

### 138. Spectroscopic Characterization of Open-Shell Cations: Emission and Laser Excitation Spectra of Rotationally Cooled $\text{CH}_3(\text{C}\equiv\text{C})_2\text{X}^+$ , $\text{X} = \text{Cl}, \text{Br}$

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(11.V.84)

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#### Summary

Gas phase emission and laser excitation spectra of the  $\tilde{\text{A}}^2\text{E} \leftrightarrow \tilde{\text{X}}^2\text{E}$  ( $\Sigma = +\frac{1}{2}, -\frac{1}{2}$ ) transition of rotationally/vibrationally cooled 1-chloro- and 1-bromo-1,3-pentadiyne cations have been obtained. The emission was excited by electron impact on a seeded helium supersonic free jet and the fluorescence by laser excitation of cations produced by *Penning* ionization and collisional relaxation. From these two sets of data the origin bands of the spin-orbit systems are located and for the bromo species this leads to better values of the spin-orbit splittings in the two electronic states and of the first adiabatic ionization energy. The vibrational frequencies of many of the fundamentals of these cations in the  $\tilde{\text{X}}^2\text{E}$  and  $\tilde{\text{A}}^2\text{E}$  states have been obtained to within  $\pm 2 \text{ cm}^{-1}$ .

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**1. Introduction.** – Various spectroscopic methods have been, and are being, developed in order to characterize polyatomic cations in the gas phase at resolution much higher than that attained by photoelectron (PE) spectroscopy [1]. Invariably, the highest resolution studies have utilized lasers and have been applied to the smaller species. Most notable recent approaches involve absorption by ions of IR laser radiation followed by detection using modulated techniques [2] or *via* dissociation channels [3], and with visible lasers-ion beams arrangements [4]. In the case of open-shell organic cations, laser-excited fluorescence spectroscopy [5] has made an important impact following the preliminary experiments using electron-beam excitation of their emission spectra [6]. The newer improvements in these areas have focused on the use of rotationally and vibrationally cooled ions using supersonic expansions [7] and collisional relaxation [8]. In this contribution we report the results of two such methods; the one being emission spectroscopy of rotationally supercooled cations and the other being fluorescence caused by laser excitation of cations cooled to liquid nitrogen temperature in the gas phase [9]. The spectroscopic characterization of concern here is the vibrational structure of the 1-chloro- and 1-bromo-1,3-pentadiyne cations in their ground,  $\tilde{\text{X}}^2\text{E}$ , and first excited,  $\tilde{\text{A}}^2\text{E}$ , electronic states.

The first study of these two cations,  $\text{CH}_3(\text{C}\equiv\text{C})_2\text{X}^+$ ,  $\text{X} = \text{Cl}, \text{Br}$ , was by PE spectroscopy [10] and this provided the basis in the search for the radiative decay from their excited electronic states in the optical part of the spectrum. In these experiments

the emission spectra were produced by electron beam impact on an effusive sample beam and the observed band systems could be attributed to the  $\tilde{A}^2E \rightarrow \tilde{X}^2E$  electronic transition (using  $C_{3v}$  symmetry classification) of these cations [11]. The vibrational analysis yielded frequencies of some of the fundamentals in the ground cationic state; however, these could only be inferred to  $\pm 10 \text{ cm}^{-1}$  due to the broadness of the bands. With the development of the technique to produce rotationally super-cold cations by means of a seeded supersonic expansion, a considerable enhancement in the accuracy and amount of information available from the emission spectra of larger organic cations was realized [12]. Thus, the reinvestigation of the emission spectra of the 1-chloro- and 1-bromo-1,3-pentadiyne cations using the technique reported here, has led to much more precise vibrational frequencies, to resolution of the two spin-orbit sub-systems of the chloro species and reassignment of the origin bands for the bromo one.

Complementary data on the vibrational modes of these cations in their lowest excited electronic state,  $\tilde{A}^2E$ , are also reported. These are obtained from the laser-excitation spectra of the  $\tilde{A}^2E \leftarrow \tilde{X}^2E$  transition. In these measurements the cations are also rotationally cooled, though not as extensively as in the supersonic expansion. Nevertheless, the cooling achieved enhances the quality of the spectra over those obtainable with a room-temperature source [5] [9].

The availability of both emission and excitation spectra leads to an unambiguous assignment of the band origins and helps in the vibrational interpretations. The result of the analyses is that the vibrational frequencies of many of the totally symmetric fundamentals ( $a_1$ ) could be deduced for the  $\tilde{X}^2E$  and  $\tilde{A}^2E$  electronic states to within  $\pm 2 \text{ cm}^{-1}$ , as well as for some of the degenerate ( $e$ ) fundamentals. Better values for the spin-orbit splitting and adiabatic ionization energy for the  $\tilde{X}^2E$  state could also be inferred for the 1-bromo-1,3-pentadiyne cation.

**2. Experimental.** – A detailed description of the experimental set-up for laser-excitation measurements has been given earlier [11] [13]. Vibrationally and rotationally relaxed cations were formed by *Penning* ionization using Ar metastables in a liquid  $N_2$  cooled discharge flow system. The thermalized ion beam was probed by a nitrogen, or Nd:Yag, laser pumped dye laser at 30 Hz. The undispersed fluorescence was detected by a photomultiplier after passing through a cut-off filter discriminating against stray laser light. The photomultiplier signal along with two photodiode pulses probing laser intensity and frequency marking interference fringes were fed into a transient digitizer and further processed by a microcomputer which also controls the scanning of the laser frequency. The wavelength scale was absolutely determined using atomic lines, excited in the observation region by the laser, in conjunction with the frequency markers.

The emission spectra were recorded with a crossed supersonic sample-electron beam apparatus which has also been described previously [9]. A mixture of 2% of the 1-halo-1,3-pentadiyne in He was expanded through a 100  $\mu\text{m}$  diameter nozzle at a total backing pressure of 1.1 bar into the ionization chamber where the pressure was  $< 10^{-3}$  mbar. Excitation was achieved with an electron beam of 200 eV energy and 4 mA current, which intersected the supersonic free jet at right angles 5–7 mm downstream from the nozzle. Emitted photons were collected at right angles to the sample and electron beams, their wavelength analyzed by an  $f/9.5$ , 1.26 m monochromator and focused onto a cooled photomultiplier connected to single-photon counting electronics. The spectra were recorded on-line with a microcomputer. The calibration was based on the observation of many He lines which were concurrently excited by the electron beam.

The syntheses and purification of 1-chloro- and 1-bromo-1,3-pentadiyne samples were carried out according to the procedure given in [14]. Both the samples contained a few percent of 2,4-hexadiyne as an impurity and the bands due to its cation are easily identifiable in the spectra.

**3. Results and Discussion.** – 3.1. *General Spectral Features.* The emission spectra recorded using an effusive source led to the identification of the  $\tilde{A}^2E \rightarrow \tilde{X}^2E$  band systems

of 1-chloro- and 1-bromo-1,3-pentadiyne cations [11]. In the case of the chloro compound the two spin-orbit components ( $\Sigma = +\frac{1}{2}$  and  $-\frac{1}{2}$ ) were not individually discernible and were inferred to be contained within each of the bands ascribed to a particular vibronic transition. Also in the PE spectrum of 1-chloro-1,3-pentadiyne the spin-orbit splitting is not resolved on either of the first two bands corresponding to the  $\tilde{X}^2E$  and  $\tilde{A}^2E$  states. According to this  $A'(\tilde{A}^2E) \approx A''(\tilde{X}^2E) \approx -160 \pm 80 \text{ cm}^{-1}$ , but the model predictions for the spin-orbit splittings show that  $A'$  is slightly larger than  $A''$ ; similar to the situation in the chlorodiacetylene cation [10].

In the emission spectrum of the supersonically cooled cation, the two spin-orbit systems are now distinct (Fig. 1), and both are also apparent in the laser excitation spectrum of this transition (Fig. 3). The origins of the  $\Sigma = +\frac{1}{2}$ ,  $-\frac{1}{2}$  sub-systems are identified by comparison of the excitation and emission spectra. Whereas the two most intense bands in the emission system, separated by  $20 \text{ cm}^{-1}$ , are about equally intense, the higher energy one is less intense in the excitation spectrum. The reason for this is that the cations formed in the Penning ionization process are thermalized to the temperature of their environment, which is cooled by liquid  $N_2$ . Thus the population of the zeroth level of the  $\Sigma = -\frac{1}{2}$  component of the  $\tilde{X}^2E$  state is attenuated according to the Boltzmann-distribution. Thus it is concluded that the lower energy origin band at  $19820 \pm 1 \text{ cm}^{-1}$  is the  $0_0^0 \Sigma = +\frac{1}{2}$  component, and the one at  $19840 \pm 1 \text{ cm}^{-1}$  is the  $\bar{0}_0^0$ ,  $\Sigma = -\frac{1}{2}$  origin. (The bar above the vibrational mode designates the  $\Sigma = -\frac{1}{2}$  component, in the Figures and in the Tables.) This interpretation ( $A'' - A' = 20 \text{ cm}^{-1}$ ) is consistent with the prediction  $|A'| > |A''|$ , and the attenuation of the  $\bar{0}_0^0$  band intensity in the excitation spectrum with the inference from the photoelectron spectroscopic measurement that  $A' \approx A'' \approx -160 \pm 80 \text{ cm}^{-1}$  (the states being inverted) [10] [11].

The locations of the origins in the case of the  $\tilde{A}^2E \leftrightarrow \tilde{X}^2E$  transition of 1-bromo-1,3-pentadiyne cation is straightforward since the  $\Sigma = -\frac{1}{2}$  component system is not observed in the excitation spectrum because the spin-orbit splitting in the  $\tilde{X}^2E$  state is  $0.04 \pm 0.01 \text{ eV}$ . The  $0_0^0$  band is the most intense transition in both spectra (Figures 2 and 4). In the emission spectrum both sub-systems are observed as both  $\Sigma = +\frac{1}{2}$  and  $-\frac{1}{2}$  components in the  $\tilde{A}^2E$  state are populated in the ionisation process. However, the  $\bar{0}_0^0$  band is weaker than the  $0_0^0$  band (Fig. 2), as is to be expected in view of the measured fluorescence quantum yields by the photoelectron-photon coincidence technique [15]. The  $\bar{0}_0^0$  band lies  $304 \pm 1 \text{ cm}^{-1}$  ( $\approx 0.04 \text{ eV}$ ) to higher energy of the  $0_0^0$  band which is consistent, within error limits, with the data from photoelectron spectroscopy, i.e.  $A' = -0.09 \pm 0.01 \text{ eV}$  and  $A'' = -0.04 \pm 0.01 \text{ eV}$ . These observations lead to an unambiguous reassignment of the origin bands with respect to that given [11].

In the PE spectrum of 1-bromo-1,3-pentadiyne the adiabatic ionization energies ( $I$ ) leading to the  $\tilde{A}^2E$  state  $\Sigma = +\frac{1}{2}$  and  $-\frac{1}{2}$  components are more distinctly identifiable than for the  $\tilde{X}^2E$  state [10] [11]. These values can then be combined with the observed positions of the  $0_0^0$  and  $\bar{0}_0^0$  bands in the emission spectrum of the  $\tilde{A}^2E \rightarrow \tilde{X}^2E$  transition to predict more reliable adiabatic ionization energies for the production of this cation in the ground state than is possible by PE spectroscopy alone. The following values ( $\pm 0.01 \text{ eV}$ ) are thus recommended:

$$\begin{array}{ll}
 I_1(\tilde{X}^2E, \Sigma = +\frac{1}{2}, -\frac{1}{2}) & I_2(\tilde{A}^2E, \Sigma = +\frac{1}{2}, -\frac{1}{2}) \\
 9.02, 9.07 & 11.32, 11.41 \text{ eV,}
 \end{array}$$

and thus  $A'' = -0.05$  and  $A' = -0.09$  eV. The  $I_1(\Sigma = +\frac{1}{2})$  value, the important entity for the evaluation of the heat of formation of this cation, is 0.04 eV lower than given previously [10] [11]. For 1-chloro-1,3-pentadiyne, no improvement on the given ionization energies is possible, since the spin-orbit splittings are not resolved on either of the first two photoelectron bands, *i.e.*  $I_1 = 9.19 \pm 0.01$  eV,  $I_2 = 11.63 \pm 0.01$  eV and these refer to the mean of the  $\Sigma = \pm\frac{1}{2}$  values.

The vibrational assignment of the bands in the  $\tilde{A}^2E \leftrightarrow \tilde{X}^2E$  emission and excitation systems of the two cations is made using the numbering of the fundamentals given for the molecular ground state [14]. Under  $C_{3v}$  symmetry classification there are seven totally symmetric  $a_1$  modes,  $\nu_1$  to  $\nu_7$ , and seven degenerate  $e$  modes,  $\nu_8$  to  $\nu_{14}$ . Their approximate description is indicated in *Table 5*.

Due to the difference in the generation of the cations in the emission and excitation experiments, the vibrational structure is often different, especially in respect to the sequence transitions. In the laser excitation experiment, assuming a vibrational temperature of  $\approx 100$  K, only the lowest ( $< 200$   $\text{cm}^{-1}$ ) vibrational levels (*i.e.* of  $\nu_{13}$ ,  $\nu_{14}$ ) in the  $\tilde{X}^2E$  state are sufficiently populated for their sequence transitions to be observed. On the other hand, in the emission experiment sequence transitions between all the levels of the totally symmetric vibrations may be seen, depending on their initial population in the excited state and their respective *Franck-Condon* factors, as well as between the very low frequency  $\nu_{14}$  vibration, the first level of which is populated somewhat even at a vibrational temperature of say 50 K.

**3.2. Emission Spectra.** Compared to the emission spectra obtained using an effusive source [11], the spectra from the supersonic free jet (*Figures 1* and *2*) show a good deal of new structure previously buried underneath the inhomogeneously broadened bands at the higher rotational temperatures. The  $\Sigma = \pm\frac{1}{2}$  components become clearly discernible as well as many new bands. The maxima of the more intense, or of the assigned bands in the two spectra are collected in *Tables 1* and *2*, where the proposed vibrational assignments are given. In the *Figures* themselves some of these are also indicated.

*Table 1. Maxima of the Prominent or Assigned Bands ( $\tilde{\nu}_{\text{vac}}$ ) in the  $\tilde{A}^2E \rightarrow \tilde{X}^2E$ ,  $\Sigma = +\frac{1}{2}, -\frac{1}{2}$ , Emission Spectrum of the 1-Chloro-1,3-pentadiyne Cation. The vibrational numbering corresponds to that given in *Table 5*, (the  $\Sigma = -\frac{1}{2}$  component bands are designated by the bar) and the label numbers refer to the markers in *Fig. 1*. Tentative assignments are in parentheses.*

Label	$\tilde{\nu}_{\text{vac}}$	Transition
1	20312	$\overline{13}_0^2$
2	20289	$13_0^2$
3	20268	$\overline{7}_0^1$
4	20244	$7_0^1$
5	19840	$\overline{0}_0^0$
6	19820	$0_0^0$
7	19778	
8	19706	$5_1^1$
9	19636	( $14_9^0$ )

*Table 2. Maxima of the More Intense or Assigned Bands ( $\tilde{\nu}_{\text{vac}}$ ) in the  $\tilde{A}^2E \rightarrow \tilde{X}^2E$ ,  $\Sigma = +\frac{1}{2}, -\frac{1}{2}$ , Emission Spectrum of the 1-Bromo-1,3-pentadiyne Cation. The running numbers correspond to the markers in *Fig. 2* and the vibrational modes to those listed in *Table 5*. The  $\Sigma = -\frac{1}{2}$  bands are distinguished by the bar. Tentative interpretations are in brackets. All values  $\pm 1$   $\text{cm}^{-1}$ .*

Label	$\tilde{\nu}_{\text{vac}}$	Transition
	19705	$5_0^1$
1	18924	
2	18911	
3	18900	
4	18857	$\overline{0}_0^0$
5	18845	$\overline{13}_1^1$
6	18830	$\overline{13}_2^1$
7	18803	
8	18785	$\overline{2}_1^1$

Table 1 (continued)

Label	$\tilde{\nu}_{\text{vac}}$	Transition
10	19395	$13_2^0$
11	19377	
12	19365	$13_2^0$
13	19346	$7_1^0$
14	19317	$7_1^0$
15	18928	
16	18905	$7_1^0 13_2^0$
17	18875	$7_2^0$
18	18522	$5_1^0$
19	18507	$4_1^0$
20	18500	$5_1^0$
21	18486	$4_1^0$
22	18472	
23	18084	$5_1^0 13_2^0$
24	18052	$5_1^0 13_2^0$
25	18031	$5_1^0 7_1^0$
26	18007	$5_1^0 7_1^0$
27	17610	$2_1^0$
28	17588	$2_1^0$
29	17177	
30	17158	$2_1^0 13_2^0$
31	17141	$2_1^0 13_2^0$
32	17125	$2_1^0 7_1^0$
33	17095	$2_1^0 7_1^0$
34	16686	$2_1^0 7_1^0$
35	16655	$2_1^0 7_2^0$
36	16302	$2_1^0 5_1^0$
37	16280	$2_1^0 5_1^0$
38	15392	$2_2^0$
39	15373	$2_2^0$

Table 2 (continued)

Label	$\tilde{\nu}_{\text{vac}}$	Transition
9	18553	$0_0^0$
10	18545	
11	18540	$13_1^1$
12	18528	$(14_1^1)$
13	18518	
14	18508	
15	18491	$7_1^0$
16	18479	$2_1^1$
17	18185	$7_1^0$
18	18164	
19	18153	
20	18102	$13_2^0$
21	17820	
21	17817	$7_2^0$
22	17802	
23	17758	$6_1^0$
24	17743	$7_1^0 13_2^0$
25	17456	
25	17451	$7_3^0$
26	17364	$(7_2^0 13_2^0)$
27	17278	
27	17276	$5_1^0$
28	17255	
29	16907	$5_1^0 7_1^0$
30	16645	$(2_1^0)$
31	16632	
32	16564	$3_1^0$
33	16337	$2_1^0$
34	16314	$(2_1^0 14_1^1)$
35	16306	
36	16296	
37	16196	$3_1^0 7_1^0$
38	15972	
38	15970	$2_1^0 7_1^0$
39	15889	$2_1^0 13_2^0$
40	15606	$2_1^0 7_2^0$
41	14133	$2_2^0$

The spectrum of the 1-chloro-1,3-pentadiyne cation is the more complex one because of the overlapping of the two spin-orbit sub-systems. According to the proposed assignment  $\nu_7''$ ,  $\nu_5''$  and  $\nu_2''$  are the dominant vibrations excited, as well as  $\nu_{13}''$  in double quanta. The latter transitions lie near to the intense bands associated with the  $\nu_7''$  totally symmetric mode excitation e.g.  $13_2^0$  and  $7_1^0$ . The proximity of these transitions yields an appreciable *Fermi*-interaction (the double excitation of the e mode yields an  $a_1$  component) and accounts for the high intensity of the transitions (e.g.  $13_2^0$ ). The same pattern has already been observed and discussed for the emission spectra of the analogous transitions of the 1,3-pentadiyne cation [16] and of the halo-substituted diacetylene cations [17]. The  $\nu_4''$  mode is also, but weakly, excited in the emission spectrum and possibly  $\nu_{14}''$  in double quanta (cf. Table 1).



The assignment of the bands  $7_1^0$ ,  $13_2^0$  and their  $\Sigma = -\frac{1}{2}$  components was made on the basis of the relative intensities and the pattern in the next group of bands, *i.e.* the Fermi-triad  $7_2^0$ ,  $7_1^0 13_2^0$ ,  $13_4^0$ . The other stronger bands in this region (*e.g.* at  $19377\text{ cm}^{-1}$ ) belong to an unidentified sequence transition for which  $\nu' > \nu''$ . Also to be seen in the group of bands around  $7_1^0$  is evidence of rotational K-structure. This is similar to that observed previously in the emission spectrum of the 1,3-pentadiyne cation, where it was partially analyzed from the measurements taken at various stagnation pressures (*i.e.* rotational temperatures) [16]. As in the latter study, the apparent spin-orbit splitting between the  $7_1^0$  and  $7_1^0$  bands ( $29\text{ cm}^{-1}$ ) and between the  $13_2^0$  and  $13_2^0$  bands ( $30\text{ cm}^{-1}$ ) is larger than that observed for the origin bands ( $20\text{ cm}^{-1}$ ) or for the  $5_1^0$  and  $5_1^0$  bands ( $22\text{ cm}^{-1}$ ) or the  $2_1^0$  and  $2_1^0$  bands ( $22\text{ cm}^{-1}$ ). The explanation proposed is the same as discussed in detail and quantitatively for the 1,3-pentadiyne cation; namely, that this reflects the quenching of the spin-orbit splitting in the  $\tilde{X}^2E$  state by vibronic effects. These arise due to the excitation of the  $\nu_{13}''$  mode by two quanta, and its interaction with the  $\nu_7''$  mode. According to the observed spin-orbit splittings, the two wavefunctions are about equally mixed in each of these levels (*i.e.*  $\nu_7''$  and  $2\nu_{13}''$ ) as is also suggested by the intensities (*cf.* Fig. 1). In the case of the 1,3-pentadiyne cation the intensity of the  $13_2^0$  band was less than that of the  $7_1^0$ , and also the spin-orbit splitting was larger in the former. Quantitative evaluation of the quenching parameters in the present study is not feasible since the spin-orbit splittings in the  $\tilde{X}^2E$  and  $\tilde{A}^2E$  states are not known with sufficient accuracy.

In the emission spectrum of the 1-bromo-1,3-pentadiyne cation (Fig. 2), although the two spin-orbit systems are well separated, the only bands belonging to the  $\Sigma = -\frac{1}{2}$  system which are clearly discernible are located around the origin ( $0_0^0$ ) band. In the  $\Sigma = +\frac{1}{2}$  system, the excitation of five of the totally symmetric modes is apparent ( $\nu_7''$ ,  $\nu_6''$ ,  $\nu_5''$ ,  $\nu_3''$  and  $\nu_2''$ ) in the  $\tilde{X}^2E$  state, as well as the excitation of the overtones of the  $\nu_{13}''$  mode. In this case, however, the  $13_2^0$  transition lies to lower energy of the  $7_1^0$  transition and the intensity difference is larger, the two are more separated ( $83\text{ cm}^{-1}$ ) than in the chlorine spectrum ( $48\text{ cm}^{-1}$ ). In the next group of bands involving the  $\nu_7''$  and  $\nu_{13}''$  modes, the  $7_2^0$  band is by far the most intense, and in addition shows the splitting ( $3\text{ cm}^{-1}$ ) due to the  $^{79}\text{Br}$  and  $^{81}\text{Br}$  isotopes. The inferred vibrational frequencies of the various fundamentals from the respective emission spectra are collected in Table 5, where the molecular ground state values are also reproduced from [14].

3.3. *Laser Excitation Spectra.* The laser excitation spectra of the  $\tilde{A}^2E \leftrightarrow \tilde{X}^2E$  transition of rotationally and vibrationally cooled cations of 1-chloro- and 1-bromo-1,3-pentadiyne are reproduced in Fig. 3 and 4. These spectra were recorded with  $0.02\text{ nm}$  laser band-width. Selected portions of the spectra were also scanned with a  $0.005\text{ nm}$  band-pass. From such measurements, the data in Tables 3 and 4 were assembled where the maxima of most of the clearly discernible bands are listed.

Fluorescence signals were detected from vibrational levels in the  $\tilde{A}^2E$  state of these cations lying up to  $\approx 2500\text{ cm}^{-1}$  above the zeroth level. The reason for the decreasing intensity of the excitation bands with excess energy is twofold. Firstly the respective Franck-Condon factors for the population of the levels in the  $\tilde{A}^2E$  state, starting from the lowest level in the  $\tilde{X}^2E$  state, drop off. Secondly, as the photoelectron-photon coincidence measurements have shown, the fluorescence quantum yields decrease from 0.55 to 0.07 and from 0.23 to 0.08 for the zeroth level to  $2500\text{ cm}^{-1}$  excess energy for the

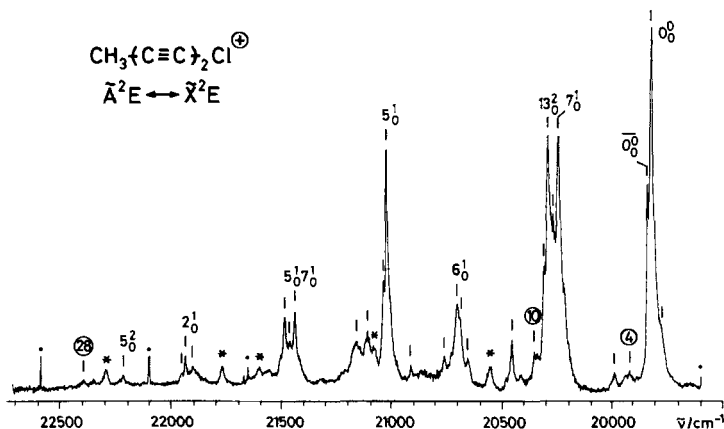


Fig. 3. Laser excitation spectrum of the  $\tilde{A}^2E \leftrightarrow \tilde{X}^2E$  transition of the 1-chloro-1,3-pentadiyne cation in the gas phase cooled by liquid  $\text{N}_2$ . The optical band pass was 0.02 nm. (See also remarks under Fig. 1).

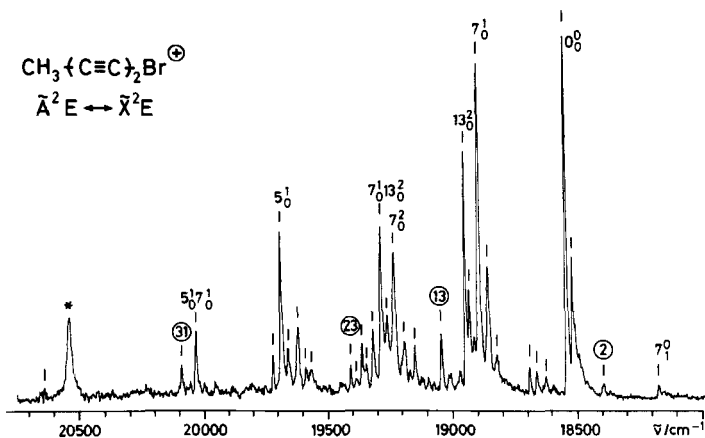


Fig. 4. Laser excitation spectrum of the  $\tilde{A}^2E \leftrightarrow \tilde{X}^2E$  transition of the 1-bromo-1,3-pentadiyne cation cooled by liquid  $\text{N}_2$ . The optical band pass was 0.02 nm. (See also remarks under Fig. 1).

chloro- and bromo-species, respectively [15]. The intensity of an excitation band is proportional to both these factors.

The proposed vibrational assignments of the band systems in the excitation spectra are given in *Tables 3 and 4* and some of these are labelled in *Fig. 3 and 4*. In both spectra the  $\nu_7'$  and  $\nu_5'$  modes are most strongly excited in the  $\tilde{A}^2E$  state. Bands associated with the excitation of the  $\nu_6'$  and  $\nu_2'$  fundamentals are also identified. Various combination bands involving these vibrations are evident. In addition, for both the cations, strong excitation of the  $\nu_{13}'$  degenerate mode in double quanta is observed. As in the emission spectra, the respective transitions lie close to the allowed ones involving the  $a_1$  modes e.g.  $13_0^2$  and  $7_0^1$ . In the case of the spectrum of the 1-chloro-1,3-pentadiyne cation (*Fig. 3*), the separation of the  $7_0^1$  and  $\bar{7}_0^1$  and  $13_0^2$  and  $\bar{13}_0^2$  bands is about equal ( $\approx 25 \text{ cm}^{-1}$ ). This is slightly larger than the separation of the  $0_0^0$  and  $\bar{0}_0^0$  bands ( $20 \text{ cm}^{-1}$ ) and



less than the corresponding bands in the  $\tilde{X}^2E$  state as discussed in *Sect. 3.2*. This indicates that the effects of vibronic coupling in quenching of the spin-orbit splittings are less in the excited state. This again follows the trend established for the parent cation of 1,3-pentadiyne [16]. A few weak bands at the higher energy side of the origin bands, and of the strong progression bands in the excitation spectra of the two cations, could also be due to the excitation of other degenerate modes in double quanta, *i.e.*  $\nu_{14}$  and  $\nu_{12}$ . These assignments are tentative and are made on the basis of the corresponding molecular values. All the deduced vibrational frequencies are given in *Table 5*.

Table 3. *Maxima of the Prominent Bands* ( $\tilde{\nu}_{\text{vac}}$ ) *in the*  $\tilde{A}^2E \leftarrow \tilde{X}^2E$  *Laser-Excitation Spectrum of the 1-Chloro-1,3-pentadiyne Cation*. The running numbers refer to the labels in *Fig. 3*. The vibrational assignments use the numbering of the fundamentals given in *Table 5* and the transitions of the  $\Sigma = -\frac{1}{2}$  component are designated by a bar.

Tentative assignments are in parentheses.

Label	$\tilde{\nu}$ (cm <sup>-1</sup> )	Transition
1	19783 ± 3	
2	19820 ± 2	0 <sub>0</sub> <sup>0</sup>
3	19840 ± 2	$\bar{0}_0^0$
4	19926 ± 5	
5	19996 ± 3	(14 <sub>0</sub> <sup>2</sup> )
6	20244 ± 2	7 <sub>0</sub> <sup>1</sup>
7	20269 ± 2	$\bar{7}_0^1$
8	20291 ± 2	13 <sub>0</sub> <sup>2</sup>
9	20313 ± 3	$\bar{13}_0^2$
10	20358 ± 5	
11	20458 ± 2	(12 <sub>0</sub> <sup>2</sup> )
12	20661 ± 3	7 <sub>0</sub> <sup>2</sup>
13	20700 ± 5	7 <sub>0</sub> <sup>1</sup> 13 <sub>0</sub> <sup>2</sup>
14	20709 ± 3	6 <sub>0</sub> <sup>1</sup>
15	20768 ± 2	13 <sub>0</sub> <sup>1</sup>
16	20921 ± 3	
17	21027 ± 2	5 <sub>0</sub> <sup>1</sup>
18	21042 ± 2	$\bar{5}_0^1$
19	21116 ± 2	4 <sub>0</sub> <sup>1</sup> ; 6 <sub>0</sub> <sup>1</sup> 7 <sub>0</sub> <sup>1</sup>
20	21167 ± 5	6 <sub>0</sub> <sup>1</sup> 13 <sub>0</sub> <sup>2</sup>
21	21445 ± 2	5 <sub>0</sub> <sup>1</sup> 7 <sub>0</sub> <sup>1</sup>
22	21470 ± 4	$\bar{5}_0^1 \bar{7}_0^1$
23	21493 ± 3	5 <sub>0</sub> <sup>1</sup> 13 <sub>0</sub> <sup>2</sup>
24	21909 ± 5	5 <sub>0</sub> <sup>1</sup> 6 <sub>0</sub> <sup>1</sup>
25	21944 ± 2	2 <sub>0</sub> <sup>1</sup>
26	21961 ± 3	$\bar{2}_0^1$
27	22225 ± 3	5 <sub>0</sub> <sup>2</sup>
28	22405 ± 5	

Table 4. *Maxima of the Prominent Bands* ( $\tilde{\nu}_{\text{vac}}$ ) *in the*  $\tilde{A}^2E \leftarrow \tilde{X}^2E$  *Laser-Excitation Spectrum* ( $\Sigma = +\frac{1}{2}$  component) *of the 1-Bromo-1,3-pentadiyne Cation*. The label-numbers refer to the markers in *Fig. 4*. The vibrational assignments use the numbering of the modes given in *Table 5*. Tentative assignments are in parentheses.

Label	$\tilde{\nu}$ (cm <sup>-1</sup> )	Transition
1	18185 ± 2	7 <sub>0</sub> <sup>0</sup>
2	18405 ± 3	
3	18528 ± 1	14 <sub>0</sub> <sup>1</sup>
4	18553 ± 1	0 <sub>0</sub> <sup>0</sup>
5	18637 ± 2	
6	18675 ± 2	
7	18704 ± 1	14 <sub>0</sub> <sup>2</sup>
8	18833 ± 2	
9	18867 ± 2	
10	18903 ± 2	7 <sub>0</sub> <sup>1</sup>
11	18942 ± 1	(7 <sub>0</sub> <sup>1</sup> 13 <sub>0</sub> <sup>2</sup> )
12	18959 ± 1	13 <sub>0</sub> <sup>2</sup>
13	19057 ± 1	7 <sub>0</sub> <sup>1</sup> 14 <sub>0</sub> <sup>2</sup>
14	19164 ± 1	(12 <sub>0</sub> <sup>2</sup> )
15	19206 ± 3	
16	19244 ± 2	7 <sub>0</sub> <sup>2</sup>
17	19274 ± 2	
18	19298 ± 1	7 <sub>0</sub> <sup>1</sup> 13 <sub>0</sub> <sup>2</sup>
19	19333 ± 1	6 <sub>0</sub> <sup>1</sup>
20	19361 ± 2	13 <sub>0</sub> <sup>1</sup>
21	19378 ± 1	
22	19400 ± 3	7 <sub>0</sub> <sup>2</sup> 14 <sub>0</sub> <sup>2</sup>
23	19423 ± 1	
24	19583 ± 3	7 <sub>0</sub> <sup>3</sup>
25	19605 ± 2	
26	19635 ± 1	7 <sub>0</sub> <sup>2</sup> 13 <sub>0</sub> <sup>2</sup>
27	19677 ± 2	6 <sub>0</sub> <sup>1</sup> 7 <sub>0</sub> <sup>1</sup>
28	19704 ± 1	5 <sub>0</sub> <sup>1</sup>
29	19737 ± 1	6 <sub>0</sub> <sup>1</sup> 13 <sub>0</sub> <sup>2</sup>
	20017 ± 1	6 <sub>0</sub> <sup>1</sup> 7 <sub>0</sub> <sup>2</sup>
30	20050 ± 1	5 <sub>0</sub> <sup>1</sup> 7 <sub>0</sub> <sup>1</sup>
31	20108 ± 1	5 <sub>0</sub> <sup>1</sup> 13 <sub>0</sub> <sup>2</sup>
32	20694 ± 1	(2 <sub>0</sub> <sup>1</sup> )

Sequence structure is only clearly discernible in the excitation spectrum of the 1-bromo-1,3-pentadiyne cation (*cf. Fig. 4*). This lies to lower energy of the main bands and thus implies that for the sequence modes the frequencies are less in the  $\tilde{A}^2E$  state than in the  $\tilde{X}^2E$  state. On the basis of the argument presented in *Sect. 3.1*, that only the lowest frequency vibrations come into consideration, these must involve the  $\nu_{14}$  and  $\nu_{13}$  modes, *i.e.*  $14_1^1$ ,  $14_2^2$  and  $13_1^1$  transitions. The  $7_1^0$  band is also weakly seen, and its intensity, as well as that of the sequence bands, increases relative to say the  $0_0^0$  band in the excitation spectrum recorded at room temperature. From these changes in intensity, it appears that the vibrational temperature is probably around 150 K when the environment is cooled with liquid nitrogen. In the excitation spectrum of the chloro species the bands are broader due to the overlap of the rotational profiles of the bands of the  $\Sigma = +\frac{1}{2}$  and  $-\frac{1}{2}$  components, and the sequence structure is hardly apparent. The corresponding  $\nu_{14}$  and  $\nu_{13}$  sequence bands are assumed to be buried within these rotational envelopes.

Table 5. *Fundamental Vibrational Frequencies ( $\pm 2 \text{ cm}^{-1}$ ) of 1-Chloro-1,3-pentadiyne and 1-Bromo-1,3-pentadiyne Cations in the Ground,  $\tilde{X}^2E$ , and First Excited,  $\tilde{A}^2E$ , Electronic States Deduced from the Emission and Laser Excitation Spectra, Respectively. The values refer to the  $^{35}\text{Cl}$  isotope or to the mean of the  $^{79}\text{Br}$ ,  $^{81}\text{Br}$  isotopes of the  $\Sigma = +\frac{1}{2}$  components. Tentative assignment are given in parentheses. The ground molecular state values are taken from [14].*

Species/State	$\text{CH}_3(\text{C}\equiv\text{C})_2\text{Cl}^+$			$\text{CH}_3(\text{C}\equiv\text{C})_2\text{Br}^+$			
	$X^1A_1$	$\tilde{X}^2E$	$\tilde{A}^2E$	$X^1A_1$	$\tilde{X}^2E$	$\tilde{A}^2E$	
a <sub>1</sub>	$\nu_1$ (CH <sub>3</sub> sym. str.)	2935		2933			
	$\nu_2$ (C≡C sym. str.)	2257	2232	2123	2256	(2141)	
	$\nu_3$ (C≡C as. str.)	2175			2158	1989	
	$\nu_4$ (CH <sub>3</sub> sym. def.)	1381	1334	1296	1381		
	$\nu_5$ (C–C as. str.)	1228	1320	1207	1210	1276	1151
	$\nu_6$ (C–C sym. str.)	862		888	815	795	780
	$\nu_7$ (C–X str.)	437	503	424	356	368	350
e	$\nu_8$ (CH <sub>3</sub> as str.)	2977		2975			
	$\nu_9$ (CH <sub>3</sub> as. def.)	1446		1446			
	$\nu_{10}$ (CH <sub>3</sub> rock)	1029		1029			
	$\nu_{11}$ (as. skel. bend)	457		460			
	$\nu_{12}$ (sym. skel. bend)	339		(319)	332		(306)
	$\nu_{13}$ (C≡C–X bend)	241	228	235	223	226	203
	$\nu_{14}$ (skel. bend)	101	(92)	(87)	92	(101)	76

The rotational envelopes are shaded to the red (as in the spectra of the corresponding transitions of the halodiacetylene cations [17]) implying that the rotational constant (for end-over-end rotation) is smaller in the excited state *i.e.*  $B'(\tilde{A}^2E) < B''(\tilde{X}^2E)$ . Since the largest relative frequency changes are associated with the  $\nu_7$ (C–X stretching) and  $\nu_5$ (C–C asymmetric stretching) modes,  $\nu_7'' > \nu_7'$  and  $\nu_5'' > \nu_5'$  (*Table 5*), the main changes accompanying the  $\tilde{A}^2E \leftrightarrow \tilde{X}^2E$  transition seem to be changes in the C–X and C–C distances, both being larger in the  $\tilde{A}^2E$  state of the cations.

This work is part of project No. 2.817-0.83 of the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung*. *Ciba-Geigy AG*, *Sandoz AG* and *F. Hoffmann-La Roche & Co. AG*, Basel are also thanked for financial support.

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