PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Infrared Spectroscopy of Carbo-Ions [and Discussion]

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Infrared spectroscopy of carbo-ions

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The recent development of high-resolution, high-sensitivity laser infrared spectroscopy has enabled us to study many fundamental molecular ions for which there had previously been no spectroscopic studies. We summarize our recent work here on carbo-ions, CH_3^+, C_2^-, $C_2H_2^+$ and $C_2H_3^+$.

1. Introduction

It is well known that the development of science occurs stepwise rather than continuously. In the area of molecular spectroscopy, the burst of activity in microwave spectroscopy after World War II, the electronic spectroscopy of free radicals in the 1950s and 1960s, the discoveries of many molecular lasers in the 1960s, and the radio-astronomical discoveries of interstellar molecules in the late 1960s and 1970s all occurred in this mode. I think we are now experiencing such a period in the field of molecular-ion spectroscopy. This Royal Society Meeting is very timely.

My venture in molecular-ion spectroscopy started with H_3^+, the simplest stable polyatomic system. Figure 1 shows the first 15 lines that were observed nearly seven years ago (Oka 1980). Since then a great many papers have been published on this fundamental molecular ion and its isotopic species (see, for example, a review by Sears 1987). Two weeks ago I was greatly excited by the discovery of the millimetre-wave spectrum of ArH_3^+ and ArD_3^+ complexes reported by Bogey *et al.* (1987). Last week I was also very surprised to hear from J. B. A.

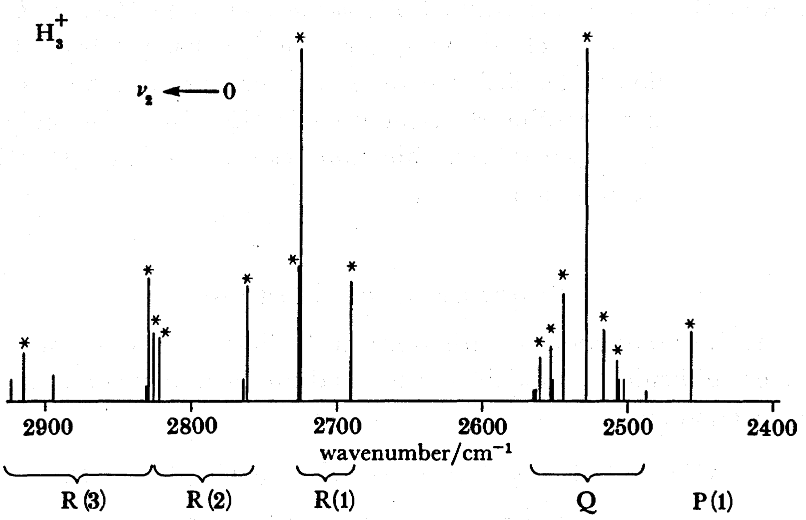

Figure 1. First 15 observed lines of the ν_2-band of H_3^+ (Oka 1980). Note that there is no obvious symmetry or regularity in the spectrum, although H_3^+ is a well-bound equilateral triangle. The analysis of the spectrum is by Watson (Watson 1984; Watson *et al.* 1984)

Mitchell that Smith & Adams (see Smith, this symposium) have now found that the electronic recombination rate constant of H_3^+ is less than $10^{-11}\ \mathrm{cm^3\ s^{-1}}$, nearly that of atomic recombination. I look forward to hearing more about these most recent developments at this Meeting.

The H_3^+ ions are formed in a laboratory hydrogen discharge as well as in molecular clouds through the ion–molecule reaction

$$H_2^+ + H_2 \longrightarrow H_3^+ + H, \tag{1}$$

which will be formally written as a hydrogen-extraction reaction

$$H_2^+ \xrightarrow[-H]{H_2} H_3^+. \tag{2}$$

Likewise, protonated water H_3O^+ and protonated ammonia NH_4^+ are formed through the chains of hydrogen-extraction reactions

$$O^+ \xrightarrow[-H]{H_2} OH^+ \xrightarrow[-H]{H_2} H_2O^+ \xrightarrow[-H]{H_2} H_3O^+ \tag{3}$$

and

$$N^+ \xrightarrow[-H]{H_2} NH^+ \xrightarrow[-H]{H_2} NH_2^+ \xrightarrow[-H]{H_2} NH_3^+ \xrightarrow[-H]{H_2} NH_4^+. \tag{4}$$

The reactions in (3) are all exothermic, with large Langevin cross sections. The same is true for the reactions in (4) except for the last step, which has a much smaller cross section. All the molecular ions in (3) and (4) have now been observed through their infrared spectra: OH^+ (Crofton *et al.* 1985); H_2O^+ (Dinelli *et al.* 1987); H_3O^+ (Begemann *et al.* 1983); NH^+ (Amano, this symposium); NH_2^+ (Rehfuss *et al.* 1987); NH_3^+ (Bawendi *et al.* 1987); and NH_4^+ (Crofton & Oka 1983).

Having studied some of these ions, it was natural to proceed to carbo-ions (here defined as molecular ions composed of only carbon and hydrogen atoms); we started searching for protonated methane CH_5^+ in the spring of 1983. The polyatomic hydrocarbon cations CH_n^+ ($n = 2$–5) and $C_2H_n^+$ ($n = 1$–7) are fundamental ionic species that play important roles in chemical kinetics in the laboratory and in space, yet there had previously been no spectroscopic studies of these in gaseous phase in any spectral region. In the concluding section of Herbert Brown's controversial book (1977) entitled *The nonclassical ion problem*, P. R. Schleyer notes: 'Major problems remain to be solved. No general method has yet been developed for the experimental determination of detailed structures of carbocations in the gas phase. No direct experimental information concerning the structure of CH_3^+ exists!' The only high-resolution studies of polyatomic carbo-ions had been Callomon's classic work on $C_4H_2^+$ (Callomon 1956), and work by Maier (this symposium).

2. Production of carbo-ions

We found that the production of carbo-ions in discharges in sufficient amount for spectroscopy was more difficult than for the oxygen and nitrogen analogues in (3) and (4). The corresponding reaction chain

$$C^+ \nrightarrow CH^+ \longrightarrow CH_2^+ \longrightarrow CH_3^+ \nrightarrow CH_4^+ \longrightarrow CH_5^+ \tag{5}$$

has two hangups between C^+ and CH^+, and CH_3^+ and CH_4^+ (Huntress 1977). The diatomic-carbon reaction chain is

$$C_2^+ \longrightarrow C_2H^+ \longrightarrow C_2H_2^+ \longrightarrow C_2H_3^+ \tag{6}$$

but does not extend further. The last reaction goes only for vibrationally excited $C_2H_2^+$ (Huntress 1977). The major difficulty in the production of carbo-ions results from the efficient polymerization of carbo-ions. Almost all reactions between carbo-ions and neutral hydrocarbons such as $CH_3^+ + CH_4(C_2H_4, C_2H_6$, etc.) have large Langevin cross sections and produce polymeric hydrocarbons, eventually leading to a large amount of soot deposited on the wall of a discharge tube. The best method to cope with this difficulty is to simply dilute the discharge gas mixture with a large amount of He. Helium also increases the efficiency of ion production through Penning ionization and, because of its high ionization potential, tends to increase the electron temperature in the plasma, thus fragmenting the larger carbo-ions. It is this use of He developed by my student Mark Crofton that has made possible the spectroscopy not only of carbo-ions but also of OH^+, H_2O^+, NH_2^+, NH_3^+, etc. We thus use a discharge gas mixture of $He:H_2:CH_4$ of *ca.* 700:20:1 with a total pressure of *ca.* 7 Torr† for the production of CH_3^+ and the same mixture with C_2H_2 for the production of $C_2H_3^+$. For a liquid-nitrogen-cooled discharge we used the former gas mixture even for $C_2H_3^+$ because C_2H_2 was frozen.

The relative abundance of different carbocations in (5) and (6) is very sensitive to the ratio of H_2 to hydrocarbon. The $C_2H_2^+$ lines disappear almost completely with an increased amount of H_2 in the discharge, whereas the $C_2H_3^+$ lines are not much affected. This fact was very useful to discriminate between the spectra of these two species that appear intermixed in the same region with similar spacings.

For the spectroscopy of carbo-ions, various multiple-inlet–outlet discharge tubes have been used. We have used an air-cooled discharge tube (nicknamed 'spider'), a water-cooled tube ('tarantula') and a liquid-nitrogen tube ('black widow') depending on purposes. The water-cooled tube is schematically shown in figure 2. A fresh mixture of gases is introduced into the discharge through the eight inlet ports. Blue-green emission, which Herzberg witnessed when he visited our laboratory and ascribed to CH, was noticed in the region of discharge around each inlet, indicating that hydrocarbon reactions are taking place vigorously in the optical path.

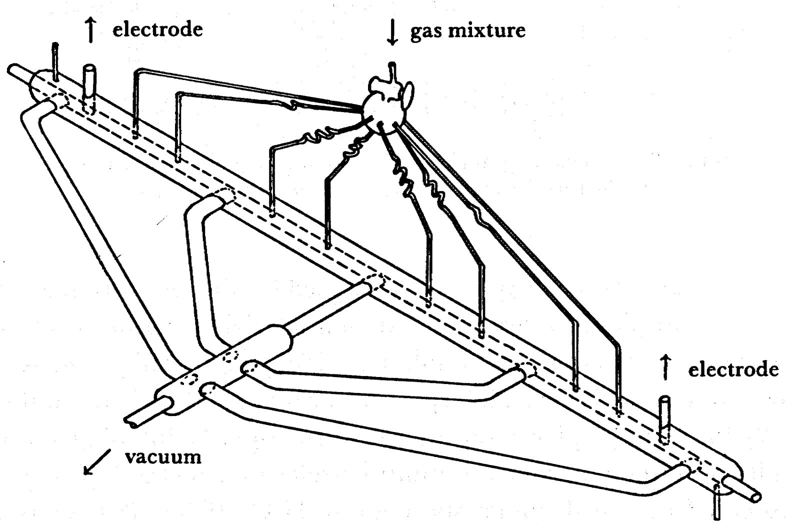

FIGURE 2. The water-cooled multiple-inlet–outlet discharge cell ('tarantula').

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† 1 Torr ≈ 133.3 Pa.

3. Spectroscopy

The success of infrared molecular-ion spectroscopy is caused by the great increase in sensitivity of infrared absorption spectroscopy brought about by laser spectroscopic techniques. The minimum detectable absorption is on the order of $\Delta I/I \approx 10^{-6}$–$10^{-7}$, indicating that this method is more sensitive than the traditional grating infrared spectroscopy by a factor of perhaps *ca.* 10^4–10^5.

We use three frequency-tunable laser infrared radiation sources for spectroscopy; they are a difference-frequency laser system, a diode-laser system, and a microwave-modulation sideband system on CO_2 laser lines. A diagram of the difference-frequency spectrometer is shown in figure 3. The radiation ν_A from a single-mode Ar ion laser (blue to green) and the radiation ν_D from a single-mode ring dye laser (yellow to red) are mixed in a temperature-controlled $LiNbO_3$ crystal to generate the infrared difference frequency $\nu_A - \nu_D$. This radiation source, initially developed by Pine (1974), generates continuously tunable infrared radiation over the infrared range of 2.2–4.2 μm with a power of *ca.* 100 μW.† This radiation source was indispensable for my first work on H_3^+ (Oka 1980) and is still the most powerful tool in our laboratory.

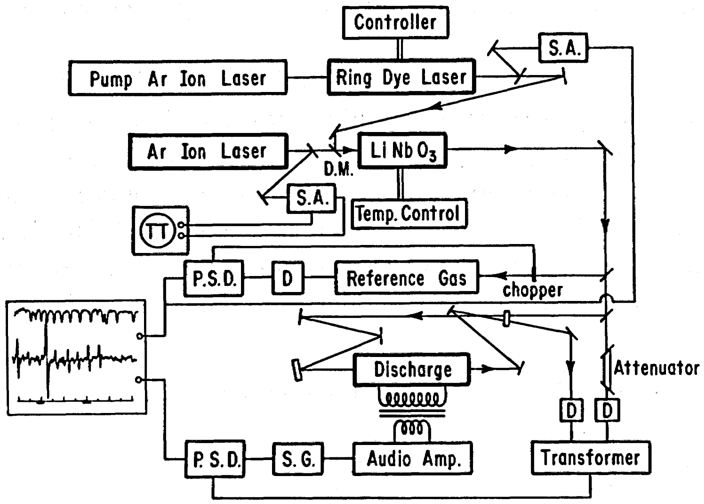

Figure 3. A block diagram of the difference-frequency spectrometer applied to the infrared molecular-ion spectroscopy.

The diode-laser system (Spectra Physics LS-3) is used for the lower frequency range down to *ca.* 350 cm^{-1}. This system played a great role in characterizing the inversion motion of H_3O^+ (Liu & Oka 1985). The microwave-modulation sideband technique generates frequency-tunable infrared radiation with very high spectral purity ($\Delta\nu \leqslant 50$ kHz) and sufficiently high power (*ca.* 3 mW) for sub-Doppler saturation spectroscopy. Combining the ultra-high-resolution sub-Doppler spectroscopy and the multiple-reflection method (Chen *et al.* 1986), we have recently observed the sub-Doppler spectrum of H_3O^+ (Chen & Oka 1987).

To both discriminate the ion spectral lines from much stronger neutral absorption lines and

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† 1 μW = 10^{-6} J s^{-1}.

to increase the sensitivity of ion spectroscopy, the powerful velocity-modulation technique developed by Gudeman *et al.* (1983) is used. This method is even more effective for carbo-ion spectroscopy because a great many neutral hydrocarbon molecules are present in the discharge and absorb infrared very strongly. We increase the optical path length by using a multiple-reflection mirror system. We use a unidirectional multiple path so that we can still use the velocity modulation.

4. Observed spectra

In March 1985 M. W. Crofton found many lines by using the air-cooled multiple-inlet discharge tube with the discharge gas mixture of He, H_2 and C_2H_2. Velocity modulation and chemistry indicated that the carriers of these spectral lines were hydrocarbon cations. About 1000 lines were observed in the region 3250–2990 cm^{-1}. These lines have been repeatedly studied under different chemical and plasma conditions. It has been revealed that these lines are caused by at least three carbocations and probably a few more. The beautiful spectral patterns of fundamental bands of the methyl cations CH_3^+, the acetylene ion $C_2H_2^+$, and the protonated acetylene $C_2H_3^+$ gradually emerged from this bush of lines.

(*a*) CH_3^+

A group of lines stood out as being caused by molecular ions with larger rotational constants because of their larger spacing of *ca.* 8 cm^{-1} and larger extension of R- and P-branches. Their larger linewidths also indicated smaller molecular masses. With CH_4 instead of C_2H_2, the intensities of these lines increased greatly. Initially we thought that the spectrum was caused by CH_5^+, for which *ab initio* calculation (Raghavachari *et al.* 1981) predicts $2B \approx 8\ cm^{-1}$. It was soon found that the spectrum was too simple for that of CH_5^+ and that the observed spacing of 8 cm^{-1} corresponds to the spacing of $2\ (C-C\zeta)$ characteristic of the perpendicular band of an oblate top. More detailed analysis has established that this group of spectral lines correspond to the ν_3 fundamental band of CH_3^+.

Altogether 165 lines have been assigned up to the highest J of 16 and K of 16. A computer-generated stick spectrum of the observed vibration–rotation transitions is shown in figure 4. The spectrum is that of a typical perpendicular band for an oblate symmetric top. This appearance and the 2:1 intensity ratios for the $K = 3n$ and $K = 3n \pm 1$ transitions point to an equilateral triangle equilibrium structure. The absence of $J =$ even lines in the $^rQ_0$ branch reflects the planarity of the molecule and a totally symmetric A_1' electronic state. The D_{3h} geometrical structure of this ion had been expected from Herzberg's Rydberg spectrum of CH_3 (Herzberg 1961) and from *ab initio* theory. We have also observed and analysed the ν_3-band of $^{13}CH_3^+$.

Molecular constants determined from the spectrum by M.-F. Jagod are listed in table 1. A preliminary paper has been published (Crofton *et al.* 1985). More details of the results will be published soon (Crofton *et al.* 1987*a*). We have taken this opportunity to work out vibration–rotation interactions for this type of molecule in detail.

The methyl cation CH_3^+ plays a crucial role in interstellar chemistry of both diffuse clouds (Black & Dalgarno 1977) and dense clouds (Smith, this symposium). A chemistry chart in a diffuse molecular cloud is shown in figure 5. Future detection of this species in interstellar space through its infrared spectrum is awaited.

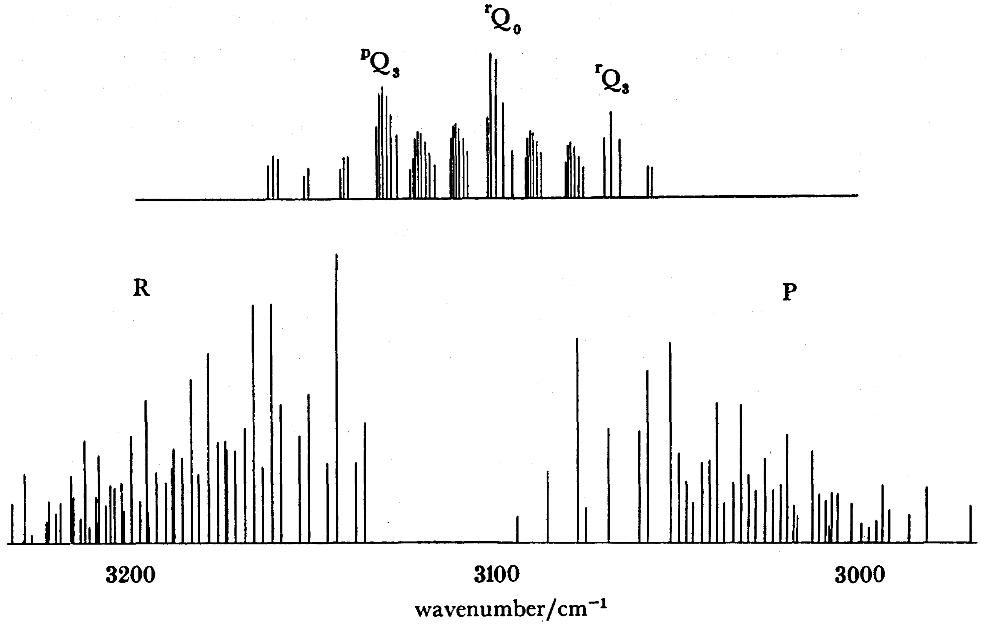

FIGURE 4. A computer-generated stick diagram of the observed ν_3 fundamental band of CH_3^+.

TABLE 1. DETERMINED MOLECULAR CONSTANTS OF CH_3^+ AND $^{13}CH_3^+$ (RECIPROCAL CENTIMETRES)

	CH_3^+	$^{13}CH_3^+$
$\nu_3 - C'\zeta_{33} - \frac{1}{4}\eta_K$	3107.8559 (53)	3095.2133 (97)
B'	9.27224 (44)	9.2727 (17)
$C'(1-\zeta_{33}) + \eta_K$	4.04591 (84)	4.0969 (22)
$C' - C'' + \frac{3}{2}\eta_K$	−0.04006 (27)	0.0405 (17)
D'_{JJ}	0.7104 (78) × 10^{-3}	0.679 (51) × 10^{-3}
D'_{JK}	−1.313 (21) × 10^{-3}	−1.274 (99) × 10^{-3}
$D'_{KK} - \frac{1}{4}\eta_K$	0.469 (16) × 10^{-3}	0.481 (57) × 10^{-3}
η_J	−0.643 (44) × 10^{-3}	−0.60 (19) × 10^{-3}
B''	9.36227 (31)	9.3621 (16)
D''_{JJ}	0.7482 (65) × 10^{-3}	0.720 (50) × 10^{-3}
D''_{JK}	−1.337 (16) × 10^{-3}	−1.275 (99) × 10^{-3}
$D''_{KK} - D'_{KK}$	0.019 (13) × 10^{-3}	0.011 (61) × 10^{-3}
$H'_{JJJ} = H''_{JJJ}$	0.106 (41) × 10^{-6}	
$H'_{JJK} = H''_{JJK}$	−0.31 (11) × 10^{-6}	
$H'_{JKK} = H''_{JKK}$	0.23 (11) × 10^{-6}	
$H'_{KKK} = H''_{KKK}$	−0.16 (13) × 10^{-6}	
q	−8.6 (10) × 10^{-3}	−11.4 (10) × 10^{-3}
q_J	−0.026 (15) × 10^{-3}	
q_K	−1.40 (38) × 10^{-3}	
β_2	−0.0367 (25) × 10^{-3}	−0.0414 (71) × 10^{-3}
h_3	−0.0112 (61) × 10^{-6}	

(*b*) C_2^-

Infrared spectra of C_2^- were observed first in the 2.6 μm region by using the difference-frequency system and later in the 4.6 μm region with the diode-laser system. These spectra are different from other carbo-ion spectra in various ways: (*a*) they are electronic transitions $A^2\Pi_u \leftarrow X^2\Sigma_g$ instead of the usual vibrational transitions; (*b*) the carrier of this spectrum is

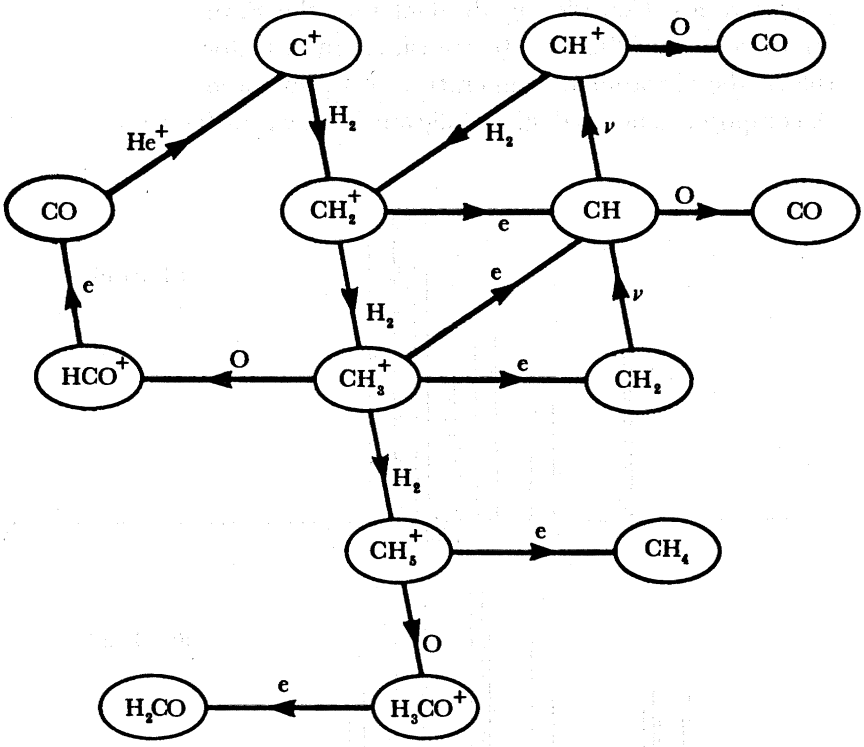

FIGURE 5. Interstellar chemistry diffuse molecular cloud after Dalgarno.

an anion; and (*c*) quantum mechanics of this ion had earlier been studied in relation to its electronic spectra. However, our study of this ion and thus the $^2\Pi$ state was essential in assigning the $C_2H_2^+$ spectrum discussed in the next section.

The first spectroscopic study of C_2^- is described in a classic paper by Herzberg & Lagerqvist (1968), in which they report a new system of Σ–Σ bands in the region 4800–6000 Å† and point out the possibility that the bands are caused by C_2^-. Milligan & Jacox (1969) observed the same transition in inert gas matrices and reported that the band is very likely from C_2^- because its intensity increased with the presence of an electron donor. The final confirmation came when Lineberger & Patterson (1972) observed the two-photon photodetachment spectrum of C_2^-. These results characterised the $B^2\Sigma_u^+$ state and the $X^2\Sigma_g^+$ state with high accuracy. More recently, Mead *et al.* (1985) observed the $B \leftarrow X$ transition with sub-Doppler resolution and by using the perturbations on the B state from the high vibrational states of the $A^2\Pi_u$ state, determined some molecular constants for the $A^2\Pi_u$ state. We used their constants, in particular the $A \leftarrow X$ energy separation, as the guide for our search of the spectrum.

The infrared spectrum of C_2^- was found by B. Dinelli and M.-F. Jagod in January 1986. It was found that a mixture of a large amount of He (7 Torr) and a small amount of C_2H_2 (*ca.* 50 mTorr) was optimum for the most effective production of C_2^-. We estimate the C_2^- concentration in the discharge to be *ca.* 10^8 cm^{-3}. Although this is considerably less than the concentration of other carbo-ions, the spectrum is rather strong because the transition dipole moment is much larger. The vibrationally hot bands $(1 \leftarrow 1)$ and $(0 \leftarrow 1)$ were observed with

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† 1 Å = 10^{-1} nm = 10^{-1} m.

good signal-to-noise ratios. Considering the fact that the Franck–Condon factors for these bands are lower than that of the $(0 \leftarrow 0)$ transition by a factor of 2.0 and 3.2, respectively (Mead *et al.* 1985), the vibrational temperature of C_2^- in the discharge must be very high: $T \gtrsim 5000$ K. A computer-generated stick diagram is shown in figure 6.

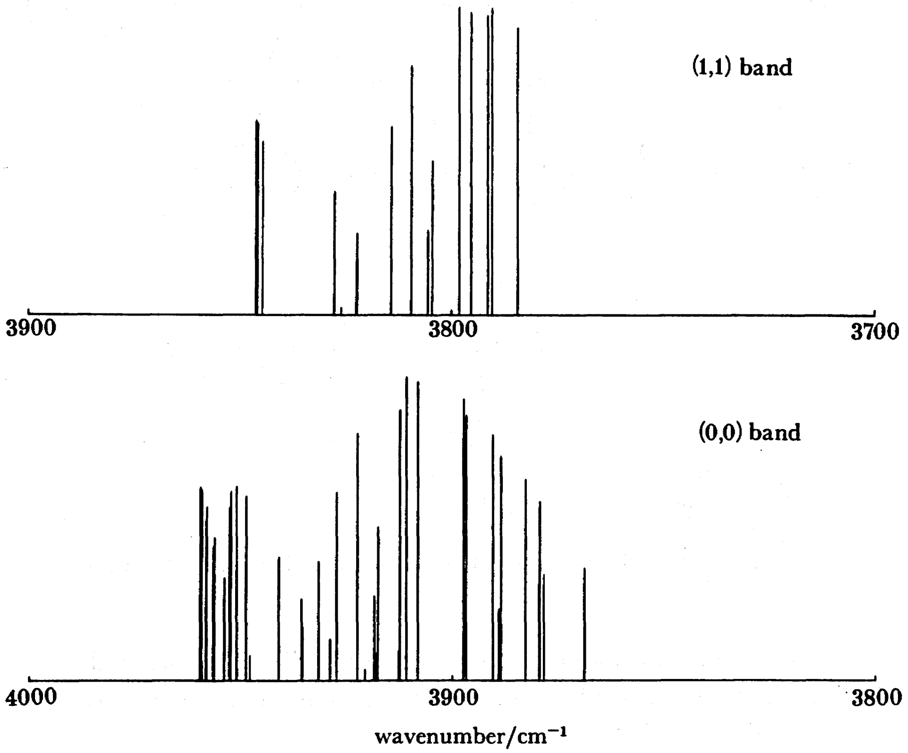

FIGURE 6. A computer-generated stick diagram of the observed $^2\Pi \leftarrow {}^2\Sigma_g^+$ transition of C_2^-.

Since the initial theoretical work by Hill & Van Vleck (1928), a great many papers have been published on the hamiltonian for the $^2\Pi$ state. We used the hamiltonian by Brown & Watson (Brown *et al.* 1979).

$$H = BN^2 - DN^4 + \tfrac{1}{2}[(\tilde{A} + \tilde{A}_D N^2), L_z S_z]_+ + \tfrac{1}{2}p(\Lambda_+^2 S_- N_- + \Lambda^2 S_+ N_+) - \tfrac{1}{2}q(\Lambda_+^2 N_- + \Lambda^2 N_+^2). \tag{7}$$

For the derivation of this formula and the definition of the parameters and operators, refer to the paper by Brown *et al.* (1979). For the ground $^2\Sigma_g^+$ state the usual hamiltonian

$$H = BN^2 - DN^4 + \gamma \boldsymbol{N} \cdot \boldsymbol{S} \tag{8}$$

was used. The 104 observed lines for the three observed bands have been fitted simultaneously by a least-squares computer program. The parameters determined for the $A^2\Pi_u$ state are shown in table 2, where previously determined parameters are also shown. The agreement with the results of Mead *et al.* (1985) is remarkable considering the indirect nature of their determination.

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Table 2. Molecular constants (reciprocal centimetres) of C_2^- in the $A^2\Pi_u$ state

	this work	Mead *et al.* (1985)
T_0	3928.660 (17)	4002 (91)
ν_0	1644.803 (51)	1637 (10)
A_0	−24.989 (62)	−24 (1)
A_e	−25.032 (56)	
α_A	−0.084 (69)	
B_0	1.63494 (26)	1.622
B_e	1.64307 (51)	1.630 (5)
α_B	0.01625 (72)	0.0152
r_e	1.30767 (20) Å	1.313

(*c*) $C_2H_2^+$

After our excursion to C_2^-, we went back to the complicated spectrum in the 3.3 μm region that we thought was all caused by $C_2H_3^+$. *Ab initio* calculations on this molecular ion have indicated that two structures are possible, the formaldehyde-type (classical) structure and the bridged (non-classical) structure, and that they are very close in energy (Weber *et al.* 1987; Raine & Schaefer 1984). In the classical structure, the C_2-axis for permutation of the two equivalent protons is along the *a*-axis, whereas in the bridged structure the axis is along the *b*-axis. The former will show *K*-doubling spectral lines with equal intensities whereas the latter will give a ratio of 3:1.

There was a series of doublet lines with equal intensities in the bush of the spectrum that initially led us to think $C_2H_3^+$ has the classical structure. However, after more careful analysis with combination differences together with the newly gained understanding of the $^2\Pi$ state, and after the chemical experiment discussed earlier, we realized that they were caused by the ν_3-band $^2\Pi \leftarrow {}^2\Pi$ transitions of the acetylene ion $C_2H_2^+$. Extremely weak Q-branch lines expected for a $\Pi \leftarrow \Pi$ transition played a crucial role in the final assignment. A preliminary paper has been published (Crofton *et al.* 1987*b*). The molecular constants determined are listed in table 3. A computer-generated stick diagram of the observed transitions is shown in figure 7. Whereas low J transitions $J < 10$ fit well to the usual $^2\Pi$ hamiltonian, higher J transitions deviate markedly from the calculated spectrum. More detailed analysis is in progress. The present results confirm the earlier estimate by Hollas & Sutherlay (1971) that the C–C bond length increases by about 0.04–0.05 Å upon ionization of acetylene.

Table 3. Molecular constants (reciprocal centimetres) of $C_2H_2^+$ $^2\Pi_u$

$\nu_3 = 3135.975\ (5)$
$B' = 1.09895\ (13)$ $A' = -29.6\ (15)$
$B_0 = 1.10456\ (7)$ $A_0 = -30.1\ (15)$
$\alpha_3 = 0.00561\ (15)$
$D_0 = D' = 1.44 \times 10^{-6}$

(*d*) $C_2H_3^+$

After assigning many spectral lines of CH_3^+ and $C_2H_2^+$, we were left with more than 1000 lines in the 3200–3090 cm^{-1} region. It is possible that these lines are caused by more than one carbocation, but a major portion of them are believed to be from protonated acetylene

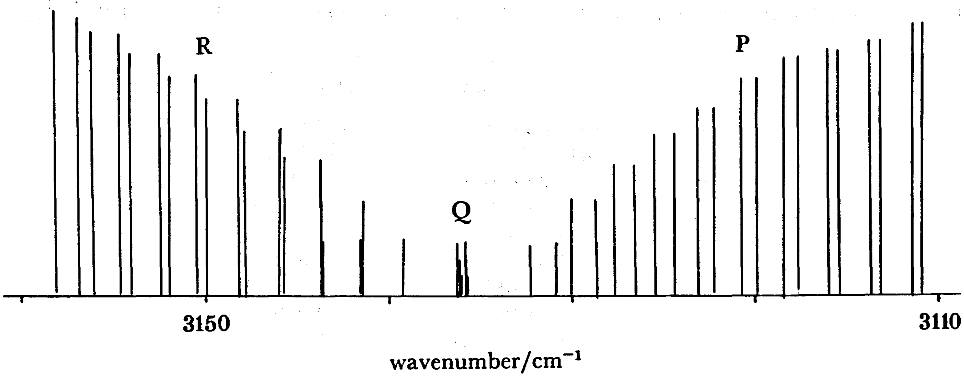

FIGURE 7. A computer-generated stick diagram of the ν_3-band $^2\Pi \leftarrow {}^2\Pi$ transition of $C_2H_2^+$.

$C_2H_3^+$. A computer-generated stick diagram of the central portion of the observed spectrum is shown in figure 8. The $C_2H_3^+$ lines are intermixed with CH_3^+ and $C_2H_2^+$ lines as shown in figure 9. In particular, both the band origins and the spacings of groups of lines of $C_2H_2^+$ and $C_2H_3^+$ are very close; this confused us at the initial stage of the assignment.

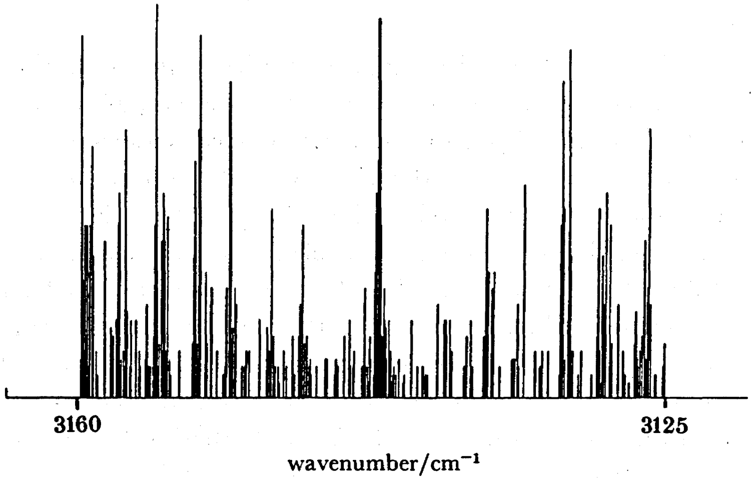

FIGURE 8. A stick diagram for the central portion of the observed $C_2H_3^+$ spectrum.

Although the intensities of the $C_2H_2^+$ lines depend critically on the hydrogen concentration, the $C_2H_3^+$ lines are produced in almost any discharge containing hydrocarbon, H_2 and He. We obtained similar spectra when we used C_2H_4, C_2H_6, C_2H_3Br, and CH_2CCH_2, as when we used C_2H_2. We produced the spectrum with D_2 instead of H_2 in various mixing ratios and ^{13}C-enriched HCCH. These results were not inconsistent with the carrier of the gas being $C_2H_3^+$.

Low J spectral lines assigned so far are listed in table 4. There are other lines that are assigned, but their assignment is not as definitive as those listed in table 4. These spectral lines are close to the asymmetric rotor pattern expected for the rigid non-classical structure. The 'staggering' behaviour of the $K = 1$ K-doubling lines clearly shows that the ion has the bridged structure.

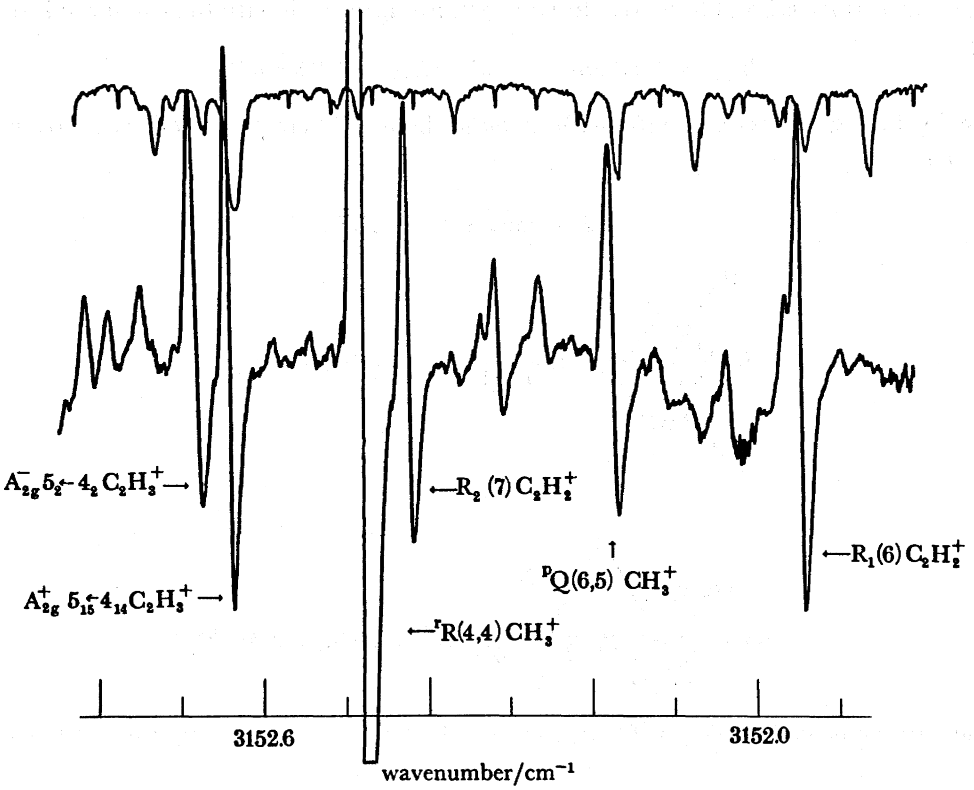

FIGURE 9. An example of carbo-ion spectral lines.

TABLE 4. TENTATIVE ASSIGNMENT (RECIPROCAL CENTIMETRES) OF THE LOW J LINES OF $C_2H_3^+$

$9_{28} \leftarrow 8_{27}$	A^-_{2g}	3161.160	$2_{11} \leftarrow 1_{10}$	A^+_{2g}	3146.708
$9_{19} \leftarrow 8_{18}$	A^+_{2g}	3161.042	$2_{02} \leftarrow 1_{01}$	A^-_{2g}	3146.633
$8_{17} \leftarrow 7_{16}$	A^+_{2g}	3159.511	$2_{02} \leftarrow 3_{03}$	A^-_{2g}	3135.690
$8_{08} \leftarrow 7_{07}$	A^-_{2g}	3159.316	$2_{11} \leftarrow 3_{12}$	A^+_{2g}	3135.540
$8_{26} \leftarrow 7_{25}$	A^-_{2g}	3159.041	$3_{13} \leftarrow 4_{14}$	A^+_{2g}	3133.453
$8_{18} \leftarrow 7_{17}$	E^-_g	3159.189	$4_{14} \leftarrow 5_{15}$	E^-_g	3131.292
$7_{16} \leftarrow 6_{15}$	E^-_g	3157.396	$4_{04} \leftarrow 5_{05}$	A^-_{2g}	3131.232
$7_{17} \leftarrow 6_{16}$	A^+_{2g}	3156.962	$4_{13} \leftarrow 5_{14}$	A^+_{2g}	3130.776
$7_{26} \leftarrow 6_{25}$	A^-_{2g}	3156.931	$5_{15} \leftarrow 6_{16}$	A^+_{2g}	3129.104
$6_{15} \leftarrow 5_{14}$	A^+_{2g}	3155.204	$5_{05} \leftarrow 6_{06}$	E^+_g	3128.870
$6_{24} \leftarrow 5_{23}$	A^-_{2g}	3154.756	$5_{24} \leftarrow 6_{25}$	A^-_{2g}	3128.636
$6_{16} \leftarrow 5_{15}$	E^-_g	3154.672	$5_{14} \leftarrow 6_{15}$	E^-_g	3128.406
$5_{14} \leftarrow 4_{13}$	E^-_g	3152.989	$6_{24} \leftarrow 7_{25}$	A^-_{2g}	3126.363
$5_{05} \leftarrow 4_{04}$	E^+_g	3152.897	$6_{15} \leftarrow 7_{16}$	A^+_{2g}	3126.150
$5_2 \leftarrow 4_2$	A^-_{2g}, E^+_g	3152.678	$7_{17} \leftarrow 8_{18}$	A^+_{2g}	3124.876
$5_{15} \leftarrow 4_{14}$	A^+_{2g}	3152.637	$7_{07} \leftarrow 8_{08}$	E^+_g	3124.534
$4_{04} \leftarrow 3_{03}$	A^-_{2g}	3150.908	$8_{08} \leftarrow 9_{09}$	A^-_{2g}	3122.168
$4_{13} \leftarrow 3_{12}$	A^+_{2g}	3150.889	$8_{26} \leftarrow 9_{27}$	A^-_{2g}	3121.776
$4_{14} \leftarrow 3_{13}$	E^-_g	3150.540	$8_{17} \leftarrow 9_{18}$	A^+_{2g}	3121.535
$3_{13} \leftarrow 2_{12}$	A^+_{2g}	3148.438			

If we take combination differences in the ground state, the 23 differences can be fitted fairly well to an asymmetric rotor model (standard deviation of the fit is *ca.* 0.02 cm^{-1}) with the following rotational constants:

$$B = 1.1412\ (19)\ \mathrm{cm}^{-1} \quad \text{and} \quad C = 1.0467\ (19)\ \mathrm{cm}^{-1},$$

where the uncertainty is 3σ. These rotational constants agree well with the calculated rotational constants

$$B_{\text{calc}} = 1.13\ \text{cm}^{-1} \quad \text{and} \quad C_{\text{calc}} = 1.04\ \text{cm}^{-1}$$

predicted by Lee & Schaefer (1986) with *ab initio* theory. Their predicted structure is shown in figure 10.

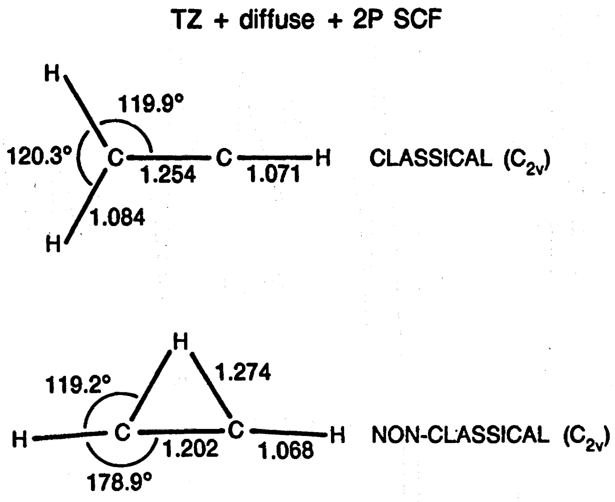

FIGURE 10. Theoretical prediction of $C_2H_3^+$ structure (TZ + diffuse + 2P SCF) (Lee & Schaefer 1986).

Although these results establish the carrier of the spectrum to be $C_2H_3^+$, with the non-classical structure dominating (a conclusion earlier obtained by Kanter *et al.* (1986) from their Coulomb explosion experiment), there are various indications that the spectrum is not that of a usual well-behaved asymmetric rotor. They are as follows. (1) The standard deviation of fitting is larger than the normal case by a factor of 10. In particular, the lowest J transitions ($J = 0$, 1, 2) have large residuals. (2) The observed intensity ratios of the stronger lines to weaker lines of K-doublets (which have nearly equal transition matrix elements except for the spin weight) are closer to 2:1 rather than the 3:1 expected from the usual permutation of two protons. (3) Spectral lines with higher K values ($K \geqslant 3$) are more difficult to assign if we impose combination differences involving Q-branch lines. (4) For each group of lines, there are extra lines with significant intensities. These observations may be associated with the proton tunnelling expected from the theoretically calculated small energy difference between the non-classical and classical ions and the small barrier separating them (Weber *et al.* 1976).

Recently Hougen (1987) and Escribano & Bunker (1987) developed a theory in which the three protons in $C_2H_3^+$ are tunnelling through the barrier and rotating in the plane of $C_2H_3^+$. In such a model the three protons are all equivalent in contrast to the rigid C_{2v} model, in which only two protons are equivalent. The spin-weight ratio is then 2:1 as in NH_3 rather than 3:1 as in H_2. We should use for symmetry argument the full permutation–inversion group

$$S_3 \otimes S_2 \otimes E^* = G_{24},$$

which is isomorphic to D_{6h} ($E^* \equiv \{E, E^*\}$). A simple symmetry argument shows that the symmetry of the total wavefunction should be either A_{2g}^+ or A_{2g}^- and that of the spin wavefunction $4A_{1g}^+$ (for $I = \frac{3}{2}$) and $2E_g^+$ (for $I = \frac{1}{2}$). The correlation table (below) shows that the stronger components of the K doublet that have a spin weight of 3 are split into two lines with the weights of 2 and 1:

C_{2v}	$K_a K_c$	G_{24}
A_1	ee	E_g^+
A_2	oo	E_g^-
$3B_1$	oe	$2A_{2g}^+ + E_g^+$
$3B_2$	eo	$2A_{2g}^- + E_g^-$

Hougen (1987) calculated the magnitude of the splitting based on the internal-rotation hamiltonian used for the analysis of the microwave spectra of CH_3BH_2 and CH_3NO_2 (Wilson *et al.* 1955; Tannenbaum *et al.* 1956). The application of Hougen's programme to the analysis of the $C_2H_3^+$ is in progress.

5. CONCLUSIONS

Spectroscopy of simple carbo-ions has just begun. None of the work described in this paper has been completed yet. Many spectral lines have been observed but their identity is unknown at present. A great many other carbo-ions will be studied. We have already invested a considerable amount of time searching for the spectra of C_2H^-, $C_3H_3^+$ and CH_5^+. Their spectra and many others will be observed and characterized in the near future. The CH_5^+ spectrum will be particularly interesting. The permutation of five protons, S_5, will be involved. This group, which has a high degeneracy, has never been used in molecular spectroscopy. These results will provide fresh information for quantum chemistry, chemical kinetics, plasma physics and astrophysics. Above all, together with spectroscopy of other ions reported in this Meeting, they enrich chemistry at the most fundamental level.

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Discussion

R. SAYKALLY (*Department of Chemistry, University of California, Berkeley, U.S.A.*). Regarding Professor Oka's tentative assignment of the vibrational spectrum of protonated acetylene to a model with the hydrogens tunnelling between the classical and non-classical forms with an apparent barrier near 600 $\mathrm{cm^{-1}}$, it is a bit troublesome that the most recent energy-level *ab initio* calculations on this system indicate a large separation of the two isomers (*ca.* 3 kcal; 1 kcal = 4.18×10^3 J). Also the Argonne Coulomb explosion experiment provides evidence only for the non-classical structure. Can he reconcile these facts with his assignment?

T. OKA, F.R.S. We have not attempted to determine the barrier by fitting the spectrum. The barrier is probably much higher than initially predicted by Weber *et al.* (1976).

R. SAYKALLY. Has Professor Oka observed hot bands for either the methyl cation or the acetylene cation in his spectra? In the latter case, the complex Renner–Teller interactions may make identification very difficult. Also, what are the rotational temperatures observed for these two ions? Do these change substantially with conditions?

T. OKA, F.R.S. We have observed many extra lines for CH_3^+ and $C_2H_2^+$, but none of them have so far been definitively assigned to hot bands. The bending-excited hot bands of $C_2H_2^+$ will be very complicated by the Renner–Teller effect. We have not attempted to determine rotational temperatures, but typical values are 200–300 K for a liquid-N_2 cooled discharge, 500 K for a water-cooled discharge and 800–1000 K for an air-cooled discharge. We used an air-cooled discharge tube for observing high J, K lines of CH_3^+.

H.-J. FOTH (*University of Kaiserlauten, F.R.G.*). Could Professor Oka give more information about the last experiment of H_3O^+? By which techniques did he obtain sub-Doppler resolution. Is it a kind of saturation spectroscopy?

T. OKA, F.R.S. We used the inverse-Lamb dip technique for this observation. Mixing microwave radiation (ν_m) and CO_2 infrared laser radiation (ν_L) in a CdTe crystal, we obtain frequency-tunable infrared radiation in the 10 μm region with high spectral purity and sufficient power for saturation. We combined this source with a low-pressure (30 mTorr) hollow cathode discharge to observe the sub-Doppler spectrum.

E. Hirota (*Institute for Molecular Science*, *Okazaki* 444, *Japan*). There are three 'C–H' stretching states in protonated acetylene. Which one is the upper state of the transition that Professor Oka assigned?

T. Oka, F.R.S. The observed excited state corresponds to the antisymmetric C–H stretching vibration of the bridged (non-classical) structure. The band origin is 3142 cm^{-1}.