The anharmonic infrared spectra of polycyclic aromatic hydrocarbons

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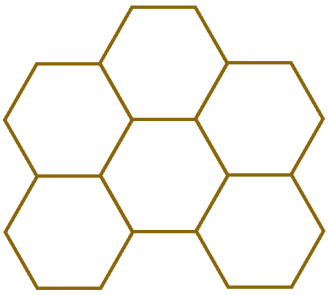

Accounting for large numbers of resonances in temperature dependent infrared spectra

A Wang–Landau statistical approach, making use of anharmonic quartic force fields, has been shown to reproduce temperature shifts and broadenings in the theoretical infrared spectra of small molecules. However, in order to reproduce the low–temperature gas–phase experimental infrared spectra of large molecules, it is crucial to account for a large number of resonances. A second order vibrational treatment, again making use of anharmonic quartic force fields, can account for these resonances through a polyad approach. Therefore, accurate reproduction of high–temperature gas–phase infrared spectrum of large molecules requires the combination of these two approaches. This work harmonizes these two distinct anharmonic effects into one theoretical treatment.

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6.1 Introduction

As computational power increases and theoretical methods improve, the calculation of highly accurate ab–initio molecular properties is being extended into the domain of larger molecules. Previously, due to computational limitations these larger molecules have been largely overlooked, but can ironically show a greater need for improved theoretical treatments. For example, the inclusion of anharmonicities through a quartic force field (QFF) potential energy surface (PES) has been shown to alter dramatically the resulting theoretical infrared (IR) spectra of polycyclic aromatic hydrocarbons (>20 atoms)[25, 26, 27, 105, 125, 132]. These changes to the spectra have been attributed large numbers of resonances that occur between the ever increasing number of normal modes. These large groups of resonances, so–called *polyads*, are handled sufficiently using a modified second order perturbation theory (VPT2) method akin to degenerate perturbation theory[51, 58].

Other effects attributed to anharmonicities are also known. Band shifts and broadenings are directly related to the temperature of the species due to anharmonic mode interactions. Again, the use of a QFF as the PES allows for accurate reproduction of these effects. Quantum statistical methods, such as a Wang–Landau approach have been shown to reproduce the high–temperature spectrum of small to medium sized molecules[133].

In order to reproduce the high–temperature spectrum of medium to large molecules, the VPT2 and Wang-Landau approaches need to be applied simultaneously. The same anharmonic PES of a molecule can be used to account for both of these effects in a simple manner. This work combines these anharmonic phenomenon (polyads and temperature) into one harmonized theoretical approach.

6.2 Theory

6.2.1 Polyads

In a VPT2 treatment, the anharmonic transition energies between neighboring vibrational levels ($n_k \rightarrow n_k$+1) is written as

$$\Delta E_k(n) = \omega_k + 2\chi_{kk} + \frac{1}{2}\sum_{i\neq k}\chi_{ik} + 2\chi_{kk}n_k + \sum_{i\neq k}\chi_{ik}n_i \tag{6.1}$$

where ω_k is the harmonic frequency of the k^{th} fundamental mode, n_k and n_l are the number of quanta in the respective k and l fundamental modes, and χ_{kl} are the anharmonic constants joining the k and l fundamentals.

The anharmonic constants are calculated in the VPT2 treatment using the calculated QFF of the molecule (see reference 87). During the calculation of these anharmonic constants there exists terms that are inversely proportional to the sums and differences of the harmonic frequencies (see equations A1 and A2 of reference 58). This opens up the possibility for mathematical singularities to occur when these sums and differences are equal (or nearly equal) resulting in divisions by zeros. These singularities are referred to as *resonances*. Four types of resonances

are possible within a VPT2 perturbation treatment: 1) Fermi 1; a fundamental band is approximately equal to two times another, 2) Fermi 2; a fundamental is approximately equal to the sum of two others, 3) Coriolis; two fundamentals are approximately equal, 4) Darling-Dennison; two first overtones are approximately equal. When a resonance occurs, the offending terms must be removed from the regular VPT2 treatment and instead treated in a degenerate VPT2 treatment. A two-by-two matrix is constructed with the diagonals consisting of the *deperturbed* transition energies (equation 7.6), and the off–diagonals with the appropriate coupling terms (Fermi 1, Fermi 2, etc.) (see reference 51). Once solved, this matrix provides the corrected band positions as the eigenvalues, and the degree of mixing between the modes as the square of the eigenvectors. In a physical sense, the offending modes push each other apart slightly in energy, and one mode can borrow intensity from the other. The degree of mode mixing is used to estimate this redistribution of intensity between the resonating modes[105].

Complications arise when modes are in simultaneous resonances with other modes. Treating each resonance individually leads to erroneous results. Instead the group of resonances need to be treated together in what is known as a *polyad*. The polyad resonance matrix is constructed in a similar manner, however additional "2-2" interactions need to be included to account for interactions between combination bands (see reference 51). Again, these matrices are diagonalized, giving the final band positions and intensities (see ref. 105, 125 for more details).

6.2.2 Temperature spectra

The temperature dependent IR spectra of a molecule can be produced in one of two ways. Either a full "exact" method or a Monte–Carlo "sampling" method. In the exact method, thermal populations of the lower levels are calculated at a specific temperature, then band energies and intensities are calculated for every possible transition between the sufficiently populated upper and lower states (see 84 for more details). In the sampling method, a biased sampling known as the Wang–Landau method[134, 135] is performed over vibrational energy space. The use of this method for PAHs was pioneered by Basire et al and applied to a variety of applications[133, 136, 137, 138]. The incorporation of polyads into this biased sampling method is straightforward and will be explained below.

The sampling method begins with calculating the vibrational density of states (DoS) through a random walk over internal vibrational energies, given for an asymmetric top as

$$\begin{aligned} E(\{n\}) = &\sum_{i=1}^{m} h\omega_i \left(n_i + \frac{1}{2}\right) \\ &+ \sum_{1 \le i \le j} \chi_{ij} \left(n_i + \frac{1}{2}\right)\left(n_i + \frac{1}{2}\right) \end{aligned} \tag{6.2}$$

The Wang–Landau method is a biased sampling method in which each time an energy bin is visited it is penalized slightly against further visits, forcing the walk to visit each energy bin a roughly equal amount of times (see 133, 139 for a full

description). This penalization factor converges to the DoS over enough iterations of the walk. Once complete, a second Wang–Landau walk is performed (using the previously calculated DoS to again bias the walk), however during this run the spectrum at each given step is recorded resulting in an absorption spectrum at each energy bin visited given by

$$\mathcal{S}(\nu, E) = \sum_k (n_k + 1)\sigma^k_{0\to1}\delta[h\nu - \Delta E^{(k)}] \tag{6.3}$$

With $\sigma^{(k)}_{0\to1}$ being the absorption cross section of mode k. For combination bands, the corresponding anharmonic cross sections are used with n_k taken to be the lower of the quanta of the two modes. $\Delta E^{(k)}$ becomes the asymmetric top term for the combination band (sum of the individual $\Delta E^{(k)}$'s).

Once complete, the energy dependent spectra are normalized by the number of visits to each energy bin. This results in the microcanonical absorption spectra of the molecule as a function of internal energy I(ν,E).

Transforming from an energy dependent spectrum to a temperature dependent spectrum is then simply a Laplace transformation

$$I(\nu, T) = \frac{1}{Z(T)} \int_{E_{min}}^{E_{max}} I(\nu, E)\Omega(E)e^{(-E/k_BT)}dE \tag{6.4}$$

With Z being the partition function

$$Z(T) = \int \Omega(E)e^{(-E/k_BT)}dE \tag{6.5}$$

The advantage of the sampling method over the exact method is that once the DoS and $I(\nu, E)$ are calculated then producing the spectrum at any desired temperature can be performed in a matter of seconds. In contrast, the exact method needs to be started from scratch for each desired temperature. Additionally, as long as enough steps are performed and the bin sizes are small enough, the sampling method rapidly converges to the exact method. More importantly, it can be seen easily where polyads readily fit into the Wang–Landau sampling method.

6.3 Temperature polyads

Incorporating polyads into the Wang–Landau method is straightforward. At each iteration of the second Wang–Landau walk used to construct $I(\nu, E)$, a polyad matrix is constructed as in a regular anharmonic treatment, except the diagonal terms are replaced by the new transition energies given by equation 7.6. The off–diagonal coupling terms of the polyad matrix are left unchanged in the VPT2 treatment, as they do not depend on the vibrational energy levels occupied, but only on the change in number of quanta in a given mode (equations 4-7 in reference 51 (here $\Delta(n_k)$ is always 1). Therefore, the polyad matrices only need to be constructed once, and at each iteration only the diagonal terms need to be replaced and the new matrix diagonalized. As before, the eigenvalues of the new polyad matrix gives the transition energies of the vibrationally excited states (i.e., a new set of Δ

$E^{(k)}(\{n\})$, and the squared eigenvalues give the intensity sharing percentages over the resonating modes (i.e., a new set of $\sigma^{(k)}_{0\rightarrow 1}$). It is possible, but not necessary to perform these polyad corrections within the Wang–Landau walk used to construct the DoS, but as resolution of the bin sizes is low (typically 25cm^{-1}) the corrections are insignificant. All other steps during the Wang–Landau creation of the temperature dependent spectrum remain the same as references 133, 139.

6.4 Methods

To demonstrate the of inclusion of polyads into a temperature dependent spectrum of a medium sized molecule, phenanthrene ($C_{14}H_{10}$) was chosen as a test case. A non–temperature dependent and temperature dependent (1000 K) spectrum were produced, each including and excluding polyads. Additionally, tetracene ($C_{18}H_{12}$) was chosen to demonstrate the changes that can occur in resonances as temperature is increased (from 100 K – 700 K).

The methods for producing the anharmonic IR spectra follow our previous work [105, 125, 132]. The software package Gaussian09[53] is used to optimize the geometry, calculate the QFFs, and produce the ground state IR intensities. Density functional theory is used (DFT) using the B3LYP functional[126] and N07D basis[128]. For the VPT2 treatment, and to produce the initial polyad matrices, a locally modified version of the SPECTRO software package[54] was used after transforming the QFF produced by Gaussian from normal to Cartesian coordinates[97].

The parameters used for the Wang–Landau walks were comparable to the values given in reference 133. For the initial Wang–Landau walk the vibrational quanta number probability increase/decrease parameter was set to 5%. The DoS energy bins were set to 25 cm^{-1}. The energy range of the walk was 0 – 15 eV (0 – 120983 cm^{-1}). Twenty iterations of decreasing penalization factors (f) were run, with each iteration consisting of 1×10^7 steps. For the second Wang–Landau walk, which was used to produce the energy dependent spectrum, the spectral bin size was set to 0.1 cm^{-1}. The second walk was performed until each energy bin was visited 2,500 times.

6.5 Results

Figure 6.1 shows the theoretical spectrum of phenanthrene computed at 0 K with and without including polyads compared to a high–resolution low–temperature gas–phase experimental spectrum[26]. As can be seen, additional bands are present due to intensity borrowing, as well as shifts in band positions, both occurring due to resonances and the inclusion of polyads in the calculations. Many features are absent and shifted incorrectly when polyads are ignored, and as a result the match to the experimental spectrum is quite poor. In contrast, the polyad results give very satisfactory comparisons to experimental data (see references 25, 26, 27 for more comparisons). Figure 6.2 shows the comparison of the theoretical spectrum at 1000 K computed with and without polyads. Significant differences can still

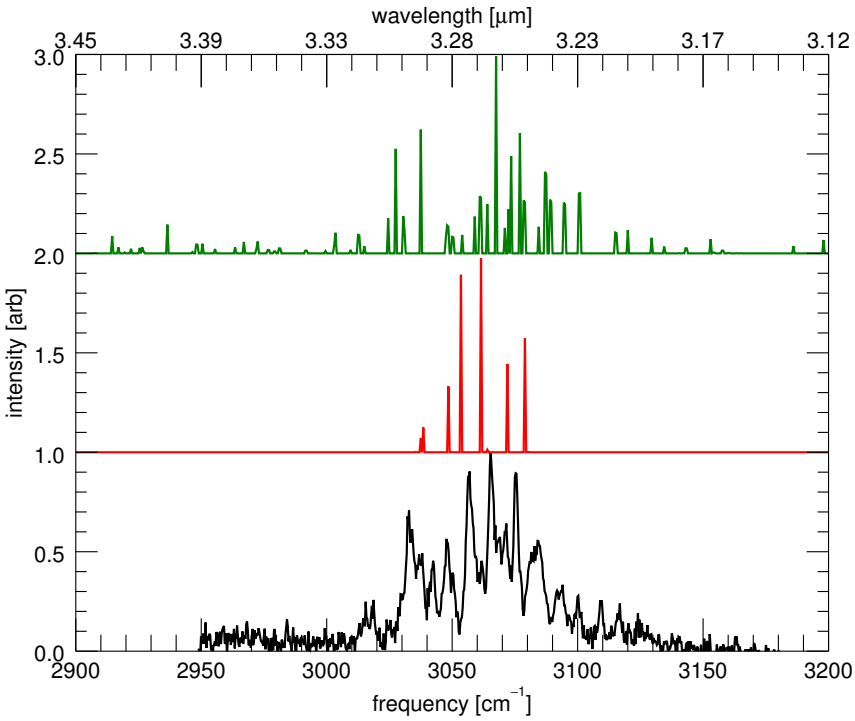

Figure 6.1 Comparison of the 0 K theoretical spectrum of phenanthrene including polyads (green), and excluding polyads (red), compared to a high–resolution low–temperature gas–phase experimental spectrum[26].

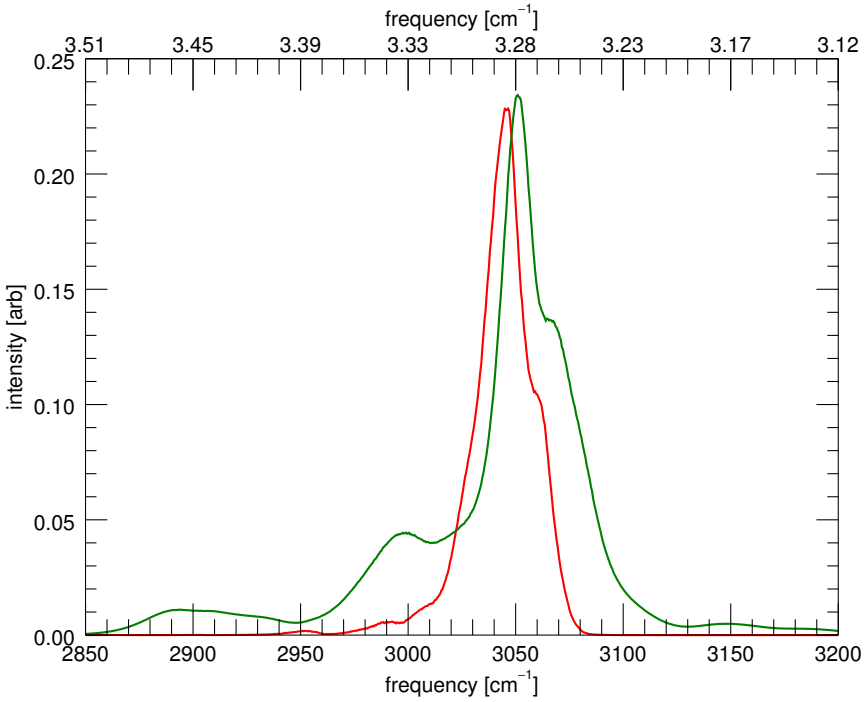

Figure 6.2 Comparison of theoretical spectrum of phenanthrene at 1000 K including polyads (green), and excluding polyads (red).

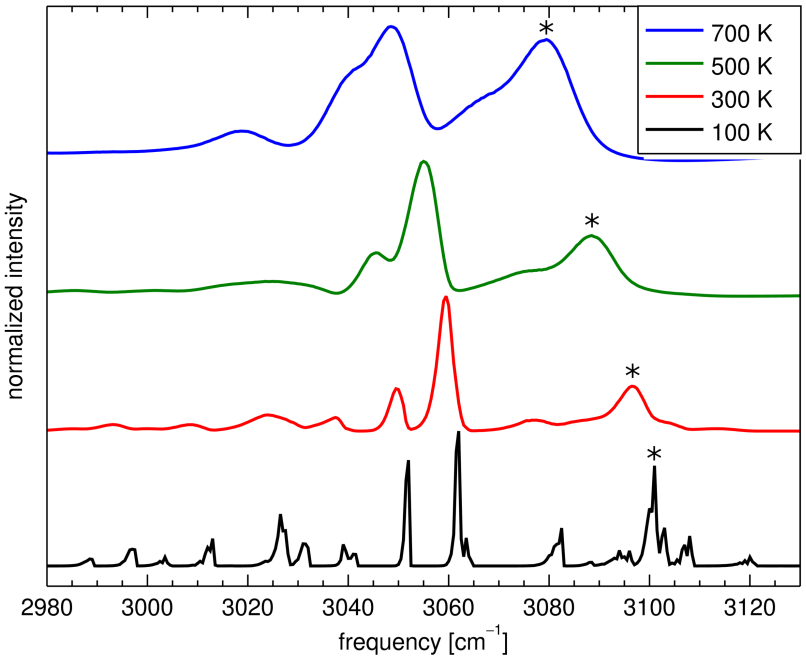

Figure 6.3 The theoretical infrared spectrum of tetracene showing an increase in relative intensity of a combination band (marked with a "*") as the internal temperature is increased.

be observed even in this highly broadened spectrum. Besides frequency shifts, the effects of intensity borrowing can also be observed, especially for the feature at 3000 cm^{-1}. The minor features arising from intensity borrowing are also still visible, now as an extended pseudo–continuum under the main spectral features. There is also an overall shift and broadening of the main spectral features when moving from the non–polyad to the polyad spectrum.

The anharmonic constants and quantum occupations of the CH–stretching modes, and the combination bands which resonate with them, were found to differ enough that it was possible for the combination bands to "catch–up" to the position of the CH–stretching modes. In other words, the resonance between a particular combination band and a fundamental can wax or wane as thermal population of vibrational levels increases. Since the strength of the interactions between resonating modes depends on the energy separation of the modes, as the combination bands catch–up they begin to borrow more intensity from the fundamentals. This has the effect of a gradual increase in intensity of the combination bands as the internal energy of the molecules is increased. For example, this effect was found to be very strong for a particular combination band in tetracene. The combination band was observed to gain significant intensity up to an internal energy of approximately 2.5 eV before decreasing again at higher energies. Figure 6.3 shows the effect this has on the temperature dependent spectrum. It can be seen that the combination band marked with a "*" initially drops in intensity (due to thermal broadening), but then grows again at higher temperatures compared to the two strongest fundamentals.

The methods described in this work have also been applied successfully to a larger set of PAHs (including hydrogenated, methylated, nitrogen–substituted, and cationic PAHs), which are the topics of future work. Similar behavior is found.

6.6 Conclusions

Incorporating resonances and polyads into a Wang–Landau statistical approach to temperature dependent spectra is straight forward. As shown previously[25, 26, 27, 105, 125, 132], the change in the IR spectrum of molecules where resonances play an important role is significant at low temperatures. The same holds true for high temperatures. Changes in both band positions and widths, as well as the appearance of additional features is observed even in the unresolved spectrum at high temperatures. The predicted temperature effects on an IR spectrum can be significantly underestimated when polyads are neglected. Additionally, resonances may wax and wane as the temperature increases, which can dramatically alter the measured spectra at specific internal energies or temperatures. The low effort and high impact of including polyads into the Wang–Landau approach warrants their inclusion in all temperature calculations of large molecules.

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