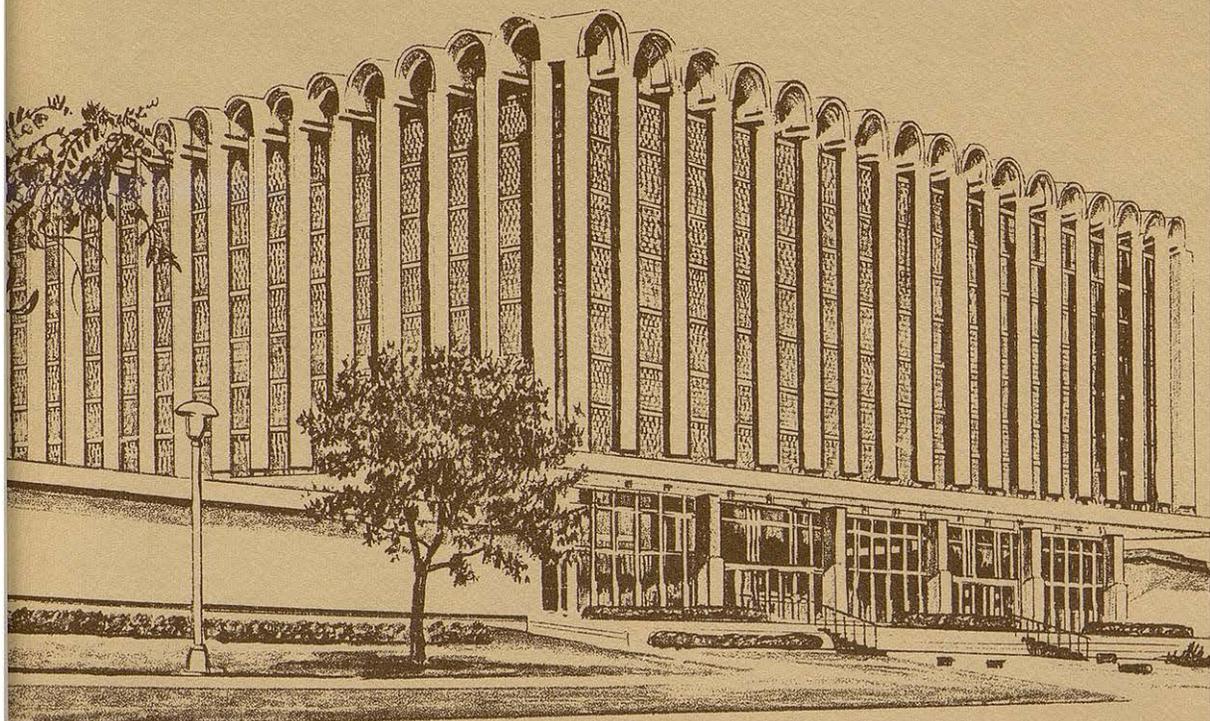


GRADUATE STUDIES TEXAS TECH UNIVERSITY

Excited States of Matter

Edited by *Charles W. Shoppee*



No. 2

April 1973

TEXAS TECH UNIVERSITY

Grover E. Murray, President

Regents.—Bill E. Collins (Chairman), R. Trent Campbell, Waggoner Carr, Clint Formby, John J. Hinchey, Frank Junell, Field Scovell, Charles G. Scruggs, and Judson F. Williams.

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PREFACE

A symposium on "Excited states of matter" was held to coincide with the dedication of the addition to the Chemistry Building of Texas Tech University. This symposium was made possible by generous financial support from the University, the Graduate School, Atlantic Richfield Company, New York, New York; Cosden Oil and Chemical Company, Big Spring, Texas; E. I. du Pont de Nemours and Company, Wilmington, Delaware; Gulf Oil Corporation, Houston, Texas; Petro-Tex Chemical Corporation, Houston, Texas; Texas Instruments Foundation, Dallas, Texas; and Celanese Corporation, New York, New York.

The symposium consisted of six plenary lectures by scientists of international reputation, together with the ensuing discussions led by three distinguished workers in the field. The plenary lectures covered a wide purview and included topics in bio-organic, inorganic, organic, and metallo-organic chemistry. Also recorded are the formal proceedings of the dedication ceremony and the symposium banquet oration by one of the most distinguished of American photochemists.

The writer wishes gratefully to acknowledge the expert advice and assistance of Dr. Dilford C. Carter, Associate Dean of the Graduate School and Managing Editor of Academic Publications, at all stages of the production of this symposium volume.

Charles W. Shoppee,
M.A., D.Phil., Ph.D., D.Sc., F.A.A., F.R.S.
Welch Professor of Chemistry,
Texas Tech University

MULTIPLE EXCITATION IN COMPOSITE MOLECULES: BIPROTONIC PHOTOTAUTOMERISM

MICHAEL KASHA

It is a particular pleasure for me to be here today, partly because I am from a university which has many analogies to this one. About 20 or 25 years ago, Florida State University was relatively unknown as the Florida State College for Women; I don't know what Texas Tech University was in those days, but it might have been equally small. We have also aspired to the development of a great university with great faculties and facilities, as this one has done, and we have hosted some national and international symposia. I was reminded, on coming here, of one such event in Florida; we held an International Symposium on Molecular Mechanisms in Photobiology in 1964, and it was attended by some of the people at this conference, and a few from other parts of the world. There was one particularly notable scientist from Italy, A. A. Buzzati-Traverso. He is a biologist, and he was frequently seen busily writing in a corner, while other people were socializing in between sessions. It turned out that he is also a journalist, writing for an Italian periodical as a highly knowledgeable science writer. I was fortunate to get a copy of his writings on that conference and had them translated. There was a particularly interesting paragraph that went something like this: "So I came to Florida expecting to find a small, local, provincial college in the vast swamplands of northern Florida. To my great surprise, there was a major university, aspiring to compete with other major universities in the country and in the world. In fact, the Symposium they were holding was one that would do credit to any institution. Would this not be a good model for universities in other underdeveloped parts of the world?" I thought that was a very nice viewpoint by a European. And I see by the development of this university, by this fine new building, and by the aspiring motives behind this symposium that this university also has its inspirations and aspirations.

MULTIPLE EXCITATION IN COMPOSITE MOLECULES

This section is based on a detailed study by Ashraf El-Bayoumi (Michigan State University) and myself, the results of which are in preparation. My own research has been directed along lines from my own curiosity, just exploring phenomena, trying to discover new ones and characterizing them. Unlike many chemists, I do not fall in love with a single molecule; I fall in love with phenomena. So, if a particular molecule is uncooperative, I simply switch to another. In forming these ideas, I usually think in terms of patterns of thought, rather than trying to hit on something by chance; although, quite often, one does discover something new accidentally. One of the recent ways of thinking, one which I have been trying to develop with one of my colleagues, Ashraf El-Bayoumi, now a professor of biophysics at Michigan State University,

and with other colleagues, is to think of molecular multiple excitation events. Normally we think of light absorption as involving a single photon interacting with a single molecule. Now, in fact, we know that many of the systems we are interested in (biological systems, aggregate and solid state systems, solvated systems) present the possibility of multiple interactions. We could consider the interaction of several molecules with one photon, or the interaction of several photons with one molecule. In a study of the literature, there seems to be some confusion, at times, between rather similar or overlapping phenomena, such as excimer, exciton, and charge transfer interactions, etc. It seemed that a theoretical treatment that could unify many of these in a systematic fashion would not only teach us the distinctions between these phenomena, but perhaps also a more interesting thing, transitional cases that are intermediate between what we would characterize as pure cases. A listing of such multiple-excitation events might be given as

- Successive excitation
- Triplet-triplet annihilation
- Nonlinear absorption
- Simultaneous transition
- Molecular exciton
- Molecular excimer
- Contact charge transfer
- Charge transfer
- Biprotic phototautomerism

As this listing shows, there are a significant number of phenomena in the category involving multiple excitation. Some of these are very well studied. One of the best known is the charge transfer interaction, in which a new electronic state is evidenced by a new (single photon) absorption or emission band for a molecular pair, not related to the electronic states of the separated components. Then there are the cases where a single photon excitation causes interaction in excited states which do not exist in the ground states of a pair of molecules (contact charge transfer; excimer and exciplex interaction). Molecular-exciton effects in absorption and emission may represent the interaction of one photon with two (or many more) molecules in a preformed aggregate in an excitation resonance interaction. Simultaneous transitions are observed as one-photon, two-molecule state superposition ("photon-pooling") events in absorption and emission, which occur in molecular aggregates, or in favorable cases, in collision pairs.

Multi-photon processes are of several types. The most familiar in principle is the "biphotonic" case of successive excitation, commonly applied in molecular triplet-triplet absorption studies for molecules with singlet ground states. As ordinary a two-photon process as this is, with simple kinetic limitations on the time sequence of the successive excitations, it is of considerable practical importance in locating upper excited states of molecules, or in exciting high energy states with two low-energy photons for photochemical studies. With

metastable singlet lowest excited states (and high intensity laser pulses), vacuum ultraviolet transitions may be observed in the visible and near ultraviolet. Both synchronized-flash spectroscopy and steady state techniques have been used in successive biphotonic excitation. Triplet-triplet annihilation generally is evidenced as a delayed fluorescence from the lowest excited singlet state of a molecule when a pair of molecular triplet states or triplet exciton states interact to yield a photon-pooling. Finally, the truly biphotonic (triphotonic, . . .) absorption can be observed from nonlinear components in electromagnetic radiation as produced with ultrahigh intensity photon fields obtainable with pulsed lasers. Here, an excited state is reached by using a photon of half the normal (one-photon) excitation energy for a biphotonic process, or a third the normal excitation energy for a triphoton process, etc.

The biphotonic nonlinear absorption case is a good example of the shortcomings of textbooks in spectroscopy and quantum chemistry. Radiation theory as treated in standard texts omits any mention of nonlinear terms in the electromagnetic vector potential, or any terms suggesting any phenomenon aside from single-photon linear perturbations. We of course rely on theoretical physics for our reschooling.

The simultaneous transition case has been equally unfamiliar to the average well-trained physical chemist, spectroscopist, or photochemist. And yet, experimentally, observations indicating the ubiquitousness of simultaneous transitions in condensed or aggregate systems have been known for decades. Starting with the recognition of simultaneous electronic transitions for molecular oxygen pairs in liquid and solid oxygen, also well recognized are the more recent observations, *e.g.* those of electronic states evidenced for pairs of transition metal ions in solid state spectroscopy, in addition to infrared vibrational transitions for (heterogeneous) pairs of molecules in highly compressed gases, etc. Currently, a great deal of interest is centered on the observation of heterogeneous molecular pair electronic absorptions in condensed phases. Solute-solvent pair states could be expected to occur under favorable circumstances.

The search for qualitatively new types of multiple excitation in composite molecules, in addition to new cases from the substantial list of known types, is one of the frontiers of spectroscopy today.

Of considerable interest to the photochemist and photobiologist is the realization that some of the multiple excitation phenomena can be directly detected by the "action spectrum" or "excitation spectrum" for the absorbing system, and some, in contrast, would not be evidenced at all in the action or excitation spectrum, occurring only as a subsequent event to the primary absorption act.

SINGLET MOLECULAR OXYGEN

The "rediscovery" of singlet molecular oxygen involves some examples of simultaneous transitions, which have been studied in our laboratory,^{1,2} and

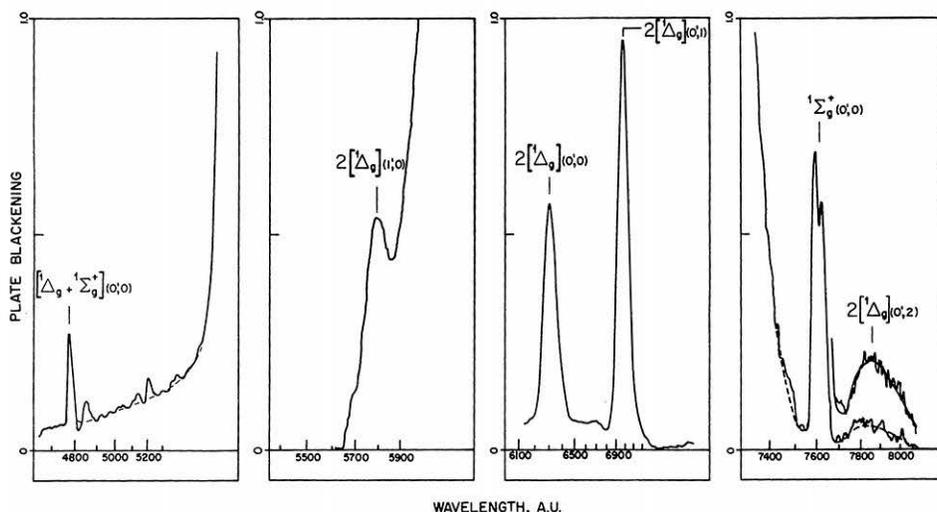


FIG. 1.—Singlet molecular oxygen single-molecule emission and molecular-pair simultaneous emission bands observed at 20°C as the chemiluminescence for reaction of hydrogen peroxide with sodium hypochlorite.¹

by numerous other investigators. This is a typical example of how a neglect of general classifications may put us in the dark for many years. Singlet molecular oxygen has been known since the 1930's, but it has only been in the last six or seven years that singlet molecular oxygen has become important as a chemical, photochemical, spectroscopic, and even a biological reactant. Fig. 1 shows some aqueous chemiluminescence produced by the reaction of 10 per cent aqueous hydrogen peroxide with commercial sodium hypochlorite bleach solution. The most prominent emission bands occur in the red-orange region. It was not commonly recognized that a red-orange chemiluminescence glow is produced by the reaction of hypochlorite with peroxide, but a weak chemiluminescence had been reported in the literature. One gets a nice, bright, orange-red glow, and with a good apparatus, it is relatively easy to photograph these spectra. One of the features of the greatest interest, of course, is that several different sets of bands shown are two-molecule one-photon emissions. They require, for example, a collision of two singlet ${}^1\Delta_g$ molecules ($7.88 \times 10^3 \text{ cm}^{-1}$) to give one photon at double the energy ($15.76 \times 10^3 \text{ cm}^{-1}$). The ultimate result is that one finally recognizes that the species excited via the two infrared transitions for molecular oxygen, 12,687 and 7621 Å, which were thought to be only of astrophysical interest, thus turn out to be species that are easily generated in the laboratory by several methods.¹ The great activity in the field on the part of numerous chemists, photochemists, photobiologists, and others has served to indicate the general importance of singlet molecular oxygen in numerous oxidations and photooxidations. This all could have been described accurately and fully in 1935 or so, but it was not until rather recently that researchers began to pay attention to the possibilities of singlet molecular oxygen involvement in ordinary chemistry and photochemistry.

BIPROTONIC PHOTOTAUTOMERISM

One of the new general interests that my colleagues and I are exploring is how protons, and hydrogen atoms, move about within and between molecular skeletons in excited states of molecules and molecular pairs respectively. Our recent study of biprotonic phototautomerism,³ in 7-azaindole, is just one example of what we believe may prove to be a general phenomenon. In our usual description of molecular electronic excitation, we do not consider atomic rearrangement beyond a slight geometrical distortion, but it could well be that some key phenomena do involve proton or hydrogen atom transfers with an alteration of a molecular skeleton.

We have studied the 7-azaindole molecule for a number of years because it offers a nice system for studying doubly hydrogen-bonded base pairing. One of our particular interests has been in exciton interaction in hydrogen-bonded dimers. Molecular exciton interaction leads to new states, which we call exciton states, that represent a delocalization of excitation energy. We were interested in knowing the influence of this delocalization of excitation energy on spectral properties. For 7-azaindole pairs, the lowest electronic states represent a weak coupling interaction. A weak coupling interaction means that the molecular exciton effect would not show up significantly in absorption, but it might show up significantly in emission, depending on the case (such as dimer geometry, transition moment magnitude, mean intermolecular separation, etc). The work I am describing was carried out in my laboratory by Carl Al Taylor in collaboration with Ashraf El-Bayoumi. Taylor's research directions were to make 7-azaindole dimers at low temperatures to find what effect dimerization (and the molecular exciton effect) had on emission. There was a small possible phosphorescence versus fluorescence enhancement effect for the dimers (as obtained in a hydrocarbon solvent at low temperature), compared with the total emission for the 7-azaindole monomer (as obtained in a hydroxylic solvent at low temperature). This is interesting because it would be an example of a nonspin-orbital perturbation effect, which enhances triplet state excitation. This sounds contradictory, but there are kinetic factors in intersystem crossing, and this present case would represent an enhancement that arises from such kinetic competition factors, not from a spin-orbital perturbation itself. In other words, the lowest molecular exciton singlet state may become metastable, thus favoring triplet excitation.

One of the things that I have an aversion to doing is the study of luminescence of molecules at room temperature. As spectroscopists, we are interested in positions, band envelopes, vibrational intervals, but at room temperature one generally gets smeared out, uninteresting spectra. I particularly told Al Taylor: "Don't bother to obtain luminescence spectra at room temperature." But Taylor is a very systematic and persistent fellow; he wanted to do his own work in his own way, so he insisted on doing all his spectral experiments at room temperature as well. He quickly discovered that there were two fluorescences for 7-azaindole in hydrocarbon solvents at room temperature (Fig. 2).

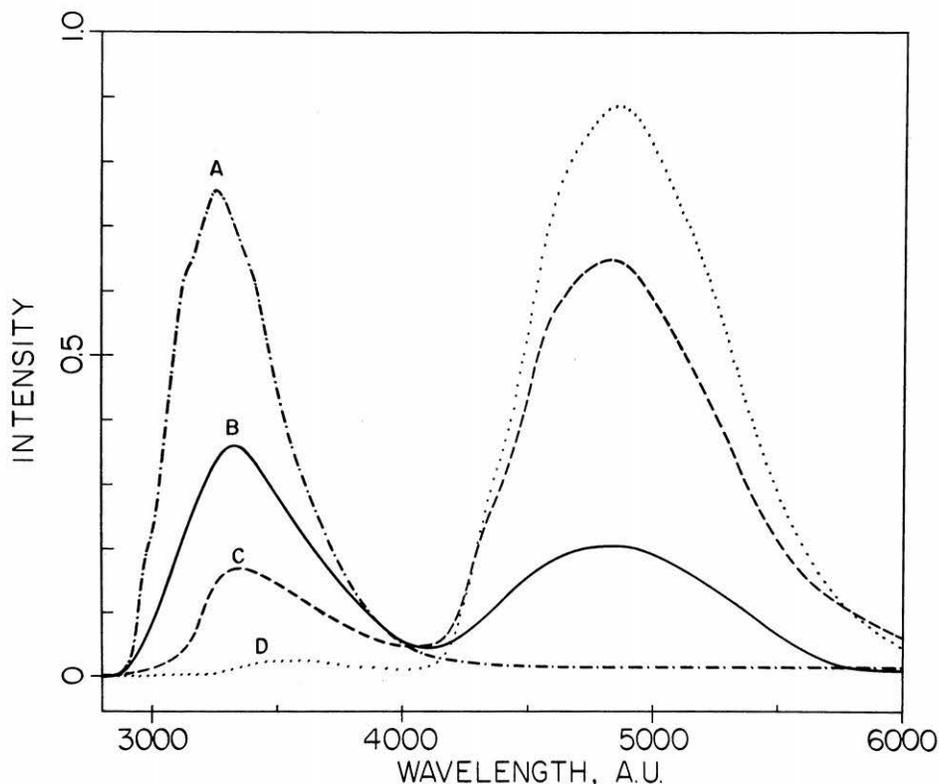


FIG. 2.—Fluorescences of 7-azaindole in 3-methylpentane at 20°C as a function of concentration³ in which A = 1.00×10^{-5} M, B = 1.00×10^{-4} M, C = 1.00×10^{-3} M, and D = 1.00×10^{-2} M.

Now, there are many lovely ways for getting two fluorescences for one molecule at room temperature. There is the method of using dirty solvents. There is the method of using dirty glassware. There is the method of using dirty chemicals. We are very proficient in all of these methods in our laboratory, and our chief problem is to learn how to avoid them. On the other hand, there are also some excellent molecular phenomena known that do give two authentic emissions for one molecular species. Especially pertinent are those cases where the second emission is shifted to longer wavelength than the normal expected fluorescence, with the shifted emission appearing as a diffuse, structureless band. Excimer emission is such a phenomenon, low energy charge-transfer states can give similar results, and then exciton interaction can lead to new emissions or enhancement of phosphorescence emission. All these cases are for molecular pairs or higher aggregates. Also, there is the consequence of excited state chemistry, and quite often by experiencing a proton addition or removal in the excited state, a molecule can exhibit a new emission that does not correspond to any feature observed in the absorption spectrum.

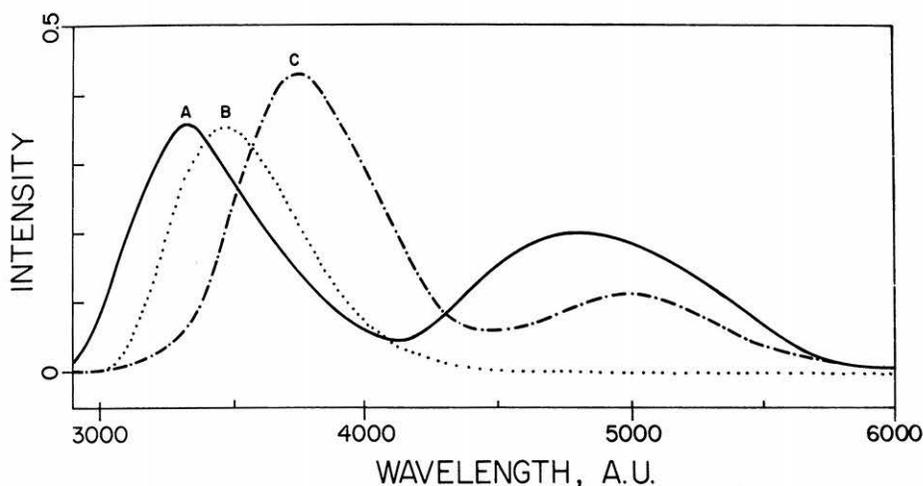


FIG. 3.—Effect of solvent on fluorescence of 7-azaindole at 20°C, 1.00×10^{-4} M: A, 3-methylpentane; B, ethyl ether; C, absolute ethanol.³

Taylor proceeded to prove, after several months of careful experimentation, that he had a genuinely nontrivial phenomenon. We then had to prove which one of those possibilities I described was applicable. It turned out to be none of the five or six types of behavior that we could think of as pertinent, and we were pressed to realize that we had observed a really novel phenomenon. Curve A of Fig. 2 shows the emission of the monomer in hydrocarbon solvent, which appears as a violet emission (*i.e.*, the tail of the emission is violet), and there is no emission in the green region. Curve D represents the emission of the practically pure dimer of 7-azaindole, which is obtained in 10^{-2} molar solution in hydrocarbon at room temperature, and you see that curve D indicates mainly a green fluorescence emission. The variation in the two intensities (violet/green) is directly connected with the shift of the dimer equilibrium, which was known before to us from infrared studies on the NH vibrational frequency change. As this phenomenon was studied further, more complex features appeared. For example, in Fig. 3, curve A is one of the hydrocarbon solution emission curves for 7-azaindole at intermediate concentration, showing some dimer emission in the green and some monomer emission. Curve B is the emission of an ether solution, and proves to be a uniquely displaced normal fluorescence with no appearance of a second emission at any concentration to saturation. So, in ether solvents, in which there is no dimerization, one never finds a second emission. We concluded, in addition, that an excimer phenomenon is not present,³ inasmuch as the unique violet fluorescence of 7-azaindole is obtained at all concentrations in ether in its solubility range.

We then proposed that in the dimer, a biprotonic tautomerization, occurs during the lifetime of the excited state, represented in Fig. 4. Because the 7-

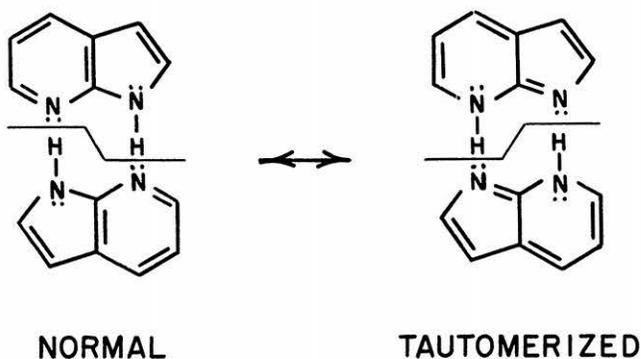


FIG. 4.—Hydrogen-bonded dimer structure of 7-azaindole.

azaindole molecule is not symmetrical, the tautomerized form could be expected to have quite different electronic state energies compared with normal molecules. We speculated that the lowest allowed transition for the tautomer could come substantially below that of 7-azaindole itself. Our hypothesis would require a shift of $10,000\text{ cm}^{-1}$ for the lowest transition energy to account for the violet to green fluorescence emission shift. In the literature, we found that Robison and Robison⁴ had synthesized and determined the lowest absorption spectrum of the N-methyl tautomer of 7-azaindole (7-methyl-7H-pyrrolo[2,3-b]-pyridine), Fig. 5. The lowest absorption spectrum of the tautomer occurred in the appropriate region to correlate well with the observed green fluorescence.

Direct confirmation of the assignment of the green fluorescence of 7-azaindole dimer as the tautomer fluorescence was obtained by Ingham *et al.*⁵ who showed that the fluorescence of the N-methyl tautomer (Fig. 5) is essentially identical to the green fluorescence of the 7-azaindole.

Finally, a self-consistent field calculation by the Pariser-Parr-Pople method, with careful parametrization and with inclusion of configurational interaction, has been carried out by Horowitz *et al.*⁶ for N-perturbation in the indene skeleton, from indole, thru 7-azaindole, to purine and adenine. For 7-azaindole the tautomer first singlet excited state was found to lie approximately $10,000\text{ cm}^{-1}$ below the normal molecule first excited singlet state, with a convergence of the gap steadily with increasing number of ring N-atoms.

COOPERATIVITY REQUIREMENT OF BI-PROTONIC PHOTOTAUTOMERISM

The effects of solvation by hydroxylic solvents of the biprotonic photo-tautomerism in 7-azaindole lead to a realization of the demand on synchronous cooperativity of the two-proton transfer.

In the 7-azaindole dimer (in hydrocarbon solvents at room temperature) the existence of a synchronous cooperativity is guaranteed by the exciton state characteristic of the excited dimer.³ In other words, even though an inter-

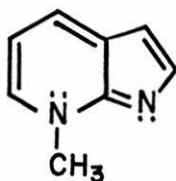


FIG. 5.—Structure of 7-methyl-7H-pyrrolo[2,3-*b*]-pyridine, or the N-methyl tautomer of 7-azaindole.

mediate coupling case may be at hand, the delocalization of excitation between the two molecules of the dimer offers the means for a synchronous cooperative transfer of 2 protons: as one proton becomes more acidic (positive) in the excited state, the increased basicity (electronegativity) of the complementary N-atom offers a transfer site. The intramolecular charge rearrangement and intermolecular-bridge atom $\dots\text{N}-\text{H}:\text{N}\dots$ network electronic changes are synchronized. Biprotonic phototautomerization hence is unrestricted at room temperature, where there is no potential barrier limitation (see below).

In ethyl alcohol solvent, quite a different behavior of the 7-azaindole phototautomerization is involved. As curve C (Fig. 3) shows, a violet normal fluorescence and a green tautomer fluorescence are both observed, the latter being slightly displaced in comparison with the green fluorescence of the 7-azaindole dimer. However, the violet/green fluorescence ratio is now concentration independent in ethanol. We interpret this to be a consequence of the synchronous cooperativity requirement. As Fig. 6 (left) indicates, a cyclic ethanol solvate must necessarily be involved in the biprotonic phototautomerism.

For 7-azaindole in ethanol, the noncyclic solvates would not provide a synchronous cooperativity and would not be capable of excited state tautomerism. Hence, the concentration-independence indicates a fixed ratio of cyclically solvated 7-azaindole and the chain-solvated molecule.

For 7-azaindole in water, no green fluorescence is observed in any part of its solubility range. This observation offers a striking contrast to the behavior of 7-azaindole fluorescence in ethanol solutions and is very puzzling at first sight. However, if water molecules are more strongly chain-hydrogen-bonded, then as Fig. 6 (right) indicates, the two N-atom positions of 7-azaindole would be bridged to different water chains. This circumstance would prevent synchrony of electronic charge migration as apparently required for the cooperative phenomenon of biprotonic phototautomerism. It can be expected that an isolated HOH molecule in water could cyclically hydrogen-bond to 7-azaindole for a synchronous cooperativity of biprotonic transfer in the excited state, but that the availability of single molecules of HOH in water would be infinitesimal; or, in other words, water molecules are too wet (solvated) in liquid water.

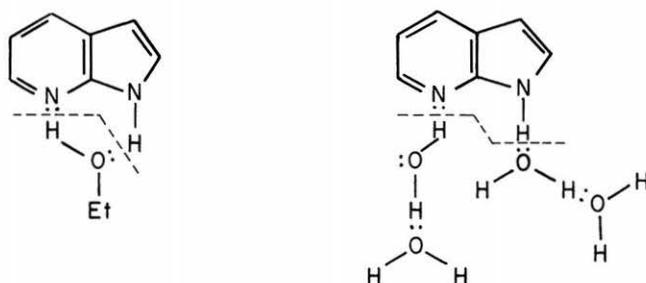


FIG. 6. — Structure of cyclical ethanol solvate (left) and chain water solvate (right) of 7-azaindole.

THE DOUBLE MINIMUM POTENTIAL FOR BIPROTONIC PHOTOTAUTOMERISM

A schematic representation of the double minimum potential function for tautomerization of 7-azaindole dimer in its ground and its lowest singlet excited state is given in Fig. 7. The asterisks indicate the excited dimer in its lowest exciton state.³ The normal molecule dimers correspond to the minima in the potential curves on the left side of the diagram, and the tautomerized molecule dimers correspond to the potential minima on the right side of the diagram. The absorption of the normal dimer, corresponding to the UV (violet) fluorescence is shown by an upward arrow, and the green fluorescence of the tautomerized dimer is shown by the downward arrow.

Ingham *et al.*⁵ has studied the temperature dependence of the violet/green fluorescence of the dimer. They established the fact that the Boltzmann or thermal mechanism (over-the-barrier) greatly predominates as the mode of formation of the tautomer at room temperature. The approximate barrier height in the excited state was found to be quite small, $\sim 140 \text{ cm}^{-1}$. At temperatures below approximately 100 down to 4°K, a temperature independent proton tunneling was observed.

In another place⁷ we have presented a discussion of the competition between proton tunneling, excimer formation, and the biprotonic phototautomerism phenomenon in N-heterocyclic base pairs. The idea that various tautomeric possibilities exist and could be altered in excited states of the molecules in the DNA base pairs has been considered in the earliest studies of the DNA base pairing scheme by Watson and Crick.⁷

There has been a long history of speculative ideas on proton tunneling in such heterocyclic base pairs, and a number of years of effort in quantum mechanical calculation of potential functions and tunneling rates. Now the studies of biprotonic phototautomerism offer a beginning of quantitative experimental information on this aspect of excited states of hydrogen-bonded N-heterocyclic base pairs.

We anticipate that the extension of these studies to other base pairs, including those of biological interest will provide a fruitful development of this subject. When we know more about the double minimum potential barriers in

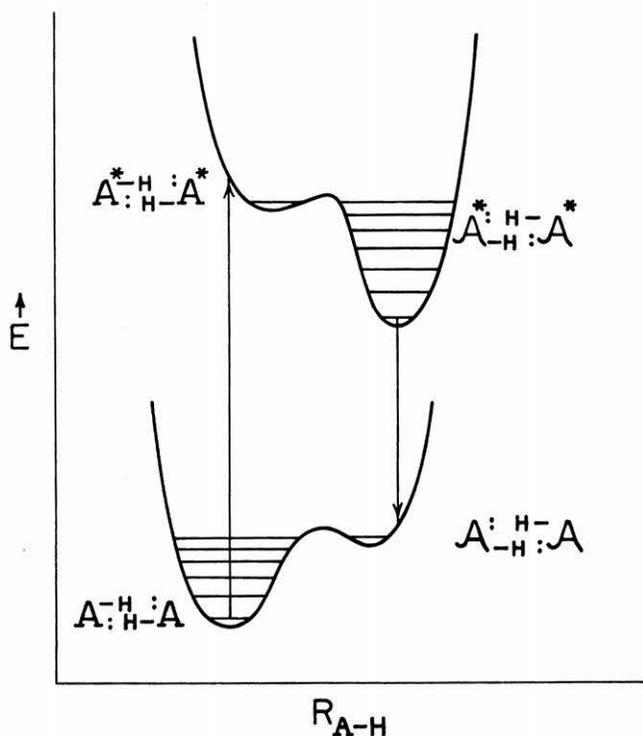


FIG. 7.—Schematic double minimum potential diagram for biprotonic transfer in ground state and exciton states of 7-azaindole hydrogen-bonded dimer.

excited and ground states, we will be in a position to evaluate the participation of the cooperative biprotonic transfer phenomenon in chemical, photochemical, and radiobiological events.

ACKNOWLEDGMENTS

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DISCUSSION: LEADER, DR. E. C. LIM

Dr. Song.—Indoles usually show relatively long phosphorescence lifetimes of one to seven seconds in rigid matrices. Is it possible to expect relaxation in the triplet state that may favor a tautomer, which then emits corresponding phosphorescence analogous to the long wavelength fluorescence?

Dr. Kasha.—Yes. The nature of Dr. Song's question and the appropriate answer are very important, and represent the kind of detail I left out in my presentation. It certainly is only proper to talk about the entire electronically excited manifold. There are singlet L_a and singlet L_b states in the indoles and purines, and there may even be low-lying $n-\pi^*$ singlet excited states in some of the purines. Where are the lowest triplet states and what are they doing in terms of this biprotonic interaction? What possibility is there that the tautomer lowest singlet state can cross back to the triplet manifold of the untautomerized base? That is a complex and uninvestigated point. We do not know, for example, where the triplet state of the tautomerized 7-azaindole is. But, inasmuch as the stabilized methyl derivative is available, that certainly is amenable to study. The diagrams that I showed you are the most primitive, and the simplest showing the allowed lowest singlet excited states—you have raised the question of a sort of Pandora's box of excited state complexity that will come into these cases.

Dr. Song.—If we look at the charge distributions in the excited singlet L_a and L_b states, and in the excited triplet L_a and L_b states, the calculations that you mentioned (and our analogous calculations) show that the ρK 's of the excited triplets are very similar to those of the ground state as far as indole itself is concerned. Perhaps the electronic structure in the excited triplet state becomes very much like the ground state, and does not favor the tautomer. Is this reasonable?

Dr. Kasha.—No. I see a more complicated possibility. If you think of a left side and a right side diagram, with the left side representing the normal molecule in a dimer and the right side representing the tautomeric form, then what I see as a new possibility is that the triplet states of the normal molecule may cross radiationlessly with the triplet states of the tautomer. So, we may have a new path to get back to the ground state, which we have not really taken into account here at all. The triplet states of the tautomer, we believe, will be beyond our present range of observation in the infrared, and I do not think they will be a primary participant in the phenomena that I have described. But that other possibility is interesting. You see, we do not usually think of two systems of molecules interacting; we usually have just one manifold of states, which is normally complicated enough. Here I see the spilling back into the normal molecule manifold by a new intersystem crossing event. That is the kind of thing that I was thinking of. However, even if the ρK 's of the lowest normal triplet and the ground state are similar, one cannot assume that the corresponding electronic structures are identical.

Dr. Shulman.—When we started to work on the excited states of DNA, we had a list, almost as long as Dr. Kasha has shown, of possible explanations of the different excited states; a number of the entries on that list have now been eliminated, *e.g.*, $n-\pi^*$ states, as lowest energy excited states of purines and pyrimidines. The important point is what are the actual mechanisms, not what are the possible mechanisms and explanations of the different excited states of the nucleic acids. Inasmuch as you did not say that biprotonic tautomerism is an explanation of any of the results that we have, I need not defend myself in any way now; the rest of the defense will be conducted at great length tomorrow! There is one question, however, that I have about tunnelling at lower temperature. I did not understand why the rate went up and came down before leveling off. Why did it not level off at the highest value?

Dr. Kasha.—I think that there were three competing phenomena. I would like to make another remark about the work of yours that I reported on. We see a clear indication of three competitive phenomena, not two, in that temperature dependence study. Certainly, the rise with lowering of temperature in the relative yields of the two emissions is directly connected with the dimerization equilibrium shift. Now, if there were a temperature independent tunnelling, it would taper off at a high level and remain there. But, because the fluorescence yield ratio drops sharply, it must be true that we are freezing out the Boltzmann mechanism when the temperature is lowered and all dimers are formed. The rate of dropping for the left side of the curve is an indication of the magnitude of the ΔH° for the barrier, and that is estimated by Ingham and El-Bayoumi to be relatively low, approximately 200 cm^{-1} . If the yield ratio dropped finally to zero near 0°K , you could say that only the Boltzmann mechanism was present. But the $F_2:F_1$ ratio tapered off at a high ratio of about two, indicating that there is still a significant phenomenon at all temperatures below a critical temperature. That effect must be due to tunnelling; it is a temperature independent proton transfer process. However, in dimer at room temperatures, the thermal or over-the-barrier mechanism dominates, with a yield ratio of more than 10 to 15.

Dr. Shulman.—Yes, so the chemical change is occurring at the lower temperatures. I think it would be well to mention that there is a sizeable body of opinion that has severe reservations about the role of proton tunnelling in mutation. In fact, if X is the body that includes Löwdin and his coworkers, $1 - X$ is the scientific body that is opposed.

A question, which so far as I know has never satisfactorily been answered, relates to the very short lifetimes of excited states and the known rate of replication; similarly, how can excited state tautomers, or ground state tautomers, with very short lifetimes, have any mutagenic effect?

Dr. Kasha.—We have the greatest reservations (I think analogous to yours) about the role of very fast phenomena of this kind in any biological effect, particularly in genetic changes during replication. The only possibility that has occurred to us is that if one found a barrier, which was really rather larger than anything presently seen, one could trap a tautomer. I can only say that it is something to investigate. If the proton transfer barrier in a biological base is of the character of the barriers we are now working with for 7-azaindole, I would say that proton transfer would have limited biological significance. We believe that the radiation chemistry of biological base pairs could, however, involve proton transfer processes.

Dr. Shulman.—But, of course, during replication the hydrogen bonds break, so a tautomer that is trapped, even if you bind it, by the existence of the hydrogen bonds, is not relevant for the DNA when it is single stranded during replication.

Dr. Kasha.—The only other thing I wanted to say is that we know that the chemistry of the tautomer, in the excited or ground state tautomer, would be significantly different from the chemistry of the normal molecule, and we could expect side events to take place in competition with events we normally expect to occur.

Dr. Gouterman.—Just a couple of questions and one comment. First of all, what happens to the residual green fluorescence at low temperature if you deuterate? Second, has anyone taken a concentrated solution of 7-azaindole and irradiated it in what would be the anti-Stokes region, corresponding to the emission? There may be a significant amount of the tautomeric dimer in the ground states, as you could show very clearly by direct excitation. As for the comment, the most elegant examples of trapping of polymeric forms, are those of D. S. McClure and others, mono-protonic shifts, in which there is an ancillary geometric isomerization that helps trap them.

Dr. Kasha.—The question about deuteration is being investigated. Because the weak coupling exciton model seems to be working here, it might be this very situation in which vibronic interactions become especially important. So deuterium in the hydrogen-bonding location would sensitively indicate a dependence.

Dr. Gouterman.—What about irradiation in the anti-Stokes region?

Dr. Kasha.—The low values for the tautomerization energy versus the normal base or base pairs suggest that you could, in fact, do direct excitation. There are parts of the problem that I left out. If you study absorption spectroscopy of this particular base, 7-azaindole, as a function of concentration, there are vast changes in the spectrum as with dimer formation or solvated molecules. And these changes are of the character of shifting bands—with new bands appearing at long wavelength. These spectral effects look like exciton effects because they are of the right character, but they are entirely of the wrong magnitude. So it turns out that they are electronic state interchanges that occur owing to electronic perturbation transversely to the main axis of the molecule. Those are now well understood as solvent effects. There has been no effort to excite beyond that region to even longer wavelengths. But, I think, perhaps with sufficiently intense light sources, it is a feasible experiment and a good idea.

Dr. Burr.—Milliken Daniels at Oregon has been able to observe the room temperature fluorescence of thymine, cytosine, and uracil, and the excitation spectra for these compounds. From these he can deduce a lifetime for the singlet state of 10^{-12} seconds, which would reduce the time available for the polymer to have any effect on the replication, and it seems to me, introduces some question as to whether there would be time enough for proton transfer from a pyrimidine-purine pair. Do you have any comment about this lifetime consideration?

Dr. Kasha.—Of course what one means by such lifetimes are the lifetimes after the competitive events have taken place because, obviously, they are not what we might call the Einstein radiative lifetimes. Therefore, the plethora of events reducing the lifetime to the observed magnitude could include much slower processes, because they are not competing with that observed lifetime but are competing with the normal radiative lifetime; that is, that calculable from the transition moments for that excited state. That is analogous to the observation of excimer emission versus thymine dimer formation through excimers. What is observed as emission is certainly competing with thymine dimer formation.

Dr. Song.—Have you examined the temperature dependence of the $F_2:F_1$ ratio in a matrix where alcohol complication does not come in?

Dr. Kasha.—There is some disagreement between my laboratory and Ashraf El-Bayoumi's laboratory on that question. Al Taylor's thesis was a study of such events, and he showed that in very dilute hydrocarbon solutions where all dimers formed at low temperature, the F_2 phenomenon disappeared entirely. So our conclusion was that we were observing a purely nontunnelling Boltzmann mechanism. On the other hand, there is another complication; as one increases the concentration to high values at room temperature, such as 10^{-2} molar, and then freezes such samples, one observes a high degree of irreproducibility. Each time one freezes a particular sample one gets a different result, but always one gets the green emission. After a long study of this, we finally concluded that microcrystals were interfering and that in the solid state we were fighting this and the nonequilibrium in viscous media. Ingham and El-Bayoumi at Michigan State have established the ethanol-complex competition with trace amounts of ethanol. That is one of the unspoken complications. There are some unresolved things there.

Dr. Shulman.—I want to take up Dr. Burr's point, which I think has not been completely answered. I think those times of 10^{-12} seconds are important; my colleagues have measured times of about the same magnitude. If your answer is correct, then proton transfer mechanisms have to compete with these short lifetimes. My colleagues have seen that these lifetimes are quite independent of the state of protonation, or of the solvent at room temperature, and therefore, one expects that the short lifetimes do not arise from proton transfer.

Dr. Kasha.—Your statement is general for mononucleotides?

Dr. Shulman.—Particularly for mononucleotides.

Dr. Kasha.—I'll accept that as a complication.

Dr. McGlynn.—The thermal glow curve you presented for the temperature dependence of emission had a peak. It looked extremely like the standard thermal glow curves that one finds in solid state physics, and which are very difficult to interpret. First, did this low curve exhibit hysteresis, dependent upon whether one measured it going up in temperature, or going down in temperature? Secondly, how was the information utilized to extract the potential barrier height?

Dr. Kasha.—I don't believe that the yield ratio versus temperature curve could be called a thermal glow curve. This is simply the fluorescence ratio intensity upon constant excitation as a function of temperature.

Dr. McGlynn.—The reason I asked the question was that I was concerned with a possible heat defect of this sort for some curves. At LSU we have produced the same effect.

Dr. Kasha.—But the measurement is done in such an utterly different fashion. I'd love to find a "defect." That would be the answer to all of the dreams of someone trying to make this a useful phenomenon because then you would have a trapping mechanism.

PHOTOCHEMISTRY OF URBAN ATMOSPHERES

J. N. PITTS, JR.

This subject represents a fascinating blend of basic science and relevance, and I would like to set forth in rather straightforward terms some physical and chemical aspects of photochemical smog. I will also comment on some biological aspects and certain key economic and political factors involved in the total air pollution system.

I should state in advance that the ultimate solutions to the air pollution problem in an area such as the South Coast Air Basin (the Los Angeles Basin) or the New York area (the east coast megalopolis) are going to be social, political, and economic solutions. Technology alone is far from solving these problems.

Fig. 1 illustrates the relevance of photochemical air pollution. Emphysema is recognized as a major cause of death today, and its occurrence is rapidly increasing. I talked to Dean Goerke of the School of Public Health, University of California at Los Angeles about this point. He said he has recently accumulated evidence showing signs of emphysema in 18-year-old students living in the South Coast Air Basin.

I want you to remember a number; the number is the air quality standard for oxidant for the state of California. Oxidant here means mostly ozone and some peroxyacetyl nitrate. Air is drawn through an iodide solution, and the intensity of the iodine color formed is measured. Anything that oxidizes iodide to iodine is defined as oxidant. The number you want to remember is 0.1 ppm of oxidant, which is the health-related air quality standard; health-related means that above this oxidant level health effects have been shown to occur.

During 218 days of the year, including every day in August and September, the people of Pasadena were exposed to oxidant levels that exceeded the health standard (Fig. 2). A similar situation occurred in Riverside. At an oxidant level of 0.27 ppm the school children in Riverside County are called in off the school grounds and all outdoor physical education is ceased. There were more than 78 such days in Pasadena and 45 in Riverside! In Sacramento, where the Legislature is located, we do not see a single solid bar. I showed this to some state legislators, and they got the message.

One of the things that might be said is that air pollution is the challenge of the 70's. What is a challenge in the 1970's was also a challenge in the 1670's, as shown in a book by John Evelyn, "Fumifugium, or the inconvenience of the aer and smoake of London dissipated together with some remedies humbly proposed." The author did not just complain about air pollution, he had some remedies, and this was in 1661. He said, "It is this which scatters and strews about those black and smutty atomes upon all things where it comes, insinuating itself into our very secret cabinets and most precious repositories. Finally, it is this which diffuses and spreads yellowness on our choycest

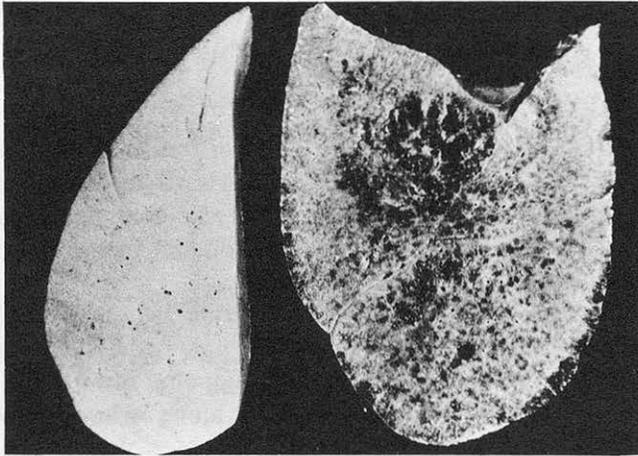


FIG. 1.—Sections of human lungs showing normal lung (left) and lung damaged by emphysema (right).

pictures and hanging, . . . adverse to fowls and kills our bees and flowers . . .” and then speaking as a plant pathologist, “. . . suffering nothing in our gardens to bud, display themselves or ripen.” Obviously Evelyn was a well-cultured seventeenth century scholar, but he was also an epidemiologist:

But, without the use of calculations it is evident to every one who looks on the yearly bill of mortality, that near half the children that are born and bred in London die under two years of age. Some have attributed this amazing destruction to luxury and the abuse of spirituous liquors: these, no doubt, are powerful assistants; but the constant and unremitting poison is communicated by the foul air, which, as the town still grows larger, has made regular and steady advances in its fatal influence.

A child born in a country village has an even chance of living nearly 40 years. Much has been said against mothers who put out their children to nurse, and where they live in a healthy air, the practice is generally unjustifiable; but the chance for life in infants, who are confined in the present foul air of London, is so small, that it is highly prudent and recommendable to remove them from it as early as possible.

Now, not only was Evelyn an epidemiologist and a plant pathologist, he was also an engineer. He wrote, “Till more effectual methods can take place it would be of great service . . . to carry their chimnies much higher into the air . . . to convey the smoke away.” “Workmen,” he stated, “should be consulted and encouraged to make experiments whether a particular construction of the chimnies would not assist in conveying off the smoake.” Finally, he recommended economic incentives. “Premiums should be given to those that were successful in it.”

In modern times there are two types of air pollution, the London type and the Los Angeles type. London smog is worst early in the day, with low temperatures, high humidity, and a radiation inversion at the surface. The atmosphere is a chemically reducing mixture of particulates and gases. The symptom is primarily lung irritation, leading to death in many cases. Los Angeles photochemical smog is worst around noon in Los Angeles, and around 4 or 5

OXIDANT LEVELS
1969

 DAYS OXIDANT EXCEEDED 0.10 PPM FOR 1 HOUR
 (CALIFORNIA HEALTH-RELATED AIR QUALITY STANDARD)
 DAYS OXIDANT EXCEEDED 0.27 PPM
 (RIVERSIDE COUNTY MEDICAL ASSOCIATION SCHOOL ALERT LEVEL)

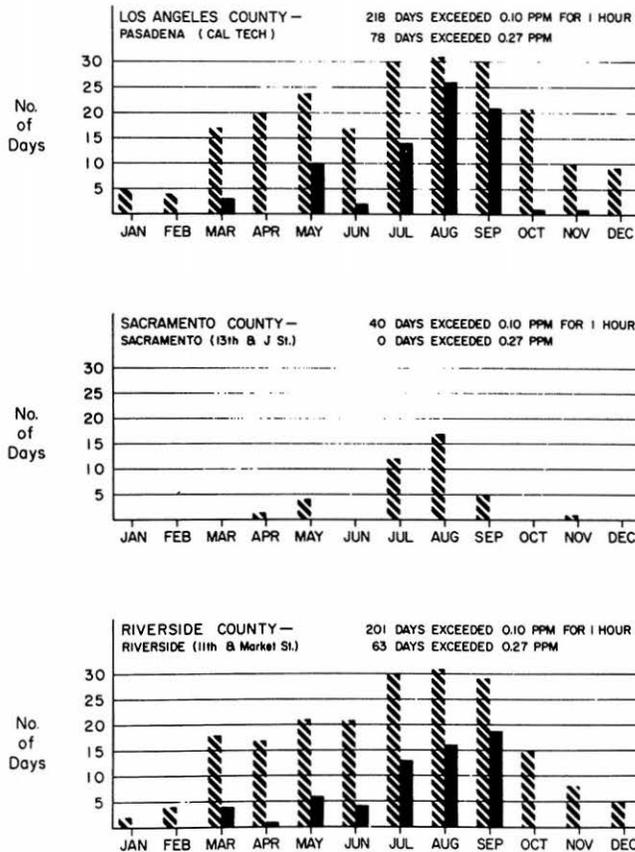


FIG. 2.—Monthly oxidant levels for Pasadena, Riverside, and Sacramento. The diagonal bars indicate the number of days that the oxidant level exceeded the health standard 0.1ppm. Solid bars indicate the number of days that the oxidant level exceeded 0.27ppm.

PM in Riverside, with high temperatures, clear skies, and an inversion layer at 2000 or 3000 feet overhead. This atmosphere is chemically oxidizing. Symptoms, which include eye irritation and disturbance and destruction of pulmonary function, depend upon individual sensitivity. Photochemical smog was originally discovered because of still another characteristic. A crop of spinach had been destroyed, and the cause of the destruction was unknown. When an investigation was first initiated, the cause was thought to be an unknown plant disease. It turned out, as you know, to be photochemical air pollution.

Professor Haagen-Smit at the California Institute of Technology suggested the original theory of the production of photochemical air pollution. His

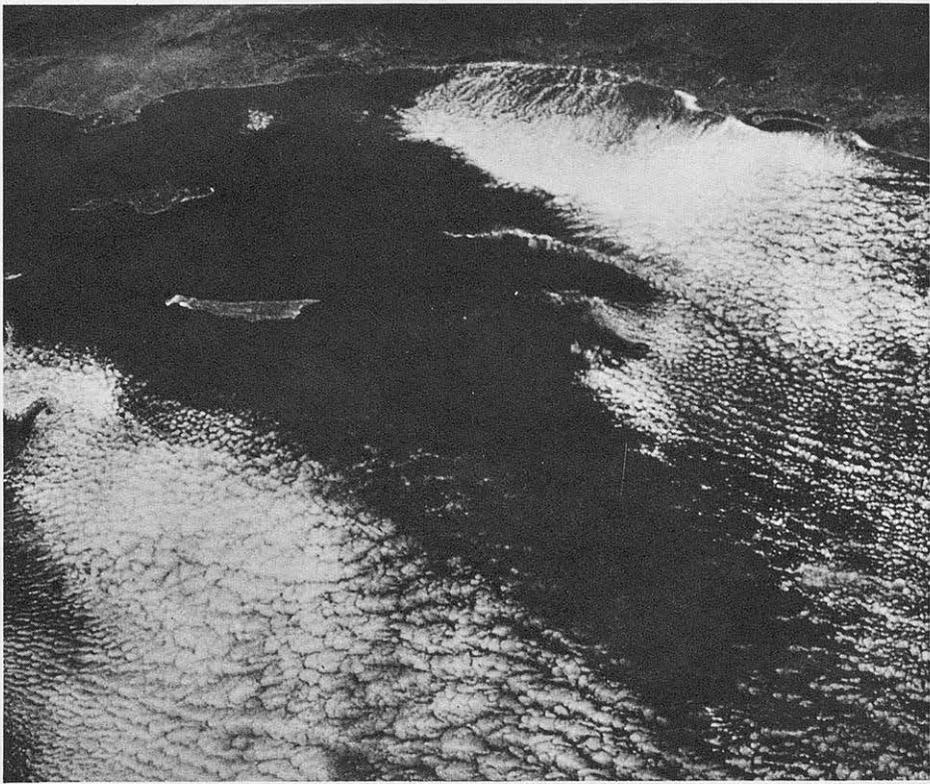


FIG. 3.—Photograph of the South Coast Basin taken from Gemini 5. The white patches are photochemical smog (the oxidant level was 0.25ppm).

theory, which proved to be generally correct, was that oxides of nitrogen, hydrocarbons, and sunlight react to produce this environmental problem.

We shall now be talking, not about the London type of smog, but about the Los Angeles type, so named because it was first discovered there. It has been a major problem on the East Coast during the summer, and was a serious problem in Tokyo in August 1970. Severe plant damage, due to photochemical smog, has been discovered in numerous portions of Holland. Photochemical smog is a global problem.

Incidentally, New York has both types of smog, the Los Angeles and the London type. Recently, I was talking to the head of health effects for the Environmental Protection Agency (EPA). We were trying to predict where a major tragedy would hit, if it should come. I predicted Riverside in the South Coast Air Basin for a variety of reasons, but he thought New York was the place because they get the worst of both worlds. The leading question is how can a reducing atmosphere and an oxidizing atmosphere coexist? For many years the people of New York made the claim that their atmosphere was essentially free from photochemical oxidant. Oxidant meters were cali-

brated and checked and showed no oxidant in the atmosphere of New York. The incident was dropped until a plant pathologist found plants showing all the symptoms of PAN (peroxyacetyl nitrate) damage and ozone damage. Clearly, both oxidant and reductant were present in the atmosphere. In the gas phase the two species react slowly, but in the liquid phase SO_2 neutralizes the oxidant rapidly. Oxidant meters use liquid phase systems, and thus the meter does not register. This is actually a major problem; in many cases people are misusing their analytical equipment and misunderstanding their results. When one is talking about millions of dollars spent on control systems and billions of dollars in economic losses, one has to be very sure of his analytical chemistry and of his basic reasoning.

Fig. 3 shows our "environmental reactor" in southern California. The South Coast Basin is approximately 80 to 90 miles long and 50 to 60 miles wide, and the entire area is surrounded by mountains. Prevailing winds are from the west and the southwest. This is our reactor; the mountains hem in the area like walls of a flask, and the atmospheric inversions act as a stopper in the flask, photochemical smog being held beneath the inversion layer.

An important point is that this smog is photochemical smog and is not from agricultural burning, forest fires or factories. Perhaps 20 per cent of the total particles present are primary particulates emitted by industry and motor vehicles, but at least 50 per cent of the total particles are generated photochemically. The particles are generated by the photochemical reactions of sunlight with the oxides of nitrogen and hydrocarbons, and a small amount of SO_2 increases the production. These particles are so small that they are capable of staying aloft and remaining stable; this is why visibility is reduced so drastically.

One of the things I want to stress is that, when dealing with smog in the real world, one is in fact dealing with a heterogeneous system. Most chemists work with homogeneous systems and even there run into problems, but smog is a system with gas-gas, gas-solid, gas-liquid, and liquid-solid interactions. Probably about 10 per cent of the solids present are lead particles. More than 50 per cent of the lead that is emitted by automobiles is in the size range below one micron. There are two important points to be made: these small particles can remain suspended in the atmosphere for many hours, and they are just the right size to be deposited efficiently in the lungs. I think the message is clear; if one is going to think about real air pollution problems one must think about heterogeneous systems, whether one is a chemist, biologist, or physician. It is known that in the London smog episode people were not killed by the concentration of the oxides of sulfur, or by particles alone, but by the synergistic effects of both pollutants. There is amazingly little known about the actual biological synergistic effects of a photochemical oxidizing system like ours. In formulating atmospheric models for the urban atmosphere people have usually ignored particles. Some time ago I attended an atmospheric modeling session. One particular atmospheric model contained 120 equations,

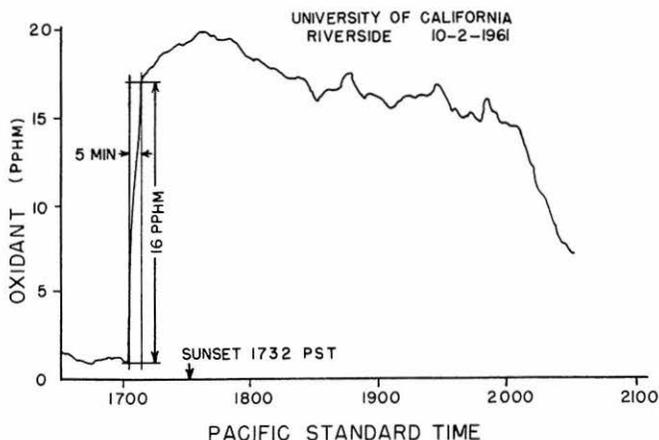


FIG. 4.—Oxidant level tracing made as a smog cloud developed.

but unfortunately not one of the equations involved a heterogeneous reaction. Our thinking needs to change here.

There are two sources for particulates—some come directly from refuse burning, automobiles, smoke stacks, and the like, whereas others are formed photochemically in the atmosphere from gases. These gases can come from people's activities or from natural sources. The haze in the Great Smoky Mountains is primarily a natural aerosol. One can form natural aerosols in the laboratory. A piece of lemon peel is crushed and placed in a flask containing ozonized air. There is an immediate formation of the white aerosol. This is an example of a natural aerosol that is formed by the reaction of ozone with the terpenes in the lemon peel.

There is an important question one can ask, "we see the particles, but how do we know whether noxious gases are present?" To measure gases we must use special instruments designed for that purpose, oxidant analyzers being among the most frequently used. Fig. 4 is a tracing made by such an analyzer. It was a beautiful October afternoon until 5:00 PM when the smog cloud suddenly developed. In Los Angeles this phenomenon is common; oxidant is present along with the particles.

In addition to the reduction in visibility, this cloud of particles and oxidant drastically reduces the ultraviolet light reaching the earth's surface. Fig. 5 is a graph, done many years ago by Stair, of solar energy versus the time of the day prepared from data collected in Pasadena. The top curve represents the standard curve for the sun, simply a curve on a clear day. The second curve was taken on a smoggy day. Notice that at about 11:00 AM the smog appears and suddenly there is a drastic reduction in the ultraviolet radiation band at 3200 to 3500 Ångstroms.

One of the questions critical to us as photochemists is, how much radiation is lost due to Rayleigh scattering and how much is lost due to absorption. Ab-

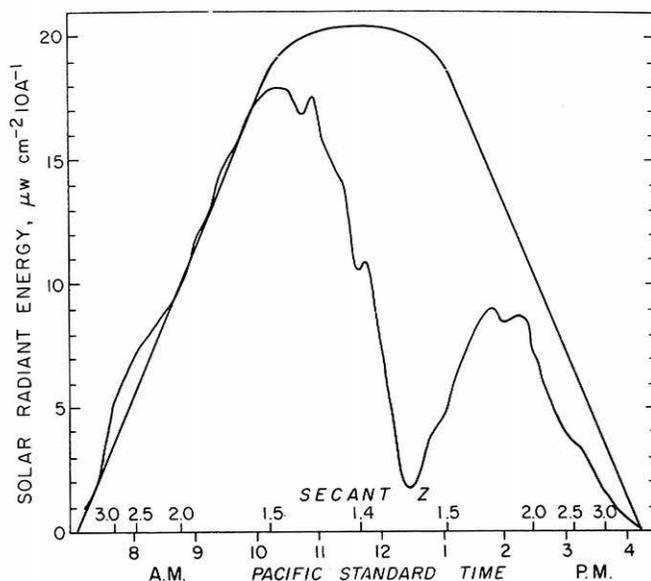


FIG. 5.—Two curves for solar energy plotted against the time of day.

sorption of ultraviolet radiation by gases, liquids, or solids is very important because if one has absorption one can have energy transfer processes that can cause chemical reactions that otherwise would not occur. Radiation lost by scattering does not cause chemical reactions. We have not sorted out yet how much ultraviolet radiation loss is due to absorption and how much is due to scattering.

Hundreds of millions of dollars in damage is being done presently to important agricultural crops. The tobacco crop of the East Coast is very sensitive to oxidant, and millions of dollars have been lost because of damage to this crop. Fig. 6 shows a grape leaf, the bottom of which is undamaged, but the flecked and speckled top illustrates ozone damage. Another type of plant damage is caused by peroxyacetyl nitrate, frequently referred to as PAN. The structure of PAN is $\text{CH}_3\text{CO}_2\text{-ONO}_2$. Silvering on the underside of leaves is usually characteristic of damage due to PAN, which also affects humans. It is an eye irritant and severely attacks the lungs. Another type of plant damage is due to ethylene, only one part per billion being sufficient to ruin an orchid crop. For that reason, orchids are no longer grown in the Los Angeles or San Francisco areas.

Fig. 7 is perhaps the most dramatic example of plant damage I have ever seen. These photographs were provided by Dr. Paul Miller of the Forest Service, U.S. Department of Agriculture. In 1961 (Fig. 7A) this tree was in good condition, but nine years later (Fig. 7B), the tree was badly damaged. It must be understood that this damage is occurring not only to one tree, but to millions of them. Timber in this area of southern California is primarily of

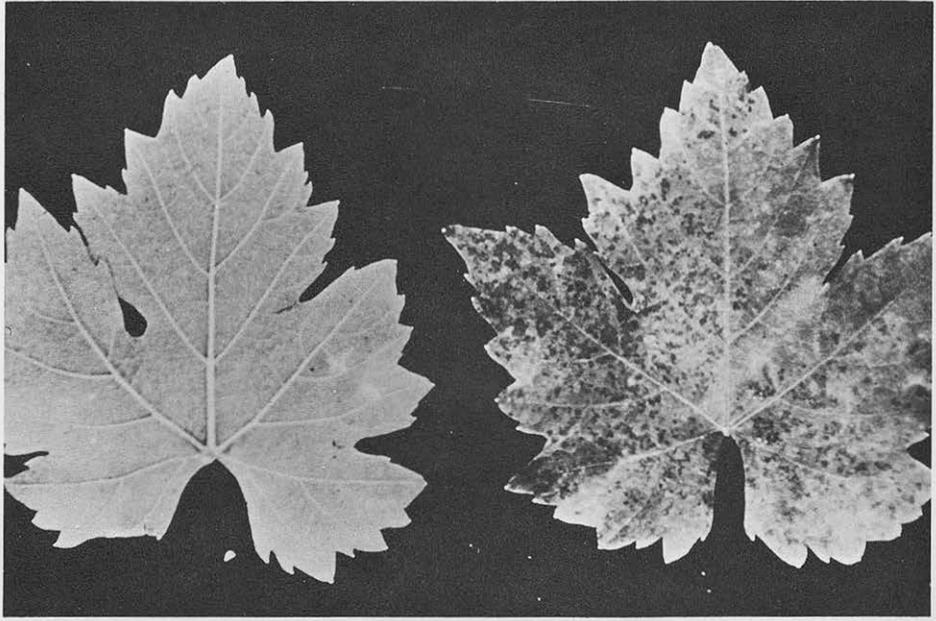


FIG. 6.—Grape leaf damaged by ozone.



FIG. 7.—Photographs of a pine tree in San Bernadino National Forest illustrates damage caused by smog: A, photograph taken in 1961; B, photograph taken in 1970.

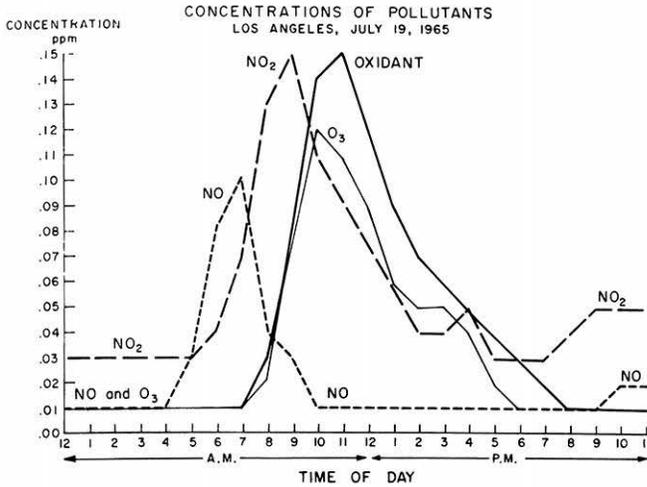


FIG. 8.—Concentrations of pollutants plotted against time of day.

scenic value, and land developers, owners, and vacationers are terrified at what is happening. Actually, the ozone and PAN affect the tree just enough to make it ill, and then natural enemies of the tree take over and kill it.

Now that we have seen some of the effects of photochemical smog, let us consider the chemical reactions in the atmosphere that cause these effects. When dealing with the chemistry of the atmosphere one must consider two types of pollutants, primary and secondary. Primary pollutants are those emitted directly into the atmosphere, for example carbon monoxide, hydrocarbons, and NO_2 from automobiles. Secondary pollutants are species such as ozone and PAN. The oxides of nitrogen that are emitted from cars and power plants consist of approximately 5 per cent NO_2 and 95 per cent NO. Nitric oxide NO is then oxidized in the atmosphere to the brown nitrogen dioxide NO_2 . Certain key primary pollutants are converted to secondary pollutants. For example, in the presence of sunlight and hydrocarbons NO is converted very rapidly to NO_2 . There is no known mechanism that can account for this extremely rapid rate of reaction.

Concentrations of pollutants in downtown Los Angeles as a function of time of day are shown in Fig. 8. The concentration of NO increases until about 7:00 AM when the sun rises. As the day progresses there are two competing factors; the traffic tapers off, but the sun appears and photochemical oxidation occurs. As the concentration of NO_2 peaks the concentration of NO becomes essentially nil. Another thing important to recognize is that the concentration of ozone remains low until NO levels are low, because the reaction of NO with ozone is very rapid. As the level of NO reaches its lowest concentration, the concentration of O_3 reaches its maximum point.

What does this mean to persons living in the South Coast Air Basin? As the smog cloud moves from west to east photochemical reactions are occurring.

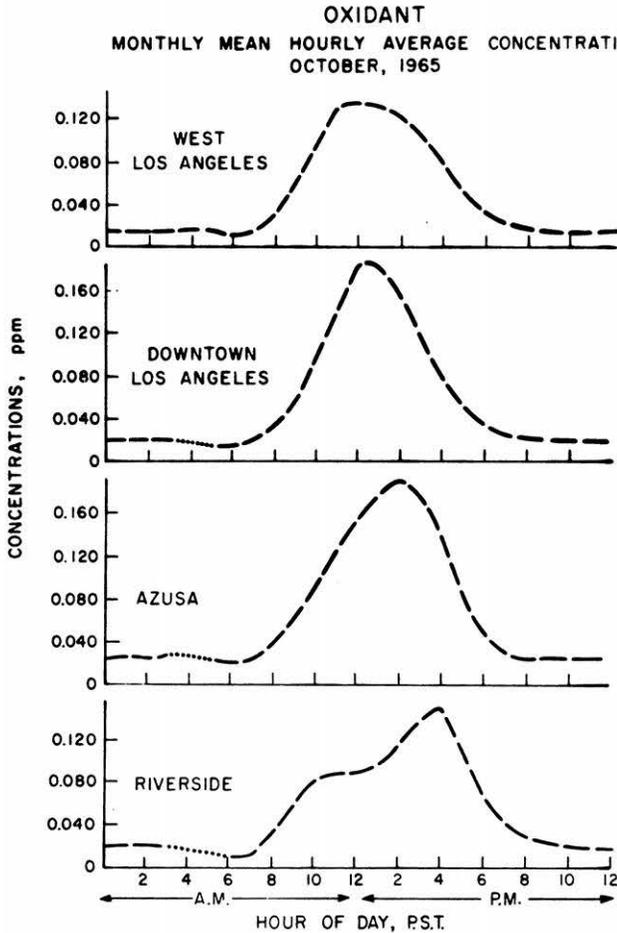


FIG. 9.—Oxidant level plotted against time of day at four locations in the Los Angeles area.

By the time the cloud reaches the east end of the basin the concentrations of PAN, ozone, and other noxious pollutants have nearly reached their maximum level. However, we still are not sure how this cloud moves from one end of the basin to the other in a matter of a few hours.

Basically, in the South Coast Basin 80 per cent of our problems are due to automobile exhaust. Incredible as it may seem we do not have a good material balance for automobile exhaust; that is, we do not have a complete analysis of its components. A chemist usually knows what is put into the system and then observes what comes out. So when dealing with an automobile one observes the compounds in gasoline, runs the gasoline through the engine, and then wonders what components are present in the exhaust. It is very difficult to do good atmospheric chemistry unless emission constituents and concentrations are known.

Fig. 9 shows the oxidant level versus the time of the day for four locations. The first (upper) graph is for West Los Angeles, the second for downtown Los Angeles, the third for Azusa, east of Los Angeles, and the fourth for Riverside farther to the east. In West Los Angeles, the oxidant level peaks just before noon; in downtown Los Angeles, at noon; in Azusa, about 2:00 PM; and in Riverside, about 4:00 PM. Not only the time of the oxidant peak but also the characteristics of the particulates seem to change at different locations. Last summer a cooperative study of aerosol chemistry was made at California Institute of Technology by S. Friedlander, Whitby of Minnesota, Charlson of Washington, and Mueller of the California State Department of Public Health. They studied not just particle size distribution but also composition. The study of the influence of aerosols on atmospheric chemical reactions is now a major area for new research.

Where do the primary pollutants come from? The primary pollutants are oxides of nitrogen, carbon monoxide, and hydrocarbons. It has been calculated and shown that 97 per cent of the carbon monoxide in the South Coast Basin originates from automobiles. An average pre-1968 car releases about 29 pounds of CO for every 10 gallons of gasoline burned. With four million cars in the South Coast Air Basin, they burn so much gasoline and drive so far that the average daily emissions of CO exceed 10,000 tons.

About 10,000 tons of the oxides of nitrogen are also produced daily in the basin. About 70 per cent of this is from autos and much of the rest from power plants. Of course, as car emissions are controlled, power plants are going to become a greater factor. When automobiles and power plants are controlled, what will be a major source of emission 10 years from now? The answer is household hot water heaters. Hot water heaters produce small concentrations of oxides of nitrogen. Combine 10,000,000 hot water heaters in one small basin and you may have problems. All such heaters may be redesigned or changed.

Other primary pollutants are particulates and sulfur oxides from the combustion of fuels. The sulfur oxides are primarily from automobiles, the sulfur being present in gasoline. These sulfur oxides are changed photochemically to sulfuric acid which is important in producing atmospheric haze.

Exactly how do atmospheric photochemical reactions occur? I am just going to mention briefly a couple of points in the mechanism. The spectrum of the sun represents that of a black body at about 6000°K. In the troposphere the solar spectrum is cut off at about 3000Å, so we are concerned with light in the region 3000Å and above. The major absorber of light in the atmosphere, as pointed out by Philip Leighton in his classic book, "Photochemistry of air pollution," is NO₂.

The absorption spectrum of NO₂ is shown in Fig. 10. In the region around 4300Å, it leads into a continuum. The primary quantum yield of the absorption process is zero at 4300Å, and becomes unity in the 3500Å region. Irradiation of an NO, NO₂, air and propylene mixture below 4300Å has yielded typical

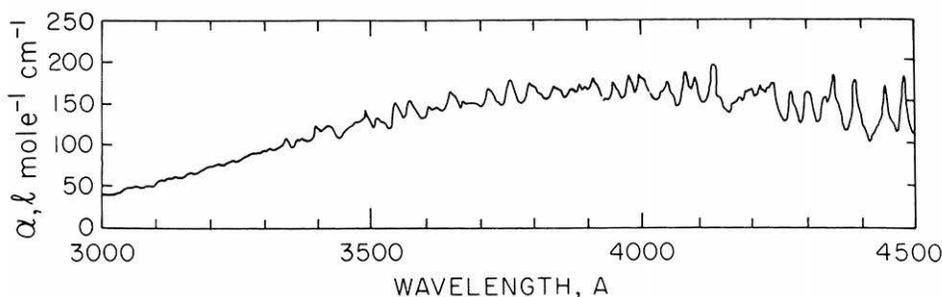
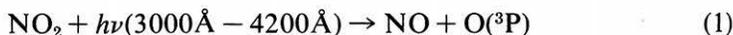


FIG. 10.—Absorption spectrum of NO₂.

photochemical smog products. Irradiation of the same mixture with light above 4300Å does not produce smog—at least not the typical gaseous products. This situation bothered us for some time because liquid products are possible, as well as reactions or condensations or both with reaction vessel walls. Two post-doctoral fellows in my research group were looking at the importance of wall reactions when they discovered one can isomerize a *cis*-olefin to *trans*-olefin or *vice versa* in a dark reaction with NO₂. The reaction is very clean and the kinetics are superb. The rate is slow but measurable. We are presently involved in irradiating NO₂-hydrocarbon mixtures in the visible region where preliminary results indicate compounds are forming and being deposited on the reaction vessel walls. More investigation is needed. The reaction is that of an excited state. Previous investigators did not see products simply because gaseous products or liquid deposits were not observed. One needs a total analysis.

Reactions 1 through 4 summarize the inorganic photochemical system.



With no hydrocarbons present one photolyzes NO₂ to get NO and O. The ozone then reacts to form O₂ and NO₂, with the NO₂ in a highly excited state, possibly a singlet state. We have been attempting to determine if singlet oxygen is present; however, the excited NO₂ emission is so intense it overlaps the 1.27-micron band where the singlet oxygen emission occurs. If no hydrocarbons are present, and just air or oxygen and NO₂, one obtains a dynamic equilibrium (reaction 4). With the addition of a hydrocarbon, the dynamic equilibrium is unbalanced, and NO is converted to NO₂, the hydrocarbon is oxidized, and reaction products such as aldehydes, nitrates, PAN, *etc.* are formed. When all of the NO has reacted, the amount of ozone begins to increase rapidly. Other pollutants such as PAN and aldehydes begin to form at

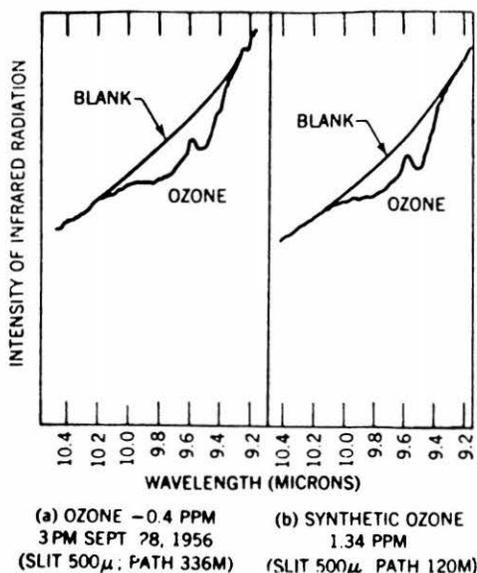


FIG. 11.—Detection of ozone in ambient air in south Pasadena, by LPIR.

various times. Incidentally, one of the most eye irritating substances identified in laboratory studies has been the phenyl analogue of PAN, peroxybenzoyl nitrate. It was identified by the General Motors Laboratories. The compound has not been observed in the atmosphere, but Dr. Stephens in our group, the discoverer of PAN, is now searching for it.

In the past, to analyze smog it was collected and condensed out of the air. Obviously, as the mixture was warmed the constituents would react with one another. One technique, long path infrared spectroscopy, has helped solve the problem. The instrument is basically a typical infrared spectrophotometer, but the cells are about one meter in length and about one third of a meter in diameter. The cells have multiple reflection mirrors that are adjusted to give a total path length of about 40 meters. The top of one of the tanks has windows for irradiation. Fig. 11 is a "classic" because it actually shows the first detection (about 15 years ago) of ozone in the atmosphere. The measurements were taken using a spectrophotometer with a path length of 336 meters.

Much of our understanding of atmospheric chemistry is derived from the results of "smog chamber" experiments. A smog chamber is simply a reaction vessel with an irradiation source that simulates sunlight. Frequently these facilities are large, with a volume of several hundred cubic feet, and have expensive instrumentation. Fig. 12 illustrates that atmospheric conditions can be closely simulated in chambers. During irradiation the concentration of NO drops as the concentration of NO₂ comes up. Also notice the increasing concentration of ozone and PAN. One can isolate many of the components of automobile exhaust and test them for reactivity individually. By testing the

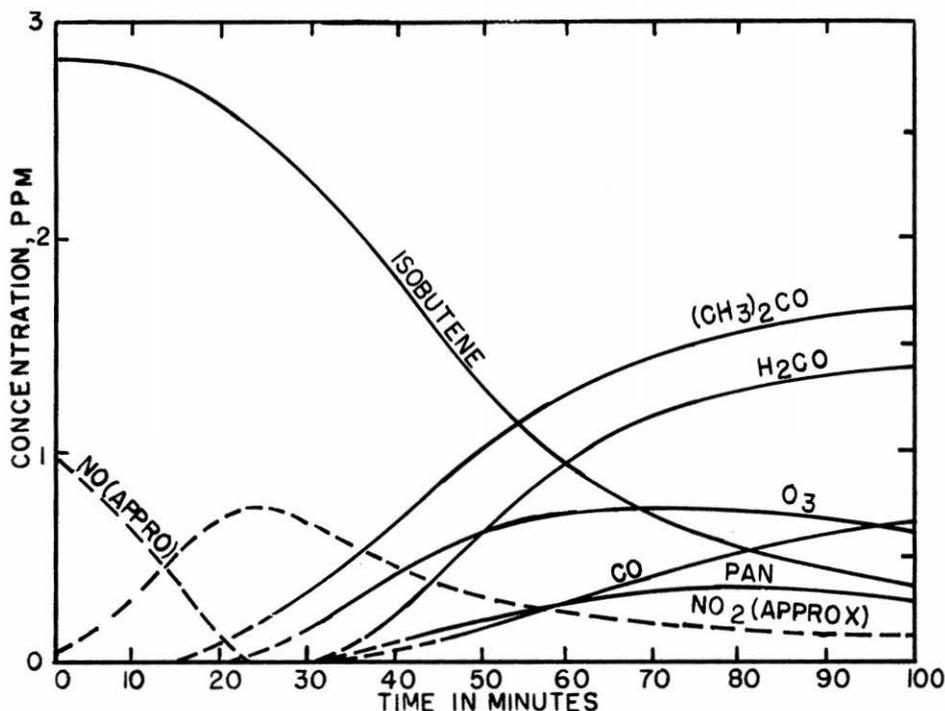


FIG. 12.—Concentration changes on irradiation of a mixture of nitric oxide (with some nitrogen dioxide) and isobutene in air. The times of first appearance of products are approximate.

individual components one can determine which are photochemically reactive and which we can use safely in an area plagued by photochemical smog. About a year ago, a firm decided to check the results from chamber studies. Known mixtures of propylene, air, and NO were irradiated in the chambers in various parts of the country. In all of the chambers used there was good qualitative agreement; however, there was no quantitative agreement. This study indicated that we need to know more about the influence of such fundamental chamber characteristics as surface-to-volume ratios, surfaces, light sources, and the effects of stirring.

Table 1 lists reactivities based on chamber-type studies. The reactivity can be measured in a variety of ways. How fast is NO converted to NO₂? How much ozone is produced? What is the eye irritation index? Table 1 ranks classes of compounds according to their chemical reactivities; this does not necessarily correspond to their reactivities based on eye irritation. Aromatics are sufficiently reactive to be of real concern. If lead is removed from gasoline the aromatic content may be increased to compensate. If the aromatics in automobile exhaust are to be increased one must be concerned as to whether the increase will produce more smog due to the photolysis of the aromatics. It is a highly debatable question.

TABLE 1.—Relative hydrocarbon "photochemical reactivities" in the system HC-NO-NO₂-AIR.*

Substance	Molar reactivity	Substance	Molar reactivity
C ₁ -C ₃ paraffins	0	Acetylenes	0
C ₄ and higher paraffins	1	Benzene	0
Ethylene	4	Toluene and other	
1-Alkenes	7	mono-alkyl benzenes	3
Internally double bonded olefins	8	Dialkyl and trialkyl benzenes	6

* Data from John Maga, California Department of Public Health, September 1966.

We will be carrying out some chamber studies at the Statewide Air Pollution Research Center. We are going to try to resolve some of the differences in results found among the various chambers. Our system will consist of two chambers, each with a capacity of 250 cubic feet. One of the chambers will be a glass cube and illuminated by black lights. This system will be similar to others in existence. Adjacent to this chamber will be a cylindrical chamber six feet in diameter with quartz windows. A large parallel beam of light will fill nearly the entire diameter of this cylinder. The chamber will be evacuable, so degassing is possible. The light source is a 10-kilowatt solar simulator that has been used for NASA studies of outer space. It will be possible to operate both chambers side by side using a set of common intake gases and analytical techniques. By using both chambers it is hoped that many chamber problems will be solved and a lot of atmospheric photochemistry will be conducted. We also hope to insert particles into one of the chambers to simulate aerosols and observe what chemistry occurs.

The evacuable chamber has been designed so that it can also be used to simulate the atmosphere at 65,000 feet. A solar simulator is available, and the windows are quartz, so chemistry at 65,000 feet can be more easily simulated. This will help scientists determine what chemistry will occur if the SST flies in this region of the atmosphere.

Dr. Coomber in my group showed that one can actually have energy transferred to produce singlet oxygen in the ppm range. The energy transfer has been done by other techniques, but he did this by using tetramethylethylene as a trap and showed, in fact, that one can produce singlet oxygen in a variety of ways. One method of producing singlet oxygen is by direct absorption; another method is by energy transfer. The photolysis of ozone is another definite source of singlet oxygen. The last method, the exothermic chemical reaction, is interesting. Professor R. W. Murray of the University of Missouri at St. Louis has shown that when various compounds react at low temperatures singlet oxygen is released. We tried many of them in the gas phase. Dr. Steer (a member of my group) showed that the reaction of diisopropyl ether and ozone produces singlet oxygen.

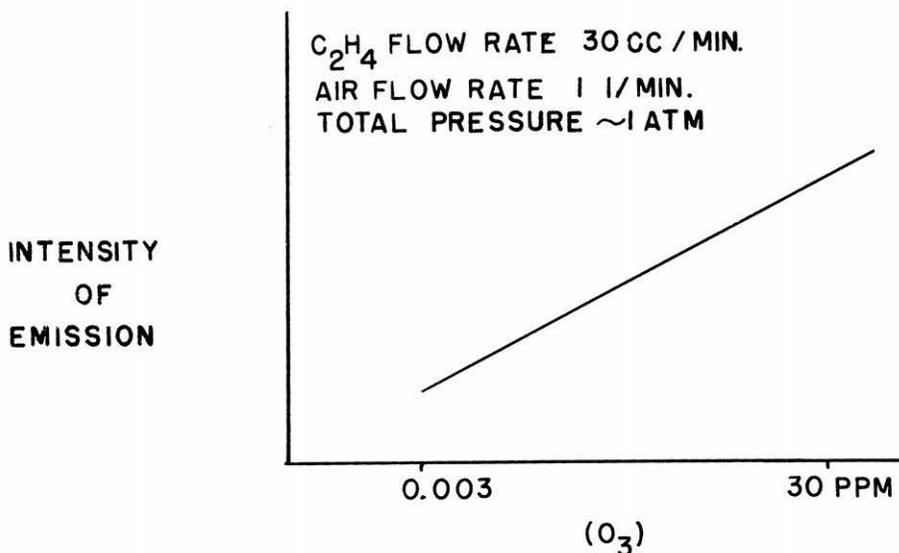


FIG. 13.—Ozone monitoring using ethylene-ozone chemiluminescent reaction (J. A. Hodgeson, personal communication).

This interest in exothermic chemical reactions led us to look at the base-catalyzed hydrolysis of PAN, which was known to yield oxygen (reaction 5).



Could this oxygen be singlet oxygen? If the oxygen were singlet oxygen, one then could have a way of bringing singlet oxygen to the cell tissues of the lung, inasmuch as we breathe PAN daily. Dr. Steer and Dr. Darnall (also a member of my group) tried the experiment and singlet oxygen was detected upon hydrolysis of PAN. So it is possible that when one breathes PAN it is hydrolyzed and singlet oxygen is produced in the lungs.

After finding the reaction of ozone with isopropyl ether yielded singlet oxygen, we began further investigations of the reactions of ozone with olefins. Dr. Steer detected no singlet oxygen in his experiments. We did know, however, that one of the most accurate techniques for measuring ozone was by a very clean chemiluminescent reaction involving the reaction of ozone with ethylene. The nature of the emitting species is not clearly defined at present. This reaction is utilized in a commercial instrument that has a linear response from 0.03 to 30 ppm of ozone (Fig. 13). The work has been conducted primarily through an APCO contract.

Other olefins yielded no chemiluminescence when reacted with ozone at one atmosphere, so other investigators ignored them. We tried some reactions at 0.5 torr and it appears that this emission occurs with ozone plus many other olefins in addition to ethylene. The emission is also noted with mercaptans and with disulfides. Ethylene, which is apparently the only olefin that

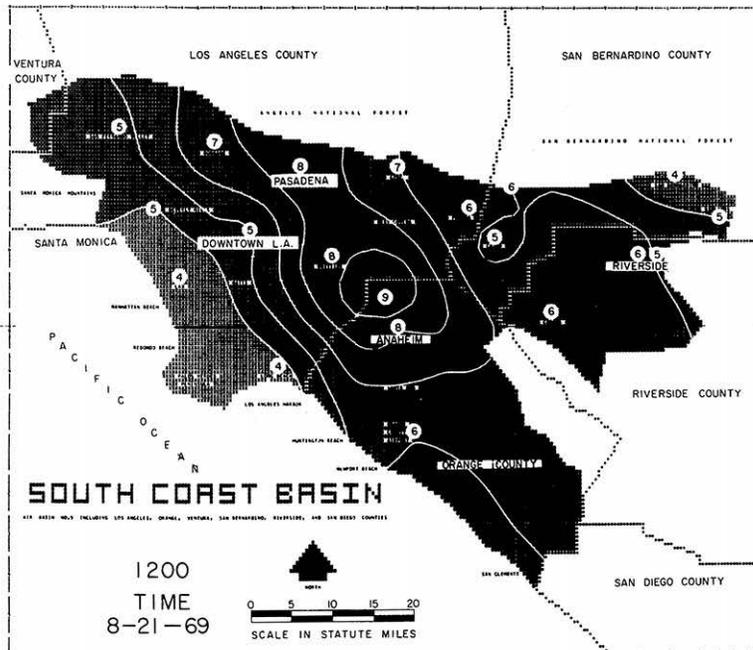
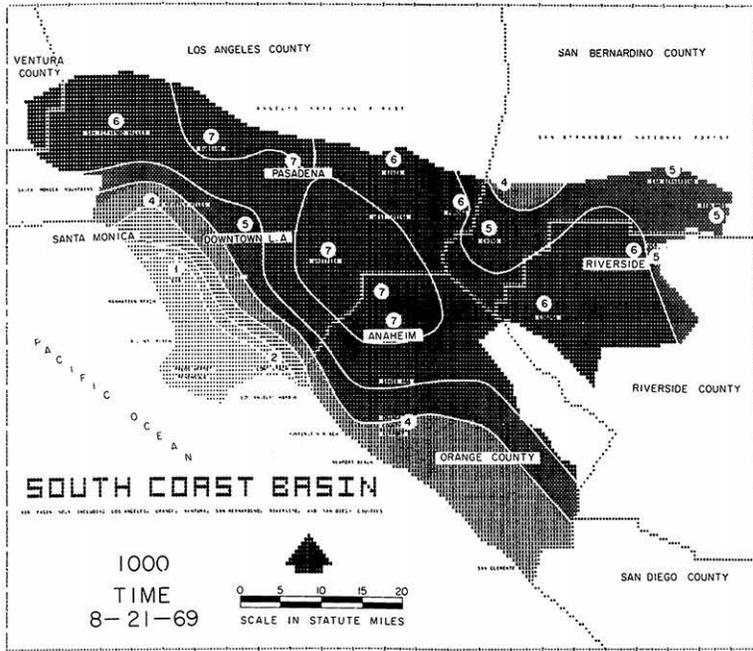


FIG. 14. — A series of computer-drawn contour maps based on data from 20 monitoring stations in the South Coast Air Basin recorded 21 August 1969.

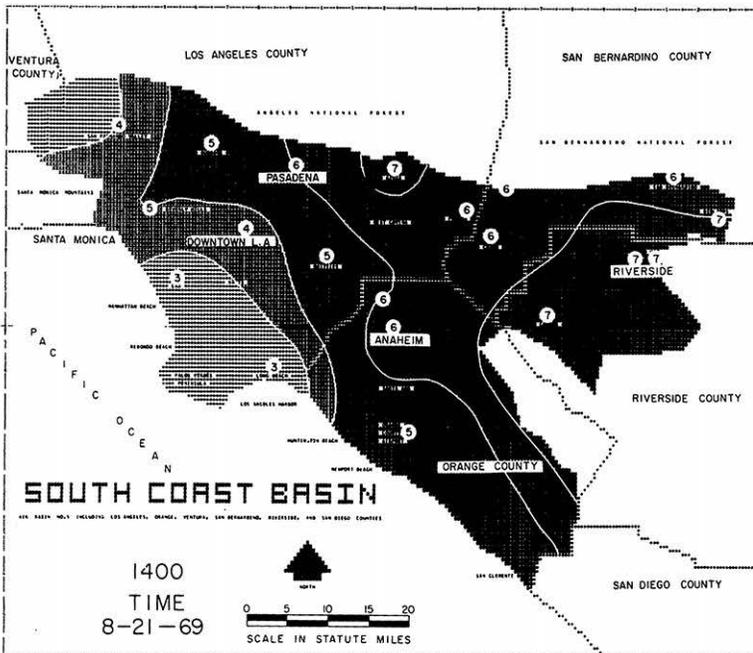
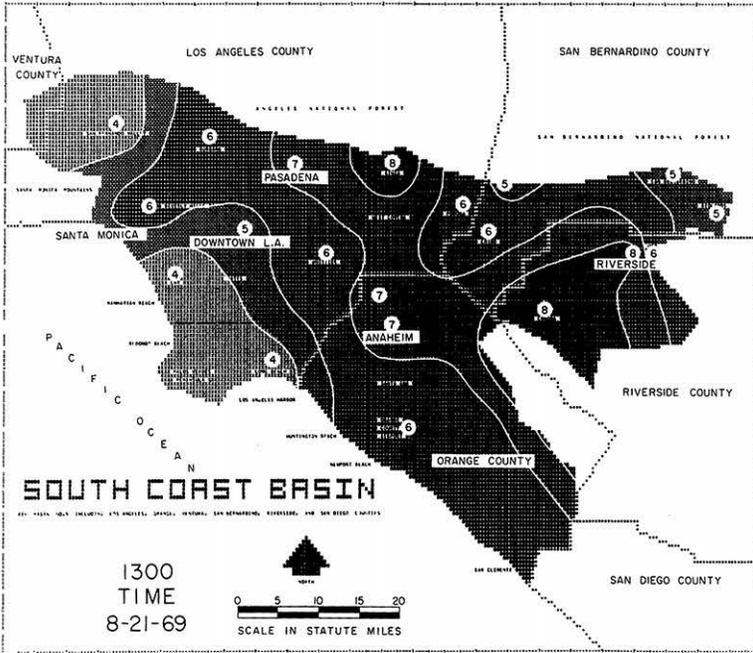


FIG. 14. - Continued.

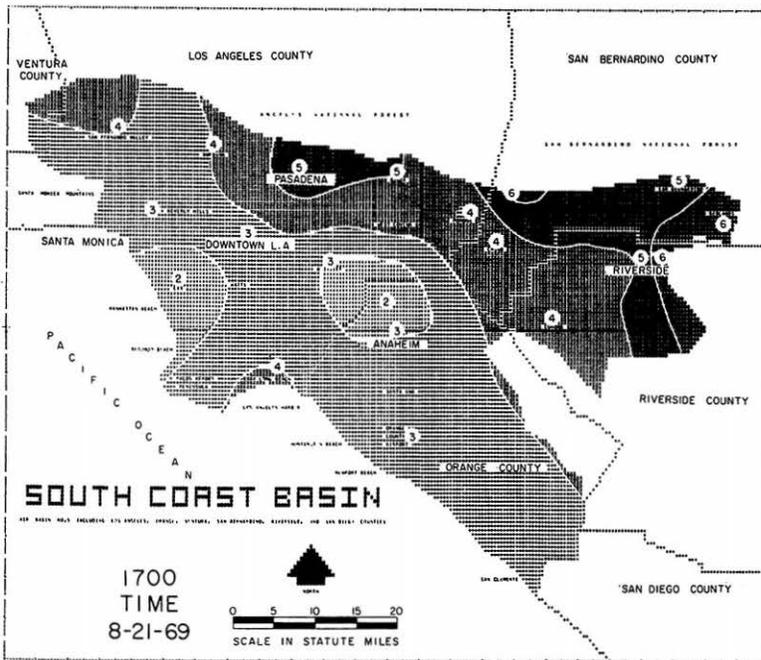
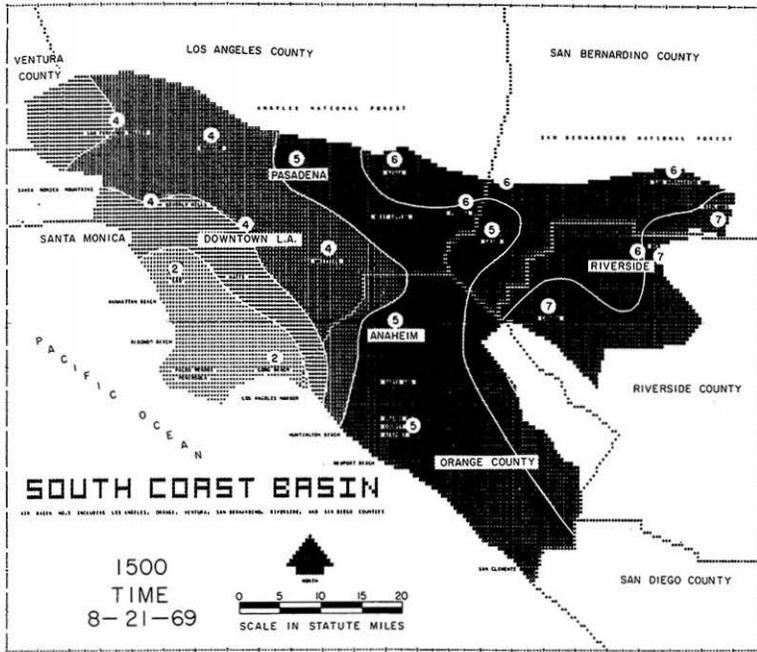


FIG. 14.—Continued.

emits at one atmosphere, is the poorest emitter at 0.5 torr. Butene is about 10 times as sensitive as ethylene, hydrogen sulfide about 25 times, and methyl mercaptan 2000 times as sensitive. We are looking at this phenomenon now from the viewpoint of fundamental pressure studies. It may prove valuable in the design of a new ozone detection system.

Getting back to pollution control, one would like to have a model that would allow prediction of the effect of a particular control method on the atmospheric conditions. Inasmuch as there is generally not enough information for this complete model, what can be done with the data that are available? For example, in the South Coast Air Basin there are 20 monitoring stations recording air quality data. One doesn't get a good overall picture of the basin from these sparse, widely scattered points. However, a group at Harvard has developed a computer program to produce contours from these data. Last year, Dr. Behar of the Statewide Air Pollution Research Center used this program to calculate the oxidant levels throughout the basin on a given day using the hourly average oxidant levels for 21 August 1969, obtained from each of the 20 air monitoring stations. The level of oxidant is shown by degree of blackness. The California health related standard for oxidant is 0.10 ppm for one hour. The area of the calculation is bounded by the coastline and by the 1500-foot elevation contour.

At 6:00 AM, the oxidant level was very low (<0.05 ppm) throughout the basin. After sunrise, the oxidant increased rapidly, and by 10:00 AM a high concentration of oxidant had formed in the middle of the basin. During the afternoon you can see that the oxidant moved east across the basin (Fig. 14). By 8:00 PM the oxidant level was again down to background level.

DISCUSSION: LEADER, DR. N. C. YANG

Dr. Shulman.—Lloyd Kruetzer in our laboratory has an operating tunable infrared laser spectrometer with a source of power more than 1,000,000 times higher than glow bar, and its sensitivity is correspondingly about 1,000,000 times greater. He goes out into our parking lot with a little one-cubic centimeter flask and fills it up by capping it and brings it in. He analyzes the sample with this spectrometer by looking at the nitric oxide lines, which is what you were looking at. If he dilutes by a factor of 1000, he gets it to go onto the scale. This is one centimeter of path and one centimeter of light. So this is an operating machine.

Dr. Pitts.—I think we should get together; I would like to hear more about this.

Dr. Kasha.—Every time I go to Los Angeles and read the *Los Angeles Times*, I see horrendous news. I think that the last time I was there, a year ago, there was a plan exposed by some county commissioners on how to cope with the doubling of the population of Los Angeles. Now, you mentioned that this is an economic problem. It appears to me that fighting that kind of propagandistic concept of the disaster area is the hardest thing in the world, because you are dealing, at least, with a doubling of input at the same time that you are trying to control it with these smaller decrements.

Dr. Pitts.—I am glad you made the point, because it is critical, mechanistically.

Dr. Kasha.—George Hammond and I were talking about socioeconomic effects.

Dr. Pitts.—At the University we provide both fundamental and applied data and provide options to people. We do not take a protagonistic or antagonistic approach; we write options. If you accept an air quality standard for oxidant of 0.1 ppm, then these things must follow. You have either so many power plants or so much freeway. The reason I said earlier that technology is not going to solve the problem is that so much of the total problem is socioeconomic. "What do you really want to do here? What are we going to do?" Bob Brattain, whom a number of you know, made a survey based on the assumption that everything worked. He took the best case estimate where the 1975 and 1976 controls worked, and the power plants were controlled; he then made the second assumption that the population followed normal growth in the Los Angeles Basin, and then assumed that smog intensity was proportional to emissions. Do you know what he found for 1980? In the South Coast Air Basin and in the San Francisco area, instead of having 213 days you would have 100 days when you exceed the health standard. Instead of oxidant reaching 0.70 ppm, as it did last year, it would reach only 0.35 ppm. That's 10 years of controls with everything working. Then he made the calculation for 1985 assuming that everything was working and predicted 50 days when the health standard was exceeded. So, our committee reported this to the state. People listened, but they did not believe we meant that in order to reach accepted air quality levels in the South Coast Basin, energy would have to be rationed. Option one: ration gasoline. The only time that emissions dropped in the last 30 years was during World War II. I am not saying it is a great idea, but it is a possibility. You can ration fuel for power plants. You can change completely the whole concept of the city Chamber of Commerce. You can think of urban transit systems. There is a whole variety of these options. I might say that people are taking it seriously enough that we are now preparing a set of options, socioeconomic options, technological ideas, assessment of feasibility, assessment of cost, and assessment of impact on society. These are being prepared now by the Air Resources Board of the State of California.

Dr. Hammond.—I would like to say, in response to what Michael Kasha said, that a lot of the rap is hung on the Chamber of Commerce, which does stupid things like wanting to increase the population; yet the fact of the matter is that we reached the point a few years ago where the population of our migration into the Basin became negative. The total population is still increasing because of births, but I think some of the most important studies that I have seen are those by John West at California Institute of Technology, relating to things that Jim Pitts was talking about. That is, given all this optimization in terms of air pollution, and an absolutely constant population but with an annually increasing per capita power consumption (which has been the standard established over the last 30 years, and which is used in most extrapolations by power companies at the present time), then by 1990, which is pretty soon, the principal problem in the Valley will be related to thermal loading. The increase in the ambient temperature will be very large and will overwhelm this particular problem. It is amazing to see how little that particular kind of projection is affected by moderate adjustments in the population growth. If the population grows 2 or 3 per cent per year, or even if it stays constant, it makes very little difference. The thing that really counts is our individual appetite for using power, and that is what Jim Pitts is talking about; we've got to change our appetites.

Dr. Kasha.—In biological phenomena, one of the most startling things is periodicity related to the rising of the sun, and here, of course, you are very conscious of the diurnal periodicity of the smog components. Have you ever tried to estimate what would happen if Los Angeles was turned upside down in working schedule? Suppose everyone drove their cars at night, and in the daytime they either slept or went out into the sun—it's there, you know, on the beach. Is it possible that the delivery of the nitric oxide, say at midnight instead of at dawn, would change the entire problem?

Dr. Pitts.—That is a good point, and it is not at all farfetched, because starting work two hours earlier has been proposed by one of our county supervisors.

Dr. Hammond.—If you do that, and do not change anything else, the rate of power consumption will rise even faster! This is a very serious thing, because work at night does increase, for a very

natural and normal reason, power levels. It may be engineerable, but it is going to take a very different kind of home and industrial engineering than those with which we are now familiar.

Dr. Pitts.—Zero population growth would never allow it. It is very strong in Beverly Hills.

Dr. X.—Do we have a figure for how many BTU's are recorded by the sun as opposed to man's engines?

Dr. Pitts.—We can get the number.

Dr. Y.—Professor Pitts, I wonder why the smog is less in January than in June?

Dr. Pitts.—It just rains more, the temperature is lower. We have had some of our worst days in January when we had bright sun; smog is just less frequent in January than in June. I was out there 15 years ago; there was no problem, just a couple of days each year. Pasadena hasn't gotten any worse. This is the interesting thing—Pasadena is just as bad now as it was 15 years ago, no worse. What has happened—Phil Leighton predicted this—is that when you double the size of a city and double the population, thus keeping the same density, the activity that George Hammond was referring to does not merely double but increases by a factor of 20. People do not realize that men's activity is not a linear function of population. Another part of our problem is that in the United States as a whole, cars reproduce faster than people, and the birth rate is two cars per child.

PHOTOCHEMICAL DYNAMICS

GEORGE S. HAMMOND

Chemical changes caused by light hold as much natural fascination for man as almost any known chemical phenomena. Storage of solar energy by photosynthesis in green plants is basic to sustaining life on this planet. Vision depends on photochemical response to light falling on the rods and cones in the eye; animals without eyes and most plants show phototropic response to light. Sunlight initiates the sequence of chemical changes by which polluted atmospheres are ripened to form the noxious mixture that we call smog, and sunlight is involved in the slow degradation of many materials in ordinary outdoor usage. Ten years ago this phenomenon was studied by chemists in industrial laboratories with the object of prolonging the outdoor lifetime of synthetic fibers, films, and other products. At present, the emphasis is changing, as values of society change, and attempts are being made to incorporate additives in some plastic materials to increase their rates of destruction on outdoor exposure, because industrialists are sensitive to mounting concern about the problem of solid waste disposal.

The greatest technological future of photochemistry probably lies in two areas: one already developed but still growing, and a second, which is in its infancy. Photochemical changes have characteristics that make them almost uniquely attractive for use in control systems, and for information transfer and storage. Speed of response and very modest requirements for energy to make significant response are responsible for this potential. Interestingly, the most dramatic functional example has been developed by nature, rather than by human technology. The speed with which a light signal falling on the human eye registers in the brain is so familiar that no one marvels at the phenomenon. However, the common feeling for the concept expressed in the word "instantaneous" is directly related to the rate of visual response. Remember that "seeing" involves a whole series of chemical changes. First, absorption of a photon by the retina of the eye initiates a series of reactions that change the chemical structure of a protein molecule in one of the visual rods. This change triggers a chain of chemical responses that propagate a message sent along the optic nerve. Finally, a completely unknown chemical change registers the signal in the brain. Careful study has led to the conclusion that a single photon falling on a rod in a dark-adapted human eye can evoke a detectable response in the brain. The energy required to evoke this response is approximately 7×10^{-19} calories, a billionth of a billionth of one calorie.

The most spectacular technological exploitation of the speed and sensitivity of photochemical response is the photographic process. A common photographic film contains fine grains of a silver halide. The surface of a grain is changed by light, thereby storing information. The information is then read out by the developing process in which the changed chemical reactivity of a

light activated grain is exploited to magnify the effect of the original photochemical change manifold.

Work goes on continuously in many laboratories aimed at development of new and different photoimaging systems based entirely upon organic compounds, rather than silver halides. The reasons for this effort are obvious. Silver halide photography is expensive and not adaptable for all conceivable uses. Moreover, there is an inevitable prospect that the known reserves of silver ores in the world will be largely exhausted early in the next century if we continue consumption at the present rate; half of the silver now mined finds its way into photographic film. At the present time I know of no completely organic system that approaches the speed and contrast achievable with silver bromide film. However, nonsilver photoimaging systems have been developed for many kinds of applications, such as the omnipresent office copying machines, which help to fill our lives with paper and information. Is anyone old enough to remember life before Xerox?

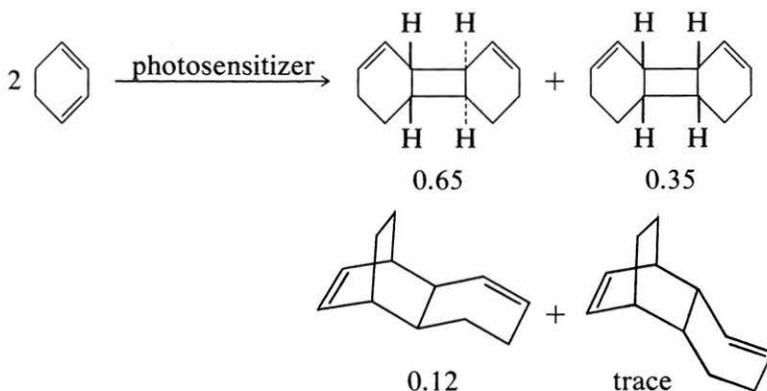
Use of photochemistry in the world's energy economy has a principal long range focus, increased storage of solar energy in usable form. Solar energy arrives at the earth's surface at the rate of about 10 calories per square meter per minute, which is equivalent to 1.7×10^9 watts per square mile. A maximum of about two per cent of the incident solar energy can theoretically be stored in the form of carbohydrates by photosynthesis. However, much of the earth's surface, though well bathed in sunlight, is almost totally barren for various other reasons. Whether or not we can potentially count on use of the oceans to become the site of greatly extended photosynthetic activity is a moot question because of the delicacy of the oceanographic ecological balance. However, the current rate at which energy is stored by photosynthesis probably does not exceed one-tenth of one per cent of the total incident solar energy. Perhaps this amount can be increased several fold by ingenious management, but I believe that at some future time man will augment the natural photosynthetic process by use of photochemical systems which are far less dependent on the natural water cycle. I doubt that any of us will live to see the deserts of the world "farmed" photochemically. However, the prospect should be thought about, along with consideration of the future consequences of the rate at which we are depleting reserves of energy stored in the form of fossil fuels.

A photochemist derives some emotional benefit from consideration of the ways in which his field of science might impact on the affairs of man. However, most of us require some more modest goals to sustain our interest and enthusiasm. This is the short range game-playing that constitutes the backbone of scientific progress. The last dozen years have been an especially active period in photochemistry, although the field has been active at least since the time of Cannizzaro. I propose to talk about recent progress and the kinds of problems that lie immediately before us as I see them. Examples will be drawn mainly from the work of our own research group, not because they are the best examples, but because they are the easiest with which to deal.

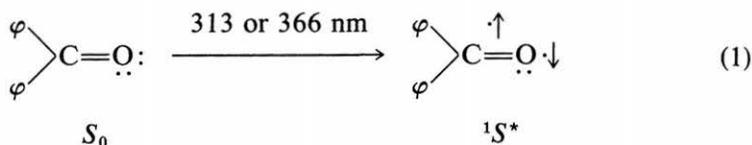
In principle, we wish to be able to give a detailed description of the course of a photochemical reaction, from the time that a molecule is excited by absorption of light to the time when a new chemical species is produced in thermal equilibrium with its environment. In some ways study of photochemical mechanisms is more difficult than study of thermal reactions and in some ways photochemistry is easier. The advantages arise because the excess energy injected into the system by light absorption is usually localized in individual molecules and one does not begin with a problem involving statistical partition of energy among all the molecules in the system. The critical changes occur while excitation energy is still localized at the molecular level. Difficulties arise because the time scale on which the critical events occur is short enough to require special techniques to monitor the behavior of excited transients directly.

Sorting out the steps and quantitative documentation of the partitioning process that occurs during decay of excited molecules is an important and fascinating game. However, our real objectives are to produce viable generalizations concerning the relationships between chemical structure and photochemical reactivity. This is the point at which we encounter problems entirely different from those known from study of thermal reactions. The familiar semi-empirical theory of the rates of thermally activated reactions turns out to be inapplicable in principle to systematic description of photochemical dynamics. The same is true of any chemical dynamic phenomenon that is an energy relaxation process, so it is not surprising that people who work in hot atom chemistry have arrived at essentially the same basic outlook as photochemists. The fact of the matter is that our dynamic problems have much in common with those encountered in understanding the decay of unstable nuclei.

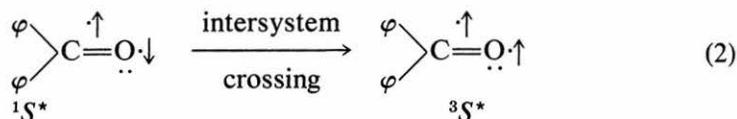
I would like to look at a few familiar photochemical reactions as a help to establishing ground rules. Consider the photochemical dimerization of 1,3-cyclohexadiene, a relatively simple hydrocarbon—work first carried out by Nicholas Turro and Donald Valentine.



The reaction can be effected by any number of photosensitizers, of which benzophenone is a familiar example. Absorption of light in the region around the 345 nm maximum in the spectrum of the ketone gives rise to an excited singlet state having the n,π^* configuration in which an electron is promoted from a nonbonding oxygen orbital to an antibonding π orbital.



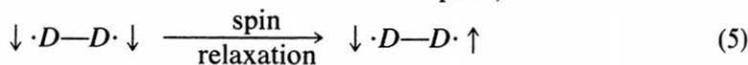
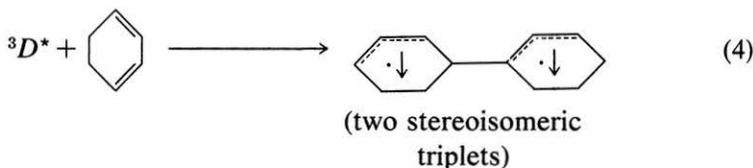
Many lines of evidence indicate that the excited singlet state of the sensitizer crosses very rapidly to a triplet state.



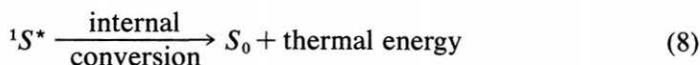
The triplet state has a relatively long lifetime, about 10 microseconds in hydrocarbon solvents at room temperature. Although phosphorescence from the triplet is weak, it has been observed in many laboratories. However, the sensitizer triplet is efficiently deactivated by collision with many kinds of molecules, such as cyclohexadiene. The deactivation process involves transfer of electronic excitation energy to the quenching molecule.



Reaction of diene triplets with diene ground state molecules leads to formation of the observed dimeric products. We have a strong predisposition to formulate the addition reaction as involving three discrete steps.



Beginning with the absorption process, we believe that there are probably five discrete steps leading to formation of the product. Each step is actually, or potentially, competitive with other decay modes. The excited singlet state of the sensitizer might decay to the original singlet ground state by either radiative or nonradiative paths.



The popularity of benzophenone as a sensitizer arises in part from the fact that reactions 7 and 8 are negligible in competition with reaction 2, intersystem crossing. With other useful sensitizers this is not the case. For example, naphthalene sensitizes the dimerization reaction, but the quantum yields at any given diene concentration are lower than those observed using benzophenone. The reason is made evident by the fact that the familiar fluorescence of naphthalene is readily observable. Obviously intersystem crossing is not overwhelming in competition with radiative decay. By adding the limiting quantum yields for the triplet sensitized reaction and the quantum yield for fluorescence, we find that, within experimental error, the sum is unity. Apparently naphthalene does not undergo unimolecular nonradiative decay from the ${}^1S^*$ to the ground state. This is a rather common observation with fluorescent molecules and has led some workers to the conclusion that nonradiative decay, ${}^1S^* \rightarrow S_0$, is an uncommon process. Consideration of nonfluorescent materials shows this to be a specious generalization. An excited singlet state of 1,3-cyclohexadiene is produced by absorption of 254 nm radiation, which is close to the first absorption maximum in the spectrum of the diene. However, no fluorescence is observed. Furthermore, chemical evidence shows that decay does not occur by way of the triplet state because triplet dimers, formed in the sensitized reaction, are not produced by direct excitation. The only important reaction caused by radiation of wavelength 254 nm has been shown by Dr. Thomas Penner to be ring opening to *cis*-hexatriene.



Reaction 9 occurs with a fairly high quantum yield, about 0.4; but it is clear that a large fraction of the electronic excitation energy is degraded to thermal energy without destruction of the original molecular structure.

Still more can be learned by study of cyclohexadiene. In order to complete the mechanism for sensitized dimerization we must add the steps which lead to unproductive decay of sensitizer and diene triplets.

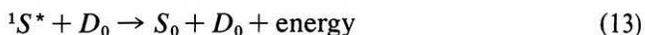


We can then formulate the predicted relationship between the quantum yield for dimerization and the concentration of diene.

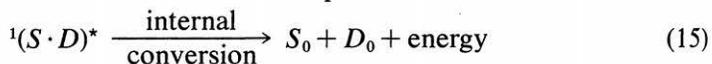
$$\Phi_D = \left(\frac{k_2}{k_2 + k_7 + k_8} \right) \left(\frac{k_3[D]}{k_3[D] + k_{10}} \right) \left(\frac{k_4[D]}{k_4[D] + k_{11}} \right) \quad (12)$$

distribution of $^1S^*$ distribution of $^3S^*$ distribution of $^3D^*$

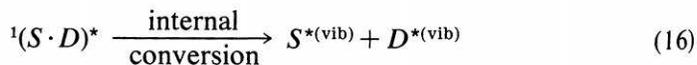
Dr. George Vesley found that equation 12 fits data obtained by study of the naphthalene sensitized reaction for low concentrations of the diene. However, at concentrations of the diene above 0.5 molar, the quantum yields fell off sharply instead of increasing as predicted. Superficially, this is a kinetic atrocity since the rate of a bimolecular reaction falls as the concentration of the reactant increases. Obviously the mechanistic model is inadequate. The inadequacy was easily resolved by correlation of Vesley's results with those obtained essentially simultaneously by Dr. L. M. Stephenson. At high concentrations the diene quenches naphthalene fluorescence.



The process is clearly an example of accelerated nonradiative decay. Electronically excited states of the diene are not produced, inasmuch as chemical reactions characteristic of excited diene triplets or singlets are not observed. Our model for this reaction is:



We conceive the exciplex as being weakly bound by a variety of forces, including excitation resonance and charge transfer. Most striking, however, is the enormous acceleration of the nonradiative decay process. I believe that there must be some close connection between the "catalyzed" process and the very efficient nonradiative decay of the diene from its own excited states. There must be some way in which the exciplex "borrows" the rapid decay properties of the quencher. Nonradiative decay is often called "internal conversion," reflecting a model in which electronic excitation energy is transferred to nuclei and appears as molecular vibrational energy. In our model for the catalyzed process, we visualize weak electronic interactions between the partners as being required to allow excited electrons to "get their fingers on" nuclei, and appropriate vibrational modes in the quencher. A clear prediction of the model is the fact that a large part of the vibrational energy produced by internal conversion should be deposited in the quencher.



This view is confirmed by a number of examples in which we have observed isomerization of quenchers as a part of such nonclassical quenching reactions.

Returning to cyclohexadiene, I would like to mention still another phenomenon recently discovered by Drs. Penner, McGregor, and Boharel in our laboratory. In the process of doing control experiments for another study, Penner irradiated neat cyclohexadiene with light of 313 nm, a wavelength longer than is usually absorbed appreciably by the diene. Chemical reaction occurred, leading to some ring opening (reaction 9), but dimeric products were also formed. Included are the dimers produced by triplet sensitization, but in new relative amounts. Three new dimers are also formed. This phenomenon is of obvious interest because a great deal of the effect of sunlight on various materials arises from absorption of light at wavelengths longer than those normally expected to be absorbed by the materials. We believe that the new chemistry is turned on by absorption by pairs of neighboring molecules, or possibly by molecular aggregates, to produce excited dimers having configurations different from those produced by diffusive encounters between a preexcited molecule and a ground state species. If this view is correct, we must visualize decay processes that channel the system into new chemical paths that are faster than configurational equilibration in the exciplex.

I have illustrated the multiplicity of decay paths for electronically excited molecules. Really useful theory must help us to think systematically about all of these dynamic processes. Only one, radiative decay, is at all well understood at this time. It is clearly the microscopic reverse of light absorption and all of the accumulated theory transition probabilities for absorptive interaction of molecules with electromagnetic radiation are directly applicable to emission.

It is my own view that all other modes of decay of excited states, chemical and nonchemical, involve essentially the same phenomenon—transfer of energy from electrons to nuclei. Because of the enormous differences in masses and velocities of electrons and nuclei, such energy transfer is relatively improbable. That is of course, the reason that stationary state molecular quantum mechanics has been so successfully based upon the separation of the electronic and nuclear factors in molecular wave functions. Now we know that some coupling between electronic and nuclear motion must be introduced in order to have even a correct formalism for dealing with the dynamic problems. A great deal of effort has been invested in calculation of electronic wave functions for excited states of molecules and the effort is being extended to include very extensive exploration of potential energy surfaces in some simple cases. This kind of information is potentially valuable, because the problems in transition probability can be set in a common form.

$$p = |\langle \psi_0 | \alpha | \psi_{ex} \rangle|^2 \quad (17)$$

However, molecular wave functions of even the finest quality will help us only in an intuitive way unless we can also develop credible models for the perturbation operator, α , which mixes the initial and final states. Because we recognize that electronic-nuclear coupling is a part of the process, we know

that the operators and perhaps the most useful kinds of wave functions will be of types unfamiliar to most of us.

At the present time my own hope is to find experimental solutions to equation 17 by looking at such quantitative results as we may be able to achieve in laboratory study. Perhaps continued reflection about the pattern of these results will lead through stages of semiempirical generalizations to a new generation of viable, nearly *ab initio*, theories of excited state dynamics.

ACKNOWLEDGMENTS

This paper is dedicated to the memory of William P. Baker, Jr., who initiated photochemical studies in our research in 1952. Dr. Baker's untimely death on 13 March, 1971 brought to an end a relationship of great personal value and at the same time reemphasized to me the importance of truly seminal work in science. This is contribution no. 4456 from the Gates and Crellin Laboratories of Chemistry.

DISCUSSION: LEADER, DR. N. C. YANG

Dr. Yang.—You may perhaps know that Peter Rentzepis of Bell Telephone Laboratories measured the rate of intersystem crossing in benzophenone derivatives using a mode-lock picosecond laser source, and obtained a rate of $\sim 1.4 \times 10^{11}$.

Dr. Hammond.—Yes, that's right. He is within a factor of two of Hochstrasse's results.

Dr. Yang.—This same point brings another comment: in this type of molecule (benzophenone and other related carbonyl compounds that we have been investigating), intersystem crossing may actually compete favorably with vibrational relaxation within the singlet manifold.

Dr. Herndon.—I wanted to make the comment that dimers of two molecular species that are the same are not necessarily repulsive. It depends on the relative geometry of the two molecules and their symmetry. We have experimental evidence from NMR spectra for isoprene dimers in solution, and also for a complex of isoprene and benzene. The evidence comes from looking at the chemical shift of the isoprene as you dilute it in benzene. The chemical shift is dependent on both the chemical structure of the solvent and the concentration. The equilibrium constant for the formation of that molecular complex is of the order $K = 2-3$ and the temperature dependence gives $\Delta H = 4-5$ kcal/mole. The complex is quite a stable species.

Dr. Shulman.—I have two questions. First, how does equation 5 differ from equation 6, and second, was there oxygen in your neat cyclohexadiene?

Dr. Hammond.—It is hard to write formulae that might make this model a little clearer. There would be the singlet, if you will pardon the expression, biradical, which then undergoes the geometric accommodation for ring closure. If anyone had a strong reason to want to try to compress equations 5 and 6 into a single step, I could offer no argument against that; this is simply a model. The question about the effects of oxygen: in the peculiar photochemistry that we see on irradiation of cyclohexadiene, very concentrated solutions are needed, and as to long wavelength radiation—apparently there is none. Now, we religiously did as we always do, and got the oxygen concentration as low as possible; this is a fetish with photochemists. However, we did not rigorously exclude oxygen in the absorption spectral measurement, and now realize that we must do so in order to be certain that the observed absorption is related directly to the photochemistry.

Dr. Shulman.—Is there a wavelength dependence of the dimer product yield in the irradiation at 313 nm of the cyclohexadiene?

Dr. Hammond.—The only wavelength-dependence we really know is that if you jump to 254 nm the dimerization becomes negligible. We presume that this is a consequence of the fact that all of the light is absorbed by monomeric species.

Dr. Shulman.—I was wondering whether there might be hot triplets dimerizing. Could that be possible in a concentrated solution?

Dr. Hammond.—Well, there is a hot something! The furthest one can go toward making hot triplets, knowing what you are doing, is to put a little benzophenone into neat cyclohexadiene and hope that you will make triplets with some excess energy because the energy transfer step is exothermic. So it does not mean a whole lot. That does not change the dimer distribution.

Dr. Shulman.—The second point relates to what was mentioned before about the NMR spectra. Is it possible that the divergence of your equation 14 at high cyclohexadiene concentrations would show up in some NMR shifts of either S_0 or D_0 ? If there were a ground state complex you would see it.

Dr. Hammond.—No. Fluorescence quenching fits perfect bimolecular kinetics. The case studied by Vesley is one example from probably 50 or 70 cases of such quenching. We have looked for ground state interaction, occasionally by NMR spectroscopy, but principally by absorption spectroscopy. We see no evidence, and the kinetics of quenching fit ordinary second order kinetics with limiting rates that approach the diffusion controlled limit.

Dr. McGlynn.—Relative to Dr. Herndon's comment and your own concerning the necessity for a complex entity to have some stability in order to have absorptivity associated with it, I would like to point out that this is not at all necessary. It merely is necessary only to have interaction. This interaction might very well be repulsive and still provide all the absorptive intensity that is needed. A case in point here is some calculations connected with what are called contact-charge-transfer entities and also some other calculations in the literature concerned with things that are called contact excimers, even though they do not, in fact, exist. My second comment is in the nature of a question. The diene that you have studied is analogous to *s-cis*-butadiene. I recall that in the case of ethylene, the first singlet-singlet absorption band (vibrational) that was observed in the gas phase, is probably the 0-0 or 0-11 member of a vibronic progression in the electronically excited state. There is no reason why, to my lack of knowledge at the moment, a similar sort of occurrence might not occur in butadiene, so, if one surmized that the shift is associated with conjugation, a very peculiar Franck-Condon excited state, one might have to go to the neat liquid in order to see transitions to the lowest vibrational levels of the upper state. Is there any possibility of such?

Dr. Hammond.—I completely agree that you do not have to have attractive interaction, you just have to have contact to get absorption. The second interpretation would inevitably have been my instantaneous explanation of the absorption tail if I had known only that the stuff is absorbing a little at 313 nanometers in the pure diene. The thing that guides me into all of this rather fancy handwaving is the turning on of the new chemistry. The chemistry, rather than the long wavelength absorption, which is characteristic of dienes just as with ethylene, guides me more to this model.

Dr. McGlynn.—I should like to note in passing that the number of photochemical processes initiated by absorption of light by molecules in regions in which they are not supposed to absorb is growing larger every day.

Dr. Kasha.—The paper which George Hammond gave inspires a couple of hours of questions on my part and hearing other questions even reminds me of things I forgot to ask about, so I suppose the Committee should have allowed a day for George Hammond's paper. I would like to bring out one or two things. I do think that this question of the spectroscopy of absorption tails becomes more and more important from the point of view of transient metastable interactions between molecules and other things which Sean McGlynn mentioned. First, I was going to ask, in reference to Robert Shulman's question about wavelength dependence, whether energy de-

pendence had been checked from the point of view of sensitizer; for example, by comparing pyridine as a sensitizer with benzophenone, because pyridine would be one of the higher energy triplets with a moderately good yield.

Dr. Hammond.—I do not think we have done it with pyridine, but we have done it with many sensitizers, with rather considerably different triplet excitation energies. We keep grinding out, over and over again, the same characteristic mixture of dimeric products.

Dr. Kasha.—I go to the second point. I wonder if the tail absorption could be a mixed high-energy triplet and low-energy singlet absorption, inasmuch as the complexity of photochemical products seems to be reflecting that. Blackwell and Stoner worked together on an interesting problem, which had to do with aggregate spectroscopy in solid matrices. They used the well-known cryogenic mixture of benzene and cyclohexane, which forms isomorphous solid crystalline solutions over a wide concentration range. They discovered that, by going to very low benzene concentrations, they got absorption spectra of essentially monomers of benzene, whereas when they went up in concentration, they got dimers and higher aggregates of benzene. It seems to me that this might be an interesting thing to extend to this kind of work.

Dr. Hammond.—Do you have in mind study of the fall-off in the 313-nm absorption with dilution?

Dr. Kasha.—Well, of course, at low temperature you would possibly be stabilizing dimers quite a bit.

Dr. Hammond.—We tried another thing, simply because Tom McCall likes to do things differently; he said, "Let's squeeze it." So he built a little cell where he could easily irradiate at 25 or 30 atmospheres in the hope that by squeezing the liquid he could change the average configuration, and therefore the relative yields of dimers. However, nothing happened. It would have been a neat experiment, if it had worked!

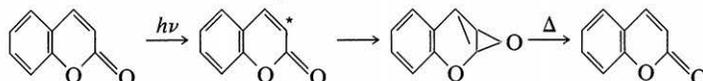
Dr. Kasha.—I do not like your remarks about equation 8; that is, that internal conversion from singlets may be common. You said you would not defend it, but I should like to make a few comments about it. Old books on spectroscopy and photochemistry are always fascinating because they contain so many unexplained phenomena. R. W. Woods, "Physical optics," is full of really fascinating photochemistry and spectroscopy; also Plotnikov's "Allgemeine Photochimie," and E. J. Bowen's book, "Chemical aspects of light," which was published in 1946. Every time there was a failure of a photochemical reaction or luminescence, it was attributed to equation 8. Now that largely has proved not to be true, and I would simply like to make one comment. Although there may be special cases, I think the ethylenic type of system is especially prone to phenomena involving equation 8. On the other hand, we know that benzophenone, a largely nonluminescent molecule, does not exhibit process 8. The failure to fluoresce is due to the very rapid rate of intersystem crossing to the triplet. I do not know how general your statement was intended to be, but it does seem to me to be a specialized statement for particular molecularly twistable excited states rather than for molecules as a whole.

Dr. Hammond.—I was about to disagree with you until you added the last phrase. My bland assertion that this was very common is simply based upon the fact that if you look at molecules as a whole, most of them are molecularly twistable.

Dr. Kasha.—The reason, of course, that we may be agreeing now is that, as you know, molecular potential functions that involve stretchings and expansions usually involve increase of energy with the distortion, whereas twisting usually involves decrease in the excited state, and that, of course, favors ground state interaction.

Dr. Hammond.—I have some other thoughts about this. Very commonly in the case of molecules that do apparently undergo process 8 with very high efficiency, you can formulate some "chemical path for decay." I will give you an example of a rather stiff-looking molecule. Coumarin has some interesting photochemistry; but perhaps the most interesting thing about the molecule

is its nonphotochemistry. Direct excitation gives chemistry which under the best circumstances gets up to quantum yields of no more than 0.05 and fluorescence is barely detectable. So 95 per cent of the excited states decay nonradiatively. We find that on irradiation at low temperature, the material photobleaches but reverts to coumarin on warming. Clearly we are generating some kind of high energy isomer, which under normal conditions reverts to the ground state of the molecule with great efficiency. The high energy isomer is not the ketenelike molecule that we expected to find. We now think that the process is:



Dr. Kasha.—I have to make a remark about the Einstein emission probability, because it is not at all clear that we know everything about it well enough to put it into a tomb. The Einstein relationship itself is of thermodynamic, not quantum mechanical, origin. It applies to two linelike atomic levels. The trouble with excited molecular states is that they are usually imbedded in the manifold of other states. The main problem is to find the best way of treating the interaction of radiation with the molecule and its manifold of states. One of the things coming out of the most recent studies by Yortner, Rice, and others is that you can have surprisingly bad Einstein cases; transition probabilities can double when there is no apparent reason for them to do so; pulsating emissions have now been observed; and there are other really strange new things happening. No one should be discouraged with so many new things coming out, when he sees the richness developing; but on the other hand, nothing seems secure either.

Dr. Hammond.—Yes, but I still believe that the theory of emission is more secure than almost anything else that we have talked about.

Dr. Kasha.—The equation I like best is 16. Long ago, when I first became interested in excited states, I had the rare opportunity to talk with Lothar Nordheim, who is interested in the matrix mechanics of excited nuclei and molecules, and with Jane Strawn. One of the things they were convinced of, and a very interesting point that physicists were asking, was, "why do not excited molecules simply get quenched by the solvent? Why do you ever see fluorescence?" Nordheim established that it is impossible to transfer energy directly from an excited state to vibrational levels of the solvent. There is no energetic reason for that to be true, but there is a fundamental reason, apparently, from the matrix elements studied by Nordheim. Your mechanism provides the first probable path by which real electronically excited energy, if I can put it that way, can be transferred intermolecularly directly to vibrational energy. There is no problem intramolecularly with what we call radiationless transitions, but your equation provides a very efficient intermolecular mode, and therefore belongs in the category of things that are proving to be very interesting these days.

Dr. Hammond.—I am sure that in some way the electronic excitation has to leak a little into the quencher, otherwise there is no communication.

Dr. Lim.—I want to refer to the question of internal conversion, discussed between you and Professor Kasha. In nitrogen heterocyclic compounds, in which $n-\pi^*$ and $\pi-\pi^*$ excited states are extremely close, one can have a pseudo Jahn-Teller effect, leading to nonplanar distortion of the lowest excited singlet. When this happens, Franck-Condon overlap involving the nonplanar vibration is fairly large between ground state and excited singlet state. In this case, the major path of deactivation is actually internal conversion to ground state. Going back to the case of coumarin, isomerization is a possibility, as you have suggested. On the other hand, is it also possible to have something similar to the case of quinoline, where a pseudo Jahn-Teller effect leads to internal conversion to the ground state?

Dr. Hammond.—Without being quantitative I can say that isomerization is involved, because we do see photobleaching at low temperature. A metastable material having an absorption spectrum different from that of coumarin is formed.

UNIVERSITIES

W. A. NOYES, JR.

It is a very great pleasure to be able to attend the dedication of the beautiful chemical laboratories at Texas Tech University, which most of us have seen for the first time today, as well as to participate in the fine conference which has been organized in honor of the occasion.

When one reaches my age one begins to be tired of hearing one's own voice. When asked to give a talk such as this, it is evident that one has nothing really new to say. Therefore, the problem one confronts, is of taking some well worn and possibly outmoded subject and of dressing it up in new terms, preferably embellished with 1971 slang, and of presenting it as though it is earth, if not world or universe, shaking. An honest person knows full well the dishonesty he is perpetrating on his audience and his only excuses must be that such a role is expected of him and that if he did not accept the invitation some other person, who might, heaven forbid, do it even worse, would accept.

Once, at a banquet in London, a British Cabinet Minister stated that the long suffering British public was subjected to more words per square meal than any other people. In this respect we extend our most sincere sympathy to our British friends, but without wishing to appear to be arrogant and egotistical we put forward the candidacy of the American people for first place in this contest.

I agreed to give a talk and I must perforce do so. The extent to which you think it to be good or bad will depend entirely on your benevolence.

Americans love to deal with clichés, with unproven generalizations, particularly if they are based on inadequate statistics, and with making predictions. We may not have the remotest idea either where we are headed or where our actions will guide us, but we insist on being told. As a people, I believe we have become the worst worriers ever created. This is all part of a great game that may lead to economic chaos, to euphoria, to peace, or to war. Nobody knows, but we all have opinions. Knowledge, even though superficial, is now wide spread. Many people talk and write, and nonsense is hard to distinguish from sense. For many years I had the very great misfortune to be editor of scientific journals. Acceptance of an editorship was my greatest mistake. I do not have a single feeling of accomplishment from this part of my life. I often wished that I could devise some scheme for paying authors not to publish. The present student generation, along with its predecessors, criticizes the idea of "publish or perish" for faculty members. They have a point, but as an ex-Dean (another low-down occupation) I was never able to devise a system of promotion based on failure to publish.

One of our pet clichés is that we are at a crossroads. Indeed there are so many crossroads that the entire country must be paved with asphalt. Tonight I have chosen to talk about universities because they are at a crossroads. I

was almost born on a campus, even though not already clothed in cap and gown. My entire life, except for the war years, has been spent in academe, and until recently I never wanted to lead any other kind of life. I do not know whether my present feelings of frustration are due to the generation gap (another cliché) or whether in fact university life today lacks the basic qualities that many of us always wanted and few really found.

Humanity has always had institutions where some relief from the trials and tribulations of life could be found. The religions of the world have provided asylum to persons unable or unwilling to confront the animosities, the hatreds, and the lusts that seem, alas, to be part and parcel of human behavior. Before the population explosion it was possible to go into the mountains or the deserts and eke out an existence far from the madding crowd. Many members of the present younger generation long to do this. They fail to realize that, with the present number of people in the world, this way of escaping anxiety can be indulged in by only a small fraction of the human race and then only if a sufficiently large number make possible the maintenance of some kind of organized society. Have the universities ceased to be good places for reflective thought?

The origins of universities in western Europe are a little vague and there can not be said to be a definite date on which they were born. Students wanted training for professions, mainly law and medicine, and later theology. They employed professors and often they could fire them. The rather rigid university structure we now know probably had its origins in France and it was the Sorbonne that began to offer centers for the study of logic. Indeed the Sorbonne was the mother of British universities.

The rigid structure of higher education in France was at least one of the main causes of the serious troubles in the spring of 1968. But this was not all. By the middle of the 20th century, European universities in most countries were training through the doctorate more persons than could be assimilated into intellectual life at home. Many migrated to colonies and to the United States, many went into industry, some into politics. But in the last 70 years, the number of university-trained persons has increased to the point that they are by no means all doing intellectual work. Universities could train mainly for the professions, including teaching, when they were training a few per cent of the population, but this can no longer be true when half or more of young people enter universities.

We have a strong tendency to forget some of the lessons that can be learned from history. I say this with a full realization that often there is little real agreement about the lessons that can be learned from history. It is always dangerous to relate present events to any period in history, because of necessity the facts of the present day are not completely known. As former President de Kiewiet of the University of Rochester, an historian, once said: "Current eventing is not a way to learn any discipline."

In one of our large state universities there are more than 800 graduate students in the Department of History alone. With this kind of an output of more

or less trained historians one might surmise that we Americans would go to history for guides as to the future. Unfortunately this is too infrequently the case.

Let us take courage in our hands and look at history. The first thing we should remember is that university unrest is not at all new. The second thing we should remember is that it is always worst in the spring and that it is most common among those students not strongly oriented toward a vocation or a profession. The third thing we should remember is that it is not confined to students. Fourth, university unrest is not limited to periods of economic unrest and it sometimes is worst among students from the upper middle class. Indeed its origins may be mainly with young faculty members. Lastly, the results of turmoil started in universities are by no means always good. Witness the unhappy university situations in our neighboring countries to the south. Many Europeans blame the rise of Hitler at least partly on an unhappy intellectual class. As for France I do not think any one really knows what ultimate effect the turmoil of 1968 will have on university life in that country. The intellectual life today in French universities seems to be at a rather low level.

But let us take a different kind of a look at recent American history. If about 25 years are subtracted from the date of the first Sputnik one goes back to the early days of the depression when the birth rate had fallen to about 60 per cent of what it had been in 1929. To use other terms, the number of young people of ages to receive Ph.D.'s was passing through a very low level about the time the clamor for a large number of trained scientists began to increase. Because any move to increase training in science takes several years to have an effect, it is perhaps most unfortunate that this clamor began to pay off at a time when the number of young people of university age began to increase due to the post-war birth rate. Few people, and least of all the scientists, were willing to see the handwriting on the wall during the halcyon days of the mid 1960's when candidates were few and jobs plentiful. We are now faced with finding jobs for a vast number of young people trained not only in the sciences but also in other intellectual pursuits.

What might this mean? For one thing, it is becoming evident that the so-called American way of life could not be provided to the present population of the world. This could mean a substantial decrease in the standard of living of middle class America. But one other fact, or more appropriately one other jaundiced glance to the future, must be kept in mind: an unhappy educated class may take the reins into its own hands and demand change. This time the intellectual class would be considerably more numerous than it has ever been before. Even then it would not be a majority of the population, or would it be very well organized in a military sense. It might be well to remember that the events of the past few years have bred a hatred of university people, which would make many citizens only too happy to shoot them down.

It is absolutely essential that those of us in university life take a good look at ourselves and make some realistic plans for the future. In so doing, we will

of necessity indulge in one other of the American vices against which I issued a warning. We will be trying to predict the future and this can never be done with certainty.

We scientists have allowed ourselves to be duped. We tell each other that research, pure research of any type, is always good and should be encouraged. In science and engineering, we were willing to allow the fears raised by Sputnik, by reports from intelligence sources, often inexact and often deliberately misinterpreted for the sake of obtaining increased budgets, to blind us to what really was happening. We were willing to forget the sources of the funds because we believed research always to be good. When total expenditures for research and development were a total of perhaps a billion dollars per year, there was no great outcry about wastage or extravagance. When they reached a total of 25 billion per year after a period of annual increase of around 20 per cent, the situation was bound to change. We are now forced to do what we should have done many years ago, establish priorities. When research could be done figuratively with test tubes and bunsen burners there was no great need for this. I once asked the advice of G. N. Lewis as to whether or not I should accept an offer from another university; I was not then at Berkeley. His reply was that a real research man would do research even in a penitentiary, but that there were pleasanter places to do it. He advised me to stay where I was. Today, with the need for expensive equipment and for research teams, the question of priorities has become one of immense importance. To err in such decisions could adversely affect the future of the country and of science for many years to come.

Science goes by fads just as do women's fashions. The popularity of nuclear physics is on the wane. Photochemistry is one of the present fads, but will it be five years from now? Should we follow the line of least resistance and provide money for what is now popular or should we employ a crystal ball and predict what will be popular in the years to come?

Guessing future popularity of fields of research is dangerous, but it simply cannot be avoided. We must, however, maintain high standards and realize that desire to do fundamental and publishable research is not an adequate reason for providing money for an investigator. Panels which pass on research proposals always maintain that there are many more good proposals than can be accommodated. Even allowing for the fact that some investigators apply to several agencies, one is very much inclined to doubt this statement. During my miserable years as an editor, we estimated that science would lose very little if we rejected 85 to 90 per cent of the articles we received. Our rejection rate usually ran about 30 per cent. Possibly we accepted too many but how could we be sure that the ones we took were the right ones?

The questions facing universities are not solely connected with scientific research. There has been a great hue and cry for educating students to be "well-rounded" citizens. We are supposed to educate the whole man. Perhaps we do not fully understand what we mean by this term and even less where this

kind of so-called broad education would ultimately lead. Anyone who has ever participated in a committee charged with the responsibility of revising degree requirements will realize that unanimity is impossible to achieve, and that compromise must be the order of the day. The result is always a hodge-podge, which pleases no one, least of all a majority of the students. Do students, who meet these distribution requirements and yet have relatively little training in depth in any one discipline, really go into the job market with much to offer? If they do not, will they be content to do menial tasks and look upon their university years as having provided an enrichment of life in their spare time? No one really can answer these questions, but the evidence seems to point to the fact that the granting of university degrees has created many frustrated individuals out of persons who might otherwise have been content to be useful members of society.

Suppose each one of you asks the question, what might most improve my standard of living? Would it help to have decent and reliable repair work on your car, a cleaner environment, some one to help with the house work (or for those of us in universities, better secretarial help), better and more mechanics, glassblowers, and electronics technicians? Americans are among the greatest litterbugs in the world and yet we are unwilling to pay the taxes necessary to clean up the mess we create daily. Is all of this service work to be done by college graduates? The answer is quite obviously that if the entire population or even a large fraction of it is to be composed of college graduates, this kind of work will be done by college graduates. Either that or it will not be done. In fact one might go a step further and express the belief that if we continue to expand the granting of advanced degrees as some people advocate, the lab boys, the glassblowers, and the technicians will all have Ph.D.'s.

It is easy enough to wax eloquent about the possibilities of having persons with doctor's degrees doing everything. This kind of socialism or communism would to some be the perfect society and yet we all know the end result would not be good. In fact life would become impossible. Every great social upheaval has been followed sooner or later by the reestablishment of differentiated classes. An upper class may be annihilated or banished as happened during the French and Russian revolutions, but before long a new upper class takes its place. The life of the common man may improve but a long period of uncertainty and reorganization must elapse before improvement becomes evident.

Thus we must decide whether to adopt what is the common practice in Europe of differentiating early and decisively between young people who will be permitted to go to universities or of putting all of them through universities and allowing the hard knocks of later competition to fit them into their proper places. Great disadvantages can be cited either for the European system or for ours. The advantage of the American system, at least in principle, is that the doors are open to all who wish to enter and the weeding out process is left to a period of life when character, habits, and originality can be more easily judged than it is for adolescents.

Many of the problems of American universities may be ascribed to numbers, to the fact that we admit to universities more than half of our young people and in so doing we admit bright ones, stupid ones, ethical ones, and criminals. The number of young people of college age in the United States should pass through a peak early in the 1980's. Perhaps an even greater fraction will enter universities then, than now; no one knows, for there are signs of disillusionment with higher education on the part of the public. But with population growth, with environmental problems that inevitably get worse as population density increases, one can predict (I am sinning again) that the standard of living of the middle class must decline in order for the standard of living not only of our own disadvantaged but for the rest of the world to improve.

If the same fraction of the world's population were to indulge in research as do so in Western Europe and North America, the resulting explosion of facts and theories would swamp our libraries, possibly our computers and certainly our brains. Chemical Abstracts publishes some 250,000 abstracts per year and perhaps a third are abstracts of papers published in the United States with six per cent of the population of the world. Thus, a *pro rata* increase would bring us up to a million or more abstracts a year.

American industry has been trying to tell us for some time that we are not producing the kinds of graduate students they think they need. One must not believe as a matter of course that industrialists know what is good for them. Patients are notoriously poor at diagnosing their own maladies, but nevertheless they must be listened to. Students and faculty members should also be listened to, but it is far from certain that they should have decisive voices in the reorganization of the university system. It is so much easier to feel that something is wrong than to suggest satisfactory remedies and this applies to social problems just as it does to psychological and medical problems.

But a few things would seem to be obvious. We now have enough knowledge to improve considerably our environment, to alleviate the suffering of much of the human race, to give the leisure for real intellectual enjoyment of literature, of art, of music. That we are not satisfactorily on the road to doing these things is almost disgraceful. Where are the difficulties? Some are so great that so-called educated people do not apply the careful thought to these problems that they deserve. *Science Magazine* in one of its recent editorials quoted statistics from one of our great universities that indicated near unanimity that population control was one of the great problems facing the human race, but that the average number of children per family wanted by those replying to the questionnaire was nearly four. This figure did not vary much from undergraduates to graduate students to faculty members. As the editorial correctly pointed out this lack of understanding of the simple principle of compound interest does not bode well for the human race.

I come therefore to the concluding thoughts in this somewhat rambling discourse. Of course we believe in research. It is necessary for progress and because the beauty of research well done should put it on a par with great

literature, great art, and great music. But let us recognize quite frankly that research is not to provide the solution to all human ills. Technology, the use of what we already know is essential. Most of all we must pay more attention to the vast majority of human beings both students and nonstudents who will not do much research, indeed not do much careful thinking. We must guide them to realize that disaster will overtake us unless somehow we not only choose intelligent leaders, but trust them to present the guidelines for the future. It will not be enough merely to follow the paths of democracy unless we put into public life persons with high ideals and great administrative ability. We must learn that to criticize might do more harm than good if helpful suggestions are not made at the same time.

Finally, perhaps we should heed what I said earlier in this talk. "Publish or perish" might not be the alternatives; to publish with no plan for action might be worse than useless. It might be psychologically upsetting, lead to turmoil, and ultimately to chaos. We scientists owe more to the world than just research and technology.

EXCITED STATES OF PORPHYRINS AND RELATED RING SYSTEMS

MARTIN GOUTERMAN

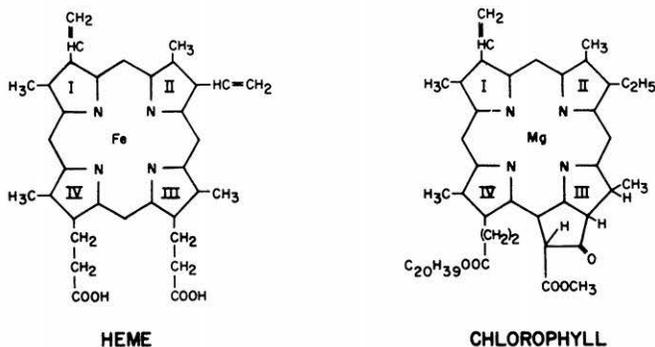
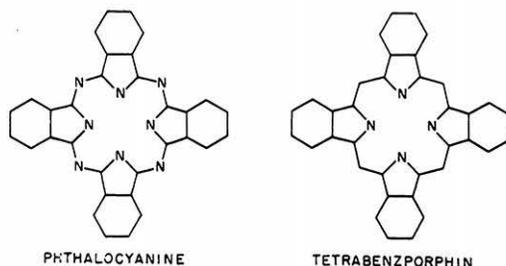
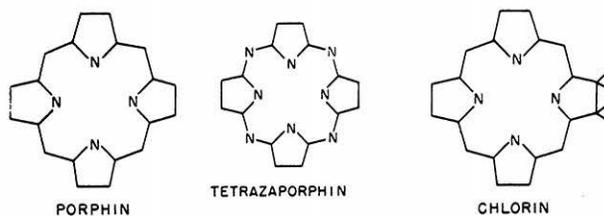
This paper is retrospective, covering some 15 years of research on porphyrins and related molecules. These systems provide a wide range of interesting problems, some of which have obvious biological significance. Also because of their primary role in biological use of solar energy, an understanding of their physics and chemistry may lead to new methods for using this basic energy source. Because of time limitations in preparing the manuscript, this paper does not have adequate references to other workers in the field, to whom apologies are offered. However, references to their work can be found in the "Literature Cited."

BACKGROUND

Fig. 1 shows the basic skeleton for the porphyrins and related ring systems. We see the porphin ring, which is the parent molecule for compounds properly called porphyrins. This class consists of molecules obtained from the parent porphin ring by substitution. The chlorin ring, *i.e.* dihydroporphin, is the parent for chlorophyll. Tetrahydroporphin (not shown in Fig. 1) is the parent for bacteriochlorophyll. Fig. 1 also shows three related ring systems: tetrazaporphin, tetrabenzporphin, and phthalocyanine. These are not parents of any compounds that occur in nature, but are synthetic compounds whose structures were determined in the 1920's and 30's. The phthalocyanine structure was one of the first determined by X-ray diffraction using the heavy atom effect rather than by classical chemical methods. This same technique was used much later in the X-ray studies of hemoglobin and myoglobin, which are proteins that contain iron porphyrin.

Fig. 2 shows two very important natural compounds, chlorophyll and heme. Notice that both have a similar set of external substituents. A principal difference is that chlorophyll contains magnesium, whereas heme contains iron. Also, chlorophyll has one ring reduced and contains a fifth ring. The heme molecule plays a key role in oxygen transport and in biological oxidation-reduction enzymes. Chlorophyll is the primary photoabsorber in photosynthesis, and either chlorophyll or bacteriochlorophyll (a closely related molecule with rings II and IV reduced) must be present for photosynthesis to occur. A basic question for our studies is why these particular molecules play such key biological roles. Our approach to this many-faceted question is to study the electronic structure of these systems by understanding the electronic spectra.

Some basic electronic absorption spectra are shown in Fig. 3. The solid curve is that of magnesium tetraphenylporphin (Mg TPP). The visible band has an extinction coefficient of $\sim 15,000 \text{ M}^{-1} \text{ cm}^{-1}$ whereas the near ultraviolet band has an extinction coefficient that can reach $500,000 \text{ M}^{-1} \text{ cm}^{-1}$.



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FIG. 1.—Basic carbon and nitrogen skeletons for porphyrin and related molecules.

FIG. 2.—Heme and chlorophyll. Ring IV rather than ring III of chlorophyll should be reduced.

The dotted curve is the absorption spectrum of magnesium tetrazaporphin (Mg TAP). Both spectra show visible and near ultraviolet bands. The visible bands of Mg TAP are far stronger than those of Mg TPP. The near ultraviolet bands have about the same integrated intensity in both molecules, but the peak maximum of Mg TAP is rather lower than that of Mg TPP because its band width is far broader. These two spectra represent extreme types that occur among metalloporphyrins and related systems.

Another important and general spectral phenomenon is shown in Fig. 4. The neutral parent porphin molecule contains two hydrogen atoms in the center, as shown in Fig. 5, which can be replaced by a divalent metal. While the metalloporphyrins generally show a two-banded visible spectrum, the metal free parent—known as the free base—shows a four-banded spectrum. Similar changes occur for every porphyrin-type ring that shows square (*i.e.*, D_{4h}) symmetry in the metalloderivative. Spectra such as that shown in Figs.

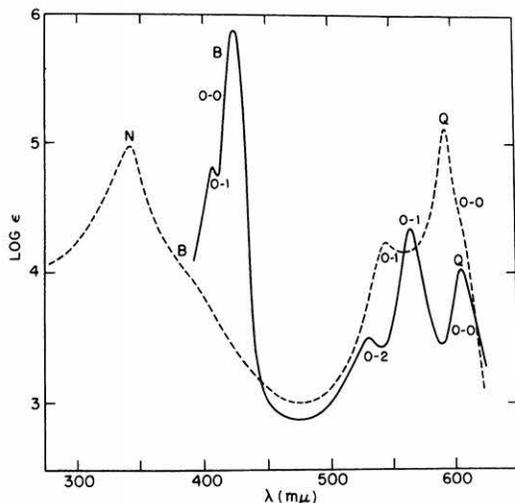


FIG. 3.—Absorption spectra of two typical symmetrical porphyrins: solid line, Mg tetraphenylporphyrin in benzene; dashed line, Mg octamethyltetrazaporphin in amyl alcohol.^{1,6}

3 and 4, and their variation with substitution, form the primary data to be interpreted by the theory of porphyrin electronic structure.

It might be useful to characterize a common thread that unites the class of molecules grouped as “porphyrins and related molecules.” All possess an inner 16-membered ring, as shown in Fig. 1, with four nitrogen atoms near the center. Because two of the nitrogen atoms are pyrrole type and two are aza type, the 16-atom ring contains 18 π electrons. In free base porphyrin, as shown in Fig. 5, the principal resonance structure consists of an 18-membered ring with 18 electrons. With the few exceptions to be discussed below, the molecules of square symmetry show a visible electronic band system of variable intensity and a near ultraviolet band system that is always very intense and is called the Soret band. When square symmetry is broken by replacing the central metal by two protons, by reducing one or more pyrrole rings, by unsymmetrical azasubstitution at the methine bridges, or by unsymmetrically fusing on benzene rings, the two-band systems show some splitting such as shown in Fig. 4. Thus the characteristic spectrum of visible and Soret bands can be attributed to an 18-electron ring, with various details affected by the actual skeleton and central metal atom.

MODEL THEORIES

The first successful treatment of the spectra of the porphyrins was provided by Platt and Simpson between 1949 and 1956.^{1,2} The simplest model would treat the molecules as a free electron ring with 18 electrons. The two highest energy filled orbitals have angular momentum around the ring axis of $l_z = \pm 4$ and the lowest energy empty orbitals have $l_z = \pm 5$. Transitions $\pm 4 \rightarrow \pm 5$ give rise to two pairs of excited states with total angular momentum

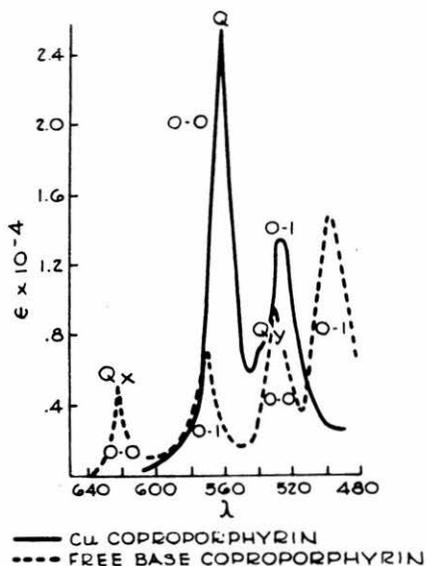
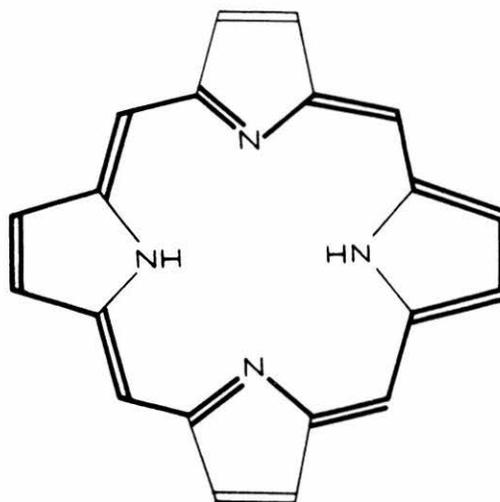


FIG. 4.—Coproporphyrin (octalkylporphyrin) absorption spectra in the visible: Cu and free base.¹

$L_z = \pm 1$ and $L_z = \pm 9$. Following Hund's rule for atomic spectra, the states ± 1 are at higher energy than the states ± 9 , due to the effect of electron interaction terms. Because the ground state is a closed shell with total angular momentum 0, the normal selection rule $\Delta L_z = \pm 1$ predicts that the higher energy pair is allowed and the lower energy pair is forbidden. In this model, the average transition energy depends only on the size of the ring and from the molecular geometry is expected in the visible to near ultraviolet region. Thus the weak visible bands can be identified as $\pm 9 \leftarrow 0$ and the Soret band as $\pm 1 \leftarrow 0$.

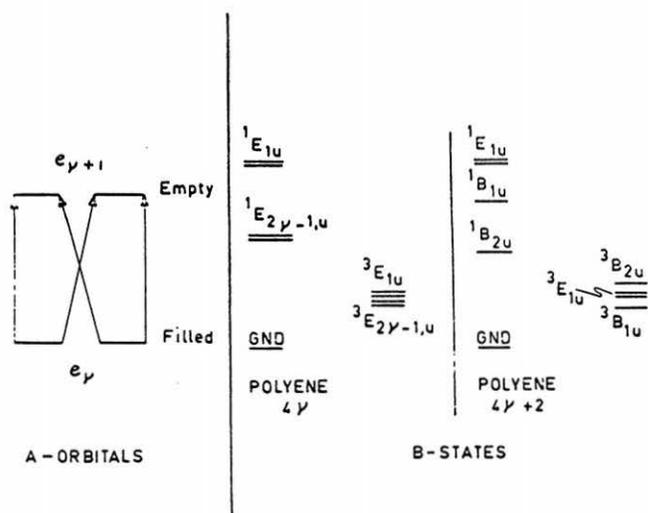
A similar picture is obtained from a cyclic polyene model. If we have a polyene of either 4ν or $4\nu + 2$ atoms containing $4\nu + 2$ electrons, the highest energy filled orbitals can be characterized by quantum numbers $\pm\nu$ and the lowest empty orbitals by $\pm(\nu + 1)$. This situation is shown in Fig. 6.³ The resulting state pattern is also shown there, including the effect of two-electron interactions. For a 16-atom polyene with 18 electrons there are two degenerate singlets in the near ultraviolet, two degenerate singlets in the visible, and four degenerate triplet states at lower energy. For an 18-atom polyene with 18 electrons, degeneracy of the lower energy singlets and of the triplets is removed as shown.

When as a graduate student I first saw the identification of the visible bands as corresponding to excited states with orbital angular momentum ± 9 , I thought the model somewhat silly as this value seemed grossly high. Years after the model was first proposed, Malley *et al.*³ made a Zeeman measurement that gave just this value. However other measurements of magnetic cir-



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SPECTRA OF PORPHYRINS



6

FIG. 5.—Principal resonance structure for free base porphyrin. The heavy bonds indicate the eighteen-membered cyclic polyene.¹

FIG. 6.—Orbitals and states of cyclic polyenes.²

cular dichroism (MCD) as well as calculations based on more rigorous PPP theory, to be described below, suggest that values around ± 5 are more correct. The near ultraviolet states are found to have small values, no more than ± 0.5 . Thus, even though these new results do not confirm the exact angular

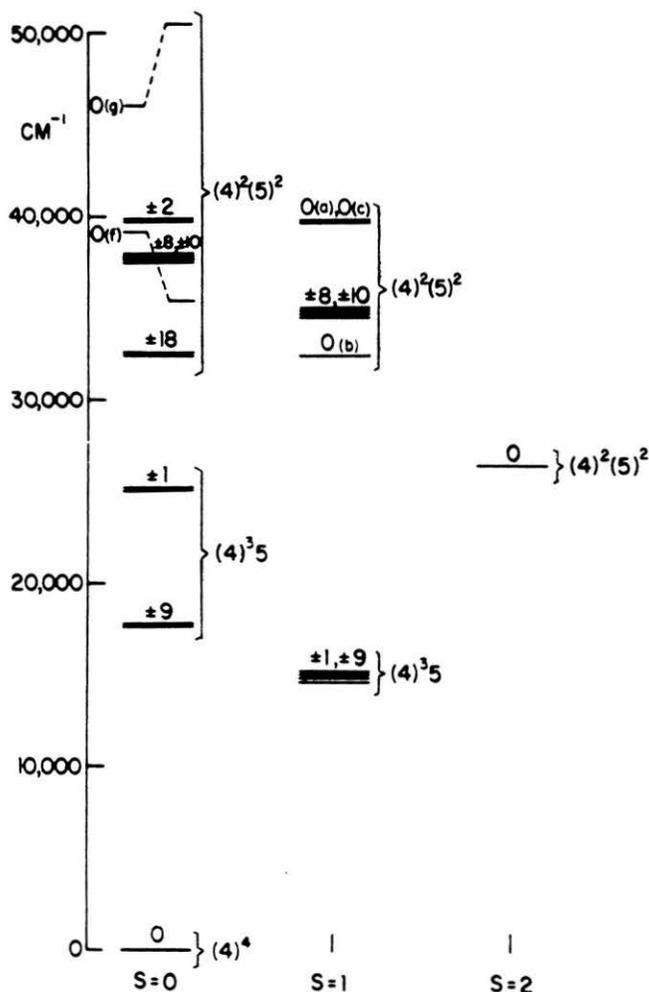


FIG. 7.—Porphin energy levels for circular box model of the electronic configurations $(4)^4$, $(4)^3 5$, $(4)^2(5)^2$. S is the spin. The numbers on the levels are L_z values.^{4a}

momentum results of free electron theory, the naive model is surprisingly good.

Fig. 7 shows an extension of the model to cover doubly excited states;^{4a} *i.e.*, states with configuration $(4)^2(5)^2$. The diagram shows the singlets and triplets arising from the configuration $(4)^3 5$ as well as higher states. The energies for the states arising from $(4)^2(5)^2$ were calculated by using the orbital energies and electron repulsion integrals determined from the known states of $(4)^3 5$. The results were used to interpret the triplet-triplet spectrum of zinc

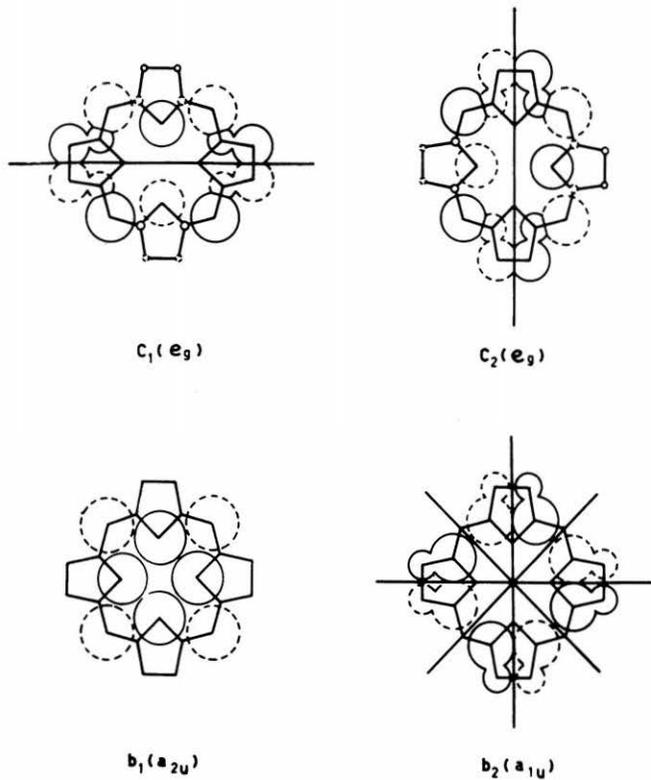


FIG. 8.—The top filled MO's b_1 , b_2 and lowest empty MO's c_1 , c_2 of porphyrin. The atomic orbital coefficients are proportional to the size of the circles. Solid or dashed circles indicate sign. Symmetry nodes are drawn in heavy lines.²

porphyrin, which had been taken by Linschitz in 1958. A good part of his spectrum could be interpreted as transitions from the lowest triplet of the $(4)^35$ configuration to higher triplets of the $(4)^2(5)^2$ configuration.^{4a} Note that this configuration also generates a quintet state, which has yet to be found experimentally. Ronald Felton^{4b} used this model to interpret negative ion spectra where the major intensity is due to transitions $(4)^45 \rightarrow (4)^3(5)^2$.

The last semiquantitative model to be developed was the four-orbital.^{2,5} Fig. 8 shows the top filled orbitals b_1 , b_2 generated by a simple Hückel MO calculation and the lowest empty orbitals c_1 , c_2 . The orbitals b_1 , b_2 can be related to orbitals $\cos 4\Phi$, $\sin 4\Phi$ that are the real forms of the free electron orbitals with $l_z = \pm 4$. This relation can be seen from the fact that these orbitals show four nodal planes. Similarly, the lowest empty orbitals c_1 , c_2 can be related to the free electron orbitals with $l_z = \pm 5$. In square symmetric porphyrin, the orbitals b_1 , b_2 are not necessarily degenerate whereas c_1 , c_2 are. However it can be shown that if b_1 and b_2 are accidentally degenerate, then configuration interaction will bring about states much like those predicted by the free electron model; *i.e.*, the molecule will have weak visible and

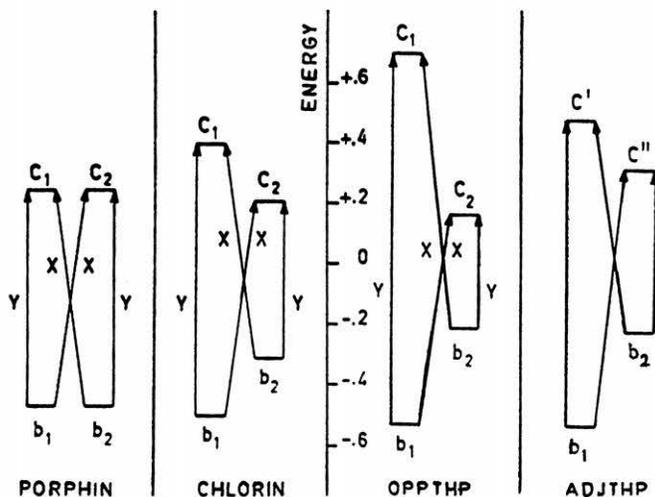


FIG. 9.—MO levels in porphin, chlorin, opposite tetrahydroporphin, and adjacent tetrahydroporphin. Energies from a corrected Hückel model.²

strong ultraviolet bands. Furthermore, it can be shown that if the degeneracy of b_1 , b_2 is lifted then the visible bands will gain intensity from the near ultraviolet bands.

It is possible to see how this works for the reduced porphyrins. Fig. 9 shows energy levels for the four orbitals of reduced porphyrins generated in a simple way.² To the energies of b_1 and b_2 , generated by a simple Hückel model for the molecules shown, an amount ϵ is subtracted from the energy of b_1 and added to that of b_2 so as to make the two degenerate in porphin. The spectrum of chlorin and related chlorophyll are then easily explained. The two X polarized transitions are nearly degenerate, giving a strong Soret and weak visible, as in the free electron model. The two Y-polarized transitions are not degenerate, giving rise to a strong red band. The resulting strong red absorption, but weak absorption out to the Soret band, produces the strong green color of chlorophyll.

Whereas Fig. 9 was used only for qualitative purposes, the four-orbital model was later used semiquantitatively.⁵ The Hückel parameters were arbitrarily adjusted to force b_1 , b_2 into degeneracy. Two electron terms were extrapolated from porphyrin to other molecules. In this way a reasonably good account of the spectra of porphyrins and related ring systems was obtained. However, the bond orders generated by the arbitrary Hückel parameters were in rather poor correspondence with experimental bond lengths, and it was apparent that this approach was inadequate.

PARISER-PARR-POPLE (PPP) THEORY

Around 1963, when computers of sufficient size and speed became available, we wanted to show that the ideas of the four-orbital model could be

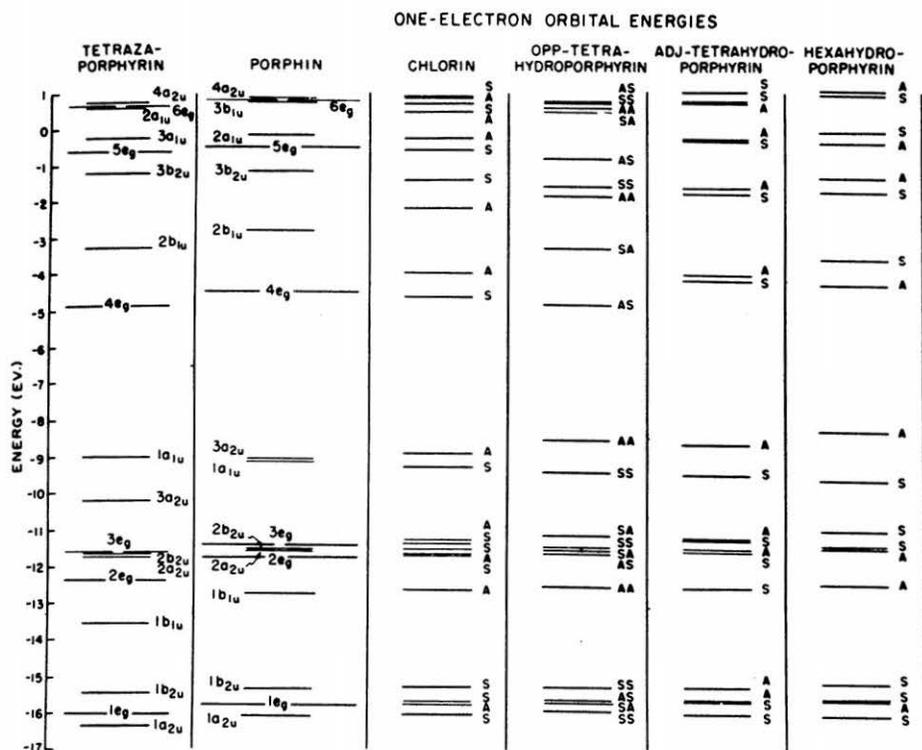


FIG. 10.—Orbital energies for porphin, reduced porphyrins, and tetrazaporphin. S, A means symmetric or antisymmetric with respect to reflections in planes through symmetry axes.⁶

verified by self-consistent molecular orbital (SCMO) theory. Using the PPP method, Weiss *et al.*⁶ were able to show that the postulated near degeneracy of the top filled orbitals in porphin are predicted by SCMO theory. Comparison of Fig. 10 generated by SCMO theory to Fig. 9 generated by arbitrary "correction" of naive Hückel energies shows a very similar pattern of orbital energies. In tetrazaporphin, we see that the degeneracy of $b_1(a_{2u})$ and $b_2(a_{1u})$ is strongly lifted and thus accounts for the strong visible bands (see Fig. 3). In bacteriochlorin (opposite tetrahydroporphyrin) the energy gap between the top filled and lowest empty orbital is small, accounting for the fact that bacteriochlorophyll absorbs in the 800-nm region, unlike chlorophyll, which absorbs around 650 nm.

Fig. 11 shows some more details of the PPP calculations on metalloporphin. The left column shows the excited states with their combined oscillator strengths generated by the four-orbital model only. We also see the transitions omitting configuration interaction (CI) and the result of a full CI treatment. Notice that the theoretical oscillator strength for the Soret band (labelled B) is 5.86 whereas the experimental value is only ~ 1.5 . This type of disagreement is shown by all π electron treatments that calculate intensity from the transition dipole.

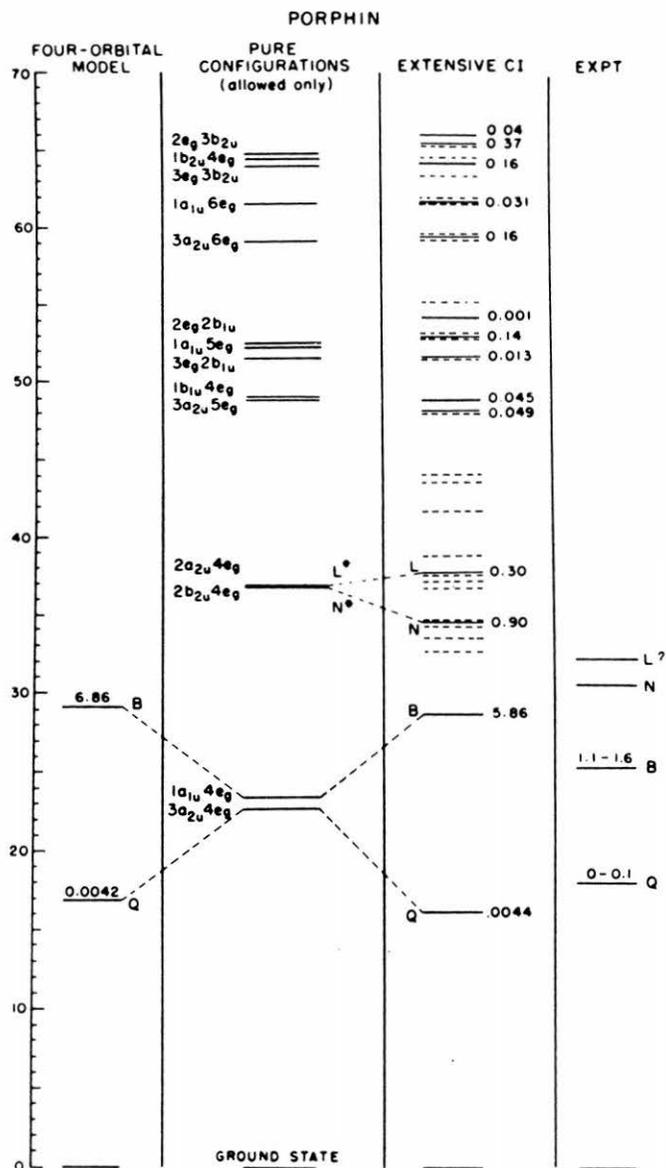


FIG. 11.—Metal porphin energy level diagram. Full lines are doubly degenerate allowed levels; dotted lines are forbidden levels of g symmetry. Numbers are dipole oscillator strengths.⁶

Fig. 12 to 14 show more recent SCMO-PPP calculations⁷ done for the metal complexes of tetrazaporphin (TAP), tetrabenzporphin (TBP), and phthalocyanine (Pc). The theoretical oscillator strengths f_1 and f_2 for these three figures should be doubled before comparison with experiment, as they represent only one of the two degenerate components. We see that in these molecules, in contrast with porphin, the lowest two transitions are not at all

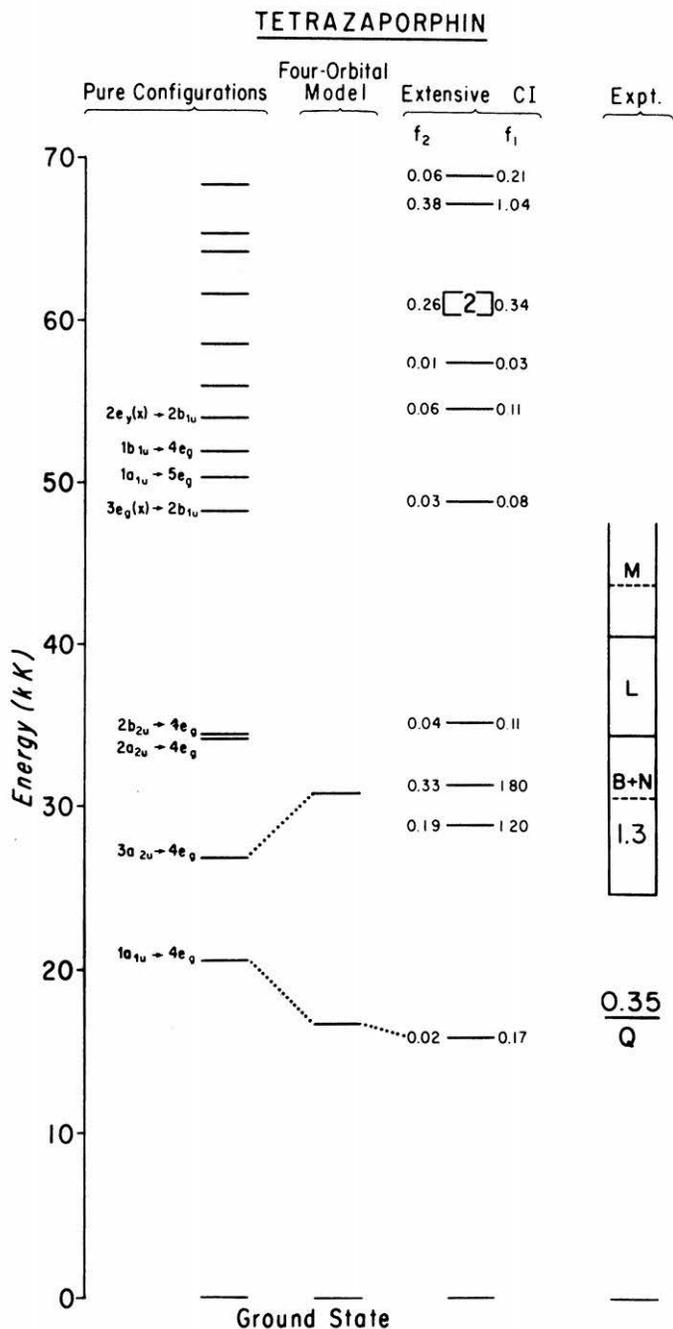


FIG. 12.—Allowed transitions with and without CI with theoretical oscillator strengths f_1 (dipole) and f_2 (gradient). Integers in theoretical boxes give number of predicted levels. Experimental data from R. P. Linstead on Mg TAP in methanol. Continuous absorption above 24.6 kK indicated by box; solid lines show minima and dashed lines peaks. Numbers give experimental f values.⁷

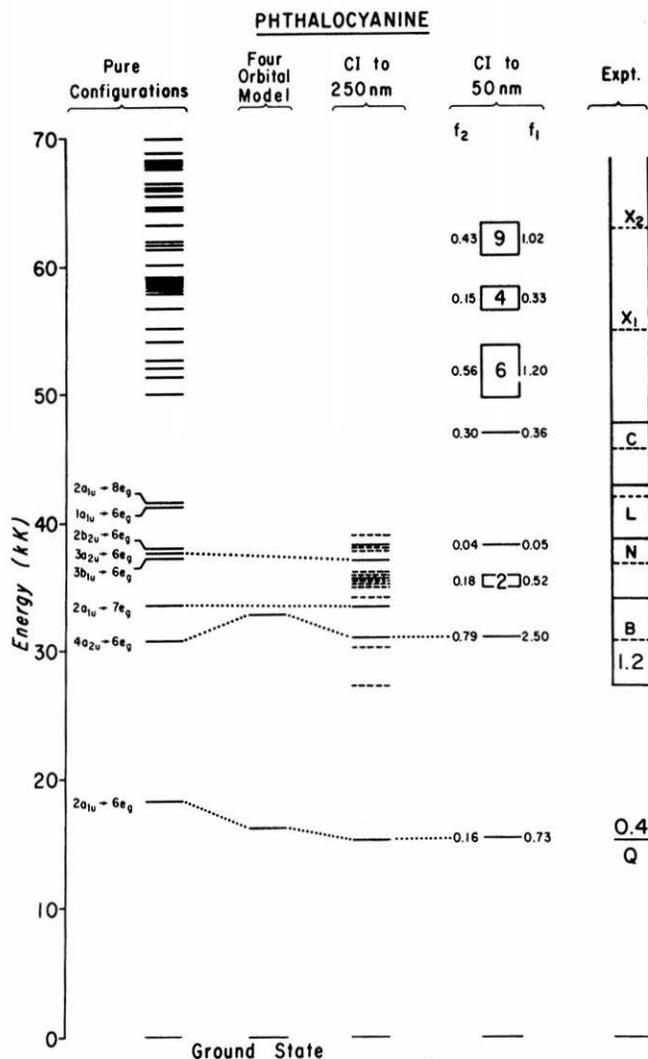


FIG. 13.—See legend for Fig. 12. Forbidden levels in the region 20 to 40 kK shown as dotted lines,⁷ experimental data from Edwards and Gouterman.¹¹

degenerate before CI, and after CI the visible bands are predicted to be much more intense than in porphyrin. Oscillator strengths f were calculated using transition dipoles, and generally are about a factor of four too high. Oscillator strengths f_2 were calculated using the transition gradient and generally are of the right order of magnitude. For exact wave functions, f_1 and f_2 should give the same values. However for our approximate π electron SCMO functions, it is apparent that although f_1 is grossly in error and f_2 agrees quite well with experiment, this same result had been shown for polyacenes before application to porphyrin.⁸

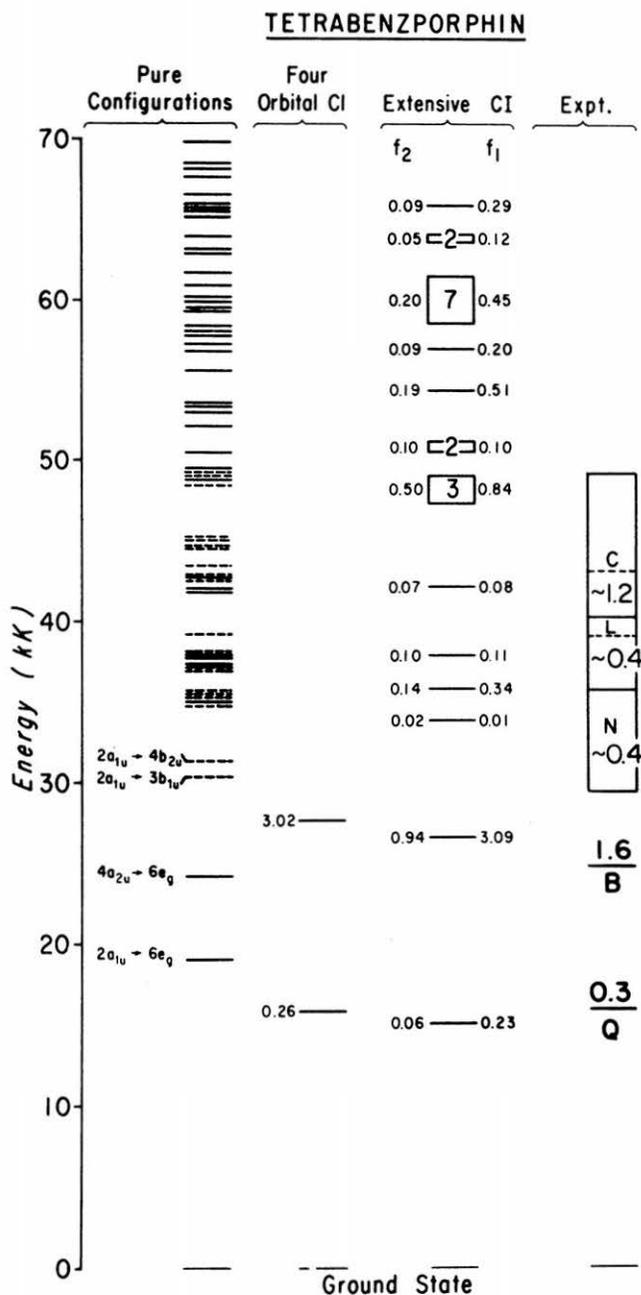


FIG. 14.—See legend for Fig. 12. Experimental data from Edwards³⁰ and Bajema and Gouterman.²⁷

We have found that f_2 values are sufficiently accurate that they can be used to criticize experiments. Thus the original experimental values for the absorption intensity of zinc tetrabenzporphin were lower than those shown in Fig. 14, and rather lower than those calculated from f_2 . Meanwhile Dr. Charles Rose at the University of Nevada had synthesized new material and found higher absorption coefficients than reported in the literature. On the basis of our f_2 values, we felt that we could confirm his finding. One would be more reluctant to do this with f_1 , which is routinely high by a factor of four. We also found that f_2 makes the Q_x band weaker than Q_y in porphin, as found experimentally; however f_1 predicts Q_x to be stronger.⁹

Of course the question remains, why is f_1 so badly in error and f_2 nearly correct? At present we do not have an altogether satisfactory answer to this question, and I leave that question to a more profound quantum theoretician. However for porphyrins and for polyacenes we have found "empirically" that f_2 seems to work well enough to begin to be useful in criticizing data. Because f_1 and f_2 are equally valid theoretically, it would seem that f_2 would be more useful to persons trying to interpret spectra with π electron functions.

Figs. 13 and 14 also show some results of experimental work carried out by a former student of mine, L. Edwards,^{10,11,12,13} who studied the absorption spectra of porphyrins in the vapor, in some cases going into the vacuum ultraviolet. We find one striking difference between tetrabenzporphin and porphin and also between phthalocyanine and tetrazaporphin. Both in theory and in the experiments, the molecules with fused benzene rings show strong intensity around $50,000\text{ cm}^{-1}$. This intensity can be attributed to the benenoid rings acting in some sense independently from the inner 18 electron porphyrin macrocycle. Thus, we see from these benenoid absorptions that even though rings are fused onto the 18 electron macrocycle, this latter still in some sense preserves its integrity.

Most recently⁷ we have used SCMO-PPP theory to calculate excited state angular momentum. As mentioned above, this can be measured either through a direct Zeeman experiment or through magnetic circular dichroism (MCD). The top filled orbitals, which by free electron theory have angular momentum ± 4 , are found by direct calculation on 10 different "porphyrins and related molecules" to have angular momentum $\pm(2.1 \pm 0.1)$, *i.e.*, the ± 0.1 was the range of values for the 10 skeletons. Likewise, the lowest empty orbitals, which by free electron theory have angular momentum ± 5 , are calculated to have angular momentum $\pm(2.0 \pm 0.1)$. The angular momentum for the visible excited states is basically determined by the sum, whereas the angular momentum for the Soret excited states is determined by the difference. Inasmuch as the difference is small, the Soret band value will be strongly affected by other terms whose contribution to the angular momentum of the visible bands is relatively small. Thus, the SCMO-PPP model gives values for excited state angular momentum that is quite reminiscent of free electron theory.

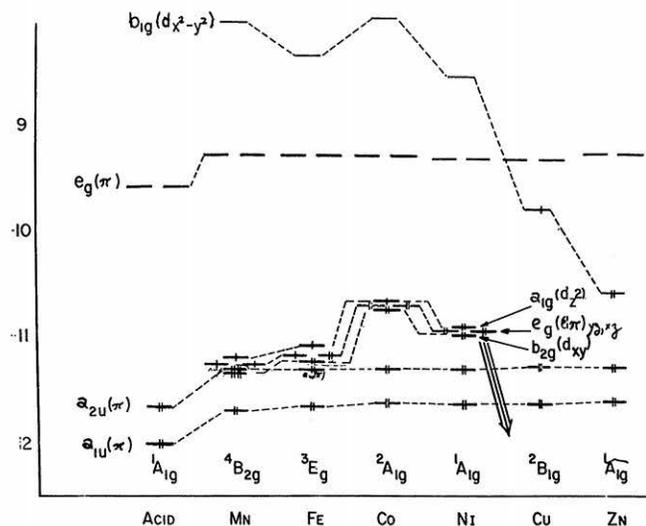


FIG. 15.—Calculated energies for top filled and lowest empty orbitals by EH model for various metal porphyrins. The state for Mn should be ${}^4A_{2g}$.¹⁴

EXTENDED HÜCKEL (EH) THEORY

After successfully completing the π electron work, the next theoretical question was how the electrons of a metal atom interact with the π electrons. About half the atoms of the Periodic Table have been introduced into the middle of a porphyrin or phthalocyanine ring, including some rare earths. In spite of the fact that many metals have incomplete d shells, generally the visible and near ultraviolet absorption spectra are little affected by changing one metal for another. This was rather a puzzle, and we wanted to explain it theoretically. The method we used was the extended Hückel model. A student of mine, Michael Zerner, prepared a computer program for a molecule with two planes of symmetry. At the time treating such a large system by this method, including a self-consistent charge procedure for adjusting parameters, represented a considerable computer challenge.

Fig. 15 gives the results of Zerner's calculation on the transition metals, Mn through Zn.¹⁴ Much of what we know about d orbitals through electronic and ESR spectra, tends to substantiate the picture given here. In the case of Zn, the energy of the d electrons is considerably below that of the top-filled π orbital. The highest filled orbital is largely a nitrogen p_σ type with little $d_{x^2-y^2}$ character. In Cu this orbital is calculated to have about 30 per cent $d_{x^2-y^2}$ character, although from ESR experiments it is found to be about 70 per cent. The other d orbitals remain deeply buried. In the case of planar nickel porphyrin with no ligands, the $d_{x^2-y^2}$ orbital is empty and calculated to have energy far above that of the top filled orbital. The other four d orbitals

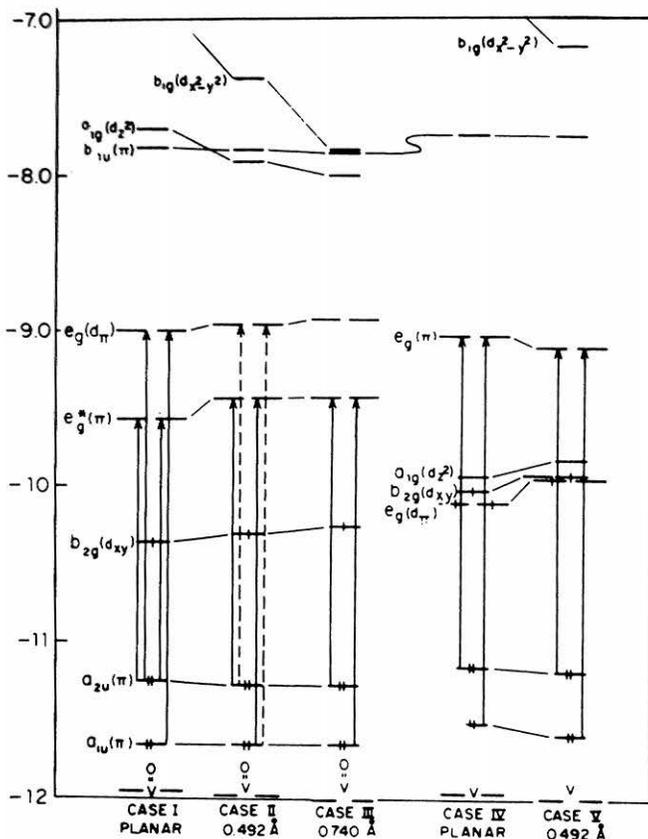


FIG. 16.—Calculated orbital energies by EH model for vanadyl and vanadium porphyrins in different geometries.¹⁵

are filled with calculated energies comparable to the top-filled π orbitals. Experimentally, Ni porphyrin can be made paramagnetic by pyridine complex formation. EH calculations suggest strongly that the Ni atom is out of plane in the paramagnetic complex. The last simple metal in the figure is Co, which is calculated to have one hole in the low energy d_{z^2} orbital, a result confirmed by ESR studies. As might be expected from the diagram of Fig. 15, the negative ion of cobalt porphyrin adds the electron to the d shell. Fig. 15 also shows calculations on Mn and Fe. The calculations were done assuming a planar geometry. It can be seen that the calculations predict $d_{x^2-y^2}$ to have very high energy while the energy of four d orbitals is quite close. As a result ferrous porphyrin is predicted to have two unpaired d electrons, and Mn three. As we shall see, this prediction is rather naive.

Fig. 16 shows the result of EH calculations on vanadyl, which had predictive value.¹⁵ The left column shows results with the V atom in plane. The calculation showed heavy mixing between the empty $e_g(\pi^*)$ and $e_g(d_\pi)$ orbitals. As a result, twice as many transitions are predicted as in the four-orbital

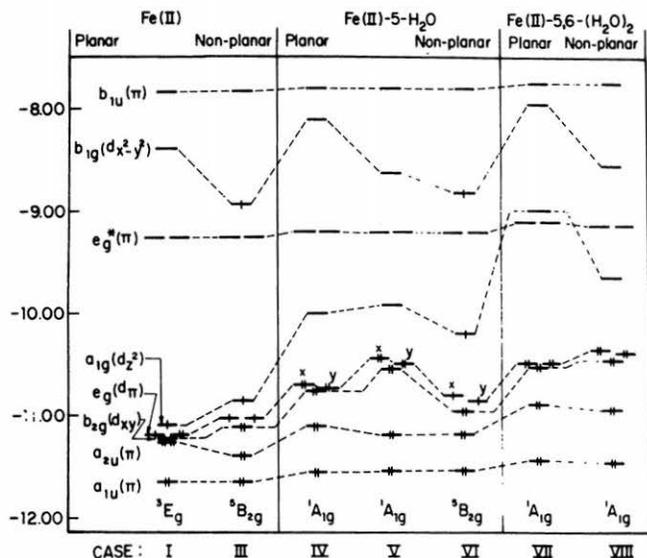


FIG. 17.—Calculated orbital energies by EH model for ferrous porphyrin and ferrous porphyrin hydrate with planar and out of plane iron.¹⁷

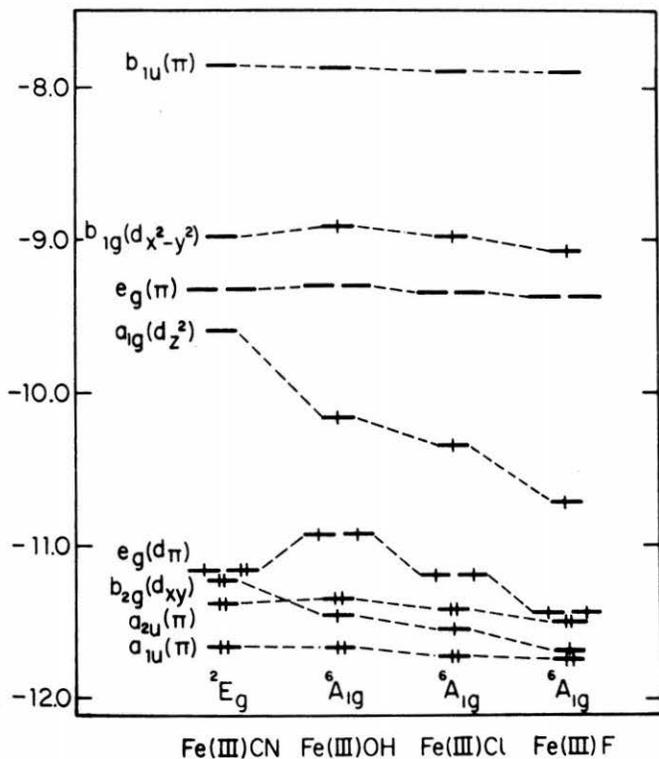


FIG. 18.—Calculated orbital energies by EH model for out of plane ferric porphyrin complexes.¹⁷

model, and the absorption spectrum should be quite perturbed. Inasmuch as the spectrum is rather normal, we knew this calculated mixing was incorrect. However, by lifting the V atom out of the porphyrin plane, we could reduce the mixing and obtain normal transitions. Three years after our calculations were published, Peterson¹⁶ in studying a VO derivative of chlorophyll, found the VO group half an Ångstrom out of plane.

Figs. 17 and 18 show the results of EH calculation on ferrous and ferric porphyrins.¹⁷ These calculations were carried out to answer a very old problem. In 1936, Pauling and Coryell found that, depending on the ligands, heme compounds show either high or low spin, but not intermediate spin as suggested by Fig. 15. To see why this happens we had to incorporate into the EH model a method for estimating exchange integrals. This was done¹⁷ and we were able to provide a simple explanation for the existence of high spin states—to obtain high spin the iron atom must be out of plane. Basically non-planarity lowers the energy of $d_{x^2-y^2}$ whereas ligands raise the energy of d_{z^2} by an amount that depends on the strength of the ligand interaction. If the iron atom remains in the plane, ligands can only effect a change between intermediate and low spin. These results are shown for ferrous porphyrin with none, one, or two water molecules in Fig. 17. Fig. 18 shows the same calculation on nonplanar ferric porphyrin with ligands CN^- , OH^- , Cl^- , and F^- . So far, our prediction that high spin iron porphyrins must have the iron out of plane has been in accord with X-ray structures that have been determined.

More recent EH calculations⁹ by my student, A. M. Schaffer, provide an explanation for a spectral effect clearly seen in Fig. 3. It is apparent that the Soret band of tetrazaporphin is very diffuse compared to that of porphin. The same contrast occurs between the Soret bands of phthalocyanine and tetrabenzporphin. Hochstrasser and Marzocco¹⁸ have shown that in a number of azines $\pi-\pi^*$ bands lying on top of $n-\pi^*$ bands are quite diffuse. Schaffer, using EH calculations, predicted that the aza nitrogen atoms would produce an $n-\pi^*$ transition in the Soret region and could thus explain the observed diffuseness.

Although the extended Hückel calculations have yielded many results that throw considerable light on the electronic structure of metalloporphyrins, the model nature of the calculations must always be kept in mind. The results of an individual calculation cannot always be taken at face value. Explaining empirical facts by an EH calculation is like posing a question to the Oracle at Delphi. A given answer has to be subjected to critical interpretation.

METAL EFFECTS ON ABSORPTION

As stated above, replacement of one metal by another in general has very little effect on the visible and near ultraviolet absorption spectra but can have considerable effect on emission spectra. In this section I shall discuss in more detail the metal effect on absorption, which will lead to the definition of an

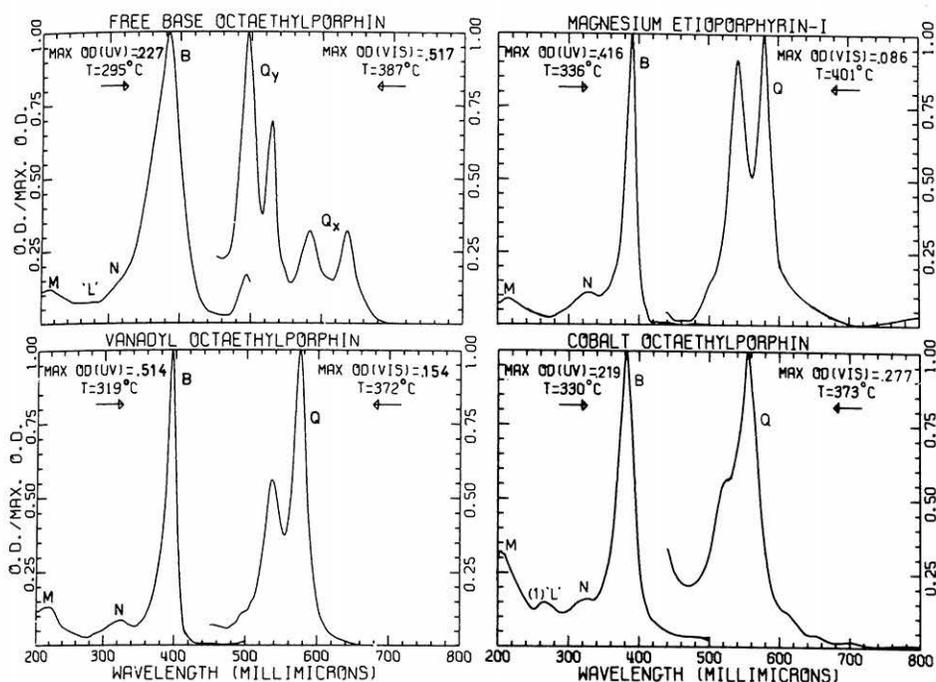


Fig. 19.—Vapor phase absorption spectra. Temperature and maximum OD (corrected to 1-cm path length) for two runs are indicated.¹²

outstanding theoretical problem. In the next section I shall discuss studies on emission spectra.

Figs. 19 and 20 show some porphyrin absorption spectra taken in the vapor.¹² All the metals show a strong Soret band and a weaker two banded visible absorption. For these latter, there is some variation in the ratio of the intensities of $Q(1,0)$ to $Q(0,0)$. This was explained some years ago by perturbation theory.¹ Otherwise there is very little metal effect on the visible and Soret bands. Note that there is very little difference between these vapor spectra and solution spectra. As in the solution spectra of Fig. 4, change from the metal to the free base changes the visible spectrum from two to four bands. Fig. 19 also shows that in the free base, the Soret band is far broader than in a metal complex, as is expected when the electronic degeneracy is lifted by the central protons. Although the metals have little effect on the visible and Soret bands, there are larger variations in the region between 340 and 200 nm. A very strong effect is shown by Ni phthalocyanine in this region.¹¹

A few metals cause rather more serious changes in the visible and Soret regions. The spectra of the heme moiety of hemoglobin show very strong near infrared absorption, depending on the complex.¹⁷ Thus, in Fig. 21 we see a relatively strong near infrared absorption in the O_2 complex and in free hemoglobin but not in the CO complex. Fig. 22, top panel, shows Mn (III)

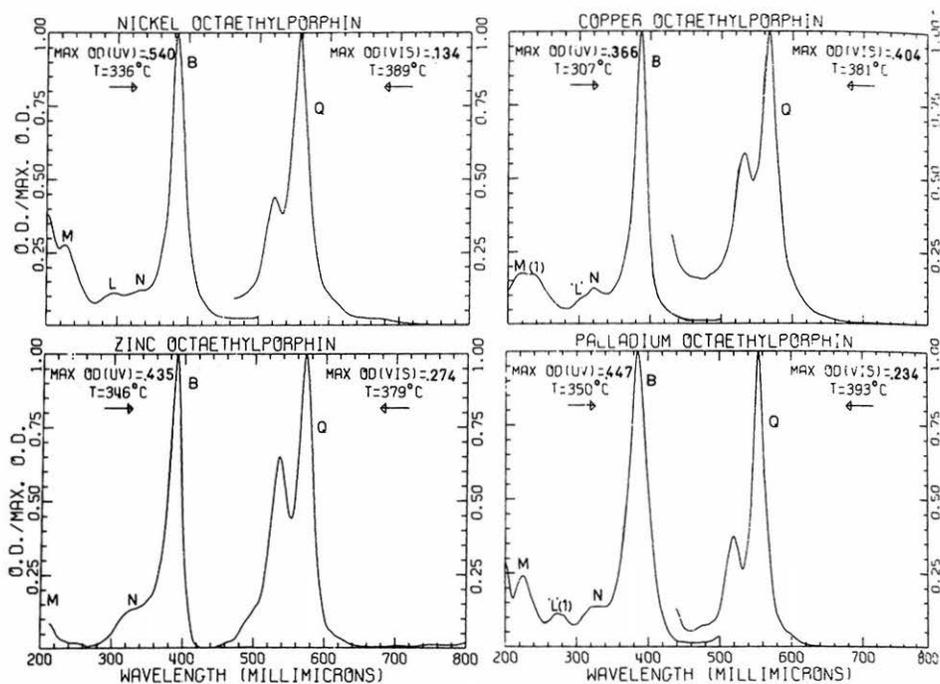


FIG. 20.—Vapor phase absorption spectra. Temperature and maximum OD (corrected to 1-cm path length) for two runs are indicated.¹²

acetate porphyrin.¹³ Instead of the normal Soret band there are two strong bands, one at 360 nm and one at 460 nm. Fig. 22 also shows that reduction to Mn (II) porphyrin produces a normal spectrum. Fig. 23 shows two vapor spectra of Mn (III) Cl TPP. The upper left panel taken early in the run shows a strong 460-nm band, which disappears later as shown in the upper right panel. We believe that this shows that vapor Mn (III) Cl TPP converts spontaneously to Mn (II) TPP by homolytic cleavage of the bond to the chlorine. A similar phenomenon is shown by Sn porphyrin in the vapor. We believe the rather complicated vapor spectrum shown in Fig. 23 consists of Sn (IV) and Sn (II). Fig. 23 also gives what we believe to be the spectrum of Sn (II) made by chemical reduction of Sn (IV) in solution. The spectrum is rather similar to Mn (III). As in the case of Mn (III), in the vapor Sn (IV) seems to convert spontaneously to Sn (II).

An interpretation of the curious Sn (II) spectrum has been given on the basis of EH calculations.¹⁹ There are two extra electrons in Sn (II) in a metal orbital of $5p_z$ character. This orbital can mix with $a_{2u}(\pi)$, a mixing that gets stronger if the metal assumes the expected out of plane geometry. The result is three top filled orbitals. Thus Sn (II) porphyrin might be described by a five-orbital model.

The curious spectra of Mn (III) porphyrin have been studied extensively by Boucher (see *Coordination Chemistry Reviews*). However a quantitative

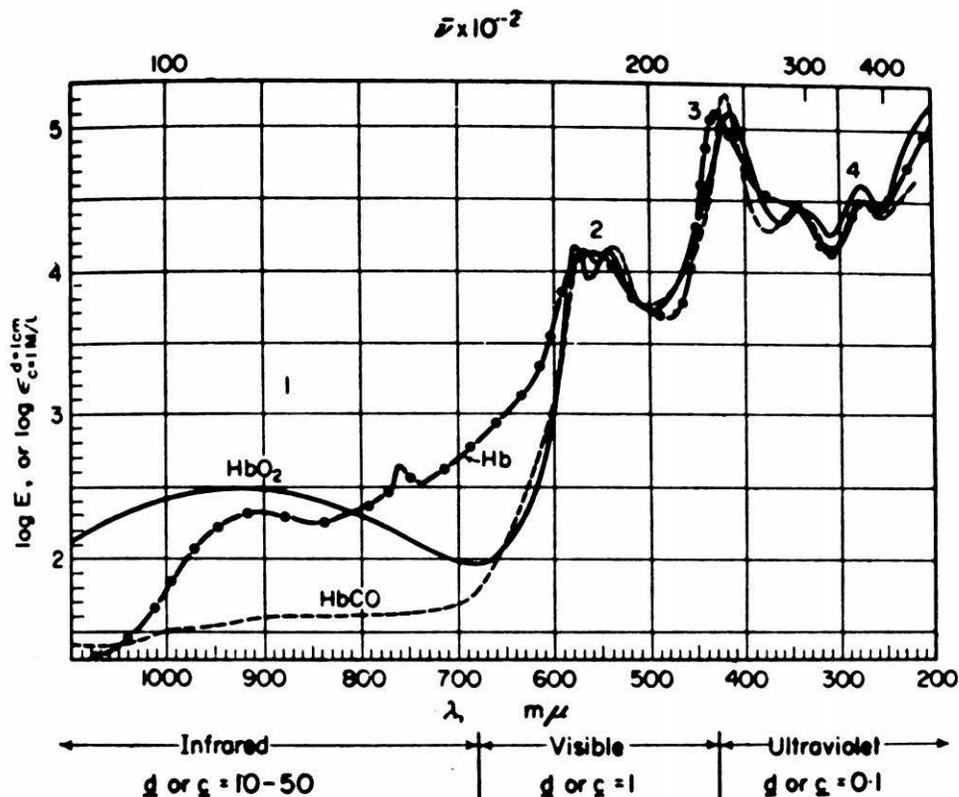


FIG. 21.—Absorption spectra of oxyhemoglobin, HbO_2 , deoxygenated hemoglobin, Hb , and carbonyl hemoglobin, HbCO . The d or c refer to cuvette thickness, d , or concentration, c , for optimal spectrophotometry.

explanation for the curious spectra has not been given. I suggest qualitatively that there is a strong resonance between the $e_g(\pi^*)$ and $e_g(d_\pi)$ levels. As mentioned above, a resonance of this sort was predicted for vanadyl porphyrin if the V atom were in the porphyrin plane. In such a case the molecule would be characterized by two pairs of e_g orbitals to which excitation can occur and the system might be described by a six-orbital model. Indeed, Mn (III) shows near infrared bands, visible bands, and two Soret bands, as might be expected qualitatively if such were the case. Calculations have yet to verify this hypothesis, and to show why Mn (III) uniquely shows this effect. This remains an outstanding problem in the theory of porphyrin excited states.

METAL EFFECTS ON EMISSION

General Discussion

Much of the experimental work of my research group has been a study of metalloporphyrin emission spectra. As stated above, the metal has a very

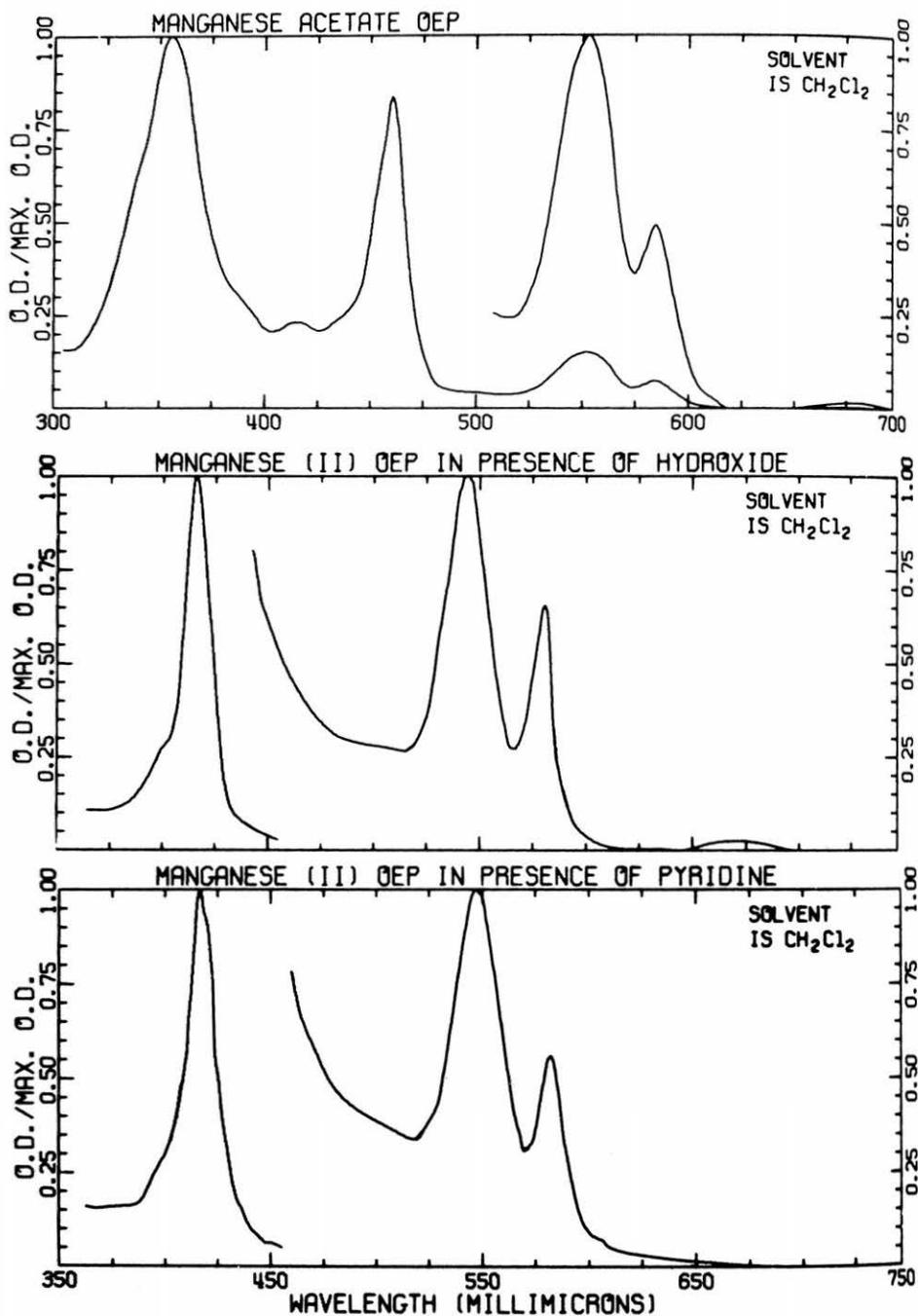


FIG. 22.—Lower two panels show the spectra produced by electrolytic reduction of Mn acetate octaethylporphin, whose spectrum is given in the top panel.¹²

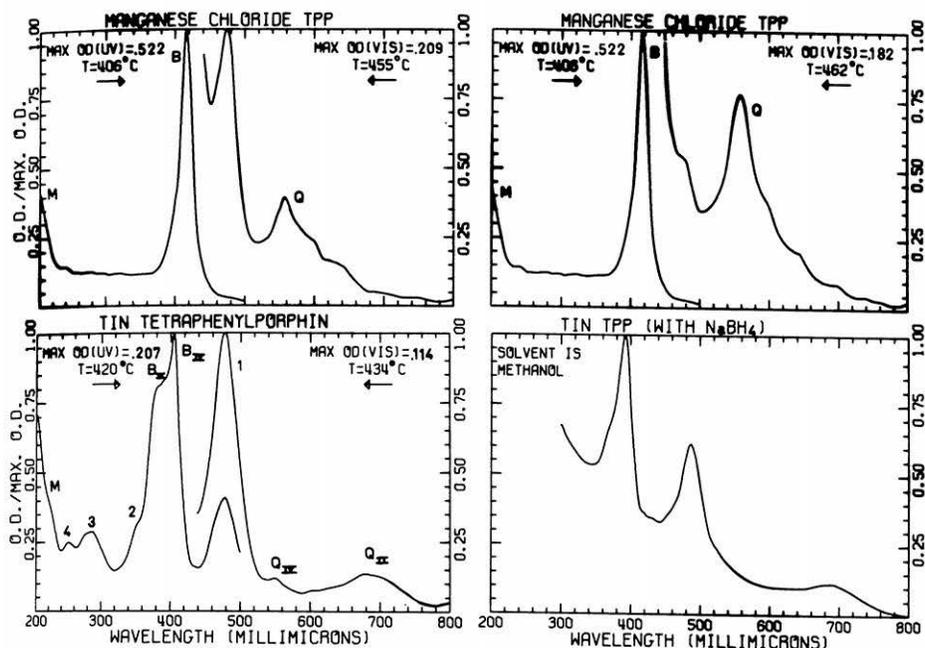


FIG. 23.—Three vapor phase spectra and one liquid spectrum (room temperature). The upper left spectrum appears initially and contains some Mn (III), while the upper right spectrum taken after 10 minutes is largely Mn (II). The Sn vapor spectrum is attributed to a mixture of Sn (II) and Sn (IV).¹³

strong effect on emission spectra. We therefore hope that by understanding emission spectra we can get an insight into the interaction between the metal and the porphyrin electrons. We can also gain a knowledge of radiationless decay routes, which in chlorophyll are crucial for the molecule's role in photosynthesis.

Fig. 24 is a classic diagram for molecular luminescence. The diagram indicates photon absorption K from S_0 to the lowest excited singlet S_1 . Because excitation to states at higher energy than S_1 is generally followed by very fast relaxation ($\sim 10^{-12}$ sec) to S_1 , the initial excited state is generally not important for the luminescence processes. From S_1 there can be fluorescence (k_f) back to S_0 , radiationless decay (k_1) back to S_0 , or intersystem crossing (k_2) to the triplet. The triplet can phosphoresce (k_p) back to S_0 , radiationlessly decay (k_3) back to S_0 , or perhaps undergo thermal radiationless conversion (k_{-2}) back to S_1 . The rate k_{-2} is responsible for thermal delayed fluorescence. If this rate is negligible, the two principal emissions will be fluorescence and phosphorescence. The yields for these processes are respectively:

$$\Phi_f = \frac{k_f}{k_f + k_1 + k_2}$$

$$\Phi_p = \frac{k_f k_p}{(k_f + k_1 + k_2)(k_p + k_3)}$$

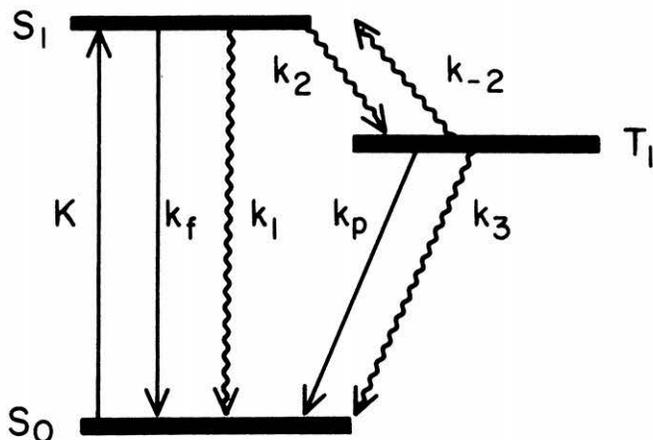


FIG. 24. — Decay scheme for singlet and triplet relaxation. Radiative rates are given by straight lines; radiationless rates by curly lines.²²

The lifetime of the triplet is:

$$\tau_p^* = (k_p + k_3)^{-1}$$

In a classic work, Becker and Allison studied the emission spectra of a large number of metal complexes of mesoporphyrin, an octalkylporphin. This pioneering survey laid down the experimental facts. We will start from these results, given in Table 1, and then show what our own work has added to this picture.

The top of Table 1 shows metals with either empty or full d shells, in order of increasing atomic number. From Be through Ba we see a decrease in fluorescence yield and a rise in phosphorescence yield. The phosphorescence lifetime tends to decrease in this series with Be and Sn somewhat exceptional. Hg and Pb both show very weak emissions.

For the open shell cases Becker and Allison reported no fluorescence. Strong or very strong phosphorescences were reported only for Cu, Pd, and Pt. We ourselves have studied only one metal not studied by Becker. As Table 1 shows, Rh (III) has a strong phosphorescence. There is a report that an Ir porphyrin phosphoresces.

We shall now present some of the results of emission studies carried out in our laboratory and show how they complement and modify the original results of Becker and Allison.

Quantum Yield Studies

Table 2 presents the results of quantum yield studies carried out in our laboratory. Although these numbers might be in error by perhaps ± 20 per cent, they are considerably more accurate than those of the original qualita-

TABLE 1.—Emission of metalloporphyrins. Data reported by Becker and Allison,²⁸ except for Rh (III) (my own laboratory) and Ir (G. Crosby, personal communication).

Metal	Be	Mg	Ca	CLOSED SHELL						Hg	Pb
				Zn	Sr	Cd	Sn	Ba			
F	vs	s	s	m	vw	w	w	vw	0	0	
P	vw	w	m	m	m	m	s	s	w	vw	
τ_p (ms)	12	160	63	83	7	7	21	8	f	f	
Metal	VO	Mn (II)	Mn (III)	OPEN SHELL				Ni	Cu		
				Fe (II)	Fe (III)	Co (II)	Co (III)				
P	w	vw		vw	vw	w	w	vw	vs		
τ_p (ms)	f	f		f		f		11	0.1		
Metal							Rh(III)	Pd	Ag		
P							s	vs	0		
τ_p (ms)							0.7	2			
Metal							Ir	Pt			
P								vs			
τ_p (ms)							0.1	0.14			

Abbreviations: vs, very strong; s, strong; m, moderate; w, weak; vw, very weak; 0, none; f has lifetime under 0.5 milliseconds.

tive report. Some of these compounds have been measured by Russian scientists, whose yields generally agree with ours.

Consider first the closed shell cases. We can see that there is, indeed, a fall off in Φ_f as the metal atomic number rises. Generally this is presumed to be due to an increase in k_2 rather than k_1 , although this is not yet fully established. Of the open shell compounds with weak phosphorescence, we have studied four. For two of these, Co and Ni, we could obtain no phosphorescence and currently believe that Becker's report of weak phosphorescence was in error. We did verify Becker's finding of no phosphorescence for Ag (II) porphyrin, and we did find a weak phosphorescence from VO porphyrin. In the Co and Ni cases, we tend to believe that lack of luminescence is due to low energy excited states of $d-d$ character lying between the lowest $^3(\pi, \pi^*)$ state and the ground state. This hypothesis has yet to be confirmed theoretically or experimentally. In the case of Ag (II) porphyrin we observed some evidence for a photochemical process.²⁰

In our laboratory we have not yet investigated the emission properties of Mn or Fe porphyrins. We believe that for these metals, low lying $d-d$ states between the lowest $^3(\pi, \pi^*)$ state and the ground state will generally provide an efficient pathway for radiationless decay. Thus, for most spin and oxidation states of Fe and Mn porphyrins, we believe luminescence is unlikely. One possible exception, however, is the d^6 , $S=0$, Fe (II) complex. We (Louise Hanson, work in progress) have observed strong phosphores-

TABLE 2.—Quantum yields.^{20,21,22,29}

CLOSED SHELL			OPEN SHELL (weak phosphorescence)	
Compound	$\Phi_f(300^\circ\text{K})$	$\Phi_p(77^\circ\text{K})$	Compound	$\Phi_p(77^\circ\text{K})$
H ₂ Etio	0.09		VO Etio	>0.01
H ₂ TPP	0.11		Co Etio	<0.0005 (?)
Mg TPP	0.13		Ni Etio	<0.0005 (?)
Zn Etio	0.04	~0.04	Ag Etio	0
Zn TPP	0.03	<0.001		
Cd TPP	<0.002			
OPEN SHELL (strong phosphorescence) $\Phi_p(77^\circ\text{K})$				
Skeleton				
Metal	TPP	P	Etio	
Cu	0.06	0.09	0.6	
Pd	0.2	0.25	0.5	
Pt	0.45	0.7	0.9	
OPEN SHELL (strong phosphorescence) $\Phi_f \times 10^4 (300^\circ\text{K})$				
Pd TPP	Pd P	Pd OEP	Pt Etio	
1.5	2.2	3.0	<0.2 (?)	

Abbreviations: Etio, etioporphyrin; TPP, tetraphenyl; P, porphin, OEP, octaethylporphin; (?), not established.

cence from a d^6 , $S = 0$, Rh (III) etioporphyrin chloride with two dimethylamine ligands, and believe that the compound has a large ligand field gap between the filled and empty d orbitals.

Table 2 shows that we verified Becker's report of strong phosphorescence from Cu, Pd, and Pt complexes.^{20,21} However, the table shows that the yield is considerably influenced by the porphyrin skeleton. In addition, we found a fluorescence yield from Pd porphyrins that was not previously reported.²² These fluorescence spectra are given in Fig. 25. The fluorescence was measured in liquid methylmethacrylate (MMA). We first discovered these fluorescences as delayed fluorescence in solid polymethylmethacrylate (PMM), where the triplets have lifetimes of ~1 millisecond at room temperature. In liquid MMA the triplet is quenched by collision with oxygen, and there is only prompt (as opposed to delayed) fluorescence. These fluorescences have been verified by excitation spectra. Fig. 25 also shows a delayed fluorescence from Pt etioporphyrin in a degassed solution where the triplet had a lifetime of 63 microseconds. Inasmuch as we believe that this compound should show observable prompt fluorescence, a point to be discussed below, we think that any such fluorescence was masked by an impurity. The Rh (III) compound that was mentioned above as showing phosphorescence also shows some prompt fluorescence.

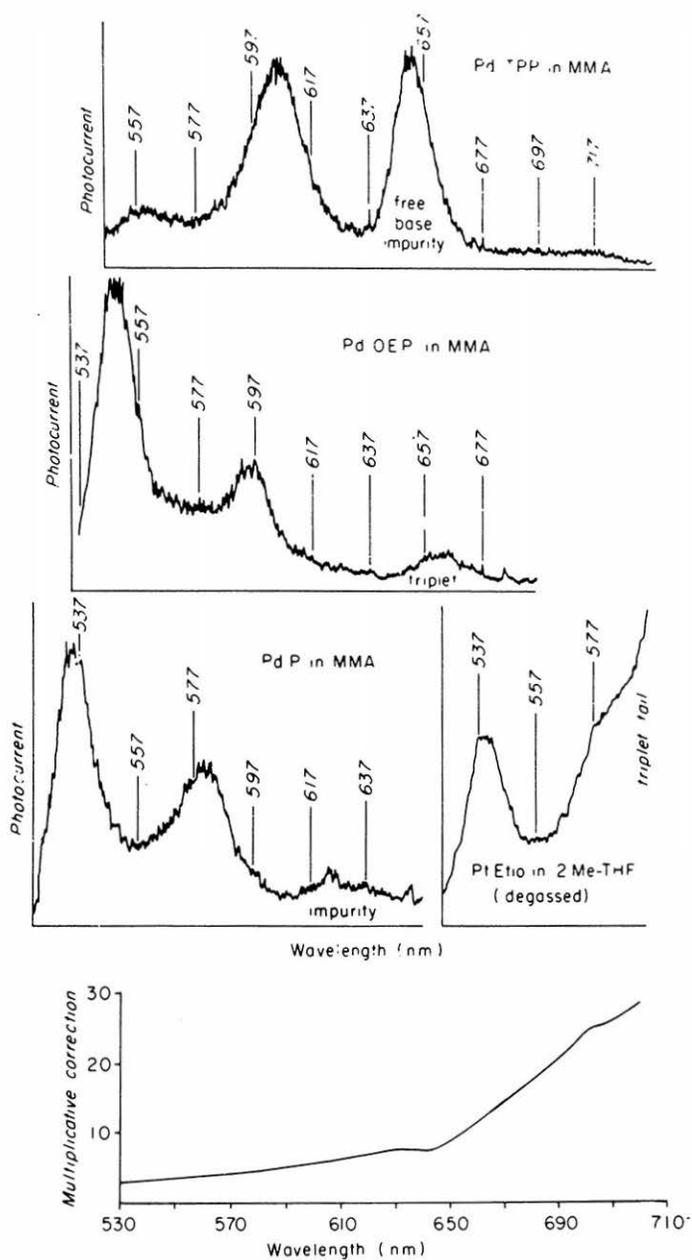


FIG. 25.—Original data showing fast fluorescence from three Pd porphyrins in liquid methylmethacrylate and delayed fluorescence from Pt etioporphyrin in degassed 2-methyltetrahydrofuran, all at room temperature. A multiplicative correction curve for detector quantum efficiency is shown.²²

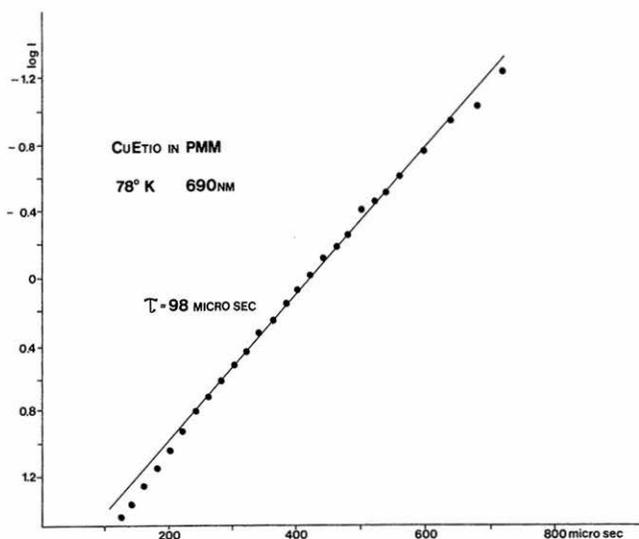


FIG. 26. — Luminescence decay of Cu etioporphyrin in polymethylmethacrylate at 78°K; detection wavelength, 690 nm.

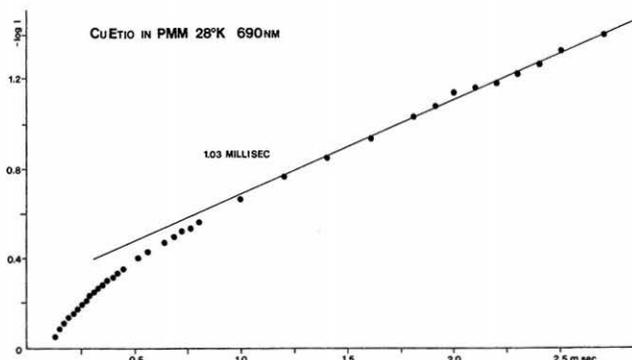


FIG. 27. — Luminescence decay of Cu etioporphyrin in polymethylmethacrylate at 28°K; detection wavelength, 690 nm.

Odd Electron Metals

For a long time I was fascinated by the phosphorescence Becker reported in VO and Cu porphyrins. These complexes have one odd electron in the ground state, which is formally a doublet. If one π electron is excited to form a normal $^1(\pi, \pi^*)$ singlet, the molecule as a whole remains a doublet. However if one π electron is excited to form a normal $^3(\pi, \pi^*)$ triplet, the triplet spin can couple with that of the odd d electron to give either a quartet or a doublet. We call such a doublet, a tripdouplet. The question then arose, does the

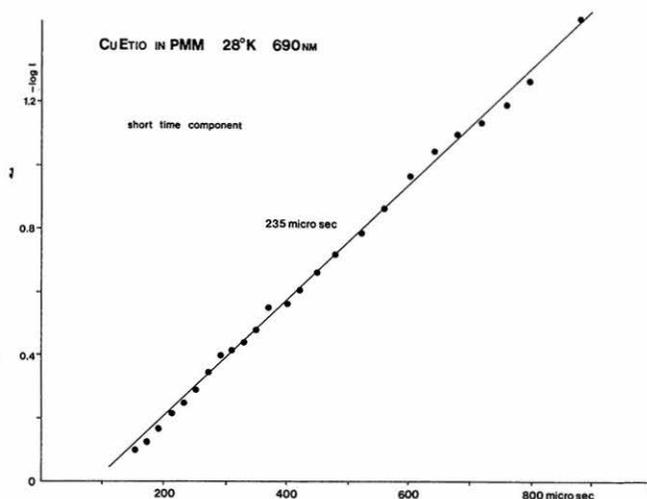


FIG. 28.—Same as Fig. 27 after subtraction of long-time decay.

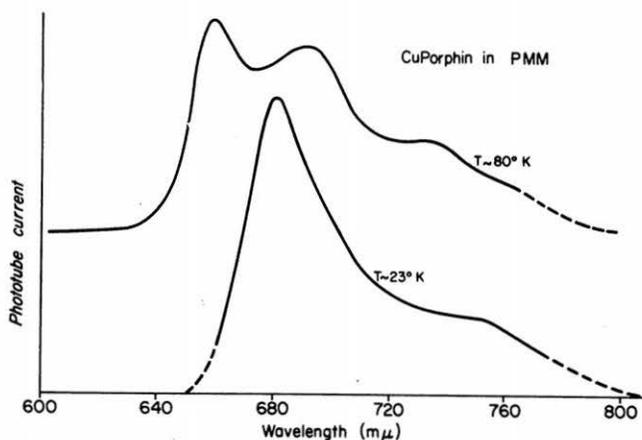


FIG. 29.—Luminescence spectra of Cu porphin in polymethylmethacrylate at two different temperatures.²³

phosphorescence of VO and Cu porphyrins originate from the $^3(\pi, \pi^*)$ quartet or from the tripdouplet?

Several experimental and theoretical papers from our laboratory provide an answer to this question.^{21,23,24,25} In brief, the tripdouplet and the quartet are separated by an energy gap ΔE_{DQ} , which depends on $d-\pi$ exchange integrals. Emission can come from either the tripdouplet or the quartet depending on the molecule and on the temperature. The phosphorescence lifetime will depend on which state is luminescing. Nonexponential lifetimes are observed.

TABLE 3.—Lifetimes and energy gaps for VO and Cu porphyrins.^{21,23,25}

Molecule	temp (°K)	λ_{det} (nm)	τ (μ sec.)	ΔE_{DQ} (est.)
Cu P	78	650	750/155	~ 500 cm^{-1}
	78	685	860/185	
	25		1870	
Cu Meso	74	690	97	130 cm^{-1}
	59	690	190/72	
	41	690	1040/150	
	21	690	1240/220	
	21	725	1140/190	
	11	715	1300/145	
Cu TPP	78	738	610/145/25	> 700 cm^{-1}
	25		1140	
VO Etio	78	710	85	40 cm^{-1}
	50	713	108	
	35	713	175/40	
	21	713	360/66	
	9	710	2100/340	
VO TPP	81	726	16	?
	81	745	10	
	73	726	13	
	73	745	8	

Some of the data on which these conclusions are based are shown in Figs. 26 to 30. Fig. 26 shows the essentially exponential decay of Cu etioporphyrin at 78°K, the lifetime being ~100 microseconds. Fig. 27 shows the luminescence decay from the same sample at 28°K. The long time behavior is exponential with decay time ~1 millisecond. However it is clear that there is also a short time decay component that, as shown in Fig. 28, has a decay time ~200 microseconds. Fig. 29 shows two different spectra obtained from a sample of Cu porphin at different temperatures. Fig. 30 shows the spectral changes with temperature observed for four different copper porphyrins. The two VO porphyrins studied show no spectral changes over the temperature range studied, but VO etioporphyrin showed distinct lifetime changes. The variation of lifetime with temperature is given in Table 3, which indicates cases where two lifetimes are observed. In Cu TPP three lifetimes are observed.

Basically these phenomena are interpreted as follows: As expected from Hund's rule the tripdouplet 2T_1 is at higher energy than the quartet 4T_1 . The transition $^2T_1 \rightarrow ^2S_0$ is far more allowed than $^4T_1 \rightarrow ^2S_0$, where 2S_0 is the ground state. Thus, in many cases as temperature drops the phosphorescence spectrum shifts to the red and the lifetime increases. The energy gap between 2T_1 and 4T_1 that best fits the data is listed in Table 3. The reason for the nonexponential decay is not clear, but it is attributed to slow relaxation among the quartet spin sublevels.

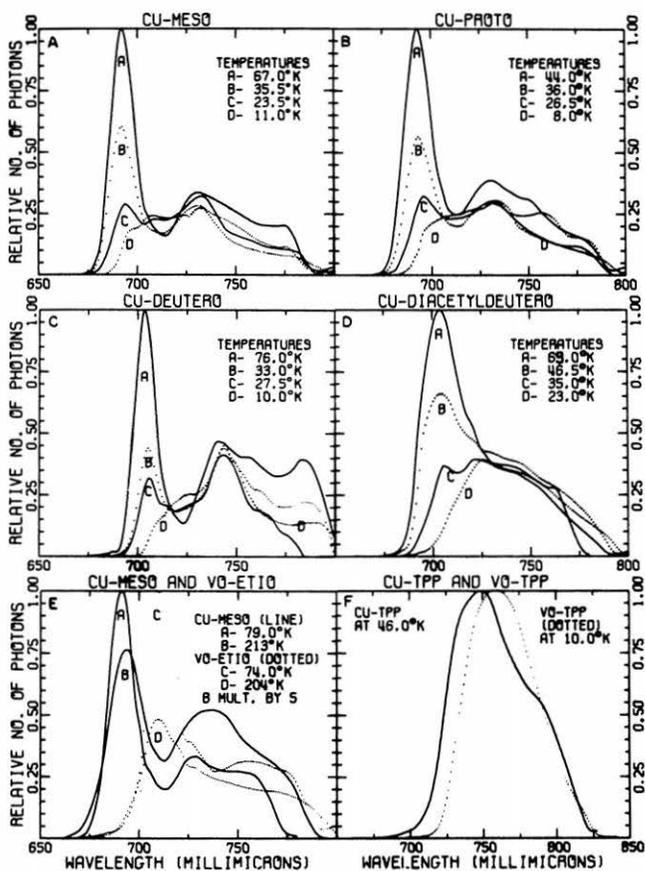


FIG. 30.—Luminescence spectra of Cu and VO porphyrins in polymethylmethacrylate at various temperatures.²⁵

Although the complete picture of the tripdouplet and quartet states is not fully understood, the basic nature of the problem has been exposed both theoretically and experimentally.

Tin Porphyrin

The reason for the very different behavior between Sn and Pb porphyrins was not appreciated by Becker because of a chemical confusion. Because tin porphyrin was made from stannous chloride, it was not generally realized that the product is a stannic porphyrin. Recently we (Paul Smith, work in progress) have studied the effect of the counter ions on the emission spectra by making Sn (IV) porphyrin with hydroxide, fluoride, chloride, bromide, and benzoate counter ions. Although the absorption spectra in these cases are almost identical, the emission spectra are quite effected. Thus for bromide we find that the fluorescence is very largely quenched and the phosphores-

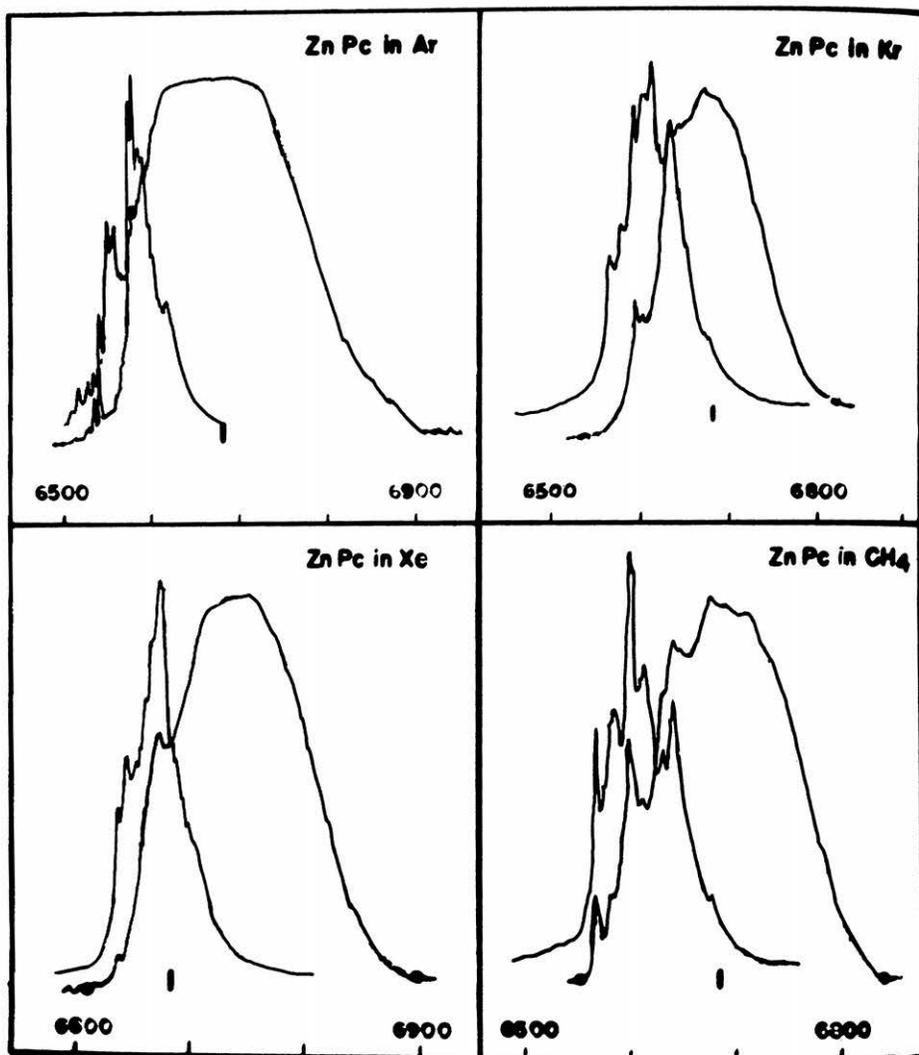


FIG. 31.—Traces of absorption and fluorescence plates of Zn phthalocyanine in various matrices. Circles indicate fluorescence curves, and the bar indicates the Hg $2 \times 3341.5\text{-}\text{\AA}$ line.²⁶

cence lifetime is much shorter. This may seem peculiar, at first glance, because Br is considerably less heavy than Sn.

An explanation for the effect of the counter ions on emission can be proposed. It turns out that because of the highly symmetric position of the Sn atom in the porphyrin skeleton, the only way it can affect spin-orbit coupling between the porphyrin $^3(\pi, \pi^*)$ and $^1(\pi, \pi^*)$ states is by the mixing of $4d_{\pi}$ orbitals into the ring $e_g(\pi^*)$ orbitals. The Br atom can influence spin-orbit coupling by mixing in $4p_x, 4p_y$ orbitals into $e_g(\pi^*)$. This latter should occur to a far larger extent. Thus qualitatively we can explain why Br with atomic

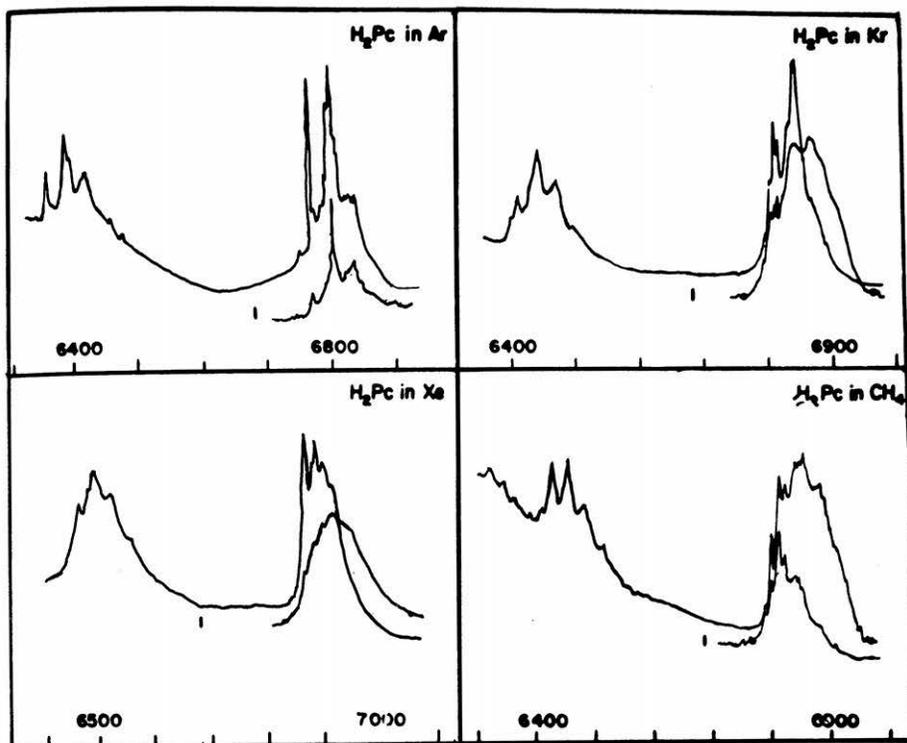


FIG. 32.—Same as Fig. 31 for free-base phthalocyanine.²⁶

number 35 has more effect on phosphorescence than Sn with atomic number 50.

QUASILINE SPECTRA

Spectra in Gaseous Matrices

The latest spectral work to be undertaken in our laboratory is the investigation of porphyrin quasilines. The existence of such lines was first reported in 1963 by Personov, who reported Shpol'skii spectra for phthalocyanine. Shpol'skii first observed sharp lines in the spectra of polyacenes in linear hydrocarbons such as pentane, heptane, *etc.* The general explanation attributed these lines to a matching of the length of the aromatic to the alkane. I had some skepticism about this general interpretation. Because a colleague of mine, Beat Meyer, had experience with matrix deposition techniques, we decided to try such experiments on the phthalocyanines.²⁶

Figs. 31 and 32, show densitometer traces of plates taken of the absorption and fluorescence spectra of Zn P_c and H₂P_c in matrices of Ar, Kr, Xe, and CH₄. Sharp lines can be observed both in absorption and in fluorescence. The sharpest lines were observed in Ar, showing that a matching of solute and solvent lengths is unnecessary for the observation of quasilines. We also drew several other interesting conclusions:

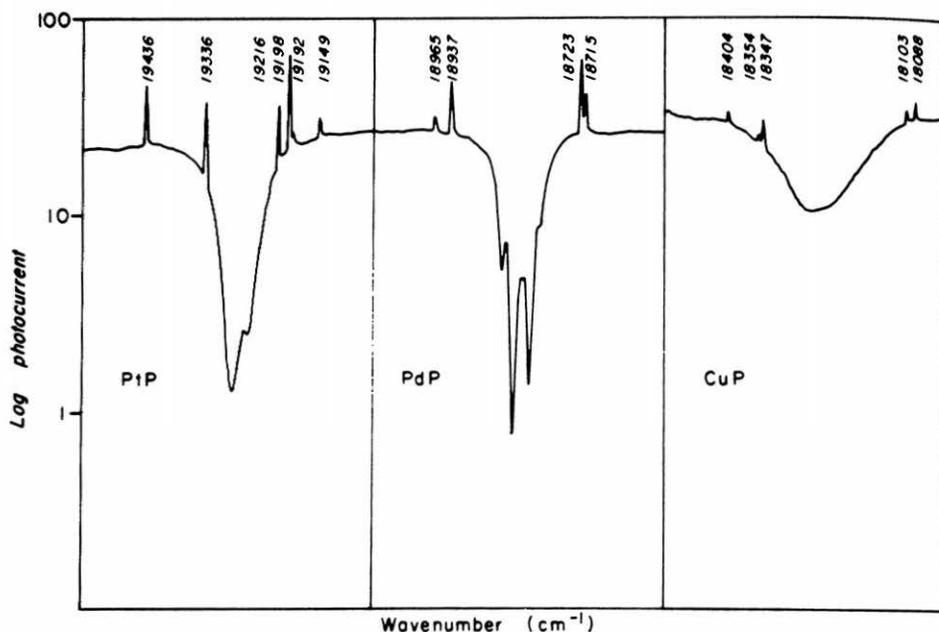


FIG. 33.—The $Q(0, 0)$ absorption band of Pd, Pt, and Cu porphyrin in *n*-octane at 77°K. Emission lines are Ne.²²

1) The lower energy Q_x band of the free base is considerably sharper than the higher energy Q_y band, a result we attribute to uncertainty broadening due to radiationless decay from Q_y to Q_x . A similar effect observed in free base porphyrin was explained in the same way by Hochstrasser.

2) There is considerable evidence that in the case of Zn Pc, the electronic degeneracy is slightly lifted by the environment in the matrix. The size of this crystal field type splitting can be estimated from the data to be 10 to 20 cm^{-1} .

3) Another conclusion, never previously mentioned in publication, is that the molecules are oriented with their planes parallel to the target surface. This conclusion was tentatively reached on the basis of a negative result of a Zeeman experiment performed by Beat Meyer and Larry Bajema and was confirmed by Paul Kasai, who examined the ESR spectra of matrix-deposited Cu Pc.

Uncertainty Broadening

Our most recent publications attempt to relate the lifetime of porphyrin excited states to the quasiline halfwidth.^{22,27} We believe that this can be studied quantitatively from the uncertainty relation

$$\Delta\tilde{\nu}_{1/2}\tau_f^* > (2\pi c)^{-1}$$

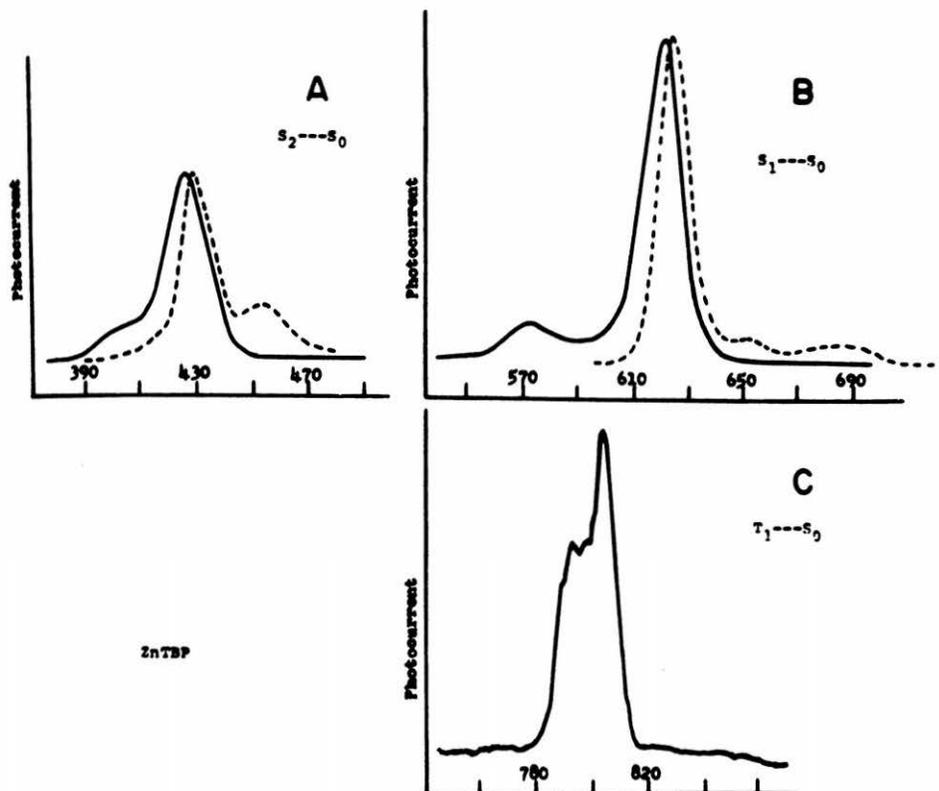


FIG. 34.—Zn TBP in octane (plus 0.5 per cent pyridine): A, excitation ($\lambda_{\text{det}} = 687 \text{ nm.}$, solid line) and fluorescence ($\lambda_{\text{exc}} = 403 \text{ nm.}$, dashed line) spectra at room temperature; B, excitation ($\lambda_{\text{det}} = 687 \text{ nm.}$, solid line) and fluorescence ($\lambda_{\text{exc}} = 430 \text{ nm.}$, dashed line) spectra at room temperature; and C, phosphorescence ($\lambda_{\text{exc}} = 678 \text{ nm.}$) spectrum at 77°K. ²⁷

Here $\Delta\tilde{\nu}_{1/2}$ is the halfwidth of the quasiline in wavenumbers, τ_f^* is the excited state lifetime, and c is the velocity of light. The excited state lifetime relates to the quantum yield inasmuch as $k_f\tau_f^* = \Phi_f$, where k_f is the natural radiative decay rate. Thus, states that show narrow quasilines must show some fluorescence.

Fig. 33 shows a Shpol'skii study done in our laboratory on Pd, Pt, and Cu porphyrin.²² Now, as discussed above, PdP shows a measurable fluorescence yield, which is more than the minimum consistent with the observed quasiline halfwidth of 8 cm^{-1} . The quasiline halfwidth of PtP is $\sim 16 \text{ cm}^{-1}$, implying a lower minimum fluorescence yield than PdP. Although this yield could have been detected by our apparatus, it was masked by an impurity in the sample of Pt etioporphyrin that we studied. As discussed above, the CuP absorption is not due to an excited singlet but to a state better called a sing-doublet. Radiationless decay to the lower energy tripdoublet, discussed above, should be particularly fast. Thus we expect a very broad quasiline, and

in fact none is observed. Russian workers previously reported that the absorption spectra of PdP showed quasilines whereas CuP did not. They did not, however, relate this finding to uncertainty broadening, and did not look for PdP fluorescence.

Soret Emission $S_2 \rightarrow S_0$

Very few molecules are known that show fluorescence from any state except the lowest excited singlet S_1 . One of the few well-studied cases is azulene, where it is attributed to the very large energy gap between the second singlet S_2 and S_1 . In the course of study of Zn tetrabenzporphyrin in Ar matrices, we found a quasiline halfwidth for the Soret band of $\sim 6 \text{ cm}^{-1}$, not much larger than $\sim 4 \text{ cm}^{-1}$ observed for the visible band. Guided by the uncertainty principle, we deduced that there should be an easily observable quantum yield for the emission $S_2 \rightarrow S_0$. This was indeed observed as shown in Fig. 34. It has the high quantum yield of $\Phi_f \sim 0.0016$. Because the molecule shows a quantum yield of $\Phi_f \sim 0.35$ for $S_1 \rightarrow S_0$ and a yield of $\Phi_p \sim 0.02$ for $T_1 \rightarrow S_0$, the molecule Zn TBP is unique in showing three fairly strong luminescences. We hope that the relation between quasiline structure and luminescence yields might prove generally useful for discovering other cases where the transition $S_2 \rightarrow S_0$ occurs.

SUMMARY

In this paper I have considered the electronic structure and spectra of porphyrins and related ring systems. We have seen that the basic spectra of the visible and near ultraviolet region arise from transitions between molecular orbitals that are analogous to the top filled and lowest empty orbitals of a free electron ring of 18 electrons. The various spectral changes in the visible and near ultraviolet region that occur among the various rings such as porphin, chlorin, phthalocyanine, *etc.* that preserve the inner ring arise mainly from the variations of these principal four orbitals caused by changes of the ring skeleton. For a given skeleton, changes among closed shell divalent metals or metal counterion groups, *e.g.* Mg, Zn, Sn and Cl cause only small variations in the electronic structure and spectra. Change from a divalent metal to H_2 (*i.e.*, free base formation) lifts the electronic degeneracy of the (π, π^*) transitions. Among these closed shell metalloporphyrins and the free base, the electronic spectra down to 200 nm appear to be largely (π, π^*) in character. For molecules with aza nitrogens in the bridge positions (*e.g.*, phthalocyanine), the diffuseness of the Soret region combined with the predictions of EH theory suggest that (n, π^*) transitions may occur in the near ultraviolet region.

Metals with other electrons can show a variety of effects depending on the interaction of these electrons with the basic four (π, π^*) orbitals. The best understood cases are Cu and VO, where a single unpaired d electron changes the ground state to a doublet and the lowest triplet $^3(\pi, \pi^*)$ to a tripdoublet

and quartet. Another well-understood case is Sn (II) where an extra pair of electrons in the $5p_z$ orbital seem to be in resonance with the top-filled $a_{2u}(\pi)$ level. The low energy spectrum then may be thought of as due to transitions from three top filled to two lowest empty orbitals. Clear effects on the low energy absorption are also seen in certain iron and manganese porphyrins. In these cases the effect may be due to resonance between the partly filled $e_g(d_\pi)$ and $e_g(\pi^*)$ orbitals. Other effects of a partly filled d shell occur in the absorption spectrum between 340 and 200 nm. Such effects are particularly clear in Ni phthalocyanine. Another effect of partly filled d shells may be in the quenching of luminescence (*e.g.* in Co and Ni porphyrins). This might be due to the presence of $d-d$ transitions between the lowest energy ${}^3(\pi, \pi^*)$ state and the ground state. The outstanding theoretical problem is to be able to calculate the energy and interaction of the metal electrons with the π electrons in those cases where these interactions affect the lower energy excited states.

Finally, it should be noted that porphyrins show quasiline spectra. These spectra seem to indicate the splitting of the electronic degeneracy by the environment. It also seems possible to relate the quasiline width to the lifetime of the excited state by the uncertainty principle.

So far, we have not related our understanding of the electronic spectra and structure to the biological function of chlorophyll and heme. However we have at least made clear why Mg would not do for heme or Fe for chlorophyll: Fe would never sustain an excited state long enough for photosynthesis; Mg does not have the variety of oxidation states, spin states, and relation to ligands that Fe has. Hopefully the knowledge we have of the electrons in porphyrins will be helpful to those engaged in biological studies when they try to understand how these molecules function.

ACKNOWLEDGMENTS

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DISCUSSION: LEADER, DR. R. M. PEARLSTEIN

Dr. Lim.—It is possible that the emission (not identifiable) that you see is actually fluorescence from an S_2 state. When the electronic energy gap is very small, the density of the lower electronic state near the electronic origin of the upper state is so small that the emission from the upper state may compete with slow radiationless transition between the two close-lying excited states. The observation of $T_2 \rightarrow S_0$ emission in *p*-benzoquinone and its methyl derivatives can, for example, be traced to this origin.

Dr. Gouterman.—Yes. Let me comment on that. I might say that one has to be careful if the energy gap is small. About five years ago, we reported the vapor luminescence of free base phthalocyanine. In the vapor there are two electronic states in the visible separated by ~ 1500 cm^{-1} . We saw luminescence from S_2 , which we attributed to thermal repopulation. If the energy gap is small, one has to be careful that an observed $S_2 \rightarrow S_0$ emission is due to a slow radiationless decay and not a thermal equilibrium.

Dr. Lim.—The experiments on *p*-benzoquinone and derivatives were carried out at 4°K at which temperature thermal repopulation of the upper state can be ruled out. Slow radiationless transition arising from the very low density of states is also a possibility in your case.

Dr. Gouterman.—Yes. But I doubt that this was the reason for our observation of $S_2 \rightarrow S_0$ in free base phthalocyanine. We were working at 500°C and thermal repopulation was extensive. The fluorescence $S_2 \rightarrow S_0$ was absent at low temperature. I think that the emission $S_2 \rightarrow S_0$ that we observe in zinc tetrabenzporphyrin is a borderline case for luminescence to occur in competition with radiationless decay. Although the density of states is relatively high, I suspect that the vibronic coupling between S_2 and S_1 is relatively small because the two states may be very

similar in shape. As a result, the rate of crossover could be low. On the other hand we know that the natural radiative decay rate is very high. I think that it would be interesting to study some closely related molecules to see which show $S_2 \rightarrow S_0$ and which do not; *i.e.*, what is the behavior of molecules in this borderline region.

Dr. Song.—How are the assignments of Q_y and Q_x made in the visible bands? In certain diagrams, such as for example chlorin, the diagram shows Q_y lowest. In other cases Q_x is lowest. Do you make assignments on the basis of the relative intensities of those two bands, or do you actually carry out polarization studies, for example photoselection?

Dr. Gouterman.—That is a very good question. Recently we completed a paper (Porphyrins XXV) which explores this problem using the extended Hückel model. For all skeletons except chlorin and bacteriochlorin we adopted the convention that calls Q_x the lower energy visible band and Q_y the upper energy visible band. Thus the question becomes how do x and y relate to the molecular geometry—in particular to the H-H axis of the central free base protons. Assuming these protons to be bonded to the central nitrogen atoms, we predict relatively unambiguously that in porphin and tetrazaporphin Q_x is parallel to the proton axis, whereas in phthalocyanine it is perpendicular to this axis. In tetrabenzporphin, our calculations do not give an unambiguous answer. The cases of chlorin and bacteriochlorin are different, because it has been the biochemical convention to draw the geometry with the reduced rings on the x axis. We calculate the polarization of the lowest band to be Q_y in the metalloderivatives. Resonance structures force the proton axis of the free bases to be on the y axis, and in the free bases we also predict Q_y to be the lowest energy band.

Experiments have shown that Q_x and Q_y are polarized perpendicular to each other. There is very little work relating polarization to the molecular axes. One study by Anex and Umans confirms our prediction for free base porphyrin.

Dr. X.—I have a question about the data of Allison and Becker. They found that changes from light to heavier alkali earth complexes caused the fluorescence to go down and phosphorescence to go up. However, Hg and Pb are both very heavy but have very weak phosphorescence. Why is that?

Dr. Gouterman.—That is a good question. Although Hg is isovalent with the alkaline earth metals, the absorption spectra of Hg porphyrin is rather peculiar. This may reflect something unusual about the compound that causes the irregularity. Perhaps the metal may be out of the plane, or perhaps the species may be dimerized. In general, if there is an anomaly in the absorption spectrum, an anomaly in the emission spectrum is not surprising. We understand the case of Pb far better. It is not equivalent with the alkaline earths, for Pb(II) has two extra valence electrons. Becker erred on this point; he thought he was studying Pb(II) and Sn(II), but his Sn porphyrin was actually Sn(IV). We have recently studied Sn(II) and Pb(IV). Although our studies are not complete, they indicate that Pb(II) porphyrin differs from the alkaline earth complexes because of the two extra electrons. We might note that the phosphorescence Becker reported for Pb(II) porphyrin is above 800 nm, rather to the red of normal porphyrin phosphorescences. On the other hand, we have found a relatively strong phosphorescence from Pb(IV) in the normal wavelength region.

Dr. McGlynn.—The cases of the palladium and platinum complexes are interesting. There is another series of flat planar compounds, the palladocyanides and the platinum cyanides, which show phenomenology conditioned by a weak conjugation of sigma-type between the palladium atoms of different compounds. For example, platinum cyanide does not emit in true solution; but at 10^{-4} molar, in what supposedly is a true solution, actually has a substantial number of these flat platelets joined together to form complexes. Then it emits very beautifully and very strongly. At the same time, there is a change in the absorption spectrum, which can be related to the sigma conjugation of d electrons from one platinum through the others. I wonder if perhaps the effects associated with this sort of phenomenon, rather well documented in those instances, might have some bearing on your luminescences in the particular cases of those platinum porphyrins? That

is question 1. Question 2: You used a gradient operator for transition probability and apparently got good results. I am mystified. As I understand it, there is no basic difference between the gradient operator and any other form of the transition probability operator that we use. Therefore, a better result using one form must imply that you are making up for some deficiency in your wave functions. But it is really in truth no better than using the Murrell mystic number of 3.7 to reduce your calculated number on the dipole length formalism to correlate it with the experiment. In other words, it is not particularly esthetic; I would like to know if you have any reason to suppose it should be. A further comment, with regard to lead, is that increased spin orbital coupling does not necessarily give production of phosphorescence, because increased spin orbital coupling will assuredly simultaneously increase all intersystem crossing routes, presumably at the same or different rates. That covers all possibilities, so I have to be right! Therefore, there is no *a priori* reason to suppose that it should be the luminescence route. Lead is described in the introductory inorganic chemical literature of the freshman chemist as being soft and fluffy. I think by this they mean that it is rather readily polarizable and that it readily involves itself in charge transfer phenomena: namely, let us say, from the porphyrin into the lead, or *vice versa*, even from the lead to the porphyrin. If these states get mixed into the lower states of your total system, and they can, because in the case of lead they are of quite low energy, no one knows what they are going to do. Do you have any reason to suppose they should increase the luminescence?

Dr. Gouterman.—Let me say about the third point, yes I would agree. A spin orbital effect would tend to increase both radiationless rates and radiative rates. One would hope that for a series of metal porphyrins, all of which have similar structures, there will be systematic changes with the heavy atom. However, lead is rather different in that it has two extra electrons and is out of plane. Thus it is not unreasonable to find that the radiationless rates are much more enhanced than the radiative rates by comparison with the alkaline earth complexes.

About the dipole, again I would agree that, as is well known, approximate wave functions do better on some measurables than on others. When you have equivalent measurables, such as the gradient and the dipole, that are supposed to be measuring the same thing, it is strange that the gradient fits the data and the dipole does not. I hope that someone will provide a good answer as to why the one is good and the other is not. In the meantime should one use the fudge factor of 3.7 or the gradient operator? The answer, of course, depends upon the final analysis of why the one operator comes closer to experiment. In our case we found the following, which is evidence for the gradient operator. One of the interesting features of porphyrins is that experimentally the Q_y band is always stronger than Q_x . We could not obtain this result with the dipole operator, but it did come out very nicely with the gradient operator. That is a small piece of evidence that the gradient operator was better in that case. But one case does not prove the point. It is a kind of inductive proof. As to the palladium and platinum, I would say that they are very, very regular as far as their other behavior as porphyrins goes; they give very sharp spectra and they have regular wavelength and intensity patterns. Therefore, I do not believe that they are showing any peculiar chemical forms, such as a dimer. As I mentioned, mercury porphyrin has a peculiar absorption spectrum indicating that some peculiar phenomenon may be occurring. Nothing like that occurs in palladium and platinum porphyrins, so I think these are monomers.

Dr. Kasha.—Martin, I wanted to make a comment about the uncertainty broadening limitation of the band wave. A long time ago, in looking at spectra, admittedly poor spectra of published cases of molecules in solution, it looked as if there were a general rule that emitting states seem to show sharp transitions whereas nonemitting levels in fact broadened. It seemed clear that a correlation of uncertainty broadening with very rapid radiationless processes was present. One reason I set out to talk about this is that I saw a very magnificent manuscript of 50 new spectra done at high resolution in the vapor phase covering many heterocyclic and aromatic molecules by Burn and Ross in Australia (*Australian Journal of Chemistry*, in the press). In this study, they went to the trouble of getting very carefully observed spectra over a very wide spectral range to establish whether it was possible that uncertainty broadening was the limiting factor.

They did find that, with one curious exception, which they did not understand, the rule seems to hold: essentially nonemitting levels are very much uncertainty broadened. I am curious about your statement that you were now applying uncertainty broadening limitations to emitting states. I, therefore, have a question. Does that come about because, in fact, they are of such high oscillator strength? Does the lifetime now get so short that even emitting states can be uncertainty broadened? You made the statement that they were in conformity with uncertainty broadening, but I do not remember whether there was a greater than or an equal sign. It is an equality. Did you show it that way, or not?

Dr. Gouterman.—Uncertainty broadening has been applied quantitatively in vapors. Hochstrasser implicitly used the idea to discuss line broadening at low temperature of molecules in the condensed phase. Although we have not yet used the uncertainty principle as an equality in the case of palladium and platinum porphyrin, I believe it is possible. The observed quasiline halfwidths are 8 cm^{-1} and 16 cm^{-1} respectively. Inasmuch as the two molecules are as alike as peas in a pod with regard to spectra and other properties, we believe that this difference is due to the faster radiationless decay of S_1 in the platinum case. However, the linewidth is sufficiently narrow for platinum for a small prompt fluorescence to be observable. That the molecule shows delayed fluorescence in a degassed solution encourages this view. Unfortunately our sample showed impurity luminescence at too high a level for us to observe the prompt fluorescence predicted by the uncertainty equality. If we can reduce impurities by a factor of three to five, we should be able to apply the principle as an equality.

Dr. Kasha.—I would like to make a second comment about the form of the transition probability operator in relation to its accuracy. I suppose the general idea is that the wave functions are more sensitively involved in determining areas in transition probability than they are in energy, because of the nature of the perturbation energy calculations. But I remember one study, made by a Russian quantum chemist, Selkolnikof, to show that even though mathematically equivalent operators are used, the wave functions differ with regard to where they are in error. He had a very clever way of integrating up to a certain radius from the atomic center and then replacing it by the next form, and the next form, and he was getting much better fits. I think that such a study might be very pertinent to your empirical discovery, and from that point of view it is much more esthetic than the fudge factor. On that point, it really comes up to the configuration interaction. I think that you used very high configurations—doubly or triply excited states.

Dr. Gouterman.—No, we used very high singly excited states.

Dr. Kasha.—It is known that inclusion of double excited states has a strong effect on oscillator strength, but usually only for the upper excited states. The reason that I make that point is that the error in the wave functions might be partly due to correlation, and the including of doubly excited states reduces the correlation effect. Thus the gradient and dipole operators come closer in value and the disagreement with experiment is reduced.

Dr. Y.—This is a remark of basically the same type. It has been shown that if you make some reasonable approximations for your resonance integrals and if you do complete configuration interaction, you get identical results for the gradient and length operators because the commutation relation between position and momentum is then satisfied. I believe this work was done by someone in Denmark. Your statement that one operator is better than the other depends, as you pointed out, on how much configuration interaction with multiply excited configurations was included in the wave function.

Dr. Gouterman.—Yes, I remember that now. Hansen [Mol. Phys. **13**, 425 (1967)] showed that for a Hartree-Fock ground state and a single configuration excited state the errors of the transition dipole and transition gradient due to correlation effects tend to be complementary. On this basis Hansen concluded that it is better to use their geometric mean value rather than either one. Inasmuch as we found that the gradient agrees with experiment, Hansen's formula would still give results high compared with experiment. So I do not think this fully answers the question.

EXCITED STATES OF DNA

R. G. SHULMAN

I would like to relate to you the excitement my colleagues and I have had in trying to pull ourselves up out of the depths of solid state physics into something that is biologically interesting and relevant. It has been a group effort, because we all wanted to do something of this sort; so that while this paper will be partially reminiscent, I hope that the reminiscences will be to a point, which is that when you do studies on biological molecules, you had better try to make them biologically interesting. In fact, almost the worst thing you can do is make them interesting to chemists and physicists. Hence if this story interests you today, I apologize, because it should not. To tell you where this started; about eight or nine years ago, someone who had been my roommate at one time at the California Institute of Technology and was a biologist, said to me "the Russians have found that DNA has one unpaired electron per base pair by electron spin resonance." I knew what electron spin resonance was; I did not know what DNA was, but I did not let him know that and we continued talking. Before long, he told me what DNA was, and I think that if we have had any success in understanding DNA, it is really because we have not been discouraged by everything we did not know when we started. None of us had worked on excited states of molecules, and certainly no one knew anything about organic chemistry. I did have a colleague who claimed to know what DNA was, but upon subsequent discussion, it turned out that he was bluffing. But there was something that we did know about DNA, and that was that it did seem unlikely there could be one unpaired electron per base pair (whatever a base pair was). We got the idea that a base pair was not very large, so that meant a lot of unpaired electrons in the ground state of DNA. To repeat those experiments Mickey Walsh and I studied the electron spin resonance of DNA and, sure enough, there was a very big electron spin resonance signal. However, it turned out that the intensity of that signal was temperature independent, with a g -factor different from the free electron g -factor of 2.0 (it was a little higher and asymmetric). We fairly soon concluded that it was ferromagnetic. If electrons are ferromagnetic, they are all coupled together, and flip together and so they act as if they have a much larger magnetic moment than if they are isolated paramagnetic electrons. When we converted the intensity of that signal to the number of electrons responsible, it turned out to be 1000-fold smaller than was required on the assumption of paramagnetism. We concluded that the signal was ferromagnetic in origin. Then the question was: What was ferromagnetic? For about three weeks we believed that DNA was ferromagnetic, and there were collective electrons involved, working together in some way. We were very excited by that, and, luckily, we kept doing experiments; we did not publish anything, we would just come in each day and oscillate with excitement because DNA was obviously ferromagnetic. Finally,

it turned out that DNA was not ferromagnetic; there were some ferromagnetic impurities which had come into DNA during preparation. You can get rid of these impurities, but it is difficult. We tried hand-picking under a microscope, but that did not work. But, in one sense, it was too late, the hook was set; DNA was not ferromagnetic, but we were now extremely interested in DNA. By that time, we knew what DNA was, and I will tell you what it is today. Then, we thought we would try something a little more tractable. John Platt has been quoted as saying that physicists getting interested in biology do one of three kinds of experiments: they either do physical experiments which are good and biologically irrelevant; or they do biological experiments which are bad and physically irrelevant; or they do radiation damage. The one thing we did know was that there was some biological importance of radiation upon DNA; in fact, there really is a very nice curve, which shows that for bacteria the optical absorption spectrum of DNA is the action curve for killing. So we started irradiating DNA with high energy radiation, using cobalt, and a Van der Graff accelerator. Then Ronald Rahn came along, and irradiated DNA with ultraviolet. I told him not to do it, but he did it, and he got a free radical, the same free radical that we had been seeing by use of ionizing radiation. Then we measured a lot of hyperfine interactions of that free radical and proved that the free radical was formed in thymine, one of the four bases in DNA. We had identified one particular place in this enormous molecule, a repeating unit, where free radicals are formed upon irradiation. We thought maybe we ought to find out what goes on before that free radical is formed, so we started studying the excited states of DNA, because that obviously had something to do with the free radical, which might in turn have had something to do with lethality or mutagenesis. So, we read Dr. Kasha's papers and many other papers, and it was hard work, but fun. And we read and read and read and measured and measured and measured for years and years and years. And that is what I am going to tell you about today.

The first slide shows you what DNA looks like in a schematic way. It is, as you know, the repository of the genetic code. It is the molecule that makes the bacterium, *Escherichia coli* like its parents, and makes people like their parents, and so on. As seen in Fig. 1, it has an alternating sugar-phosphate backbone. There are two different directions of polarity of this, depending upon whether the phosphate is attached to the 3' or the 5' end of the sugar; one chain goes one way and one the other. Sugar does not absorb in the near ultraviolet, and phosphate does not either, so that the only ultraviolet light absorbers are the four bases, thymine (T), adenine (A), guanine (G), and cytosine (C), which are hydrogen bonded, as Watson and Crick showed by analysis of the X-ray diffraction data, so that T is always hydrogen bonded to A, (thymine to adenine), and G to C (guanine to cytosine). The helical structure is represented only schematically by the ribbons indicating the sugar-phosphate backbones, and the flat plates indicating the pseudoaromatic bases. There are two hydrogen bonds between adenine and thymine, very specific hydrogen bonds, which

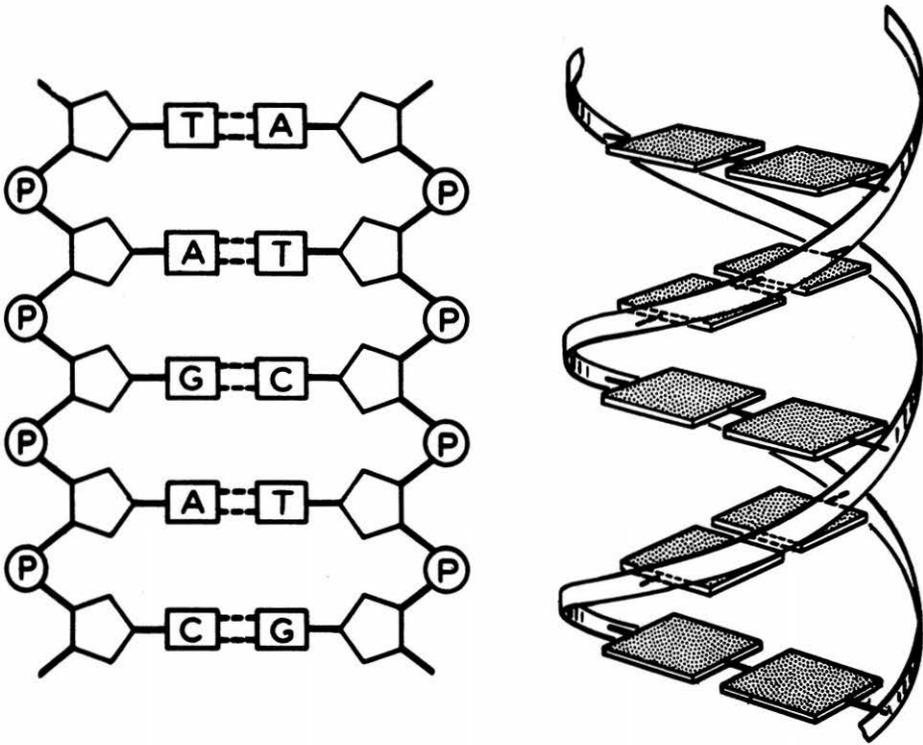
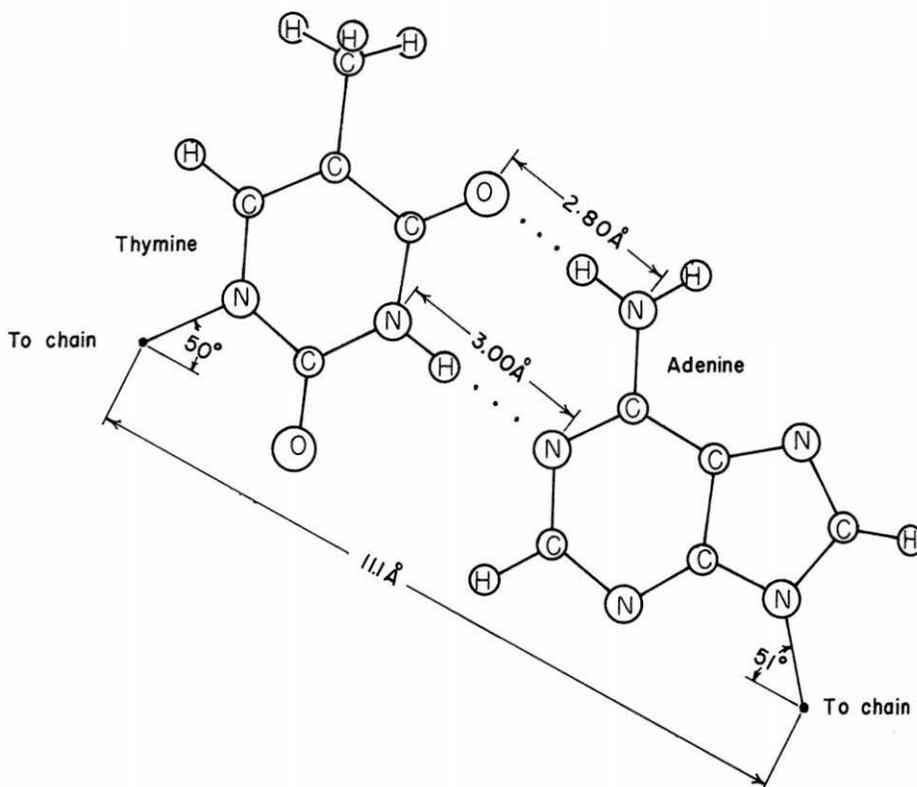


FIG. 1.—Schematic of DNA.

means that adenine always chooses thymine as a partner, and three between guanine and cytosine, so that during replication the hydrogen bonds break and a new DNA strand is formed upon each half. You end up, then, in this semi-conservative way with two strands of DNA, each of which contains one of the original strands and one of the daughter strands. So, you have two for one, which is growth.

There are smaller units of DNA. First of all, there are the four separate bases; sometimes they will be discussed in terms of A, T, G, and C, at other times I shall use AMP, TMP, GMP, and CMP. There are dinucleotides, which consist of two nucleotides together, sometimes with two phosphates, sometimes with only one. The most commonly discussed dinucleotide would be a base, a sugar, a phosphate, a sugar, a second base. DNA is, of course, a polynucleotide with a molecular weight for bacteria of the order of billions, and larger for man as far as one can tell. Synthetic polynucleotides are made by putting together the individual bases as monomers and, with enzymes, zipping them up. So there could be, for example, poly A, in which all the bases are A, or poly-dAT, which is ATATAT, and so on. The chemical formulae of the AT base pair is shown in Fig. 2. Adenine is one of the purines; the other naturally



Adenine-thymine pairing in DNA

FIG. 2.—A-T base pair.

occurring purine is guanine; thymine is one of the pyrimidines, the other naturally appearing pyrimidine is cytosine; uridine is sometimes also found and occurs in RNA, but not in DNA, in place of thymine. There are two hydrogen bonds between A and T. The N-3 nitrogen of thymine has a hydrogen bond to the ring nitrogen of adenine. Adenine is well conjugated whereas thymine has one double bond in the ring. The absorption spectra of these molecules, adenine, thymine, guanine and cytosine, to a first approximation are similar. That is, their first absorption is a broad band centered at about 260 nm, but there are small differences between them, and those differences became very important in distinguishing the bases. We worked, at the beginning, only at low temperatures (generally at liquid nitrogen temperatures, 77°K), dissolved the nucleotides or the polynucleotides in ethylene glycol-water glasses (50 per cent ethylene glycol, 50 per cent water), and we tried to monitor the state of the molecule whenever there was any doubt by using optical rotatory dispersion or the optical absorption. Ethylene glycol water is a very good water-type solvent for the secondary and tertiary structures of DNA polynucleotides. It

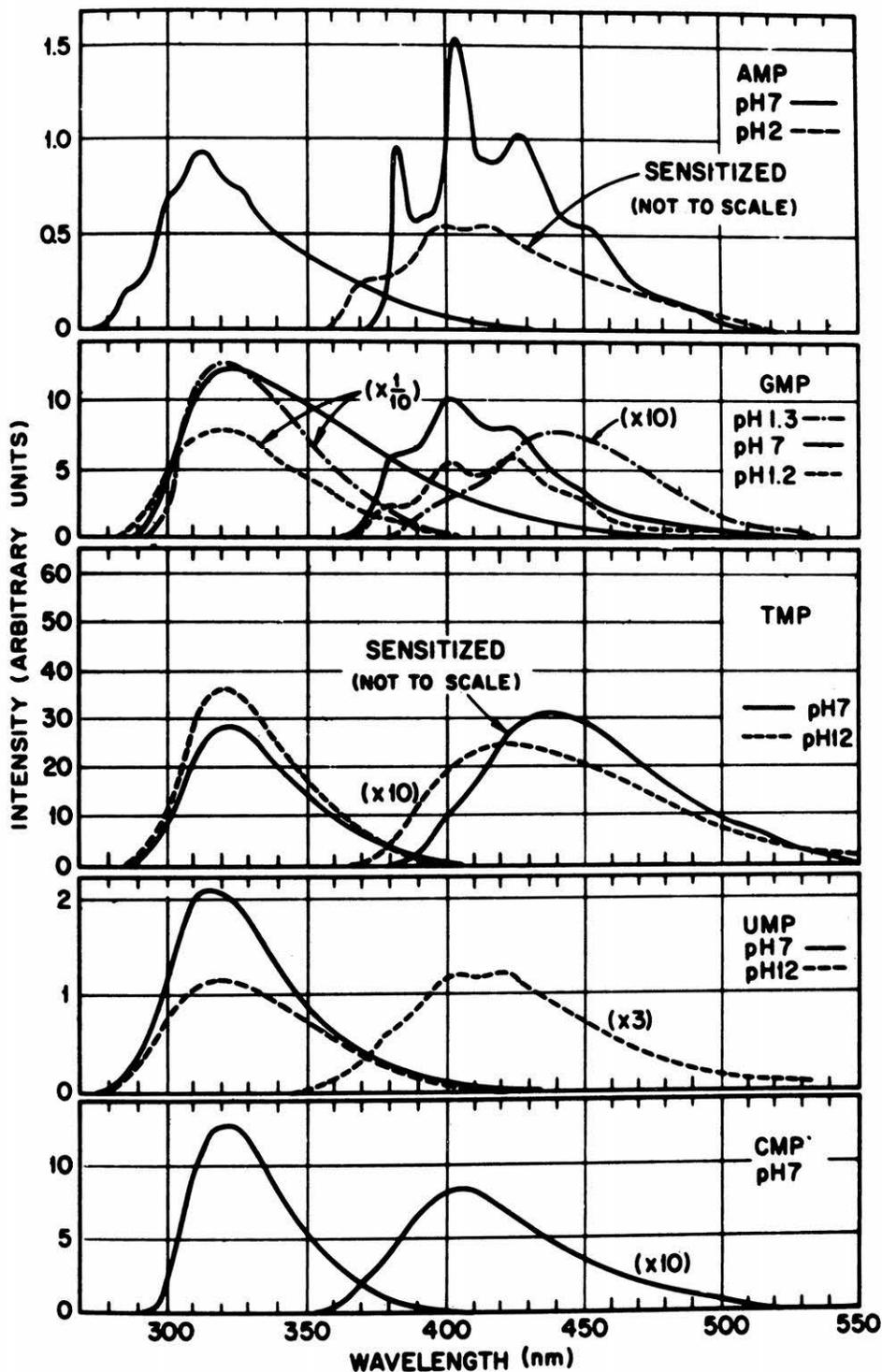


FIG. 3.—Emission spectra of nucleotides.

TABLE 1.—Triplet and singlet energies in nucleotides and sensitizers.

	E_T	E_S	ΔE_{S-T}
U ⁻	28.40	35.00	6.60
Acetone ¹³	28.20	~33.0	
C	27.90	33.70	5.80
AH ⁺	27.35	34.80	7.45
G	27.25	34.00	6.75
T ⁻	27.00	34.35	7.35
A	26.70	35.20	8.50
Acetophenone ¹²	26.50	27.40	
T	26.30	34.10	7.80

does not interfere with them any more than water does, and gives a nice glass so you do not get freezing out of the nucleotides in aggregation, which tends to confuse things. Fig. 3 shows the emission of some nucleotides. Consider the fluorescence and phosphorescence of AMP; it is one of the most characteristic of the emissions, because it is strongly structured. Guanine phosphorescence, also, is somewhat structured. The fluorescence yields of all of these compounds at liquid nitrogen temperature are very low. They range from less than one per cent to about 10 per cent. Thymine at high pH has the largest yield, about 10 per cent. The intersystem crossing rates have all been determined by measuring the intensities of the phosphorescence, and particularly by measuring the intensities of the triplet state using electron spin resonance. Measuring the phosphorescence yield only tells you how many triplets are emitting light when they decay to the ground state. If only a fraction of the triplets return to the ground state by emission, then you are measuring a lower limit of the triplet yield. You can use interactions with dienes as Hammond and Lamola have done, or you can use electron paramagnetic resonance to measure the actual yield of the triplets. The triplet yields measured in this way vary from, for example, thymine at neutral pH where the intersystem crossing yield is below 0.01 per cent, up to a few per cent in the case of guanine. In the case of molecules like thymine, neutral TMP, pH 7, which has no intersystem crossing, we were able to populate their triplets by sensitization, which Angelo Lamola did when he came to our laboratory. Given the energy levels shown in Table 1 it was possible to excite the sensitizer, in this case, acetone, and let acetone form triplets, and transfer this triplet energy into TMP, properties of which can then be measured, as we did. You can also study the excitation spectra of these emissions, and Fig. 4 compares the absorption spectrum and fluorescence of CMP; the absorption and the fluorescence have a nice mirror image relation, which does not hold in AMP and GMP, but does hold in both of the pyrimidines. Several points here are of particular interest with respect to energy

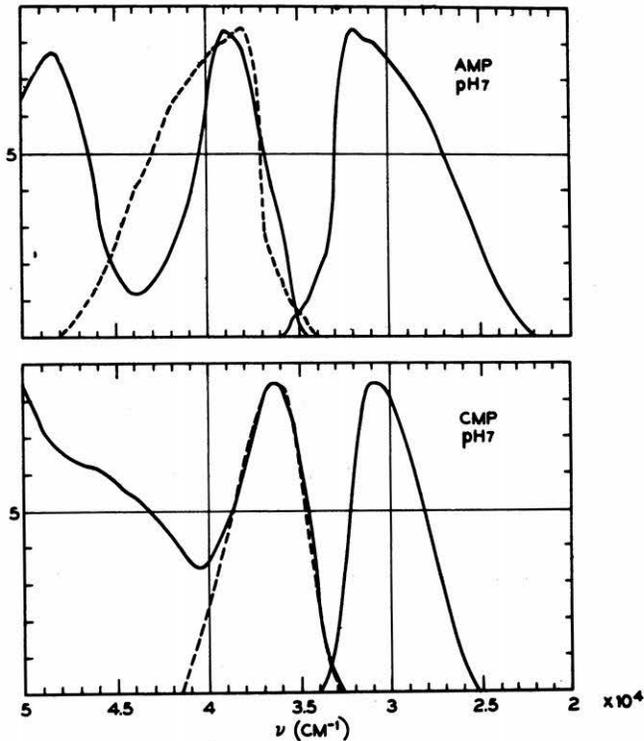


FIG. 4.—Excitation and emission spectra of AMP and CMP.

transfer in DNA. Notice that the low quantum yield of fluorescence, meaning that there is a very short singlet lifetime, prohibits extensive singlet energy transfer. Furthermore, the overlaps between absorption and emission are very small, which again argue against extensive energy delocalization. The third point to be mentioned, in this respect, is that the optical absorption spectrum of DNA, is identical with that of a mixture of its constituent nucleotides, except that there is a slight reduction in the intensity (the so-called hypochromism) again showing that there are no strong interactions at the excited singlet level.

Let us now consider, having characterized the excited singlet states of the various mononucleotides, what happens to the next degree of complication, which is the dinucleotide, consisting of two bases joined together by a sugar-phosphate bond between them. Fig. 5 shows the fluorescence of a particular dinucleotide, ApC (the p represents the phosphate) in 50 per cent ethylene glycol-water at 77°K, and compares it with the fluorescence of an equimolar mixture of A + C. Those are the only two chromophores. The fluorescence of the dinucleotide is considerably red shifted from the sum of the monomers and depends upon the environment. Nearly all of the dinucleotides show this red shift of the fluorescence. We have attributed this shift to the excimer (or exciplex) interaction that we spoke about briefly yesterday after Professor

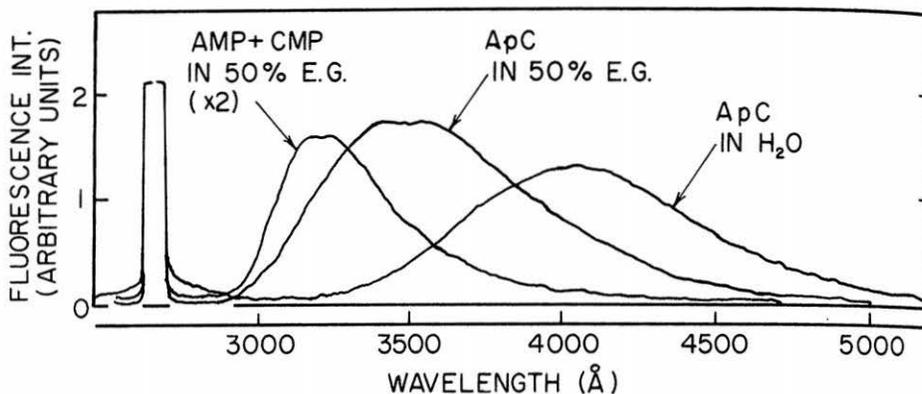


FIG. 5.—Fluorescence of dinucleotide ApC compared with the sum of AMP and CMP.

Kasha's paper. We have measured the optical rotatory dispersion of a number of these dinucleotides, and when this indicates that the bases are stacked, one on the top of another, we get excimer fluorescence; when optical rotatory dispersion gives no indication of stacking, we find no excimer emission. For example, the optical rotatory dispersion of CpC at neutral pH shows it to be stacked and it gives a nice red shift, and looks just like poly C. However, for CpC at pH 2, with both bases protonated, the optical rotatory dispersion shows no stacking, as you would expect from these charged particles, and there is no excimer emission; just the monomer emission. What is an excimer? Excimer (or exciplex is really a better word to use) is a contraction of excited state dimer (or excited state complex) and an excimer is produced when two chromophores form a dimer or complex in an excited state that is not stable in the ground state. The fluorescence is red shifted, first because the excited state energy is stabilized, and second because the ground state energy is destabilized by the proximity of the two chromophores. There was a little bit of luck in finding this explanation, and I think Dr. McGlynn must take his share either of the credit or the blame; we were reading as fast as we could, but people were publishing faster, and one depended upon hearing things by chance. A few years ago, Dr. McGlynn came to Bell Laboratories and gave a talk about a molecular orbital model of excimer formation; it was very interesting and we listened, and then we knew about excited state dimers. About a month later, Eisinger and I looked at the emissions from these dinucleotides, and they were red shifted, just as Dr. McGlynn had said excimers were. So, we concluded they were excimers. One of the points that Dr. Kasha mentioned yesterday, which I said I would come back to, is whether these really are excimers. A biprotonic transfer leading to tautomerism would require hydrogen bonds between the nucleotides. We have a number of cases, *e.g.*, Fig. 5, where there is no possibility of hydrogen bonding such as between A and C, and yet the fluorescence is red-shifted fairly extensively. So we feel fairly confident about the explanation of these red shifts in terms of excimer or exciplex forma-

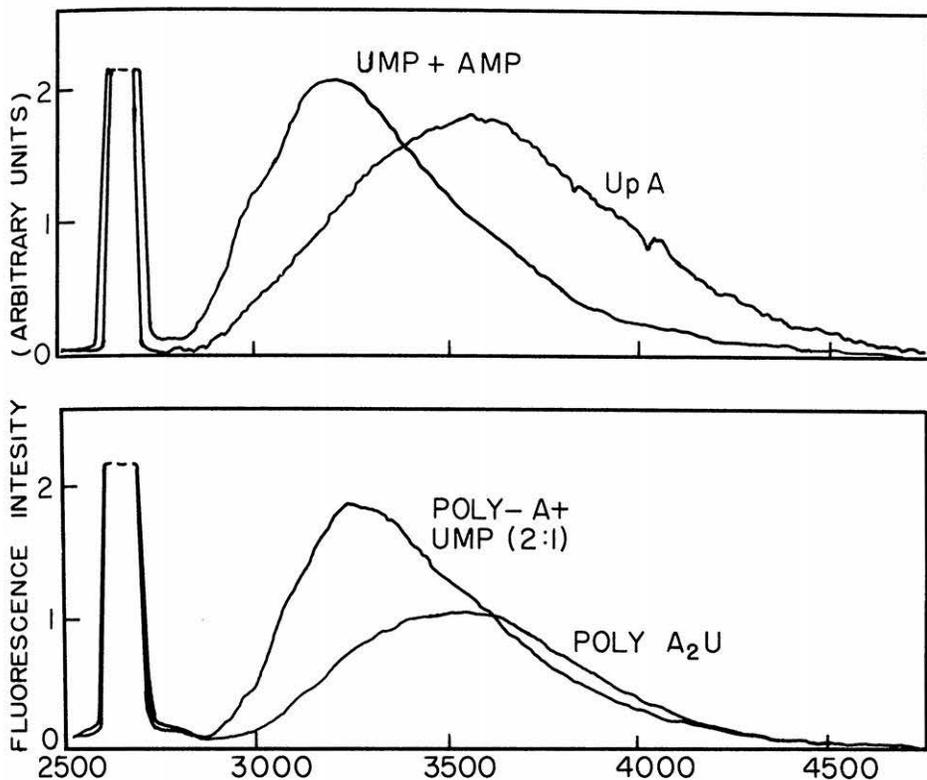


FIG. 6.—Comparison of fluorescence from UMP + AMP with that from the dinucleotide UpA showing a red shift similar to that observed in the polynucleotide poly-A₂U.

tion. Fig. 6 shows a comparison between the fluorescence of UMP and AMP monomers, and the dinucleotide UpA, which also was red-shifted. I would like to call your attention to the interesting lower curve in Fig. 6 for polyA₂U, which gives just an excimer emission. This poly-A₂U is a single-strand, synthetic polynucleotide, with the A's and the U's in the stoichiometric ratio of 2:1 inserted into the strand randomly. You would expect that nearly every A would have a U next to it, and every U would have an A next to it. What happened was that within the experimental accuracy we observed only an excimer-type emission. Now, consider the case of poly-A₆U, which has a considerable excess of A's. If singlet-energy transfer occurs along the strands of roughly six A's until the excitation reaches the one U and forms an AU excimer, the excimer, being of lower energy, should be a trap. In this case one would expect that all the light collected either by A or U would diffuse through these six bases, get over to the AU region, form an AU excimer, be red-shifted, and trapped. But, that is not what Eisinger observed. What he observed was some excimer emission and some emission looking just like normal poly-A, that is, at the nonexcimer position. Hence, there was not

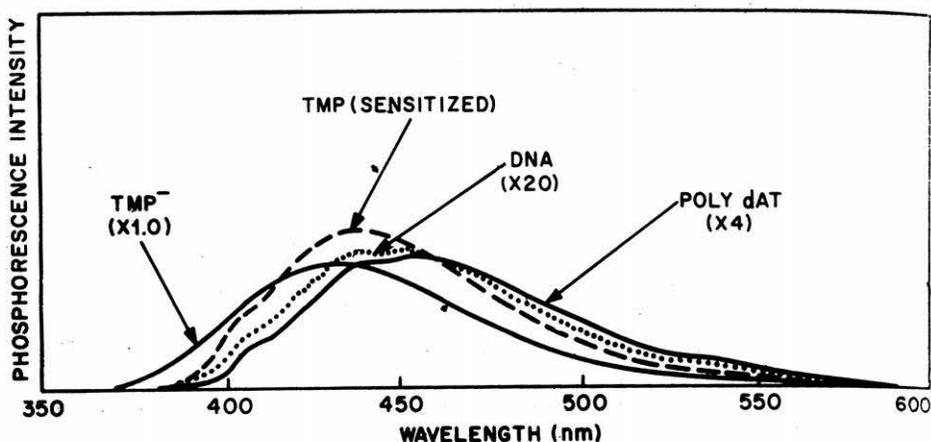


FIG. 7.—Phosphorescence of DNA, poly-dAT, neutral TMP and TMP.

extensive delocalization at the singlet level. The reasons for this can be seen when one calculates the Forster probabilities for transfer; they really are very small, showing it to be uncertain for most neighbors as to whether or not the excitation is going to jump one base. The singlet energy delocalization in poly-A and in polynucleotides is limited at 77°K. We have not been able to measure this at room temperature, but inasmuch as the lifetimes of the excited state become so much shorter at room temperature, there is really no reason to expect the transfer to be any more extensive at room temperature than at the lower temperature.

Next we turned to the phosphorescence of DNA; this was a hard job, and Ronald Rahn and Jim Longworth worked for more than a year trying to understand it. It was hard because it turned out that the phosphorescence of DNA is the phosphorescence of thymine and the fact is that neutral thymine does not phosphoresce. Eventually we were able to observe the neutral thymine triplet phosphorescence by sensitization but it took a long time to identify the triplet state of DNA. Fig. 7 shows that the phosphorescence of DNA looks like that of thymine. Notice that a comparison of phosphorescence from the different species, *viz.* TMP^- at pH 11, TMP at pH 7, which had been sensitized, DNA and poly-dAT suggests that the polynucleotides are similar to neutral TMP, although they all are very close together. Electron paramagnetic resonance, shown in Fig. 8 for the $\Delta m = 2$ transitions of T, G, and A, gave the spectra shown. In the electron paramagnetic resonance of the triplet state, the molecule is excited into the triplet state by light and the so-called $\Delta m = 2$ transition is studied. The position of that resonance in a magnetic field is very sensitive to the dipole-dipole interaction between the two electron spins of the triplet. Therefore, in a molecule like thymine where the spins are closer to each other, there is a larger spin-spin interaction, which shifts that resonance to low fields, compared to those for the purines, guanine and adenine, which are fairly close

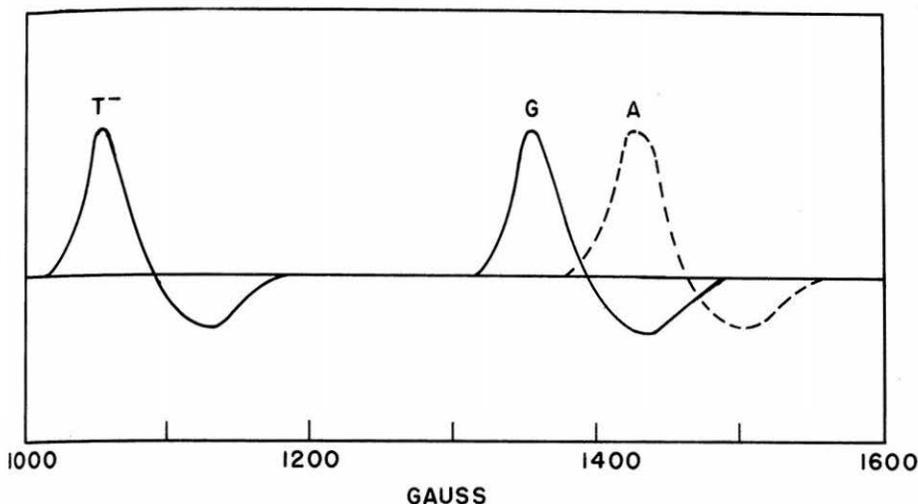


FIG. 8.—Electron paramagnetic resonance of the $\Delta m = 2$ transition of A, G, and T.

to each other and at much higher fields than the position of the electron resonance of thymine. Fig. 9 compares thymine with poly-dAT and DNA, and the resonances are similar. The scale in Fig. 9 is expanded enormously compared to that of Fig. 8. It was this that led us to believe that the triplet state of DNA was the triplet state of thymine. This assignment has been supported by the energy levels that we have of the nucleotide triplets, which show that neutral thymine has the lowest energy triplet of all the bases.

Now what can be said about triplet energy transfer? The simplest place to look for triplet energy transfer was in poly-A; this is the polynucleotide with only A components. Bersohn and Isenberg had shown that paramagnetic metal-ions quench the phosphorescence of poly-A, also of DNA. We repeated these experiments, and the results were as follow. Paramagnetic metal ions, like cobalt and manganese, are known to bind to the phosphate group of DNA. They are a little away from the bases, but they were shown to quench the phosphorescence and not the fluorescence as Bersohn and Isenberg had reported. It really did look as though the metal ions were operating on the triplet state, and furthermore, the range of this quenching was fairly large. In poly-A, Eisinger and I were able to show that one metal ion could quench as many as 150 bases in a line, fitting the diffusion curves to the quenching. In DNA, the quenching was harder to measure; the phosphorescence yields were low but the quenching seemed to have a range of ~ 10 bases. Eisinger and Lamola have repeated these experiments, and it seems that one metal ion quenches the triplets of about a dozen bases in two-stranded DNA. Fig. 10 shows the quenching in Ap_7 by Co^{2+} , and the phosphorescence intensity goes down as the amount of cobalt goes up. I will not trouble you with the formulae but the solid line is the limiting case, where we assume that each cobalt ion

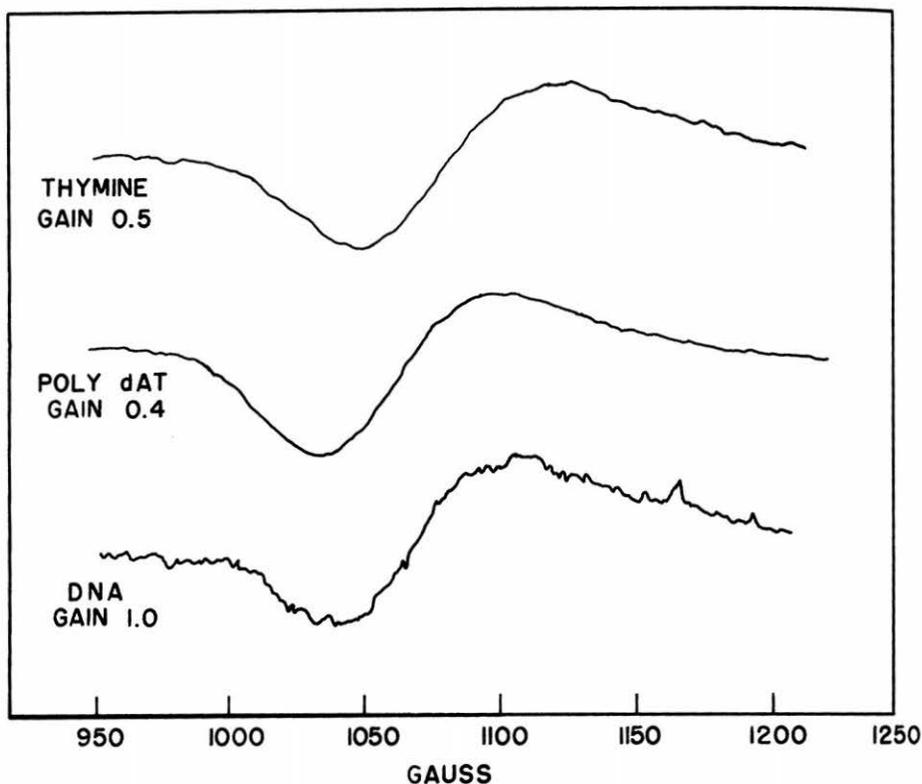


FIG. 9.—Electron paramagnetic resonance of the $\Delta.\gamma = 2$ transition of thymine, poly-dAT and DNA.

quenches seven different triplets. For the other two lines it is assumed that each cobalt ion quenches nine and five bases. The data fall nicely around the line of seven, and it does look as if quenching is complete over the whole range of seven bases. For longer strands of poly-A, shown in Fig. 11, the phosphorescence intensity is plotted on a log scale versus the cobalt to phosphate ratio; S is the sedimentation velocity of the poly-A. In the high molecular weight poly-A with the largest S value it will be seen that when the ratio of cobalt to phosphate is about 4 per cent, the quenching is a factor of ~ 25 . These are fits to diffusion curves. They determine the number I mentioned before—*i.e.*, that in the very longest poly-A, one cobalt ion can quench ~ 130 bases. We do not know why the range is limited to ~ 130 , which is less than the number of bases in the polynucleotides. It might be there are kinks when the polynucleotide is frozen in solution—we do not know. However, the triplet transfer is very fast in the poly-A because the lifetime is not at all reduced; that is, in the quenching experiments shown, when we go down to 10 per cent or even one per cent of the initial phosphorescence, those bases that still phosphoresce have the life time of A, which is about 3 seconds. You would expect that if the triplet is diffusing into a quenching center, especially when there is a

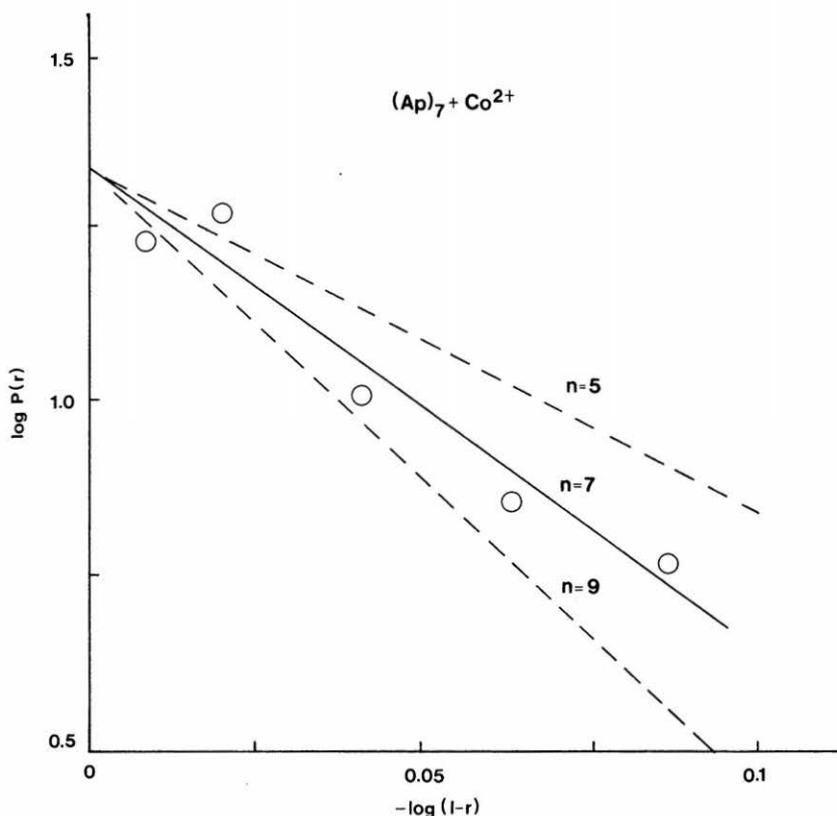


FIG. 10.— Ap_7 triplet quenching by Co^{2+} .

lot of quenching, there would be heterogeneity in the lifetime. That does not happen. That is why we must postulate a definite range. DNA was a problem like that for a while. Fig. 12 shows the quenching of DNA phosphorescence in exactly the same way. These are old data, measured by electron paramagnetic resonance. Notice that the intensities fall off rather fast with $[Mn^{2+}]$ whereas the lifetime of the triplet of DNA after quenching was *unchanged* within experimental error. The lifetime was constant, even though the quenching varied almost an order of magnitude. Recently, Lamola has been able to explain this qualitatively with the following model. Given the energy of the triplets, thymine < adenine < guanine < cytosine, you can write the expression for triplet transfer, and it is very sensitive to the energies of the triplet states that are involved. It turns out that quite a number of triplet transfers to near neighbors in stacked nucleotides will occur within the lifetime of the triplets, which is 0.2 of a second at low temperatures. But there are a few that will not; for example thymine to guanine or thymine to cytosine triplet transfer, which are across the biggest energy intervals, will not occur within 0.2 second, and they represent, therefore, impenetrable walls for the triplet diffusion.

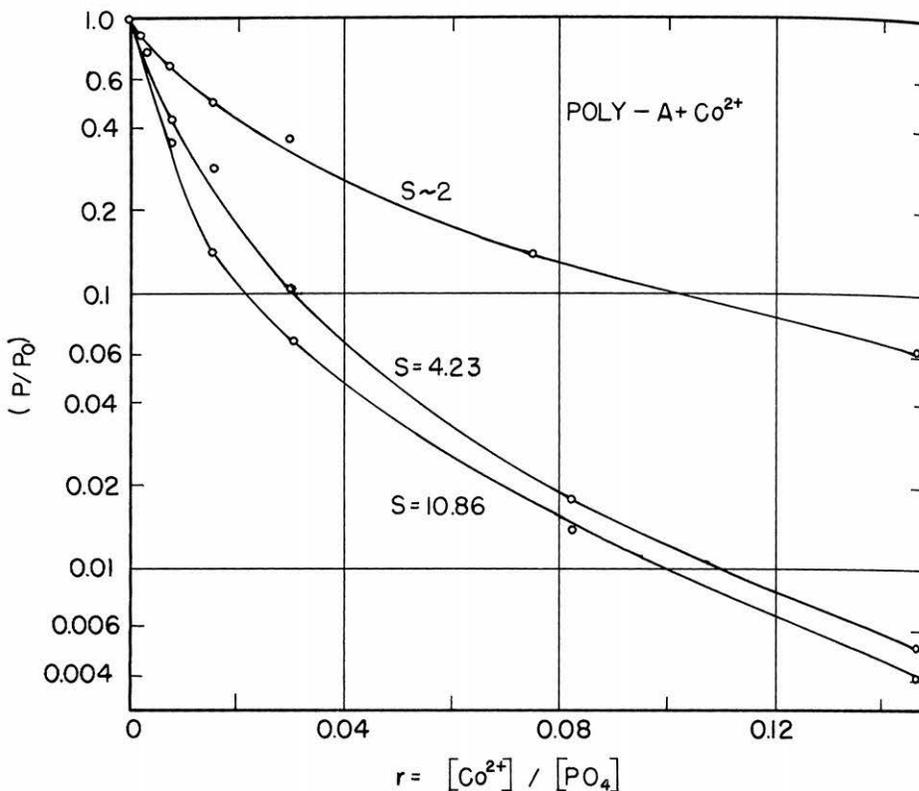


FIG. 11. — Poly-A triplet quenching by Co^{2+} paramagnetic metal ions.

Let us turn to something more interesting biologically. I wish to tell you about the experiments that Meistrich did with Lamola and myself. These were experiments on sensitization of DNA using a derivative of acetophenone. If you excite DNA with ultraviolet light near 280 nm, you excite all four of the bases to their first excited singlet states. This direct irradiation of the excited singlet state of DNA forms about 10 products that have been identified. The mutations that occur in a bacteriophage after direct irradiation of the phage have been shown by Drake to be of two different kinds. These two different kinds of mutations are expressed in the DNA as follows. Consider a sequence of bases in DNA: A, B, C, D, E, F, G, H, I, *etc.*, containing the genetic information. One type of mutation is the so-called base transition, where one of the bases changes to another, so that you have A, B, then instead of C you have X, then D, E, F, *etc.*; the other type of mutation is an insertion or deletion called a frame-shift mutation, say that between B and C another base Y is inserted, thus obtaining A, B, Y, C, D, E, F, *etc.* These two kinds of mutations have been characterized by study of the bacteriophage. The question was: Did one of the photoproducts give one particular kind of mutation, say the base transition, and another photoproduct the frame-shift mutation? We did the

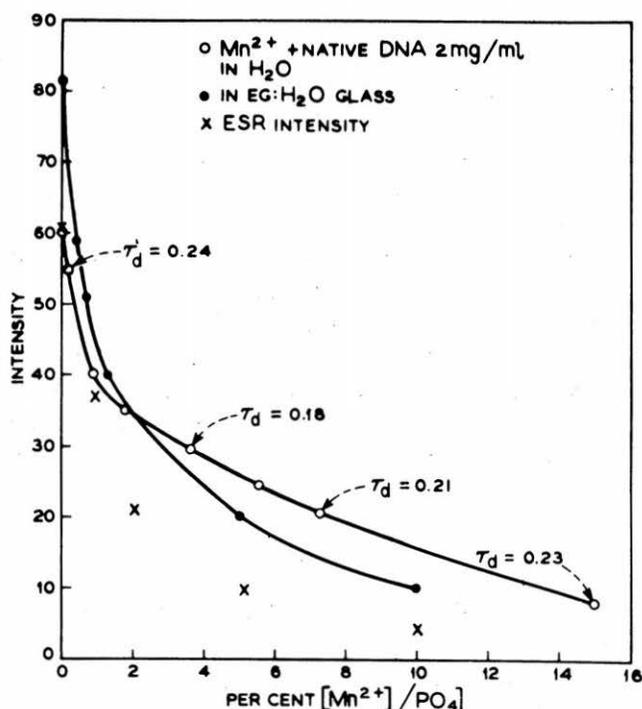


FIG. 12.—Quenching of the triplet state electron paramagnetic resonance signal in DNA by Mn^{2+} .

experiment by modifying acetophenone, which had been shown to act as a sensitizer for the thymine triplet state alone of all the excited states of the DNA bases. Gabbay took acetophenone and put a dipositive tail on it, two quaternary ammonium salts, which then fit onto the phosphate groups of DNA. The DNA is in the phage head, and in fact bacteriophage is a package of DNA with a protein coat. There are certain bacteriophage that are osmotic shock resistant; if they are placed in distilled water from an 0.1N NaCl solution they live, but all the others die. Electron micrographs of these osmotic-shock resistant phages have shown that they have holes in their heads; the protein coat has big holes, and the reason they are osmotic-shock resistant is that small molecules can run in and out of the holes. So we took the phage that had holes in their heads and the acetophenone derivative with the two positively charged quaternary ammonium ions on the tails, just the right distance away to sit on the two phosphate groups on the DNA, and sent this sensitizer through the holes in the head in order to sensitize the phage DNA in solution. It worked. Acetophenone did not work; phage without holes in the head did not work. By using the sensitizer, which attaches to the DNA and transfers energy only into the triplet state of thymine, we were able to show that essentially the only photoproduct introduced into the DNA was thymine dimers. With this simplification of the photochemical products we were able to study the

genetics. The interesting result was that upon introducing just thymine dimers into the DNA, as opposed to the whole spectrum of many different mutants, we got exactly the same distribution of these two types of mutants in the phage as had previously been obtained with direct irradiation. The conclusion that could be drawn from this was that the changes in the DNA upon irradiation were not specific to the mispairing of the bases, because thymine dimers were able equally well to form both types of mutation.

At this point I shall end the story. The reason that it is the end of the story is because from these results we saw that mutagenesis depended upon some subsequent step in the biological synthesis, which was a little too complicated, biologically, for us to study. However by starting with the excited states of nucleic acids at low temperatures and extending that knowledge to the photosensitization of bacteriophage at room temperature we were able to obtain information about the nature of mutagenesis that had not been obtained by any other methods.

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DISCUSSION: LEADER, DR. R. M. PEARLSTEIN

Dr. Pearlstein.—At a symposium on Biological Molecules and Excited States a year and a half ago, Dr. Shulman was the after-dinner speaker. He shocked us when he issued a plea for more rather than less quantum mechanics in biology. One consensus that came out of that meeting was that more work needs to be done on polynucleotides at room temperature. I would now like to call on Dr. James Gill, of the Lawrence Radiation Laboratory at Livermore, who will present some recent data on that subject.

Dr. Gill.—Encouraged by Dr. Shulman's success at low temperature, and desiring to do something that was biologically relevant at room temperature, we have looked for a long time for ways of observing luminescence in DNA at room temperature and at neutral pH. Besides the four bases that Dr. Shulman described, DNA contains a minor base, 5-methylcytosine, which has the interesting property of being very weakly fluorescent at room temperature and neutral pH. Using enzymology developed by Wells, we have succeeded, very recently, in producing several synthetic DNA's that contain 5-methylcytosine. We have found that they are weakly luminescent at room temperature and neutral pH, and I would like to present these few results to you now. The first and most obvious polynucleotide that we made was polydeoxy-5-methylcytosine. The excitation spectrum of polydeoxy-5-methylcytosine closely matches the absorption spectrum of the polynucleotide. 5-Methylcytosine absorbs maximally at about 278 nm, which puts the maximum out a little into the red for most nucleotides. This close match indicates that there is no increased intersystem crossing at higher energies and that the quantum yield for fluorescence is fairly uniform across the first absorption band. The minimum is at about 255 nm. The next polynucleotide that we have worked with is a copolymer between 5-methylcytosine and inosin. It is an alternating copolymer: I-5-methylC-I-5-methylC. We believe it is an ordered structure. It melts at about 42°C

under normal TCL. It sediments as a single band in alkaline cesium chloride. Comparison of the fluorescence excitation spectrum with the absorption spectrum, although there is a great deal of background noise, shows that the 5-methylcytosine excitation, and the excitation spectrum generally, does not match the absorption spectrum. We see predominantly only 5-methylcytosine excitation. However, in one region, there is a shoulder. Last week, when I saw this shoulder, I got tremendously excited and called Dr. Pearlstein, because I thought it represented energy transfer. After sober reflection, I realized that there are at least four explanations for this shoulder. One is energy transfer, another is impurity fluorescence, another is inosin fluorescence, and the other one escapes me at the moment. To test which of these occurred, we did membrane dialysis on the sample and succeeded in getting a cleaner spectrum, but the shoulder persisted. We argue that if inosin fluorescence was occurring, that, like many purines, the fluorescence maximum ought to be at somewhat longer wavelength, about 385 or 390 nm, than the 5-methylcytosine fluorescence, which occurs at about 350 nm. So, we excited in the region of the shoulder and measured the fluorescence emission spectrum, and compared those two emission spectra, and, sure enough, when we excited, we saw increased emission at about 385 nm over what we saw when we excited at 278 nm. Thus it appears that what we saw was predominantly 5-methylcytosine fluorescence and a little of inosin fluorescence. I had not believed that inosin was fluorescent at all at room temperature, but in reviewing the literature hurriedly I discovered that in 1963, Eva Wallace in Norway had published a report of inosin fluorescence at neutral pH. Briefly, what we have here, I think, is a useful tool for looking for evidence of energy transfer or biprotonic phototautomerism. We do not see evidence for either of those in this particular instance. There is clearly a great deal of work that needs to be done. It is much too soon to draw any kind of generalizations from these data, and I would certainly invite all of you, who care to join in the search for luminescence from polynucleotides at room temperature, to unravel some of the mysteries of the excited states in these molecules.

Dr. Pearlstein.—I would like to make a comment and ask two questions. I would not agree with the explanation offered for the extent of delocalization of the triplet energy in poly-A, because it is well known from diffusion theory that even in one dimension there is predominantly only a single exponential decay brought about by quenching or trapping of energy, even if it is extensively delocalized. The rate constant for this is simply the sum of the rate constants for the quenching process plus that of all the other radiative and nonradiative processes that would be present in the absence of quenching. I believe that at Arden House, Guéron offered the explanation that there may be traps, that is host traps, in the adenine and there appears to be evidence for these (Longworth and Pellin, in the press) from triplet-triplet annihilation studies of poly-A. Having brought up the possibility of host-traps in poly-A and conceivably in other polynucleotides, I would like to ask, as the first question, about the possibility of host-trapping playing a role with respect to the excited singlet states. It occurs to me that perhaps host-traps might provide an alternative explanation to the apparent lack of energy transfer in the singlet states; for example, if you have host traps present, the singlets may migrate rapidly, and then what one sees is competition between host-trapping and other processes, and this would account for the apparent lack of energy transfer—the energy simply transfers too fast for it to be seen. The second question is, that I seem to recall with respect to Lamola's barrier model to explain the short extent of triplet delocalization in DNA's, that poly-dAT was anomalous. That is, was not the delocalization there either much less or much greater than predicted, and could you comment on that?

Dr. Shulman.—About your comment disagreeing with my explanation of the quenching, one does not expect a single exponential after quenching on the basis of diffusion theory as has been shown by Bersohn and Isenberg [*J. Chem. Phys.* **40**, 3175 (1964)], but rather that, after considerable quenching, the lifetimes of the surviving triplets will be reduced. Inasmuch as this nonexponential decay is not observed, simple triplet diffusion to the quencher is not the mechanism.

In answer to your second question, yes. What Lamola predicted in poly-dAT was that you could transfer energy very easily from T to A, and that the triplet delocalization should be very extensive. He and Eisinger repeated the experiments on poly-dAT lately, and it is true that there is a tail

on the phosphorescence decay versus metal ion plot, which gives 10 or 12 bases quenched per metal ion, as Isenberg originally claimed. But, it is also true that the quenching is very rapid at first, and in the first part where they have extensive data, they found that approximately 100 bases are quenched per metal ion. Afterwards the quenching is less effective, *i.e.* about 10 bases quenched per ion, but the main part of the quenching, which had been overlooked until now, does agree with the calculations.

Dr. Kasha.—I was thinking about it while you were talking. I have spoken with Angelo Lamola about this, and here is how I feel it goes; it is really in accord with what Dr. Pearlstein said. The way I would put it is that you should think of four different realms of energy transfer in terms of time. The frightening time is for free excitons, 10^{-15} seconds or shorter. We do not know anything about such times, and we do not have ways of directly observing them. The only way we know that such things exist is from gross displacement of absorption spectra. Now, obviously, that is out, so we never think about free excitons in DNA. At the opposite end of the scale is the Forster mechanism, and you are quite right that the criteria empirically show that it is going to be very limited in DNA. But Forster's analytical comparisons of the four different energy-transfer cases shows that that one is, of course, the slow one. That is called the very weak coupling case, and it is usually in the realm of longer than 10^{-9} to 10^{-11} seconds, which could hardly compete with, say, the decay of the excited state of DNA. The interesting cases are the two that really are not considered here and I would discuss them in this way. Intermediate coupling, which goes from 10^{-13} to 10^{-15} seconds, requires not a shift of the spectrum but a gross change in its Franck-Condon envelope. We know that is out, also. On the other hand, the very presence of hypochromism is in itself a demonstration that we have interface interaction. So the question is, is it possible that the weak coupling mechanism, which must be present in order to have hypochromism appear as a second order consequence, can give a fast energy transfer mechanism? The answer is, absolutely, yes. Here is a good, short process, 10^{-11} to 10^{-14} seconds in range; it is going to be a mechanism that will provide very fast energy transfer, will never show up in the absorption spectrum, and would possibly show up only in subtle ways. It is deserving of study. There is nothing in this concept that would interfere with the broad spectrum of results that you already have. It would, maybe, contribute to them.

Dr. Shulman.—I was suggesting that in poly-A at the singlet level and in DNA, energy transfer does not seem to be particularly long range. I did not mention Longworth's lack of fluorescence depolarization in poly-A. However, couplings resulting in near neighbor interactions of the sort you have just mentioned certainly do occur, and we have lots of evidence for that which I did not mention. For example in poly-dAT with alternating AT bases, we can show that exciting A or exciting T gives the same excimer yield and gives the same thymine triplet yield. So, certainly those two bases, A and T, are intimately related. It might be that the transfer occurs at the triplet level or at the excited singlet level. But is there anything of longer range than near-neighbor interaction, and if so, where does the barrier occur? The evidence seems to be against longer range interaction in DNA.

Dr. Pearlstein.—It comes to the question of your energy balance again. You suggest that 90 per cent or more of your energy is dissipated when you get these things alike. Do you have any ideas on the mechanism of this particular energy displacement process? Do you think it has something to do with the hydrogen bonding of the solvent?

Dr. Shulman.—In regard to hydrogen bonding and biprotonic transfer, let me refer to some facts that I had not mentioned. When you form the hydrogen bond between A and T, for example in double-strand poly-dAT, there is no quenching of the fluorescence compared to the separate dinucleotide. There is a similar sort of excimer singlet emission. Furthermore there is no quenching of the thymine triplet. However, when we form either of the other two possible base pairs, that is, GC base pairs or AU base pairs, there is complete quenching at the singlet level; that is, of the fluorescence and consequently of the phosphorescence. It is quite possible that biprotonic transfer, particularly in the case of GC, could occur, and in contrast to the case of 7-azaindole,

it does not shift the fluorescence but it quenches it. In addition, note the fascinating difference between U and T; in the former hydrogen bonding quenches the fluorescence and in the latter it does not. The case of GC quenching is a possible role for biprotonic transfer, and important because GC is quenched in DNA.

In regard to your question about the low overall yields, we do not understand the quantum yields but they are intramolecular in view of their independence of solvent. From the viewpoint of evolution it may be a very good thing that most excitation energy is harmlessly dissipated as heat.

Dr. X.—Would you comment on the rather striking difference between the excitation spectrum of adenine as opposed to its absorption spectrum?

Dr. Shulman.—That is a striking difference. As you know, there are other π - π^* bands in adenine, which may be close to each other, and n - π^* contributions are also possible, but we have not been able to interpret that. It is interesting that in both the pyrimidines there seems to be one predominant low energy π - π^* transition, showing up as a nice mirror image of emission and absorption but not in the two natural purines.

Dr. Gouterman.—Did you ever study temperature dependence of the barrier between T and G in the triplet state? Was that effected by temperature at all?

Dr. Shulman.—No, we have not studied it. We would not expect much temperature dependence of the overlap terms although there will of course be a temperature dependence of the hopping, as Professor Gouterman suggested.

Dr. Kasha.—I have one expensive experiment for you to do. You must have thought of it. How about studying perdeuterated DNA? Or, to make it easy for you, perdeuterated dinucleotides? The idea behind it is to try to get the yields up. We do not know where 99 per cent of the excitation energy goes, and if ring skeletal C-H frequencies are important, you could perhaps double or multiply yield by a larger factor. Have you thought of doing things like that?

Dr. Shulman.—Yes, we have thought about it.

Dr. Kasha.—A very expensive idea. Could I make one comment? I like to see phenomena, and if there are excimers in DNA, so much the better. But, on the other hand, has it occurred to you that you have a little paradox in the thymine case, because the adenine-thymine excimers are apparently clearly shown. On the other hand, your sensitization experiment shows that you get the thymine dimers even without the excimer.

Dr. Shulman.—There is no reason to believe that the excimer is necessary for the dimer formation.

Dr. Kasha.—No, precisely. But, I am saying that it could be that the excimer is a side phenomenon, which might or might not contribute to the thymine dimer formation.

Dr. Shulman.—It is possible that it is a side phenomenon. Poly-dAT does not dimerize, so it seems that when the dimer path is closed, the excimer path is available. Conversely, there are the various experiments done either with TT dimers, or with stacked dimethylthymine in water, and so on, in which the quantum yields for dimer formation are unity, and the quantum yields for excimer fluorescence of any sort are zero. So, all that we can say is that in the one extreme, that is, where the geometry allows dimerization, we get no fluorescence of any sort, and in the other extreme where the geometry does not allow dimerization we get excimers. But I agree with you, that whether the excimer is the path to the dimer or an off-shoot is an unanswered question.

GENEALOGY IN MOLECULAR SPECTROSCOPY

S. P. MCGLYNN, P. HOCHMANN AND H. J. MARIA

We intend to discuss genealogy as a tool for the classification and interpretation of molecular electronic spectroscopy and the identification of molecular electronic states. The term "genealogy" covers a vast number of attitudes embracing many different areas—all of them helpful in some generic way for the induction of order in a jumble of otherwise unrelated observations. In organic chemistry, for example, "homology" falls within the compass of common genealogical attitudes; in atomic spectroscopy, "seniority" serves similar purposes; and in molecular spectroscopy, we use what is known as "the correlative attitude." Wherever found, the basic idea is the same: To induce understanding for a specific entity from information available concerning related species.

The identification of electronic states and the classification of electronic spectra for molecules are difficult. As a result, few state identifications are ever made completely conclusive, and most (including many of those already hoary with age and proper pedigree certification) can be questioned. Indeed, the number of experimental works that lead to full and precise labelling of an excited electronic state are few and far between. It is precisely this facet of molecular electronic spectroscopy that leads to the dominance of circumstantial evidence and the use of genealogical attitudes.

Despite the extensive use of correlatory attitudes in the field of molecular electronic spectroscopy, it has grown clear recently^{1,2} that not all the available approaches have been investigated fully, and that many avenues of ingress remain totally untried. In view of this, and because of our own concerns with the excited states of small polyatomic molecules and ions, it is one of our present intentions to attempt systematization of some of the genealogical approaches which appear to hold promise in this area.

We know quite a lot about the spectroscopy of diatomic molecules. It is true, as Professor Kasha so aptly points out, that we rarely use all that is known—a case in point³ being "singlet oxygen." Nonetheless, our knowledge of diatomic molecules is quite exhaustive and the reasons for this are not hard to find. These molecules are small, possessing only one doubly degenerate degree of rotational freedom and one degree of vibrational freedom; the united atom-separated atomic correlation diagrams, as developed by Mulliken,⁴ provide an invaluable diagnostic tool; many specific state identifications are available in the early works of physicists who thought they could understand all of molecular spectroscopy by concentrating on the diatomic molecules; and a rather restrictive relationship exists between the Λ quantum number of a given diatomic state and the m_l quantum numbers of the constituent atomic orbitals composing that state.

Statements similar to the above are also valid for the type of ion spectroscopy termed "ligand field." The spectroscopy under study, in this instance,

is atomic in nature and the effects of the ligand field might be classified as "nursery variations on a primal atom rhyme." The ligand field is, or should be, a small perturbation of which the effects are predictable from a knowledge of geometries, parent ion electronic states, and the possession of some authoritative treatise.⁵

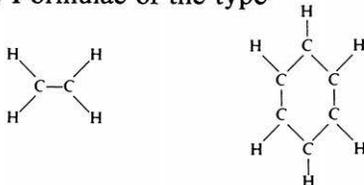
The electronic spectroscopy of the diatomic and of the ligand field variety of molecule is rather well traveled and well understood. The extent of our understanding, however, is squarely based, in both instances, on our ability to relate back to the electronic affairs of the atomic precedents. We now consider a third area, one which may not so readily be related to the affairs of its constituent atoms and yet one which is in surprisingly good repair; we refer, of course, to the molecular electronic spectroscopy of aromatic hydrocarbon molecules. The type of genealogical approach used here is quite different from that applicable in the diatomic or crystal-field areas, and is of interest for its own sake as well as for its great interpretive utility. In view of this, and because of our own prejudices, we will concern ourselves with the topological content of aromatic π -electron spectroscopy.

TOPOLOGICAL STUDIES OF CONJUGATED HYDROCARBONS

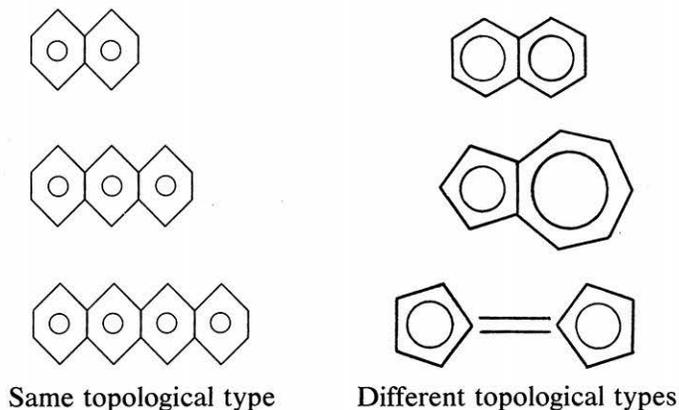
The largest known pool of genealogically related molecules is available in organic chemistry. Organic molecules exhibit broad variations in structure and contain very large populations of each structural type—this, despite the fact that such molecules may consist of only a few kinds of atom. Thus, it is hardly surprising that the correlation of various physicochemical properties of organic molecules has proceeded apace, and that even though we understand little, we can interpret much.

We will illustrate our point by considering the relative importance of molecular topology and molecular geometry in determining the energy of the absorption maxima of the p -band (Clar's classification)⁶ or, equivalently, the 1L_a -band (Platt's classification)⁷ in the spectra of conjugated hydrocarbons. In the electronic absorption spectra of conjugated hydrocarbons, the p -band is usually the lowest energy intense band. Within the framework of π -electron molecular orbital models, this band is associated with the excitation of an electron from the highest energy occupied MO to the lowest energy unoccupied MO of the ground configuration.

In order to proceed, a few definitions are needed. Molecular topology consists of a listing of all pairs of atoms which, in a given molecule, are linked by formal covalent bonds. Formulae of the type



can be viewed as graphical representations of molecular topologies. Inasmuch as we will restrict ourselves to the π -electron approximation (which neglects the presence of carbon-hydrogen covalent bonds), the only topology of interest is that of the carbon skeleton of a given hydrocarbon molecule. In lieu of any formal definitions of the topological differences and similarities of various types of hydrocarbon molecules,^{8,9,10} we will assume that such relationships are intuitively obvious. Thus, for example, we consider naphthalene, anthracene, and tetracene to be topologically similar, whereas naphthalene, azulene, and fulvalene are considered to be topologically different:



However, a more quantitative representation of molecular topology than that provided by skeletal formulae is desirable; consequently, we now introduce the notion^{8,9} of the *topological matrix* T . If the carbon atoms of a molecule are numbered consecutively from 1 to N , if the matrix elements $T_{ij} = 1$ when the atoms with indexes i and j are linked by a formal covalent bond and if $T_{ij} = 0$ otherwise, then $T \equiv [T_{ij}]$. Fig. 1 provides examples of topological matrices T for several conjugated hydrocarbons. When combined with simple stereochemical assumptions based on averaged values of bond lengths and angles, the molecular topology, as defined, will serve as a primary rationale for the interpretation of the physicochemical properties of hydrocarbon molecules.

Molecular geometry, in contrast to molecular topology, provides knowledge of the detailed spatial relationships of the atoms in a molecule. We define molecular geometry as the set of equilibrium interatomic distances for the molecule in its ground state.

We may now reformulate our goals in more precise terms. Molecular topology and geometry are viewed as static components of that ill-defined entity known as chemical structure. Thus, we wish to examine the extent to which the spectral characteristics of conjugated hydrocarbon molecules are determined solely by molecular topology and the degree to which additional knowledge and input of geometric information becomes mandatory.

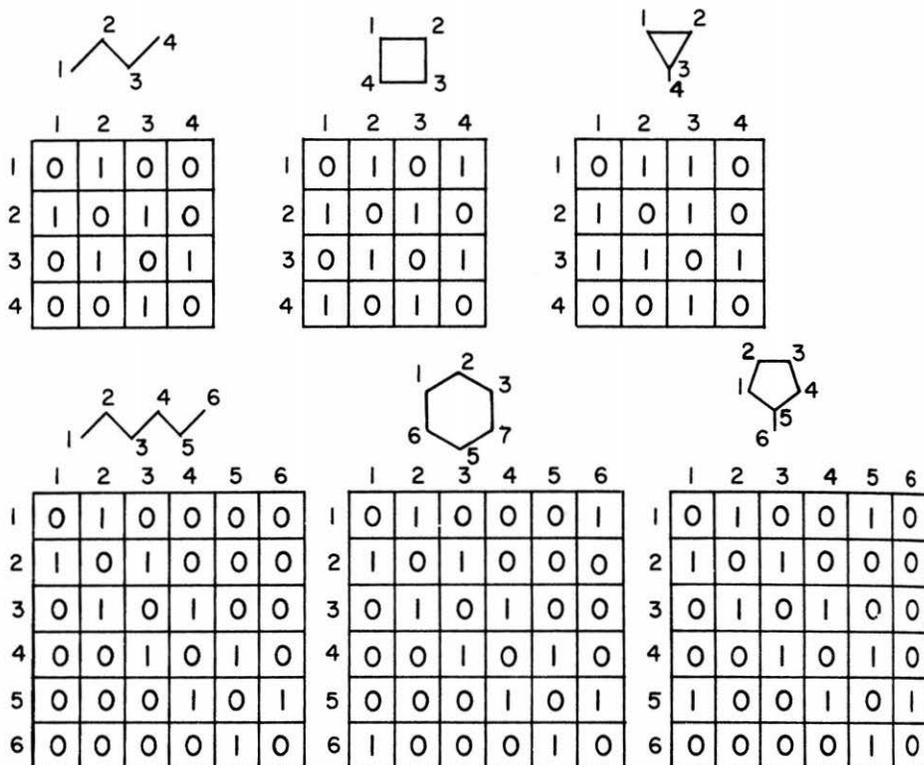


FIG. 1.—Topological matrix representations of various molecules.

Topological Considerations

One observes that the topological matrix T of the carbon skeleton of a hydrocarbon molecule is identical with the matrix representation of the effective π -electron Hamiltonian within the strictures of the simple Hückel (or HMO) method.¹¹ It follows that the molecular orbitals and their energies as obtained by HMO means, are merely the eigenvectors and eigenfunctions of the topological matrix. Consequently, when we correlate p -band energies with the corresponding HMO results,¹¹ we are, in essence, correlating a spectroscopic characteristic of the molecule with its topology—in other words, the HMO method provides a correlative algorithm whose sole input is topological. There is, we emphasize, no obscurity in this statement. The simple HMO method is based on the assumption that short-range interactions (which act only between nearest-neighbor atoms and which, therefore, reflect molecular topology) are dominantly important. The HMO method also implies that the long-range interactions as well as various perturbations of the short-range interactions, which are dependent on the detailed molecular geometry, may be neglected. In this same connection, we emphasize that

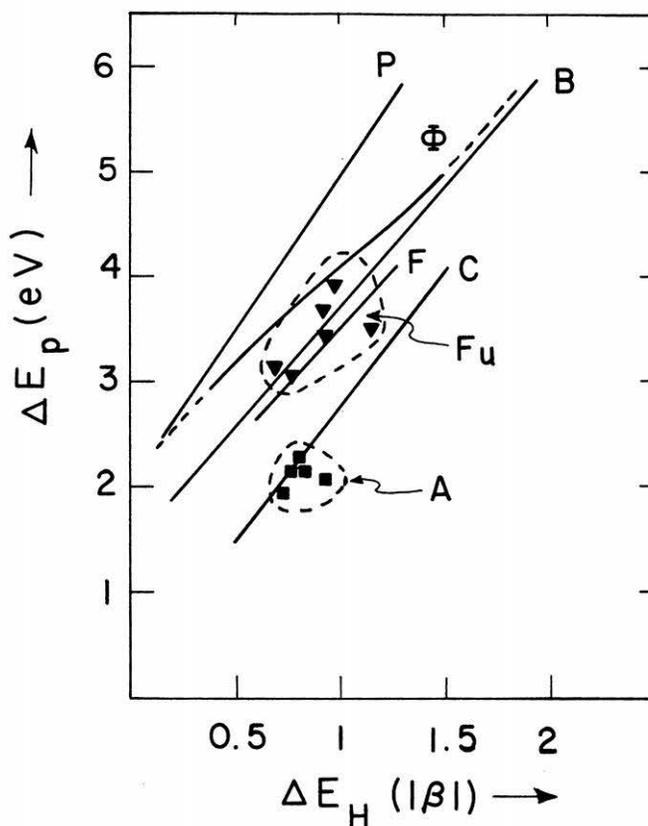


FIG. 2.—A plot of p -band energies (units of eV) versus simple Hückel excitation energies (units of $|\beta|$) for various types of unsaturated hydrocarbon molecules. The notation used is as follows: A (squares), Benzo-derivatives of azulene; B, Benzenoid hydrocarbons; C, Benzo-derivatives of tropylium cation; F, Benzo-derivatives of fluoranthene; Fu (triangles, apices down), Benzo-derivatives of fulvene and; heptafulvene; P, Linear polyenes; Φ , α -Phenylpolyenes and α,ω -diphenylpolyenes.

the concept of the formal covalent bond was introduced empirically on the basis of the very same sort of approximations.

The results of such a correlative attempt¹²⁻¹⁵ are shown in Fig. 2, in which the experimental p -band energies, denoted ΔE_p , are plotted against the appropriate HMO quantity given by $\Delta E_H = \epsilon_1 - \epsilon_1$, where ϵ_1 is the energy of the lowest-energy unoccupied MO and ϵ_1 is the energy of the highest-energy occupied MO of the ground configuration. Three types of correlative dependence may be discerned in Fig. 2:

1. The benzenoid hydrocarbons (B), the linear polyenes (P), the benzo-derivatives of fluoranthene (F) and of the tropylium cation and the cyclopentadienyl anion (C) exhibit a statistically significant linear correlation.

2. The group of α -phenylpolyenes and α,ω -diphenylpolyenes (Φ) exhibit a significant correlation, which, however, deviates from linearity. The pro-

nounced S-shape of this curve, with its upper end approaching the regression line for benzenoid hydrocarbons (B), and its lower end approaching the regression line for the linear polyenes (P), reflects the fact that the lowest members of this group (*i.e.*, biphenyl and styrene) are chemically similar to the benzenoid systems whereas the higher members, which contain enlarged polyenic chains, are more or less wholly polyenic in nature.

3. The benzo-derivatives of azulene (A) and of fulvene and heptafulvene (Fu) exhibit no obvious correlative dependence whatever.

One may conclude from Fig. 2, that significant correlations of ΔE_H with ΔE_p can be established only within structurally homogeneous groups of hydrocarbons. For those structural types exhibiting a linear correlation, the slopes of all regression lines are approximately identical. However, the non-zero values of the regression line intercepts, the relatively large intercept variation from one structural type to another, and the lack of any simple correlation in the azulenic group (which, according to chemical experience, contains a rather closely related set of molecules) indicate that there are factors other than topology that are determinative of p -band energies. We will return to this point on page 139.

In order to clarify some defects of the mostly excellent $\Delta E_p \sim \Delta E_H$ correlation of Fig. 2, we emphasize that debatable points devolve on the shape of that correlation curve, which is deemed acceptable, and on those criteria of statistical significance chosen for use. For example, more rigid significance criteria can effect a separation of the benzenoid hydrocarbon group into two subgroups,¹⁶ one for the catacondensed hydrocarbons and one for the pericondensed hydrocarbons (see Koutecky *et al.*¹⁷ for similar scissioning of other hydrocarbon sets). Koutecky *et al.*¹⁶ suggested ways of representing the topological dependence of ΔE_p , which are free of the above weaknesses. The Koutecky technique consists of making separate plots of the experimental values of ΔE_p and of the various theoretical estimates of ΔE_p against suitable structural parameters; these parameters might be the number of benzene rings, which is a parameter suited to the case of benzenoid hydrocarbons and benzo-derivatives of nonalternant systems, or the number of $-C=C-$ groups, which would suit the case of molecules with long polyenic chains. This type of dependence is illustrated in Fig. 3, where the quantities ΔE_p and ΔE_H for a group of catacondensed hydrocarbons are plotted against the number of carbon atoms, N , in the molecule. It seems obvious from Fig. 3 that the changes of ΔE_p attributable to benzene ring annelation⁶ are qualitatively reproduced by ΔE_H and that these changes, consequently, are more or less completely determined by molecular topology. A plot of ΔE_{PPP} versus N , where ΔE_{PPP} is a Pariser-Parr-Pople estimate of ΔE_p (*vide infra*) is also given in Fig. 3. Apart from a better estimate of absolute energies, the ΔE_{PPP} correlation with N contributes nothing that is not already resident in the ΔE_H correlation.

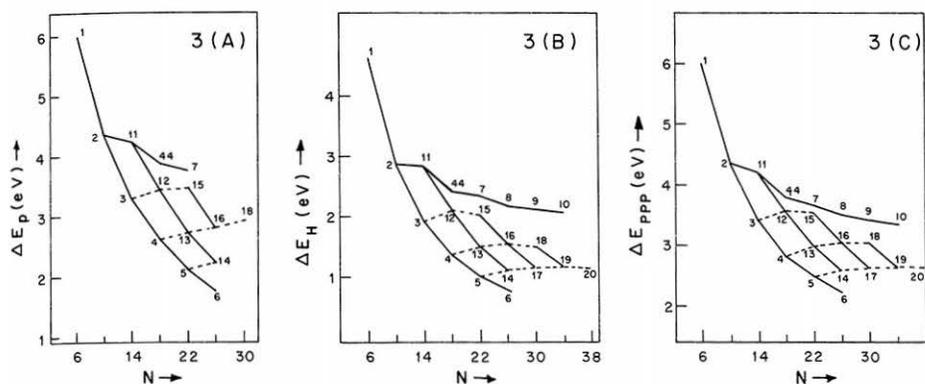


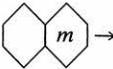
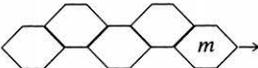
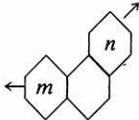
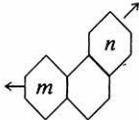
FIG. 3.—A plot of experimental p -band energies (eV) versus N , the number of C-atoms in the molecule, is given in Fig. 3A. A plot of $\Delta E_H = \epsilon_1^- - \epsilon_1$ (in eV) versus N is given in Fig. 3B. A plot of ΔE_{PPP} versus N , where ΔE_{PPP} is obtained from a Pariser-Parr-Pople type of calculation discussed later in the text, is given in Fig. 3C. The molecules correlated in Fig. 3 are of cata-condensed type and are fully identified in Table I. The correlations shown here are adapted from the work of Koutecky and others.

Similar HMO correlations have been established for a number of other energetic characteristics of hydrocarbons. Nepras and Zahradnik,¹³ in the case of π -complexes of the conjugated hydrocarbons, found a significant correlation between the energy of the first charge-transfer band and the HMO energy ϵ_1 , provided that the benzenoid hydrocarbons, the polyenes, and the α,ω -diphenylpolyenes were treated as separate groups. Koutecky¹⁴ found a significant correlation between the polarographic reduction and oxidation half-wave potentials and the HMO energies ϵ_1^- and ϵ_1 , respectively—again provided that the benzenoid hydrocarbons, the polyenes, and the α,ω -diphenylpolyenes were treated as separate groups. Therefore, we conclude that the variation of ΔE_p and the other characteristics specified above, at least as evidenced within structurally homogeneous groups of conjugated hydrocarbons, are determined by molecular topology. The changes of ΔE_p between different hydrocarbon classes, however, are not explicable within the HMO framework. In other words, the topological factor alone does not provide any simple relation between ΔE_p and changes in structure when these latter changes are gross.

GEOMETRIC CONSIDERATIONS

Progress toward a correlative algorithm that permits the input of molecular geometry will require two modifications. The tight-binding approximation of the HMO model must be relaxed; in other words, the short-range interactions (which, in the HMO method, reflect the topological pattern of the molecule) must be augmented by those long-range interactions that are demanded by any molecular model that is explicitly dependent on the mole-

TABLE 1.—Identification of catacondensed molecules discussed in Fig. 3.

Structural type	Individual representatives ^a (and their numbers in Fig. 3)
	$m: 0, 1, 2, 3, 4, 5$ (No. 1, 2, 3, 4, 5, 6)
	$m: 0, 1, 2, 3$ (No. 7, 8, 9, 10)
	$m: 1; n: 1, 2, 3, 4$ (No. 11, 12, 13, 14)
	$m: 2; n: 2, 3, 4$ (No. 15, 16, 17)
	$m: 3; n: 3, 4$ (No. 18, 19)
	$m: 4; n: 4$ (No. 20)

^aThe number of benzene rings annelated in the direction indicated by the arrow is denoted by m or n .

cular geometry. Secondly, any precise consideration of detailed molecular geometry requires an accounting of the effects of bond length variations on the short-range interactions. The Pariser-Parr-Pople scheme¹⁸ provides a model that satisfies both of these requirements.¹⁹

It seems desirable to isolate the effects of inclusion of the long-range interactions from those of the bond-length dependence of the short-range interactions. In view of this, the computational results of two different versions of the Pariser-Parr-Pople (PPP) scheme will now be explored. These are:

Version 1.^{12,17}—A simplified molecular geometry is used. All carbon-carbon bond lengths are set equal to 1.39 Å. All bond-bond angles within a ring system are set equal to the inner angles of the corresponding regular polygon. For some structural types of hydrocarbons (*e.g.*, tricyclic or tetracyclic per-condensed systems containing odd-member rings), the topology does not permit this choice of bond-bond angles. In such cases, if the bond lengths are maintained equal, certain ambiguities occur in bond-bond angle values. However, the resulting ambiguity in the non-nearest neighbor interatomic distances produces rather insignificant, and completely unworrisome, variations in the quantities computed by PPP methods.²⁰ A value of 120° is assigned to the angle between all exocyclic bonds. HMO's are used as the basis MO set for construction of Slater determinants. For the resonance integral β_0 pertinent

to a bond length of 1.39 Å, the value -2.318 eV is adopted. This value of β_0 produces an energy match of ΔE_p and ΔE_{PPP} for benzene.¹²

The electron repulsion integrals γ_{ij} are approximated by the Mataga formula

$$\gamma_{ij} = 14.399/(1.328 + R_{ij}) \quad (1)$$

where R_{ij} is the distance (in Å units) between carbon atoms i and j . The energy of the p -band calculated by these means is denoted ΔE_{PPP} . With the exception of some effects caused by configuration interaction, this method differs from the simple HMO model only insofar as it includes the π -electron repulsions, which in this approach, represent the intramolecular long-range forces.

Version 2.—A self-consistent field set of molecular orbitals (SCF-MO's) is used as a basis for construction of Slater determinants. The dependence of both short-range and long-range interactions on bond length is simulated as follows. In each SCF step, the bond length is evaluated as:

$$R_{ij} = A_0 + A_1 p_{ij} + A_2(\Delta p_{ii} + \Delta p_{jj}) + A_3(\Delta p_{ii} \Delta p_{jj} - \frac{1}{2} p_{ij}^2) \quad (2)$$

where p_{ij} is the π -electron bond order of the $C_i - C_j$ bond; where Δp_{ii} and Δp_{jj} are the net π -electron charges on the i -th and j -th carbon atoms, respectively; and where the parameters A_0, \dots, A_3 are estimated empirically. The results of version 2, as presented here, are based on the following values of the A parameters:

$$A_0 = 1.508; A_1 = -0.158; A_2 = -0.162; A_3 = 0.049$$

With these values, equation 2 provides rather good agreement with those experimental values of C-C bond lengths available for a group of 25 hydrocarbons. The values of R_{ij} appropriate to each SCF iterative step are used to reevaluate the resonance integrals for the next step as:

$$\beta_{ij} = -2.318 \exp [-2.0(R_{ij} - 1.39)] \quad (3)$$

and to reevaluate the electron repulsion integrals between nearest-neighbor atoms C_i and C_j , (*i.e.*, γ_{ij}), for the next step using equation 1. The energies of the p -band obtained in version 2 are denoted $\Delta E_{PPP(+)}$. These two PPP versions constitute correlative algorithms that contain input of both molecular topology and an average molecular geometry; version 2, however, transforms the topology into a fairly detailed geometric data set *via* equation 2. The results of both versions are illustrated in Figs. 4 and 5. The plot of ΔE_p versus ΔE_{PPP} given in Fig. 4 illustrates a satisfactory agreement for benzenoid and fluoranthene types of hydrocarbons. However, ΔE_{PPP} values for the linear polyenes, α -phenylpolyenes, α, ω -diphenylpolyenes, azulenes, fulvenes and heptafulvenes appear to be much too small. Because it is expected that all of these molecules (the azulenes, perhaps, excepted) should possess rather pronounced bond-length alternations, Fig. 4 suggests that the averaged geometry used in version 1 is inadequate. In accord with this supposition, it is found

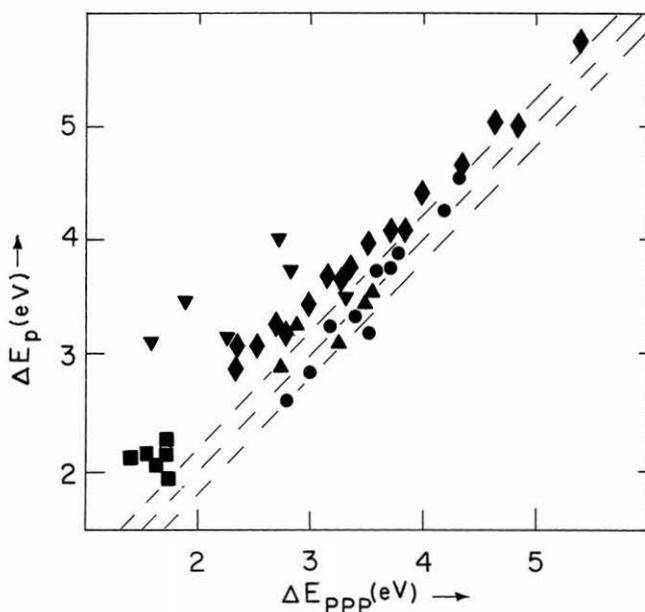


FIG. 4.— A plot of ΔE_{PPP} , as obtained from version 1 of the Pariser-Parr-Pople approach, versus the experimental energies of p -band maxima. Molecule types are identified as follows: triangles (apices down), benzologs of fulvene and heptafulvene; triangles (apices up), benzologs of fluoranthene; squares, azulenes; diamonds, linear polyenes (including α -phenyl- and α,ω -diphenyl-polyenes); circles, benzenoid molecules. The center 45° line represents exact coincidence of experiment and computation. The outer 45° lines bracket the "acceptable agreement" limits of ± 0.2 eV between experiment and theory.

that the plot of ΔE_p versus $\Delta E_{PPP(+)}$ given in Fig. 5 produces a completely acceptable agreement of experiment and computation.

We may conclude, from inspection of Figs. 2, 4, and 5, that both molecular topology and molecular geometry must be considered in order that different structural types of hydrocarbons should produce a single acceptable correlational dependence between ΔE_p values and their theoretical estimates.

The reader might take exception to the fact that version 2 differs from version 1 not only with regard to explicit bond-length dependency input but also insofar as SCF-MO's are used instead of HMO's. Inasmuch as SCF-MO's for certain types of hydrocarbons (*e.g.*, nonalternant or polyenic types) differ substantially from the corresponding HMO's, it is possible that these differences might produce relatively large changes in the computed p -band energies. In order to allay this suspicion, Table 2 provides a compilation of variously computed p -band energies for a number of alternant hydrocarbons. The second and third columns of Table 2 contain the computed values ΔE_{PPP} and $\Delta E_{PPP(+)}$, respectively. The fourth column contains p -band energies calculated according to version 1, except that SCF-MO's are substituted for HMO's. If we accept column 3 of Table 2 as providing a good representation of experiment (see

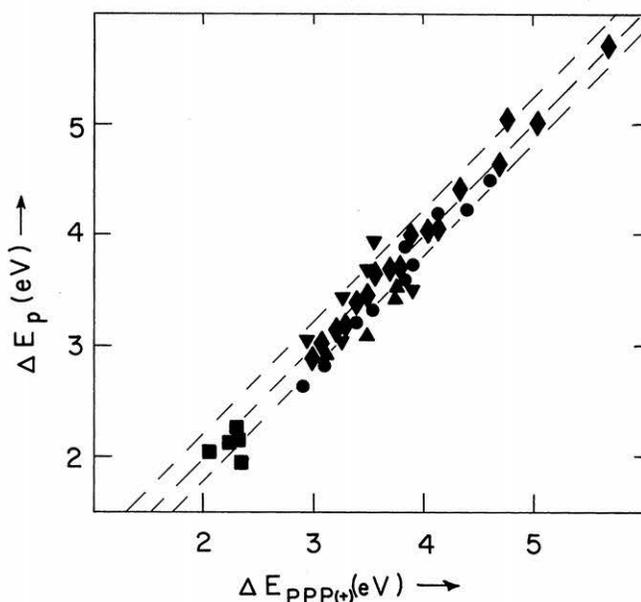


FIG. 5.—A plot of $\Delta E_{PPP(+)}$, as obtained from version 2 of the Pariser-Parr-Pople approach, versus the experimental energies of p -band maxima. All other identifications pertinent to Fig. 4 (See caption to Fig. 4) apply here also.

Fig. 5), it is clear that the use of SCF-MO's, without the concomitant use of bond-length variations, actually provides a correlation with experiment that is generally poorer than that given by the unadulterated version 1. The fifth column of Table 2 collects results of a PPP calculation that uses an HMO basis set, but also uses SCF bond orders and charges in order to evaluate bond lengths (*via* equation 2) and to correct for resonance and repulsion integral variations (*via* equations 1 and 3). The results of Table 2 fully support the conclusion that it is the allowance for the bond-length dependence of the resonance integral, β_{ij} , and the nearest neighbor repulsion integral, γ_{ij} , that provides the superiority of version 2 (see also Bloor *et al.*²² and Koutecky¹⁴ for similar conclusions concerning oxidation and reduction potential correlations).

In summary an analysis of the relative importance of topologic and geometric input in PPP computational models must concern itself with the observations:

1. Almost all quantities computed by PPP means are grossly sensitive to nearest-neighbor bond-length variations. Proper account for the deviations of bond-lengths from their average values usually improves correlation with experiment. On the other hand, most computed quantities are rather insensitive to variations of non-nearest neighbor distances.²⁰

2. The last comment is particularly pertinent to bond-orders and π -electron charges. Indeed, the computed values of carbon-carbon bond

TABLE 2. — *A comparison of different Pariser-Parr-Pople estimates of ΔE_p (Hochmann²¹).*

Molecule	Version 1	Version 2	Version 1 but with use of an SCF-MO set	Version 1 but with geometry input via equation 2
Naphthalene	4.35	4.58	4.37	4.45
Anthracene	3.41	3.66	3.44	3.53
Butadiene	5.38	5.71	5.19	5.81
Hexatriene	4.36	4.68	4.11	4.73
Octatetraene	3.74	4.08	3.46	4.07
Styrene	4.85	5.04	4.76	5.16
Biphenyl	4.66	4.76	4.63	4.82
1,2-Biphenylethylene	3.83	4.13	3.77	4.21

lengths (*i.e.*, R_{ij} of equation 2) are quite independent of the particular values for non-nearest neighbor distances which are adopted in any given computation. Thus, we may conclude that the computed R_{ij} values are more or less wholly determined by that part of the interatomic interactions, both short-range and long-range, which reflect the topological pattern of a molecule.

3. The computed values of R_{ij} obtained using equation 2 and version 2 are in fair agreement with the known experimental values of C-C bond lengths.

It follows immediately that the pattern of C-C bond length variations within a given molecule is topologically enforced. Indeed, it has also been established that HMO bond orders yield a qualitatively correct picture of the bond-length variations in many molecular types.¹¹ Consequently, the simulation of bond-length variations provided in version 2 may be concluded to be an implicit topological input. Further indirect support for this point of view is provided by HMO computations based on a variable β scheme.²³ In this approach, the effective resonance integrals of HMO theory, β^{eff} , are made bond-length dependent and are given as

$$\beta_{ij}^{eff} = \exp [-\alpha(R_{ij} - 1.39)] \quad (4)$$

where R_{ij} is computed from the Coulson equation

$$R_{ij} = 1.517 - 0.180\rho_{ij} \quad (5)$$

The resulting eigenproblem, when solved in an iterative manner and with a suitable choice for the value of α in equation 4, provides²⁴ a good single correlative dependence of ΔE_p on $\epsilon_1 - \epsilon_1$ for both the benzenoid and polyenic hydrocarbons. Analogously, good correlation was also found for lowest-

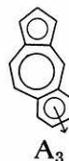
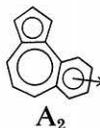
energy π -electron ionization potentials and for the final values of R_{ij} (*i.e.*, R_{ij} at convergence). Indeed, this set of R_{ij} 's is in substantially better agreement with experiment than those obtained using equation 5 in conjunction with simple HMO bond orders. Therefore, for a structurally heterogeneous group of hydrocarbons, topological information conjoined with knowledge of average distances for non-nearest neighbor atoms are sufficient to induce a single correlative dependence between the value of a given experimental quantity and its counterpart theoretical estimate; however, a molecular model which is topologically conditioned in explicit ways (*via* short-range interaction patterns) and in implicit ways (*via* bond-length variations) must be used. We will illustrate this last point in the next section where we will attempt to separate those parts of $\Delta E_{PPP(+)}$ that are explicitly and implicitly dependent on topology.

The Explicit and Implicit Topological Dependence of ΔE_p

The relatively good agreement between ΔE_p and $\Delta E_{PPP(+)}$ indicates that an analysis of $\Delta E_{PPP(+)}$ might yield understanding of the correlative dependence of ΔE_p and ΔE_H . In this regard, the most interesting content of Fig. 2 concerns those groups of molecules showing linear or nearly-linear correlation between ΔE_p and ΔE_H ; such groups exhibit very little variation of regression line slopes, but considerable variations of regression line intercepts.

Figs. 6 and 7 provide plots of ΔE_{PPP} and $\Delta E_{PPP(+)}$ versus ΔE_H , respectively; both figures, with some exceptions, exhibit nearly linear correlative dependencies as long as narrow structural groups are considered. Exceptions are:

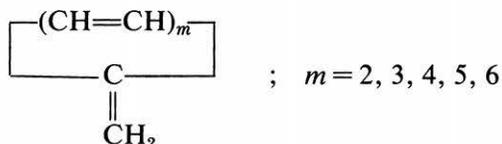
1. Azulenes exhibit a nonlinear, but nonetheless simple interdependence, but only when these molecular types are subdivided into three groups distinguished A_1 , A_2 , and A_3 :



2. Analogous results to that above obtain for the benzo-derivatives of fulvene and heptafulvene, but again, only when narrow structural subgroups of these molecules are considered.

3. Similar effects (not graphed here) are also observed for the benzo-derivatives of fluoranthene.¹⁷

4. Fulvene and heptafulvene belong to a correlating group of molecules (see Fu dependencies on Figs. 6 and 7), which is of formula



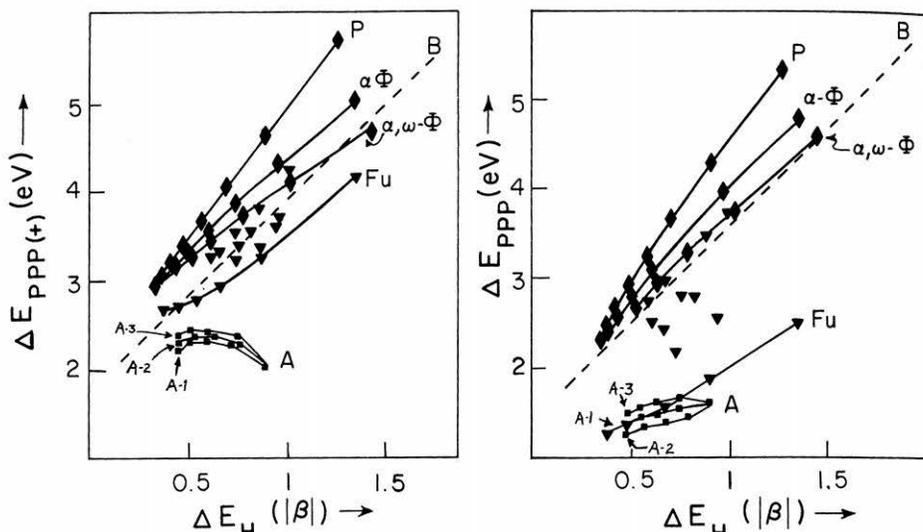


FIG. 6.—A plot of $\Delta E_{PPP(+)}$ (units of eV) versus ΔE_H (units of $|\beta|$). Notation is identical to that in Fig. 4, with the following exceptions: the fulvene correlation line, proceeding from top to bottom runs sequentially through fulvene, heptafulvene, nonafulvene, etc. The subclassification A_1 , A_2 , and A_3 for azulenes is discussed in the text.

FIG. 7.—A plot of $\Delta E_{PPP(+)}$ (units of eV) versus ΔE_H (units of $|\beta|$). Notation is identical with that used in Fig. 6. Compare Figs. 2, 6, and 7.

Because of the above results, and because of the good congruence of $\Delta E_{PPP(+)}$ and ΔE_p values, we may expect the existence of rather simple correlations between ΔE_p and ΔE_H even for hydrocarbons such as the benzoderivatives of azulene, fulvene or heptafulvene—providing that we seek such dependence only among the members of a structurally very narrow group. However, the necessity to create narrow groups (and the possibility that the correlation dependence might be nonlinear) restricts the practical value of such correlations (*i.e.*, of ΔE_p versus ΔE_H).

The striking similarities of Figs. 2 and 7 must also be noted. Therefore, in order to understand the characteristic features of the ΔE_p versus ΔE_H correlation of Fig. 2, we will attempt a separation of the expressions for ΔE_{PPP} and $\Delta E_{PPP(+)}$ into two parts so that the first part correlates with the molecular topology *via* the eigenvalues of the topological matrix, whereas the second part correlates with the molecular topology *via* nearest neighbor bond-length variations and nearest-neighbor geometry. Such a separation is effected (see also reference 22) in equation 6

$$\left. \begin{array}{l} \Delta E_{PPP} \\ \Delta E_{PPP(+)} \end{array} \right\} = \quad (6)$$

$$(\beta_0 - \frac{1}{3}\gamma_{12})\{\tilde{C}_1TC_1 - \tilde{C}_1TC_1\} + \tilde{C}_1\Delta FC_1 - \tilde{C}_1\Delta FC_1 + 2K_{1\bar{1}} - J_{1\bar{1}} + \Delta E_{Cl}$$

where β_0 and γ_{12} are resonance and electron repulsion integrals, respectively,

at a carbon-carbon distance of 1.39 Å; where $C_{\bar{i}}$ and C_i are vectors constituted from the coefficients of the MO's of energy $\epsilon_{\bar{i}}$ and ϵ_i , respectively; and where $J_{i\bar{i}}$ and $K_{i\bar{i}}$ are coulombic and exchange integrals,¹⁸ respectively. The matrix elements of ΔF are defined as

$$\Delta F_{ij} = F_{ij} - (\beta_0 - \frac{1}{3}\gamma_{12})T_{ij} \quad (7)$$

with F_{ij} being an element of the atomic orbital representation of the effective SCF π -electron Hamiltonian in a Pariser-Parr-Pople scheme. The quantity ΔE_{CI} represents the contribution of configuration interaction to the values ΔE_{PPP} or $\Delta E_{PPP(+)}$ and is found to be quite negligible in PPP calculations of ΔE_p .

If the basis MO's are of the HMO type, it is found that $\tilde{C}_{\bar{i}}TC_{\bar{i}} - \tilde{C}_iTC_i = \Delta E_H$. For an SCF-MO basis, $\tilde{C}_{\bar{i}}TC_{\bar{i}} - \tilde{C}_iTC_i$ is generally different from ΔE_H . Nonetheless, for most molecules considered here, this quantity is strongly correlated with ΔE_H and the corresponding regression line has a slope of ~ 1 . Consequently, the quantity $(\beta_0 - \frac{1}{3}\gamma_{12})$ provides a theoretical estimate of the slopes of the $\Delta E_p \sim \Delta E_H$ lines when these lines are linear or nearly so. It is found here that $(\beta_0 - \frac{1}{3}\gamma_{12}) = -4.08$ eV is in excellent accord with the average regression line slope of -4.15 ± 0.1 eV shown in Fig. 2.

The quantity

$$\left. \begin{array}{l} \delta\Delta E_{PPP} \\ \delta\Delta E_{PPP(+)} \end{array} \right\} = C_{\bar{i}}\Delta FC_{\bar{i}} - C_i\Delta FC_i + 2K_{i\bar{i}} - J_{i\bar{i}} \quad (7)$$

represents, for the most part, the contributions of electron repulsion interactions and of the variation of resonance integrals and nearest neighbor repulsion integrals with bond lengths to the values of ΔE_{PPP} or $\Delta E_{PPP(+)}$. Because of the acceptable agreement of $\Delta E_{PPP(+)}$ with ΔE_p , we may interpret the quantity $\delta\Delta E_{PPP(+)}$ to be that part of the p -band energy that depends on the average non-nearest neighbor distances and the variations in bond lengths. This bond effect, of course, is clearly not present in $\delta\Delta E_{PPP}$.

As pointed out by Bloor,²² the values of $\delta\Delta E_{PPP}$ and $\delta\Delta E_{PPP(+)}$ are quite constant within those groups of molecules that exhibit nearly linear dependencies of ΔE_{PPP} versus ΔE_H or $\Delta E_{PPP(+)}$ versus ΔE_H . On the other hand, the average values of these quantities are highly group dependent. The group averages of $\delta\Delta E_{PPP}$ and $\delta\Delta E_{PPP(+)}$ for different molecular types are listed in Table 3 where they are also compared with the regression-line intercepts of the $\Delta E_p \sim \Delta E_H$ plots. The consistency of agreement in Table 3 is quite remarkable.

Conclusions

Within a structurally homogeneous molecular group, the gross variance of p -band energy is correlated with molecular topology *via* the eigenvalues of the topological matrix.

In order to interpret the variance of ΔE_p among molecular groups possess-

TABLE 3.—Regression line intercepts (in eV) and regression line slope as obtained by various means.

Hydrocarbon type	PPP Calculation		From Fig. 2 experiment
	Version 1, eV	Version 2, eV	
REGRESSION LINE INTERCEPTS			
Benzenoid	1.5	1.6	1.4
Fluoranthenoid	1.5	1.7	1.4
Polyenic	1.2	2.0	2.0
α -Phenylpolyenic	1.6	2.1	2.0
α - ω -Biphenylpolyenic	1.6	2.1	2.0
Fulvenic ^a	0.9	1.8	
β -Fulvenic ^b	0.2	1.3	~1.7
REGRESSION LINE SLOPE			
	$(\beta_0 - \frac{1}{3}\gamma_{12}) = -4.08$ theoretical	
	$(\beta_0 - \frac{1}{3}\gamma_{12}) = -4.18 \pm 0.1$ from ΔE_p versus ΔE_H plots of Figure 2	

^aSee molecular formula on page 139.

^bThe benzoderivatives of fulvene and heptafulvene.

ing diverse structures, the molecular geometry (in addition to the molecular topology) must be included in the correlative algorithm. However, only a very simplified geometry (that which provides average non-nearest neighbor distances but rather precise bond lengths) is required.

The bond-length tabulation can be supplanted by a computed bond-length set. Because these, in turn, are evaluable from topology and non-nearest neighbor distances, it appears that the molecular topology and simple stereochemical considerations comprise the totality of basic information required for correlative purposes pertaining to ΔE_p .

SMALL POLYATOMIC MOLECULES AND IONS

The molecular electronic spectroscopy of small polyatomic molecules and ions found primary systematization at the hands of A. D. Walsh,²⁵ who made use of isoelectronic sequence ideas and of correlation diagrams concerned with the dependence of molecular orbital energies on molecular geometry. He achieved considerable success, particularly with regard to prediction of ground state geometries. Nonetheless, this field of molecular electronic spectroscopy is not in as good a state as that of the diatomic, ligand field, or aromatic types of molecule. In view of this, the remainder of this article will concern itself with small polyatomic molecules and their electronic spectroscopy.

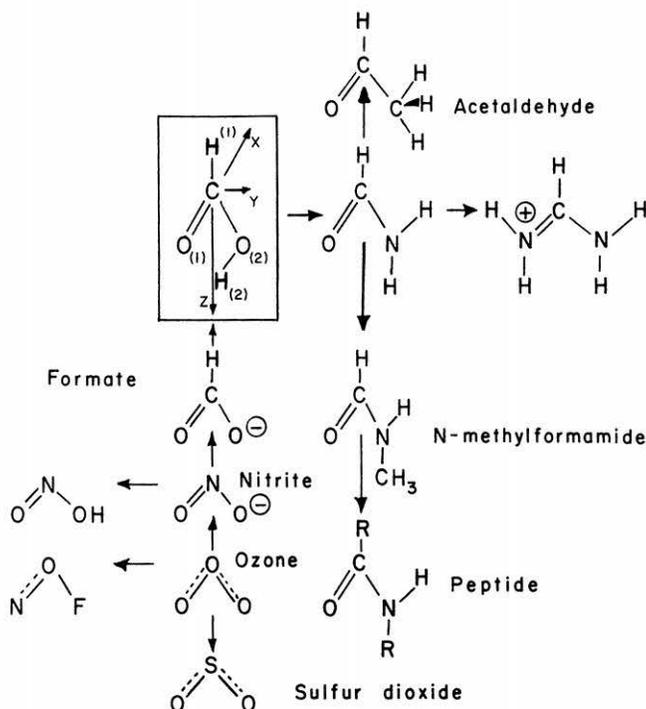


FIG. 8.—Molecular genealogy of the peptide grouping. Axes and atom numbering conventions are provided for HCOOH in the top left corner.

*Specification of Isoelectronic Sequences
for Simple Polyatomic Molecules and Ions^{1,2}*

The type of isoelectronic sequence to be discussed is best described in terms of an example. Fig. 8 shows a series of nonlinear triatomic groupings, each of which contains 18 valence electrons. This diagram may be considered to represent a “proton push-pull synthesis” of the peptide linkage from ozone. The steps involved in this “synthesis” are:

1. Extraction of a proton from the central oxygen atom of ozone produces nitrite ion. A return of this proton, by chemical fixation, to one of the oxygen atoms yields nitrous acid.
2. Extraction of a proton from the nitrogen atom of nitrite ion and its chemical fixation to a carbon center thereby generated yields formate ion. Chemical addition of another proton does not affect the number of valence electrons and yields formic acid.
3. Extraction of a proton from the oxygen atom of the hydroxyl group of formic acid and its chemical fixation to the nitrogen center thereby generated yields an amino group and, hence, formamide.

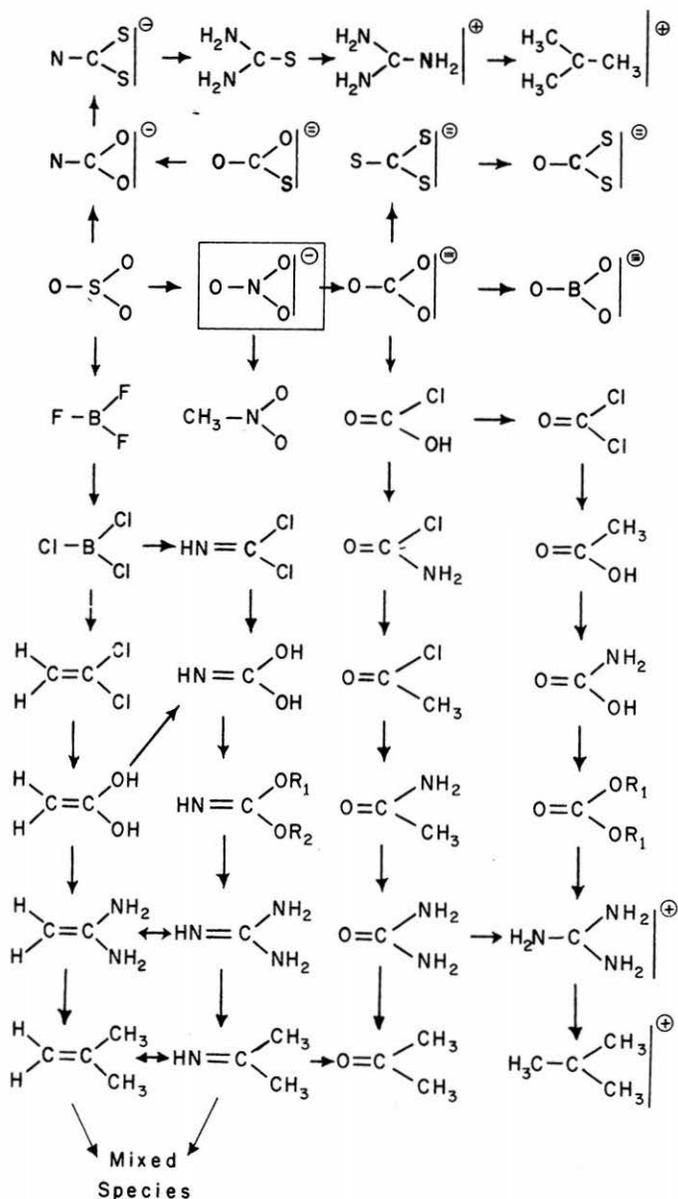


FIG. 9.—A short list of molecules which are isoelectronic with the nitrate ion.

4. The additional steps from formamide to *N*-methylformamide to peptide are trivial in a spectroscopic sense.

5. The "peptide synthesis" illustrated in Fig. 8 also includes a number of "subsyntheses" whose "reaction paths" are obvious. These lead to the formamidinium ion (which is the zeroth member of the series of amidinium

salts), to the nitrosyl halide molecules, to acetaldehyde, and to sulfur dioxide. The reader should not experience much difficulty in conjuring up other series members not shown in Fig. 8.

An isoelectronic sequence of which each member contains 24 valence electrons is shown in Fig. 9. We will speak of this series as the "nitrate series" because the nitrate ion is one of the more common series members. This short list spans the range of purely organic (*e.g.*, acetone), purely inorganic (*e.g.*, nitrate ion), and purely biological (*e.g.*, urea) molecules. We now inquire about the extent to which we understand the spectroscopy of such molecules. Consider acetone, for example, and inquire about the energetic whereabouts of the lowest energy $\pi^* \leftarrow \pi$ transition; few knowledgeable spectroscopists would care to choose between the two most likely candidate absorption bands in the near vacuum ultraviolet. Consider urea, our knowledge of the spectrum of this molecule is, at best, primitive; it is rather difficult to interpret that which we do not know. The spectrum of boron trifluoride has never been measured. That reported for sulfur trioxide is assuredly erroneous. Indeed, it is quite probable that the presently accepted interpretation of the absorption spectrum of nitrate ion itself is as much fairytale as it is wishful thinking. The facts are that few data are available, and no existing interpretation of the known data is wholly acceptable. Thus, these molecules provide fertile ground for application of genealogical attitudes.

A number of other isoelectronic sequences are readily generated. Their presentation here would merely indicate the generality of an attitude and would not introduce any new ideas. Such new series will be discussed in the following when and if needed.

Correlatory Attitudes for Simple Polyatomic Molecules and Ions

We now progress to the core matter of this presentation. The question raised is whether correlatory attitudes can provide any significant systematization of the spectroscopy of simple polyatomic molecules and ions. The answer is a resounding affirmative that is amply validated in the work of A. D. Walsh.²⁵

The purpose of the present work is not to discuss the contribution made by Walsh, but rather to ask whether his attitudes are capable of extension, and whether correlatory aids other than the one he used can be developed. We answer this question by specifying correlatory ideas that we have found useful and exemplifying this utility, in each instance, using an apt molecular sequence.

Attitude 1, the crystal field approach.—Ionic materials are rather difficult to investigate spectroscopically. They may not be gasified and investigated under low-pressure conditions; it is more or less impossible to deposit films sufficiently thin to provide adequate transparency in wavelength regions of high optical density; and the ionicity of the material may induce large solute-solvent interactions that cause extensive band broadening and structure loss in solution. Yet, ionic materials come equipped with variational characteris-

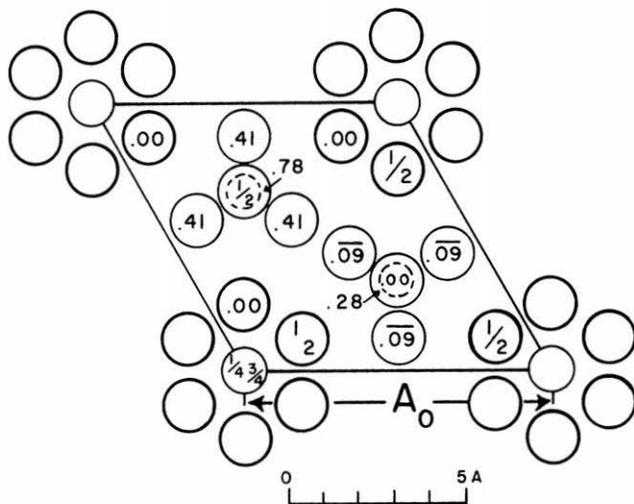


FIG. 10.—A projection on the c face of the hexagonal structure of $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$. Lithium atoms, as represented by small lightly ringed circles, are considered to be at the centers of octahedra of water molecules (heavily ringed large circles). The chlorate oxygen atoms are shown as large lightly outlined circles.

tics that are ideally suited to correlative study: the dependence of crystal habit and site symmetry on salt composition, and the facility with which salts of similar sizes and geometries cocrystallize. The first characteristic may be used to alter the effective symmetry of the “crystalline” ion, and thus, to split degeneracies, or change quantum mechanical selection rules governing electronic transition probabilities, or both. The second characteristic may be used as a diluent device for strongly absorbing materials, the absorber having the status of “guest” in a nonabsorbing “host” crystal.

The above is best illustrated by example. Permanganate salts cocrystallize readily, in virtually all molar ratios, with perchlorate salts. Similar statements are true for the $\text{CrO}_4^{2-}/\text{SO}_4^{2-}$ and $\text{VO}_4^{3-}/\text{PO}_4^{3-}$ couples. The hypothetical isolated MnO_4^- ion presumably possesses tetrahedral (T_d) symmetry; the site symmetry of MnO_4^- in a $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}/\text{LiMnO}_4 \cdot 3\text{H}_2\text{O}$ mixed single crystal is C_{3v} ; that in $\text{Ba}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}/\text{Ba}(\text{MnO}_4)_2 \cdot 3\text{H}_2\text{O}$ is C_3 ; that in $\text{NaClO}_4/\text{NaMnO}_4$ is C_{2v} ; and that in $\text{KClO}_4/\text{KMnO}_4$ is C_s . The C_{3v} site symmetry of ClO_4^- in LiClO_4 is best illustrated in Fig. 10. The lithium salt and barium salt crystals are uniaxial and measurements using polarized light are easy to effect and to interpret. The use of the nonabsorptive perchlorate host medium allows one to control the absorber MnO_4^- concentrations so that relatively large, easily manipulatable crystals may be fabricated and used.

The electronic states of a tetrahedral molecule-ion containing an even number of electrons span a total of five representations. These are shown in Table 4. The manner in which the degeneracy of these states is removed by a decrease of the effective molecular symmetry is also shown in Table 4, as

TABLE 4.—Absorption characteristics expected for a tetrahedral ion in crystal sites of different symmetries. The notations used are as follows: ${}^1\Gamma_1$ is a totally symmetric singlet ground state; ${}^1\Gamma_i$ is an arbitrary excited singlet state; (f) denotes electric-dipole forbidden; (i) denotes electric-dipole allowed and isotropically polarized; (\parallel), as (i) but polarized parallel to the principal c axis; (\perp), as (\parallel) but polarized perpendicular to the principal axis; (a), as (i) but polarized parallel to the a axis; (b), as (i) but polarized parallel to the b axis; and (ac), as (i) but polarized in the ac plane.

Site symmetry	State representations (and electric dipole characteristics of a ${}^1\Gamma_i \leftarrow {}^1\Gamma_1$ transition)					
	T_d	A_1 (f)	A_2 (f)	E (f)	T_1 (f)	T_2 (i)
T	A (f)	A (f)	E (f)	T (i)	T (i)	
C_{3v}	A_1 (\parallel)	A_2 (f)	E (\perp)	$A_2 + E$ (f) (\perp)	$A_1 + E$ (\parallel) (\perp)	
C_3	A (\parallel)	A (\parallel)	E (\perp)	$A + E$ (\parallel) (\perp)	$A + E$ (\parallel) (\perp)	
C_{2v}	A_1 (a)	A_2 (f)	$A_1 + A_2$ (a) (f)	$A_2 + B_1 + B_2$ (f) (b) (c)	$A_1 + B_1 + B_2$ (a) (b) (c)	
C_s	A' (ac)	A'' (b)	$A' + A''$ (ac) (b)	$2A'' + A'$ (b) (ac)	$2A' + A''$ (ac) (b)	

are the electric dipole transition characteristics of an electronic excitation that connects these states to a totally symmetric ground state. It is clear that the predictive content of Table 4 is adequate to the task of identifying any ${}^1\Gamma_i \leftarrow {}^1\Gamma_1$ transition of a tetrahedral molecule, provided that experiment can discriminate small crystal-field splittings and distinguish different polarization directions. Thus, a transition for which the origin band exhibits no splitting and which is clearly discernible and \parallel -polarized in $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}/\text{LiMnO}_4 \cdot 3\text{H}_2\text{O}$ is of species ${}^1A_1 \leftarrow {}^1A_1$ in both the C_{3v} and T_d point groups; a transition whose origin band splits into two observable components in C_{3v} , one \parallel -polarized, one \perp -polarized, is clearly correlatable with a ${}^1T_2 \leftarrow {}^1A_1$ transition of the tetrahedral molecule. Indeed, success is dependent only on the ingenuity of the researcher with regard to growing good crystals and achieving high spectroscopic resolution.

Example of attitude 1, the far-red absorption band of MnO_4^- .—The far-red absorption bands of MnO_4^- comprise a weak absorption system,²⁶⁻²⁹ the origin of which lies in the region of $14,000 \text{ cm}^{-1}$. These bands have been inves-

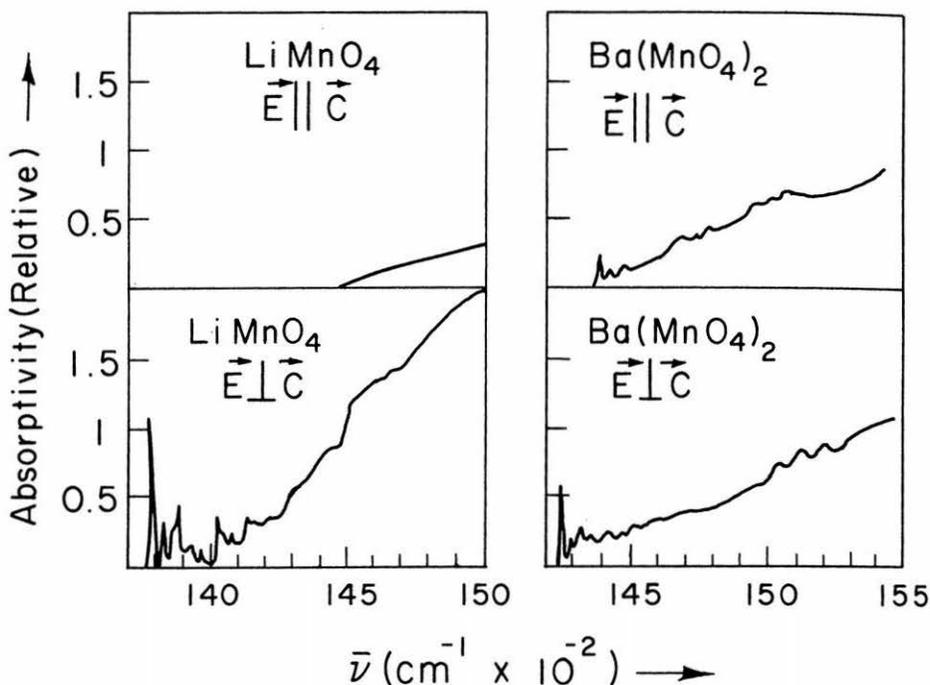


FIG. 11.—Polarized absorption spectra of mixed single crystals $\text{ClO}_4^-/\text{MnO}_4^-$ at 4.2°K (from reference 30).

tigated by Teltow,²⁶ Ballhausen,²⁷ and Day,²⁸ all of whom seem to agree on a tentative ${}^1T_1 \leftarrow {}^1A_1$ assignment.

The far-red absorption spectra of MnO_4^- in C_{3v} and C_3 environments³⁰ are shown in Fig. 11 in both \perp and \parallel -polarizations. It will be seen that the origin band is clearly discernible in all instances except the \parallel -polarization of the C_{3v} entity. These observations are fully consistent with an electric-dipole-forbidden transition of $T_1 \leftarrow A_1$ type in the tetrahedral molecule. The components of such a transition should attain electric dipole allowedness as follows (the electric field vector is denoted \vec{E}):

$$\vec{E} \parallel \vec{c} \text{ and } \vec{E} \perp \vec{c} \text{ in } C_3 \text{ and } \vec{E} \perp \vec{c} \text{ in } C_{3v} \text{ with } \vec{E} \parallel \vec{c} \text{ forbidden}$$

Inasmuch as these are precisely the characteristics observed, we consider the $T_1 \leftarrow A_1(T_d)$ assignment proven. A number of evidences dictate the further spin designations ${}^1T_1 \leftarrow {}^1A_1$ and enable the possibility of magnetic dipole character of the far-red bands to be discounted.³⁰

The experimental work performed was adequate for precise transition type determination for the far-red bands of MnO_4^- . Identification was based on straightforward genealogical point-group processing and no computational arguments were used.

Unfortunately, such precise identifications are rare; where available, they usually serve as cornerstones for the construction of correlative identification

TABLE 5.—Correlation of electronic state representations among various point groups for 16 valence electron molecules isoelectronic with CO₂.

Point group	Ground state	$\pi \rightarrow \pi^*$ states			$\sigma \rightarrow \pi^*$ state(s)
$D_{\infty h}$	${}^1\Sigma_g^+$	Σ_u^-	Δ_u	Σ_u^+	Π_g
$C_{\infty v}$	${}^1\Sigma^+$	Σ^-	Δ	Σ^+	Π
D_{2d}	1A_1	B_1	A_2 A_1	B_2	E
C_{2v}	1A_1	A_2	A_2 B_2	B_2	A_2 B_2
C_s	${}^1A'$	A''	A'' A'	A'	A'' A'

schemes in other related molecules. In this regard, it is worth noting the large population of tetrahedral or nearly tetrahedral molecules which are isoelectronic with MnO₄⁻. Some of these are: ClO₄⁻, BrO₄⁻, IO₄⁻, SO₄⁼, S₂O₃⁼, PO₄⁼, CrO₄⁼, VO₄⁼, RuO₄, OsO₄, TcO₄⁻, ReO₄⁻, WO₄⁼, CrO₂Cl₂, MnO₃F, POCl₃, MoO₄⁼, and SiO₄⁼.

Attitude 2, the molecular field approach.—The molecules in an isoelectronic sequence may possess different symmetries even when viewed as isolated entities. This statement is readily verified by reference to the two tabulations of Figs. 8 and 9, but is made more obvious by consideration of the following representative set of 16 valence-electron molecules:

- $D_{\infty h}$ point group: CO₂, CS₂, N₃⁻ (azide ion)
- $C_{\infty v}$ point group: OCS, NCO⁻, NCS⁻, NCCI, NCI, NCB
- D_{2d} point group: H₂CCCH₂ (allene)
- C_{2v} point group: H₂CCO (keten), HNCNH (carbodi-imide)
- C_s point group: HNCO, HNCS, HN₃ (hydrazoic acid)

As in the case of attitude 1, these alterations of point symmetries lead to the removal of electronic degeneracies and to the alteration of electric dipole selection rules governing electronic transition probabilities. Indeed, the only difference between attitudes 1 and 2 lies in the fact that one type of symmetry is environmentally determined (*i.e.*, attitude 1), whereas the other is intrinsic to the isolated molecule and is subject to alteration during the course of "proton push-pull synthesis" (*i.e.*, attitude 2).

*Example of attitude 2, the electronic states of linear triatomic groupings that contain 16 valence electrons.*²—A short list of molecules of this type, categorized with regard to point group symmetry, is given above. The manner in which the expected set of low-energy states transforms in the various point groups is shown in Table 5, wherein predictions concerning degeneracy-loss are quite evident. The observed electronic states of the same molecules are correlated in Fig. 12, the basis for correlation being band intensities, band shapes, and associated vibronic structure. Two correlated sets of states ex-

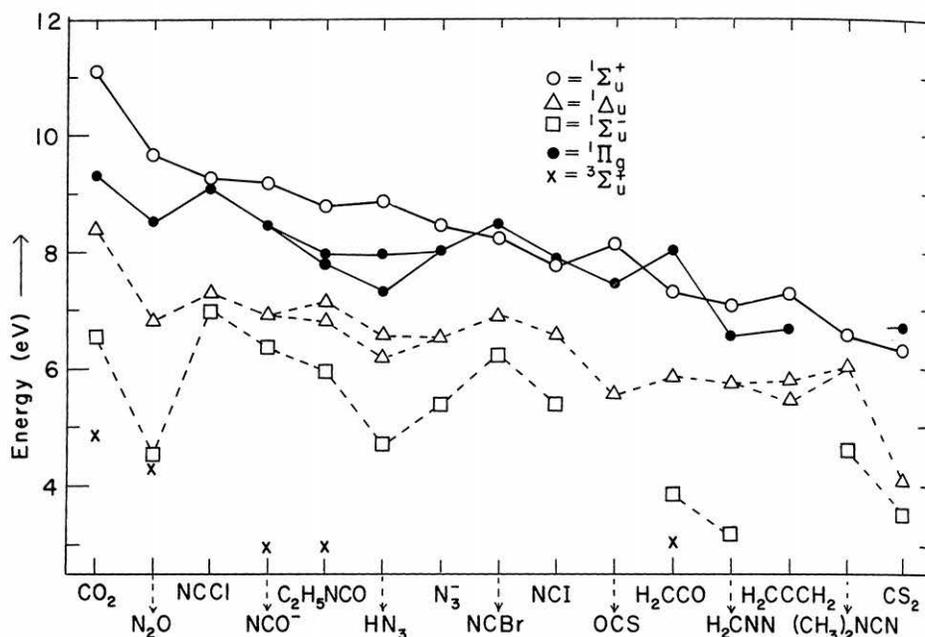


FIG. 12.—Correlation diagram for excited states of molecules isoelectronic with CO_2 . The states marked with an X are triplet states.

hibit bifurcation in molecules of low symmetry indicating that these sets are either Π , Δ , Φ , ... states, whereas all the other sets must be of Σ type ($C_{\infty v}$ point group). In particular, the fact that bifurcation persists only in one of these two sets in allene is adequate to identify the nonbifurcating set as Π and the bifurcating set as one of Δ , Φ , ... in $C_{\infty v}$. Specifically, in allene, a 1Δ state should split into $1A_1$ and $1A_2$ states and the two transitions $1A_1 \leftarrow 1A_1$ and $1A_2 \leftarrow 1A_1$ initiating in the $1A_1$ ground state should be electric dipole forbidden. Thus, if these two transitions are observed at all, they should be weak. On the other hand, in allene, the 1Π ($C_{\infty v}$) state becomes a $1E$ state and the transition which is of $1\Pi \leftarrow 1\Sigma$ type in $C_{\infty v}$ becomes $1E \leftarrow 1A_1$ in D_{2d} and remains dipole-allowed and doubly degenerate just as in the $C_{\infty v}$ point group. The discussion to follow will note the observation in allene of just those simple characteristics we have specified above.

The predicted oscillator strengths of the various possible low-energy transitions are collected in Table 6. The appearance of a zero in this table indicates a group theoretic forbiddenness; the absence of a zero indicates group theoretic allowedness. However, the large range of allowed oscillator strengths—computed to lie between a low of $\sim 10^{-5}$ (weakly allowed) and a high of ~ 0.5 (strongly allowed)—provides a diagnostic tool significantly more powerful than the simple “yes-no” of group theory. The appearance of two different numbers in a given columnar tabulation connotes a removal of degeneracy. The experimental data available for this same set of molecules are given in

TABLE 6.—Computed oscillator strengths for transitions from the ground state to the indicated upper states of molecules isoelectronic with CO_2 . For identification of states in molecules of other than $D_{\infty h}$ symmetry, see Table 5.

Molecule	${}^1\Sigma_u^-$	${}^1\Delta_u$	${}^1\Sigma_u^+$	${}^1\pi_g$		
OCO	0	0	0.417	0		
SCS	0	0	0.502	0		
NNN ⁻	0	0	0.278	0		
OCS	0	0	0.482	1.22×10^{-4}		
NNO	0	0	0.386	7.61×10^{-4}		
NCS ⁻	0	0	0.302	3.59×10^{-4}		
NCO ⁻	0	0	0.286	1.44×10^{-3}		
H ₂ CCCH ₂	0	0	0.344	3.84×10^{-3}		
H ₂ NCN	0	0	1.09×10^{-3}	0.355	0	0.259
H ₂ CCO	0	0	4.09×10^{-3}	0.420	0	0.391
HNCS	9.81×10^{-5}	1.92×10^{-4}	0.383	0.458	9.64×10^{-4}	8.21×10^{-2}
HNNN	3.86×10^{-4}	1.13×10^{-3}	0.317	0.385	5.03×10^{-3}	3.97×10^{-2}
HNCO	5.02×10^{-4}	1.33×10^{-3}	0.328	0.411	8.48×10^{-5}	2.43×10^{-3}

Table 7. Comparison of Tables 6 and 7 indicates a decided similarity of patterns relating to branching and the presence of large or small numbers in the various tabular slots. Some discrepancies surely do occur but are allowed to stand because of other correlative evidences. The reader should study the recorded allene data with respect to the predictions made in the text and implied in Table 6.

In summary, this method appears to possess much power. However, realization of this power is dependent on the availability of highly resolved gas-phase spectra. Without such spectra and other correlative evidence, it is possible that the tactic adopted in this section might not succeed. Indeed, despite the use of a number of other correlative devices in the construction of Fig. 12 and Table 7, it is quite probable that much of the induced state level schematization presented here is wrong. Nonetheless, the gambit would seem to be a good one and should find general utility. In particular, it does provide a windmill that is admirably suited to experimental tilting.

Attitude 3, heavy atom spin orbit coupling.—The generation of an isoelectronic series may involve consideration of ionic members. A case in point is the nitrite ion of the series in Fig. 8. In this instance, we might consider certain of the salts of this anion to represent an extension of the isoelectronic series. Thus, the series of salts $NaNO_2$, $AgNO_2$, $Cd(NO_2)_2$, $Pb(NO_2)_2$, $TlNO_2$ can all be considered to be isoelectronic with NO_2^- . Inasmuch as some of these cations are rather heavy, and because in the case of weak acids such as nitrous

TABLE 7.— Observed energies (eV) and intensities (oscillator strengths, f) of electronic absorption bands of molecules isoelectronic with CO_2 .

D_{wh}	${}^1\Sigma_u^-(f)$	${}^1\Delta_u(f)$	${}^1\Sigma_g^+(z)$	${}^1\Pi(f)$
C_{wp}	${}^1\Sigma^-(f)$	${}^1\Delta(f)$	${}^1\Sigma^+(z)$	${}^1\Pi(x, y)$
D_{2d}	${}^1B_1(f)$	${}^1A_2(f)$	${}^1B_2(z)$	${}^1E(x, y)$
C_{2v}	${}^1A_2(f)$	${}^1A_2(f)$	${}^1B_2(z)$	${}^1A_2(f)$
C_s	${}^1A''(z)$	${}^1A''(z)$	${}^1A'(x, y)$	${}^1B_2(z)$
			${}^1A'(x, y)$	${}^1A''(z)$
				${}^1A'(x, y)$
CO_2 (D_{wh})	6.53 eV $f \sim 1 \times 10^{-5}$	8.41 eV $f \sim 6.2 \times 10^{-3}$	11.08 eV $f = 0.12$	9.31 eV $f \sim 7.5 \times 10^{-3}$
CS_2 (D_{wh})	3.49 eV $f \sim 8 \times 10^{-5}$	3.89 eV $f = 2.7 \times 10^{-4}$	6.29 eV $f = 1.1$	7.20 eV $f = 2.9 \times 10^{-2}$
NNN^- (D_{wh})	5.39 eV $f = 2 \times 10^{-3}$	6.52 eV $f = 0.5$	8.43 eV $f = 3.0$	8.00 eV $f = 1.0$
OCS (C_{wp})		5.54 eV $f = 1.8 \times 10^{-3}$	8.12 eV $f = 0.38$	7.44 eV $f = 0.13$
N_2O (C_{wp})	4.54 eV $f \sim 5 \times 10^{-6}$	6.81 eV $f = 1.4 \times 10^{-3}$	9.66 eV $f = 0.36$	8.52 eV $f = 7.2 \times 10^{-3}$

TABLE 7. — Continued

NCS ⁻ (C _{∞v})	5.64 eV $f \sim 3 \times 10^{-5}$					
NCO ⁻ (C _{∞v})	6.36 eV $f = 2.3 \times 10^{-2}$		6.92 eV $f = 4.1 \times 10^{-2}$	9.17 eV $f = 2.0$		8.43 eV $f = 0.18$
H ₂ CCCH ₂ (D _{2d})		5.45 eV $f \sim 1 \times 10^{-3}$		5.76 eV $f \sim 3 \times 10^{-3}$	7.23 eV $f = 0.34$	6.70 eV $f = 3.0 \times 10^{-2}$
H ₂ CNN (C _{2v})	3.14 eV $f \sim 1 \times 10^{-4}$			5.70 eV	7.06 eV	6.53 eV
H ₂ CCO (C _{2v})	3.84 eV $f \sim 2.3 \times 10^{-4}$			5.82 eV $f = 9.9 \times 10^{-3}$	7.29 eV $f \sim 0.3$	8.00 eV $f \sim 1 \times 10^{-1}$
HNCS (C _s)	5.06 eV	6.29 eV				
HNNN (C _s)	4.70 eV $f = 6.0 \times 10^{-4}$	6.20 eV $f = 9 \times 10^{-3}$		6.56 eV $f = 1.5 \times 10^{-2}$	8.84 eV $f = 0.3$	7.29 eV $f = 1 \times 10^{-2}$
C ₂ H ₃ NCO (C _s)	5.96 eV $f = 2.1 \times 10^{-3}$	6.82 eV $f = 2.4 \times 10^{-2}$		7.13 eV $f = 3.0 \times 10^{-2}$	8.77 eV $f = 0.30$	7.80 eV $f = 7.6 \times 10^{-2}$

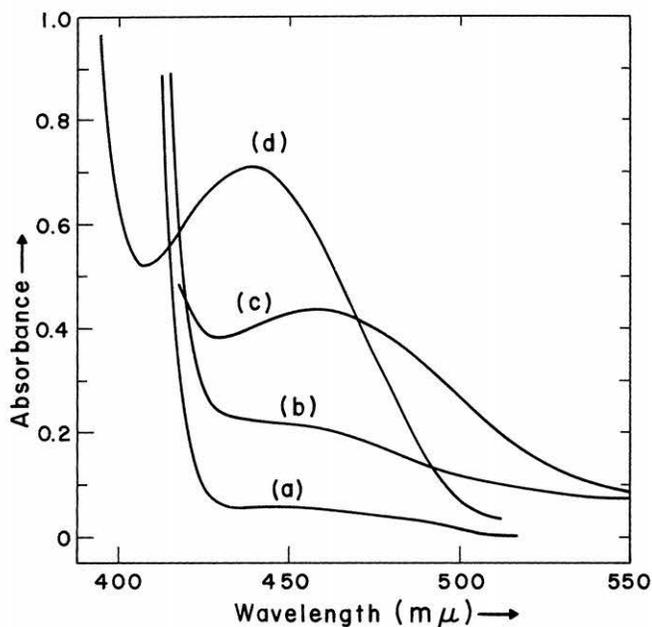
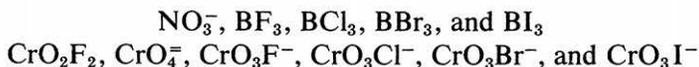


FIG. 13.— Absorption spectra of nitrite complexes in the visible region: a, 1.5M-NaNO₂, 10-cm. cell; b, 0.02M-AgNO₃ in excess NaNO₂, 10-cm. cell; c, 0.14M-TlNO₃ + 0.28M-NaNO₂, 10-cm. cell; d, 0.08M-Pb(NO₃)₂ + 0.16M-NaNO₂, 1-cm. cell.

acid, the salts might exhibit considerable covalency, we should not be surprised to see a spin orbit coupling enhancement in the $(-\text{NO}_2)^{\delta-}$ moiety brought about by the attachment of the heavy-atom metal counter ions. In this connection, it would seem proper, at least initially, to avoid salts of the various transition metal series. The transition metal ions invariably complicate the spectrum of the polyatomic anion by introducing their own complement of $d-d$ or $f-f$ transitions and various charge-transfer excitations of types cation \rightleftharpoons anion and, therefore, lead to obscurity of the spectrum of interest (*i.e.*, that of the polyatomic anion as modified by spin orbit coupling effects).

The generation of an isoelectronic series may also involve consideration of molecules that contain integral heavy-atom components. Cases in point are the two series



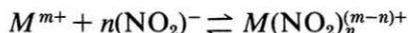
Because all of these molecules contain an even number of electrons, the regular substitution of "heavy atoms" implies a step-wise left-to-right enhancement of the probabilities of spin-forbidden transitions of type $T_j \leftarrow S_0$ where S_0 denotes a singlet ground state and T_j denotes an arbitrary excited triplet state. The spin orbit coupling increase should vary regularly with the increase of atomic number of the appended heavy atom. Thus, weak transitions sus-

pected of being intercombinations in nature may be so substantiated by appropriate study.

Numerous examples of the type of study referred to here are available in the area of the emission spectroscopy of organic molecules and such studies possess an excellent experimental and theoretical basis.³¹ Similar studies relating to small polyatomic molecules and ions have only recently become available. We now illustrate these latter investigations.

Example A of attitude 3, the visible absorption band of nitrite ion.—The visible absorption spectra of a number of nitrite salts³¹ are shown in Fig. 13. Despite decreasing nitrite concentrations, it is obvious from the diagram that the absorptivity increases as one proceeds through the salt series: $\text{Na}^+ \rightarrow \text{Ag}^+ \rightarrow \text{Tl}^+ \rightarrow \text{Pb}^{++}$. This observed effect is that expected for a spin orbit coupling enhancement of an $T_j \leftarrow S_0$ transition. In view of the fact that the absorption is observed in the "isolated" NO_2^- ion (see the NaNO_2 spectrum), simplistic attitudes dictate that such an enhancement should be a function of spin orbit coupling available at the metal center (as measured by the spin orbit coupling constant ζ) and of the extent to which the nitrite electrons sample this heavy-metal environment (as measured by the degree of metal-anion covalency or the equilibrium constant for the metal-anion complex).

An investigation of a presumed equilibrium



in the solutions of Fig. 13 leads to the experimental results³² of Table 8. The extinction coefficient data of Table 8 may be used to evaluate an intrinsic emissive decay lifetime for a possible $T_j \rightarrow S_0$ phosphorescence emission. Such an emission has, in fact, been detected³² and the lifetimes calculated from the absorption data are compared with those measured experimentally in Table 9. The agreement is impressive.

The $T_j \rightarrow S_0$ phosphorescence is now established as the $T_1 \rightarrow S_0$, ${}^3B_1 \rightarrow {}^1A_1(C_{2v})$ transition of the nitrite ion.³³⁻³⁵ Spin-polarization measurements relating to the emissive lifetime of the three spin components of the 3B_1 state are available in two instances³³ and quantum chemical calculations of the ${}^3B_1 \rightarrow {}^1A_1$ process have also been carried out.³⁶ The results of the spin-polarization studies are compared with the quantum chemical results in Table 10. Again, the agreement must be considered impressive.

The conclusions of the previous few paragraphs seem fully substantiated in the case of the nitrite ion and have served as guides in similar investigations of the following anions: formates and acetates,³⁷ thiocyanates and isothiocyanates,³⁸ cyanates and isocyanates,³⁹ azides,⁴⁰ and benzoates.⁴¹ These observations have also been developed into a viable rationalization⁴² of the fairly common development of color in the non-transition heavy-metal salts of otherwise colorless polyatomic anions.

Example B of attitude 3, the 3000Å absorption band of NO_3^- .—The discussion we give here solves few problems concerning the nature of the 3000Å

TABLE 8.—Triplet energies, molar extinction coefficients, and formation equilibrium constants for some nitrite complexes.

Metal ion	n	$\bar{\nu}_{\max}$ (kK)	ϵ [$\text{cm}^{-1} \cdot (\text{moles/liter})^{-1}$]	K [(moles/liter) $^{-n}$]
Na(I)	0	22.2	3×10^{-3}	0
Ag(I)	...	22.2
Cd(II)	1	23.4	2.3×10^{-2}	55
Pb(II)	1	22.8	11.7	42
Tl(I)	2	21.9	0.64	43

TABLE 9.—Measured and calculated lifetimes of the phosphorescence of nitrite complexes.

Central metal ion	Mean lifetime τ (sec)	
	Measured	Calculated ^a
Na(I)	...	1×10^{-1}
Cd(II)	3.3×10^{-1}	5×10^{-2}
Pb(II)	7.0×10^{-5}	5×10^{-5}
Tl(I)	9×10^{-5}	6×10^{-4}

^aMean lifetime is calculated using

$$\tau = 3.47 \times 10^8 (\bar{\nu}_{\max}^2)^{-1} (g_u/g_l) (\int \epsilon d\nu)^{-1}$$

where g_u and g_l are the degeneracies of the upper and lower states, respectively.

absorption process in nitrate salts; it merely questions existing interpretations and generates further conundrums. However, it does exemplify the correlative approach and it is only in this spirit that we present it.

The molecules NO_3^- , CH_3NO_3 , BF_3 , BCl_3 , BBr_3 , and BI_3 are isoelectronic. It would, therefore, be expected that their spectra would be more or less identical, the total spectrum of any one molecule merely being displaced energetically with respect to that of any other. Insofar as data are available on the gaseous vacuum ultraviolet spectra of these molecules,⁴³ this supposition is confirmed in all cases except NO_3^- where such spectra were not, of course, obtainable.

The parallelism of spectra referred to above is quite remarkable (after the appropriate energy displacements) with regard to both band shapes and oscillator strengths. The one instance in which the parallelism with regard to oscillator strengths does not exist is in that band which we suppose to be the analog of the 3000Å absorption band of NO_3^- . The absorption bands in question are abstracted in Fig. 14, wherein it is clear that the most striking effects are an increase of extinction and a decrease of energy in quite regular ways as one proceeds from BF_3 to BI_3 ; a displacement toward higher energies as

TABLE 10.—*Experimental emissive lifetimes for the ${}^3B_1 \rightarrow {}^1A_1$ process compared to those calculated in a first-order perturbation theory format.^a*

	τ_x	τ_y	τ_z
NaNO ₂			
Experimental	—	$3.3 \times 10^{-2} - 3.3 \times 10^{-3}$	—
Calculated	∞	2.3×10^{-2}	1.76
AgNO ₂			
Experimental	1×10^{-4}	3.5×10^{-3}	6×10^{-4}
Calculated	1.6×10^{-4}	1.8×10^{-2}	6.3×10^{-4}

^aThis tabulation is taken from Harris *et al.*³⁶ and this paper should be consulted for full explanation concerning interpretation of the experimental data. The z -axis is the principal axis of the C_{2v} point group and the x -axis is perpendicular to the molecular plane. The computations on AgNO₂ reported here presume nonplanarity of the AgNO₂ molecule.

one progresses from NO₃⁻ to CH₃NO₃; and a slight enhancement of absorptivity in Pb(NO₃)₂ relative to N(CH₃)₄NO₃.

The first conclusion we may draw relates to the strictly D_{3h} boron halide spectra. It is clear that although the transition in question may be considered to be forbidden in BF₃ and BCl₃, it is rather more difficult to posit such for BBr₃ and BI₃. It is also obvious that the intensifications underway conform rather well to that which one would expect for spin-orbit enhancement of a triplet ← singlet absorptive transition. In order to validate this latter hypothesis, the data are abstracted in Table 11 where they are correlated with the results of a simple spin-orbit interaction model. The compilation of Table 11 indicates that intensity data which vary over a range of 10³ are correlatable within a factor of ~3 by a simple spin orbit model. On this basis, it would seem that the 3000 Å absorption band of nitrate must be represented as a triplet ← singlet transition. In any event, no second order vibronic phenomenon—such as has previously been held accountable⁴⁴ for the intensity of this band—can account for the observations on the boron halides, and it is doubtful, therefore, that such an interpretation retains validity even for nitrate ion.

We now enquire into the absolute values of excitation energies of this transition in the various molecules. To this end, we have used Mulliken-Wolfsberg-Helmholtz (MWH) computational techniques⁴⁵ to generate the energy level diagram of Fig. 15. The first point of note in Fig. 15 is that the π , n and σ -MO's are all more or less nonbonding, in the sense that the MO amplitudes on the central atom (*i.e.*, B or N) are either zero or very small. Consequently, the transition energy associated with configurational excitations $a_2'' \leftarrow e''$, $a_2'' \leftarrow e'$, $a_2'' \leftarrow a_2'$, where a_2'' is the π^* MO, is largely determined by the VOIE (valence orbital ionization energy) of the np peripheral-atom valence orbital. Thus, the transition energies should decrease in the order BF₃ > BCl₃ > NO₃⁻ \approx BBr₃ > BI₃, which is precisely the order observed.

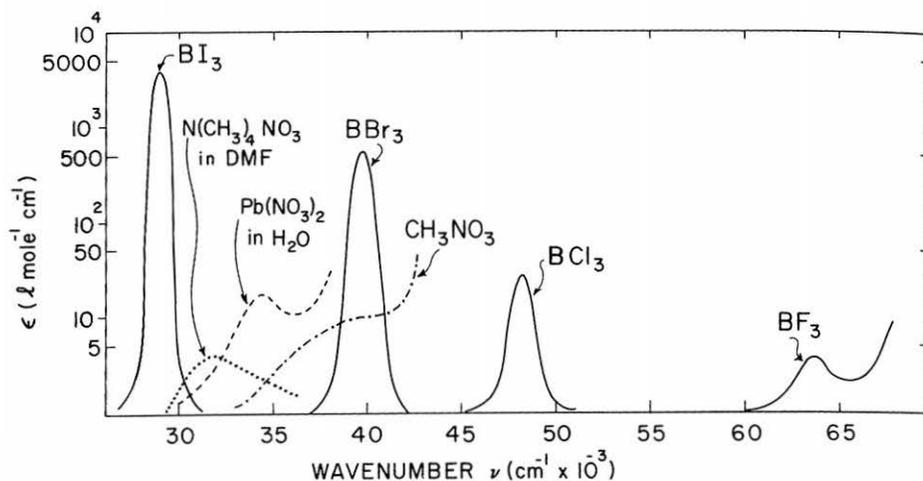


FIG. 14.—The low-energy absorption bands of boron halides, nitrate ion, and methyl nitrate. All spectra are for the gas phase except as noted.

All extant observations^{46,47} on the 3000Å absorption band of NO_3^- indicate that it is in-plane (*i.e.*, xy) polarized. Inasmuch as this band is usually assigned as a forbidden ${}^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ transition in D_{3h} , we must now enquire into the manner in which such an excitation might acquire intensity. A ${}^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ transition should be forbidden by electric dipole, magnetic dipole, electric quadrupole and all first-order vibronic effects; therefore, the source of intensity input must be sought elsewhere. The obvious choice is to devise a mechanism that would enable a ${}^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ transition to borrow intensity from the in-plane-polarized strongly allowed ${}^1\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ transition at 1900Å. Such a mechanism was devised by Kasha and Strickler⁴⁴ and was based on a per-

TABLE 11.—Spin-orbit coupling model applied to spectroscopic data for the first distinctive absorption bands of the boron halides and nitrate ion. The subscript *m* denotes "maximum"; ζ is the atomic spin-orbit coupling constant for a halogen atom or for an oxygen atom; all data are normalized to the BCl_3 data because the absorption data in this instance are more secure than those for BF_3 : BF_3 tends to react with almost everything and the data here for BF_3 are conceivably not entirely free of error in the ϵ_{max} measurements; since the absorption bands are situated at different energies, the absorption data are rendered independent of $\bar{\nu}_m$ (see column 6) in order to achieve proper comparison with the ζ^2 expectations (see column 5).

Molecule	ϵ_m (l/m. cm)	$\bar{\nu}_m$ (cm^{-1})	ζ (cm^{-1})	$\zeta^2/\zeta_{\text{Cl}}^2$	$\frac{\epsilon_m/\bar{\nu}_m}{(\epsilon_m/\bar{\nu}_m)_{\text{BCl}_3}}$
BF_3	3.6	63600	272	0.215	0.101
BCl_3	27.3	48200	587	$\equiv 1$	$\equiv 1$
BBr_3	560	39700	2460	17.56	24.9
BI_3	3940	28900	5060	74.30	241
NO_3^-	4.0	31900	152	0.067	0.22

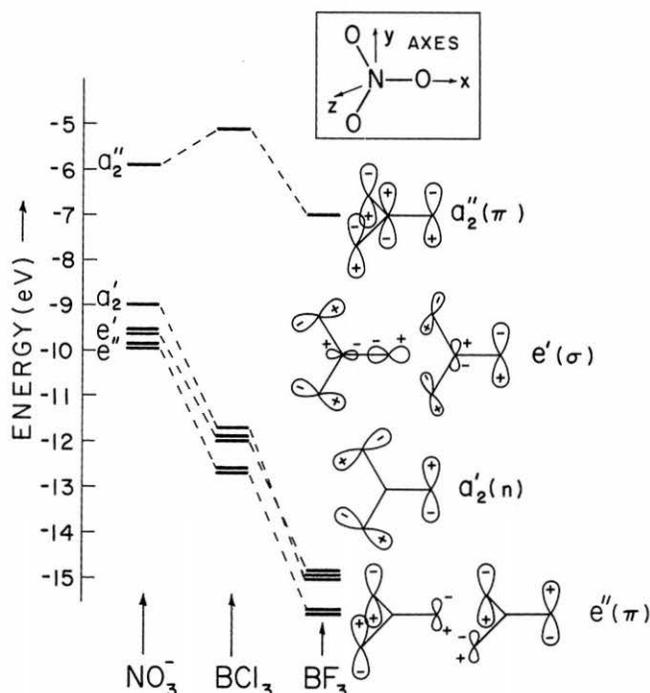


FIG. 15.—Molecular orbital energy diagram for NO_3^- , BCl_3 and BF_3 . The form of the MO's are represented roughly in pictorial form on the right of the diagram. Axes are also designated.

turbation operator of second-order vibronic nature. The calculations performed⁴⁴ were necessarily crude and indicated an intensity borrowing commensurate with $f = 3.0 \times 10^{-7}$, all of it in-plane polarized. The experimental value, at $8.0 - 15 \times 10^{-5}$, is considerably larger.

Let us now suppose, as is indicated by the data of Fig. 14 and Table 11, that the 3000Å absorption band is best assigned to a triplet ← singlet absorptive event. Let us suppose further, per Table 11, that the specific designation of the excited state achieved in the absorption event might be any one of ${}^3\Gamma_{n\pi^*}$, ${}^3\Gamma_{\sigma\pi^*}$, or ${}^3\Gamma_{\pi\pi^*}$. A first-order spin orbit mechanism would enable either of the transitions ${}^3\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ or ${}^3\Gamma_{\sigma\pi^*} \leftarrow {}^1\Gamma_1$ to borrow in-plane intensity from the intense ${}^1\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ transition and must be investigated as a possible interpretation of the intensity resident in the 3000Å nitrate band. Such an investigation, processed using conventional techniques,⁴⁸ is reported for NO_3^- , BF_3 and BCl_3 in Table 12. The results of Table 12 do, in fact, indicate that transitions of type ${}^3\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ or ${}^3\Gamma_{\sigma\pi^*} \leftarrow {}^1\Gamma_1$ can account for the intensity observed in the 3000Å nitrate band. In fact, both transitions are computed to have oscillator strengths $10^{-5} < f < 10^{-4}$, and to be in-plane polarized in exact coincidence with experiment.

Granted the vagaries of any semiempirical calculational route, it still appears proper to make the following judgments:

TABLE 12.—Oscillator strengths in different polarizations for various ${}^3\Gamma_1 \leftarrow {}^1\Gamma_1$ transitions of NO_3^- , BF_3 and BCl_3 . The energies and wave functions used were those of Fig. 15. The procedural spin orbit computational route followed along lines outlined by Carroll et al.⁴⁸ The principal axis, z, is perpendicular to the molecular plane.

Transition	Molecule	Oscillator strength		
		f_x	f_y	f_z
${}^3\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$	BF_3	1.49×10^{-4}	1.51×10^{-4}	2.15×10^{-7}
	BCl_3	5.6×10^{-4}	5.6×10^{-4}	4.8×10^{-6}
	NO_3^-	2.4×10^{-5}	2.4×10^{-5}	2.4×10^{-8}
${}^3\Gamma_{\sigma\pi^*} \leftarrow {}^1\Gamma_1$	BF_3	6×10^{-7}	1.4×10^{-6}	4.9×10^{-8}
		5.6×10^{-7}	1.8×10^{-6}	7.3×10^{-4}
	BCl_3	9.2×10^{-7}	1.7×10^{-6}	4.4×10^{-10}
		9.6×10^{-7}	1.6×10^{-6}	2.0×10^{-5}
	NO_3^-	1.3×10^{-5}	1.9×10^{-5}	6.2×10^{-9}
		1.3×10^{-5}	1.9×10^{-5}	1.3×10^{-7}
${}^3\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$	BF_3	0	0	1.9×10^{-7}
	BCl_3	0	0	5.1×10^{-6}
	NO_3^-	0	0	2.2×10^{-8}

1. Second-order vibronic effects cannot account for the observed intensities of Fig. 14 for the lowest energy distinctive transitions in BCl_3 , BBr_3 , or BI_3 . Spin orbit coupling can account for the observed effects if the transition in question is assigned as either ${}^3\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ or ${}^3\Gamma_{\sigma\pi^*} \leftarrow {}^1\Gamma_1$.

2. Spin orbit coupling can account for the observed intensities in BF_3 and NO_3^- if a similar assignment to that immediately above obtains. It is not clear that any second-order vibronic mechanism coupled with a ${}^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ assignment can provide comparable rationalization.

3. In any event, it is clear that either $\pi^* \leftarrow n$ or $\pi^* \leftarrow \sigma$ configurational excitation can lead to rationalization of the observed energy and intensity and that the point under debate here relates to the identification of the excited state as either spin singlet or spin triplet. In the case of BI_3 and BBr_3 , where strong $j-j$ coupling exists, this point of debate is redundant and in the case of BCl_3 , NO_3^- and BF_3 it may very well be academic. This latter point will be illustrated now for ${}^1\Gamma_{n\pi^*}$ and ${}^3\Gamma_{n\pi^*}$ states. The ${}^1\Gamma_{n\pi^*}$ and ${}^3\Gamma_{n\pi^*}$ states are closely degenerate, the exchange integral $K_{n\pi^*}$ being approximately 1000 cm^{-1} , and $E({}^1\Gamma_{n\pi^*}) - E({}^3\Gamma_{n\pi^*}) \leq 2000 \text{ cm}^{-1}$. Thus, the two transitions ${}^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ and ${}^3\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ should be encompassed within the same single (if unstructured) absorption band. Under these circumstances, a spin orbit perturbation would cause enhancement of T \leftarrow S character and make this absorption band behave as if it were ${}^3\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$; such effects could be held responsible for the boron halide enhancement phenomenon and for the intensification observed in $\text{Pb}(\text{NO}_3)_2$ (see

Fig. 14). Similarly, another type of perturbation might elicit dominance of the ${}^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ character and make the band appear to be of singlet \leftarrow singlet type. Thus, we conclude that the 3000Å band could be assigned as ${}^1,{}^3\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$. Inasmuch as the characteristics discussed also apply in identical fashion to a ${}^1,{}^3\Gamma_{\sigma\pi^*} \leftarrow {}^1\Gamma_1$ possibility, it is clear that these latter two designations must be retained as equally valid assignment candidates.

4. With regard to the eliciting of a singlet \leftarrow singlet character referred to immediately above, we must emphasize that we know of no perturbation that produces such for NO_3^- ion. The intensity enhancement in HNO_3 (C_s point group) and CH_3NO_3 (approximate C_s point group), where both ${}^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ and ${}^1\Gamma_{\sigma\pi^*} \leftarrow {}^1\Gamma_1$ transitions are formally electric-dipole allowed, are quite negligible experimentally. The intensity enhancement of the 3000Å band in covalently bound nitrate salts, in which the metal ion does not function as a significant electron acceptor (*e.g.*, Cd^{2+} , Zn^{2+} ; *vide infra*) is also quite negligible.⁴³ Nonetheless, gross changes do occur in the nitrate spectrum when its transition metal salts are investigated under conditions favorable to the presence of metal-nitrate covalencies. These changes (previously adduced as evidence for the 3000Å transition probability enhancement of $S_1 \leftarrow S_0$ type) are, in fact, caused by the generation of new band systems appropriate to a nitrate-metal entity. It is our contention that these new band systems are of a charge-transfer nature.⁴³

We depart from the topic of nitrate ion spectroscopy at this point. However, in order to provide proper topic closure, we present an energy level diagram for NO_3^- in Fig. 16. We make no comment on this diagram other than to note that it is discussed in some detail in Maria *et al.*⁴³

*Attitude 4, the dependence of electronic transition energies on effective nuclear charges.*¹—The most obvious difference between the isoelectronic molecules BCl_3 and BBR_3 is that the electrons associated with the bromine atoms of the latter are much less tightly bound than are those associated with the chlorine atoms of the former. Thus, the energy of a charge-transfer transition of type halogen $\xrightarrow{e/h\nu}$ boron should decrease in the series $\text{BF}_3 \rightarrow \text{BCl}_3 \rightarrow \text{BBR}_3 \rightarrow \text{BI}_3$ whereas that of a charge-transfer transition of type boron $\xrightarrow{e/h\nu}$ halogen might be expected to decrease in precisely the opposite direction. Qualitative conclusions of this sort are elaborated quantitatively in Fig. 15 and are used to validate the charge-transfer (oxygen to nitrogen) nature of the lowest energy transitions of nitrate ion.

In a similar way, the deprotonation of nuclei leading from ozone to the peptide linkage (See Fig. 8), which undoubtedly generates some very tightly-held covalently bonded σ -electrons, must also produce a number of less tightly bound electrons. The rationale here is relatively straight forward: the nuclear deprotonations depress nuclear charges and decrease the effective nuclear potentials which bind electrons. In other words, valence orbital ionization energies (VOIE's) decrease. Thus, deprotonation should produce a group

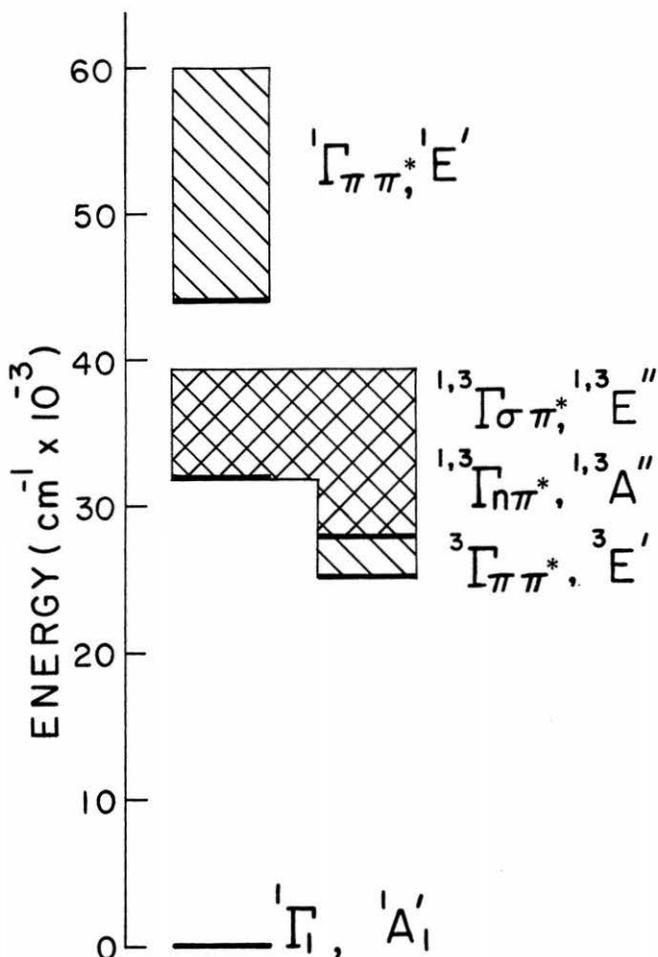


FIG. 16.—An energy level diagram for nitrate ion. Character notation refers to the D_{3h} point group tables. In view of the MO diagram of Fig. 15, it is expected that low energy transitions of type $\pi^* \leftarrow \sigma$ (i.e., $a_2'' \leftarrow e'$) should also occur at low energies; the corresponding transitions, ${}^1{}^3E'' \leftarrow {}^1A_1'$, are orbitally forbidden and more or less degenerate. Some authors⁴⁹ have predicted the ${}^1E'' \leftarrow {}^1A_1'$ excitation to be the lowest energy transition in the singlet manifold, and the arguments presented in this paper are not adequate to distinguish ${}^1{}^3A_1''$ from ${}^1{}^3E''$ pair states (see Fig. 15 and Table 12).

of covalently σ -bound electrons, more tightly held than formerly—and which will be discussed under *attitude 5*—and a group of nonbonding or π -bonding electrons, which might be expected to be less tightly bound than previously—and which are the subject of discussion here. The nuclear deprotonation leading from $[\text{O-N-O}]^-$ to $[\text{O-CH-O}]^-$ ties up two σ -electrons in a new C-H bond which was not present in the nitrite ion. Thus, two weakly bound electrons of the nitrite ion have been incorporated into a strong C-H σ -bond in the formate ion. These electrons are more strongly bound than they were

TABLE 13.—Molecular orbitals for NO_2^- . The axes designations and atom numbering conventions are given in Fig. 8. MO energy and type are given in brackets immediately below the analytic form of the orbital.

C_{2v}	Nitrite ion
a_1	$(0.61)2p_{xN} - (0.56)(2p_{xO_1} + 2p_{xO_2})$ [-6.63 eV; π^* MO]
b_1	$(0.10)2s_N + (0.52)2p_{zN} - (0.60)(2p_{zO_1} + 2p_{zO_2}) - (0.07)(2p_{yO_1} - 2p_{yO_2})$ [-8.07 eV; σ MO]
b_2	$(0.11)2p_{yN} - (0.44)(2p_{zO_1} - 2p_{zO_2}) - (0.54)(2p_{yO_1} + 2p_{yO_2})$ [-8.73 eV; σ_n MO]
a_2	$(0.707)(2p_{xO_1} - 2p_{xO_2})$ [-9.53 eV; π MO]

prior to the nuclear deprotonation act. On the other hand, the four π -electrons of the nitrite system, subject as they are to a potential supplied by an NO_2^{5-} nucleus-plus- σ -electron system, are more tightly held than the same set in the potential supplied by an effective CO_2^{5-} system in the formate ion because, as a result of incomplete nuclear shielding, the nuclear potential due to $\text{C}^{\delta(\pm)}$ is less than that due to $\text{N}^{\delta(\pm)}$.

Predictions analogous to those based on the boron halide example presented above are relatively simple. Such consideration, in a qualitative way, constituted a very large part of the classic Walsh approach²⁵ to the serialization of isoelectronic spectra. Predictions concerning atomic VOIE changes caused by deprotonation are also easy to come by; however, the molecular effects produced by such VOIE changes are not necessarily simple and any consideration of such changes is best guided by some primitive type of molecular orbital calculation (the Mulliken-Wolfsberg-Helmholz (MWH) MO type of computation, for example).

The detailed results of such computations need not be believed because such calculations have had notoriously poor interpretive success; indeed, the advocacy here is merely that they be used to establish the perturbative trends, which ensue in proceeding from one species to another in the series under investigation.

*Example of attitude 4, the ozone to formate series.*¹—The MWH molecular orbitals of a representative molecule are shown in Table 13. Only those MO's involved in the generation of the lower energy excited electronic states are shown. These MO's will now be used to discuss the trends in MO and state energies as the central atom varies from carbon to nitrogen to oxygen (*i.e.*, from formate to nitrite to ozone).

The a_2 MO is of π nature; it consists of a group orbital that is localized, in its entirety, on the two end atoms. Since the two end atoms are oxygen in all

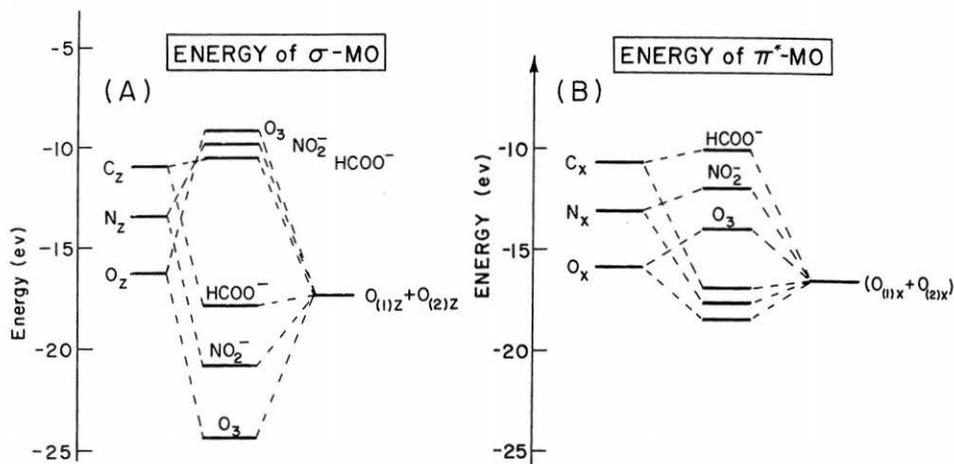


FIG. 17.—(A) Illustration of the formation of the a_1 MO; large (*i.e.*, σ) overlap. C_z , N_z , and O_z denote VOIE's of $2p_z$ AO's located on the specified centers. The symbol O_{1z} represents a $2p_z$ AO on oxygen, of Fig. 8.

(B) Illustration of the formation of the b_1 MO; small (*i.e.*, π) overlap.

three molecules, the energy of the a_2 MO should be more or less invariant in these molecules. The same conclusion is also applicable to the b_2 MO: this MO consists almost wholly of end-atom atomic orbitals (Table 13) and these pertain to oxygen in all three molecules.

The a_1 MO however, is not energy invariant. This MO, in nitrite ion, possesses dominant amplitude in the $2p_z$ AO of nitrogen and the $2p_z$ group orbital (GO) of the end oxygen atoms and is antibonding in the combination. Therefore, the topmost of the two a_1 MO's that result from the AO-GO mixing (*i.e.*, the σ MO of Table 13) will be destabilized relative to the $2p_{zN}$ AO by an amount that will be inversely proportional to the energy separation between $2p_{zN}$ and $(2p_{zO_1} + 2p_{zO_2})$. Furthermore, the $(2p_{zN}, 2p_{zO})$ -overlap integral is large and, as a result, this destabilization will be severe. Indeed, we compute a bonding-antibonding a_1 MO interval of 9.0 eV for NO_2^- and 7.5 eV for HCOO^- ; the same interval has been computed, by different means, as 10.73 eV for formate ion⁵⁰ and as 14.83 eV for ozone.⁵¹ Both sets of numbers show a predictable trend. In O_3 , the $2p_z$ AO of the central oxygen and the $2p_z$ GO of the end atoms are in close energy proximity and the interaction is stronger than in nitrite or formate where the energies of the interacting orbitals are more widely separated. Thus, the antibonding a_1 MO is in an energetic order in O_3 , NO_2^- , and HCO_2^- that is precisely opposite to that expected from the valence orbital ionization energies (VOIE's) for the $2p_z$ AO's of carbon, nitrogen, and oxygen. In other words, it is the off-diagonal terms of the energy matrix which are responsible for the energetic ordering of the a_1 antibonding MO. These considerations are schematized in Fig. 17A.

The same considerations applicable to the a_1 MO also pertain to the b_1 MO with one exception: inasmuch as the overlap of the $2p_x$ AO of the central atom

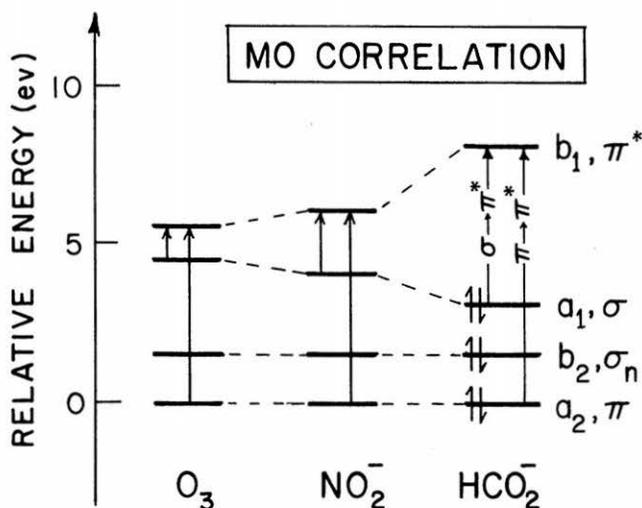


FIG. 18.—Trends in the orbital energies of ozone, nitrite, and formate.

with the ($2p_{x0_1} + 2p_{x0_2}$) GO on the end atoms is relatively small (being of π nature) the energy of the resulting π^* MO (*i.e.*, antibonding π) is dominantly determined by the diagonal terms of the interaction matrix. The results are shown in Fig. 17B where it is seen that central atom VOIE's are the primary determinants of energy.

All of these conclusions are summarized in Fig. 18. The lowest energy excitation is predicted to be $b_1 \leftarrow a_1$ (*i.e.*, ${}^1B_1 \leftarrow {}^1A_1$); it is of $\pi^* \leftarrow \sigma$ type and its energy should increase in the order ozone < nitrite < formate. The transition $b_1 \leftarrow a_2$ (*i.e.*, ${}^1B_2 \leftarrow {}^1A_1$) is of $\pi^* \leftarrow \pi$ type and is predicted to increase energetically in the same order as does the ${}^1B_1 \leftarrow {}^1A_1$ transition; however, its increase should be less rapid and the $\pi^* \leftarrow \sigma$ and $\pi^* \leftarrow \pi$ energies should converge as we progress toward formate. The energy of the $b_1 \leftarrow b_2$ (*i.e.*, ${}^1A_2 \leftarrow {}^1A_1$; $\pi^* \leftarrow \sigma_n$) transition should parallel that of the $\pi^* \leftarrow \pi$ transition, but should be of lower energy.

The results of these conclusions are embodied in the three appropriate columns of Fig. 19 concerned with the molecules in question. It will be seen that the conclusions drawn fit observation remarkably well. The remainder of the molecules for which data are tabulated in Fig. 19 will be discussed under *attitude 5*. Indeed, if the three columns (first, fourth, and fifth) are abstracted from Fig. 19, they will be seen to match every predictive detail present in Fig. 18.

Attitude 5, conversion of nonbonding electrons into tightly bound σ -electrons.—The removal of two protons from each oxygen nucleus of CO_2 and their reinstatement as extranuclear protons (or H-atoms), as in allene, $\text{H}_2\text{C}=\text{C}=\text{CH}_2$, utilizes a total of eight electrons to bind the newly created protons to the molecular skeleton. Since the C-H bond is a relatively tightly

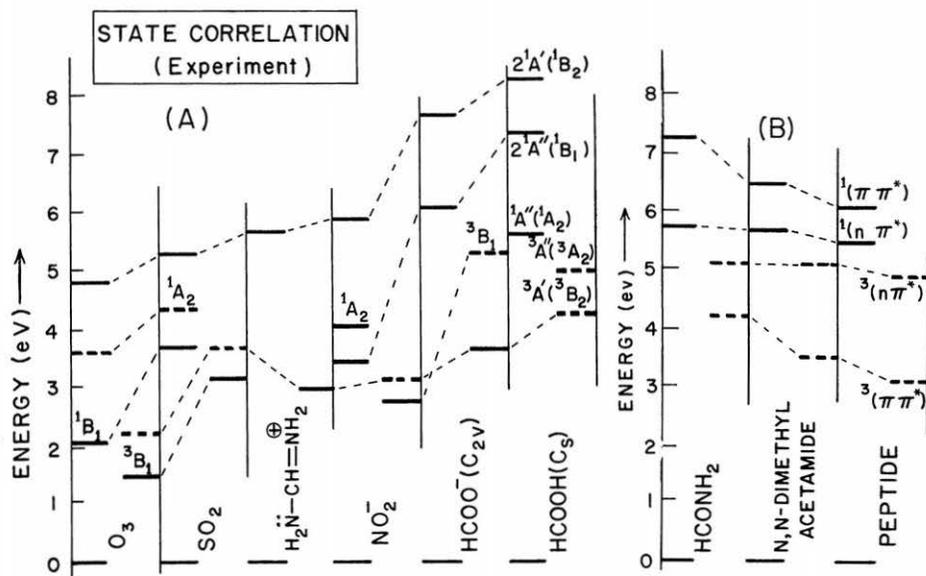


FIG. 19.—Electronic-state correlation diagram. Dashed levels are in doubt experimentally. The experimental data required are extensive and must be used judiciously. The sources of data are given elsewhere.¹ The symmetry notation used for HCOOH is: Γ in C_s (Γ in C_{2v}).

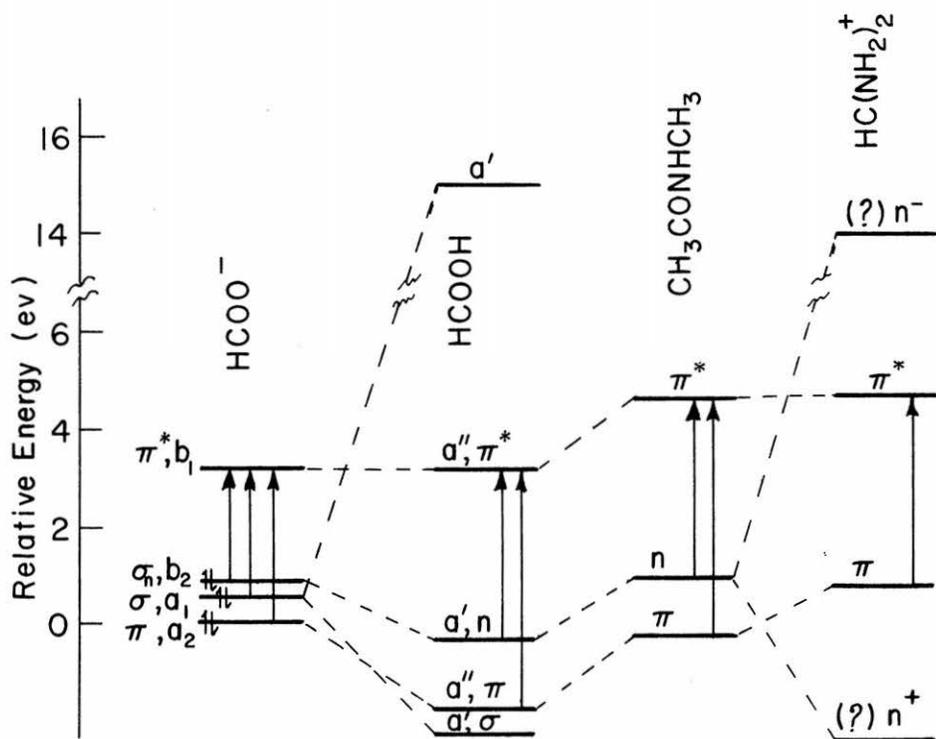


FIG. 20.—Molecular orbitals of some isoelectronic groupings.

tions of the other MO's are fixed using computed energy differences. For example, the π^* MO in formic acid is very similar analytically to that of formate ion and, therefore, the energies of these two MO's are equated. In formate ion, we note that the rate of descent of the a_1 MO indicated in Fig. 18 is such that this MO actually falls below the b_2 MO. Nonetheless, formate ion still possesses two σ MO's intermediate between the π and π^* MO's. Thus, one would expect to observe two transitions of $\pi^* \leftarrow \sigma$ type of lower energy than the $\pi^* \leftarrow \pi$ transition.

The effects of the protonation that leads to formic acid are threefold. First, the a_1 MO interacts strongly with the $1s_H$ AO to form bonding and antibonding combinations. Thus, the bonding a' component drops energetically below the π MO, and we might expect to find in formic acid a considerable increase in energy of the transition which is analog to the ${}^1B_1 \leftarrow {}^1A_1 (b_1 \leftarrow a_1)$ excitation of formate ion. Secondly, the $b_2 (\sigma_n)$ MO evolves toward an atomic-like orbital located on the carbonyl oxygen (*i.e.*, on O_1). Thirdly, the a_2 MO interacts with the $2p_{xC}$ AO, and the MO relevant to our purposes (*i.e.*, the MO that consists of the bonding combination) is lowered in energy. The π MO's, therefore, attain a substantially greater energy spread. Thus, we expect a relative blue shift of the spectrum of formic acid; we expect to observe the ${}^1B_1 \leftarrow {}^1A_1 (b_1 \leftarrow a_1)$ analog transition either at higher energy than, or close to, the $\pi^* \leftarrow \pi$ transition; and we expect the ${}^1A_2 \leftarrow {}^1A_1 (b_1 \leftarrow b_2)$ analog transition to be readily observable because it is no longer forbidden and because it should now have the lowest energy of all singlet \leftarrow singlet transitions.

The situation in *N*-methylacetamide is similar to that in formic acid, with some exceptions. The -C-H bonding a_1 component drops sufficiently low in energy that the $b_1 \leftarrow a_1$ transition might no longer be observable spectroscopically. The π and π^* MO's are destabilized relative to those of formic acid because of the smaller electronegativity of the nitrogen atom that replaces oxygen. The π MO is further destabilized because bonding interactions with the carbon atom decrease. Similarly, the n orbital destabilizes relative to its energy in formic acid because of a decrease in the bonding interactions with the second oxygen atom of formic acid and because it localizes completely on one oxygen center.

The situation obtaining in formamidinium ion is sketched on the extreme right of Fig. 20. The evolution of $=O_1$ to $=NH_2^+$ causes σ bonding between the n AO and the $1s_H$ AO's of the amide hydrogen atoms. As a result, the splitting shown on the extreme right of Fig. 20 is obtained, and it is predicted that this molecule should possess only one low energy transition, which should be of $\pi^* \leftarrow \pi$ nature.

The conclusions of this section may be compared with experiment by a study of Fig. 19. It will again be seen that every prediction made here appears to be in excellent accord with the observed spectroscopic characteristics of Fig. 19.

At this point, it is well to note that the correlation studies leading to Fig. 19 used other information than that provided here under *attitudes* 4 and 5.

Specifically, the considerations of *attitude 3* were used in inducing correlatory order among the triplet levels. Finally, simple transition intensity deductions were also of immense help. The interested reader should consult the original source.¹

CONCLUSION

The purpose of this article has been to discuss genealogical attitudes and their importance in molecular electronic spectroscopy. The emphasis has been two-fold.

The topological approaches for the unsaturated hydrocarbons have been dissected in an effort to ascertain the relative weighting of pure topology on the one hand and molecular geometry on the other in determining the spectroscopic affairs of these molecules. It was concluded that the geometric information required for a good statistical fit of experiment and theory for *p*-band energies was, in large measure, an implicit topological input. In this way, the somewhat satisfactory state of the molecular spectroscopy of unsaturated hydrocarbons was seen to be associated with the large population densities of genealogically-related molecules and the overwhelming importance of topology as a simple correlative device for unsaturated systems.

A genealogical relation based on a "proton push-pull synthesis" has been devised and used in order to increase the population densities within isoelectronic series based on various simple polyatomic molecules and ions. In conjunction with this series broadening device, five different correlative attitudes have been developed and applied to different series in order to identify electronic states of the series constituents and to test the utility of the correlative attitudes themselves. It has been concluded that all five approaches possess considerable power. A number of other correlative approaches are also possible, but are not yet adequately developed to merit discussion here.

We believe that the series broadening genealogy used here and the five correlative attitudes that have been developed will lead to increased experimental knowledge and understanding of the neglected field of small polyatomic molecules and ions. We also believe that our dissection and generation of correlative algorithms for the π -electron spectroscopy of unsaturated hydrocarbons will provide considerable assurance of common sense in a somewhat confused area.

ACKNOWLEDGMENTS

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DISCUSSION: LEADER, DR. E. C. LIM

Dr. Kasha.—In 1951 or thereabouts, A. D. Walsh published 10 papers in which he took the Kynch-Penney numerology on electrons in triatomic molecules and showed why stable molecules of different geometries were formed. In a sense, he transformed small polyatomic-molecule spectroscopy into a correlative science. To me, it looks as if the approach just outlined will deal similarly with other molecules for which no correlative approaches are presently available. So, I favor the method. I certainly believe that Sean McGlynn's topological correlation will greatly extend our understanding of molecular electronic spectra and structure.

On the other hand, there is always a problem that arises, even with Walsh diagrams: namely, one must believe in the derived correlation and, simultaneously, in the existence of a nice simple physicochemical reality. In a number of cases that you have correlated, one must surely satisfy such simple physicochemical criteria. For example, a singlet-triplet transition (*i.e.*, a spin-orbital perturbation) is not usually influenced by ordinary hydration of the solute; therefore if hydration produces a 10-fold increase in the intensity of a transition that has been assigned as singlet-triplet, one must conclude that at least a large part of the intensity associated with that transition can not be of singlet-triplet character. I would say, therefore, that the absorption bands illustrated for BCl_3 , BF_3 , and NO_3^- exhibit dual nature (*i.e.*, $S_1 \leftarrow S_0$ and $T_1 \leftarrow S_0$) in that sense.

Dr. McGlynn.—I should, in answer, thank you for your complimentary remarks. The initial work on nitrate ion relating to fourth-order effects was by Kasha and Strickler (I use fourth-order in the sense of fourth-order in intensity but second-order in wave function) and yielded $f \approx 10^{-7}$. Your comments, then, are pertinent and, in part, I am in full agreement with you. The $T_1 \leftarrow S_0$ interpretation provided here implies an $\pi^* \leftarrow (n \text{ or } \sigma)$ MO excitation; this designation, coupled with the very small calculated singlet \leftarrow triplet split for such an MO excitation, says that these two transitions are almost degenerate. In the case of nitrate ion, where presumably both transitions ought to have approximately equal intensity, it is probable that both excitations are encompassed by the same single absorption band. Thus, different perturbations might elicit dominance of either singlet character or triplet character. Consequently, hydration effects might indicate singlet-singlet character whereas heavy atom effects might suggest triplet-singlet character.

Dr. Lim.—When you say fourth order, you are exaggerating. It is actually second order squared.

Dr. McGlynn.—Second order squared. Right. That is fourth order.

Dr. Song.—Formic acid was luminescent? Do you mean neutral, undissociated formic acid?

Dr. McGlynn.—Yes.

Dr. Song.—Is undissociated acetic acid also luminescent?

Dr. McGlynn.—The ester appears to be luminescent, and the ester assuredly is undissociated. We believe that only the undissociated, uncomplexed, undimerized, or unpolymerized entity exhibits luminescence.

Dr. Song.—Why cannot you expect, then, to have luminescence from an aliphatic amino acid? Some of the amino acids you listed were undissociated—depending, of course, on the pH condition. If neutral acetic acid is luminescent, there exists no reason why the amino acid should be nonluminescent.

Dr. McGlynn.—This whole question is very complicated. Let me pose a question. Formic acid exhibits a weak low energy luminescence. Oxalic acid is a very nice luminophore; it emits a very definite $\pi^* \rightarrow n$ luminescence, which, however, is at higher energy than that observed in formic acid. If we are to rationalize the observation on formic acid, we must conclude either that this luminescence is not intrinsic to this molecule or that the low energy of this luminescence implies considerable distortion of the $\pi^* \rightarrow \pi$ state of this molecule. Which is correct? I do not know!

Now, consider some other observations. In the case of oxalic acid, only the covalent salts, the ester, and the unionized acid exhibit the $\pi^* \rightarrow n$ luminescence. If we now look at oxalic acid in an ionizing medium or at one of its ionizable salts, we find an emission almost identical with those which we proclaim we are examining in the case of unionized formic acid. I do not know why this should be.

Finally, none of the simple amides emits. Therefore, should we be surprised if none of the saturated amino acids emits? As far as I know, they do not. And like you, I do not understand. On the other hand, I am willing to be surprised.

Dr. Hammond.—I would like to comment on the question of luminescence or nonluminescence. To take the question of the amino acids, if it turned out that bimolecular quenching of the luminescence of a simple ester was caused by a tertiary amine, I would have a ready explanation—one modeled on a lot of bimolecular quenching experiments, which we have done, but which I do not want to go into here. I think it entirely possible that other interactions, as well as effects caused by very modest distortions of the excited states of some of these molecules, can accelerate non-radiative decay enormously. This, in fact, is related to my discussion yesterday. However, I also think it important to get a digest of all of the available numbers, so that we might plan appropriate experiments. If these low lying triplet states exist, we can experimentally deduce their presence and their character, *etc.* by doing some fairly well devised triplet quenching experiments. These are easy and nice to do, and will, I think, provide another sensing technique.

Dr. McGlynn.—I agree with you fully. I believe such experiments should be done.

Dr. Song.—Because you said that the anions of carboxylic acids do not emit, the pH at which you worked becomes pertinent. Was it sufficiently acidic?

Dr. McGlynn.—The amino acids were looked at under almost every possible condition. They are, in fact, now being looked at as deposits in a xenon matrix. We have covered the whole set of amino acids. We find no emission by these acids, under any condition.

DEDICATION CEREMONY

Dr. Henry J. Shine.—President Murray, Mrs. Murray, Regent Collins, kind friends, visitors, members of the campus community, members of the Lubbock community: It is a pleasure to see you here on this occasion. It is a great occasion for us; I thank you for attending. There were times when we thought we would not really reach this stage; as a matter of fact, at some time in March, we thought we might be asking you to come here, as it were, to launch a ship and then help us outfit it. However, it has all worked out and I am very pleased that you are here at this dedication ceremony.

This is not the occasion for too many introductions, but I would like to introduce to you Mr. R. White, the representative of the architectural firm, Pitts, Phelps, and White, that designed this building. I would like to call your attention to Dr. R. G. Rekers; Dr. Rekers was the Departmental representative who was the liaison officer between us and the architects. I want to acknowledge that here, and to thank him very much. I would like to call to your attention two members of our staff emeritus, Professor Slagle and Professor Craig, who worked in our old building. The addition to the Chemistry Building is much larger than the original building, and we now refer to the original building as the North Wing.

The first speaker that we were to have had was Mr. Frank Junell, Chairman of the Board of Regents of Texas Tech University. Mr. Junell is not able to be with us, and Mr. W. Collins, one of the newest members of the Board of Regents, is going to speak instead; he will explain why Mr. Junell is not here today. I now invite Mr. Collins to address you.

Mr. Bill E. Collins.—Dr. Shine, President Murray, ladies and gentlemen: I am representing the Chairman of the Board of Regents, Mr. Junell. It was his full intent, early this morning, to be here. Health problems in his family, along with the weather existing between Lubbock and San Angelo at the moment, prevent Mr. Junell from being here. So if you will, I would ask that you bear with me in trying to express the words that Mr. Junell transmitted to me over the telephone this morning.

First of all, a telegram has been handed to me by President Murray; it is my pleasure to read a telegram from the Governor of the State of Texas:

Dr. Grover E. Murray,
President, Texas Tech University
Lubbock, Texas

I sincerely regret the inability to be with you on Monday on the occasion of the ceremonies dedicating the new Chemistry Building. I know that you are proud of this facility and that it will be a meaningful addition to this great institution. Please convey my warmest personal greetings to all participating, and sincere best wishes for a memorable occasion.

Preston Smith
Governor of Texas

And another telegram that came to the Board of Regents:

The President
Texas Tech University
Lubbock, Texas

I am pleased to take this opportunity to congratulate the students, faculty, and administration of Texas Tech University on the dedication of the new addition to the Chemistry Building and on convening the symposium on "Excited States of Matter." These new facilities will enable Texas Tech University to continue its tradition of excellence and education and to provide a supply of talent for this State in the 20th century. I regret that I am unable to join you, but I send you my best wishes for every continued success.

Ben Barnes
Lt. Governor of Texas

And now the words that Chairman Junell has asked to be quoted; I shall read from his notes: "It is most fitting that a symposium on 'Excited States of Matter' be held in conjunction with the new five and one half million dollar addition to the Chemistry Building. The very air we breathe, the water we drink, the wood in the furniture that we use, the steel in the automobiles that we drive, are of course all made of matter, and most of our means of living as well as our life processes, depend on interactions of energy. The natives, who occupied this continent long ago, had the same materials that we have today, and the many great differences, that lie between their way of life and ours, come from our greater knowledge of how to make matter, which exists in millions of forms, do the things that we want it to do today. A number of important scientific developments took place during the year 1970, many of them on university campuses. Some of these are: 1) a new table of atomic weights, 2) a new element, man made, of atomic weight 105, which may lead to a revision of some currently existing theories, 3) a group succeeded in synthesising the molecular structure of chlorophyll which gives hope for the elucidation of the mechanism of photosynthesis. In his State of the Union message in January 1970, President Nixon stressed what may well be the great question of this decade. 'Shall we surrender to our services or shall we make our peace with nature and begin to make reparation for the damage that we have done to the air that we breathe, to the land that we use, and to the water that we use?' At last the problem of the human environment has received official recognition at the highest governmental level and the environmental problems that now confront us are real. It is important to recognize that they are not insoluble, that disaster is by no means inevitable; it could be that important work in this area will be done here in this building. The people of Texas, through The Board of Regents of Texas Tech University, are pleased to make this magnificent structure available to the staff, to the students, that they may engage more effectively and more efficiently in research and in study; we know that they will make good use of it.

In dedicating this building, it is well that we remember the scientists of the past who discovered chemistry, and those of the more recent times who have explored it. It is indeed a pleasure to have this portion of time on this important and auspicious occasion this morning."

Dr. Shine.—Thank you very much Mr. Collins. Many of you will know that Mr. Collins is a graduate of Texas Tech; he is a member of the class of 1932. Therefore, he is one of those present who has had a very long-standing connection with Texas Tech University, and I think it is fitting that he has been able to speak on this occasion. I am now going to ask the President of this University, who has had a much shorter connection with the University than the previous speaker, to address the gathering. I would like to point out that, although this building was planned before Dr. Murray became President, it is entirely suitable for such a building to be dedicated during his presidency. An enormous growth has taken place in the last few years on the campus in the number of disciplines studied; the latest is the Medical School. Dr. Murray, it is a great pleasure to have you present and to invite you to address the meeting.

Dr. Grover E. Murray.—Dr. Shine, Dr. Dennis, Dr. Doherty, Mr. Collins; I think I might say that Mr. Junell has well summed up what can be said about the role of chemistry in the modern world. Whether we like it or not, this is a technologically and scientifically based culture, and those who would dispute that simply do so with their eyes closed. I can think of no discipline which is more germane to the world of today in the environmental area, in the field of human welfare, in medicine itself, than chemistry. The dedication of this building is indeed a great step forward in the growth of this university and its sister institution the Texas Tech University School of Medicine. On behalf of both institutions it is my pleasure to welcome you here. To those of you who are on the campus anew, I hope that you enjoy your stay. I hope that you have an "excited symposium" and that it is so exciting that you will return again someday. Welcome, have a good stay, and we look forward to seeing you again in the future.

Dr. Shine.—We have with us today, Dr. W. T. Doherty, President of the Welch Foundation. I do not think that we could have present on this occasion, a more fitting visitor from a foundation that has spent so much time and money in encouraging the growth of chemistry in this State. As a matter of fact, I do not think that we can speak of chemistry in Texas any more without also

including the Welch Foundation. There are in this department, fourteen grantees of the Welch Foundation, and the Welch Foundation has endowed a chair of chemistry in this university now held by Professor C. W. Shoppee. The Welch Foundation has influenced chemistry in Texas enormously and has influenced chemistry in the United States, and I think I can say throughout the rest of the world, by what it has done here in Texas. Dr. Doherty holds a Doctor of Science degree from this university, which he received in 1963; he comes back to this university each year to visit with the Welch Grantees, and it is a great pleasure to be able to welcome him on this occasion, and ask him to address you.

Dr. W. T. Doherty.—Mr. Chairman, President Murray, Mr. Collins, honored guests, ladies and gentlemen. It is indeed an honor and a pleasure for me to say a few words to you today on this important occasion of the dedication of the new addition to the Chemistry Building. And the theme of the symposium "Excited States of Matter" is appropriate. We of the Robert A. Welch Foundation have been excited for some time, not excitement of the type that is produced in molecules by radiation or other means, but nevertheless excited because of our participation in the development of excellent and higher education in the State of Texas. At the end of our fiscal year of 1970, we were supporting a total of 1367 people, consisting of 337 principal investigators, 194 postdoctoral fellows, 493 predoctoral fellows, and 343 undergraduate students. At this time we have invested, and you notice that I use the word invested, not given, over 43 million dollars in the support of basic research in chemistry in the State of Texas. Our grantees have published over 1000 scientific papers in accepted scientific journals. We believe our continuing grant and aid program has been, and still is, a major factor in the development of desired quality in basic research in chemistry in the State of Texas. And we are most happy that Texas Tech University has been an important part of this program. At this time, we have 14 grants here, involving 14 principal investigators, nine postdoctoral fellows, 28 predoctoral fellows, and 15 undergraduate students. This gives a total of 66 people we are now supporting in Texas Tech University and we are definitely excited about the results that they are going to obtain through research in this new building. Our overall investment in basic research in chemistry in Texas Tech University now totals \$1,743,786, plus the Welch Chair of Chemistry endowed with \$1,000,000, and occupied by an eminent chemist, Dr. Charles W. Shoppee, F.R.S.; including the check, which we are sending to you in a few days, our support will approach \$3,000,000. In our association with Texas Tech University, it has been a pleasure to work with your past president, Dr. Goodwin, your present president, Dr. Murray, and with Dr. Barnett, Dr. Shine, and Dr. Joe Dennis. I want to mention Dr. Joe Dennis in particular, because he has been very helpful to us in working out and maintaining our program at this school, and we wish him every success and happiness in his retirement from the chairmanship of the Chemistry Department. The Robert A. Welch Foundation wishes you every success in your drive to excellence, and since we are a perpetual trust, we hope we can continue to be helpful in your accomplishment of this goal. It is a pleasure to be here and to take part in this important dedication ceremony.

Dr. Shine.—I think that there is no other person here that should make the closing remarks in this dedication ceremony than Dr. Joe Dennis. As Dr. Doherty has just pointed out, Dr. Dennis is a former chairman of the Department of Chemistry; he joined this department in 1938, became head in 1950, and relinquished those responsibilities in 1969. He was responsible for getting this building started, but apart from that I would like to point out that he was also responsible for seeing that we had a proper building for work, in what we now call the North Wing. The North Wing of this building was originally the Science Building of Texas Technological College and it housed not only the Chemistry Department but also the other science departments. As these other departments were moved out over a period of years, under the leadership of Dr. Dennis that building was converted into what we thought was a pretty good chemistry building. The design of this addition was completed and the commencement of the construction was begun when he was chairman of this department. I would say also, that not only do we owe this building to his leadership, but I would also point out that most of us on the staff would not be here if it were not for him, because most of us were appointed when he was chairman. As a matter of fact, it occurs to me that none of us would be here today if it were not for the hard work of Dr. Dennis whilst

attempting to get Texas Tech University to build a building like this. Dr. Dennis, I invite you to make the concluding remarks in this dedication ceremony.

Dr. J. Dennis.—Thank you Dr. Shine, thank you ladies and gentlemen: I had a vision, I have a dream; others share this dream, perhaps even others dreamed before us. Yes, certainly they did. All we have and are, is rooted in the past surrounded by the present and reaching for the future. No one without a sense of history, an awareness of the present, and a vision for the future, deserves to dream the impossible dream or accomplish the impossible task. We remember Dr. D. M. Wiggins, whose help was invaluable in earlier days, and Dr. E. N. Jones, who helped us to continue the work that had been started. Especially, do we remember Dr. R. C. Goodwin, who was the second chairman of this department and who was our president when this addition to the chemistry building was planned, under whose leadership the great leap forward at Texas Tech University commenced, which has been continued so ably and admirably under our present leadership. We remember those former members of the departmental staff who remain with us as continuing inspirations, and who have been introduced, Professor W. M. Craig, Professor W. M. Slagle, and Professor O. C. Southall, who is not here today. We think of Dr. R. G. Rekers, who has worked so hard and so faithfully as chairman of the building committee; without his efforts we might not stand here today. We thank Mr. Harold Hinn, whose advice and diligence helped us to see the larger picture and paved the way for the acceptance of our place in this picture. We salute the Welch Foundation, which has aided us materially and intellectually in achieving the present goal. We thank the architect and the builders for a job well done. We express our confidence in the present university and the departmental administration as we reach for the future. Yes, I have a dream, a continuing dream; a dream of a Chemistry Department, growing in wisdom, in stature, and in favor with God and man, growing in the diligence of its pursuit of truth, the acquisition of knowledge, and the application of this knowledge for the betterment of man, for the betterment of all creatures. I am certain others share this dream. The dedication of a building is a symbolic act. The dedication of a man, of men and women, is a vibrant, living thing, which is capable of growth, capable of a rendezvous with destiny, which may change the lot of mankind for the better. Let us dedicate ourselves to the ideal of the pursuit of truth and a rendezvous with destiny. Let your young men have visions, and your old men dream dreams; where there is no vision, the people perish.

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