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Anharmonicity and deuteration in the IR absorption and emission spectrum of phenylacetylene

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ABSTRACT
Anharmonic cascade emission simulations, herein evinced by full reproduction and deep insights into recent emission spectroscopy experiments of phenylacetylene, are integral to the future successful analysis of JWST observational spectra. Experimental infrared absorption experiments conducted in this study reveal a complex spectrum dominated by quantum effects that are uncovered by anharmonic computational analysis. From this work, it becomes clear that phenylacetylene exhibits strong resonance coupling between fundamental and two-quanta combination modes as well as giving indication for coupling with higher-order, three-quanta combination bands. This study benchmarks the development of advanced computational methods that will be extended to larger systems of astronomical relevance and those including isotopic substitution and side group functionalization with groups such as acetylene. The astrophysical implications of these results, including the potential for detection of acetylenic C–H stretches in space, are discussed in the vein of the impact polycyclic aromatic hydrocarbons have on astronomical infrared emission bands.

KEYWORDS
Infrared spectroscopy; astrochemistry; anharmonicity; emission spectroscopy; polycyclic aromatic hydrocarbons

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Preamble
We dedicate this article to the memory of Timothy J. Lee, who recently passed away. Tim was a long-standing and highly valued member of our consortium to study the infrared characteristics of polycyclic aromatic hydrocarbon species of astrophysical relevance. With his deep knowledge of quantum chemical methods and techniques, his insights in the intricacies of PAH vibrational spectroscopy, and his expertise with quantum chemical tools, Tim guided several students and postdocs in their spectroscopic journey exploring the aromatic Universe and to a successful career in academia and beyond. With Tim, they were blessed with the best possible teacher and mentor quantum chemistry had to offer, as he was beyond generous in sharing his insights, knowledge, and expertise. He will be dearly missed.

1. Introduction
The aromatic infrared bands (AIBs) are a set of astrophysical infrared (IR) emission features that dominate
the spectrum of many interstellar medium sources in our own and other galaxies. Their measured band positions—namely 3.3, 6.2, 7.7, 11.2, and 12.7 μm—coincide with those found for polycyclic aromatic hydrocarbons (PAHs). PAHs are a class of molecules made up of fused hexagonal rings of sp²-hybridized carbon atoms with hydrogens decorating the periphery. The AIBs are generally attributed to PAHs. The emission originates from a fluorescence process where the PAHs are electronically excited by UV photons and relax, after internal conversion to the electronic ground state, through a vibrational cascade in the IR (see Tielens 1, for a review;[1]). Over the past three decades, the astronomical and physical chemistry communities have expended much effort in trying to elucidate the physical characteristics of these species and their behaviour in space [2–7]. Much of this effort has focused on understanding the spectral characteristics and relied largely on quantum chemistry using density functional theory (DFT). The resultant harmonic spectra have been assembled in readily accessible databases [3,5,8,9] that are widely used to analyze and interpret astronomical PAH spectra in terms of the make-up of the underlying population [10–16].

These DFT-computed spectra have been largely validated against matrix isolation studies of a few, small neutral and cationic PAHs in argon and N₂ matrices. This comparison reveals a systematic frequency shift that can be corrected by a (frequency-dependent) scaling factor, on the order of 0.96, implicitly reflecting the importance of anharmonicity effects and basis set errors [3]. However, in turn, the laboratory-measured spectra are affected by matrix effects that limit their accuracy to ±6 cm⁻¹ [17] and influence band intensities [18,19], thus putting constraints on where this approach can be effectively used. Therefore, more recent studies have been focused on using a Resonance Enhanced Multiphoton Ionisation (REMPI) ion-dip technique to measure low-temperature gas-phase absorption spectra at high spectral resolution and without the use of an external matrix [19–23]. These have been compared to the results from DFT studies that include anharmonic effects, using second order vibrational perturbation theory (VPT2), where the vibrational potential energy surface is expressed as a fourth-order Taylor expansion. These studies also account for Fermi and Darling-Dennison resonances, which are particularly important in the 3 μm region [24–26]. In the anharmonic approach, no correction factor is needed, and very good agreement is reached with an accuracy in peak wavelength position of about 0.1% [25].

Before a proper quantum chemical and theoretical comparison with astronomical spectra can be made, the calculated, low-temperature absorption spectra need to be converted into emission spectra using an approach that takes the full cascade from the initial high internal energy to very low internal energies into account. During this radiative vibrational relaxation, anharmonicity and resonances have profound effects on the peak position and profile of the spectral features that arise from the molecular vibrational modes [27–29]. In recent years, sophisticated models have been developed to quantify anharmonic effects on the IR emission spectrum [27,30]. These emission models can be validated against experimental studies on the IR vibrational emission of highly excited PAH molecules with the first results being very promising [25,26,31,32]. Here, this methodology is applied to a recent study of the IR emission spectrum of the aromatic and acetylenic C—H and C—D stretching bands in phenylacetylene measured during the collisional cascade [33]. Besides assessing the validity of the cascade simulations of astronomical spectra, this study receives additional impetus from the recent detection of pure rotational transitions of phenylacetylene in the dark cloud TMC-1 in the interstellar medium [34].

2. Methods

2.1. Experimental methods

Molecular beams of phenylacetylene and D-phenylacetylene (the singly deuterated isotopologue of phenylacetylene with deuteration taking place at the acetylene hydrogen) are formed by an Ar-seeded source composed of an external reservoir and a series 9 pulsed valve from General Valve. The source is operated at room temperature using an Ar backing pressure of 4 bar and at a repetition rate of 10 Hz. The gas expands into vacuum and is collimated by a 2 mm skimmer, providing an internally cold molecular beam. Following, the beam enters the extraction zone of a reflectron time-of-flight mass spectrometer (m/Δm = 2200 at 100 amu), as depicted in the scheme of Figure 1. (1 + 1) Resonance Enhanced Two-Photon Ionisation (R2PI) takes place in between the extraction plates of the spectrometer using a UV laser beam provided by a Nd:YAG laser (InnoLas Spit-Light1200) pumped dye laser (Radiant Dye) operating on Coumarin 153 in ethanol. Mass-resolved ion detection is performed using a reflectron time-of-flight mass spectrometer (R.M. Jordan D-850) equipped with a 40 mm dual microchannel plate (MCP) detector (Jordan Co. C-726).

In order to record the infrared spectrum of phenylacetylene and D-phenylacetylene molecules, the UV laser was tuned to a specific S₁ ← S₀ electronic transition of each species and was preceded by the tunable laser light of a high-resolution OPO/OPA laser (Laser
Figure 1. Schematic representation of the molecular beam setup, composed of a pulsed source seeded with Ar gas and a reflectron time-of-flight mass spectrometer. In between the extraction plates of the mass spectrometer, a nanosecond dye laser with a second harmonic generation unit is used for ionisation, while a counterpropagating nanosecond OPO/OPA infrared laser is employed for resonant vibrational excitation.

Vision), covering the 2550–3400 cm\(^{-1}\) range. The bandwidth of the OPO/OPA laser is approximately 0.1 cm\(^{-1}\), which is also the step size used for the measurements. Infrared spectra are measured via IR-UV ion dip spectroscopy [35] in which resonant infrared absorption is probed via a decrease in ion count at the mass of the molecular ion. To record such spectra, mass spectra are consecutively obtained with and without the excitation of the OPO/OPA laser. The UV and infrared lasers are operated at 10 Hz, but a shutter running at 5 Hz is used to block every other infrared pulse.

2.2. Computational methods

2.2.1. Anharmonic absorption spectrum

The methods utilised in this study have been described in detail elsewhere [20,24–26,31,36,37]. Here, therefore, only an abbreviated description is included. Computation of the optimised geometry, harmonic normal modes, and quadratic, cubic, and quartic normal coordinate force constants (quartic force field; QFF) of phenylacetylene and its deuterated isotopologue in the acetylene hydrogen is performed using the B3LYP [38] DFT functional in conjunction with the N07D basis set [39] within Gaussian 16 [40]. The N07D basis set is based on the 6-31G(d) basis with additional diffuse and polarisation functions that have been shown to improve the anharmonic treatment for PAH molecules [41]. A QFF is a truncated Taylor series expansion of the potential surrounding equilibrium, and follows the formula,

\[
V = \frac{1}{2} \sum_{i,j}^{3N} \left( \frac{\partial^2 V}{\partial X_i \partial X_j} \right) X_i X_j + \frac{1}{6} \sum_{i,j,k}^{3N} \left( \frac{\partial^3 V}{\partial X_i \partial X_j \partial X_k} \right) X_i X_j X_k + \frac{1}{24} \sum_{i,j,k,l}^{3N} \left( \frac{\partial^4 V}{\partial X_i \partial X_j \partial X_k \partial X_l} \right) X_i X_j X_k X_l
\]

However, a simple Hessian cannot be constructed due to the non-linear nature of the new potential term. Instead, 2nd order vibrational perturbation theory (VPT2) [42–45] is utilised. The VPT2 model implemented in Gaussian 16 fails to properly treat the redistribution of intensities between the resonant normal modes. Therefore, a locally modified version of the VPT2 code SPECTRO [46] is used to compute the anharmonic vibrational absorption spectrum.

SPECTRO has the advantage that it uses resonance polyads in the anharmonic computations [47,48]. When a resonance occurs between nearby normal modes leading to a near-singularity in the VPT2 perturbation, these modes are removed from the standard VPT2 treatment and are included in a resonance polyad matrix. The resonance polyad matrix allows for the computation of resonance effects, as well as for the treatment of modes that participate in multiple resonances simultaneously. Another advantage of the polyad matrix is the proper redistribution of intensities that is not captured with standard VPT2.

SPECTRO takes the optimised geometry and QFF from the Gaussian computation as input. The QFF is computed in normal mode coordinates, and a linear transformation is performed to produce a Cartesian coordinate QFF [61]. The resonances are determined via two parameters: the difference in energy between the two states (\(\Delta\)) set to the default value of 200 cm\(^{-1}\), and the minimum value of the interaction between the two states (W) is also set to the default value of 10 cm\(^{-1}\) [24]. The resultant anharmonic vibrational absorption spectrum is produced by convolving the anharmonic stick spectrum output of SPECTRO with a Lorentzian line shape function with a full-width at half-maximum (FWHM) of 1 cm\(^{-1}\).

2.2.2. Anharmonic cascade emission spectrum

While the quantum chemical procedure has been well-established for vibrational absorption [42,43], emission is not as commonly computed as the actual physics is
much more complicated. Following absorption of a UV photon inducing excitation to an electronically excited (singlet) state, rapid internal conversion to the ground electronic state occurs, populating the vibrational states of the ground electronic state with an energy equal to the initial UV photon energy [49]. From there, the molecule radiatively relaxes by emitting infrared photons until all the energy is dissipated. The probability of emitting an IR photon at a given internal energy is proportional to the magnitude of the vibrational frequency of the corresponding normal mode multiplied by the energy-dependent emission at the given internal energy. This process is modelled via a straightforward cascade emission process previously described in detail in Refs. [25,28,29,50]. In this method, an IR photon derived from the anharmonic vibrational frequency calculations is chosen based on the criteria described above, resulting in the loss of energy of the IR photon. In short, this process uses VPT2 to calculate the anharmonicity constants $x$ via the following equation:

$$E(v) = \sum_k \omega_k \left( n_k + \frac{1}{2} \right) + \sum_{k \leq l} x_{kl} \left( n_k + \frac{1}{2} \right) \times \left( n_l + \frac{1}{2} \right)$$

where $\omega$ represents the harmonic frequency and $n$ represents the number of quanta in the vibrational mode. Transition energies between adjacent vibrational levels of a given mode are then calculated by,

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

where $n_k$ is relative to the upper state and the $n_i$ represents a ‘spectator’ mode that is populated but is not involved in the transition. At this new internal energy, the energy-dependent emission spectrum is recalculated, giving a new set of emission probabilities. This is repeated until the molecule has relaxed to its vibrational ground state, and the entire process is repeated on-the-whole to improve accuracy, yielding a cascade emission spectrum. The resultant spectra were then smoothed with a boxcar average of width 120 cm$^{-1}$. Prior to the recalculation of the energy-dependent spectrum, the chosen IR photon loss results in a probability distribution at discrete internal energies. Please refer to reference [25] for a fully detailed explanation of the anharmonic cascade procedure. These simulations are performed using the IDL code suite developed and validated by Mackie et al. [25,31].

3. Results

Figure 2 displays the R2PI excitation spectra of phenylacetylene (top, green) and D-phenylacetylene (bottom, purple) with respect to their $S_1 \leftrightarrow S_0$ 0–0 transition found at 35875.7 and 35888.6 cm$^{-1}$, respectively. This spectrum agrees nicely with a previous R2PI study of phenylacetylene which reported, however, only the initial 600 cm$^{-1}$ range above the $S_1 \leftrightarrow S_0$ 0–0 transition [51]. In the spectrum reported here, up to 2200 cm$^{-1}$ above the 0–0 transition, vibronic transitions involving C–C modes and out-of-plane C–H modes are observed, with higher frequency vibronic transitions attributed to C–H stretching expected above the measured range. Details of these modes in the electronic ground state are discussed later. While overall the spectra of phenylacetylene and D-phenylacetylene are similar, small differences are observed. For example, D-phenylacetylene has a clear additional peak at 471 cm$^{-1}$, and in general, a more congested spectrum above 1000 cm$^{-1}$. The similarities in the spectra are expected, given that both species have similar vibrational modes below 2200 cm$^{-1}$, except for the modes directly involving the D atom. A detailed analysis of the vibrational spectra of both complexes in the range below 2200 cm$^{-1}$, and, therefore, of the corresponding vibronic transitions seen in the R2PI excitation spectra is beyond the scope of the current study.

3.1. IR absorption spectrum of phenylacetylene

Figure 3 displays the gas-phase experimental absorption spectrum (top) and the computed anharmonic absorption spectrum (bottom) of phenylacetylene in the C–H stretch fundamental region from 3000–3400 cm$^{-1}$. Between 3300 and 3400 cm$^{-1}$, four clear bands at 3317, 3325, 3340 and 3353 cm$^{-1}$ are observed experimentally, in excellent agreement with previous studies [52–54]. Between 3000 and 3120 cm$^{-1}$ a group of bands with lower intensity are detected, seven of which can be clearly distinguished from the noise level, at 3032, 3043, 3065, 3074, 3088, 3094 and 3107 cm$^{-1}$. The bands in this range arise from the aromatic benzene-ring C–H stretches, as well as combination bands and overtones of the lower-frequency C≡C stretching and in-plane (IP) and out-of-plane C–H bending motions. There is good visual agreement between the experiment and theory in this region. Many small features as well as side bands and shoulders are observed in the experimental spectrum compared to the computational spectrum. These can be attributed to possible lower intensity transitions not accounted for in the computations as well as blending of features resulting from the lower resolution in the experiment. From 2550–3000 cm$^{-1}$ no major infrared
bands are experimentally observed for phenylacetylene, in agreement with the computations.

The most intense feature in the experimental spectrum at 3340 cm\(^{-1}\) (bandwidth = 2.6 cm\(^{-1}\)) is assigned to the acetylene C–H stretch fundamental \((v_1)\), which is calculated at 3351.9 cm\(^{-1}\) and, thus, only differs from the experimental value by 0.35%. The lower-intensity feature observed at 3353 cm\(^{-1}\) partially arises from a two-quanta combination band involving one quantum of the acetylene C≡C stretch \((v_7)\) plus one quantum of a C–H IP bending motion \((v_{14})\) and is predicted at 3369.8 cm\(^{-1}\) with an absolute difference of 16.8 cm\(^{-1}\) (0.49%) when compared with the experimental band centre. This band has a double peak structure that will be discussed later in this Section.

Difficulties arise when attempting to identify the two features experimentally detected at 3317 and 3325 cm\(^{-1}\) as the computations predict only a single intense feature at 3346.3 cm\(^{-1}\). While an exact assignment of the features at 3317 and 3325 cm\(^{-1}\) cannot be determined at this time, these features most likely stem from a mixture of the strong \(v_7 + v_{15}\) acetylenic C≡C stretch + IP C–H bend combination band at 3346.3 cm\(^{-1}\) and three-quanta levels exhibiting \(A_1\) symmetry. Similarly, the three-quanta transitions probably contribute to the double-peak nature of the feature observed at 3352 cm\(^{-1}\). This suggests that the original implementation of the anharmonic theory, which includes transitions up to two-quanta levels, does not capture the entire picture in the case of phenylacetylene, and that higher-order transitions have to be considered [22].

To explore the impact of higher-order transitions, 71 three-quanta transitions in the range between 3300–3370 cm\(^{-1}\) are chosen for inclusion in the resonance polyad VPT2 treatment. The resultant anharmonic vibrational transitions are displayed in Table 1 with their anharmonic computed frequency, level build-up, and symmetry. Intensity information is not currently available in this higher-order treatment. As a result, the computed intrinsic intensity (in km mol\(^{-1}\)) of the one- and two-quanta transitions are included for reference. The inclusion of the additional three-quanta transitions leads to an improvement in the agreement between the experimental and computational spectra, as shown in Figure 2. The experimental spectrum is compared with the anharmonic computational results in Figure 3.
Table 1. Computed anharmonic vibrational frequencies (cm\(^{-1}\)), vibrational level build-up, computed intensities (km mol\(^{-1}\)) and mode symmetry of phenylacetylene, including 1, 2, and 3 quanta modes.

<table>
<thead>
<tr>
<th>Anharmonic frequency</th>
<th>Mode</th>
<th>Computed Intensity</th>
<th>Symmetry</th>
<th>Anharmonic frequency</th>
<th>Mode</th>
<th>Computed Intensity</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>3303.2</td>
<td>(v_7 + v_{29} + v_{35})</td>
<td>A(_2)</td>
<td>3335.9</td>
<td>(2v_{10} + v_{14})</td>
<td>B(_1)</td>
<td></td>
<td></td>
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<tr>
<td>3317.4</td>
<td>(v_7 + v_{19} + v_{35})</td>
<td>B(_2)</td>
<td>3336.1</td>
<td>(v_{10} + v_{14} + v_{17})</td>
<td>B(_2)</td>
<td></td>
<td></td>
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<tr>
<td>3321.4</td>
<td>(v_7 + v_{29} + v_{31})</td>
<td>A(_1)*</td>
<td>3336.3</td>
<td>(2v_{16} + v_{18})</td>
<td>A(_1)*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3321.6</td>
<td>(v_9 + v_{12} + v_{33})</td>
<td>B(_1)</td>
<td>3336.8</td>
<td>(v_{12} + v_{18} + v_{20})</td>
<td>A(_2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3323.4</td>
<td>(v_7 + v_{25} + v_{33})</td>
<td>B(_2)</td>
<td>3338.3</td>
<td>(v_{8} + v_{9} + v_{35})</td>
<td>A(_2)*</td>
<td></td>
<td></td>
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<tr>
<td>3325.5</td>
<td>(v_7 + v_{21} + v_{25})</td>
<td>B(_1)</td>
<td>3339.3</td>
<td>(v_{11} + v_{20} + v_{22})</td>
<td>B(_1)</td>
<td></td>
<td></td>
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<td>3327.4</td>
<td>(v_9 + v_{19} + v_{25})</td>
<td>A(_2)</td>
<td>3403.0</td>
<td>(v_{9} + v_{15} + v_{29})</td>
<td>A(_2)</td>
<td></td>
<td></td>
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<tr>
<td>3328.3</td>
<td>(v_9 + v_{27} + v_{30})</td>
<td>A(_2)</td>
<td>3404.4</td>
<td>(v_{9} + v_{15} + v_{29})</td>
<td>A(_2)</td>
<td></td>
<td></td>
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<tr>
<td>3328.8</td>
<td>(v_9 + v_{17} + v_{25})</td>
<td>A(_2)</td>
<td>3405.3</td>
<td>(v_{13} + v_{17} + v_{31})</td>
<td>A(_2)</td>
<td></td>
<td></td>
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<tr>
<td>3329.4</td>
<td>(v_9 + v_{15} + v_{32})</td>
<td>A(_1)*</td>
<td>3433.2</td>
<td>(v_{9} + v_{20} + v_{25})</td>
<td>A(_1)*</td>
<td></td>
<td></td>
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<td>3330.0</td>
<td>(v_9 + v_{17} + v_{27})</td>
<td>A(_1)*</td>
<td>3435.9</td>
<td>(v_{12} + v_{15} + v_{23})</td>
<td>A(_2)</td>
<td></td>
<td></td>
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<tr>
<td>3331.9</td>
<td>(v_{12} + v_{16} + v_{23})</td>
<td>A(_2)</td>
<td>3436.1</td>
<td>(v_{10} + v_{16} + v_{26})</td>
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<td></td>
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<tr>
<td>3333.2</td>
<td>(v_7 + v_{24} + v_{33})</td>
<td>A(_2)</td>
<td>3436.5</td>
<td>(v_{9} + v_{17} + v_{26})</td>
<td>B(_1)</td>
<td></td>
<td></td>
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<tr>
<td>3333.5</td>
<td>(v_7 + v_{18} + v_{36})</td>
<td>B(_1)</td>
<td>3447.1</td>
<td>(v_{7} + v_{15} = 85%)</td>
<td>10.96</td>
<td>A(_1)</td>
<td></td>
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<tr>
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<td>(v_7 + v_{16})</td>
<td>B(_2)</td>
<td>3348.9</td>
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<td>A(_2)</td>
<td>69.58</td>
<td>A(_1)</td>
</tr>
<tr>
<td>3333.9</td>
<td>(v_8 + v_{17} + v_{24})</td>
<td>A(_2)</td>
<td>3350.9</td>
<td>(v_{1} = 68% v_{7} + v_{14} = 17% v_{7} + v_{15} = 15%)</td>
<td>A(_1)</td>
<td></td>
<td></td>
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<td>3334.0</td>
<td>(v_{10} + v_{12} + v_{31})</td>
<td>A(_1)*</td>
<td>3351.0</td>
<td>(v_{15} + 2v_{17})</td>
<td>A(_1)*</td>
<td></td>
<td></td>
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<tr>
<td>3334.5</td>
<td>(v_{15} + v_{16} + v_{20})</td>
<td>A(_2)</td>
<td>3352.2</td>
<td>(v_{8} + v_{20} + v_{24})</td>
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<td>3334.7</td>
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<td>3357.1</td>
<td>(v_{9} + v_{12} + v_{24})</td>
<td>A(_1)*</td>
<td></td>
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<td>3334.7</td>
<td>(v_9 + v_{11} + v_{33})</td>
<td>B(_2)</td>
<td>3358.6</td>
<td>(v_{9} + v_{11} + v_{22})</td>
<td>B(_2)</td>
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<td>3334.9</td>
<td>(v_{13} + v_{14} + v_{23})</td>
<td>A(_2)</td>
<td>3358.7</td>
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<tr>
<td>3335.6</td>
<td>(v_{10} + v_{17} + v_{24})</td>
<td>B(_2)</td>
<td>3369.7</td>
<td>(v_{7} + v_{14} = 79%)</td>
<td>v(_{1} = 21%)</td>
<td>22.56</td>
<td>A(_1)</td>
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<tr>
<td>3335.9</td>
<td>(v_8 + v_{14} + v_{30})</td>
<td>B(_1)</td>
<td></td>
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</table>

to the resonance polyads causes a small shift in the predicted frequencies of the three intense features in the bottom panel of Figure 3. For example, the frequency of \(v_1\) shifted by 1.0 cm\(^{-1}\) from the computed frequency of 3350.9 cm\(^{-1}\) in the higher-order computations. This agreement with the previous computation validates that the higher-order transitions can be included in this case without significantly affecting the lower-order ones.

The symmetry of the transitions is important to consider when analyzing the potential impact of the newly included three-quanta transitions because Fermi resonance coupling will occur between states of the same symmetry. In this case, the acetylene C–H stretch fundamental \(v_1\) along with the \(v_7 + v_{14}\) and \(v_7 + v_{15}\) combination bands have A\(_1\) symmetry, all of which participate in intensity sharing with the intrinsically weak combination bands growing in intensity via the Fermi resonance. From Table 1, many three-quanta levels have A\(_1\) symmetry and the ability to strongly couple with \(v_1, v_7 + v_{14},\) and \(v_7 + v_{15}\). The difference between the observed and computed frequencies for the two assigned higher energy features, \(v_1\) and \(v_7 + v_{14}\), is on the order of 10 - 20 cm\(^{-1}\). This indicates that looking in the region from approximately 3330–3350 cm\(^{-1}\) may help identify transitions contributing intensity to the features at 3317 and 3325 cm\(^{-1}\). There are seven three-quanta levels, indicated with an asterisk in Table 1, that have A\(_1\) symmetry and can participate in resonance sharing with the intense fundamental and two-quanta combination bands in this region. It is likely that coupling with three-quanta levels is responsible for the additional bands and intensity distribution in the experimental spectrum that are not predicted by the two-quanta calculations.

3.2. IR absorption spectrum of D-phenylacetylene

Figure 4 presents the gas-phase experimental absorption spectrum (top) and calculated anharmonic absorption spectrum (bottom) in the region between 2550–3150 cm\(^{-1}\) of D-phenylacetylene. Some striking differences are observed in the absorption spectrum following deuteration. The most intense feature is detected at 2608 cm\(^{-1}\), which is in agreement with previous measurements performed in an \(N_2\) matrix [54]. This feature is assigned to the acetylenic C-D stretch fundamental \(v_9\) predicted at 2626.9 cm\(^{-1}\) - a difference in the observed compared to computed frequency of 18.9 cm\(^{-1}\) - implying an experimental (computational) isotopic shift of 725 (731) cm\(^{-1}\). In contrast to the spectrum of phenylacetylene, a single strong peak exists for D-phenylacetylene due to the difference in the frequency and intensity of the acetylenic C=C stretch fundamental. As mentioned above, in the case of phenylacetylene, Fermi resonances between the \(v_7 + v_{14}\) and \(v_7 + v_{15}\) combination bands (\(v_7\) is the acetylenic C=C stretch fundamental) with the \(v_1\) fundamental results in an intensity redistribution to the
Figure 4. Experimental (top) and anharmonic computational (bottom) absorption spectrum of D-phenylacetylene in the acetylenic C-D and aromatic C-H stretching region (2600 - 3150 cm$^{-1}$). Insets are an expanded look at the 3000–3150 cm$^{-1}$ region of the spectrum.

combination bands and that coupling of these intense transitions to nearby three-quanta transitions may lead to the fourth band observed in that experiment. Here, the acetylenic C-D stretch occurs at a much lower frequency and therefore no longer participates in a strong resonance coupling with any nearby combination levels.

Above 3000 cm$^{-1}$, a group of clear bands, mainly arising from the aromatic C–H stretch fundamental transitions, are observed at 3029, 3033, 3042, 3064, 3069, 3074, 3088, 3095 and 3107 cm$^{-1}$. The region where these bands are present is the same as for phenylacetylene but given the slightly higher signal-to-noise ratio of the D-phenylacetylene spectrum, more bands can be distinguished. Given that deuteriation takes place at the terminal end of the acetylene side group, very small differences are expected between the two isotopologues, which is indeed confirmed here.

3.3. Anharmonic cascade emission spectra

Figure 5 displays the emission spectrum of phenylacetylene (left) and D-phenylacetylene (right). In both panels, the experimental data obtained by Lacinbala et al. [33] is plotted as the black line, and the anharmonic cascade emission simulations at the various starting internal energies are plotted as the coloured lines. For phenylacetylene, the cascade simulations are normalised to match the peak intensity of the 3.0 μm feature whereas for D-phenylacetylene, the intensity is normalised to the feature at 3.3 μm.

In both cases, the band centred at 3.3 μm arises from the aromatic C–H stretch fundamentals of each molecule. For phenylacetylene, the more intense feature centred at 3.0 μm comes from the intrinsically more intense acetylene C–H stretch. The anharmonic cascade simulations match the band position of the 3.0 μm feature well for all internal energies with only a slight blue shift observed. The simulated bands at 3.0 μm have a narrower width, which may be attributed to the larger separation between the two band centres in the simulations and/or the lower resolution of the experiments. The band position of the 3.3 μm feature in the cascade spectra at 2 and 3 eV shows good agreement with the experiment while the agreement is slightly reduced for the 3 and 4 eV internal energies which are shifted to longer wavelengths. Nevertheless, there is still good agreement overall. Compared to the experiment, there is a longer ‘red wing’ on the long wavelength side of the 3.3 μm feature in the cascade spectra at 4 and 5 eV, which is absent in the 2 and 3 eV cascade spectra. This ‘red wing’ stems from anharmonicity and the higher levels of excitation.

In D-phenylacetylene (right panel), the band position and width of the 3.3 μm feature for all internal energies of the cascade spectrum and the experimental spectrum show excellent agreement with only a slightly broader width on the high-energy side of the experiment. Similarly, the cascade spectra agree well with the band centre of the 3.9 μm feature. The band position of the cascade spectra moves to longer wavelengths as the energy increases. There is less agreement for the intensities with the cascade simulation which predicts a larger relative intensity for the 3.9 μm feature compared to the 3.3 μm band than observed in the experiment. Importantly, the band observed in the experiment at 4.2 μm is missed completely in the harmonic model used by Lacinbala et al. [33]. In the present work which includes anharmonicity, the cascade spectrum simulations reproduce this feature quite nicely albeit with a slight bathochromic (red) shift.
Figure 5. Anharmonic IR cascade emission spectrum of phenylacetylene and D-phenylacetylene at starting internal energies of 2 (green), 3 (dark blue), 4 (light blue), and 5 (red) eV compared to the experimentally observed emission spectrum (black) of Lacinbala et al. [33].

In order to model the energy flow within the experiment, IR photon emission probabilities at different internal energies along the cascade spectrum are simulated and presented in Figure 6. Beginning with D-phenylacetylene in the right panel, the aromatic C–H stretch features at 3.3 μm and all experimental times are well modelled with the 4 and 5 eV internal energies. The best agreement with the red wing of the 6–12 μs experiments occurs with the 5 eV simulation. Moving to the acetylene C-D stretch at 3.9 μm, all internal energies agree with the blue threshold. These differ in their amplitude, with 3 and 4 eV matching the peak intensity of the 12 μs experiment. The 4 eV simulation displays a longer red wing than in the experimental spectra at each time. In phenylacetylene (left panel), each internal energy agrees well with the blue threshold of the 3.0 μm feature, and the 3 eV internal energy nicely matches the red wing of the longer time experiments (10–16 μs).

There are some interesting properties to note in the anharmonic characteristics of phenylacetylene. Large coupling constants between the acetylene C–H stretching mode and various other modes— including the C≡C stretch and other out-of-plane C–H bending modes— exist, which have a clear influence on the emission spectrum (see Figures S1-S2 in the Supplementary Information). To test whether these large couplings are a product of the specific B3LYP/N07D level of theory, additional anharmonic frequency computations were performed at the B3LYP/aug-cc-pVDZ, M06-2X/aug-cc-pVDZ, and MP2/aug-cc-pVDZ levels of theory. In each case, the large coupling constants are reproduced, indicating that they are correct and not an anomaly of the chosen method. To further explore this point, a deeper dive into the weeds of the anharmonicity is needed. This includes exploring the contribution of individual resonances and cubic and quartic force constants to the total anharmonicity constant. This is deferred to a future study as the basis of a concerted effort to understand the intricacies of the influence of PAH substitution on interstellar emission bands in the 3000 cm⁻¹ region.

4. Discussion

4.1. The emission of phenylacetylene

Overall, the experimental and theoretical emission spectra compare well. In phenylacetylene, the calculated acetylenic C–H stretch emission bands show a blue shift with decreasing internal energy (Figure 6). The same holds for the aromatic C–H stretches and the acetylenic C-D stretch in D-phenylacetylene. These shifts are of the same order as the measured blue shift with time, supporting the interpretation that the measured shifts result from the (collisional) energy relaxation process. The calculated, aromatic C–H stretch in phenylacetylene reveals a more complex behaviour (Figure 6). As emphasised in Section 3.1, the aromatic C–H stretching modes are very sensitive to resonance interactions.
Figures 3 and 4 show that this leads to a noticeable spread of the infrared activity over a $\sim 100 \text{ cm}^{-1}$ range. The spectral changes so apparent in Figure 6 reflect, then, the increased excitation in the low-lying C–H and C–C modes involved in these resonances and the resulting redistribution of the intrinsic intensity of the modes in this frequency range. As discussed in Section 3.1, the acetylenic C–H stretching mode is also susceptible to resonance interactions. However, in this case, appreciable intensity only occurs over a $\sim 40 \text{ cm}^{-1}$ range, and these interactions have little influence on the emission profile at high energies (Figure 6). The aromatic C–H stretching mode in D-phenylacetylene does not show similar, profound profile variations with increasing energy. This suggests that the interacting modes important for the resonance behaviour of phenylacetylene involve the C–H IP wagging and bending modes of the acetylene group in the 800-950 cm$^{-1}$ range that shift to 500-550 cm$^{-1}$ upon deuteration.

In agreement with earlier studies [27,31], the emission bands show a very similar blue rise for low energy initial excitations, but with increasing internal energy the emission bands start to shift appreciably. This implies that the measured emission bands could be good tracers of the internal energy of the emitting species. Figure 6 illustrates that for both species the best visual ‘fit’ between the calculated and measured spectra is obtained for low energies ($E \lesssim 2 \text{ eV}$) when examining the relative intensity and peak position. In making this assessment, the small difference between the experimental and calculated acetylene stretch position (Table 2) is ignored, as the measured and calculated absorption spectra are known to differ by a small amount (Figures 3 and 4, Table 2). For phenylacetylene, the relative intensity variations between the acetylenic and aromatic modes are particularly revealing. For D-phenylacetylene, intensity variations are much more modest. Relative intensity variations reflect (systematic) variations in internal excitation. In this respect, the microcanonical temperature of these species is recognised to drop from 1550 K at 5 eV of internal energy to 1000 K at 2 eV of internal energy [55]. Over this range, the high frequency (3300 cm$^{-1}$) mode of phenylacetylene becomes very sensitive to the actual temperature as is quantified in Figure 7. The internal excitation would have to drop substantially to yield similar relative intensity variations between the modes in D-phenylacetylene.

From this comparison it can be concluded that in the experiments reported in Ref. [33] phenylacetylene is already deexcited from the initial internal energy of 6.5 eV to $\sim 2 \text{ eV}$ at the beginning of the measurements (2 $\mu$s). Subsequent de-excitation occurs on $\sim 10$ times slower timescale, as on a timescale of $\sim 10$ $\mu$s the molecule loses only about another 1 eV. Apparently, collisional energy transfer becomes much less efficient with decreasing internal energy. In contrast, models imply that the average energy transferred in a collision is not very sensitive to the internal energy of the PAH molecule, varying by less than a factor 2 over the relevant internal energy range[33,56].

### 4.2. Astronomical implications

The interstellar aromatic infrared bands represent the emission of excited species integrated over the full cascade from the initial excitation energy set by the absorbed UV photon energy to full relaxation. Therefore, the
Figure 7. Emission band position of the aromatic C-H stretch and acetylenic C-H stretch of a) phenylacetylene and b) D-phenylacetylene at discreet internal excitations of 1 (red), 2 (orange), 3 (yellow), 4 (green), and 5 (blue) eV. Computational emission data from this work is represented by diamonds while experimental data from Lacinbala et al. [33] is shown as a circle. Note the difference in frequency range for the x and y axes.

Table 2. Absolute difference and relative percent difference of the experimentally determined and computationally predicted aromatic and acetylenic C-H stretch absorption and emission frequencies.

<table>
<thead>
<tr>
<th></th>
<th>Absorption</th>
<th>Absolute Difference (cm⁻¹)</th>
<th>Relative Percent Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph Aromatic</td>
<td>1 eV</td>
<td>13.0</td>
<td>0.423</td>
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<tr>
<td></td>
<td>2 eV</td>
<td>17.6</td>
<td>0.573</td>
</tr>
<tr>
<td></td>
<td>3 eV</td>
<td>2.0</td>
<td>0.066</td>
</tr>
<tr>
<td></td>
<td>4 eV</td>
<td>27.7</td>
<td>0.903</td>
</tr>
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<td></td>
<td>5 eV</td>
<td>55.4</td>
<td>1.681</td>
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<table>
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<th>Emission</th>
<th>Absolute Difference (cm⁻¹)</th>
<th>Relative Percent Difference</th>
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<tbody>
<tr>
<td>Ph Aromatic</td>
<td>1 eV</td>
<td>63.7</td>
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<tr>
<td></td>
<td>2 eV</td>
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<td></td>
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<td></td>
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<td>27.7</td>
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<td></td>
<td>5 eV</td>
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profiles of the emission bands represent the effects of this cascade. This is illustrated in Figure 5. Since much of the emission originates at low internal energies, the calculated bands start their blue onset at about the low temperature absorption position [27], but the peak reveals a very modest shift toward the blue with increasing initial excitation energy. As the internal energy increases, the profile develops a pronounced, red-shaded tail. This is a characteristic of all bands [27,28,31].

With the launch of the James Webb Space Telescope (JWST), routine but sensitive observations of the aromatic infrared bands at moderate spectral resolution become feasible for a variety of interstellar sources. As these and earlier studies [27,31] demonstrate, the detailed profiles of the aromatic infrared bands provide a sensitive probe of the internal excitation energy of the emitting species and, with an initial excitation energy fixed by the UV photon energy distribution, a probe for the size of the emitting species. As the present computations demonstrate, this effect is most easily quantified for isolated bands that are not much affected by resonances. That is quite well illustrated by the behaviour of the C-D stretch in D-phenylacetylene. In contrast, the C–H stretch in phenylacetylene is much more susceptible to resonance effects.

Phenylacetylene has long been considered too small to be a viable interstellar PAH. However, recently the presence of this molecule was established in the shielded environment of the TMC-1 dark cloud core [34], and this raises the possibility that this species could be contributing to the interstellar aromatic infrared band spectrum. In this regard, the C-D bond strength in phenylacetylene is 4.8 eV [57], and experiments show that for toluene, the appearance energy of fragments is ∼10 eV [58,59]. Acetylenic derivatives of larger PAHs could be produced by similar chemical processes as those leading to the formation of phenylacetylene in dark cloud cores but could also act on preexisting large PAHs. Fragmentation of the acetylene groups in such large PAHs
would have even higher appearance energies than for phenylacetylene. The acetylenic C–H stretch is sufficiently removed from the aromatic stretch to be readily separated and identified (cf. Figures 5 and 6). Present observations do not show an emission feature at the acetylenic frequency [60], but more extensive studies may be required to detect acetylenic functional groups.

Finally, the C-D stretch in D-phenylacetylene is well shifted from the C–H stretching modes, and this band may provide a good ‘hunting’ target for the presence of deuterated PAHs in the interstellar medium.

5. Conclusions

Anharmonic cascade emission spectra, benchmarked against emission experiments, fully reproduce experimental findings and capture features missed by harmonic models. To realise fully the power of JWST, accurate prediction of small features, demonstrated in this work, is integral to analyzing new high-resolution emission data. Many small features missed by previous missions (e.g. ISO, Spitzer) will be resolved in the JWST observations for the first time, and understanding their origin will allow for the probing of conditions in the local astronomical environment.

Anharmonic absorption computations have provided detailed insight into the complex experimentally observed structure in the acetylene C–H stretch region of phenylacetylene. Various strong resonances between the acetylene C–H stretch and combination bands involving the C≡C stretch and strong C–H IP bending motions redistribute intensity. Additionally, three-quanta levels are implicated in additional strong couplings leading to a further redistribution of intensity in the absorption spectrum. Deuteration is used to help verify the source of the anomalous behaviour in phenylacetylene. This study is another piece of evidence that points to the need for inclusion of anharmonicity in databases used for observational analysis such as the NASA Ames PAH IR Spectroscopic Database (PAHdb) [3,8,9], as observational data continues to outpace available reference data for interpreting the results.

The hand-in-hand relationship between experiment and theory is shown here to provide deep chemical insights that drive innovation toward understanding the astronomical environment. Recent detection of phenylacetylene in TMC-1 challenges the adage that small aromatic molecules will be destroyed in space relatively easily. Although this is a well-shielded dark cloud, there are environments where all sizes of PAHs and related aromatic molecules may exist. Future investigations of the emission spectra of larger PAHs and substituted PAHs, such as those with an acetylene side group, will lead to a better understanding of the main contributors to the interstellar aromatic infrared band spectrum.

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Significance statement

The experimental infrared absorption spectrum of phenylacetylene is complicated due to the presence of strong Fermi resonances, particularly in the acetylene CH stretch fundamental region. Anharmonic computations are required to assign the experimental spectrum because higher-order vibrational transitions (combination bands and overtones) gain strength due to strong coupling. In a similar vein, an anharmonic cascade emission simulation matches the experimental band position with no scaling factors included. Additionally, the anharmonic computations capture the presence of small features missed by the harmonic model; an integral result given the high-fidelity JWST data will resolve new, low-intensity emission features.

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