

FOCUS: ION SPECTROSCOPY

Electronic Spectra of C_6H^+ and $C_6H_3^+$ in the Gas Phase

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Measurement of the $^3\Pi - ^3\Pi$ transition of C_6H^+ in the gas phase near 19486 cm^{-1} is reported. The experiment was carried out with a supersonic slit-jet expansion discharge using cavity ringdown absorption spectroscopy. Partly resolved P lines and observation of band heads permitted a rotational contour fit. Spectroscopic constants in the ground and excited-state were determined. The density of ions being sampled is merely $2 \times 10^8\text{ cm}^{-3}$. Broadening of the spectral lines indicates the excited-state lifetime to be $\approx 100\text{ ps}$. The electronic transition of $HC_6H_2^+$ at 26402 cm^{-1} assumed to be $^1A_1 - X^1A_1$ in C_{2v} symmetry could not be rotationally resolved. (J Am Soc Mass Spectrom 2010, 21, 694–697) © 2010 American Society for Mass Spectrometry

In connection with astronomical observation of absorption features through diffuse interstellar clouds [1], the measurement of the electronic spectra in the gas phase of carbon chains and their simple derivatives including H, N, and O has been a goal. Following the suggestion by Douglas [2] that bare carbon chains comprising a handful or two of carbon atoms are good candidates as carriers of these absorptions—the diffuse interstellar bands (DIBs)—it took around 20 years to obtain a number of gas-phase electronic spectra in the laboratory [3]. Thus, it became possible for the first time to make a direct comparison with the astronomical data under comparable conditions: collision-free environment and low, 10–50 K, temperatures. This was achieved in the laboratory by producing the species in supersonic expansions through which a discharge runs, coupled with sensitive laser methods such as cavity ringdown absorption, frequency modulation, and resonant multi-photon ionization [4]. Important were the observations of the neutral carbon chains C_4 , C_5 , and of their hydrogen derivatives, C_nH , the latter being well known constituents of dark interstellar clouds, identified by mm-wave astronomy. These species listed were selected because they have electronic transitions in the visible part of the spectrum, where the DIBs are observed.

In all these cases, the comparisons with the DIB data were negative, leading to upper limits of column densities of around 10^{12} cm^{-2} [3]. Only in the case of C_3 could very weak interstellar absorptions be detected and the species unambiguously identified in the diffuse medium [5]. The analyses of these data led to the conclusion that Douglas' hypothesis [2] is now excluded; carbon chains comprising up to a dozen atoms or their hydrogen containing analogues C_nH cannot be

the carriers of the stronger DIBs [6]. In turn, this pointed to future studies of potential carriers; apart from having electronic transitions in the optical regions, the oscillator strengths would have to be two orders of magnitude larger than the afore-mentioned chains. Examples of such systems are the carbon chains with odd number of atoms, starting with C_{15} , C_{17}

The electronic band systems of the C_n^+ and C_nH^+ cations have hitherto not been obtained in the gas phase because this has proven to be technically demanding. A few measurements of the electronic transitions have been achieved in 6 K neon matrices, namely for C_n^+ $n = 6-9$ [7], and C_nH^+ $n = 6, 8$ [8]. Apart from the fact that these species have electronic band systems in the visible region, the experiments in matrices indicate, as well as theory, that the oscillator strengths are quite a bit larger than for the neutral species. In this contribution the detection of the $^3\Pi - ^3\Pi$ transition of C_6H^+ in the gas phase is reported. The technique used was cavity ringdown spectroscopy coupled with a supersonic slit discharge. The identification follows by the partial resolution and analysis of the rotational structure, changes on deuteration, and comparison with the absorption spectra in neon matrices.

In addition, the study of the origin band of protonated triacetylene, $C_6H_3^+$, was investigated with this approach. An electronic transition of mass-selected $C_6H_3^+$ could already be observed in the gas phase by using ion-trapping technology [9]. However the possibility of laser power saturation in such experiments precluded a conclusion whether the excited-state structure was lifetime broadened or the resolution was just inadequate.

Experimental

The spectra have been recorded by a pulsed cavity ringdown technique using a free jet expansion discharge with a slit nozzle [10]. The molecules were

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produced in a pulsed plasma, which was generated by applying 600–900 V to a mixture of 1% HCCH or DCCD diluted in argon or helium. The slit used was 30×1 mm² and the backing pressure was kept around 11 bar. The average pressures in the vacuum chamber were 0.07 and 0.15 mbar for C_6H^+ and $C_6H_3^+$, respectively. Typical ringdown times were 15–20 μ s depending on the quality of the high-reflectance mirrors. A dye laser with 0.06 cm⁻¹ bandwidth running at 20 Hz was used, and the wavelength was calibrated with a wavemeter.

Observations

The energy region searched was based on the observation made in neon matrices, where the origin band of the $^3\Sigma^- - X^3\Sigma^-$ transition of mass-selected C_6H^+ was identified at 19387 cm⁻¹ [8]. The corresponding band was observed in the gas phase around 19486 cm⁻¹, as can be seen in Figure 1. The top trace shows the actual recording, accumulated in several scans. Apart from the band showing resolved rotational peaks in the P-branch at lower energies, the dominant features overlapping are C_2 lines ($d^3\Pi_g - a^3\Pi_u$). The middle trace shows the resulting spectrum when the C_2 lines are removed and the baseline is corrected. The C_2 peaks (synthetic spectrum shown in bottom trace) were subtracted after fitting by a Voigt line shape (of variable width and amplitude and baseline). The band is blue-shifted by 99 cm⁻¹ from the neon matrix value, similar to the 142 cm⁻¹ change observed for the $C_6H^+ \ ^2\Pi - ^2\Pi$ electronic transition [11, 12]. Both systems have similar characteristics involving $2\pi^4 3\pi^3 - 2\pi^3 3\pi^4$ for C_6H and $2\pi^4 12\sigma^2 3\pi^2 - 2\pi^3 12\sigma^2 3\pi^3$ orbital configuration for C_6H^+ with the same π electron being excited.

To confirm that the detected band is due to C_6H^+ , the following measurements were carried out. The absorption spectrum recorded in the 6 K neon matrix displays three main transitions ($6_0^1, 5_0^1, 4_0^1$) to excited

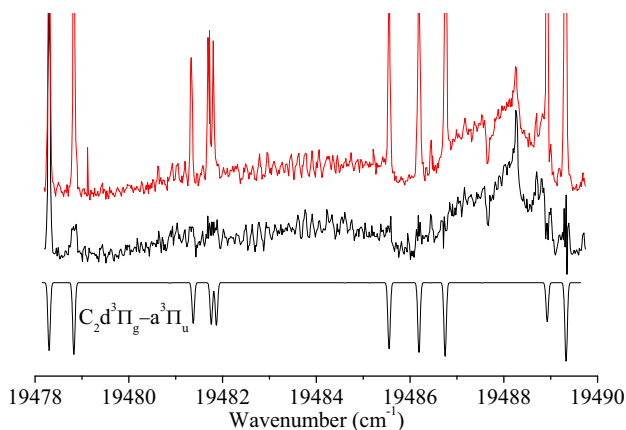


Figure 1. Absorption spectrum of C_6H^+ in the gas-phase recorded by a pulsed cavity ringdown method. The band is attributed to the $^3\Pi - X^3\Pi$ transition. The middle trace is obtained by removal of the prominent C_2 $d^3\Pi_g - a^3\Pi_u$ lines shown in the bottom trace at a temperature of 3000 K with a Gaussian line width of 0.04 cm⁻¹.

vibrational levels in the upper electronic state [8]. Of these, the most intense 4_0^1 is displaced by 1903 cm⁻¹ to higher energy relative to the origin band, with a quarter of its intensity. Thus, a corresponding band was searched for in the gas phase and found at 21402 cm⁻¹, showing the same band profile as seen in Figure 1. The energy difference between the 0_0^0 and 4_0^1 bands in the gas phase is 1916 cm⁻¹. Though the absolute neon-gas shifts are large, it is known that the vibrational frequencies generally lie within a few cm⁻¹ [13]. The second set of measurements involved using deuterio-acetylene in the discharge. An absorption band of the same profile characteristics as the one seen in Figure 1 was detected at 19538 cm⁻¹, shifted 52 cm⁻¹ to higher energy relative to C_6H^+ . This is comparable to the 51(2) cm⁻¹ displacement observed for the C_6H/C_6D pair [8]. The corresponding blue shift in the neon matrix for the cation is 38 cm⁻¹ (Table 1) upon deuteration.

As can be seen in Figure 1, the spectrum displays three band heads along with a distinct protrusion near 19486 cm⁻¹ and a band head like feature at 19487 cm⁻¹. It should be noted that the presence of the three R-band heads (at the higher energy end) readily differentiates this from absorptions belonging to a band within the $^2\Pi - ^2\Pi$ system of C_6H , which are seen throughout this wavelength region [12]. Furthermore, the assignment to a band within the $^3\Sigma^- - X^3\Sigma^-$ transition of C_6 , with observed origin at 19558 cm⁻¹ in a neon matrix [11] is excluded as the rotational spacing would be roughly twice as large as between the lines for C_6H^+ because of nuclear spin statistics.

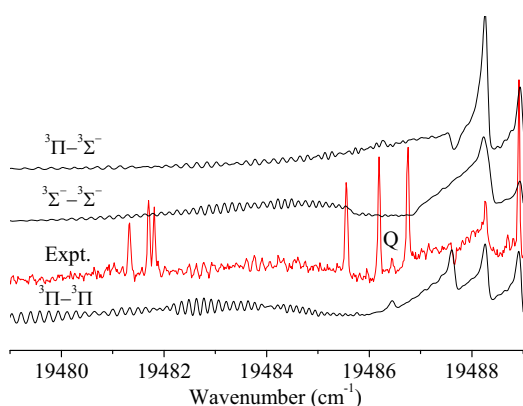
In connection with the study of the electronic absorption of C_6H^+ in the neon matrix, it was suggested that the transition being observed was $^3\Sigma^- - X^3\Sigma^-$. The first argument for this was that C_6H^+ and C_6 are isoelectronic and the $^3\Sigma^- - X^3\Sigma^-$ transition of the latter was located in a neon matrix with origin band at 19558 cm⁻¹. However, CASSCF calculations, the results of which are given in reference [8], show that the $^3\Pi$ state arising from the $2\pi^4 12\sigma^2 3\pi^3$ configuration lies just 0.04 eV lower than the $^3\Sigma^-$ ($2\pi^4 12\sigma^2 3\pi^2$) and would thus be the ground state of C_6H^+ . Furthermore, the $^3\Pi - ^3\Pi$ system at $T_v = 2.36$ eV is strong (transition moment $TM = 3.2$ D). On the other hand higher level RCCSD(T)/cc calculations indicated a preference for $^3\Sigma^-$ as the ground state (with $^3\Pi$ lying 0.33 eV higher) and that the transition is $^3\Sigma^- - X^3\Sigma^-$ at $T_0 = 2.77$ eV with $TM = 1.48$ D. The $^3\Pi - ^3\Sigma^-$ transition is predicted at 2.24 eV but is very weak ($TM = 0.03$ D). Consequently the choice of $^3\Sigma^- - X^3\Sigma^-$ for the absorption system in the neon matrix was proposed [8].

Thus, in the analysis of the rotational structure and contour of the gas-phase band seen in Figure 1 it was initially assumed that this has $^3\Sigma^- - ^3\Sigma^-$ symmetry. A simulation of the rotational features was undertaken using PGOPHER [16]. The optimized calculated ground state geometry, as given in [8], was used for the $X^3\Sigma^-$ ground state in the first instance and the constants in the excited $^3\Sigma^-$ state were the parameters, in addition to the rotational temperature. A second iteration was

Table 1. Frequencies (cm^{-1}) measured in a neon matrix and in the gas-phase for the ${}^3\Pi - X^3\Pi$ electronic transition of C_6H^+ and C_6D^+ . Previously published data for linear C_6H and HC_6H^+ electronic transitions are also given

Radical	Vibrational band	Ne matrix	Gas-phase T_{00}	Shift
$\text{I-C}_6\text{H}^+$	0_0^0	19387(8) [8]	19486(1)	-99
	4_0^1	21290(8) [8]	21402(1)	-112
$\text{I-C}_6\text{D}^+$	0_0^0	19425(8) [8]	19538(1)	-113
$\text{I-C}_6\text{H}$	$0_0^0 \quad {}^2\Pi - {}^2\Pi$	18854(5) [11]	18996(1) [12]	-142
	$6_0^1 \quad {}^2\Pi - {}^2\Pi$	19512(5) [11]	19649(1) [12]	-137
$\text{I-HC}_6\text{H}^+$	$0_0^0 \quad {}^2\Pi_u - {}^2\Pi_g$	16535(5) [14]	16654(1) [15]	-119

made by slightly varying the lower state B' constant as well. Ambiguity in the fit is caused by the lack of sufficient number of resolved rotational lines (mainly observed in the P-branch). For the final fit the ground state rotational value was also then used as parameter. However, the simulation failed to reproduce important features in the spectrum, as can be seen in Figure 2. Specifically, the peak at 19486.5 cm^{-1} labeled as Q-head above the experimental trace, is not seen, neither the prominent dip at 19487.6 cm^{-1} . Thus, it was then considered whether the transition could be of ${}^3\Pi - {}^3\Pi$ or ${}^3\Sigma^- - {}^3\Pi$ symmetry. The same procedure was followed in the simulations as above, using the calculated geometry for the lowest lying ${}^3\Pi$ state also given in [8]. A ${}^3\Pi - {}^3\Sigma^-$ transition would result in three well separated branches, by roughly 13 cm^{-1} due to the spin-orbit splitting of the ${}^3\Pi$ [17]. In this case, the intensities of the three band heads would not depend on the internal temperature of the radical. According to theory [8] this transition is much weaker. Similarly, a ${}^3\Sigma^- - {}^3\Pi$ system should show three well-separated structures, provided that the internal temperature of the radical is around 80 K. This is not in agreement with the spectra recorded in the $19050\text{--}19600 \text{ cm}^{-1}$ region: all transitions occurring nearby were identified as part of the $\text{C}_6\text{H} \quad {}^2\Pi - {}^2\Pi$ electronic transition, excluding this

**Figure 2.** Simulation of the possible transition symmetries involved for C_6H^+ at 80 K and 0.04 cm^{-1} line width. The temperature is high because the cation is probed a few mm from the slit, near the active zone between the blade-electrodes.

case also. A ${}^3\Sigma^- - {}^3\Pi$ transition does not match the observed profile as well; no Q head is apparent.

As can be seen in Figure 2, ${}^3\Pi - {}^3\Pi$ fits best (at 60–80 K) reproducing the shape especially the dip at 19487.8 cm^{-1} caused by an R-head and the Q head at 19486.5 cm^{-1} . In the corresponding band of C_6D^+ (at 19538 cm^{-1}) the rotational lines were not resolved though the profile showed the same features as for C_6H^+ . The lines in the P branch have been fitted, yielding the spectroscopic constants given in Table 2. The positions of the band heads and the observed dip while keeping the ground state rotational constant at the ab initio value and varying the upper state B' as well as T_{00} gave enough constraint so as to reproduce the overall shape of the P branch (Figure 2). The value obtained for the lower electronic state from the calculated rotational fit for ${}^3\Pi$ ($0.0486(2) \text{ cm}^{-1}$) is comparable to the value 0.0475 cm^{-1} obtained from the optimized bond distances [8]. Thus it is concluded that the ${}^3\Pi - {}^3\Pi$ transition is being observed.

As a follow-up to this, one can ask: “What is the symmetry of the ground state of C_6H^+ ?” Undoubtedly, in the neon matrix at 6 K, the absorption stems from the ground electronic state even if a near-lying excited electronic state is located just 0.04 eV above. It is not populated due to the complete relaxation at 6 K in the solid-state environment. The same transition is being observed in the gas phase (based on the gas-matrix and isotopic shifts discussed above) and, thus, the symmetry appears to be ${}^3\Pi$. It is up to even higher level of theory to prove this. Furthermore, the ab initio calculations carried out [8] predict for the ${}^3\Pi - {}^3\Pi$ transition $T_{00} = 2.36 \text{ eV}$ compared with the observed 2.42 eV. On the other hand the ${}^3\Sigma^- - {}^3\Sigma^-$ system is calculated at 2.77

Table 2. Spectroscopic constants (cm^{-1}) obtained from the rotational contour fit of the ${}^3\Pi - X^3\Pi$ transition of C_6H^+ at 19486 cm^{-1}

T_{00}	19485.776(11)
B''	0.0486(2)
B'	0.0477(2)
B'/B''	1.019
A''	-13 (fixed)
A'	-12.33(1)

eV, a region to higher energy than scanned experimentally. If the $^3\Sigma^-$ state remains sufficiently populated in the supersonic expansion, in contrast to the 6 K neon matrix, it may be possible to find this transition. Also, cavity ringdown measurements at higher temperatures may be feasible and advantageous.

In the P-branch, individual rotational lines are discernible, with $\approx 0.1 \text{ cm}^{-1}$ widths. The laser bandwidth (Gaussian) was estimated by measuring the C₂ rotational lines as $\approx 0.04 \text{ cm}^{-1}$. The Gaussian and Lorentzian components are about the same, 0.056 cm^{-1} . The kinetic temperature of the radical close to the expansion slit is $\approx 600 \text{ K}$ (corresponding to 0.04 cm^{-1} , since $\Delta\omega_{\text{Gauss}}^2 = \Delta\omega_{\text{Doppler}}^2 + \Delta\omega_{\text{Laser}}^2$). The overall natural broadening of $3 \times 10^{-5} \text{ cm}^{-1}$ calculated from the oscillator strength (≈ 0.02 [8]) is negligible relatively to the overall Lorentzian. However, the lifetime of the excited-state is expected to be $\approx 100 \text{ ps}$. Collisional effects of the spectral carrier with charged and neutral species in the plasma contribute to this. Using the oscillator strength of the transition, the rotational temperature and the estimated Voigt line shape, the density of the C₆H⁺ cations is inferred to be around $2.0 \times 10^8 \text{ cm}^{-3}$.

Electronic Transition of C₆H₃⁺

An electronic band system of C₆H₃⁺ was also observed in a 6 K neon matrix following mass-selection [18]. This was subsequently detected at 26402 cm^{-1} in the gas phase in an ion trap [9]. A two-color photon scheme was used to observe this; a bound-bound transition out of the ground electronic state was excited with one laser while the second UV laser subsequently produced the fragment ion C₆H₃⁺, which was monitored. In the latter experiment, the rotational profile was seen but the individual lines could not be resolved. Their resolution would prove the structure of the species; either the “classical” HC₆H₂⁺ with C_{2v} symmetry, or the nonclassical linear HC₆H form with a loosely bound H⁺ undergoing large amplitude motion. According to ab initio calculations [9], the electronic transition observed could correspond to $^1A_1 - X^1A_1$ in C_{2v} symmetry. On the basis of the infrared frequencies observed in measurements on mass-selected C₆H₃⁺ in neon-matrices [18], the classical H₂C₆H⁺ structure was also implied.

It was not clear whether the reasons for the rotational structure not being resolved was due to the short lifetime of the excited electronic state because of intramolecular processes or power broadening in the two-color laser approach. It was decided to measure the band with cavity ringdown spectroscopy for which the

measured signal is not dependent on the intensity of the probing laser beam, avoiding power broadening effects. This was achieved here with the cavity ringdown approach. However, the structure could still not be resolved and the same rotational profile as shown in Figure 3 in reference [9] was observed. Thus, it is concluded that the excited electronic state is short-lived as a result of lifetime broadening by intramolecular processes. The lines have a Lorentzian FWHM of 0.08 cm^{-1} and the rotational structure is smeared out. This corresponds to the excited-state lifetime of 60 ps.

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