The Infrared Spectrum of Pyrene Anion in the CH Stretching Region

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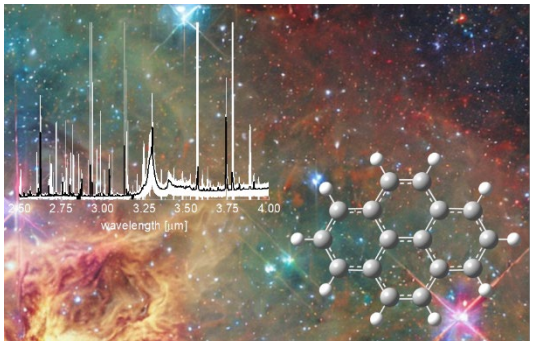
KEYWORDS.

Pyrene; polyaromatic hydrocarbons; astrochemistry; vibrational spectroscopy;

TOC Graphic



ABSTRACT

In this work, we report the infrared spectrum of pyrene anion, measured using messenger tagging with up to three Ar atoms. We assign the spectrum using density functional theory and vibrational perturbation theory. We discuss our results in the context of computed and experimental spectra from the literature as well as recent observations from astronomical sources, addressing the question whether PAH anions could contribute to the strong infrared emission bands at 3.29 μm from carbon rich regions of space.

Introduction

Polycyclic aromatic hydrocarbons (PAH) occur in many chemical contexts in nature as well as in technology. They are commonly found pollutants,[1-7] from various combustion processes,[8] and are models for graphenic materials, such as carbon nanotubes and graphene.[9-10] They are ubiquitous in astrochemistry, as they are present in astrochemical dust and ices,[11-18] and they have been widely investigated as carriers of diffuse interstellar bands (DIBs) and unidentified infrared emissions (UIEs).[19-29] A large body of work has been aimed at identifying PAHs in astrochemical environments and attribute their contributions to the DIBs and UIEs through experimental[28, 30-49] and computational studies.[26, 50-58] Computational data in current astrochemical databases[59-61] need to be validated through experimental data, particularly since improvements in observation, e.g., from the James Webb Space Telescope (JWST),[29, 62] yield increased detail of spectroscopic information. Together with laboratory data, these developments will enable more accurate modeling of astrochemical processes.

Most previous gas-phase spectroscopy work focused primarily on cationic and neutral PAHs due to the assumed relative scarcity of anions in interstellar environments. However, despite their lower abundance, anions are relevant in astrochemistry and have been detected in space.[63] In the absence of intense ultraviolet radiation in dense cold molecular clouds, anionic species potentially contribute uniquely to the astrochemical environment through electron attachment.[51, 64-67] In addition, the CH stretching transitions in PAH cations are likely weak compared to neutral and anionic PAHs,[37-38, 51, 53] lending additional importance to experimental data on anions. Similar to other PAHs with four rings, pyrene (Py, see Figure 1) has a positive electron affinity (0.406 ± 0.010 eV[68]) and can thereby form stable anions. While electronic transitions of Py^- are resonances in the electron detachment continuum,[69] the CH stretching vibrational transitions in this class of

PAHs are below the detachment limit and can therefore be expected to yield sharp vibrational bands.

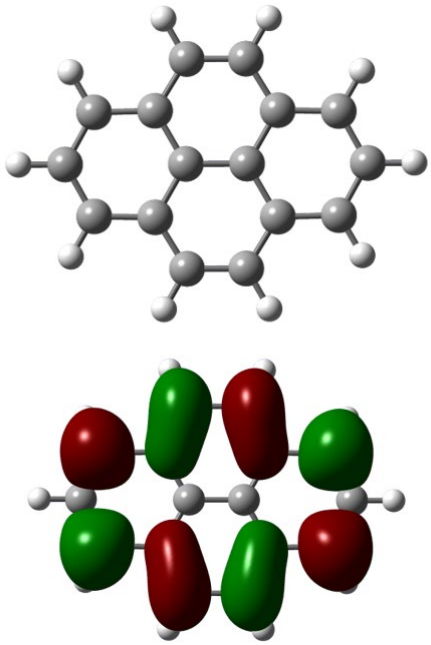


Figure 1. Calculated molecular structure (top) and highest occupied molecular orbital (bottom) of pyrene radical anion, Py^-.

Infrared spectra from carbon-rich astrochemical environments in the CH stretching region are congested and consist of contributions from many different species.[19, 27, 51] Moreover, the CH stretching region of PAHs is challenging to interpret, due to Fermi resonances of the CH stretching fundamental transitions with overtones and combination bands of CH bending modes.[26, 48-49, 52, 55-56, 58] In this work, we report the IR spectrum of gas-phase Py anions in the CH stretching region by IR messenger photodissociation spectroscopy using Ar atoms as messenger tags. We use anharmonic calculations to assign the dominant vibrational states in the spectrum.

Methods

Experimental. The photodissociation spectrometer used for this work has been described in detail in earlier work.[70-71] Cluster ions of the form $Py^-{\cdot}Ar_n$ (n = 1 – 3) were generated by entrainment of Py vapor from an oven at T = (400 ± 10) K into a pulsed supersonic expansion of Ar (Even Lavie valve, stagnation pressure 1.5 bar), where fast electrons (800 eV) created an electron impact plasma. Target anion formation resulted from the attachment of slow secondary electrons to neutral precursors in the beam. Figure 2 shows a mass spectrum of the ion source under typical source conditions. Negative ions in the expansion plume were accelerated into a custom-built Wiley-McLaren time-of-flight spectrometer, where they were mass selected by an interleaving comb mass gate and subsequently irradiated with the output of a tunable OPO/OPA laser system (pulse duration: 5-7 ns, bandwidth: 2-5 cm^{-1}, pulse energy: 5-10 mJ) in a multipass cell. The wavelength of the light source was calibrated by gathering a photoacoustic spectrum of water[72] in a 3D-printed photoacoustic spectrometer tube, and we estimate the absolute error bars of frequencies reported here to be ±3 cm^{-1}. Upon photon absorption, the weakly bound argon atoms dissociate according to

$$Py^- \cdot Ar_n \rightarrow n\,Ar + Py^- \qquad (n = 1 - 3). \tag{1}$$

Py^- fragment ions were separated from undissociated target ions in a two-stage reflectron, and their intensity was monitored on a dual microchannel plate detector. The fragment ion intensity was normalized to the photon fluence to generate IR photodissociation spectra. To ensure reproducibility and improve the signal to noise ratio, several spectra were taken on different days and averaged.

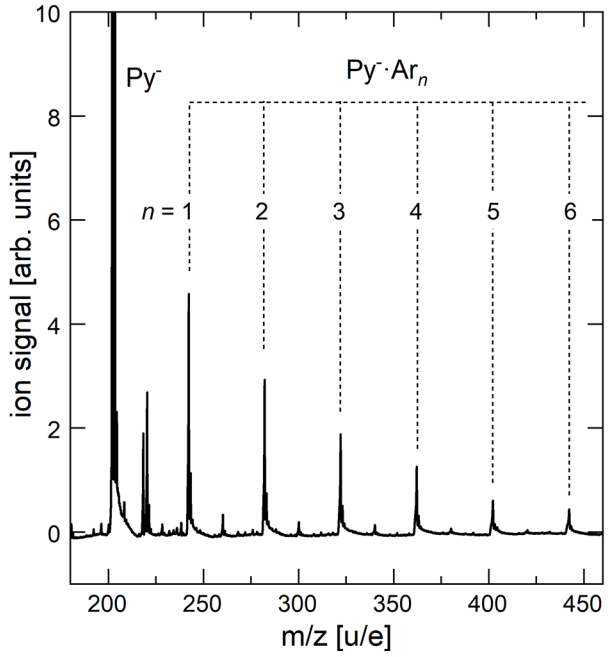


Figure 2. Reflectron time-of-flight mass spectrum under typical source conditions. The ion signal of the untagged Py^- ion is ca. 50 – 100 times greater than that of $Py^-\cdot Ar$. The weaker peaks between the $Py^-\cdot Ar_n$ progression are due to $Py^-\cdot H_2O\cdot Ar_n$ ions.

Computational. The structure of Py^- was optimized employing density functional theory (DFT) using the B3LYP[73-74] functional and 6-311+G(d,p) basis sets[75-76] for all atoms. Due to the large number of strongly coupled nearly degenerate states, the anharmonic spectrum of Py^- shows a significant basis set dependence (see Supporting Information). While spectra obtained using 6-311+G(d,p) and 6-311++G(2df,2pd) basis were in qualitative agreement, the spectra obtained using the 6-311+G(d,p) basis yielded the best fit to the experiment overall. A population analysis was performed using the same functional and the 6-311+G(d,p) basis set with the Merz-Singh-Kollman electrostatic potential (ESP).[77] Harmonic calculations are insufficient to describe the CH stretching region of the IR spectrum of PAH molecules, since many of the CH stretching

fundamental transitions are nearly degenerate with overtones and combination bands of CH bending modes, borrowing intensity through Fermi resonances and resulting in highly congested spectra.[55, 58, 78-79] We therefore used second order vibrational perturbation theory (VPT2)[80-81] calculations to assign the features in the experimental spectrum, employing the same functional and basis sets as for the structure optimization, consistent with the typical recommendation[80] that triple-ζ basis sets with polarizable (and in the present case also diffuse) functions is recommended for such calculations. To accelerate the calculations in a system the size of Py^- and to ensure that spectroscopic selection rules are obeyed, we enforced D_{2h} symmetry for some of the calculations, with the molecule in the *xy* plane. All calculations were carried out using Gaussian 16.[81] Note that we use Herzberg notation for the vibrational modes.

Analysis of the results of these calculations, showed some problematic trends. Specifically, some of the CH stretching fundamental transitions that should be forbidden by symmetry (here: a_g and b_{3g} modes under the D_{2h} point group symmetry) acquired significant intensities in the VPT2 calculations (see Supporting Information). Likewise, the VPT2 calculations predicted that some of the transitions that have two quanta of excitation in the same vibration (e. g. the $v = 2$ overtones), all of which should be forbidden by symmetry, acquired notable intensities when the symmetry was not strictly enforced. As described in the Supporting Information, we believe that the origin of the large intensities of symmetry forbidden transitions predicted by the VPT2 calculations most likely reflects numerical instabilities in the evaluation of the second derivatives of the potential, particularly for out-of-plane vibrations. These derivatives are obtained through finite difference schemes where the fourth derivatives are obtained by numerical evaluation of the elements of the Hessian in terms of the normal mode coordinates.[82-84] Analysis of the quartic contributions shows that there are a number of such terms, which couple states of different

symmetries and have values that are approaching several cm^{-1}. While these terms will have a negligible effect on the energies, they will contribute to the second order correction to the wave functions, and through this, lead to the problematic intensities that are noted above (see Supporting Information). To address this issue, the transition moments used to obtain the anharmonic intensities were evaluated only through first order in perturbation theory. Operationally, this is equivalent to using the harmonic intensities for the $\Delta v = 1$ transitions and anharmonic intensities for $\Delta v = 2$ transitions. Because of the change in the transition moments used to calculate the spectra, we also reevaluated the intensities of transitions to any state involved in a Fermi resonance, replacing the deperturbed transition moments for the fundamental transitions with the corresponding harmonic values. A similar approach was taken in our recent study of host-guest complexes.[85] To compare the harmonic and anharmonic calculated spectra with the experimental spectrum, we applied a scaling factor of 0.96088 to the harmonic frequencies. All spectra were broadened by a Lorentzian line shape with 8 cm^{-1} full width at half maximum.

Results and Discussion

Before discussing the IR spectrum, a characterization of the effects of the extra electron in Py^- seems appropriate. As outlined in earlier work,[68, 86] a zero-order orbital picture suggests that the excess electron resides in a π* orbital (Figure 1). Electron attachment distorts the molecule slightly by lengthening the C-C bonds in the molecule (on average by 0.40% or 0.56 pm), as well as the C-H bonds (on average by 0.18% or 0.2 pm). The effect on the C-H bond lengths reflects the incompleteness of the simple π* picture, which can be easily amended by realizing that a part of the excess charge is accommodated in the σ* orbitals of the C-H groups.[70-71] This result is corroborated by analyzing the charge distribution in the neutral and anion, which shows that the C

atoms accommodate -0.782 *e*, while -0.218 *e* reside on the H atoms. The spill-out of excess electron density into the C-H groups has significant consequences, since the C-H bonds are weakened as a result, and the C-H stretching frequencies in the anion are shifted to the red. This red-shift of the vibrational features is a general observation for PAHs.[53] We note that the transitions observed here are more than 200 cm^{-1} below the detachment threshold of bare Py^- (0.406 eV),[68] and Ar solvation will increase the electron binding energy further.[70] As a result, we do not expect any coupling of the C-H stretching features with the detachment continuum.

Figure 3.A shows the photodissociation spectrum of $Py^-\cdot Ar_2$ in the CH stretching region, monitoring the loss of both Ar atoms. We note that different levels of Ar solvation do not shift the observed features appreciably, as differences in the observed peak positions for $n = 1 – 3$ do not exceed 1 cm^{-1} (see Supporting Information). The near-absence of Ar-induced shifts strongly suggests that the spectrum shown in Figure 3 represents that of bare Py^- within our experimental uncertainties. Out of the 72 vibrational modes of Py^-, ten are CH stretching modes, and five of these are IR active, with b_{1u} or b_{2u} character. The experimental spectrum has several prominent features, all containing several unresolved or partially resolved transitions. Some of these features are qualitatively recovered by scaled harmonic calculations (Figure 3.C), specifically the peaks at 2982 cm^{-1} (labeled F_{25}) and around 3021 cm^{-1} (F_{23}, F_{42}, see Figure 4 for mode pattern). The anharmonic treatment (Figure 3.B) changes the frequencies and intensities of several of the fundamental CH stretching bands significantly. The feature at 3021 cm^{-1} has a low-energy shoulder at 3014 cm^{-1}. Modes ω_{23}, ω_{42}, and ω_{43} all contribute to these partially resolved, congested features. Our anharmonic analysis shows that the vibrational states in this region of the spectrum are strongly mixed in the basis of the harmonic normal modes. In particular, the b_{2u} modes ω_{42} and ω_{43} are mixed with nearly equal contributions. We assign the dominant feature to transitions

belonging to a mix of ω_{42} and ω_{43}, while the lower energy shoulder has leading contributions from ω_{23}. Table 1 lists the leading contributions in the harmonic normal mode basis for the assignable features in this region.

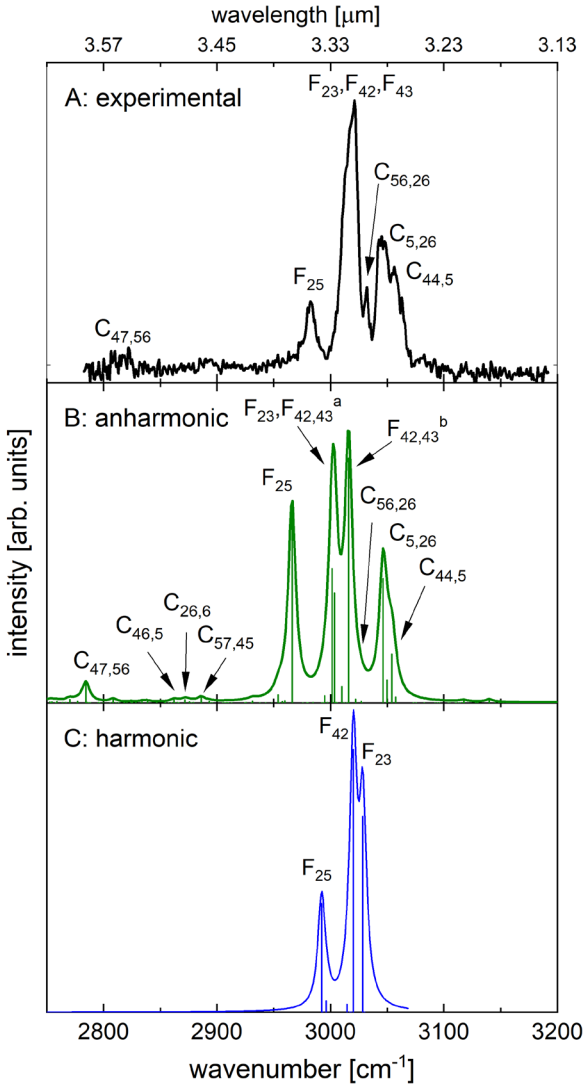


Figure 3. A: Experimental photodissociation spectrum of $Py^{-}\cdot Ar_2$. B: Anharmonic spectrum of Py^{-} with D_{2h} symmetry restriction. C: Harmonic approximation spectrum of Py^{-} with D_{2h} symmetry restriction. The labels describe the nature of the transitions: F_j = fundamental transition with leading contribution from mode j; $F_{42,43}{}^{a}$ and $F_{42,43}{}^{b}$ describe strongly mixed states (see also Table 1); $C_{j,k}$ = combination band with $\Delta v = 1$ each both modes j and k. The positions and intensities used for the calculated spectra are provided in the Supporting Information.

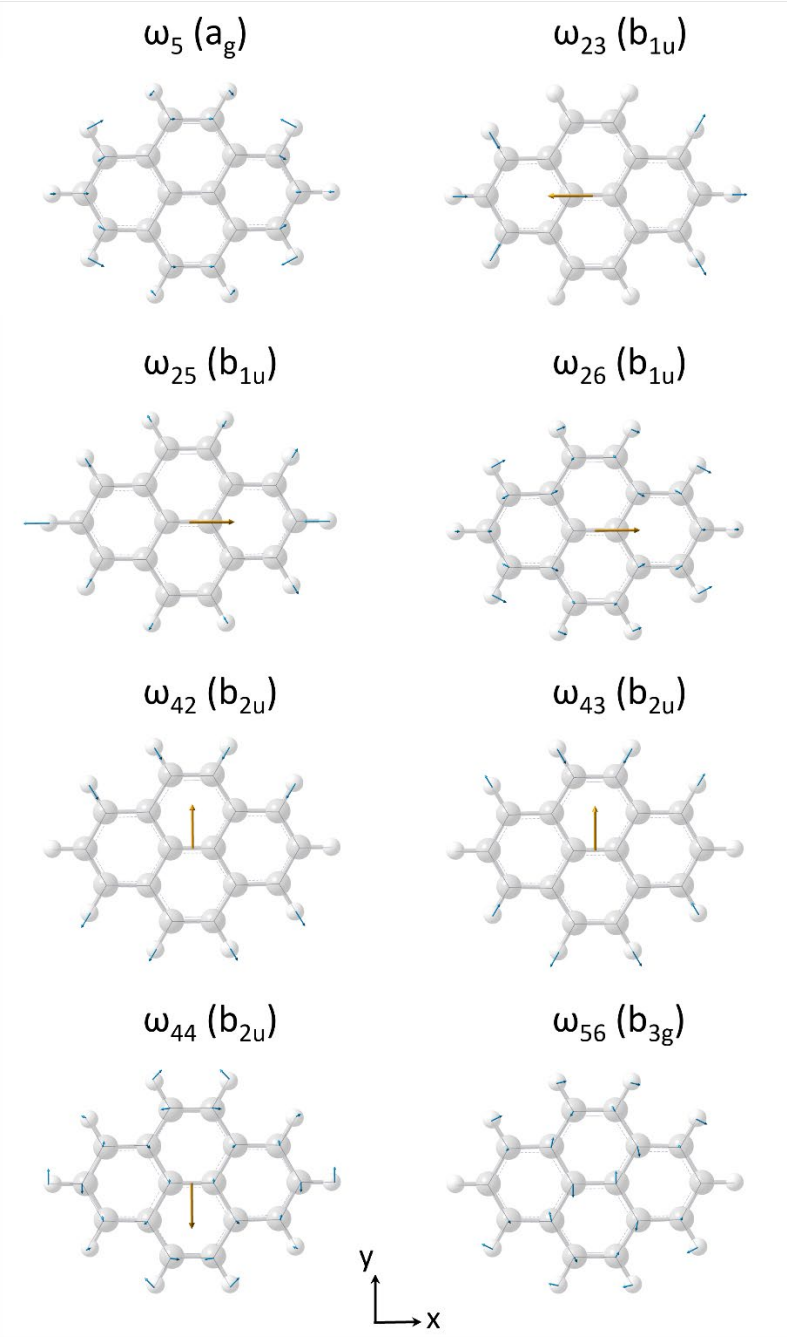


Figure 4. Vibrational normal modes (and their irreducible representations) with the most significant contributions to the IR spectrum of Py^- in the CH stretching region, either as fundamental transitions, or through Fermi interactions with CH stretching modes. Blue arrows show the normal mode pattern for each mode, while orange arrows represent dipole derivative vectors (where applicable).

None of the features at higher frequencies (above 3025 cm^{-1}) can be explained by harmonic calculations, but anharmonic calculations (Figure 3.B) agree very well with the experimental spectrum. They show that these higher frequency features are due to combination bands of vibrational modes with in-plane CH bending and CC stretching character (see Figure 4 for mode patterns). We assign the narrow peak at 3032 cm^{-1} ($C_{56,26}$) to a combination band of ω_{56} and ω_{26}. A peak at 3045 cm^{-1} ($C_{5,26}$) is due to a combination band of ω_5 with ω_{26}, and a partially resolved shoulder at 3056 cm^{-1} ($C_{44,5}$) is due to a combination band of ω_{44} and ω_5. At frequencies below the dominant group of peaks, we observe two broad, weak features and 2894 cm^{-1} and 2817 cm^{-1}, both of which are assigned to combination bands. All peaks and assignments are summarized in Table 1. We note that calculations without symmetry restriction recover the overall spectroscopic pattern with similar overall quality as the D_{2h} restricted calculations, but show some problematic intensity behavior as described in the Computational section.

Table 1. Assigned Transitions in the CH Stretching Spectrum of Py^-

observed [cm^{-1}]	calculated[a] [cm^{-1}]	assignment and symmetry[b]	calculated intensity [km/mol]
2817[d]	2784	ω_{47}/ω_{56}; $b_{2u} \otimes b_{3g} = b_{1u}$	11.3
2893[c]	2862[d]	ω_5/ω_{46}; $a_g \otimes b_{2u} = b_{2u}$	1.47
	2872[d]	ω_{26}/ω_6; $b_{1u} \otimes a_g = b_{1u}$	1.56
	2886[d]	ω_{45}/ω_{57}; $b_{2u} \otimes b_{3g} = b_{1u}$	2.68
2982	2966 (2992)	ω_{25} (75%) + ω_{44}/ω_{57} (16%); b_{1u}	110
3014	3002[e] (3029)	ω_{23} (54%) + ω_{26}/ω_5 (31%); b_{1u}	75.6
	3004[e] (3020)	ω_{43} (53%) + ω_{42} (44%); b_{2u}	61.8
3021	3016[e] (3020)	ω_{43} (47%) + ω_{42} (46%); b_{2u}	138
3032	3022	ω_{56}/ω_{26}; $b_{3g} \otimes b_{1u} = b_{2u}$	2.15
3045	3046	ω_5/ω_{26} (55%) + ω_{23} (30%); $a_g \otimes b_{1u} = b_{1u}$	69.9
3056	3054	ω_{44}/ω_5; $b_{2u} \otimes a_g = b_{2u}$	27.4

[a] anharmonic frequencies; for fundamental transitions, scaled harmonic frequencies of the leading contributions are reported in parentheses;

[b] entries with a single vibrational mode are fundamental transitions; entries with two different modes describe combination bands; fractional contributions reflect contributions from the states obtained from the VPT2 calculations, with all contributions of 10% or larger; the direct products result from the irreducible representations of each mode;

[c] broad and weak;

[d] either is a possible assignment for the feature at 2893 cm^{-1};

[e] the anharmonic frequency corrections for these features resulted in very similar frequency positions, we assign the experimental feature to the combined intensities of these transitions;

Figure 5 shows a comparison of IR data for neutral[47] and anionic Py in this range. As found previously, the CH stretching region of the IR spectrum of a PAH is strongly dependent on its charge state.[51, 53] In PAH ions, the excess charge is delocalized throughout the π system.[68] In anions, excess electron density in the π system spills out into net antibonding orbitals of the CH groups, weakening the CH bonds and shifting the bulk of the CH stretching modes to lower frequencies compared to the neutral molecule,[70] which is observed for Py (Figure 5). In contrast, the cation bands are calculated to shift to higher frequencies compared to the neutral molecules, with the peak of the envelope of their bands 20-40 cm^{-1} higher than for the neutral molecules in most cases.[51, 53]

The calculated IR intensities for Py^- are typically 3-10 times stronger than for neutral Py.[51, 53] In contrast, the CH stretching modes in PAH cations are predicted to be very weak. While Saykally and coworkers[37-38] reported experimental IR emission data on Py cations, their data in the CH stretching region are not sufficient to pinpoint individual transitions. Computational work on the different charge states of Py[53] predicts the intensities of the strongest CH stretching bands in Py cations to be ca. 10-200 times weaker than for neutral Py.[51, 53]

Based on modeling of chemistry in dense interstellar clouds, Wakelam and Herbst concluded[64] that PAHs constitute the dominant negative charge carriers in such environments. While we do not claim that Py^- itself is of special astrophysical significance, it seems appropriate to discuss the spectroscopy of PAH anions, exemplified by Py^-, in terms of possible astrophysical implications. We compare the infrared photodissociation spectrum of $Py^-\cdot Ar_2$ with astronomical observations on the right side of Figure 5, specifically with the IR emission spectrum of M17, a star forming region in Sagittarius,[29] and IR absorption in in the low-mass star-forming region Chameleon I.[62] Taking into account the average frequency positions and intensities calculated for anionic, neutral,

and cationic PAHs,[51, 53] it seems quite possible at first glance that the CH stretching features of PAH anions could contribute to the long-wavelength part of the prominent 3.29 μm (ca. 3040 cm^{-1}) feature in the emission spectrum from M17. However, the IR emission spectrum which prominently shows this feature comes from a bright region of space with significant UV irradiation, in which the survival of PAH anions is doubtful. [51] The spectrum shown on the right bottom panel in Figure 5, which originates from a dark molecular cloud (Chameleon I), shows only a broad, unresolved background absorption in the region where one would expect PAH anions to show their main IR features, on the low-frequency side of the OH stretching signatures from ice particles. Whether it is possible to attribute any features in the CH stretching region to PAH anions depends on the availability of PAHs as gaseous species, or whether their specific signatures survive ice formation.

While it would be tempting to claim that PAH anions can be spectroscopically observed in the interstellar medium, significantly more laboratory data in different frequency domains, accurate (i.e., anharmonic) calculations, and additional observational data are needed to substantiate such a claim.

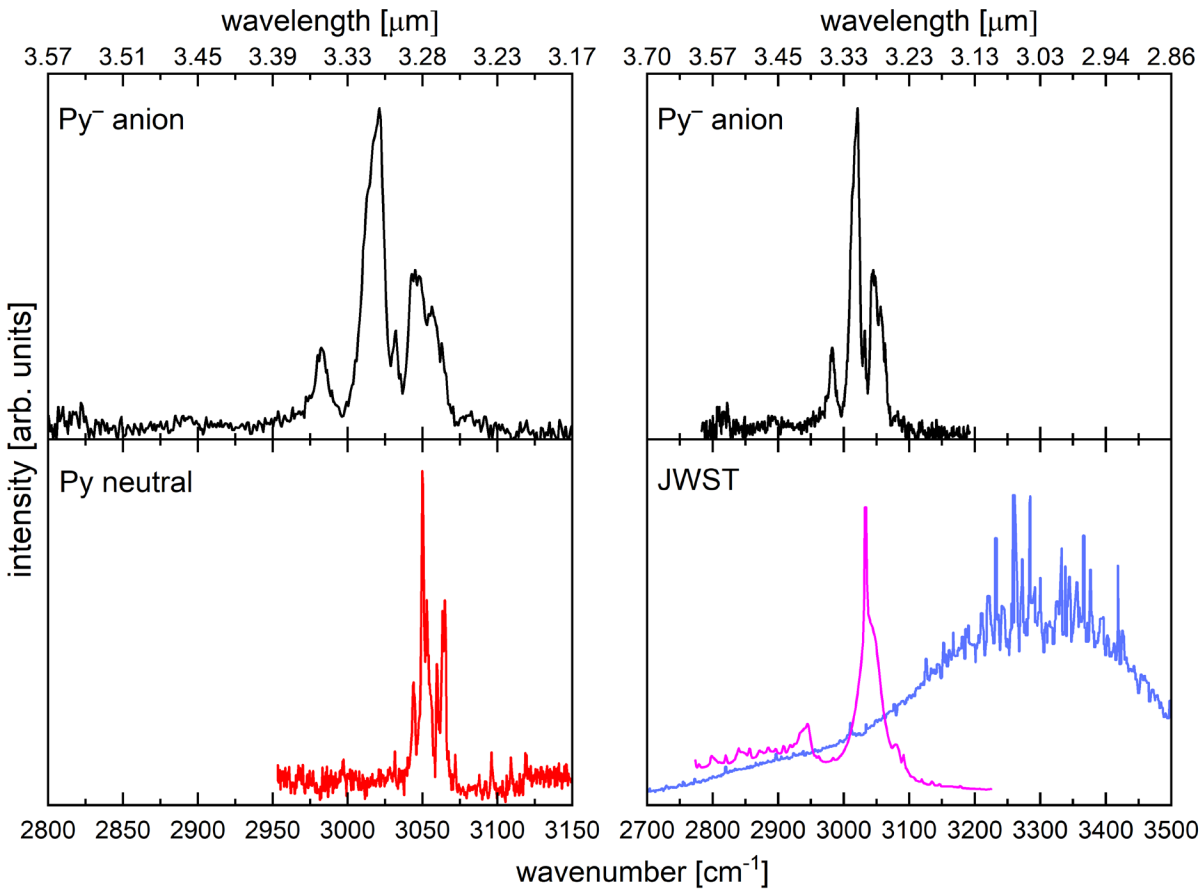


Figure 5. Left column: Comparison of experimental spectra of $Py^{-}\cdot Ar_2$ (top) and Py (bottom). The data on neutral Py (from two-color resonance-enhanced multiphoton ionization in a supersonic beam of Py seeded in Ar) was taken from ref. 47. Right column: Comparison of experimental spectrum of $Py^{-}\cdot Ar_2$ (top) with JWST data (bottom), showing IR emission[29] from M17 (magenta curve) and IR absorption (converted from flux measurements) in in the low-mass star-forming region Chameleon I,[62] probed by the background star SSTSL2J110621.63-772354.1 (blue curve). The two JWST spectra were scaled to fit to the same overall magnitude.

Conclusions

We report the IR spectrum of Py^{-} in the CH stretching region, measured using messenger tagging with Ar atoms, with the Ar induced shift of the bands less than 1 cm^{-1}. While the spectrum is dominated by several CH stretching fundamental bands, it cannot be satisfactorily interpreted with

harmonic calculations. Anharmonic VPT2 calculations recover the experimental spectrum very well, with an average error of 11 cm^{-1} (0.36% and actual deviations from the experimental values between -9 cm^{-1} (-0.29%) and 21 cm^{-1} (0.70%), and they do not require the use of an empirical scaling factor that needs to be applied to harmonic calculations. However, care must be taken to avoid problems with numerical instabilities in the evaluation of the second derivatives of the potential, which can lead to incorrect intensities. We assign several prominent bands to combination bands of in-plane CH bending vibrational modes, which gain intensity through Fermi resonances with CH stretching fundamentals. We show that messenger tagging of PAH radical anions provides an excellent approach to obtain experimental spectra for these species and to calibrate the quality of computations. Similar to the work by Mackie et al.[55] on neutral PAHs, our results show that VPT2 calculations can be used to significantly improve the predictions in computational databases.[59-61] Anharmonic calculations also will give better representations for the available states leading to possible IR emission upon electron attachment to Py and other PAHs. We hope that the present work can stimulate additional efforts towards the experimental and computational characterization of the spectroscopy of PAH anions. A better evaluation of possible astrophysical implications of PAH anions requires additional astronomical observations from regions of space with dark, carbon rich, molecular clouds.

ASSOCIATED CONTENT

Supporting Information. The following files are available free of charge.

SI_Vibrational_Analysis.xlsx (Excel file): Vibrational analysis for different basis sets.

SI_Salzmann_CH_stretches_in_Pyrene.pdf (PDF file): Dependence of the $Py^{-}\cdot Ar_n$ spectra on the number of Ar atoms, *n*; atomic coordinates of Py^{-}; comments on intensity problems in vibrational perturbation theory; basis set dependence of calculated anharmonic spectra.

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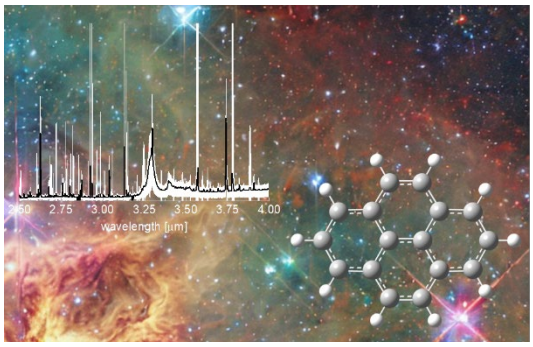
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