A Quantum Dynamical Study of the Rotation of the Dihydrogen Ligand in the
 $\text{Fe}(\text{H})_2(\text{H}_2)(\text{PEtPh}_2)_3$ Coordination Complex

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Megan E. Gonzalez, B.S.

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Approved

L. William Poirier Ph.D.
Chairperson of the Committee

Jorge A. Morales Ph.D.

Adelia Aquino Ph.D.

Mark Sheridan Ph.D.
Dean of the Graduate School

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ABSTRACT

Within the past few decades there has been a societal push towards cleaner energy and, more specifically, efficient and safe hydrogen fuel technologies. In order to progress in this avenue of research it is vital to have a clear understanding and characterization of how materials of interest interact with hydrogen. Due to the inherently quantum mechanical nature of hydrogen, any theoretical studies of these systems must be treated quantum dynamically. Many Kubas complexes have been studied both experimentally and theoretically since their discovery in 1984. This study examines the behavior of the hydrogen ligand in the $\text{Fe}(\text{H})_2(\text{H}_2)(\text{PEtPh}_2)_3$ Kubas complex, allowing two rotational degrees of freedom and quantum dynamic behavior. Our density functional theory (DFT) electronic structure calculations utilizing the B3LYP functional of the “gas-phase” molecule allows better insight into possible θ – ϕ correlation and a comprehensive look into librational ground state tunneling splittings. The success of this in-depth study indicates similar calculations can be done on similarly complex systems.

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LIST OF ABBREVIATIONS AND NOTATION

1-D	one-dimensional	PES	potential energy surface
2-D	two-dimensional	DFT	density functional theory
		ZPE	zero-point energy
STP	standard temperature and pressure	100 dataset	Dataset of 100 <i>ab initio</i> points in which only Fe and dihydrogen are frozen
MOF	metal-organic framework		
cm ⁻¹	wavenumber	216 dataset	Dataset of 216 <i>ab initio</i> points in which only Fe and dihydrogen are frozen
d.o.f.	degree of freedom		
INS	inelastic neutron scattering	316 dataset	Dataset consisting of both the 100 dataset and 216 dataset.
QD	quantum dynamics	f198 dataset	Dataset consisting of 198 <i>ab initio</i> points in which all coordinates are frozen except for the hydrides
MEP	minimum energy path		

CHAPTER 1

INTRODUCTION

Within the past few decades there has been a societal push towards cleaner energy and specifically efficient and safe hydrogen fuel technologies.¹⁻³ *Pure* hydrogen combustion results in only water as a product, i.e. no carbon is involved. Moreover, as illustrated in Fig. 1.1, based on a mass:energy ratio, hydrogen has nearly 3 times the gravimetric density of gasoline.⁴ On the other hand, there are some distinct disadvantages. Most notably, pure hydrogen is difficult to store compactly, owing essentially to the ideal gas law. Even when compressed using a pressure of 700 bar, the volumetric density is undesirably low as compared with other fuels (Fig. 1.1). Thus, there has been a particular interest in the utilization of hydride metal systems such as Kubas complexes and metal-organic frameworks (MOF) in the development of attractive materials for hydrogen storage.^{2,5} Such materials allow hydrogen to be stored much more compactly at pressures much closer to 1 bar, but still have their challenges. Kubas complexes suffer limited accessibility to binding sites, low weight-percent ratios (i.e. volumetric density), and high costs in their production.² Alternatively, MOFs suffer from instability at standard temperature and pressure (STP) due to weak binding, unfavorable kinetics, and again low specific uptake by percent weight (i.e. gravimetric density).²

In recent years, progress has been made regarding the capacities for hydrogen storage through the hydrogen spillover mechanism. The approach relies on the introduction of small metal particles on or in a high-surface area material which then act to catalytically dissociate the hydrogen molecules under saturation.³ Many of the studies that utilize this process also involve MOFs.^{3,6,7} Due to the complementary natures of MOFs and Kubas

complexes, J. Eckert and associates have shown some interest in finding a middle ground between Kubas complexes and MOFs that would increase the overall efficiency in regards to hydrogen storage.⁸

Figure 1.1: Based on mass, Hydrogen has nearly 3 times the energy capabilities of gasoline.⁴

Additional demands arise from the US Department of Energy’s 2010 targets for a hydrogen storage system. They require a capacity of 45g H₂ per L, a refueling time of $\leq$ 10 minutes, a minimum lifetime of 1000 refueling cycles and the ability to operate within the temperature range of -30 to 50 C°. ⁶ the US Department of Energy’s 2012 requirements are quite similar, but in some ways more demanding. The minimum lifetime cycles has been increased to 1500 cycles, and a larger range of operating ambient temperatures (-40 to 60 C°). ⁹ All of this is by way of stating that the demands for hydrogen storage materials are very challenging and the search for the “perfect” material requires a thorough

understanding and characterization of how those materials interact with hydrogen.

With the increasing demands on hydrogen storage targets and clean energy it is necessary to better understand the systems that are looked to as potential solutions. of particular importance is the fact that hydrogen, being the lightest element, is inherently quantum mechanical. Yet remarkably, very few previous studies of hydrogen-material interactions have incorporated quantum dynamics (QD).^{10–19}

Since 1984, when Kubas et al first reported their findings of a (η^2 -H₂) ligand in a coordination complex, there has been much interest in the behavior and mechanisms of the dihydrogen ligand.^{20–28} There are now many one dimensional (1-D) and a few two dimensional (2-D) QD models.^{27,29–31} It should be noted that previous 2-D models were not done using *ab initio* methods due to the attributed difficulty.³¹ One of the main goals of this thesis project, accordingly, has been to provide the first ever comprehensive study of the quantum rotational dynamics of the dihydrogen ligand in a Kubas complex. In these complexes both rotation of the ligand and hydrogen exchange are major contributors to the dynamics. At higher temperatures it is difficult to disentangle the role of rotation in experimental data. On the other hand, at lower temperatures rotational tunneling dynamics is not only prevalent, but also largely the only force active making the rotation of the H₂ ligand particularly important.

For this study, the Fe(H)₂(H₂)(PEtPh₂)₃ coordination complex is of particular interest due to the availability of experimental results and the depth of the studies done over the past few decades.^{21,26,27,31,32} Fe(H)₂(H₂)(PEtPh₂)₃, initially reported by Aresta et al, is a natural extension to the Ru and Os studies.^{32,33} In 1992 Eckert et al discovered, through the measurement of the stretching mode of the hydride, a measure of the σ bond strength of the metal center. This bond strength increases in order down the group of metals, Fe <

Ru < Os, as expected. However, for the dihydrogen ligand, the M-H bond strength increases as Ru < Fe < Os, which comes with a corresponding decrease in H-H interactions, Os < Fe < Ru. This led Morris and collaborators to the conclusion that, contrary to expectation, Fe is a better back donor; though no direct evidence could be obtained.²⁰ Additionally, $\text{Fe}(\text{H})_2(\text{H}_2)(\text{PEtPh}_2)_3$ has a unique staggered structure that is tied to the fluxional behavior of this complex.³² Analysis of the crystal structure in *trans*- $[\text{FeH}(\text{H}_2)-(\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2]\text{BF}_4$ reveals that when rotating the $\eta^2\text{-H}_2$ ligand off of the $\text{H}_2\text{-Fe-H}$ plane, the potential minimum is found about 20° off to the side of the planar orientation. On the other hand, Eckert et al cautioned that their use of sinusoidal functions in the rotational potential may not accurately represent the “true” potential curve even taking into account the consistency their model had with the available experimental data.²¹

The last comprehensive study done on the Fe coordination complex was performed by Eckert et al in 2011. Their 1-D study varied the azimuthal coordinate (we denote “ ϕ ”, they denote “ θ ”) while holding the polar angle (we denote “ θ ”) fixed at the crystal structure geometry. Their study analyzed the dihydrogen rotation for both partially and fully optimized $\text{Fe}(\text{H})_2(\text{H}_2)(\text{PEtPh}_2)_3$ and found that with the hybrid functional, B3LYP, the minimum is located at $\theta = 16.7^\circ$ where θ is their azimuthal coordinate defined as in Fig. 1.2 (Left).²⁷ The orientation of H_2 varied in the interval $0^\circ < \theta < 180^\circ$ in increments of 10° . The remaining geometries were held fixed in the crystal structure. While it would be best to include relaxation of neighboring molecules when calculating the rotational potential energy curve, it is currently beyond the capabilities of technology. Largely this is due to a unit cell containing close to 800 atoms. The barrier to H_2 rotation was found to be 332.269 cm^{-1} .

Figure 1.2: (Left) Orientation of the azimuthal coordinate as determined by Eckert et al in 2011.²⁷ (Right) Orientation of both the azimuthal and polar angle as defined for this study.³¹

This study examines the Fe coordination complex, $\text{Fe}(\text{H})_2(\text{H}_2)(\text{PEtPh}_2)_3$, in the gas phase, with the goal of establishing a better understanding of the H_2 rotational QD, and will expand upon Eckert’s 2011 work through a 2-D QD study. It should be noted that the gas phase calculations will likely relax with more ease than that of the crystal structure.²⁷ This can be attributed to both the crystal packing forces and the considerable intermolecular interactions.³⁴ Until this study there has not been a comprehensive QD study that allows H_2 two rotational degrees of freedom (d.o.f.). The general spherical coordinates used in this study are illustrated in Fig. 1.2 (Right). The coordinate ϕ is defined as the azimuthal coordinate and θ is the polar angle—defined relative to the M– H_2 bond. This 2-D study illustrates the role of quantum tunneling and θ – ϕ correlation, which manifest as “snaking” of the minimum energy path for hindered rotation, ground and excited state tunneling splittings, and also Fermi resonances, all of which will be explored.

CHAPTER 2

THEORETICAL BACKGROUND AND METHODOLOGIES

2.1 Kubas Complex

In 1984 Kubas et al. discovered that molecular hydrogen (H_2) can form a σ complex (η^2 or hapticity two) with transition-metal complexes.³⁵ Widely, this discovery is viewed as a key development in inorganic chemistry within the the last two decades of the 20th century.^{25,27} By 1992 H_2 had been recognized as a key component in many catalytic processes, and by the 21st century the science community showed interest in utilizing metal-hydride systems as a material for hydrogen storage.^{2,34} In addition to their potential in the field of clean energy, Kubas complexes also present the opportunity to examine a complex hindered rotor model (a dumbbell in a double-minimum potential with two-fold symmetry) with the η^2 - H_2 ligand serving as a prototype for a “ σ -bond complex”.^{23,34}

A key indicator for the coordination of the dihydrogen ligand in the solid state originates from observations of the rotational transitions from inelastic neutron scattering (INS) measurements which have subsequently led to a value for the barrier to rotation of the dihydrogen ligand.³⁴ This barrier can then be analyzed into a series of interaction terms which can be calculated through a series of experiments in which one or more factors is changed or through theoretical calculations. Further discussion of the rotational barrier will be covered in Sec. 2.3 The various forces that govern hindered rotation can be split into two main groups — electronic (bonded) or steric (non-bonded) interactions. In this manner, we can characterize the various “structural” aspects of the H_2 -complex interactions, that are independent of the hydrogen QD.

2.2 Electronic and Steric Interactions

The direct electronic interaction arises from the overlap of the corresponding molecular orbitals of the metal and dihydrogen.³⁴ A study of $M(\text{CO})_3(\text{PR}_3)_2(\eta^2\text{-H}_2)$ (where $M=\text{W}$, Mo ; $\text{R}=\text{Cy}$, $i\text{-PR}$) reveals that the direct electronic binding of the dihydrogen has a significant impact on the rotational barrier (see Sec. 2.3), roughly half or more of the experimentally determined value.²³ When the hydrogen molecule binds in an η^2 mode to the transition metal the ligand can adopt two possible conformations, σ or π (see Fig. 2.1). The preference for either conformation is determined by the π properties of the metal.^{20,31} This is due in part to the H_2 orientational independence of the σ donation. On the other hand, the orientation will strongly influence the relative stability through the π back-donation.

Figure 2.1: Definition of the z axis and illustration of the σ vs π donation between M (some transition metal species) and H_2 .³¹

In order to have any donation to the H_2 , the d orbitals (d_{yz} or d_{xz}) on the metal must be filled.³¹ This results in the highest of the two occupied orbitals determining the preferred orientation. This is partially due to the orbital being the closest in energy to the accepting $\sigma^*_{(\text{H}_2)}$. In the case that both the d_{yz} and d_{xz} orbitals are filled, the result is no strongly preferred orientation. Therefore, the barrier between the two conformations is relatively

small (generally $< 1000\text{ cm}^{-1}$). This is why only one peak can be observed for an H_2 ligand in ^1H NMR spectra in solution at room temperature. This low barrier allows the two hydrogen nuclei to go through large amplitude librational motion which can lead to an exchange of their positions (illustrated in Fig. 2.2). Further implications of this will be discussed in Secs. 2.3 and 2.4. In practice, the identity of the metal atom appears to play a major role here, for reasons that are not yet completely understood.^{20,34}

Alternatively, steric interactions can be attributed to interaction between the dihydrogen ligand and other atoms in the complex as the dihydrogen ligand rotates.³⁴ Due to the distance between the complexes in the crystal it is expected that intermolecular interactions would not largely contribute to the barrier of rotation; however, there is a possible effect on the coordination geometry which could in turn affect the bond between the metal and dihydrogen ligand as well as on the polar angle θ . This study will not be utilizing a crystal structure due to technological restrictions mentioned in the introduction. As a result, there may be some variance from the results obtained from experiments that utilized a crystallized complex.

Ligands other than the dihydrogen can strongly affect the electronic state of the metal. The more basic the ligands are the more electron density is shifted to the metal which will in turn raise the energy of the highest occupied d-orbital of the complex. This will result in an increased interaction with $\sigma_{(\text{H}_2)}^*$ which can then strengthen the back-donation enough to result in cleavage of the H-H bond (an accepted mechanism for oxidative addition to form a dihydride). Similarly, π -acceptors may compete with the back donation also resulting dihydrogen cleaving into hydride in the more π -basic transition metals (such as group 6). The presence of electron rich ligands also have this effect. Alternatively, strong σ -donors may impede the σ -donation from the dihydrogen inhibiting the binding of the

dihydrogen ligand.³⁴ On the other hand, the bulky pendant ligands provide steric constraints that tend to stabilize the complexes and discourage dihydrogen-dihydride exchange.³⁶ The following section will examine H₂–H–H exchange in more detail.

2.3 H₂–H–H Exchange and H₂ Rotation

As mentioned in Sec. 2.2, electronic interactions can result in a single peak in ¹H NMR spectra $\approx$ room temperature.^{27,36} In other words, the hydride and dihydrogen ligands are indistinguishable, indicating rapid H₂-hydride exchange dynamics.³⁷ The study done by Oldham et al shows this for cationic iridium complexes of the form [CpIr(L)H₃]BF₄ where L= various PR₃. Due to this it is impossible to determine the H–D coupling constant for an H–D ligand and the reorientation of the dihydrogen ligand happens via rotational tunneling. The barrier for this exchange can be very close to that for rotation of H₂, as in the case of IrXH₂(η^2 H₂)(PR₃)₂, but typically is found to be somewhat higher in energy.^{3,27} Normally the exchange processes would be expected to occur classically through transition states, though in previous theoretical studies these were found to be high in energy.³² In any event, for the Fe compound of this study such H₂-hydride exchange dynamics are found to be facile at least above room temperature.^{27,36} Although such exchange dynamics will form the focus of a future study, here, we examine only the dihydrogen rotation dynamics, which are most relevant below room temperature.

The origin of the rotational barrier can be attributed to intramolecular interactions. The first interaction to consider is the direct electronic interactions between the dihydrogen and the metal.³⁴ Through both experiment and theoretical calculations it has been shown that this is the major influential contributor to the barrier. Inelastic neutron scattering (INS) rotational tunneling spectra showed the profound effect of altering the metal center. Through the INS of M(CO)₃(η^2 -H₂)(PR₃)₂ (where M = W, Mo, Cr and R= Cy, *i*-PR) the

ratio of tunneling splitting is found to be approximately 1:3:5 for W/Mo/Cr. In comparison, changing the phosphine (PR_3) shifted the mean tunneling transition by around 20%. These results strongly support the origin of the barrier lying in the metal-dihydrogen electronic interaction.³⁴

In theory the barrier to rotation for dihydrogen should be zero if the ligands in the plane parallel to the rotation are highly symmetric. However, crystal structure data for $\text{W}(\text{CO})_3(\text{H}_2)(\text{P-i-Pr}_3)_2$ revealed that the structure of the MP_4 fragment is distorted and at least one of the P-M-P' axes bent back and away from the dihydrogen ligand.³⁴ This distortion rehybridizes the metal orbitals in such a way that the overlap of $\sigma_{(\text{H}_2)}^*$ shows a variation through the rotation in the plane parallel to the MP_4 fragment. This distortion can also be influenced by steric effects or crystal packing forces. Thus, it can be concluded that the use of different counter ions or solvent molecules in crystallization can result in different molecular structures and barriers to dihydrogen rotation. This may account for differences in results between crystal structure and those of the gas phase.

2.4 Hindered Rotor Symmetric Double Well and Tunneling Splittings

As alluded to in Sec. 2.2, the rotational exchange of the two hydrogen nuclei in the dihydrogen ligand (i.e. H_2 permutation symmetry) results in a symmetric double well potential energy profile (illustrated in Fig. 2.2) with a relatively low transition state barrier. Before proceeding therefore, it is essential to review the QD of symmetric double wells—especially tunneling splittings—in the context of a periodic azimuthal rotational degree of freedom (d.o.f.). This is reminiscent of the umbrella-like inversion of the ammonia molecule. In that case, the barrier for the nitrogen atom to pass through the H_3 plane cannot be too large, since the inversion occurs more than 10^{10} times per second at 300K. Conceptually, the double well is constructed by superimposing two single

minimum potential wells.

Figure 2.2: The exchange of H_2 nuclei resulting from a low rotational barrier. The metal fragment L_nM is assumed to be frozen and serves as a reference frame fixed in space.³¹

For the lowest-lying states the barrier causes a “tunneling splitting” of the hypothetical levels of the single-minimum wells. The splitting that occurs between the states increases with vibrational excitation v until it is comparable with the single-well level spacing itself. Traditionally, this is presumed to be for energies below the barrier, although in reality hydrogen can manifest clear “tunneling splitting” even above the barrier.³⁸ These splittings occur as a result of both symmetric and antisymmetric combinations of the wavefunctions of the single minimum potential wells, with the symmetric combination at a lower energy than the antisymmetric combination.³⁹

Figure 2.3 features the energy level diagram for the two-fold potential with one rotational d.o.f., the azimuthal coordinate, ϕ . As the barrier height increases, the separation between two lowest librational levels rapidly decreases. This can be viewed as a split librational ground state.^{34,40} This split librational ground state largely originates in Kubas complexes at low energy states when the behavior aligns to that of a hindered rotor. At very high energies or when the barrier is low the dihydrogen ligand will behave as a free rotor. In this limit, one again finds near degeneracy associated with the usual

Figure 2.3: Tunneling splitting as a function of the rotational barrier height.^{23,34}

degenerate $\pm m$ (azimuthal quantum number) pairs for the rigid rotor eigenstates (i.e. “left” and “right” rotation are identical). The intermediate regime, where the barrier is large enough to cause m -splitting, but too small for clearly identifiable tunneling splitting, is interesting.

Computationally the rotational “tunneling splitting” is extremely sensitive to various features of the barrier to H_2 rotation (e.g. it depends exponentially on the barrier height) and thus can be difficult to achieve accurately.²³ Additionally, ground state “tunneling splittings” are often too small for instruments to be able to detect experimentally. This is rather unfortunate as these splittings may act as a built-in scale of the relative contribution of steric effects to the barrier to rotation³⁴

It should also be noted that in addition to influencing the barrier to rotation, steric interactions also contribute θ - ϕ correlation or “snaking”.³⁴ One example in particular is the phosphine ligand on one end of $W(CO)_3(H_2)(P\text{-}i\text{-}Pr_3)_2$ which is known to have two possible orientations. The different orientations have been noted to result in slightly

different barriers and thus different tunneling splittings. Additionally, alternative complexes that do not feature structural disorder do not exhibit split tunneling peaks, which also provides evidence that nonbonded interactions also play a part in the barrier.

CHAPTER 3

COMPUTATIONAL STUDIES AND METHODS

To understand how the H_2 molecule rotates, i.e. the rotational dynamics, this motion needs to be treated quantum mechanically. In principle, this means first and foremost, the H_2 molecule must be allowed to explore the entire (θ, ϕ) solid angle space. At each (θ, ϕ) orientation the H_2 molecule will feel a completely different potential energy. It is therefore necessary to determine a global “potential energy surface” (PES), i.e. $V(\theta, \phi)$, for all possible rotational orientations (θ, ϕ) . This, in turn is achieved by first using electronic structure methods to compute V at a specific set of (θ, ϕ) points, called “*ab initio* points”. Finally, using the global $V(\theta, \phi)$ PES so constructed, we will compute the quantum hindered rotational Hamiltonian for the H_2 ligand, and use that to compute the hindered rotor quantum eigenstates—i.e., rotational energy levels and wavefunctions.

Initial electronic structure calculations were made with 100 *ab initio* points (denoted the “100 dataset”) globally distributed across the entire (θ, ϕ) solid angle space, generated by A. Aquino et al.⁴¹ For each such *ab initio* calculation, the Fe and dihydrogen ligand geometries were frozen, and all other atoms were allowed to relax. Similar calculations were performed by the author, on a 216 dataset spanning a narrower θ range, in order to gain further insight into the bottom 10% of the potential energy well ($\approx 2000 \text{ cm}^{-1}$). A PES function was fit to the 216 dataset. Although technically a “global” fit, the 216 PES is only reliable in the deep well region. In order to assure a high quality fit throughout the entire (θ, ϕ) range, both the 100 dataset and 216 datasets were combined to form the 316 dataset, and a subsequent PES fit was also performed. Further work was made to craft a blended PES between the 216 and 316 datasets (denoted b216/316). The preliminary work

for the blended potential will be discussed later in Sec. 3.2.2.

For all of the aforementioned calculations, the Fe and dihydrogen ligand were frozen while the rest of the complex was allowed to relax. While this is fine for a gas phase simulation, it may be inconsistent for comparison with condensed phase experiments, especially vis-à-vis tunneling splittings. To better address the latter, a completely different set of calculations were made for 198 *ab initio* points (denoted the “f198” dataset) in which all coordinates except for the two hydride ligands were frozen. This was done to more closely simulate solid state conditions.

For each of the 216, 316, and f198 PESs, QD calculations were performed. Specifically, a 2-D hindered rotational QD Hamiltonian matrix was constructed, and eigenstates were computed (both energy levels and wavefunctions). These were then analyzed to determine state labels, tunneling splittings and the extent of θ – ϕ correlation. The details of how this was done will be addressed in this chapter.

3.1 *Ab Initio* Calculations

3.1.1 Density Functional Theory (DFT)

The electronic structure calculations were performed by means of DFT using the hybrid Becke, 3-parameter, Lee-Yang-Parr (B3-LYP)^{42,43} functional and the SV(P) basis set.⁴⁴ The Stuttgart effective core potential⁴⁵ was used for the Fe atom. All calculations were carried out through TURBOMOLE program suite⁴⁶ in the Robinson computer cluster of the Department of Chemistry and Biochemistry, Texas Tech University.⁴⁷

3.1.2 Coordinate Systems

Two coordinate systems were involved within the calculations. The original 100 points generated by A. Aquino et al were oriented in an Cartesian xyz-coordinate system as

utilized by the Turbomole program package.⁴¹ On the other hand, the natural orientation/reference frame to use for this system is that of Fig. 1.2. It was thus necessary to define the coordinate transformation from the Turbomole “space-fixed” frame to the orthogonal “body-fixed” frame referred to the Fe-H₂ axis as defined in Fig. 1.2. This simple rotation was completed through the following matrix:

From space-fixed frame to body-fixed frame:

$$\begin{bmatrix} 0.610734 & 0.772909 & -0.172092 \\ -0.147444 & -0.102529 & -0.983742 \\ -0.777987 & 0.626179 & 0.051343 \end{bmatrix}$$

3.1.2.1 Creating more *ab initio* points

After the analysis of the original 100 global data points, it was decided that a higher resolution below the energy of $\approx 2000 \text{ cm}^{-1}$ (approximately the lowest 10% of the PES well) would highlight the behavior within this more relevant energy range resulting in more refined results (see the Results chapter).

This led to the creation of the 216 dataset. These *ab initio* points were generated as follows. First, from the 100 dataset PES, the energy contours, $V(\theta, \phi) = 2000 \text{ cm}^{-1}$ were computed, where the zero value for $V(\theta, \phi)$ is set equal to the potential well minimum. These contours are visible in the right of Fig. 3.1, from which we extracted $\theta_{\min}(\phi)$ and $\theta_{\max}(\phi)$ contour curves. Next, a set of 18 uniformly distributed ϕ values were chosen from 0 to $17\pi/18$ in increments of $\pi/18$. The $[\pi, 2\pi]$ values of ϕ can be ignored, due to the H–H permutation symmetry of the PES, which implies that $V(\pi - \theta, \pi + \phi) = V(\theta, \phi)$. For each ϕ value, a ϕ -specific set of 11 uniformly-distributed θ values was chosen, ranging from $\theta = \theta_{\min}$ to $\theta = \theta_{\max}$, in increments of $(\theta_{\max} - \theta_{\min})/10$. This accounts for 198 *ab initio* points of the dataset (see the left of Fig. 3.1). Finally, one additional fixed θ value

($\theta = 1.000$) was added, and paired with all 18 ϕ values, to form the total 216 dataset. The *ab initio* calculations for the 216 dataset were then performed in the same manner as for the 100 dataset.

Figure 3.1: (Left) The first 198 *ab initio* points for the 216 dataset. θ values are generated from the 2000 cm^{-1} contour of the 100 PES and ϕ is limited to 0 to π due to H–H permutation symmetry. (Right) The 100 PES used to determine the 198 *ab initio* points.

It was determined that though the 216 dataset largely has high enough resolution below 2000 cm^{-1} (see Chap. 4), it naturally does not behave well under higher energy conditions. In order to alleviate this issue, further analysis was performed on a set that combined the original 100 dataset and the 216 dataset. This set of data is termed the “316 dataset”. An even better global PES was later constructed using a more sophisticated “blending” procedure (see section 3.2.2).

In order to better understand the behavior of the complex under solid state conditions, a final set of data was created. The f198 “frozen” dataset was generated with the following parameters. It was determined that ϕ would vary from 0 to $17\pi/18$ by $\pi/18$ while θ was centered at $\pi/2$ and varied from $\theta_{\min} = 1.1108$ to $\theta_{\max} = 2.0308$ by $(\theta_{\max} - \theta_{\min})/10$. These 198 *ab initio* calculations freeze all coordinates to the gas phase minimum, except those of the two hydrides, which were allowed to relax.

3.2 Fitting the Potential Energy Surface

The creation of a global analytic PES requires the coordinate values θ and ϕ for all *ab initio* points, as well as the energies that correspond to these points. This PES data (see appendix A) is then fit to a global functional form. Given the rotational nature of the configuration space and the H–H permutation symmetry, a natural choice for the expansion functions are the spherical harmonics, $Y_{l,m}(\theta, \phi)$. In particular, due to the above-referenced H–H permutation symmetry, only even l values contribute. We therefore expand $V(\theta, \phi)$ in all even l $Y_{l,m}(\theta, \phi)$ functions up to some maximum value $l_{\max}$ —for which $l_{\max} = 6, 8, 10$ were considered. A test of numerical convergence was then applied by comparing the resultant $V(\theta, \phi)$ functions. Through the analysis shown in Chap. 4 it was determined that $l_{\max} = 8$ was the optimal choice. This resulted in an expansion into 45 functions (i.e. $2l + 1$ for each of $l = 0, 2, 4, 6, 8$).

3.2.1 PES Expansion Coefficients

To determine the optimal PES expansion coefficients ($C_{l,m}$), for a given dataset, a least squares fit was applied. For this particular study, there are 45 PES expansion coefficients. Equation 3.1 illustrates the relationship between $V(\theta, \phi)$ and $C_{l,m}$. Please refer to Appendix B for these coefficients.

$$V(\theta, \phi) = \sum_{l=0, \text{even}}^{l_{\max}} \sum_{m=-l}^l C_{l,m} Y_{l,m}(\theta, \phi) \quad (3.1)$$

3.2.2 The Blended Function: b216/316

In theory, the 216 PES Provides the best energy values below 2000 cm^{-1} , but breaks down catastrophically at higher energies. The 316 PES should perform well throughout the energetic range, but will still not be as accurate as the 216 PES at the lowest energies.

Indeed, the actual performance as discussed in section 4.1 is not quite as good as desired. To obtain a true “best of both worlds” PES, therefore, a “blended” b216/316 PES was constructed, wherein weighting functions were used to smoothly transition from 216 to 316 as $|\theta - \pi/2|$ increases. Specifically, the weighting function, “window(θ)”, has the form,

$$\text{window}(\theta) = \frac{1}{2}(\tanh[\alpha(\theta - \theta_o)] + \tanh[\alpha([\pi - \theta_o] - \theta)])$$

The parameters θ_o and α were varied to identify the optimal blended function, balancing smoothness with difference from either the 216 PES or 316 PES. In order for the window function to have the appropriate effect, window(θ) is multiplied to the 216 dataset, $V(\theta, \phi)$ and $[1 - \text{window}(\theta)]$ is multiplied to the 316 dataset $V(\theta, \phi)$. This allows for the 216 dataset to more strongly influence the bottom 10% of the PES well, while the 316 dataset dominates the higher energy region.

3.3 Quantum Dynamics Calculations

From the PES, it is possible to calculate a hindered rotor H_2 Hamiltonian for each dataset. From the Hamiltonian we compute rotational energy levels and wavefunctions. All such rotational states are computed up to 6500 cm^{-1} , which gives us a complete characterization of the rotational QD in the energy range of interest. From these calculations, we are then able to extract useful dynamical data such as ground and excited state double-well tunneling splittings, state labels (from wavefunction density plots), and the role of (θ, ϕ) correlation or “snaking”.

To compute eigenstates, it is necessary to represent the Hamiltonian operator $\hat{H}$ as an $N \times N$ matrix $\tilde{H}$, using a finite basis set of N functions. The Hamiltonian operator is given by $\hat{H} = \hat{V}(\theta, \phi) + \hat{T}_{\text{rot}}$ where the rotational kinetic energy is given by $\hat{T}_{\text{rot}} = \frac{\hbar^2}{2I} \hat{l}^2$ where $\hat{l}^2$ is the total angular momentum, the moment of inertia $I = \mu R_e^2$, and R_e is the H–H

separation, the matrix elements, $\tilde{H}_{l,m,l',m'}$, are therefore given by equation 3.2, where $\langle \theta, \phi | lm \rangle = Y_{l,m}(\theta, \phi)$.

$$\tilde{H}_{l,m,l',m'} = \int Y_{l,m}^*(\theta, \phi) \hat{H} Y_{l,m}(\theta, \phi) \sin \theta d\theta d\phi = \langle lm | \hat{T}_{\text{rot}} | l'm' \rangle + \langle lm | V(\theta, \phi) | l'm' \rangle \quad (3.2)$$

The kinetic energy contribution is particularly simple, resulting in a diagonal matrix because the $Y_{l,m}$'s are eigenstates of $\hat{T}_{\text{rot}}$:

$$\tilde{T}_{l,m,l',m'} = \frac{\hbar^2}{2I} l(l+1) \delta_{l,l'} \delta_{m,m'} \quad (3.3)$$

The potential energy contribution on the other hand is more complicated, as it requires a separate 2-D integral for every one of the N^2 matrix elements. On the other hand, because $V(\theta, \phi)$ is itself expressed in terms of spherical harmonics an analytic evaluation of the $\tilde{V}_{l,m,l',m'}$ matrix elements is possible, as follows.

$$\begin{aligned} \langle lm | V(\theta, \phi) | l'm' \rangle &= \int_0^\pi \sin \theta d\theta \int_{-\pi}^\pi d\phi Y_{l,m}^*(\theta, \phi) V(\theta, \phi) Y_{l',m'}(\theta, \phi) \\ &= \sum_{l''=0, \text{even}}^{l''_{\text{max}}} \sum_{m=-l''}^{l''} C_{l''m''} \int_0^\pi \sin \theta d\theta \int_{-\pi}^\pi d\phi Y_{lm}^* Y_{l''m''} Y_{l'm'} \end{aligned} \quad (3.4)$$

$$\int \sin \theta d\theta \int d\phi Y_{l_3 m_3}^* Y_{l_2 m_2} Y_{l_1 m_1} = \left[\frac{(2l_1+1)(2l_2+1)}{4\pi(2l_3+1)} \right]^{\frac{1}{2}} C(l_1 l_2 l_3; m_1 m_2 m_3) C(l_1 l_2 l_3; 000) \quad (3.5)$$

3.3.1 Coding Clebsch-Gordan Coefficients

Note that the integrals in Eq. 3.5 can be analytically expressed in terms of Clebsch-Gordan coefficients, $C(l_1 l_2 l_3; m_1 m_2 m_3)$.⁴⁸ Thus, we represent every one the N^2 matrix elements as a sum over 45 Clebsch-Gordan terms of the Eq. 3.5 form. In practice, this can get rather large, so that evaluation of these terms becomes the computational bottleneck. To reduce the necessary computational effort, we precompute all the necessary Clebsch-Gordan coefficients i.e. up to $l_{\text{MAX}} = 20$ for the even calculations and $l_{\text{MAX}} = 19$ for the odd calculations and stored within an array. This array was exported to a file and imported as needed.

3.3.2 Permutation Symmetry and Numerical Convergence

Because of the H–H permutation symmetry of the Hamiltonian, the para–H₂ and ortho–H₂ quantum states can be computed separately. In particular, the para–H₂ states have even spatial symmetry, and can be associated with $l = \text{even}$. The ortho–H₂ states have odd spatial symmetry, and correspond to $l = \text{odd}$. To compute a finite representational Hamiltonian matrix, therefore, we use all even– l or odd– l spherical harmonic basis functions, up to some maximum value l_{MAX} . By increasing l_{MAX} , recomputing eigenvalues, and comparing with smaller l_{MAX} eigenvalues, we can assess the level of numerical convergence of our calculation. Note that our convergence is variational, meaning that all computed eigenvalues converge from above, because the representation is analytic. This property is useful for analyzing convergence. In any case, we found the values $l_{\text{MAX}} = 20$ and $l_{\text{MAX}} = 19$ to be extremely well converged for para–H₂ and ortho–H₂ respectively.

3.4 Creating Wavefunction Density Plots

From the even and odd Hamiltonian matrices, eigenvectors were obtained. For each eigenvector, every coefficient was then multiplied by the corresponding spherical harmonic function, and summed. The result was squared to obtain the wavefunction density, which was subsequently plotted. The even and odd plots were then combined and ranked via their rotational frequencies which are obtained from the eigenvalues. Throughout this thesis, whenever we use a single number index for a rotational state this is what is meant. Sometimes we apply the energetic ordering label just to the even or odd states by themselves, in which case we add an “e” or “o” prefix. Finally, based on the wavefunction density plots, we assign (n_θ, n_ϕ) labels describing excitations in θ and ϕ based on the number of peaks shown in the respective direction. Each excitation in θ results in a single peak, while each excitation in ϕ results in two peaks, due to the periodic symmetry exhibited in the ϕ coordinate. Tables containing this information as well as plots can be found in Appendix C. Additionally, this analysis is where tunneling splitting can be assigned and any coupling between states can be noted.

CHAPTER 4

RESULTS

4.1 PES

Electronic structure calculations were performed for multiple datasets as defined in Chap. 3. Analysis and global PES fits were performed for individual datasets, as well as combinations of datasets. This section will discuss the PESs so obtained for datasets 100, 216, and 316 as well as for the blended combination of 216 and 316 (b216/316). All of these PES's describe a fully relaxed complex substrate, such as might be most appropriate for the gas phase. In order to better represent experiments performed in the condensed phase, we also computed the f198 “frozen” dataset, for which only the two hydride ligands in the complex were allowed to relax.

4.1.1 *Ab Initio* Points

Our first PES fit was for the 100 dataset (see Fig. 4.1 [Top] (Left)) for l values up to $l_{\max} = 6$. This is not expected to be particularly accurate, but was performed to get a rough idea of the general behavior that should be expected from the H_2 rotation. From the figure, the full PES is seen to be smooth and well behaved throughout. The PES manifests roughly sinusoidal behavior in θ , with a very large polar rotational barrier of over 20,000 cm^{-1} . On this scale, no θ - ϕ correlation is evident—nor, indeed, is any ϕ -dependence whatsoever. However, in Fig. 4.1 [Top] (Right), representing the dynamically relevant bottom 10% of the PES well (below $\approx 2000 \text{ cm}^{-1}$) significant θ - ϕ correlation can be observed, giving rise to a “snaking” behavior. The azimuthal rotational barrier can also be observed, near $\phi = 0$.

From Fig. 4.1 [Top] (Right), also, it is clear that the rotational dynamics are effectively

restricted to a fairly narrow band, extended about 20° in either polar direction above and below the $\theta = \pi/2$ equatorial plane. In order to better represent this dynamically relevant region the *ab initio* points of the 216 dataset were by design limited largely to this region. Of course, by limiting this dataset to roughly the bottom 10% of the well, it is expected that the corresponding globally fitted PES function will break down at configurations with higher energies that lie outside this region. This will be discussed in the next section in more depth. When comparing the full PES for the 100 and 216 datasets (Fig. 4.1 [Middle] (Left)) it is immediately clear that the polar rotational barrier of the 216 PES exceeds that of the 100 PES by roughly $10,000 \text{ cm}^{-1}$. Additionally, comparing the low-energy (Right) plots between 100 and 216 PES's it is clear that the more refined 216 PES exhibits somewhat less snaking/correlation, although the azimuthal barrier height turns out to be higher.

In order to combine the behavior of the 216 PES for the bottom 10% of the well with higher energy regions of the 100 PES, a third "316 dataset" was created, by simply combining the 100 and 216 datasets together. The corresponding fit PES is indicated in Fig. 4.1 [Bottom] where it is possible to see the similarities between PES 316 and the two parent data sets in the appropriate regions. This was the desired outcome resulting in a PES that is globally best across both high-energy and low-energy regions. That said, the 316 PES exhibits a bit more snaking than 216. Evidently, the true PES does exhibit snaking, although the precise details are somewhat sensitively dependent on the datasets used for the PES fitting.

Figure 4.1: [Left] Global PES from which the barrier to rotation in θ can be obtained. [Right] Local PES limited to the bottom 10% of the well ($\approx 2000 \text{ cm}^{-1}$) from which more detailed information can be obtained for the lower energy regime. From the local plots more detail on θ - ϕ correlation is available. (Top) The 100 dataset for $l_{\max} = 6$. (Middle) The 216 dataset for $l_{\max} = 8$. (Bottom) The 316 dataset for $l_{\max} = 8$.

4.1.2 PES Function

In order to determine the best value of $l_{\max}$ to set as the maximum, one is faced with several considerations. For too *large* an $l_{\max}$ value, one will have more fit functions than data points. The fit PES will, as a result, pass through all *ab initio* points perfectly, but will exhibit unphysical oscillations at points in between. On the other hand, with too *small* an $l_{\max}$, the fit will be smooth, but will not do an adequate job of reproducing the *ab initio* points. Provided that a sufficient number of *ab initio* points have been included, the “best” choice of $l_{\max}$ should exhibit only small changes to the PES when incremented or decremented.

Since it is most accurate in the dynamically relevant region, we begin with the 216 PES. Specifically, a convergence test was applied to the 216 dataset for $l_{\max} = 6, 8$, and 10. The three resultant PES's are indicated in Fig. 4.2. As expected very large discrepancies can be observed in the high-energy regions, with the $l_{\max} = 10$ PES even turning around, unphysically in the polar regions. On the other hand in the dynamically relevant region the differences between $l_{\max} = 8$ and $l_{\max} = 10$ are very small, typically no larger than 10 cm^{-1} , as indicated in Fig. 4.3.

Figure 4.2: PESs for the 216 dataset, where spherical harmonic basis set is limited to : (Top) $l_{\max} = 6$; (Middle) $l_{\max} = 8$; (Bottom) $l_{\max} = 10$. [Left] Global PES, from which the barrier to rotation in θ can be obtained. [Right] Local PES, limited to the bottom 10% of the well ($\approx 2000 \text{ cm}^{-1}$).

Figure 4.3: Results of convergence test from the 216 PES. Specifically, the difference between the 216 PES functions where $l_{\max} = 8$ and $l_{\max} = 10$.

4.1.3 Azimuthal Barrier Heights and Reaction Profiles

In order to connect with previous model calculations on the H_2 rotational dynamics that only considered 1-D azimuthal motion ($\theta = \pi/2$ is fixed at the equator), in this section we discuss various 1-D azimuthal reaction profiles, generated from our 2-D PES's. To be clear, however, no such approximations are made in our QD calculations, for which the full 2-D PES's are always used. The 2-D PES's allow more variation in the method of creating reaction profiles, as is demonstrated by the plots in Fig. 4.4 [Left].

Figure 4.4: [Left] Reaction profiles comparing “slices” at $\theta = \pi/2$ (Yellow, solid), θ equal to the global minimum (Red, solid), and the MEP as a function of ϕ with θ held fixed (Blue, dashed). [Right] An in depth view of the snaking of the minimum of the PES, where the curves are defined as above. Circles represent the minima while squares the maxima (Top) The 100 PES. (Middle) The 216 PES. (Bottom) The 316 PES.

The obvious option is to “slice” the PES using the same $\theta = \pi/2$ value as was used in the 1-D models, i.e. $V(\pi/2, \phi)$. This should be used for comparison purposes. However, it becomes apparent by looking at the 100 dataset PES “slice” plot for $\theta = \pi/2$ (Fig. 4.4 [Left](Top)) that this selection can be problematic. While this reaction profile does maintain the doubly periodic π translation symmetry caused by H-H exchange, it is immediately apparent that this θ value at no point reaches 0 cm^{-1} . This indicates that the global minimum (i.e. the bottom of the well at 0 cm^{-1}) does not lie along this path, which leads to the conclusion that this choice is unlikely to provide reliable information regarding the barrier height.

The second option, to fix θ to the global minimum (in this case $\theta = 1.61477$ radians), has a different set of complications. While this method does go through the minimum, it does not exhibit doubly periodic symmetry. As the lack of symmetry means this method does not accurately model the known behavior of the H-H system, it can be concluded that this too is a problematic solution.

The final solution is to follow the minimum energy path (MEP), for which the value of θ necessarily changes with ϕ , as a manifestation of snaking. This method more accurately models what is expected of these reaction profile plots in that it is both doubly periodic and goes through the true global minimum. From this method we can extract the most reliable rotational barrier height, which can be found in Table 4.1.

Unlike the 100 PES, which does not have high resolution in the dynamically relevant region, the 216 PES can provide a better insight to the behavior within the desired energy range. Figure 4.4 [Left] (Middle) shows a consistency not found in the 100 PES in that all three reaction profiles—the two θ “slices,” and the MEP—look similar. Indeed the two slice plots are virtually indistinguishable, owing to the fact that the equilibrium

Table 4.1: Minimum energy path barrier heights for various PESs: 100, 216, 316, b216/316, and f198

PES	Barrier Height (cm ⁻¹)
100	248.117
216	315.450
316	341.431
b216/316	315.451
f198	440.410

$\theta = 1.57151$ is very close to $\theta = \pi/2$.

The 316 PES for all three reaction profiles is much closer to the 216 PES than the 100 PES, as desired. The slices have a uniformity reminiscent of dataset 216 with the paths for $\theta = \pi/2$ and $\theta = 1.57031$ also being indistinguishable from each other. On the other hand, the 316 PES shows more deviation in the MEP reaction profile of the 216 PES. To understand these trends, one must examine the respective MEPs themselves, indicated in the right side of Fig. 4.4. From the figure, all three PESs exhibit substantial snaking (deviation in θ), on the order of 5° . However, the details vary significantly from PES to PES indicating a sensitive dependence upon the PES function utilized, and therefore a dependence on the number and choice of *ab initio* points.

For example the blue circles represent the minimum geometry of the PES. The position of this minimum corresponds to a near extremal θ value for the 100 PES, but for 216 and 316 lies very close to $\pi/2$. Of particular note is the range of the snaking for the various PESs. The 100 PES sees snaking in a range of about 0.1 Radians (or $\approx 6^\circ$). The 216 PES sees a slightly tighter range of 0.06 Radians ($\approx 3.5^\circ$). Upon analysis the 316 PES, which from the reaction profile plots on the left should echo the behavior of the 216 PES in this particular energy range, has the same range as the 100 PES. This discrepancy indicates that the snaking behavior, like the barrier height itself, is sensitively dependent on the

PES. Thus, whereas the amount of snaking is fairly consistent, the details vary from PES to PES. An additional point of interest is the symmetry of the snaking path that arises due to the permutation symmetry of the dihydrogen ligand. This is a *translational* symmetry, but not a *reflection* symmetry. Indeed, all reaction profiles are found to be highly asymmetric with respect to reflection. This effect, probably due to steric interactions, has not been much considered in prior calculations.

4.1.4 Blended PES Function: b216/316

While datasets 216 and 316 both produce consistent behavior in the low energy range, the results do show significant differences. This has motivated the development of a blended PES function that could adequately pull from both datasets to form a better global PES. The window function featured in chapter 3 can be seen in Fig. 4.5. The dashed line represents the range of influence of the 216 PES and has the greatest influence in the θ range that roughly corresponds to the lowest 10% of the PES well. Alternatively, the solid line represents the 316 PES that will be the dominant contribution outside of the θ range mentioned above. As a whole this forms the blended function b216/316.

Figure 4.5: Plot of the window functions, $\text{window}(\theta)$ (Red, dashed) and $[1-\text{window}(\theta)]$ (Blue, solid). This represents the weighting of the 216 and 316 PESs respectively as a function of θ .

Figure 4.6: (Left) Global PES for the blended function b216/316. (Right) b216/316 Local PES limited to the bottom 10% of the well for $l_{\max} = 8$.

Figure 4.6 illustrates the global b216/316 PES and this PES limited to $\approx 2000 \text{ cm}^{-1}$. By comparison with Fig. 4.1 we see that the full b216/316 PES is nearly identical to the 316 PES in the upper energy regime as is expected, but also practically identical to the 216 PES for the lowest energies. Further analysis provided in Fig. 4.7 allows for more comparisons between the blended function and that for data sets 216 and 316. The reaction profiles of the blended function closer resemble those of the 216 dataset in that the MEP reaction profile trends close to that of the minimum value for θ (1.5715 Radians) and $\pi/2$. By comparison with Fig. 4.4 it is clear that the blended function accomplished what was desired. Additionally, the MEP of the blended function is almost identical to that of the dataset 216. Taking in consideration the value of the barrier, 315.451 cm^{-1} , it becomes clear that the blended function favors the influence of 216 in the barrier and the snaking characteristics without losing consistency at higher energy states.

Figure 4.7: [Left] Reaction profile of the blended PES, b216/316 comparing “slices” as defined in Fig. 4.4. [Right] An in depth view of the snaking of the minimum of the b216/316 PES as defined in Fig. 4.4

To ensure the best blended fit, convergence tests were performed for different values of α and θ_0 . A sampling of these can be seen in Fig. 4.8. These plots feature the results of the α parameter convergence tests for the 2-D blended global PES. Overall, these plots are nearly identical with the exception of $\alpha = 15$ and $\alpha = 20$ (Fig. 4.8 [Bottom]) having a slightly higher discrepancy of 30 cm^{-1} range. This suggests that while the overall sensitivity of b216/316 to α is small, the “sweet spot” for α falls between $\alpha = 10$ and $\alpha = 20$. This study chose $\alpha = 15$ because it lies in the middle of the “sweet spot” range.

Further confirmation that the b216/316 PES converges as desired is displayed in Fig. 4.9, representing the difference PES b216/316 and either 216 PES or 316 PES, depending on θ . From this plot it is clear that the only errors occur around the points in which the blending is occurring and are limited to within 30 cm^{-1} .

Figure 4.8: Results of convergence test from the b216/316 PES. [Top] Difference between $\alpha = 10$ and $\alpha = 12$. [Middle] Difference between $\alpha = 12$ and $\alpha = 15$. [Bottom] Difference between $\alpha = 15$ and $\alpha = 20$.

Figure 4.9: Difference profile of the blended PES function b216/316 and either 216 PES or 316 PES depending on θ . Blending parameters are $\theta_o = 1.2$ and $\alpha = 15$.

Due to the method of blending the 216 and 316 PESs, it is difficult to do QD calculations with this dataset. While the integral shown in Sec. 3.3 allows other datasets to be handled analytically, b216/316 will need to be handled numerically. This was considered computationally expensive for this study, and as such further QD calculations on b216/316 will be featured in future work.

4.1.5 f198 “Frozen” PES

As described earlier, the purpose of the f198 dataset is to allow a better comparison to the results from crystal geometries. Figure 4.10 [Top] features both the full f198 PES (Left) and the limited f198 PES (Right). Analysis of the full f198 PES is very similar to that of the full global PES in figure 4.1 in that there is very little detail regarding the depth of the well to be gleaned aside from the polar angle (θ) barrier height. In comparison, however, it is clear that the θ rotational barrier height is roughly 5000 cm^{-1} above that for datasets 100 and 316.

In regards to the limited f198 PES it is clear that there is significantly more snaking than that of any of the previously discussed datasets. This implies significantly more (θ, ϕ) correlation than what is seen in the previous datasets. This could be attributed to the extra

motions needed to move around the pendant ligands frozen in place.

In comparison, the shape/features of the f198 profile plot are reminiscent of those of datasets 216 and 316 but show less uniformity though not to the extent of dataset 100. The discrepancy between the MEP, the minimum θ , and $\theta = \pi/2$, supports the concept of steric forces influencing the rotational barrier. Additionally, the f198 dataset also has a notably higher rotational barrier (see table 4.1) of 440 cm^{-1} (from MEP).

The MEP [Bottom] (Right) has far fewer features than that of any of the previous datasets, although the range of the snaking is reminiscent of that of the 100 PES and 316 PES. Additionally, it should be noted that the minima (represented as circles) deviate significantly from $\theta = \pi/2$ much like that of the 100 PES.

Figure 4.10: [Top] (Left) The f198 global PES (Right) f198 local PES. [Bottom] (Left) Reaction profiles for the F198 PES comparing “slices” as defined in Fig. 4.4. (Right) An in depth view of the snaking of the minimum of the f198 PES with the lines defined in Fig. 4.4).

4.2 Quantum Dynamics — Hamiltonian

Upon the completion of the electronic structure calculations, QD calculations were performed on the 216, 316, and f198 datasets. QD calculations were attempted on the b216/316 dataset; however, due to the window function used in its construction QD calculations require numerical integration of the potential energy matrix elements, rather than the analytic formula of Eq. 3.5. This numerical integration was too costly in our simple implementation, and so this will be set aside for future work. For each PES, an even and odd Hamiltonian matrix (corresponding to para-H₂ and ortho-H₂ respectively) was constructed (Fig. 4.11 for visual representation). From these matrices the eigenstates were tested for convergence for a varied range of l_{MAX} values to determine the “best” choice for basis set size. Next, the eigenvectors for this “best” choice Hamiltonian were extracted and used to construct wavefunction density plots. The even and odd wavefunction density plots were combined and ordered by increasing librational frequencies. These density plots were then labeled (see Appendix C) by excitations in θ and ϕ , as will be discussed in Sec. 4.3.

Figure 4.11: Plot of the even rotational quantum dynamics Hamiltonian matrix for the f198 PES

4.2.1 Eigenstates

Table 4.2 reports the eigenstate findings for the 216, 316, and f198 PESs, including the even or odd matrix origins, the number of polar excitations and azimuthal excitations, as well as the librational frequencies up to $\approx 2000 \text{ cm}^{-1}$. While the assigned (n_θ, n_ϕ) labels are identical to each other across all three PESs, it is clear that the 216 PES and 316 PES are essentially the same (i.e. energy eigenvalues within 5 cm^{-1} below 2000 cm^{-1}). In regards to the f198 frequencies, it should be noted that while the first excitation is lower in energy, it maintains a trend of higher frequencies overall. It is evident that the 216 and 316 are in strong agreement in the lower energy regime, as they were for the PES results in Sec. 4.1.3. The basis sets used for these values correspond to $l_{\text{MAX}} = 20$ and $l_{\text{MAX}} = 19$.

Tables 4.3 and 4.4 contain the convergence data for the 216 PES eigenstate calculations, for even and odd (respectively) eigenstates up to $\approx 7000 \text{ cm}^{-1}$. The convergence for the other PESs is similar. It is evident that by $l_{\text{MAX}} = 20$ and $l_{\text{MAX}} = 19$ the eigenstates have converged at least up to 6000 cm^{-1} to within an accuracy of around 0.01 cm^{-1} . As this goes well beyond the energetic region of interest ($\approx 2000 \text{ cm}^{-1}$) it is clear that this selection of basis sets is sufficient for further analysis. The even basis set that corresponds to $l_{\text{MAX}} = 20$ results in 231 functions, whereas the odd basis set corresponding $l_{\text{MAX}} = 19$ results in 210 functions.

Table 4.2: Eigenstates for the 216, 316, and f198 PESs. Columns I indicate even (e) or odd (o) matrix origins. In columns II, state labels are reported, where n_θ is the number of polar excitations, and n_ϕ is the number of azimuthal excitations [i.e. (n_θ, n_ϕ)]. Columns III report librational frequencies (up to $\approx 2000 \text{ cm}^{-1}$), relative to the computed rotational ground state energy level. Zero point energies (ZPEs) (a) 1106.05 cm^{-1} (b) 1146.43 cm^{-1} (c) 1254.51 cm^{-1}

(a) 216			(b) 316			(c) f198		
I	II	III	I	II	III	I	II	III
e1	(0,0)	0	e1	(0,0)	0.	e1	(0,0)	0.
o1	(0,1)	31.1498	o1	(0,1)	32.7009	o1	(0,1)	19.6867
o2	(0,1)	158.556	o2	(0,1)	153.292	o2	(0,1)	207.313
e2	(0,2)	316.679	e2	(0,2)	313.32	e2	(0,2)	338.797
e3	(0,2)	363.356	e3	(0,2)	359.863	e3	(0,2)	410.735
o3	(0,3)	714.981	o3	(0,3)	711.339	o3	(0,3)	744.235
o4	(0,3)	721.542	o4	(0,3)	718.929	o4	(0,3)	751.543
e4	(0,4)	1246.73	e4	(0,4)	1243.59	e4	(0,4)	1269.35
e5	(0,4)	1255.57	e5	(0,4)	1252.32	e5	(0,4)	1283.61
o5	(0,5)	1936.6	o5	(0,5)	1933.32	o5	(0,5)	1958.13
o6	(0,5)	1937.46	o6	(0,5)	1933.85	o6	(0,5)	1960.4
o7	(1,0)	2019.33	o7	(1,0)	2043.73	o7	(1,0)	2283.39

Table 4.3: The even eigenstate convergence for the 216 PES. For each eigenstate energy level up to around 7000 cm^{-1} , the difference between the $l_{\text{MAX}} = 20$ and $l_{\text{MAX}} = 16$ calculations is reported in column III (in cm^{-1}). In column IV, we report librational frequencies, relative to the computed rotational ground state energy level ZPE of 1106.05 cm^{-1} . In column II, state labels are reported, where n_θ is the number of polar excitations, and n_ϕ is the number of azimuthal excitations. It should be noted that A^* and A^{**} are the result of a Fermi resonance and can only be loosely labeled as $A^*=(1,3)$ and $A^{**}=(0,6)$.

Label	(n_θ, n_ϕ)	Convergence	Librational Frequency
e1	(0,0)	-0.0000197615	0
e2	(0,2)	-0.0000139728	316.679
e3	(0,2)	-0.0000149708	363.356
e4	(0,4)	-0.0000403214	1246.73
e5	(0,4)	-0.0000404212	1255.57
e6	(1,1)	-0.000328061	2057.48
e7	(1,1)	-0.000146315	2177.38
e8	(A^*, A^*)	-0.000177354	2759.86
e9	(A^*, A^*)	-0.000185439	2760.69
e10	(A^{**}, A^{**})	-0.000239134	2802.81
e11	(A^{**}, A^{**})	-0.000265682	2803.7
e12	(2,0)	-0.00186037	4043.64
e13	(1,5)	-0.00077479	4099.03
e14	(1,5)	-0.000769201	4099.57
e15	(2,2)	-0.00192505	4414.99
e16	(2,2)	-0.00186546	4441.68
e17	(0,8)	-0.000445632	4908.87
e18	(0,8)	-0.000446031	4908.88
e19	(2,4)	-0.0041555	5489.18
e20	(2,4)	-0.00407017	5495.11
e21	(1,7)	-0.00310365	6063.55
e22	(1,7)	-0.00306064	6063.7
e23	(1,3)	-0.0131518	6151.34
e24	(1,3)	-0.0100938	6262.24

Table 4.4: The odd eigenstate convergence for the 216 PES. For each eigenstate energy level up to around 7000 cm^{-1} , the difference between the $l_{\text{MAX}} = 19$ and $l_{\text{MAX}} = 13$ calculations is reported in column III (in cm^{-1}). In column IV, we report rotational frequencies, relative to the computed rotational ground state energy level ZPE of 1106.05 cm^{-1} . In column II, state labels are reported, where n_θ is the number of polar excitations, and n_ϕ is the number of azimuthal excitations.

Label	(n_θ, n_ϕ)	Convergence	Librational Frequency
o1	(0,1)	-0.00161495	31.1498
o2	(0,1)	-0.00099047	158.556
o3	(0,3)	-0.00214452	714.981
o4	(0,3)	-0.00186027	721.542
o5	(0,5)	-0.00575758	1936.6
o6	(0,5)	-0.0057453	1937.46
o7	(1,0)	-0.020833	2019.33
o8	(1,2)	-0.0251566	2360.92
o9	(1,2)	-0.0240899	2396.47
o10	(1,4)	-0.0588633	3357.28
o11	(1,4)	-0.0578615	3364.48
o12	(0,7)	-0.0305127	3767.95
o13	(0,7)	-0.0304536	3768.
o14	(2,1)	-0.222436	4089.42
o15	(2,1)	-0.205525	4204.93
o16	(2,3)	-0.363512	4863.15
o17	(2,3)	-0.387446	4869.27
o18	(1,6)	-0.255113	5006.28
o19	(1,6)	-0.256882	5006.32
o20	(3,0)	-1.60306	6096.97
o21	(0,9)	-0.265208	6200.64
o22	(0,9)	-0.265158	6200.64
o23	(2,5)	-1.27981	6288.35
o24	(2,5)	-1.27748	6288.72

4.3 Analysis of the Wavefunction Density Plots

With the eigenstate convergence test confirming that the basis size is sufficient, further calculations were done to construct wavefunction density plots. The even and odd plots for a PES were combined and ranked by frequency labeled for excitations in θ and ϕ and further analyzed for interesting “quirks” and discrepancies among PESs.

Figure 4.12 shows the ground state and first two excitations in ϕ for the 216 PES (Left) and 316 PES (Right). It should be noted that ϕ excitations results in additional pairs being added due to ϕ 's periodic symmetry, as illustrated in Fig. 4.13. It should be noted that the ground state and the 1st excited state are paired through tunneling splitting while the 1st and 2nd excited state are paired through (free rotor) $\pm m$ degeneracy. Additionally, Fig. 4.14 shows the ground state and first two excitations in θ for the 216 PES, where the excitations in θ result in a single additional row of peaks. It should be noted that ϕ nodes are clearly absent for states with no excitation in ϕ .

These plots are needed to identify the correct energy levels needed to extract the librational tunneling splittings. Table 4.5 compares the lowest three rotational frequencies as computed using the 216, 316, and f198 PESs. Also listed are the values previously obtained through experiment for crystal structure geometries.³² As expected, comparing the results from the gas phase calculations to those of a crystal structure reveal some discrepancies. While, the f198 PES results, though only simulating the condensed phase geometry, are more in line with experiment for the ground state, the remaining frequencies are far greater. This suggests that the majority of disagreement between the theoretical calculations and the experimental values arise primarily from the different geometries.

Figure 4.12: Wavefunction density plots featuring the ground state (Top) and the first two excited states (i.e. excitations in ϕ) (Middle) and (Bottom) respectively. [Left] 216 PES.[Right] 316 PES

Figure 4.13: f198 PES wavefunction density plots featuring states 1-6, where “o” and “e” signify if the state originates from the even or odd Hamiltonian matrix. (A) e1, (B) o1, (C) o2, (D) e2, (E) e3, (F) o3

Figure 4.14: Wavefunction density plots featuring the ground state and the first two excitations in θ . [Left] Ground state (e1). [Right] 1st excitation (o7). Frequency = 2017.33 [Bottom] 2nd excitation (e12). Frequency = 3767.95 cm^{-1} .

Table 4.5: A comparison of librational tunneling frequencies [in (cm^{-1})], where $0 \rightarrow 1$ indicates the excitation from the ground state to the 1st excited state etc. Column II: previous results from J. Eckert et al in 1990.³²

Transition	Eckert et al	216 PES	316 PES	f198 PES
$0 \rightarrow 1$	6.4	31	33	19
$0 \rightarrow 2$	170	159	153	207
$0 \rightarrow 3$	252	317	313	339

Furthermore, this study is able to glean excited state tunneling splittings through the same method. Table 4.6 allows a comparison between the ground state tunneling splitting and the θ -excited state tunneling splittings. It is clear that the f198 PES tunneling splittings remain smaller than those of the 216 and 316 PESs. Additionally, the excited

Table 4.6: A comparison of excited state librational tunneling splitting [in (cm^{-1})], where $(1,0) \rightarrow (1,1)$ indicates the excitation from the first state to the second state etc.

Transition	216 PES	316 PES	f198 PES
$(0,0) \rightarrow (0,1)$	31	33	19
$(1,0) \rightarrow (1,1)$	38	40	24
$(2,0) \rightarrow (2,1)$	46	50	30
$(3,0) \rightarrow (3,1)$	54	—	—

state tunneling splittings, while increasing, remain within the range of 30 to 60 cm^{-1} . All in all, f198 does the best job of predicting the experimental ground state tunneling splitting, as expected. However, it also clearly does worse for the 2nd and 3rd excited state frequencies, as compared with the 216 PES and 316 PES.

At higher energies, the PESs disagree vis-à-vis the order of state labels. Table 4.7 shows such discrepancies between the 216, 316, and f198 PESs. A few discrepancies occur when one pair of eigenstates is displaced for one PES relative to another, such as for the 216 PES states of (5,1), where the (n_θ, n_ϕ) notation indicates the number of excitations in (θ, ϕ) . Other discrepancies occur in a complete reordering of excitations. This can be seen in for the (8,0) state, which 216 PES this excitation occur after the (2,3) excitation, whereas, in the 316 PES it occurs before the (2,3) excitation and before the (2,2) excitation in the f198 PES.

Table 4.7: Comparison of the (n_θ, n_ϕ) state labels for the 216, 316, and f198 PESs where columns are defined as in Table 4.2. The complete state labels can be found in Appendix C.

216			316			f198		
I	II	III	I	II	III	I	II	III
o9	(1,2)	2396.47	o9	(1,2)	2417.07	o9	(1,2)	2700.16
e8	(A*,A*)	2759.86	e8	(A**,A**)	2762.54	e8	(0,6)	2794.18
e9	(A**,A**)	2760.69	e9	(A*,A*)	2763.81	e9	(0,6)	2794.45
e10	(A*,A*)	2802.81	e10	(A**,A**)	2814.03	e10	(1,3)	3068.47
e11	(A**,A**)	2803.7	e11	(A*,A*)	2818.87	e11	(1,3)	3073.23
o10	(1,4)	3357.28	o10	(1,4)	3375.4	o10	(1,4)	3630.54
o11	(1,4)	3364.48	o11	(1,4)	3384.06	o11	(1,4)	3642.52
o12	(0,7)	3767.95	o12	(0,7)	3764.07	o12	(0,7)	3781.11
o13	(0,7)	3768.	o13	(0,7)	3764.1	o13	(0,7)	3781.13
e12	(2,0)	4043.64	e12	(B*,B*)	4108.36	e12	(1,5)	4364.75
o14	(2,1)	4089.42	e13	(1,5)	4117.84	e13	(1,5)	4366.43
e13	(1,5)	4099.03	e14	(B*,B*)	4120.83	e14	(2,0)	4591.11
e14	(1,5)	4099.57	o14	(2,1)	4158.06	o14	(2,1)	4620.86
o15	(2,1)	4204.93	o15	(2,1)	4269.55	o15	(2,1)	4795.67
e15	(2,2)	4414.99	e15	(2,2)	4473.72	e15	(0,8)	4918.71
e16	(2,2)	4441.68	e16	(2,2)	4512.35	e16	(0,8)	4918.79
o16	(2,3)	4863.15	e17	(0,8)	4904.7	e17	(2,2)	4971.61
o17	(2,3)	4869.27	e18	(0,8)	4904.71	e18	(2,2)	5019.48
e17	(0,8)	4908.87	o16	(2,3)	4928.63	o16	(1,6)	5255.38
e18	(0,8)	4908.88	o17	(2,3)	4941.81	o17	(1,6)	5255.53
o18	(1,6)	5006.28	o18	(1,6)	5018.32	o18	(2,3)	5423.37
o19	(1,6)	5006.32	o19	(1,6)	5018.36	o19	(2,3)	5427.6
e19	(2,4)	5489.18	e19	(2,4)	5553.31	e19	(2,4)	6027.24
e20	(2,4)	5495.11	e20	(2,4)	5561.19	e20	(2,4)	6037.46
e21	(1,7)	6063.55	e21	(1,7)	6076.29	o20	(0,9)	6207.24
e22	(1,7)	6063.7	e22	(1,7)	6076.41	o21	(0,9)	6207.24
o20	(3,0)	6096.97	o20	(3,0)	6175.85	e21	(1,7)	6305.17
e23	(1,3)	6151.34	o21	(0,9)	6196.34	e22	(1,7)	6305.2

Occasionally, it is possible to have state pairs that sort of “blur” together due to being close in energy to each other. This occurs for the 216 and 316 PESs and can be seen in the wavefunction density plots. Figure 4.15 shows how this appeared in this study. These

plots do not maintain the same type of rigid patterning for θ and ϕ excitations as had been perviously noted. Instead it seems as if the peaks bleed together in the θ direction causing it to be difficult to attribute a specific excitation to a particular plot. Of course, these are the tell-tale hallmarks of a Fermi resonance. In this case, it is possible from examining the plots to extract that there are 12 peaks total. In the θ direction it is known that an excitation will result in adding only one peak. It is equally clear that (due to symmetry) a ϕ excitation results in 2 peaks. Additional information can be gleaned from the surrounding states to determine which states are unaccounted for. In this case, the states (3,1) and (1,6) were unaccounted for. While identifying which states are “blurring” together is rather facile, it is not trivial to assign these states uniquely. These states were assigned based largely on how apparent the θ excitation could be seen.

While the 216 and 316 PESs share the above mentioned Fermi resonance, the 316 PES also has one additional Fermi resonance occurring between the (3,0) state and the second (1,5) state. As stated previously, the 316 is considerably more accurate in the higher energy regime. Thus, this suggests that this further Fermi resonance should be further investigated. Additionally, the lack of Fermi resonance in the f198 PES suggests that the presence of a Fermi resonance is sensitively dependent on the original PES.

Figure 4.15: 216 wavefunction density plots featuring Fermi resonance. A* denotes the (3,1) state. A** denotes the (1,6) state. [Top Left] 216 e8 wavefunction density plot. [Top Right] 216 e9 wavefunction density plot. [Bottom Left] 216 e10 wavefunction density plot. [Bottom Right] 216 e11 wavefunction density plot.

CHAPTER 5

CONCLUDING REMARKS

This study initially performed 2-D electronic structure and QD calculations on datasets consisting of 100, 216, and 316 *ab initio* points, followed by further calculations on a “blended” b216/316 PES (electronic structure only) and f198 “frozen” PES. From these calculations it can be concluded through the presence of “snaking” that there is obvious θ - ϕ correlation suggesting that both rotational d.o.f.s do matter. However, it is difficult to put too much faith in specific features, considering the sensitivity that these have to various parameters. Additionally, these 2-D calculations, specifically the reaction profile plots, make it clear that previous 1-D models fail to accurately capture the full scope of the PES. The presence of Fermi resonances just under 3000 cm^{-1} (and $\approx 4000\text{ cm}^{-1}$ for the 316 PES) is a sign of coupling and presents an interesting avenue for future research, particularly as this energy regime coincides with the first *stretch* excitation. This Fermi resonance is also interesting because of its absence within the f198 calculations. Furthermore, the shifting in state labels between the 216, 316, and f198 datasets also indicates couplings.

The success of these calculations indicate that a 2-D QD study is possible for other related molecules while also providing the basis for expanding this study. Future work should include QD calculations on the b216/316 PES. The numerical integration that presented issues for this study could potentially be handled through the use of quadrature. The delocalized wavefunctions indicate that a four atom (H_2 , H, H) study could be computationally possible. Future studies should also look at utilizing crystal geometries and could possibly take into account the influence of cells though, as stated in the

introduction, this may be currently outside the realm of what is technologically possible.

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APPENDIX A

PES DATA

Table A.1: Dataset for the 216 PES

θ	ϕ	Energy (cm^{-1})	θ	ϕ	Energy (cm^{-1})
1.01362	0.	4373.21	1.91858	1.5708	1696.78
1.10301	0.	3143.89	1.99309	1.5708	2446.06
1.1924	0.	2140.16	1.25646	1.74533	1661.35
1.2818	0.	1362.95	1.33018	1.74533	1087.91
1.37119	0.	794.354	1.40391	1.74533	635.336
1.46058	0.	434.495	1.47763	1.74533	328.758
1.54997	0.	295.933	1.55136	1.74533	170.513
1.63937	0.	370.007	1.62508	1.74533	165.731
1.72876	0.	665.541	1.69881	1.74533	308.615
1.81815	0.	1176.91	1.77253	1.74533	604.753
1.90754	0.	1902.36	1.84626	1.74533	1051.66
1.01754	0.174533	4318.99	1.91999	1.74533	1643.85
1.10627	0.174533	3095.99	1.99371	1.74533	2393.46
1.195	0.174533	2102.56	1.2635	1.91986	1681.7
1.28373	0.174533	1320.17	1.33877	1.91986	1075.11
1.37247	0.174533	747.762	1.41403	1.91986	618.369
1.4612	0.174533	381.635	1.4893	1.91986	311.754
1.54993	0.174533	226.325	1.56457	1.91986	160.851
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Table A.1 – continued from previous page

θ	ϕ	Energy (cm ⁻¹)	θ	ϕ	Energy (cm ⁻¹)
1.63866	0.174533	287.358	1.63983	1.91986	168.918
1.7274	0.174533	570.852	1.7151	1.91986	337.066
1.81613	0.174533	1072.37	1.79037	1.91986	665.264
1.90486	0.174533	1786.91	1.86563	1.91986	1152.29
1.0278	0.349066	4151.69	1.9409	1.91986	1811.59
1.11678	0.349066	2940.33	2.01616	1.91986	2607.86
1.20577	0.349066	1952.49	1.27085	2.0944	1677.3
1.29475	0.349066	1181.53	1.34891	2.0944	1054.95
1.38374	0.349066	622.763	1.42698	2.0944	596.212
1.47272	0.349066	277.08	1.50504	2.0944	300.645
1.5617	0.349066	143.433	1.58311	2.0944	172.563
1.65069	0.349066	234.192	1.66118	2.0944	220.942
1.73967	0.349066	544.566	1.73924	2.0944	437.674
1.82866	0.349066	1075.98	1.81731	2.0944	826.606
1.91764	0.349066	1816.65	1.89537	2.0944	1373.05
1.04825	0.523599	3824.39	1.97344	2.0944	2127.39
1.14009	0.523599	2620.93	2.0515	2.0944	3036.88
1.23194	0.523599	1655.27	1.27546	2.26893	1691.61
1.32379	0.523599	920.091	1.35667	2.26893	1053.54
1.41564	0.523599	411.57	1.43789	2.26893	590.609
1.50749	0.523599	133.692	1.51911	2.26893	308.365
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Table A.1 – continued from previous page

θ	ϕ	Energy (cm ⁻¹)	θ	ϕ	Energy (cm ⁻¹)
1.59934	0.523599	87.5025	1.60033	2.26893	216.925
1.69119	0.523599	282.867	1.68154	2.26893	297.427
1.78304	0.523599	709.618	1.76276	2.26893	549.552
1.87489	0.523599	1368.62	1.84398	2.26893	1031.41
1.96674	0.523599	2261.91	1.9252	2.26893	1687.91
1.08022	0.698132	3358.53	2.00641	2.26893	2511.33
1.17558	0.698132	2185.84	2.08763	2.26893	3543.64
1.27094	0.698132	1273.71	1.27241	2.44346	1750.44
1.36631	0.698132	609.931	1.35666	2.44346	1091.06
1.46167	0.698132	191.528	1.4409	2.44346	618.125
1.55703	0.698132	29.7486	1.52514	2.44346	335.549
1.65239	0.698132	124.153	1.60938	2.44346	253.595
1.74775	0.698132	473.171	1.69363	2.44346	375.393
1.84312	0.698132	1072.57	1.77787	2.44346	694.143
1.93848	0.698132	1920.54	1.86211	2.44346	1185.25
2.03384	0.698132	3022.97	1.94635	2.44346	1898.82
1.12164	0.872665	2806.1	2.03059	2.44346	2815.84
1.21674	0.872665	1749.89	2.11484	2.44346	3954.79
1.31184	0.872665	938.533	1.26041	2.61799	1826.89
1.40693	0.872665	403.126	1.34727	2.61799	1162.77
1.50203	0.872665	65.4609	1.43413	2.61799	672.348
Continued on next page					

Table A.1 – continued from previous page

θ	ϕ	Energy (cm ⁻¹)	θ	ϕ	Energy (cm ⁻¹)
1.59713	0.872665	10.6854	1.52099	2.61799	374.282
1.69223	0.872665	210.106	1.60785	2.61799	290.301
1.78732	0.872665	667.462	1.69471	2.61799	394.498
1.88242	0.872665	1372.64	1.78157	2.61799	731.411
1.97752	0.872665	2320.56	1.86844	2.61799	1273.11
2.07261	0.872665	3522.27	1.9553	2.61799	2049.08
1.1662	1.0472	2282.67	2.04216	2.61799	3019.18
1.25689	1.0472	1391.72	2.12902	2.61799	4195.81
1.34758	1.0472	707.663	1.24505	2.79253	1928.53
1.43827	1.0472	261.972	1.33376	2.79253	1206.78
1.52897	1.0472	31.2213	1.42247	2.79253	697.624
1.61966	1.0472	38.3369	1.51118	2.79253	388.611
1.71035	1.0472	278.993	1.59989	2.79253	310.265
1.80104	1.0472	753.947	1.68859	2.79253	423.268
1.89174	1.0472	1513.87	1.7773	2.79253	760.609
1.98243	1.0472	2366.09	1.86601	2.79253	1316.65
2.07312	1.0472	3516.31	1.95472	2.79253	2081.33
1.20513	1.22173	1924.4	2.04342	2.79253	3073.05
1.28938	1.22173	1164.99	2.13213	2.79253	4301.51
1.37363	1.22173	600.652	1.23491	2.96706	1969.51
1.45789	1.22173	228.485	1.32444	2.96706	1233.87
Continued on next page					

Table A.1 – continued from previous page

θ	ϕ	Energy (cm ⁻¹)	θ	ϕ	Energy (cm ⁻¹)
1.54214	1.22173	79.0721	1.41397	2.96706	710.477
1.62639	1.22173	81.2083	1.50351	2.96706	405.843
1.71065	1.22173	303.213	1.59304	2.96706	312.208
1.7949	1.22173	753.863	1.68257	2.96706	442.683
1.87915	1.22173	1344.51	1.7721	2.96706	786.714
1.9634	1.22173	2153.61	1.86164	2.96706	1366.89
2.04766	1.22173	3151.61	1.95117	2.96706	2118.9
1.23239	1.39626	1715.51	2.0407	2.96706	3116.14
1.31062	1.39626	1064.8	2.13023	2.96706	4349.19
1.38886	1.39626	603.919	1.	0.	4577.1
1.46709	1.39626	277.668	1.	0.174533	4588.99
1.54532	1.39626	98.5002	1.	0.349066	4574.28
1.62356	1.39626	130.306	1.	0.523599	4551.67
1.70179	1.39626	317.323	1.	0.698132	4536.15
1.78003	1.39626	661.517	1.	0.872665	4549.5
1.85826	1.39626	1197.76	1.	1.0472	4561.17
1.9365	1.39626	1886.22	1.	1.22173	4585.45
2.01473	1.39626	2741.83	1.	1.39626	4655.94
1.24791	1.5708	1660.39	1.	1.5708	4760.09
1.32243	1.5708	1077.57	1.	1.74533	4677.86
1.39695	1.5708	611.015	1.	1.91986	4993.65
Continued on next page					

Table A.1 – continued from previous page

θ	ϕ	Energy (cm^{-1})	θ	ϕ	Energy (cm^{-1})
1.47146	1.5708	316.595	1.	2.0944	5082.38
1.54598	1.5708	154.462	1.	2.26893	5174.76
1.6205	1.5708	158.683	1.	2.44346	5149.77
1.69502	1.5708	312.54	1.	2.61799	5125.96
1.76954	1.5708	619.779	1.	2.79253	5063.04
1.84406	1.5708	1077.75	1.	2.96706	4977.64

Table A.2: dataset for the 316 PES

θ	ϕ	Energy (cm^{-1})	θ	ϕ	Energy (cm^{-1})
1.5329	-1.5708	112.299	1.40693	0.872665	364.109
1.53476	-1.25646	124.097	1.50203	0.872665	26.4443
1.54014	-0.942167	167.105	1.59713	0.872665	-28.3311
1.54853	-0.628008	226.633	1.69223	0.872665	171.089
1.55909	-0.31398	302.92	1.78732	0.872665	628.446
1.5708	-0.0000318335	278.129	1.88242	0.872665	1333.62
1.58251	0.313916	150.761	1.97752	0.872665	2281.54
1.59307	0.627945	21.8447	2.07261	0.872665	3483.25
1.60146	0.942104	-14.0011	1.1662	1.0472	2243.65
1.60684	1.25639	50.0642	1.25689	1.0472	1352.7
1.5329	-1.5708	112.432	1.34758	1.0472	668.646
1.43898	-1.26983	258.23	1.43827	1.0472	222.956
1.35705	-0.961834	632.909	1.52897	1.0472	-7.7953
1.29527	-0.644217	1123.4	1.61966	1.0472	-0.679634
1.26049	-0.317956	1596.8	1.71035	1.0472	239.976
1.25691	0.0122715	1836.32	1.80104	1.0472	714.93
1.28498	0.339931	1645.49	1.89174	1.0472	1474.85
1.34126	0.659701	1152.78	1.98243	1.0472	2327.08
1.41938	0.96973	635.824	2.07312	1.0472	3477.29
1.51138	1.27192	279.318	1.20513	1.22173	1885.39
1.5329	-1.5708	112.512	1.28938	1.22173	1125.97
Continued on next page					

Table A.2 – continued from previous page

θ	ϕ	Energy (cm^{-1})	θ	ϕ	Energy (cm^{-1})
1.35154	-1.3118	622.469	1.37363	1.22173	561.635
1.18547	-1.03195	1921.31	1.45789	1.22173	189.468
1.05017	-0.71595	3694.97	1.54214	1.22173	40.0556
0.963939	-0.35776	5295.76	1.62639	1.22173	42.1917
0.943036	0.0274737	6019.74	1.71065	1.22173	264.197
0.992156	0.405085	5452.33	1.7949	1.22173	714.846
1.10078	0.746373	3902.51	1.87915	1.22173	1305.49
1.25077	1.04604	2097.75	1.9634	1.22173	2114.59
1.4248	1.3153	667.	2.04766	1.22173	3112.6
1.5329	-1.5708	117.31	1.23239	1.39626	1676.5
1.28093	-1.38011	1089.21	1.31062	1.39626	1025.78
1.04048	-1.15873	3648.18	1.38886	1.39626	564.903
0.828101	-0.869058	7310.99	1.46709	1.39626	238.651
0.675251	-0.463873	10799.8	1.54532	1.39626	59.4836
0.629337	0.0520417	12364.	1.62356	1.39626	91.2891
0.711854	0.543684	11035.	1.70179	1.39626	278.306
0.88696	0.910309	7673.98	1.78003	1.39626	622.5
1.11013	1.1748	3958.49	1.85826	1.39626	1158.74
1.35532	1.38375	1208.28	1.9365	1.39626	1847.21
1.5329	-1.5708	115.235	2.01473	1.39626	2702.81
1.23483	-1.46948	1487.57	1.24791	1.5708	1621.37
Continued on next page					

Table A.2 – continued from previous page

θ	ϕ	Energy (cm ⁻¹)	θ	ϕ	Energy (cm ⁻¹)
0.940684	-1.34404	5201.64	1.32243	1.5708	1038.55
0.65817	-1.14971	10725.8	1.39695	1.5708	571.999
0.413925	-0.751342	16422.8	1.47146	1.5708	277.579
0.316391	0.11598	19165.3	1.54598	1.5708	115.446
0.468712	0.862352	16850.7	1.6205	1.5708	119.667
0.727846	1.1855	11206.5	1.69502	1.5708	273.523
1.01457	1.35523	5578.08	1.76954	1.5708	580.762
1.31018	1.47179	1638.15	1.84406	1.5708	1038.73
1.5329	-1.5708	112.668	1.91858	1.5708	1657.76
1.21878	-1.57078	1658.97	1.99309	1.5708	2407.04
0.904614	-1.57077	5896.34	1.25646	1.74533	1622.34
0.590451	-1.57074	12295.4	1.33018	1.74533	1048.9
0.27629	-1.57067	19184.4	1.40391	1.74533	596.319
0.0378707	1.56978	23230.8	1.47763	1.74533	289.741
0.352029	1.57069	19794.9	1.55136	1.74533	131.497
0.666186	1.57074	12847.9	1.62508	1.74533	126.715
0.980342	1.57076	6337.95	1.69881	1.74533	269.598
1.2945	1.57078	1907.48	1.77253	1.74533	565.737
1.5329	-1.5708	112.551	1.84626	1.74533	1012.64
1.23482	-1.6721	1521.77	1.91999	1.74533	1604.83
0.940667	-1.79751	5349.76	1.99371	1.74533	2354.44
Continued on next page					

Table A.2 – continued from previous page

θ	ϕ	Energy (cm ⁻¹)	θ	ϕ	Energy (cm ⁻¹)
0.65814	-1.9918	10975.5	1.2635	1.91986	1642.68
0.413871	-2.39014	16846.7	1.33877	1.91986	1036.1
0.316316	3.02558	16851.	1.41403	1.91986	579.353
0.468661	2.27912	17453.4	1.4893	1.91986	272.737
0.727815	1.95601	11616.	1.56457	1.91986	121.834
1.01455	1.78631	5859.69	1.63983	1.91986	129.901
1.31017	1.66977	1735.24	1.7151	1.91986	298.05
1.5329	-1.5708	112.224	1.79037	1.91986	626.247
1.28092	-1.76147	1163.55	1.86563	1.91986	1113.27
1.04045	-1.98283	3851.69	1.9409	1.91986	1772.57
0.828054	-2.27249	7608.51	2.01616	1.91986	2568.84
0.675186	-2.67768	11235.4	1.27085	2.0944	1638.28
0.629264	3.08954	12933.2	1.34891	2.0944	1015.93
0.711789	2.59786	11314.5	1.42698	2.0944	557.196
0.886911	2.23123	8295.91	1.50504	2.0944	261.628
1.11009	1.96675	4303.6	1.58311	2.0944	133.546
1.3553	1.75782	1395.81	1.66118	2.0944	181.925
1.5329	-1.5708	112.256	1.73924	2.0944	398.658
1.35152	-1.82978	680.117	1.81731	2.0944	787.589
1.18544	-2.10962	2060.67	1.89537	2.0944	1334.03
1.05012	-2.42562	3899.36	1.97344	2.0944	2088.38
Continued on next page					

Table A.2 – continued from previous page

θ	ϕ	Energy (cm ⁻¹)	θ	ϕ	Energy (cm ⁻¹)
0.963872	-2.78382	5583.19	2.0515	2.0944	2997.87
0.942963	3.11411	6416.42	1.27546	2.26893	1652.59
0.992087	2.73648	6029.59	1.35667	2.26893	1014.53
1.10072	2.39519	4517.65	1.43789	2.26893	551.593
1.25073	2.09552	2551.79	1.51911	2.26893	269.348
1.42477	1.82627	905.153	1.60033	2.26893	177.909
1.5329	-1.5708	112.446	1.68154	2.26893	258.411
1.43896	-1.87175	241.205	1.76276	2.26893	510.536
1.35701	-2.17975	622.833	1.84398	2.26893	992.397
1.29521	-2.49737	1149.67	1.9252	2.26893	1648.9
1.26042	-2.82363	1690.3	2.00641	2.26893	2472.32
1.25684	3.12932	2023.35	2.08763	2.26893	3504.62
1.28491	2.80165	1994.8	1.27241	2.44346	1711.43
1.3412	2.48188	1624.1	1.35666	2.44346	1052.05
1.41933	2.17185	1010.97	1.4409	2.44346	579.109
1.51135	1.86966	425.482	1.52514	2.44346	296.532
1.01362	0.	4334.19	1.60938	2.44346	214.578
1.10301	0.	3104.87	1.69363	2.44346	336.376
1.1924	0.	2101.15	1.77787	2.44346	655.127
1.2818	0.	1323.93	1.86211	2.44346	1146.23
1.37119	0.	755.338	1.94635	2.44346	1859.8
Continued on next page					

Table A.2 – continued from previous page

θ	ϕ	Energy (cm^{-1})	θ	ϕ	Energy (cm^{-1})
1.46058	0.	395.478	2.03059	2.44346	2776.82
1.54997	0.	256.916	2.11484	2.44346	3915.77
1.63937	0.	330.991	1.26041	2.61799	1787.87
1.72876	0.	626.525	1.34727	2.61799	1123.76
1.81815	0.	1137.89	1.43413	2.61799	633.331
1.90754	0.	1863.35	1.52099	2.61799	335.265
1.01754	0.174533	4279.97	1.60785	2.61799	251.284
1.10627	0.174533	3056.97	1.69471	2.61799	355.482
1.195	0.174533	2063.55	1.78157	2.61799	692.395
1.28373	0.174533	1281.15	1.86844	2.61799	1234.09
1.37247	0.174533	708.746	1.9553	2.61799	2010.06
1.4612	0.174533	342.618	2.04216	2.61799	2980.16
1.54993	0.174533	187.308	2.12902	2.61799	4156.79
1.63866	0.174533	248.341	1.24505	2.79253	1889.51
1.7274	0.174533	531.835	1.33376	2.79253	1167.76
1.81613	0.174533	1033.36	1.42247	2.79253	658.607
1.90486	0.174533	1747.89	1.51118	2.79253	349.595
1.0278	0.349066	4112.67	1.59989	2.79253	271.249
1.11678	0.349066	2901.31	1.68859	2.79253	384.252
1.20577	0.349066	1913.48	1.7773	2.79253	721.593
1.29475	0.349066	1142.51	1.86601	2.79253	1277.64
Continued on next page					

Table A.2 – continued from previous page

θ	ϕ	Energy (cm^{-1})	θ	ϕ	Energy (cm^{-1})
1.38374	0.349066	583.747	1.95472	2.79253	2042.32
1.47272	0.349066	238.064	2.04342	2.79253	3034.03
1.5617	0.349066	104.416	2.13213	2.79253	4262.49
1.65069	0.349066	195.175	1.23491	2.96706	1930.5
1.73967	0.349066	505.549	1.32444	2.96706	1194.86
1.82866	0.349066	1036.96	1.41397	2.96706	671.46
1.91764	0.349066	1777.64	1.50351	2.96706	366.827
1.04825	0.523599	3785.38	1.59304	2.96706	273.192
1.14009	0.523599	2581.91	1.68257	2.96706	403.666
1.23194	0.523599	1616.26	1.7721	2.96706	747.697
1.32379	0.523599	881.075	1.86164	2.96706	1327.87
1.41564	0.523599	372.554	1.95117	2.96706	2079.88
1.50749	0.523599	94.6758	2.0407	2.96706	3077.12
1.59934	0.523599	48.4859	2.13023	2.96706	4310.17
1.69119	0.523599	243.85	1.	0.	4538.08
1.78304	0.523599	670.602	1.	0.174533	4549.98
1.87489	0.523599	1329.61	1.	0.349066	4535.27
1.96674	0.523599	2222.89	1.	0.523599	4512.66
1.08022	0.698132	3319.52	1.	0.698132	4497.13
1.17558	0.698132	2146.82	1.	0.872665	4510.49
1.27094	0.698132	1234.69	1.	1.0472	4522.16
Continued on next page					

Table A.2 – continued from previous page

θ	ϕ	Energy (cm^{-1})	θ	ϕ	Energy (cm^{-1})
1.36631	0.698132	570.914	1.	1.22173	4546.44
1.46167	0.698132	152.511	1.	1.39626	4616.92
1.55703	0.698132	-9.26793	1.	1.5708	4721.07
1.65239	0.698132	85.1366	1.	1.74533	4638.85
1.74775	0.698132	434.154	1.	1.91986	4954.63
1.84312	0.698132	1033.55	1.	2.0944	5043.36
1.93848	0.698132	1881.52	1.	2.26893	5135.75
2.03384	0.698132	2983.96	1.	2.44346	5110.75
1.12164	0.872665	2767.08	1.	2.61799	5086.94
1.21674	0.872665	1710.87	1.	2.79253	5024.03
1.31184	0.872665	899.517	1.	2.96706	4938.63

Table A.3: Dataset for the f198 "Frozen" PES

θ	ϕ	Energy (cm^{-1})	θ	ϕ	Energy (cm^{-1})
1.1108	0.	3587.47	1.5708	1.5708	113.679
1.1108	0.174533	3637.42	1.5708	1.74533	140.488
1.1108	0.349066	3677.44	1.5708	1.91986	166.504
1.1108	0.523599	3735.86	1.5708	2.0944	227.887
1.1108	0.698132	3809.78	1.5708	2.26893	311.284
1.1108	0.872665	3900.68	1.5708	2.44346	377.71
1.1108	1.0472	3995.58	1.5708	2.61799	419.321
1.1108	1.22173	4108.5	1.5708	2.79253	445.337
1.1108	1.39626	4233.83	1.5708	2.96706	468.778
1.1108	1.5708	4376.91	1.6628	0.	707.156
1.1108	1.74533	4526.8	1.6628	0.174533	610.839
1.1108	1.91986	4670.21	1.6628	0.349066	490.544
1.1108	2.0944	4794.7	1.6628	0.523599	380.07
1.1108	2.26893	4879.51	1.6628	0.698132	283.023
1.1108	2.44346	4902.03	1.6628	0.872665	193.048
1.1108	2.61799	4890.57	1.6628	1.0472	130.197
1.1108	2.79253	4847.97	1.6628	1.22173	107.01
1.1108	2.96706	4774.16	1.6628	1.39626	124.416
1.2028	0.	2341.07	1.6628	1.5708	154.3
1.2028	0.174533	2365.24	1.6628	1.74533	157.492
1.2028	0.349066	2376.16	1.6628	1.91986	163.163
Continued on next page					

Table A.3 – continued from previous page

θ	ϕ	Energy (cm^{-1})	θ	ϕ	Energy (cm^{-1})
1.2028	0.523599	2404.33	1.6628	2.0944	216.162
1.2028	0.698132	2444.	1.6628	2.26893	294.725
1.2028	0.872665	2497.79	1.6628	2.44346	363.001
1.2028	1.0472	2563.36	1.6628	2.61799	405.274
1.2028	1.22173	2655.06	1.6628	2.79253	440.318
1.2028	1.39626	2764.88	1.6628	2.96706	478.208
1.2028	1.5708	2894.57	1.7548	0.	1245.15
1.2028	1.74533	3020.97	1.7548	0.174533	1129.08
1.2028	1.91986	3141.82	1.7548	0.349066	986.679
1.2028	2.0944	3256.86	1.7548	0.523599	856.809
1.2028	2.26893	3344.81	1.7548	0.698132	741.728
1.2028	2.44346	3380.16	1.7548	0.872665	631.923
1.2028	2.61799	3381.8	1.7548	1.0472	543.35
1.2028	2.79253	3351.46	1.7548	1.22173	492.044
1.2028	2.96706	3297.25	1.7548	1.39626	481.36
1.2948	0.	1419.71	1.7548	1.5708	484.039
1.2948	0.174533	1418.44	1.7548	1.74533	464.726
1.2948	0.349066	1400.39	1.7548	1.91986	455.487
1.2948	0.523599	1397.83	1.7548	2.0944	502.314
1.2948	0.698132	1404.6	1.7548	2.26893	576.321
1.2948	0.872665	1422.74	1.7548	2.44346	643.634
Continued on next page					

Table A.3 – continued from previous page

θ	ϕ	Energy (cm ⁻¹)	θ	ϕ	Energy (cm ⁻¹)
1.2948	1.0472	1462.	1.7548	2.61799	685.097
1.2948	1.22173	1532.78	1.7548	2.79253	726.544
1.2948	1.39626	1629.93	1.7548	2.96706	777.333
1.2948	1.5708	1743.77	1.8468	0.	2070.82
1.2948	1.74533	1845.13	1.8468	0.174533	1936.57
1.2948	1.91986	1941.78	1.8468	0.349066	1774.32
1.2948	2.0944	2043.47	1.8468	0.523599	1627.52
1.2948	2.26893	2132.63	1.8468	0.698132	1496.28
1.2948	2.44346	2179.68	1.8468	0.872665	1367.4
1.2948	2.61799	2195.66	1.8468	1.0472	1253.22
1.2948	2.79253	2180.4	1.8468	1.22173	1172.79
1.2948	2.96706	2147.21	1.8468	1.39626	1132.37
1.3868	0.	804.498	1.8468	1.5708	1105.58
1.3868	0.174533	778.143	1.8468	1.74533	1066.28
1.3868	0.349066	732.777	1.8468	1.91986	1049.13
1.3868	0.523599	700.109	1.8468	2.0944	1091.
1.3868	0.698132	676.437	1.8468	2.26893	1160.43
1.3868	0.872665	661.904	1.8468	2.44346	1223.49
1.3868	1.0472	676.264	1.8468	2.61799	1264.24
1.3868	1.22173	725.222	1.8468	2.79253	1310.31
1.3868	1.39626	808.503	1.8468	2.96706	1373.7
Continued on next page					

Table A.3 – continued from previous page

θ	ϕ	Energy (cm^{-1})	θ	ϕ	Energy (cm^{-1})
1.3868	1.5708	904.215	1.9388	0.	3198.83
1.3868	1.74533	980.229	1.9388	0.174533	3045.94
1.3868	1.91986	1053.04	1.9388	0.349066	2865.8
1.3868	2.0944	1139.78	1.9388	0.523599	2701.53
1.3868	2.26893	1229.41	1.9388	0.698132	2554.21
1.3868	2.44346	1285.01	1.9388	0.872665	2406.22
1.3868	2.61799	1312.98	1.9388	1.0472	2266.59
1.3868	2.79253	1313.59	1.9388	1.22173	2156.9
1.3868	2.96706	1301.22	1.9388	1.39626	2085.42
1.4788	0.	484.159	1.9388	1.5708	2029.42
1.4788	0.174533	433.14	1.9388	1.74533	1974.01
1.4788	0.349066	361.896	1.9388	1.91986	1954.3
1.4788	0.523599	300.586	1.9388	2.0944	1991.15
1.4788	0.698132	249.232	1.9388	2.26893	2055.24
1.4788	0.872665	206.025	1.9388	2.44346	2111.24
1.4788	1.0472	195.297	1.9388	2.61799	2151.29
1.4788	1.22173	221.312	1.9388	2.79253	2202.24
1.4788	1.39626	286.66	1.9388	2.96706	2278.28
1.4788	1.5708	362.814	2.0308	0.	4653.36
1.4788	1.74533	414.01	2.0308	0.174533	4480.26
1.4788	1.91986	462.881	2.0308	0.349066	4280.98
Continued on next page					

Table A.3 – continued from previous page

θ	ϕ	Energy (cm^{-1})	θ	ϕ	Energy (cm^{-1})
1.4788	2.0944	535.805	2.0308	0.523599	4095.66
1.4788	2.26893	623.521	2.0308	0.698132	3929.61
1.4788	2.44346	685.44	2.0308	0.872665	3762.56
1.4788	2.61799	722.382	2.0308	1.0472	3599.76
1.4788	2.79253	736.952	2.0308	1.22173	3460.26
1.4788	2.96706	743.636	2.0308	1.39626	3357.38
1.5708	0.	452.899	2.0308	1.5708	3274.54
1.5708	0.174533	378.385	2.0308	1.74533	3206.8
1.5708	0.349066	282.033	2.0308	1.91986	3186.26
1.5708	0.523599	194.53	2.0308	2.0944	3216.87
1.5708	0.698132	118.646	2.0308	2.26893	3273.87
1.5708	0.872665	50.3741	2.0308	2.44346	3321.67
1.5708	1.0472	13.793	2.0308	2.61799	3361.09
1.5708	1.22173	16.1295	2.0308	2.79253	3418.85
1.5708	1.39626	59.1738	2.0308	2.96706	3508.07

APPENDIX B

PES EXPANSION COEFFICIENT LISTS

Table B.1: PES expansion coefficients for dataset 216

Composite Index	(l,m)	Expansion Coefficient
1	(0,0)	-9837.72
2	(2,-2)	0.00104825 - 0.000849521 i
3	(2,-1)	-0.00492302 + 0.0050967 i
4	(2,0)	0.124369
5	(2,1)	0.00492302 + 0.0050967 i
6	(2,2)	0.00104825 + 0.000849521 i
7	(4,-4)	0.0000883852 - 0.0000149737 i
8	(4,-3)	0.0000680965 + 0.0000646071 i
9	(4,-2)	0.0000740541 - 0.000114668 i
10	(4,-1)	-0.000815138 + 0.00081255 i
11	(4,0)	0.0110598
12	(4,1)	0.000815138 + 0.00081255 i
13	(4,2)	0.0000740541 + 0.000114668 i
14	(4,3)	-0.0000680965 + 0.0000646071 i
15	(4,4)	0.0000883852 + 0.0000149737 i
16	(6,-6)	$6.405760243138457 \times 10^{-6} + 0.0000229726 i$
17	(6,-5)	$-0.0000251691 + 4.951476214644559 \times 10^{-6} i$
18	(6,-4)	$-0.0000888888 + 5.24723176546858 \times 10^{-6} i$
Continued on next page		

Table B.1 – continued from previous page

Composite Index	(l,m)	Expansion Coefficient
19	(6,-3)	$-0.0000625428 + 0.0000139088 i$
20	(6,-2)	$0.0000674028 + 0.0000235622 i$
21	(6,-1)	$-0.0000302004 - 0.000141539 i$
22	(6,0)	-0.00207226
23	(6,1)	$0.0000302004 - 0.000141539 i$
24	(6,2)	$0.0000674028 - 0.0000235621 i$
25	(6,3)	$0.0000625428 + 0.0000139088 i$
26	(6,4)	$-0.0000888888 - 5.247232995275099 \times 10^{-6} i$
27	(6,5)	$0.0000251691 + 4.951476449247086 \times 10^{-6} i$
28	(6,6)	$6.405760144141726 \times 10^{-6} - 0.0000229726 i$
29	(8,-8)	$0.000069299 - 4.59150036383376 \times 10^{-6} i$
30	(8,-7)	$5.711088912004586 \times 10^{-6} + 0.0000225354 i$
31	(8,-6)	$0.0000467537 + 7.243532728866881 \times 10^{-6} i$
32	(8,-5)	$-4.456656865195787 \times 10^{-7} + 1.8374493345313662 \times 10^{-6} i$
33	(8,-4)	$0.0000110075 + 4.7963837523272654 \times 10^{-6} i$
34	(8,-3)	$-0.0000291563 + 0.0000166381 i$
35	(8,-2)	$0.0000112098 + 0.0000297777 i$
36	(8,-1)	$0.0000639426 - 0.0000865164 i$
37	(8,0)	-0.000851034
38	(8,1)	$-0.0000639425 - 0.0000865164 i$
39	(8,2)	$0.0000112098 - 0.0000297777 i$
Continued on next page		

Table B.1 – continued from previous page

Composite Index	(l,m)	Expansion Coefficient
40	(8,3)	$0.0000291563 + 0.0000166381 i$
41	(8,4)	$0.0000110075 - 4.796384386607391 \times 10^{-6} i$
42	(8,5)	$4.4566251606147273 \times 10^{-7} + 1.8374504913657567 \times 10^{-6} i$
43	(8,6)	$0.0000467537 - 7.243533153940058 \times 10^{-6} i$
44	(8,7)	$-5.7110892915640634 \times 10^{-6} + 0.0000225354 i$
45	(8,8)	$0.000069299 + 4.591500425882213 \times 10^{-6} i$

Table B.2: PES expansion coefficients for dataset 316

Composite Index	(l,m)	Expansion Coefficient
1	(0,0)	-9837.76
2	(2,-2)	0.000213142 - 0.000626435 i
3	(2,-1)	-0.00139302 + 0.00487949 i
4	(2,0)	0.0992088
5	(2,1)	0.00139302 + 0.00487949 i
6	(2,2)	0.000213142 + 0.000626435 i
7	(4,-4)	0.000252672 + 0.0000211917 i
8	(4,-3)	0.00043007 - 0.000146132 i
9	(4,-2)	-0.000594245 + 0.000194135 i
10	(4,-1)	0.00114025 + 0.00223004 i
11	(4,0)	0.0102248
12	(4,1)	-0.00114025 + 0.00223004 i
13	(4,2)	-0.000594245 - 0.000194135 i
14	(4,3)	-0.00043007 - 0.000146132 i
15	(4,4)	0.000252672 - 0.0000211917 i
16	(6,-6)	$3.4556950576661812 \times 10^{-6} + 0.0000697358 i$
17	(6,-5)	-0.0000389255 - 0.000140401 i
18	(6,-4)	-0.0000272276 + 0.000230583 i
19	(6,-3)	0.000335915 - 0.000259031 i
20	(6,-2)	-0.00111478 + 0.000211516 i
21	(6,-1)	0.0014609 + 0.000266131 i
Continued on next page		

Table B.2 – continued from previous page

Composite Index	(l,m)	Expansion Coefficient
22	(6,0)	0.000619741
23	(6,1)	-0.0014609 + 0.000266131 i
24	(6,2)	-0.00111478 - 0.000211516 i
25	(6,3)	-0.000335915 - 0.000259031 i
26	(6,4)	-0.0000272276 - 0.000230583 i
27	(6,5)	0.0000389255 - 0.000140401 i
28	(6,6)	$3.455693893528235 \times 10^{-6}$ - 0.0000697358 i
29	(8,-8)	$0.0000445736 + 5.18480868446338 \times 10^{-6}$ i
30	(8,-7)	$-7.064621644411687 \times 10^{-6}$ - 0.0000464184 i
31	(8,-6)	0.0000613529 + 0.000117055 i
32	(8,-5)	-0.0000474291 - 0.000202243 i
33	(8,-4)	-0.000126338 + 0.000150181 i
34	(8,-3)	0.000507712 - 0.0000361423 i
35	(8,-2)	-0.000993784 + 0.0000713118 i
36	(8,-1)	0.000602086 - 0.000459343 i
37	(8,0)	0.000562792
38	(8,1)	-0.000602086 - 0.000459343 i
39	(8,2)	-0.000993784 - 0.0000713118 i
40	(8,3)	-0.000507712 - 0.0000361423 i
41	(8,4)	-0.000126338 - 0.000150181 i
42	(8,5)	0.0000474291 - -0.000202243 i
Continued on next page		

Table B.2 – continued from previous page

Composite Index	(l,m)	Expansion Coefficient
43	(8,6)	$0.0000613529 - 0.000117055 i$
44	(8,7)	$7.064621648845732 \times 10^{-6} - 0.0000464184 i$
45	(8,8)	$0.0000445735 - 5.184808723332278 \times 10^{-6} i$

Table B.3: PES expansion coefficients for dataset 198 "Frozen"

Composite Index	(l,m)	Expansion Coefficient
1	(0,0)	-9837.75
2	(2,-2)	0.000730665 - 0.000479937 i
3	(2,-1)	-0.00584281 - 0.00133842 i
4	(2,0)	0.125105
5	(2,1)	0.00584281 - 0.00133842 i
6	(2,2)	0.000730665 + 0.000479937 i
7	(4,-4)	0.000135618 - 0.0000521925 i
8	(4,-3)	0.000307613 + 0.000261848 i
9	(4,-2)	0.00072651 + 0.000569395 i
10	(4,-1)	-0.00575026 - 0.00365327 i
11	(4,0)	0.0298208
12	(4,1)	0.00575026 - 0.00365327 i
13	(4,2)	0.00072651 - 0.000569395 i
14	(4,3)	-0.000307613 + 0.000261848 i
15	(4,4)	0.000135618 + 0.0000521925 i
16	(6,-6)	$1.6576485694407349 \times 10^{-6} + 0.0000434331 i$
17	(6,-5)	0.0000331123 - 0.0000562989 i
18	(6,-4)	-0.000147075 + 0.0000439896 i
19	(6,-3)	-0.000182099 - 0.0000431999 i
20	(6,-2)	0.000584824 + 0.000555465 i
21	(6,-1)	-0.00329178 - 0.00222774 i
Continued on next page		

Table B.3 – continued from previous page

Composite Index	(l,m)	Expansion Coefficient
22	(6,0)	0.0071155
23	(6,1)	0.00329178 - 0.00222774 i
24	(6,2)	0.000584824 - 0.000555465 i
25	(6,3)	0.000182099 - 0.0000431999 i
26	(6,4)	-0.000147075 - 0.0000439896 i
27	(6,5)	-0.0000331123 - 0.0000562989 i
28	(6,6)	$1.6576481801757404 \times 10^{-6}$ - 0.0000434331 i
29	(8,-8)	$0.0000426727 - 4.599188638219344 \times 10^{-6}$ i
30	(8,-7)	$8.022647105703344 \times 10^{-6} + 5.100379701854022 \times 10^{-6}$ i
31	(8,-6)	0.0000435283 + 0.0000482624 i
32	(8,-5)	0.0000288603 - 0.0000510373 i
33	(8,-4)	-0.0000470382 + 0.0000211253 i
34	(8,-3)	-0.0000925294 - 0.0000366484 i
35	(8,-2)	0.000152868 + 0.000208352 i
36	(8,-1)	-0.000799641 - 0.000622232 i
37	(8,0)	0.000657423
38	(8,1)	0.000799641 - 0.000622232 i
39	(8,2)	0.000152868 - 0.000208352 i
40	(8,3)	0.0000925294 - 0.0000366484 i
41	(8,4)	-0.0000470382 - 0.0000211253 i
42	(8,5)	-0.0000288603 - 0.0000510373 i
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Table B.3 – continued from previous page

Composite Index	(l,m)	Expansion Coefficient
43	(8,6)	$0.0000435283 - 0.0000482624 i$
44	(8,7)	$-8.022646888388422 \times 10^{-6} + 5.10037944209714 \times 10^{-6} i$
45	(8,8)	$0.0000426727 + 4.5991878283014474 \times 10^{-6} i$

APPENDIX C

WAVEFUNCTION DENSITY PLOTS

Table C.1: Eigenstates for the 216 PES. Columns I indicate even (e) or odd (o) matrix origins. In columns II, state labels are reported, where n_θ is the number of polar excitations, and n_ϕ is the number of azimuthal excitations [i.e. (n_θ, n_ϕ)]. Columns III report rotational frequencies (up to $\approx 2000 \text{ cm}^{-1}$), relative to the computed rotational ground state energy level. ZPE: 1106.05 cm^{-1} . It should be noted that A* and A** are a result of fermi resonance and can only be loosely labeled as A*=(1,3) and A**=(0,6).

I	II	III	I	II	III
e1	(0,0)	0	e12	(2,0)	4043.64
o1	(0,1)	31.1498	o14	(2,1)	4089.42
o2	(0,1)	158.556	e13	(1,5)	4099.03
e2	(0,2)	316.679	e14	(1,5)	4099.57
e3	(0,2)	363.356	o15	(2,1)	4204.93
o3	(0,3)	714.981	e15	(2,2)	4414.99
o4	(0,3)	721.542	e16	(2,2)	4441.68
e4	(0,4)	1246.73	o16	(2,3)	4863.15
e5	(0,4)	1255.57	o17	(2,3)	4869.27
o5	(0,5)	1936.6	e17	(0,8)	4908.87
o6	(0,5)	1937.46	e18	(0,8)	4908.88
o7	(1,0)	2019.33	o18	(1,6)	5006.28
e6	(1,1)	2057.48	o19	(1,6)	5006.32
e7	(1,1)	2177.38	e19	(2,4)	5489.18
o8	(1,2)	2360.92	e20	(2,4)	5495.11
Continued on next page					

Table C.1 – continued from previous page

I	II	III	I	II	III
o9	(1,2)	2396.47	e21	(1,7)	6063.55
e8	(A*,A*)	2759.86	e22	(1,7)	6063.7
e9	(A*,A*)	2760.69	o20	(3,0)	6096.97
e10	(A**,A**)	2802.81	e23	(1,3)	6151.34
e11	(A**,A**)	2803.7	o21	(0,9)	6200.64
o10	(1,4)	3357.28	o22	(0,9)	6200.64
o11	(1,4)	3364.48	e24	(1,3)	6262.24
o12	(0,7)	3767.95	o23	(2,5)	6288.35
o13	(0,7)	3768.	o24	(2,5)	6288.72

Table C.2: Eigenstates for the 316 PES. Columns I indicate even (e) or odd (o) matrix origins. In columns II, state labels are reported, where n_θ is the number of polar excitations, and n_ϕ is the number of azimuthal excitations [i.e. (n_θ, n_ϕ)]. Columns III report rotational frequencies (up to $\approx 2000 \text{ cm}^{-1}$), relative to the computed rotational ground state energy level. ZPE: 1146.43 cm^{-1} . It should be noted that A*, A**, B* and B** are a result of fermi resonance and can only be loosely labeled as A*=(1,3), A**=(0,6), B*=(3,0) and B**=(1,5).

I	II	III	I	II	III
e1	(0,0)	0.	e12	(B*,B*)	4108.36
o1	(0,1)	32.7009	e13	(1,5)	4117.84
o2	(0,1)	153.292	e14	(B**,B**)	4120.83
e2	(0,2)	313.32	o14	(2,1)	4158.06
e3	(0,2)	359.863	o15	(2,1)	4269.55
o3	(0,3)	711.339	e15	(2,2)	4473.72
o4	(0,3)	718.929	e16	(2,2)	4512.35
e4	(0,4)	1243.59	e17	(0,8)	4904.7
e5	(0,4)	1252.32	e18	(0,8)	4904.71
o5	(0,5)	1933.32	o16	(2,3)	4928.63
o6	(0,5)	1933.85	o17	(2,3)	4941.81
o7	(1,0)	2043.73	o18	(1,6)	5018.32
e6	(1,1)	2083.73	o19	(1,6)	5018.36
e7	(1,1)	2195.13	e19	(2,4)	5553.31
o8	(1,2)	2380.13	e20	(2,4)	5561.19
o9	(1,2)	2417.07	e21	(1,7)	6076.29
e8	(A**,A**)	2762.54	e22	(1,7)	6076.41
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Table C.2 – continued from previous page

I	II	III	I	II	III
e9	(A*,A*)	2763.81	o20	(3,0)	6175.85
e10	(A**,A**)	2814.03	o21	(0,9)	6196.34
e11	(A*,A*)	2818.87	o22	(0,9)	6196.34
o10	(1,4)	3375.4	e23	(3,1)	6228.7
o11	(1,4)	3384.06	e24	(3,1)	6346.8
o12	(0,7)	3764.07	o23	(2,5)	6352.34
o13	(0,7)	3764.1	o24	(2,5)	6352.93

Table C.3: Eigenstates for the f198 “Frozen” PES. Columns I indicate even (e) or odd (o) matrix origins. In columns II, state labels are reported, where n_θ is the number of polar excitations, and n_ϕ is the number of azimuthal excitations [i.e. (n_θ, n_ϕ)]. Columns III report rotational frequencies (up to $\approx 2000 \text{ cm}^{-1}$), relative to the computed rotational ground state energy level. ZPE: 1254.51 cm^{-1} .

I	II	III	I	II	III
e1	(0,0)	0.	o12	(0,7)	3781.11
o1	(0,1)	19.6867	o13	(0,7)	3781.13
o2	(0,1)	207.313	e12	(1,5)	4364.75
e2	(0,2)	338.797	e13	(1,5)	4366.43
e3	(0,2)	410.735	e14	(2,0)	4591.11
o3	(0,3)	744.235	o14	(2,1)	4620.86
o4	(0,3)	751.543	o15	(2,1)	4795.67
e4	(0,4)	1269.35	e15	(0,8)	4918.71
e5	(0,4)	1283.61	e16	(0,8)	4918.79
o5	(0,5)	1958.13	e17	(2,2)	4971.61
o6	(0,5)	1960.4	e18	(2,2)	5019.48
o7	(1,0)	2283.39	o16	(1,6)	5255.38
e6	(1,1)	2307.71	o17	(1,6)	5255.53
e7	(1,1)	2488.72	o18	(2,3)	5423.37
o8	(1,2)	2641.99	o19	(2,3)	5427.6
o9	(1,2)	2700.16	e19	(2,4)	6027.24
e8	(0,6)	2794.18	e20	(2,4)	6037.46
e9	(0,6)	2794.45	o20	(0,9)	6207.24
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Table C.3 – continued from previous page

I	II	III	I	II	III
e10	(1,3)	3068.47	o21	(0,9)	6207.24
e11	(1,3)	3073.23	e21	(1,7)	6305.17
o10	(1,4)	3630.54	e22	(1,7)	6305.2
o11	(1,4)	3642.52

Figure C.1: f198 Wavefunction density plots. (A) e1, (B) o1, (C) o2, (D) e2, (E) e3, (F) o3

Figure C.2: f198 Wavefunction density plots. (A) o4, (B) e4, (C) e5, (D) o5, (E) o6, (F) o7

Figure C.3: f198 Wavefunction density plots. (A) e6, (B) e7, (C) o8, (D) o9, (E) e8, (F) e9

Figure C.4: f198 Wavefunction density plots. (A) e10, (B) e11, (C) o10, (D) o11, (E) o12, (F) o13

Figure C.5: f198 Wavefunction density plots. (A) e12, (B) e13, (C) e14, (D) o14, (E) o15, (F) e15

Figure C.6: f198 Wavefunction density plots. (A) e16, (B) e17, (C) e18, (D) o16, (E) o17, (F) o18

Figure C.7: f198 Wavefunction density plots. (A) o19, (B) e19, (C) e20, (D) o20