

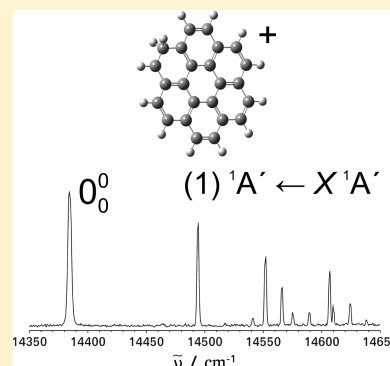
# (1) $^1A'$ $\leftarrow$ X $^1A'$ Electronic Transition of Protonated Coronene at 15 K

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**S** Supporting Information

**ABSTRACT:** The electronic spectrum of protonated coronene in the gas phase was measured at vibrational and rotational temperatures of  $\sim 15$  K in a 22-pole ion trap. The (1)  $^1A' \leftarrow$  X  $^1A'$  electronic transition of this larger polycyclic aromatic hydrocarbon cation has an origin band maximum at  $14\,383.8 \pm 0.2$   $\text{cm}^{-1}$  and shows distinct vibrational structure in the (1)  $^1A'$  state. Neither the origin nor the strongest absorptions to the blue coincide with known diffuse interstellar bands, implying that protonated coronene is not a carrier.



**SECTION:** Spectroscopy, Photochemistry, and Excited States

An experimental challenge for chemical physics is the measurement of the electronic spectra of large organic cations under the low temperatures of the interstellar medium (ISM). This is related with the concepts developed to explain the infrared (IR) emissions and optical absorptions in the diffuse ISM. The unidentified IR bands are assumed to originate from larger polycyclic aromatic hydrocarbons (PAHs) and have been suggested as possible carriers of the diffuse interstellar bands (DIBs), an enigma in observational astronomy for almost a century.<sup>1,2</sup>

The electronic spectra of a number of carbon chains and their ions can be measured in the laboratory using a variety of sensitive techniques,<sup>3,4</sup> and the comparison with astronomical DIB data seems to point toward much larger species.<sup>5</sup> Among these are PAH cations and their derivatives, composed of more atoms than initially envisaged.<sup>6</sup> Included are protonated PAHs ( $H^+$ PAHs), but the obstacle in the laboratory is how to measure the electronic absorption spectra of such transient species and equally important how to relax the vibrational and rotational degrees of freedom to the low temperatures, 10–50 K, prevalent in diffuse interstellar clouds.

Coronene,  $C_{24}H_{12}$ , is composed of six fused benzenoid rings and can be protonated easily due to its high proton affinity, 861  $\text{kJ mol}^{-1}$ . This system serves as a prototype for investigations into the roles of larger PAHs in the ISM, particularly in diffuse molecular clouds and photodissociation regions (PDRs), which are thought to possess similar physical conditions.<sup>7</sup> In a model of a PDR, it has been found that PAHs with less than 50 carbon atoms are fully dehydrogenated,<sup>8</sup> whereas those with between 50 and 90 carbons are proposed to be hydrogenated. Atomic hydrogen concentrations are on the order of  $10\text{--}100$   $\text{cm}^{-3}$  in diffuse molecular clouds, and a mechanism for hydrogen capture is  $C_{24}H_{12}^+ + H \rightarrow C_{24}H_{13}^+ + h\nu$ , having a rate

coefficient of  $1.1 \times 10^{-10}$   $\text{cm}^3 \text{s}^{-1}$  at 300 K.<sup>9</sup> Protonated coronene,  $C_{24}H_{13}^+$ , is an intermediate for understanding the mechanism of PAH hydrogenation, which takes place in the PDR and diffuse interstellar environments.

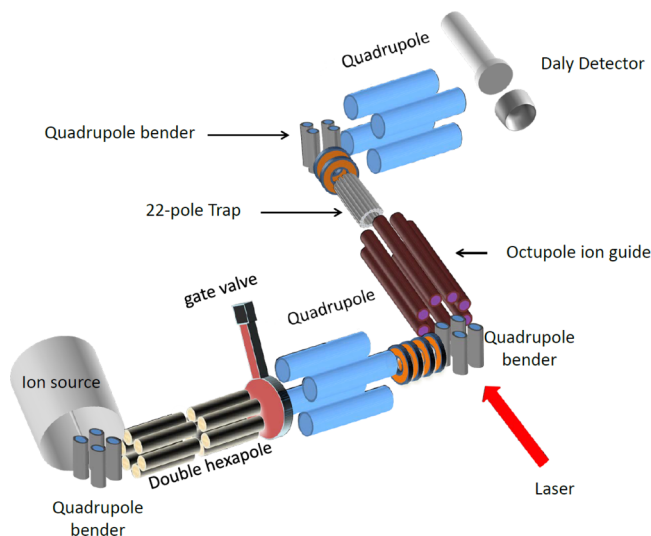
The most successful technique in chemical physics to achieve low temperatures has been the use of supersonic free-jet expansions; however, for larger species, the vibrational degrees of freedom are not always relaxed sufficiently. In this contribution, an approach that eliminates this problem is demonstrated, and the electronic spectrum of the largest PAH<sup>+</sup> derivative measured to date, protonated coronene, with 37 atoms and with rotational and vibrational temperatures equilibrated to around 15 K is presented. These low temperatures were achieved in a 22-pole radio frequency (rf) ion trap<sup>10</sup> in which mass-selected  $C_{24}H_{13}^+$  undergoes many collisions with cryogenically cooled helium. The electronic spectrum of the (1)  $^1A' \leftarrow$  X  $^1A'$  transition of protonated coronene in the visible was measured on thousands of such ions by a one- or two-color absorption–dissociation approach, by the detection of the loss of a hydrogen atom. A high signal-to-noise spectrum is obtained and compared directly with astronomical measurements. The results show that protonated PAH cations of this size are not responsible for the stronger DIBs.

Protonated species were generated by heating a solid sample of coronene to  $\sim 420$  K, followed by bombardment with 40 eV electrons in the presence of toluene ( $C_7H_8$ ) in a chemical ionization (CI) source. The proton affinities of  $C_7H_8$  and  $C_{24}H_{12}$  differ by 77  $\text{kJ mol}^{-1}$  such that the reaction

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$C_7H_9^+ + C_{24}H_{12} \rightarrow C_{24}H_{13}^+ + C_7H_8$  is exothermic. Protonated toluene ( $C_7H_9^+$ ) was produced from a CI source. There are excess protons from the electron bombardment of  $C_7H_8$ , and through ion-neutral reactions,  $C_7H_9^+$  was created. The apparatus employed is a newly built setup<sup>5</sup> and is shown in Figure 1.



**Figure 1.** Experimental scheme of the ion trap apparatus.

Briefly, ions from the CI source were deflected by  $90^\circ$  and injected into a 440 mm long hexapole, where they underwent collisions with helium and were precooled to room temperature. Protonated coronene was mass-selected by a quadrupole ( $\pm 0.5$  u) and electrostatically turned by  $90^\circ$  into an octupole ion guide and transported into a 22-pole rf trap (frequency  $\approx 7.47$  MHz; amplitude  $\approx 60$  V). Cations were then thermalized for approximately 50 ms with 6 K helium buffer gas (typically one collision per microsecond), followed by laser irradiation, extraction, and analysis by a second quadrupole.

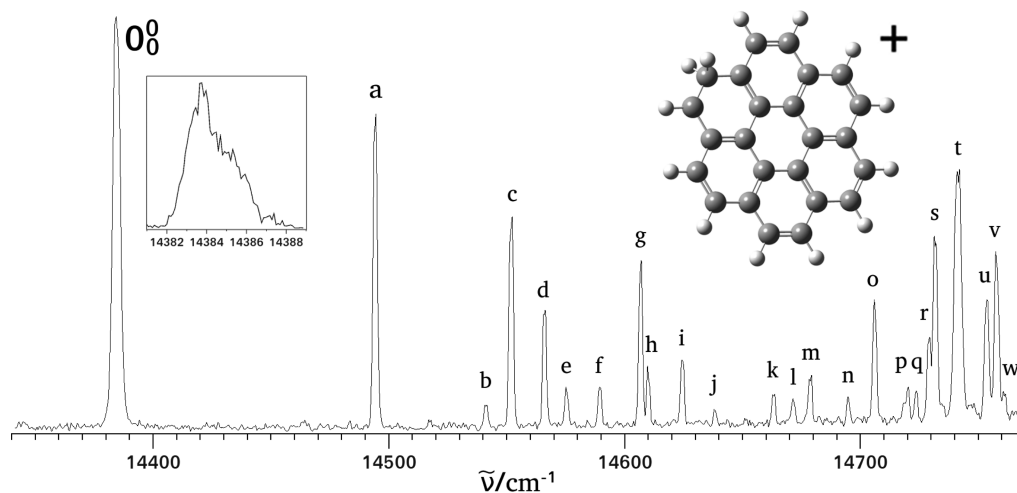
Coronene has equivalent protonation sites on the peripheral carbon atoms. No isomers with inner  $H^+$  addition are expected as these are energetically higher<sup>11,12</sup> by  $\sim 65$  kJ mol<sup>-1</sup> and are not produced in a CI source. The electronic absorption

spectrum of  $C_{24}H_{13}^+$  has been observed in a 6 K neon matrix using mass selection, with an origin band at 14 377 cm<sup>-1</sup> for the (1)  $^1A' \leftarrow X^1A'$  symmetry-allowed electronic transition.<sup>13</sup> On the basis of these data, the resonant multiphoton fragmentation spectrum of  $C_{24}H_{13}^+$  in the gas phase was sought and measured. The dissociation yield of the coronene cation,  $C_{24}H_{12}^+$ , was monitored as a function of wavelength to obtain the (1)  $^1A' \leftarrow X^1A'$  electronic spectrum of protonated coronene (Figure 2). The (1)  $^1A'$  excited state lies below the thermodynamic threshold for H loss ( $\sim 2.5$  eV); therefore, two or more photons of the same color are absorbed to bring  $C_{24}H_{13}^+$  to the fragmentation continuum. Excess energy from the excitation is sufficient for dissociation such that  $C_{24}H_{12}^+$  is detectable. Visible radiation from a tunable dye laser ( $0.07$  cm<sup>-1</sup> bandwidth with  $\sim 3$ – $8$  mJ of energy per pulse) was used. The measured electronic spectrum (Figure 2) was calibrated with a wavemeter and power-corrected, and the intensities of the recorded absorption features were scaled accordingly.

As can be seen, the spectrum (Figure 2) has a signal-to-noise ratio of  $\sim 100:1$ . Furthermore, no hot bands are observed around the origin band, indicating that the vibrational temperature is below 15 K. Previous studies of the band profiles in the electronic transitions of polyatomic cations in such an ion trap indicate a rotational temperature of around 15 K.<sup>14,5</sup> In the case of the (1)  $^1A' \leftarrow X^1A'$  electronic transition of protonated pyrene, the disappearance of the hot bands was directly demonstrated by increasing the number of collisions with helium atoms.<sup>5</sup> In the present measurements, similar conditions were chosen.

In the inset of Figure 2, the origin band of the (1)  $^1A' \leftarrow X^1A'$  electronic transition is shown. The spectrum was measured by a  $1 + 1'$  excitation–dissociation scheme, where the first color was tunable and the second was of a fixed wavelength (1064 nm). The band shows an unresolved rotational profile with a main feature centered at  $14\,383.8 \pm 0.2$  cm<sup>-1</sup> and tailing off to higher frequency, blue-shifted by 7 cm<sup>-1</sup> relative to that in a neon matrix.

Protonated coronene is of  $C_s$  symmetry and has 105 vibrations, 70 of  $a'$  and 35 of  $a''$  symmetry. Band positions and suggested assignments are given in Table 1. Calculated harmonic frequencies at the B3LYP/cc-pVTZ level of theory<sup>15</sup>



**Figure 2.** The (1)  $^1A' \leftarrow X^1A'$  electronic transition of protonated coronene measured with a  $0.07$  cm<sup>-1</sup> laser bandwidth using a resonant one-color multiphoton fragmentation scheme. The absence of hot bands around the  $0_0^0$  feature indicates rotational and vibrational temperatures of less than 15 K. A  $1 + 1'$  (1064 nm) approach was used to record the origin band (inset).

**Table 1. Band Maxima ( $\pm 0.2$  cm<sup>-1</sup>) and Suggested Assignments of the Vibrational Bands in the (1) <sup>1</sup>A'  $\leftarrow$  X <sup>1</sup>A' Electronic Transition of Protonated Coronene in Figure 2**

label	$\tilde{\nu}$ /cm <sup>-1</sup>	$\Delta\tilde{\nu}$ /cm <sup>-1</sup>	assignment
	14 383.8	0.0	0 <sub>0</sub> <sup>0</sup>
a	14 494.2	110.4	2 $\nu_{105}$
b	14 541.1	157.3	$\nu_{105} + \nu_{104}$
c	14 551.8	168.0	2 $\nu_{104}$
d	14 565.9	182.1	$\nu_{105} + \nu_{103}$
e	14 575.2	191.4	$\nu_{105} + \nu_{102}$
f	14 589.4	205.6	$\nu_{104} + \nu_{103}$
g	14 606.8	223.0	4 $\nu_{105}$
h	14 610.0	226.2	$\nu_{104} + \nu_{102}$
i	14 624.4	240.6	2 $\nu_{103}$
j	14 638.1	254.3	$\nu_{103} + \nu_{102}$
k	14 663.2	279.4	2 $\nu_{105} + 2\nu_{104}$
l	14 671.4	287.6	
m	14 678.8	295.0	$\nu_{105} + \nu_{100}$
n	14 694.7	310.9	$\nu_{102} + \nu_{101}$
o	14 706.0	322.2	$\nu_{104} + \nu_{100}$
p	14 720.2	336.4	6 $\nu_{105}$
q	14 723.7	339.9	4 $\nu_{104}$
r	14 729.1	345.3	2 $\nu_{105} + 2\nu_{103}$
s	14 731.7	347.9	$\nu_{70}$
t	14 741.5	357.7	$\nu_{69}$
u	14 753.6	369.8	$\nu_{68}$
v	14 757.6	373.8	$\nu_{67}$
w	14 761.1	377.3	2 $\nu_{105} + 2\nu_{102}$

are listed in Supporting Information Table S1. The experimental values assigned are in agreement with the calculated excited-state frequencies. There are some discrepancies in the lowest vibration  $\nu_{105}$ ; theory predicts it to be at 64 cm<sup>-1</sup>, whereas the experiment gives 55 cm<sup>-1</sup>, which is deduced from double quanta excitations. Quartic anharmonicity contributions, which are not included in the double harmonic approximation, cause an increase of the transition energy of 4 $\nu_{105}$  and 6 $\nu_{105}$ , as well as that of 4 $\nu_{104}$ , in the excited state.

Double quanta excitations of  $\nu_{105}$  (CH<sub>2</sub> rocking) and  $\nu_{104}$  lie at +110.4 and +168.0 cm<sup>-1</sup>, respectively. These are low-frequency modes, where both single quanta of these vibrations are of a'' symmetry because the lowest totally symmetric mode is at +347.9 cm<sup>-1</sup>. The intensity ratio of 2 $\nu_{105}$  to the origin band suggests that the fragmentation pathway goes through CH<sub>2</sub> rocking, leading to H loss. This dissociation is the lowest-energy channel for all smaller H<sup>+</sup>PAHs<sup>16</sup> except protonated benzene,<sup>17</sup> where H<sub>2</sub> loss dominates. Molecular hydrogen loss is not observed for C<sub>24</sub>H<sub>13</sub><sup>+</sup>. The relative intensities shown in Figure 2 are probably distorted due to multiphoton processes, where 2–3 photons are absorbed to induce fragmentation, therefore not a true reflection of those in a direct absorption spectrum.

The excitation of the in-plane a' modes in the (1) <sup>1</sup>A' state are observed at +347.9, +357.7, +369.8, and +373.8 cm<sup>-1</sup> and are attributed to the  $\nu_{70}$ ,  $\nu_{69}$ ,  $\nu_{68}$ , and  $\nu_{67}$  modes, respectively (Table 1). In the electronic absorption spectrum in a 6 K neon matrix, the excitation of the vibrational mode  $\nu_{69}$  (ring deformation) in the excited state is observed at +361 cm<sup>-1</sup>, which is comparable to the gas-phase recording at +357.7 cm<sup>-1</sup>. There are more distinct absorption bands in the (1) <sup>1</sup>A'  $\leftarrow$  X <sup>1</sup>A' electronic transition of protonated coronene observed in the gas phase than in a neon matrix. In crystalline

neon, low-frequency bending modes are not pronounced because of hindered movement, and solid-state effects broaden the spectrum.

The motivation for this study was to determine if protonated coronene could be a DIB carrier by comparing the laboratory absorptions in the gas phase at  $\sim 15$  K to astronomical data.<sup>18,19</sup> The origin band maximum of the (1) <sup>1</sup>A'  $\leftarrow$  X <sup>1</sup>A' system lies at 695.02 nm.<sup>20</sup> There is a DIB at 695.07 nm,<sup>19</sup> having a similar fwhm of  $\sim 0.07$  nm to that of the origin band absorption in the (1) <sup>1</sup>A'  $\leftarrow$  X <sup>1</sup>A' electronic transition. This is, however, not within the given error limits of both measurements. The next most intense transitions (a and c in Figure 2), 2 $\nu_{105}$  and 2 $\nu_{104}$ , involve the excitation of low-frequency modes in the (1) <sup>1</sup>A' excited state and lie at 689.74 and 687.01 nm, respectively. These features do not match with any catalogued DIBs. Therefore, C<sub>24</sub>H<sub>13</sub><sup>+</sup> cannot be a carrier of the known DIBs.

Protonated coronene has a permanent dipole moment of 3.5 D in the X <sup>1</sup>A' ground state, calculated at the B3LYP/cc-pVTZ level,<sup>15</sup> which suggests that it could be probed by rotational spectroscopy. Therefore, if it is present in dense interstellar clouds, microwave spectroscopy could be a means of identification. However, a laboratory microwave spectrum is a prerequisite.

Using the approach described in this Letter, hitherto, the absorptions in the (1) <sup>1</sup>A'  $\leftarrow$  X <sup>1</sup>A' electronic transition of protonated pyrene<sup>5</sup> and coronene in the visible could be measured at 15 K, achieved by collisional cooling with helium. Comparisons of the laboratory spectra with astronomical data are negative, implying that species of this type and size are not likely responsible for stronger DIBs. However, even larger protonated aromatic systems could be targets for the technique described.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Calculated vibrational frequencies and symmetries in the ground X <sup>1</sup>A' and excited (1) <sup>1</sup>A' states. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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