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The anharmonic infrared spectra of polycyclic aromatic hydrocarbons

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a family of related molecules. As with many labels in chemistry, the name is descriptive rather than catchy. This means however, that everything which defines a PAH is fortunately right there in the name. Therefore to understand what PAHs are, we can simply work backwards through the name. “Hydrocarbon”, refers to any molecule consisting solely of hydrogen and carbon. The next term is “aromatic”, this word requires a more in depth knowledge of chemical bonding, but in brief it refers to the delocalization of bonding electrons over the surface of a planar molecule. Instead of each atom of a molecule holding tightly onto its and its neighbor’s outer electrons (as in a non-aromatic molecule) these electrons are shared freely over the whole molecule. This particular arrangement lends extra stability, and unique chemical properties to these molecules. (In case the reader was wondering if the term “aromatic” has a connection to smell, it in fact does. When aromatic-bond containing chemicals were first isolated they were found to have quite a strong smell.) Finally, we arrive at the last term “polycyclic”. Again a simple term, referring to the fact that the carbon atoms of PAHs are arranged in rings or cycles, and there are more than two adjoined rings. Figure 1.1 shows examples of various PAH structures.

We are actually familiar with PAHs in our everyday life, perhaps without even knowing it. On Earth PAHs are one of the undesirable by-products of combustion[1, 2]. If the reader has seen the black smoke pouring out of a car’s exhaust, seen the residue left behind by candles, or dined on a flame-broiled steak, then they have come into contact with PAHs. As can be assumed, all of this acrid smoke and soot cannot be good for one’s health – PAHs have indeed been linked strongly to cancer[3]. Even ingested PAHs, such as in that steak, have been shown to cause certain types of cancers[4]. While a terrible carcinogen and pollutant, PAHs can also benefit society in the right context. PAHs have been

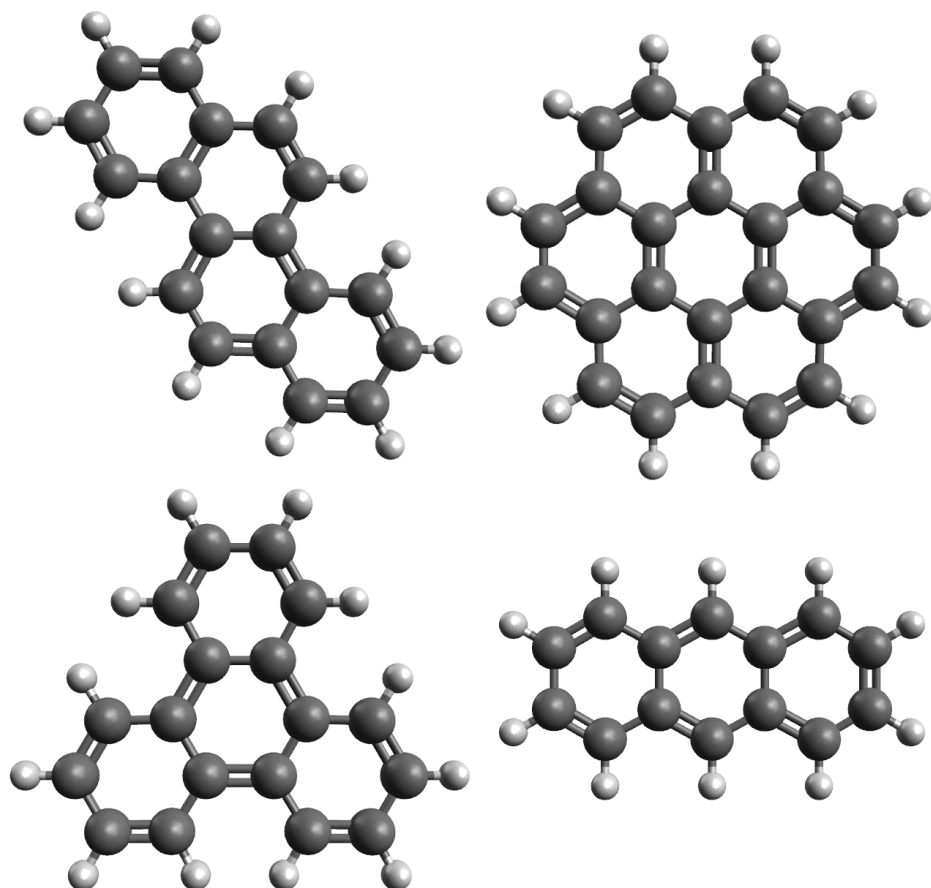


Figure 1.1 Examples of PAH species. Clockwise from top left: chrysene, coronene, anthracene, and triphenylene.

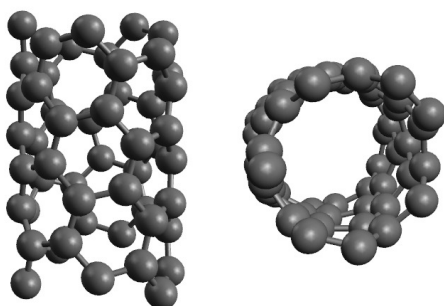


Figure 1.2 An example of PAH-like nano-structures. Side and top view of a piece of a nano-tube.

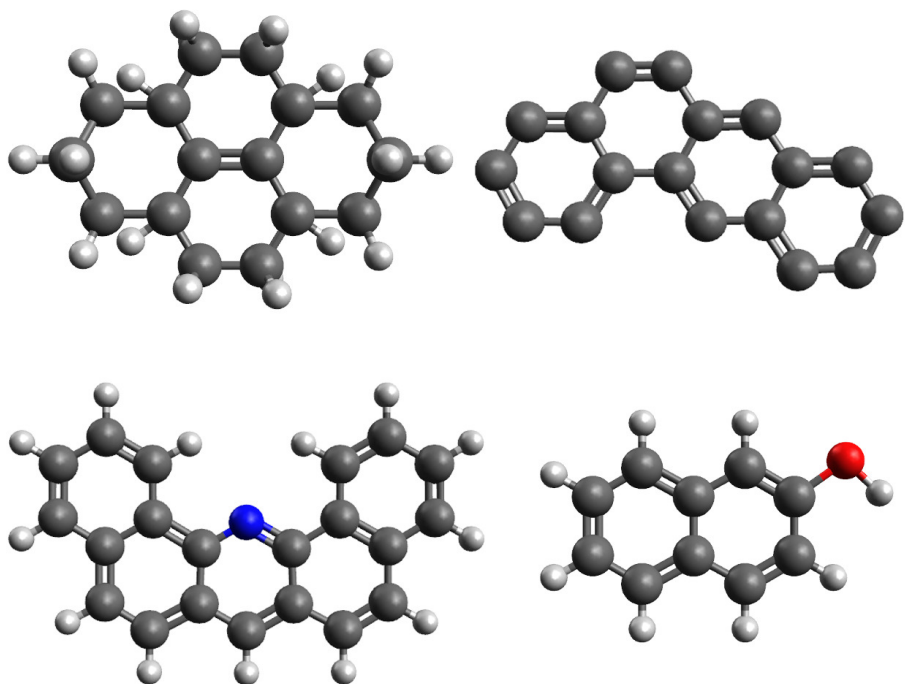


Figure 1.3 Examples of species that astronomers also consider PAHs. Clockwise from top left: super-hydrogenated pyrene, fully dehydrogenated benz[a]anthracene, 2OH-naphthalene, and dibenz[ch]acridine.

used as stand-ins for the study of nano-materials such as graphene or nano-tubes (both polycyclic carbon containing structures, as shown in figure 1.2). These super strong, super light, wonder-materials may one day replace all of our conventional building materials[5, 6, 7]. These nano-materials also exhibit interesting electrical properties, and may someday be used to replace silicon transistors in our cell phones and computers[8]. While still a fairly new area of research, the study of the structural, physical and chemical properties of PAHs and nano-carbon materials will likely lead us into the next technological age.

Now that PAHs have been defined firmly from a chemistry standpoint, the reader should put that aside, and instead focus on what astronomers define PAHs to be. Why astronomers would be interested in PAHs in the first place will be explained later, but let us take a look at the word “polycyclic aromatic hydrocarbon” again. In order to explain their observations, astronomers have to relax the definition of PAHs. Sometimes it is necessary to assume a nitrogen atom has replaced a carbon and hydrogen atom[9], or that an oxygen or hydroxy group is

inserted[9] into the PAH. This however, breaks the strict definition of a “hydrocarbon”. Sometimes astronomers need to add additional hydrogens to the PAH[10] or strip all the hydrogens away[11]. Doing so however, can disrupt the aromaticity of the molecule, leading to molecules that can no longer be called “aromatic”. Finally we arrive again at the last word, “polycyclic”. This last point is debatable, but some chemists only consider molecules containing *more* than two rings to be polycyclic. Astronomers however, accept naphthalene, a non-*poly* two ringed molecule to be a PAH. Figure 1.3 shows a few examples of these “astronomer’s PAHs”.

Chemical arguments aside, these loose definitions of what constitutes a PAH is actually important for astronomers. Interstellar space is a very different environment from Earth. How PAHs form, how they interact with the abundance of hydrogen present[10, 12], how they interact chemically in and on comets[13] or meteorites[14], how they survive high speed impacts from cosmic rays[15], how they chemically interact in the extreme environments around massive stars[16, 17], all of these considerations lead to PAHs that are less PAH-like than what is typical for a chemist on Earth. However, the behavior of these PAHs are similar enough in astrophysical environments, that from an astronomer’s point of view calling them all PAHs is acceptable and leads to some exceptional science.

We have seen how PAHs can paradoxically be both a carcinogen and a technological wonder on Earth, but are they anything but a pollutant in space? In fact they are much more. PAHs are of interest to astronomers for a number of reasons. For example: they have been shown to control temperature and charge balance in large gaseous clouds of the interstellar medium (ISM)[18]. They act as catalysts for bringing hydrogen atoms together to form molecular hydrogen H_2 [10]. They can act as nuclei for grain formation that could ultimately become planets. Even life itself could originate from the processing of interstellar PAHs. Evidence of the formation of nucleobases, the building blocks of DNA, have been found in comets and meteors[19]. These nucleobases possibly formed from the processing of PAH and PAH derivatives embedded in icy comets[20].

Unlike on Earth, scientists cannot obtain a physical sample from the ISM and test it for PAHs. Instead all they have to work with is what they can see, or more technically what their “mechanical eyes” known as spectrographs, can see. Spectroscopy is a field of science that uses the unique frequencies of light (or spectrum) emitted or absorbed by atoms and molecules to both detect the species present, and to examine their physical properties. In order to accomplish this they require an in depth understanding and high quality models of what frequencies of light they expect to be emitted from the molecules. In 2019, the James Webb Space Telescope will be launched. This will be the most powerful telescope ever sent into space, able to provide superior pictures than the Hubble Space Telescope. Attached to JWST will be a set of spectrographs able to measure infrared light in higher detail than has been achieved in the past. This coincidentally, is the same frequency of light in which PAHs emit. The wealth of knowledge we will gain from JWST about interstellar PAHs will dwarf all we know right now. However, the current spectra and models of the infrared light emitted from PAHs is not good enough for the interpretation of all of the data that will be produced by JWST.

Ideally if we could, we would measure in the lab all of the spectra of relevant

PAHs here on Earth and use those to compare to what we observe in the ISM. This however, is impossible for a number of reasons. The first being a matter of scale. There are a near infinite number of possible PAH species. For example, limiting ourselves to just ten rings or less still puts the number of possible species at over twenty thousand[11]. Add in the number of possible PAH derivatives and this set grows exponentially. Therefore, small sets of representative PAHs are selected for experimentation, and extrapolations to the larger family of PAHs are made based on them. The second issue is the low volatility of PAHs. As the size of PAH increases it becomes more and more difficult to vaporize the PAHs into the gas phase in order to measure their spectra accurately. This means that most of the experimental spectra taken to date is either at high temperatures[21] or cooled by embedding the PAHs in inert argon matrices using matrix isolation spectroscopic (MIS) techniques[22, 23, 24]. Unfortunately, this leaves PAHs in physical environments that are dissimilar to the ISM. The high temperature and pressures lead to band shifts and broadenings, and the matrix of the MIS methods leads to unpredictable band shifts due to interactions with the matrix itself.

To circumvent these two issues, a heavy reliance is put on theoretical calculations of the IR spectra of PAHs. The experimental studies can then be used to validate and improve these theoretical methods, which in turn can be applied to a vastly wider variety of PAHs and PAH derivatives, under a variety of physical conditions that cannot be accomplished with experiments. Density functional theory (DFT) methods using the harmonic approximation (explained below) are often employed to achieve these goals. However, recent work[25] has shown that the harmonic approximation reproduces poorly the IR spectra of PAHs, especially in the C–H stretching region (see the red trace of figure 1.4 compared to the experimental trace in black). To truly model the interstellar IR spectra of PAHs, *anharmonic* calculations are necessary (see the blue trace of figure 1.4 compared to the experimental trace in black).

As noted, comparisons to experimental spectra are required to develop and validate theoretical techniques. The theoretical anharmonic IR spectra presented in this work requires comparisons to state-of-the-art spectra. To make this possible, Maltseva et al.[25, 26, 27] produced new high-resolution low-temperature gas-phase infrared spectra of a variety PAHs. As will be shown, the anharmonic calculations can not only produce spectra that are far superior to the harmonic spectra (Chapters 3 through 5), but can also be used calculate the spectra of a molecule at any desired temperature (Chapters 6 and 7); which is key to understanding the IR cascade process of interstellar PAHs (Chapter 7).

The aim of this thesis then becomes clear: Improve the theoretical infrared spectra of polycyclic aromatic hydrocarbons so that we are ready to fully understand what we are looking at when we see interstellar PAHs for the first time again with the new eyes of JWST.

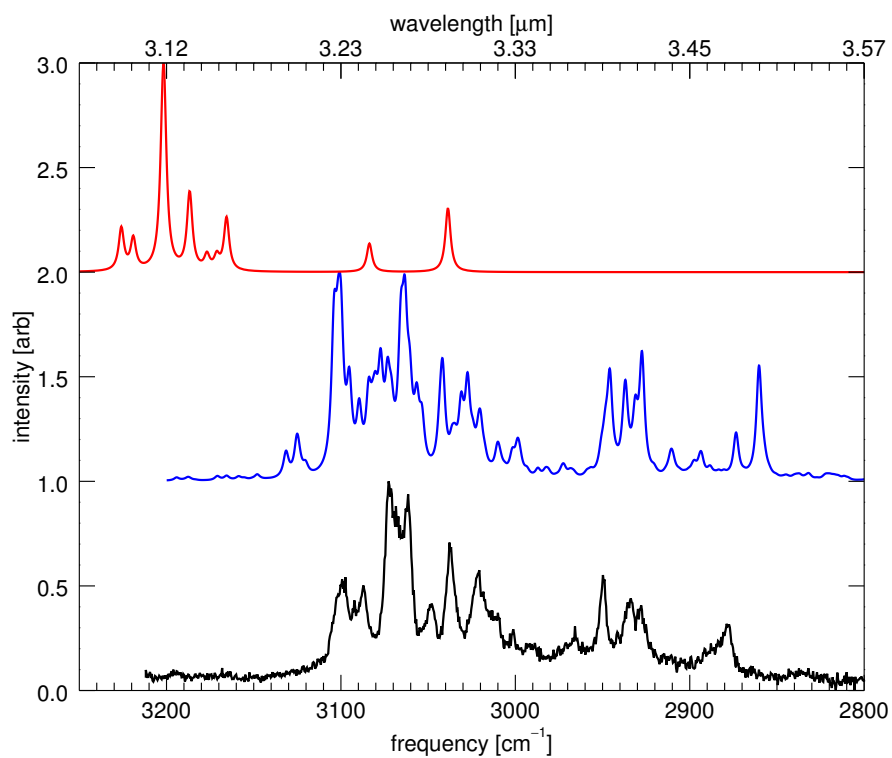


Figure 1.4 Three infrared spectra of the C–H stretching region of 9-methylanthracene: The harmonic spectrum (red, top), anharmonic spectrum (blue, middle), and the high-resolution experimental spectrum (black, bottom).

1.1 Interstellar PAH hypothesis

It may be surprising to learn that these large, complex pollutants are found in interstellar space; and not just in trace amounts, they are found *everywhere*. Every object that astronomers have observed which contains dust have been found to contain spectral lines attributed to PAHs. As long as there is enough light (ultraviolet light from stars) to excite PAHs, they are detected. The amount seen is actually staggering; it has been estimated that 10 – 20% of all of the carbon in the ISM is locked up in PAHs. These PAHs are not small either, current studies estimate that each PAH contains between 50 and 200 carbon atoms[28].

The presence of PAHs in interstellar space was first put forward in the 1980s to explain the series of IR features referred to at the time as the “unidentified infrared bands” (UIRs). In 1984, Léger and Puget[29] proposed PAHs to be the carriers of the UIR bands based on physical arguments, such as the stability of PAHs in intense UV fields. Allamandola et. al[30] in 1985, showed that the observed UIR spectra in Orion Nebula matched the spectra of PAHs by comparing it to (of all things) car exhaust, as well as the IR fluorescence of a specific PAH called chrysene. However, it was not until the 1990s that the hypothesis that PAHs are responsible for the UIR bands began to take hold. As will be explained below in the section 1.2, an infrared spectrum is not the strongest evidence to prove the presence of a particular molecule. More concrete spectral evidence, such as an electronic spectrum (in the ultraviolet (UV) region), was needed. Léger et al.[31] then argued that the observed UV absorption bump in the interstellar spectra matched the general shape of the UV absorption of PAHs. Additionally, a set of distinct visible and UV features known as the “diffuse interstellar bands” (DIBs) were put forward to be the spectral fingerprints of PAHs[31] (but has yet to be confirmed). Over the next decades, more evidence of the existence of PAHs in interstellar space began to accumulate: PAHs were found to be contained in meteorite samples[32], newly launched space telescopes provided better resolution of the UIR spectra than previously achieved with Earth-based telescopes[33, 34, 35], and theoretical models of the IR emission of PAHs were able to explain the variations seen in the UIRs from interstellar object to interstellar object[36]. Presently, the PAH hypothesis is the most widely accepted explanation for the appearance of the UIR bands. In fact these bands are now routinely referred to as the Aromatic Infrared Bands (AIBs), rather than UIRs.

Where do all of the interstellar PAHs come from? During the majority a star’s lifetime it is constantly burning hydrogen into helium through nuclear fusion. As an inert helium core builds up, eventually fusion of hydrogen in the core stops, and instead only takes place in a shell around the core. This causes the star’s outer layers to cool and puff up in size (ten to hundreds of times their original radius) into what is called a red giant. Eventually enough helium is built up in the core, and with no hydrogen burning to provide outward pressure, the core collapses. This increase in pressure ignites the helium, which begins to fuse into carbon, nitrogen, and oxygen. Once again the star builds up an inert core, this time made up of a mixture of carbon, nitrogen, and oxygen. When the helium fuel in the core has been exhausted, fusion will only occur in shells of hydrogen and helium

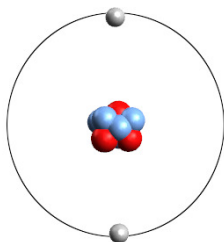


Figure 1.5 Electron particles (white) in orbit around a nucleus (blue/red).

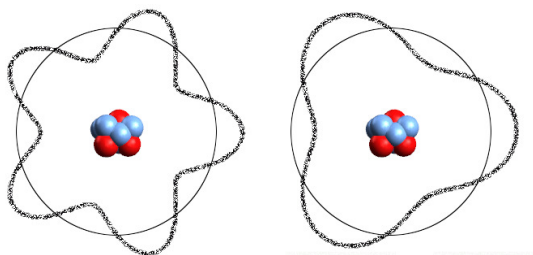


Figure 1.6 Electron waves (black dotted lines) around nuclei (blue/red). The solid line represents the division between the mathematically positive and negative values of the wave.

surrounding the core. This causes the star to swell once again into a asymptotic giant branch star or an AGB star. During the last stages of this AGB phase, large convective currents dredge up the newly formed carbon, nitrogen, and oxygen. For a mid-sized star, at this point it is as good as dead. It is not massive enough to begin burning carbon, nitrogen, or oxygen, or to go supernova, or become a black hole. Instead it will begin rapidly losing mass as it can no longer hold onto its own gases. As this outflow of gas cools it can condense into molecules, mainly carbon monoxide (CO). If there is more oxygen than carbon left over after the formation of CO, then the remaining oxygen goes into forming water and oxides, and eventually silicate grains. If there is more carbon than oxygen left over after the formation of CO, then the remaining carbon goes into forming acetylene, hydrogen cyanide, other small organics, and eventually carbonaceous grains and of course PAHs.

1.2 Spectroscopy

As stated previously, spectroscopy is the study of the interaction of atoms and molecules with light. These interactions are dictated by quantum mechanics. Quantum mechanics itself is often seen as a mysterious entity which causes odd things to happen i.e., entanglement, teleportation, Schrödinger's cat, etc., but at its core quantum mechanics is actually simple. Picture an atom. At its center

are positively charged protons, and orbiting these protons some distance away are negatively charged electrons (figure 1.5). In our everyday macroscopic world everything loses energy over time: wheels eventually stop turning, swings will stop swinging, even the orbits of planets and stars decay over time[37]. The same should hold true for electrons orbiting protons. Any accelerating (orbiting) charge, like an electron, should emit a continuous stream of energy in the form of light. Their orbits should then decay over time and the electrons should eventually crash into the protons. However, this is not what we see. In fact, if that were true we would not exist. Our universe would not exist. The reason this does not happen is explained by quantum mechanics. At the very small scale, all matter, even light, behaves both as a particle and a wave. The so-called wave-particle duality. A basic explanation of this duality is that the probability of finding the “particle” portion of matter at a particular point in space is equal to the square of the absolute value of the “wave” portion of the matter. One can never exactly pinpoint that location, but it is possible to calculate the probability that the particle will be in a particular location at a particular time. Since the particle has to be somewhere, the total of this probability has to be equal to one. If we now picture the wave portion of the electron in its orbit around the protons, we can see why it doesn’t crash (figure 1.6). It can’t. The wave itself can oscillate from positive to negative as many times as it wants as it travels around the protons, but the square of its absolute value must be equal to one. This means only certain energies of orbits are allowed. If the electron switches to a higher or lower energy orbit (say from the left wave to the right wave in figure 1.6), it must emit *exactly* the amount of energy that separates those two allowed orbits. These allowed energies are limited to particular quantities, and are *quantized*. This simple principle that energy only comes in specific quantities gives quantum mechanics its name. All of quantum mechanics stems from this basic idea.

This quantization of energy is the key to spectroscopy. Since only certain energies are allowed for any given atom or molecule, an atom or molecule can only interact with light of specific frequencies. If one were to separate the light being emitted or absorbed by the molecule using a prism, then it would produce a rainbow of colors with the spectral fingerprint, or *spectrum*, of the molecule clearly seen (see figure 1.7). Each spectra is unique to each type of atom or molecule. By analyzing this light it is possible to tell exactly which atoms and molecules are present, just like fingerprints at the scene of a crime.

While the frequency of light emitted from these orbiting electrons tends to be in the ultraviolet down to the visible region of the spectrum, this notion of quantized energy also extends to all other behavior of molecules as well. The energies of allowed rotations are also quantized, meaning molecules can only rotate at specific rates specific to their structure. The frequencies of light emitted from changes in rotation are in the microwave region of the spectrum. Vibrations of the atoms contained in molecules are also quantized, meaning the bonds between the atoms can only oscillate at specific rates, specific to the type of bonded atoms. The frequencies of light emitted by these vibrations are in the infrared (IR) region of the spectrum. See figure 1.8.

Using the spectra of a molecule in all of these regions allows us to uncover many

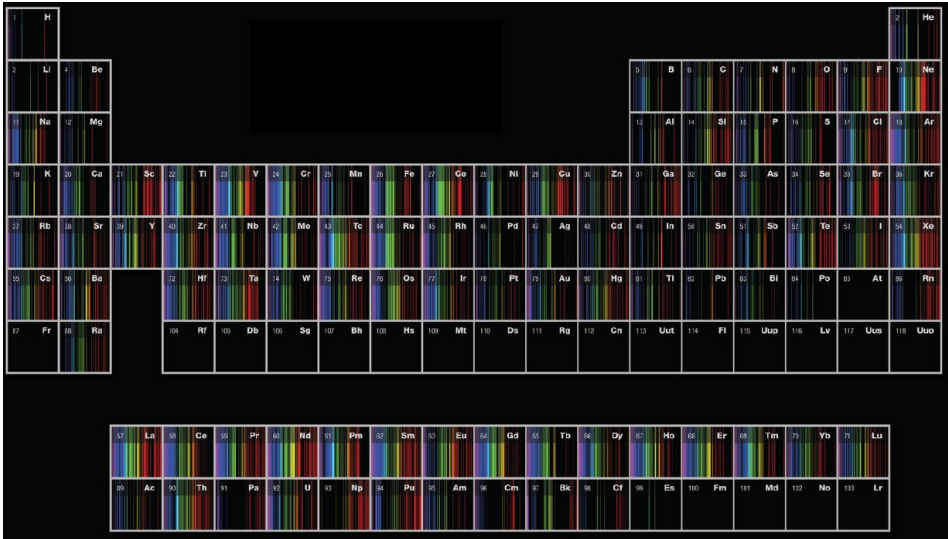


Figure 1.7 The visible light emission spectra of each element, arranged in the order of the periodic table of elements (adapted from <http://www.fieldtestedsystems.com>).

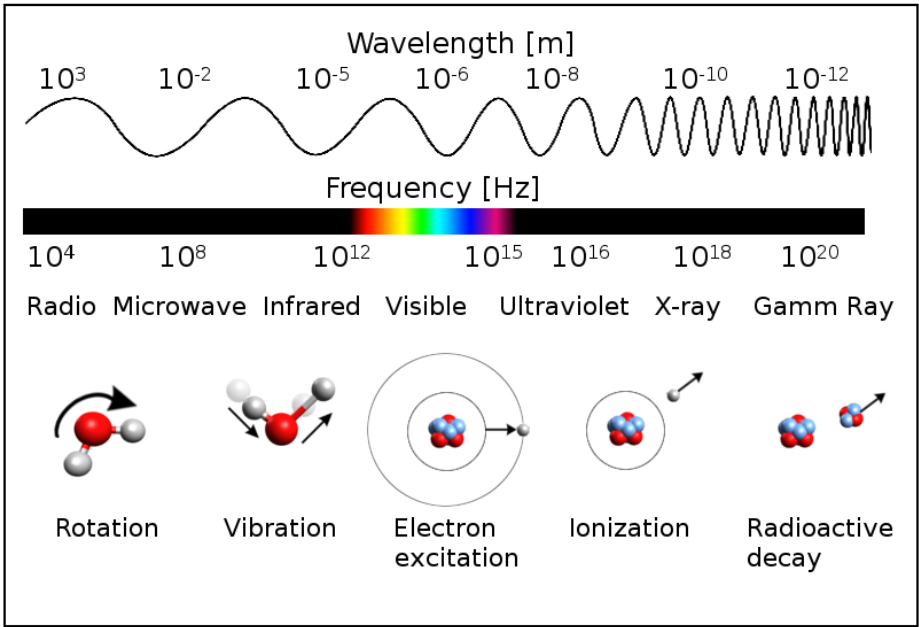


Figure 1.8 The regimes of molecular and atomic photon emissions.

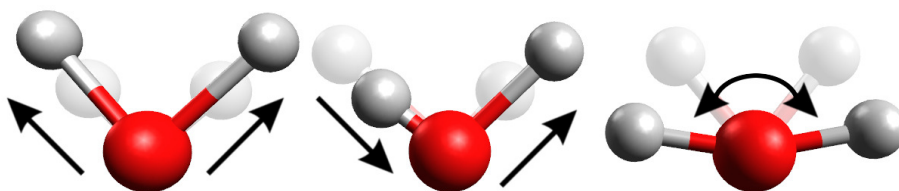


Figure 1.9 The three vibrational modes of water: symmetric stretching, asymmetric stretching, and bending.

properties of molecules such as shape, size, bond lengths, bond strengths, chemical reactivity, ionization energy, etc., as well as uniquely identify the molecules themselves.

1.2.1 Infrared spectroscopy

The focus of this thesis is on the IR spectrum of PAHs. As stated above, the IR portion of a spectrum is linked to the vibrations of the atoms inside a molecule. The atoms in a molecule can oscillate back and forth as if they were attached together by springs, or groups of atoms can bend back and forth as if a spring loaded door hinges. These motions can be described in “normal coordinates”, a set of orthogonal (independent) vibrations (see figure 1.9 for the three vibrational modes of water). Each normal coordinate motion, or *fundamental vibrational mode*, has a specific frequency at which it vibrates. For a vibrational mode to emit or absorb light its *electric dipole* must change through the course of the vibration. These properties lead to an IR spectrum with spectral bands at specific frequencies (determined by the types of normal modes) and specific intensities (determined by how much the dipole changes through the course of the vibrational motion).

While the electronic spectrum (from the orbits of electrons) is unique for each and every molecule, the IR spectrum is not as unique. Since the IR spectrum is determined by the vibrations of bonds, molecules with similar bonds have similar IR spectra. For example, all molecules containing oxygen bonded to hydrogen will have a stretching mode that shows up in the spectrum between 3200 and 3400 cm^{-1} (3.125 and 2.941 μm) (see figure 1.10 for more examples).

1.2.2 PAH IR signatures

The AIBs observed by astronomers shows great variation in the IR spectra, not only from interstellar object to interstellar object, but also spatially within an object itself[34]. The variation in the IR spectrum of PAHs is used to identify general properties of the population of PAHs, such as structure, shape, charge, temperature, and chemical make-up, as well as identify the physical conditions in which they are found, such as densities, overall charge balance, and temperature. Additionally, the variation in these observations can be used to explain the evolution of the objects in which they are found, and the evolution of carbon in the

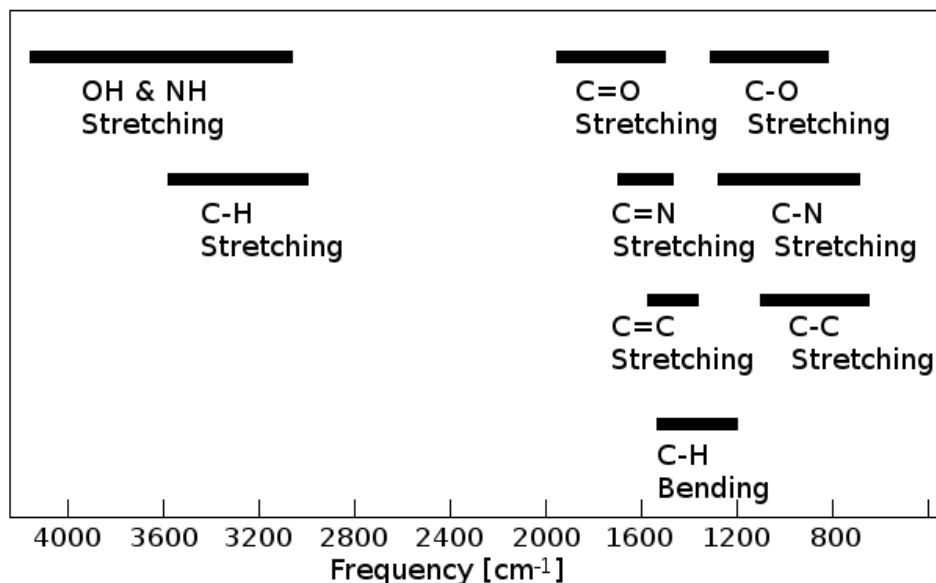


Figure 1.10 Typical infrared emission ranges for the vibrational modes of common function groups.

universe itself.

Since all PAHs contain similar bonds to one another their IR spectra are also similar. The approximate band positions of the IR features common to all PAHs are listed in Table 1.1. Although very similar overall, the IR spectra of PAHs do differ from one another in subtle ways. The edge structure (as shown in figure 1.11) can affect the position of the C-H out-of-plane bending modes[33] listed in table 1.2. The relative intensities of these sets of bands can be used to determine the edge structure of PAHs.

The charge of PAHs has also been correlated with changes in relative strengths of the $1660 - 1100 \text{ cm}^{-1}$ ($6.0 - 9.1 \mu\text{m}$) region, with the intensity of the IR features of cations increasing ten-fold compared to their neutral counterparts[38]. The

Band [cm^{-1}]	Band [μm]	Mode assignment
3030	3.3	aromatic C-H stretching
1920	5.2	combination bands: C-H bend + C-C stretch
1770	5.65	combination bands: C-H bend + C-C stretch
1610	6.2	aromatic C-C stretching
1320	7.6	C-C stretching and C-H in-plane bending
1280	7.8	C-C stretching and C-H in-plane bending
1160	8.6	C-H in-plane bending
940 - 700	10.6 - 14.2	C-H out-of-plane bending
610	16.4	C-C out-of-plane bending

Table 1.1 Typical band positions of PAH IR active vibrational modes.

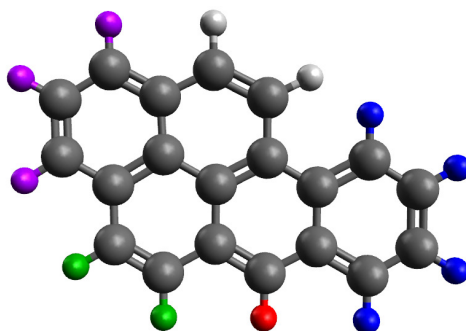


Figure 1.11 The possible variations in edge structure of a PAH. Hydrogens are classified by how many are attached to an individual ring: solo (red), duo (green), trio (purple), and quarto (blue).

Band range [cm^{-1}]	Band range [μm]	Mode assignment
940 – 880	10.6 – 11.4	C–H out-of-plane bending, solo
880 – 780	11.4 – 12.8	C–H out-of-plane bending, duo
800 – 750	12.5 – 13.3	C–H out-of-plane bending, trio
770 – 700	13.0 – 14.2	C–H out-of-plane bending, quarto

Table 1.2 The variation seen in the C–H out-of-plane bending modes due to the number of neighboring hydrogen atoms. (See figure 1.11 for definitions.)

number of carbon atoms contained within a PAH has also been correlated with shifts and changes in the features[28].

In addition to structural changes, the addition of side groups can alter the IR spectrum of PAHs. The addition of extra hydrogens[39] or methyl groups[40] cause the appearance of aliphatic C–H stretching bands around 2940 cm^{-1} ($3.4\text{ }\mu\text{m}$), and aliphatic C–H bending modes around 1450 cm^{-1} ($6.9\text{ }\mu\text{m}$). If enough hydrogens are added it will cause the loss of the aromatic C–H stretching features completely. Hetero-atomic substitutions can also alter the spectrum. For example, the insertion of a nitrogen atom into a PAH causes a shift of the 1610 cm^{-1} ($6.2\text{ }\mu\text{m}$) feature to 1590 cm^{-1} ($6.3\text{ }\mu\text{m}$), with a possible correlation of how deep the nitrogen is inserted into the PAH[9].

1.2.3 Infrared cascade spectrum of PAHs

The conditions in which interstellar PAHs emit their IR spectrum differs greatly from PAHs on Earth. The key difference being due to densities. On Earth densities of any gas are high enough that collisions between neighboring molecules are inevitable. These collisions mean that the average energy of the system (i.e., temperature of the PAHs) is uniform. Additionally, on Earth energy flows in and out of any system from its surroundings, meaning the temperature is stable and does not fluctuate wildly. For these reasons, measuring the spectra of PAHs in the

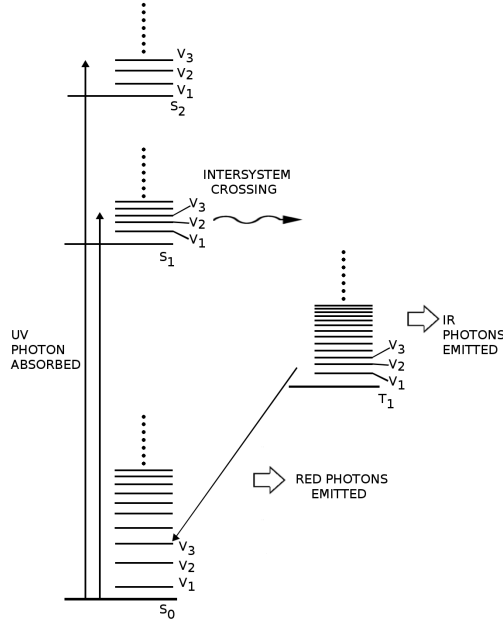


Figure 1.12 The infrared cascade emission process of interstellar PAHs. (Figure adapted from reference 41.)

lab produces a spectrum that is at one fixed temperature. Conversely, densities in interstellar space are low enough that collisions between neighboring molecules are rare. This means that the PAHs are not in thermal equilibrium, and can therefore take on different temperatures from their neighbors. In interstellar space energy also flows in and out of the system stochastically, which is to say energy comes in short bursts. For PAHs this energy comes in the form of UV photons. A PAH will absorb a UV photon, become electronically excited, then returns to the electronic ground state through non-adiabatic effects into highly excited (high temperature) vibrational states. Over the next few seconds the PAH will cool down by emitting IR photons, before eventually absorbing another UV photon and starting this process over again (see figure 1.12). This whole process known is known as an infrared cascade[41]. This stochastic process of absorbing a UV photon, becoming very hot suddenly, then slowly cooling means the IR spectrum is changing constantly. This process leads to a spectrum that is different from a spectrum recorded at a single temperature on Earth.

Attempts have been made to replicate the interstellar IR cascade emission spectrum of PAHs on Earth in the lab with some success[42, 43, 44]. However, due to the difficulty of reproducing interstellar conditions, a heavy reliance is put on theoretical models. Due to computational limits, most of these theoretical models[36, 45, 46] have relied on the harmonic approximation (explained below) to produce the IR spectrum at one temperature, after which statistical[46] and

empirically[47] derived laws are applied to account for the constant change in temperature during the cascade process. These methods have also proven to be successful, but the laboratory data from which these empirical laws are derived is limited, and a large number of assumptions still need to be made in these models. What is truly required are full anharmonic calculations (as described throughout the chapters of this thesis).

1.3 Theoretical spectroscopy

In the previous section we discussed how quantum mechanics is at the heart of spectroscopy. The equation which describes quantum mechanical systems is simple. Known as Schrödinger's equation, it can be written as follows

$$\hat{H}\Psi = E\Psi \quad (1.1)$$

where Ψ is the wavefunction that describes the system, $\hat{H}$ is a Hamiltonian that corresponds to the how the energy of the system is described and E is the total energy contained in the system. The equation simply describes the total energies contained in the system (i.e., molecule) depending on the specific state or wavefunction of the system (i.e., electron orbits) with

$$\begin{aligned} \hat{H} = & - \sum_i \frac{\hbar^2}{2M_i} \nabla_{\mathbf{R}_i}^2 \\ & - \sum_i \frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_i}^2 \\ & - \sum_i \sum_j \frac{Z_i e^2}{4\pi\epsilon_0 |\mathbf{R}_i - \mathbf{r}_j|} \\ & + \sum_i \sum_{j>i} \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} \\ & + \sum_i \sum_{j>i} \frac{Z_i Z_j e^2}{4\pi\epsilon_0 |\mathbf{R}_i - \mathbf{R}_j|} \end{aligned} \quad (1.2)$$

where $\mathbf{R}$ are the coordinates of the nuclei, $\mathbf{r}$ are the coordinates of the electrons, M_i is the mass of nucleus i , m_e is the mass of an electron. This equation accounts for all of the interactions inside the molecule. The first term describes the kinetic energy of all of the nuclei, the second term describes the kinetic energy of all of the electrons, the third term describes the energy of attraction between each electron and each nucleus, the fourth term describes the energy of repulsion between different electrons, and finally the fifth term describes the energy of repulsion between different nuclei.

Applying this Hamiltonian to a molecule and solving it will yield everything one could want to know about the spectral properties of the molecule. However, there is a caveat. As soon as there is more than one electron in the molecule, solving

this equation mathematically exact becomes impossible. It is only possible to solve mathematically exact for systems like the hydrogen atom or the helium⁺ cation, or numerically exact for very small systems. All is not lost though, approximations to this equation can be made to make it much easier (possible) to solve. For example, the Born–Oppenheimer approximation assumes that the motions of the nuclei are independent from the motions of the electrons. A fair assumption, since the electrons are so much lighter than the nucleus and therefore react much faster to stimuli. This simplifies equation 1.2 so that only three terms need to be computed, as the first term goes to zero and the last term becomes a constant.

Under this assumption a potential energy surface (PES) from the solution of the electronic part of the Schrödinger equation can be constructed simply as a function of the position of the stationary nuclei. The nuclei are adjusted in position until a minimum in total energy is found, representing the equilibrium geometry (or shape) of the molecule. Although an approximation, these approximate methods can still predict the structure of molecules fairly accurately. The accuracy is often limited by how the electron interactions are modelled in the various electronic structure methods.

1.3.1 Density functional theory

Density functional theory (DFT) is perhaps the most widely used method for modeling the electronic structure of large molecules due to it being relatively computationally inexpensive, while still remaining fairly accurate. The main assumption in DFT is that the electrons can be modeled as an electron density, which depends only on position ($\rho(\mathbf{r})$). With this electron density assumption, the second, third, and fourth terms of the Hamiltonian (equation 1.2) are replaced with functionals of $\rho(\mathbf{r})$, which are computationally much easier for a computer to handle. Errors do arise in this approximation from neglecting exchange correlation between electrons. Therefore, exchange interaction functionals must also be constructed to take into account the missing electron–electron interactions in the fourth term of equation 1.2. The choice of how these functionals are mathematically constructed impacts both the accuracy and speed of the computations. Since these functionals can be expressed in a vast number of ways, and no “universal” functional has been found, functional development is still a very active area of research in computational chemistry. For more a detailed explanation see reference 48.

1.3.2 Harmonic approximation

Once the electronic Schrödinger equation is solved (using methods such as DFT) and the equilibrium geometry is found, then the nuclear portion can be solved independently. In molecules that contain three or more atoms, the vibrations of the atoms are again too complex to handle in an exact manner. Therefore, approximations to solve the nuclear portion of Schrödinger’s equation are again needed. The most common approximation to make is the harmonic approximation, in which the potential energy (V) between each nuclei are approximated by a

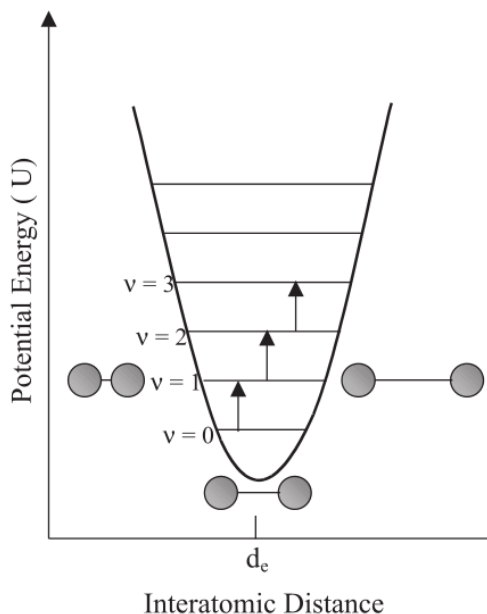


Figure 1.13 The harmonic potential of a diatomic molecule. (Adapted from reference 49.)

quadratic function given as

$$V = \frac{1}{2} \sum_i \sum_{i < j} F_{ij} X_i X_j \quad (1.3)$$

where $F_{ij} = \frac{\partial^2 V}{\partial X_i \partial X_j}$ are the quadratic force constants (strength of the bonds) between atoms i and j and X_i and X_j are the coordinates of atoms i and j . Figure 7.1 shows a visualization of a potential between two atoms. The quadratic force constants can be determined using numerical methods. Once these force constants are determined, they are mass weighted and put into a matrix. Diagonalizing this matrix gives the energies (frequencies of IR light) of the vibrational modes as the eigenvalues, and the descriptions of the vibrational motions (figure 1.9) as the eigenvectors. The intensities of these vibrational modes can then be determined by taking the derivative of the dipole moment along each of the vibrational modes.

The resulting harmonic IR spectrum for a typical PAH can be seen in figure 1.14. Databases containing the harmonic spectra of hundreds of PAHs are available online[36, 50].

1.3.3 Anharmonicities

While successful in reproducing the big picture, the harmonic approximation has many short comings. Its main problem is the potential itself. Figure 1.15 shows the

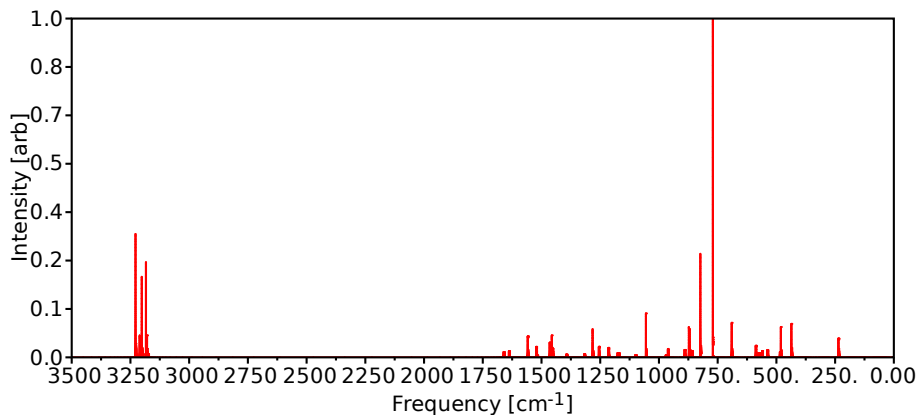


Figure 1.14 The harmonic infrared spectrum of chrysene.

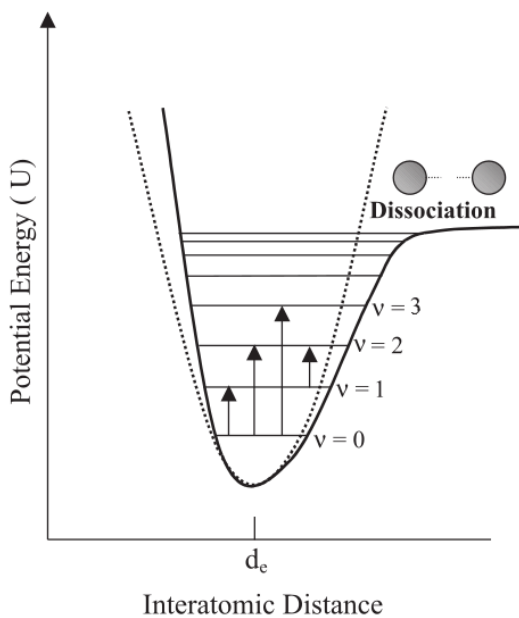


Figure 1.15 The anharmonic potential (solid black) of a diatomic molecule compared to the harmonic potential (dotted). (Adapted from reference 49.)

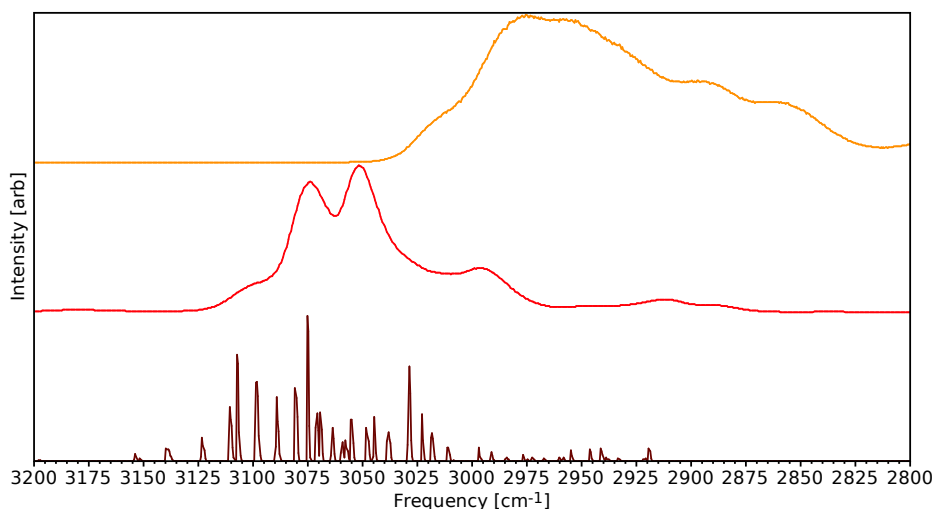


Figure 1.16 The anharmonic temperature dependent spectrum of the C–H stretching region of chrysene. Three temperatures are shown 100 K (brown), 1000 K (red), and 10,000 K (orange).

harmonic potential of a diatomic molecule next to the true potential of a diatomic molecule. There are some noticeable differences. Most importantly, the shape of the harmonic potential is incorrect. The harmonic potential is symmetric in shape, and continues to infinite energy on both sides, while the true, or anharmonic potential, is asymmetric in shape with a dissociation limit on the right side (long bond distances). Meaning, a molecule should break apart if it absorbs enough energy. This asymmetry of the anharmonic potential leads to many consequences. For one, it can be seen that the energy levels are no longer evenly spaced. This means that the photons emitted from these higher energy levels are also not evenly spaced in frequency. This uneven spacing leads to a shift in the spectrum at higher temperatures and excitations. In contrast to that, in the harmonic approximation all photons emitted from the excited vibrational levels would fall (incorrectly) at the exact same frequency as the lowest state.

In addition to the potential being incorrect, the harmonic approximation has made another fatal error. The mathematics of the eigenvalue/eigenvector solution to the potential result in a series of orthogonal vibrational modes. This means the vibrational modes do not interact with one another; exciting one vibrational mode would have no effect on the other vibrational modes. However, this is not true in nature due to anharmonicities. When a molecule is excited (such as at high temperatures) the modes interact with one another and cause shifts in the band position frequencies, and broadenings of the features themselves, as shown in figure 1.16. Additionally, *resonances* can occur between the vibrational modes. If two vibrational modes are close to one another in frequency then they can begin to

interact and resonate; much like an opera singer causing a wine glass to resonate with their voice making it shatter.

The exact nuclear potential of a molecule could be written as an infinite Taylor series around the equilibrium geometry

$$\begin{aligned}
 V = & V_0 + \sum_i \left(\frac{\partial V}{\partial X_i} \right) X_i \\
 & + \frac{1}{2} \sum_i \sum_j \left(\frac{\partial^2 V}{\partial X_i \partial X_j} \right) X_i X_j \\
 & + \frac{1}{6} \sum_i \sum_j \sum_k \left(\frac{\partial^3 V}{\partial X_i \partial X_j \partial X_k} \right) X_i X_j X_k \\
 & + \frac{1}{24} \sum_i \sum_j \sum_k \sum_l \left(\frac{\partial^4 V}{\partial X_i \partial X_j \partial X_k \partial X_l} \right) X_i X_j X_k X_l \\
 & + \frac{1}{120} \sum_i \sum_j \sum_k \sum_l \sum_m \left(\frac{\partial^5 V}{\partial X_i \partial X_j \partial X_k \partial X_l \partial X_m} \right) X_i X_j X_k X_l X_m \\
 & + \dots
 \end{aligned} \tag{1.4}$$

However, in order to account for the deficiencies of the harmonic approximation listed above, it is enough to retain only the first three non-zero terms of the equation. V_0 can be set to zero because it is arbitrary, and $\frac{\partial V}{\partial X_i}$ is zero because the Taylor series is expanded about the minimum energy structure which is a stationary point on the PES. This leaves the terms with the second, third, and fourth partial derivatives. These partial derivatives are referred to as the quadratic, cubic, and quartic force constants respectively. These sets of force constants together make up what is referred to as the quartic force field (QFF) of a molecule. To calculate the QFF, analytical 2nd derivatives are computed along the normal coordinate displacements to numerically calculate the 3rd and semi-diagonal 4th derivatives.

Once calculated, the QFF can then be used to produce the anharmonic IR spectrum of a molecule. Unfortunately, this is not as easy as the harmonic case. A simple matrix cannot be constructed and diagonalized. Instead, a second order vibrational perturbation theory (VPT2) approach is necessary. In the VPT2 treatment, the potential is first solved using the quadratic force constants only, resulting in the harmonic solution. The harmonic solution is then altered with small corrections, or in other words is *perturbed*, using the cubic and quartic force constants.

The energies of the new perturbed states are then given as

$$\begin{aligned}
 E(v) = & \sum_k \omega_k \left(n_k + \frac{1}{2} \right) + \sum_{k \leq l} \chi_{kl} \left(n_k + \frac{1}{2} \right) \\
 & \times \left(n_l + \frac{1}{2} \right)
 \end{aligned} \tag{1.5}$$

where the ω_k 's are the original harmonic frequencies, n_k are the number of quanta

in the k^{th} vibrational mode (or the vibrational quantum numbers), and the χ_{kl} 's are anharmonic constants.

The χ_{kl} values are calculated from the cubic and quartic force constant as follows

$$\chi_{kk} = \frac{1}{16}\phi_{kkkk} - \frac{1}{16}\sum_m(\phi_{kkm})^2 \times \left[\frac{8\omega_k^2 - 3\omega_m^2}{\omega_m(4\omega_k^2 - \omega_m^2)} \right] \quad (1.6)$$

and

$$\chi_{kl} = \frac{1}{4}\phi_{kkll} - \sum_m \frac{\phi_{kkm}\phi_{llm}}{4\omega_m} - \sum_m \frac{(\phi_{klm})^2 \omega_m (\omega_k^2 + \omega_l^2 - \omega_m^2)}{2\Omega_{klm}} + \sum_\alpha B_\alpha^e (\zeta_{kl}^\alpha)^2 \times \left[\frac{\omega_k}{\omega_l} + \frac{\omega_l}{\omega_k} \right] \quad (1.7)$$

with

$$\Omega_{klm} = (\omega_k + \omega_l + \omega_m)(-\omega_k + \omega_l + \omega_m) \times (\omega_k - \omega_l + \omega_m)(\omega_k + \omega_l - \omega_m) \quad (1.8)$$

and

$$B_\alpha^e = \frac{h}{8\pi^2 c I_\alpha^e} \quad (1.9)$$

where ϕ_{xxx} and ϕ_{xxxx} are the cubic and quartic force constants respectively, ζ_{kl}^α are the Coriolis coupling constants, and I_α^e are the moments of inertia.

The energy difference for a given IR transition of mode k ($n_k \rightarrow n_k + 1$) is then given by

$$\Delta E^{(k)}(\{n\}) = \omega_k + 2\chi_{kk} + \frac{1}{2}\sum_{i \neq k} \chi_{ik} + 2\chi_{kk}n_k + \sum_{i \neq k} \chi_{ik}n_i \quad (1.10)$$

with the n_x values being the number of quanta in the x^{th} vibrational mode. It should be noted that these set of equations hold for asymmetric top molecules. However, since most PAHs do not have significant symmetry these equations suffice.

Looking closely at the equations for the χ values above it can be seen that many of the terms depend inversely on the difference between harmonic frequencies. If two harmonic frequencies, or the sum of two harmonic frequencies, are equal to another harmonic frequency then some of these denominators can end up close to zero. When this happens these terms become infinitely large. This occurrence is what is referred to as a resonance in the VPT2 treatment. Four types of resonances are possible: Coriolis, when two harmonic vibrational modes are approximately equal to one another; Darling–Dennison, when two harmonic overtones (two or more quanta in one harmonic mode) are approximately equal to one another; type one Fermi, when one harmonic frequency is approximately equal to a harmonic overtone; and type two Fermi, when one harmonic frequency is equal to the sum

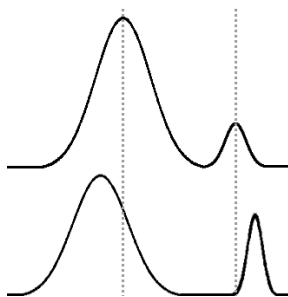


Figure 1.17 Two vibrational modes before resonance interactions (top), and after resonance interactions (bottom).

of two other harmonic frequencies. The VPT2 treatment as written is unable to handle these resonant terms, so the offending χ terms are removed completely, and a variational perturbation treatment is applied in order to account for these resonances.

In the variational treatment a resonance matrix is constructed, with the diagonal terms being the $E(\nu)$ terms with the offending χ terms removed, and the off-diagonal terms are the anharmonic coupling terms (given in reference 51). This matrix is diagonalized and the resulting eigenvalues are the new frequencies, and the square of the eigenvectors give the strength of the resonance between the modes and can be used to redistribute the intensity appropriately. Typically, the resonating IR features push each other apart in frequency, and the intensities are redistributed over both modes. (This will be discussed in more detail in the following chapters.) Figure 1.17 shows a toy example of the effect that a resonance has on two spectral features.

Resonances do not usually occur in isolation, especially in large molecule like PAHs. A particular band may be involved simultaneously in many separate resonances (and in PAHs this can be hundreds). These simultaneous resonances cannot be treated separately, but instead must be treated in what is referred to as a *polyad*. The polyad is constructed similar to the variational matrix. Each frequency of the modes involved in the chain of resonances is again inserted into the diagonal of the matrix and the appropriate coupling terms of reference 51 again make up the off-diagonals. This polyad matrix is diagonalized, and the resulting eigenvalues and eigenvectors are handled in the same manner as before. Figure 1.4 shows the dramatic effect a polyad of resonances can have on an IR spectrum of a PAH. The appearance of the multitude of features in the blue trace compared to the red trace is directly due to resonances.

In addition to anharmonic corrections to the frequencies, anharmonic corrections to the intensities can also be made involving the QFF terms. The equations describing these anharmonic intensities are pages long, so for brevity are not shown here. See reference 52 for the full set of equations.

1.4 In this thesis

Linear transformation of anharmonic molecular force constants between normal and Cartesian coordinates (Chapter 2)

This particular chapter is a slight outlier from the rest of the thesis, but without it all of the following chapters would not be possible. As will be explained in the following chapters, resonances play a dominate role in the aromatic C–H stretching region of PAHs. The software available at the start of this research (Gaussian09[53]) was not adequately able to handle the large number of resonances that occur in PAHs in its VPT2 treatment. Therefore, it was necessary to bring in a second piece of software, called SPECTRO[54], which could handle these resonances. Unfortunately, the output of Gaussian09 and the input requirements of SPECTRO were not compatible. Gaussian09 outputted the QFF of the molecules in normal-coordinates, but SPECTRO required the QFF in Cartesian-coordinates.

A coordinate transformation method from normal-coordinates to Cartesian-coordinates does exist in the literature[55]. However, this transformation is non-linear and quite complex. While working through this transformation, we realized why it was so complex: it was missing the translation and rotation eigenvectors for the normal modes. If these eigenvectors were reconstructed, then the transformation is no longer non-linear, and all complex terms (i.e., Coriolis constants) drop to zero. This transformation then becomes as simple as inverting a matrix. The exact procedure for reconstructing these missing eigenvectors, and performing the transformation are described in detail in this chapter. Example applications are also given.

The anharmonic quartic force field infrared spectra of three Polycyclic Aromatic Hydrocarbons: naphthalene, anthracene, and tetracene (Chapter 3)

With the production of high-resolution gas-phase spectra of PAHs in the aromatic C–H stretching region, it was found that current theoretical methods (i.e., the harmonic approximation) could not reproduce the experimental results. Therefore, it was proposed that anharmonic corrections were necessary. Here we perform such theoretical corrections to a set of small linear PAHs: naphthalene, anthracene, and tetracene. We apply the QFF produced by Gaussian09 and VPT2 treatment of SPECTRO to test this hypothesis. This paper marks the first proper treatment of resonances incorporated into polyads for PAHs. Comparisons to experimental high-resolution gas-phase experimental spectra, low-resolution high-temperature spectra, and matrix isolation spectra were performed. It was found that anharmonicities, and resonances indeed play a major role especially in the C–H stretching region, particularly type-two Fermi resonances. Additionally, the features from $2000 - 1820 \text{ cm}^{-1}$ ($5.0 - 5.5 \mu\text{m}$) (missing from harmonic calculations) were confirmed to be combination bands. Superior agreement between theory and experiment was achieved compared to previous harmonic calculations. All experimentally resolved

IR bands are identified and characterized.

The anharmonic quartic force field infrared spectra of five non-linear Polycyclic Aromatic Hydrocarbons: benzanthracene, chrysene, phenanthrene, pyrene, and triphenylene (Chapter 4)

This chapter extends the methods applied in Chapter 3, to a larger set of non-linear PAHs. The effect which anharmonicities and resonances have on PAHs with differing edge structures, symmetries and sizes are explored. Five PAHs were examined, benz[a]anthracene, chrysene, phenanthrene, pyrene, and triphenylene. Again, comparisons were made to experimental high-resolution gas-phase experimental spectra, low-resolution high-temperature spectra, and matrix isolation spectra. Agreement was found to within $-0.13 \pm 0.25\%$, $0.53 \pm 0.95\%$, and $0.41 \pm 0.63\%$ respectively, a vast improvement over previous techniques. It was found again, that resonances dominate the C-H stretching region, especially for PAHs with low symmetry. This work solidifies the necessity of performing anharmonic calculations to reproduce accurately the IR spectra of PAHs. All experimentally resolved IR bands are identified and characterized.

The anharmonic quartic force field infrared spectra of hydrogenated and methylated PAHs (Chapter 5)

Aliphatic C-H stretching modes of functional-group additions to PAHs are thought to be responsible for the IR features observed at 3.40, 3.46, 3.51, and 3.56 μm (2941, 2890, 2850, and 2809 cm^{-1}) in interstellar PAH emissions. In our previous work, we showed the importance of anharmonic calculations, and proper treatment of resonances for the aromatic features in this region. This work explores the impact that anharmonic corrections have on these aliphatic features. Two methylated PAHs: 9-methylanthracene, and 9,10-dimethylanthracene; and four hydrogenated PAHs: 9,10-dihydroanthracene, 9,10-dihydrophenanthrene, 1,2,3,4-tetrahydronaphthalene, and 1,2,3,6,7,8-hexahydropyrene are examined. Comparisons to high-resolution gas-phase, and matrix isolation spectra are made. Changes to the basis/functional used are also made, showing great improvement in the agreement compared to our previous work. The agreement to the high-resolution data improved to $0.00 \pm 0.17\%$, and the agreement to the matrix data improved to $-0.07 \pm 0.30\%$. Fermi resonances were found to continue to play a strong role in the C-H stretching region, even for the aliphatic modes. The changes to the spectra upon hydrogenation and methylation is also explored. All experimentally resolved IR bands are identified and characterized.

Accounting for large numbers of resonances in temperature dependent infrared spectra (Chapter 6)

The QFF used for the anharmonic IR spectra of molecules also allows for ab-initio calculations of temperature dependent band shifts, profiles, and broaden-

ings. Proper resonance treatment has been shown to be crucial for reproducing the IR spectra of PAHs. Therefore, in order to reproduce the temperature dependent spectra of PAHs the incorporation of these resonances is necessary. In this chapter a new method of incorporating these resonances into a Wang–Landau biased Monte–Carlo walk is presented. It is shown that incorporating a resonance polyad at each step of the random walk can greatly affect the resulting spectrum, and is relatively simple. Additionally, an interesting temperature dependent resonance effect is shown for tetracene, whereby a combination band gains significant intensity through resonances at particular internal energies.

Fully anharmonic infrared cascade spectrum of polycyclic aromatic hydrocarbons (Chapter 7)

The processes involved in the IR emission spectrum of interstellar PAHs are complex. PAHs absorb UV photons, then undergo an inter-conversion from an excited electronic state to their electronic ground state, but with highly excited vibrational states, then cool slowly through the emission of IR photons. To model accurately these IR cascade spectra, the temperature/energy dependent spectra must be calculated at each temperature visited by the PAHs as they cool. All methods and results of Chapters 2 through 6 are combined in this chapter to produce the full anharmonic theoretical IR cascade spectra of a set of PAHs. Anharmonic temperature dependence including the incorporation of polyads into the Wang–Landau method is employed. The advantage of this random-walk method over more exact methods is shown and discussed. The effect that initial absorbed UV photon energies has on the cascade spectra is explored. It was found, contrary to previous studies, that the cascade features do not shift (as is expected for thermal equilibrium spectra). Rather, it is shown that the statistical nature of the cascade results in cascade features that begin at their 0 Kelvin temperature, and only extend out low energy wings whose lengths are determined by initial UV energies. The “pseudo-shifting” observed in the cascade features are found to be due to changes in intensities of the lower frequency features as long wings of their higher frequency neighbors slip underneath them, rather than from “real” shifts from typical thermo-equilibrium arguments. This misinterpretation of shifting from previous experimental and theoretical studies has led astronomers to incorrectly believe that absorption spectra of PAHs cannot be used to predict the cascade emission spectra of PAHs because of these observed shifts. Our results show this to be in err. Additionally, astronomers have applied shifts of 15 cm^{-1} to their interstellar PAH models to account for these non-existent shifts. Our study paves the way for a “simple” transformation from absorption spectra to emission spectra relevant for modeling observed interstellar PAH spectra.

1.5 Outlook

The James Webb Space Telescope will mark a new era for astronomy. Its predecessor, The Hubble Space Telescope and The Spitzer Space Telescope, brought

forth beauty and wonder never imagined before. JWST will continue this legacy with even higher spatial and spectral resolution. The amount of beauty and science JWST will produce will be truly astounding. This will also mark a new era for interstellar PAH research. JWST is specifically designed to peer into the infrared universe; coincidentally, the exact wavelength range which covers PAHs. The IR spectra returned to us will show such glorious details of the AIB (PAH) bands that we will be able to confirm (or refute) all of the previous fantastic science which relied on lower resolution instruments. JWST will also allow for new science too, and answer questions such as: What is the composition of the interstellar PAH family? Is there a wide variety of PAHs or just a handful of “grandPAHs”? What are the chemical processes that go into forming PAHs? Do fullerenes really form from PAHs? And perhaps most excitingly, first time we will be able to probe the chemical variations in regions of star and planet formation; and hence take the organic inventory of habitable zones. Truly, astronomers will be seeing the universe again through new rose (PAH) colored glasses.

Yet, without quality data here on Earth, the possibilities that these new observations would bring would indeed be overly optimistic. This thesis focused on improving the quality of the infrared spectrum of PAHs through the incorporation of anharmonicities. The comparisons to available experimental data show that we have indeed achieved this goal. Anharmonic calculations are shown to dramatically improve the theoretical IR spectra, as well as being crucial to understanding the 3.3, 3.4, and 5.5 μm astronomical IR features. In addition, this thesis has shown that the incorporation of resonances into temperature dependent spectra is both simple, and important. Lastly, we arrive at the anharmonic IR cascade models. Paradoxically, the results of this study both showed the complexity in producing fully anharmonic cascade spectrum, while at the same time hinted that it may be unnecessary for astrophysical purposes. However, these conclusions can be seen as complementary. Chemists and astrochemists who want to know the gritty details, can apply these methods in full for a deeper understanding of PAHs, while the astronomers can happily apply the simplified conclusions to vastly improve their current models. With the results presented in this thesis, we can be confident that we are ready for the deluge of IR data soon to be arriving from the James Webb Space Telescope.