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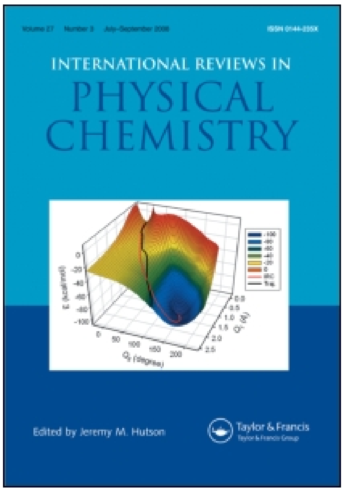

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Spectroscopic characterization of cations via their electronic transitions

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Spectroscopic characterization of cations via their electronic transitions

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Our recent studies and developments undertaken aimed at spectral characterization of open-shell cations are outlined. The analyses of the rotational structure in the laser excitation spectra of the halocyanide and diacetylene cations have enabled their complete r_s geometries to be inferred. These should serve as a benchmark for calculations in open-shell cations containing either a heavy atom or many atoms. A new direction pursued aims at spectral characterization of fragment ions. The first success is the identification of the $\tilde{B}\,{}^4\Sigma_u^-$–$\tilde{X}\,{}^4\Sigma_g^-$ transition of C_2^+, which was observed initially in absorption in a 5 K neon matrix and then in the gas phase by laser excitation. The stimulated emission pumping approach was also used to probe higher vibrational levels of the $\tilde{X}\,{}^4\Sigma_g^-$ state. In the studies of new ions by laser methods, two obstacles are encountered. One concerns the uncertainty in the energy region of the transitions sought and the other is the identification of the carrier. We have therefore been developing methods to provide such information. In one, mass-selected ions are co-deposited with neon to form a matrix at 5 K. The electronic absorption spectrum of the trapped ions can then be measured. The first results illustrate the potential of this new technique. In a gas-phase approach, mass-selected ions are investigated by two-photon absorption within a triple-quadrupole instrument. One laser photon induces a transition between bound states of the ion and the second photon leads to fragment ion production. By monitoring the fragment ions as a function of either photon wavelength, both bound–bound and bound–pre-dissociative transitions can be studied. Such results have been obtained on CS_2^+ and CO_2^+.

1. Introduction

Interest and research activity dealing with the chemistry and spectroscopy of ions have grown this decade. There are several contributing factors: the appreciation of the importance of ions in terrestrial and interstellar environments, the technological developments enabling sophisticated methods to be devised for the study of these transient species occurring in but small concentrations and the general scientific urge to comprehend the properties of a further class of somewhat exotic molecules. One must not forget that ions have long been known to a variety of scientific disciplines through mass spectrometry, a widespread analytical tool for their molecular precursors. The ability to mass-select, and to store, ions in electromagnetic fields has also allowed rich gas-phase ion–molecule chemistry to be established.

The extraterrestrial media where ions have been identified spectroscopically are dark interstellar clouds (Smith and Adams 1989) (radioastronomy has detected eight molecular ions and CH^+ had already been observed in diffuse clouds by absorption in the 1930s) and comets (Lüst 1981) (detection of resonance fluorescence of the electronic transitions of several diatomic and triatomic ions as well as the *in situ* mass spectrometry sampling of Halley's comet (Krankowsky *et al.* 1986) and the Giacobini–Zinner comet (Coplan *et al.* 1987) yielded a long list of ions). In the case of dark interstellar clouds, the identification of a variety of complex molecules has led to the generally accepted scenario that gas-phase ion–molecule reactions contribute significantly to their formation (Duley and Williams 1984). It has also been suggested that the omni-present diffuse interstellar bands are the absorption features of polycyclic hydrocarbon cations (Léger *et al.* 1986). The ions referred to in the above are primarily singly charged positive ions, The chemical composition of the Earth's outer atmosphere, as well as those of other planets, is known to be well endowed in ions and their clusters (Ferguson and Arnold 1981, Torr 1985).

In terrestrial environments both cations and anions are recognized as important constituents in flames (Calcote 1972) and plasmas (Smith and Adams 1984). The smaller ions are detectable by optical or i.r. techniques though the main wealth of data has come from direct sampling of such media by mass spectroscopy . With the rise in prominence of surface manipulation by ion beams, the characterization of the plasma ion sources is receiving increasing attention.

Many diatomic cations have been studied by electronic spectroscopy in the past (Herzberg 1985) and more recently a few have been characterized by microwave (Woods 1989), laser and i.r. techniques (Saykally and Woods 1981). Homonuclear and heteronuclear diatomic cations are produced relatively easily in electrical discharges and the analysis of their spectral features has prompted important developments in quantum-mechanical concepts and theoretical treatments (Herzberg 1970). The known spectroscopic constants up to 1978 are summarized in the compilation of Huber and Herzberg (1979) and the more recent reviews (quoted above) contain references to studies since then.

As far as polyatomic cations are concerned, prior to the mid-1970s the electronic spectra of CO_2^+, CS_2^+, OCS^+, N_2O^+, H_2O^+, H_2S^+ and $H(CC)_2H^+$ were known (Leach 1976). With the advent of photoelectron spectroscopy, a general method became available that located the dipole-accessible doublet states of ions produced from molecules with a closed-shell configuration (Turner *et al.* 1970). This information led to the identification of electronic transitions (mainly in the optical region) of around 150 open-shell cations comprising more than four atoms in the period 1975–1983 (Maier *et al.* 1983). This was accomplished by observation of the emission spectra excited by electron bombardment of an effusive jet of the molecule (Maier 1980). In subsequent years, the ions known to relax radiatively were now studied, also by other groups (Miller and Bondybey 1980), by more refined methods ranging from laser excitation spectroscopy after ion production by Penning ionization (Maier 1982, Miller and Bondybey 1982a) to the study of the ions generated in supersonic free jets by emission and laser excitation approaches (Miller and Bondybey 1982b, Klapstein *et al.* 1983a). The non-radiative relaxation of these ions was also investigated by means of photoelectron–photon (Maier and Thommen 1984) and photo-ion–photon (Leach 1986) coincidence techniques. All these aspects have been summarized in the various reviews referenced (Maier 1986).

In this article the more recent developments and approaches adopted by our group in Basel for the characterization of cations, including fragment ions, via their electronic transitions will be overviewed and the discussion is restricted to this area. It should be emphasized, however, that, since the observation of the i.r. spectrum of H_3^+ by Oka (1980), i.r. laser absorption spectroscopy of ions in conjunction with velocity modulation techniques has been applied to a variety of ions (Gudeman and Saykally 1984). Initially those were closed-shell cations such as HCO^+ and NH_4^+ (Saykally 1988), then anions (e.g. N_3^-) (Owrutsky *et al.* 1987) and most lately open-shell cations (e.g. $C_2H_2^+$) (Oka 1987). There have also been studies of high-velocity ion beams using visible (Carrington 1979) or i.r. lasers (Carrington and Softley 1983) for the excitation and pre-dissociation or charge exchange for the detection. In addition, the geometric structure of a few ions has been inferred by the Coulomb-explosion technique (Vager *et al.* 1989). In the area of negatively charged ions, a few photodetachment measurements in the visible and i.r. (Neumark 1989) have revealed long-lived autodetaching states which yield spectroscopic data. Photoelectron spectroscopy of anion beams (Arnold *et al.* 1989, Cheshnovsky *et al.* 1989), a burgeoning area, yields some information on the anions themselves. The given references are to recent reviews in these rapidly growing fields.

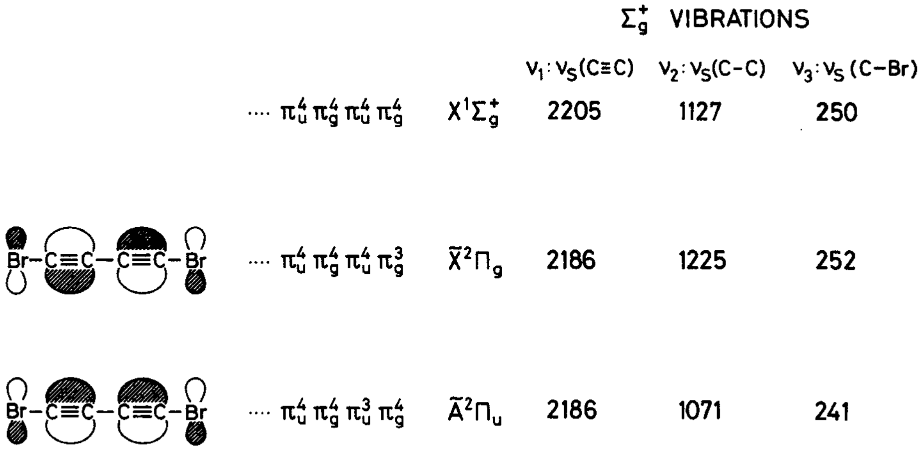
2. Electronic spectroscopy of polyatomic cations

The detection of electronic transitions of transient species has been the traditional method for obtaining structural information. This choice arose because the higher-resolution techniques of microwave and i.r. spectroscopies were not generally applicable owing to the lack of sensitivity as the species are usually produced only at low concentrations. This pattern has also evolved with open-shell polyatomic cations, whereby first spectroscopic details became apparent from the study of emission spectra, followed by the laser excitation spectra (Maier 1982). As mentioned in section 1, the more recent years have witnessed the successful introduction of i.r. laser techniques to probe the structure of ions (Saykally 1988).

The advantage in the study of the electronic transition by detection of fluorescence has been the sensitivity. The disadvantages are that only a limited set (about 150–200) of ions relax by a radiative pathway of sufficient quantum yield (higher than 10^{-4}) from their excited electronic states and that the resolution, and Doppler broadening when working in the visible part of the electromagnetic spectrum are a handicap compared with the i.r. and microwave techniques.

Our initial investigations of the emission spectra of the polyatomic cations were aimed at observation of their electronic transitions, identification of the symmetry of the states involved, and a partial vibrational analysis (Maier 1979, 1980). The laser excitation and emission spectra of ions produced at reduced temperatures in cooled discharges or supersonic free jets has led to a more detailed and precise (± 1–$2\,\mathrm{cm}^{-1}$) vibrational characterization (Klapstein *et al.* 1983a). In the case of the linear cations, often the frequencies of the majority of the modes can be inferred, especially when using in conjunction the data from the excitation and emission spectra. As an example of this, in figure 1 are summarized the vibrational frequencies of the totally symmetric stretching modes of dibromodiacetylene cation in its ground state $\tilde{X}\,^2\Pi_g$ and first excited electronic state $\tilde{A}\,^2\Pi_u$. The ground-state values come from the $\tilde{A}\,^2\Pi_u \rightarrow \tilde{X}\,^2\Pi_g$ emission spectrum of ions at a rotational temperature of about 5 K, whereas the excited-state values come from the $\tilde{A}\,^2\Pi_u \leftarrow \tilde{X}\,^2\Pi_g\ v=0$ laser excitation spectrum of ions collisionally equilibrated to about 100 K (Klapstein *et al.* 1983b). Particularly striking are the frequency changes with electronic configuration for the three, essentially localized bond vibrations. These reflect nicely the topological characteristics of the molecular-orbital description of the electronic structure (left-hand side of figure 1) (Heilbronner *et al.* 1974).

The application of the laser excitation approach with increased resolution (about $0{\cdot}04\,\mathrm{cm}^{-1}$ laser bandwidth) has enabled the rotational structure in the electronic transitions of OCS^+, XCN^+ ($\mathrm{X} \equiv \mathrm{Cl, Br}$), XCCH^+ ($\mathrm{X} \equiv \mathrm{Cl, Br, I}$) and $\mathrm{H(CC)_2H}^+$ to be resolved. The inferred rotational constants have been tabulated elsewhere (Maier



Σ_g^+ VIBRATIONS

		$\nu_1 : \nu_s(C \equiv C)$	$\nu_2 : \nu_s(C-C)$	$\nu_3 : \nu_s(C-Br)$
$\cdots \pi_u^4 \pi_g^4 \pi_u^4 \pi_g^4$	$X^1\Sigma_g^+$	2205	1127	250
$\cdots \pi_u^4 \pi_g^4 \pi_u^4 \pi_g^3$	$\tilde{X}^2\Pi_g$	2186	1225	252
$\cdots \pi_u^4 \pi_g^4 \pi_u^3 \pi_g^4$	$\tilde{A}^2\Pi_u$	2186	1071	241

Figure 1. Spectroscopically determined vibrational frequencies ($\pm 1 \text{ cm}^{-1}$) of the three totally symmetric modes of dibromodiacetylene molecule (X $^1\Sigma_g^+$ Raman spectrum) (Klaboe *et al.* 1975) and cation ($\tilde{X}$ $^2\Pi_g$ emission and $\tilde{A}$ $^2\Pi_u$ laser excitation spectra) (Klapstein *et al.* 1983b), and their relation to the molecular-orbital description of the electronic structure.

1988). Such data are also available from the analyses of the rotationally resolved emission spectra of N_2O^+, CS_2^+, CO_2^+, H_2O^+ and H_2S^+ (Saykally and Woods 1981) and of the more recently studied HCP^+ and HBS^+ ions (Maier 1988) (as well as their various isotopic derivatives). Our most recent studies have aimed at obtaining the r_s structure of some of the ions either containing a heavy atom (Cl or Br) or comprising more than four atoms.

2.1. *The r_s structure of some open-shell cations*

In order to determine the complete r_s structure of a molecule, the rotational constants of all its derivatives obtained by isotopic substitution of each atom in turn have to be known. The procedure for the evaluation of the distance z of the substituted atom i from the centre of gravity using the rotational constant B of the primary molecule and the rotational constant B^* of its isotope was developed by Kraitchman (1953).

The application of his equations leads to the formula

$$z^2 = \frac{m^*}{m(m^* - m)} \left(\frac{1}{B^*} - \frac{1}{B} \right)$$

for linear asymmetrically substituted molecules and

$$z^2 = \frac{1}{m^* - m} \left(\frac{1}{B^*} - \frac{1}{B} \right)$$

for linear symmetric species, where m and $m*$ are the masses of the isotopic derivatives. The advantage of this approach, compared with the straightforward way of determining the distances by a least-squares fit of the moments of inertia (or to their difference), is that the r_s distances are evaluated directly.

In recent years we have been able to record and analyse the rotational structure in the laser excitation spectra of the isotopic derivatives of the cations of the halocyanides XCN^+ $\tilde{B}^2\,\Pi$–$\tilde{X}$ $^2\Pi$ ($X \equiv Cl$) (Rösslein and Maier 1989), ($X \equiv Br$) (Rösslein *et al.* 1990)), haloacetylenes $XCCH^+$ $\tilde{A}^2\ \Pi$–$\tilde{X}\ ^2\Pi$ ($X\equiv Cl$) (King *et al.* 1985), ($X\equiv Br$) (King *et al.* 1984), ($X\equiv I$) (Maier and Ochsner 1985) and diacetylene $H(CC)_2H^+$ $\tilde{A}\ ^2\Pi_u$–$\tilde{X}\ ^2\Pi_g$ (Lecoultre *et al.* 1988). For the first and last category of ions a complete r_s structure has been inferred, whereas only a partial structure could be obtained for the haloacetylene cations.

2.2. *Complete r_s structures*

Prior to 1986, CO_2^+ (Gauyacq *et al.* 1979) and CS_2^+ (Callomon 1958, Balfour 1976) were the only open-shell polyatomic cations with a fully determined r_s structure, based on the rotational constants obtained from the electronic emission spectra. Since then, H_2O^+ has been characterized by i.r. laser absorption (Strahan *et al.* 1986, Dinelli *et al.* 1988); the latter methods have also led to the r_s structure of a dozen or so closed-shell cations and anions (Coe and Saykally 1989). Thus the aim of our studies in the past few years has been the determination of the r_s geometry of open-shell ions containing on the one hand a heavy atom, for example $ClCN^+$ or $BrCN^+$, and on the other hand open-shell ions comprising more than three atoms, for example $HCCCCH^+$. The r_s geometries of these ions in their ground $^2\Pi_{(g)}$ state have been established and in the case of diacetylene cation also in its lowest excited electronic state namely $\tilde{A}\ ^2\Pi_u$. For this purpose the appropriate isotopic derivatives, namely $X^{13}CN$, $XC^{15}N$ ($X\equiv Cl$, Br) and $H^{13}CCCCH$, $HC^{13}C^{13}CCH$ and DCCCCD, were synthesized and the electronic transitions of their ions have been recorded by laser excitation spectroscopy, in addition to those of the naturally occurring species $^{35,37}Cl^{12}C^{14}N^+$ (Celii *et al.* 1987), $^{79,81}Br^{12}C^{14}N^+$ (Hanratty *et al.* 1988) and $H^{12}C^{12}C^{12}C^{12}CH^+$ (Callomon 1958).

In such measurements the cations were produced by Penning ionization using argon or helium metastable ions generated in a d.c. discharge. The ions are relaxed by collisions with the rare-gas bath to a temperature in the 100–150 K range. The consequence of this is that only the lowest vibrational level in the ground state $^2\Pi$ of the ions is populated to any extent and the laser excitation takes place from there to various levels within the excited electronic state (which lies 2–3 eV towards higher energies). In addition, the presence of the heavy halogen atom results in spin–orbit separation into $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ components (inverted sequence) although only the $^2\Pi_{3/2}$ components are populated because of the cooling. The excitation is accomplished by a tunable pulsed dye laser operating with an intracavity etalon to reduce the bandwidth to about $0{\cdot}04\,cm^{-1}$. The recording, calibration and signal acquisition of the data follow standard procedures.

As an example, the $\tilde{A}\ ^2\Pi_u$–$\tilde{X}\ ^2\Pi_g$ transition of diacetylene cation is considered. The rotationally resolved origin band of this band system in the laser excitation spectrum is reproduced in figure 2. The line assignments are indicated; the band is split into the $^2\Pi_{u,1/2}$–$^2\Pi_{g,1/2}$ and $^2\Pi_{u,3/2}$–$^2\Pi_{g,3/2}$ subsystems as a result of spin–orbit splitting ($A''=-33{\cdot}5\,cm^{-1}$, $A'=-31{\cdot}1\,cm^{-1}$) and, because of their overlap, two R and two P branches are seen. The Q branches are not intense enough to be clearly discernible at the temperature of about 150 K used for the experiment.

The first step in the analysis is the establishment of the absolute numbering of the rotational lines. This was detemined only recently, even though this transition had been already observed and analysed in 1956. In this early work (Callomon 1956), two physically reasonable numbering choices (which differ by one) arose which yielded good fits to the observed line positions. It proved feasible to find the correct one by combining the information obtained from two complementary techniques, namely

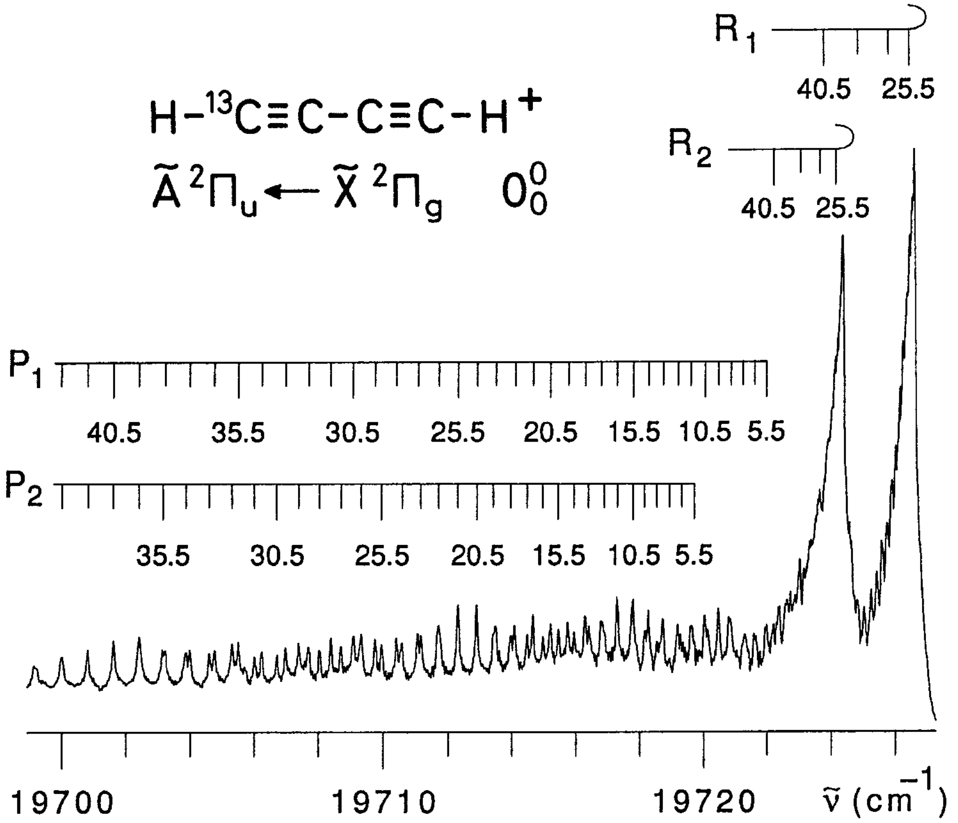


Figure 2. The rotational structure of the origin band in the laser excitation spectrum of the $\tilde{A}\,^2\Pi_u$–$\tilde{X}\,^2\Pi_g$ transition of an isotopically enriched diacetylene cation, recorded with 0·04 cm^{-1} bandwidth (Lecoultre *et al.* 1988).

from the emission spectrum of the ions cooled to low rotational temperatures and that of laser excitation (Kuhn *et al.* 1986). The basis of the experiment was the appearance of the Q_1 branch at a rotational temperatures of 10–20 K. In figure 3 are shown two recorded emission spectra: one at about 10 K (top) and one at about 100 K (bottom). The temperature was 'tuned' by changing the backing pressure of a supersonic expansion of diacetylene seeded in helium. The change in the band profile is striking; at 10–20 K the preferential population of the lowest J levels enables the Q branches to be observed because Q-line strength S_{JJ} in electronic transitions with $\Delta\Lambda = 0$ is given by $S_{JJ} = \Omega^2(2J+1)/J(J+1)$. Using the two possible numbering schemes (and hence two sets of rotational constants B_0), the position of the Q_1 lines can be calculated and compared with the experiment. The result of this is unambiguous and corresponds to the rotational line numbers shown in figure 2.

The rotational analysis is carried out using standard procedures; the positions of the rotational lines are fitted to the eigenvalues of a Hamiltonian matrix (Zare *et al.* 1973) and both spin–orbit systems are treated simultaneously. In contrast, in the case of the rotationally resolved laser excitation spectra of the halocyanide cations XCN$^+$ (X$\equiv$Cl, Br), only the $^2\Pi_{3/2}$–$^2\Pi_{3/2}$ component is observed (owing to the depopulation of the $\tilde{X}\,^2\Pi_{1/2}$ levels by the collisional relaxation and the large spin–orbit splitting

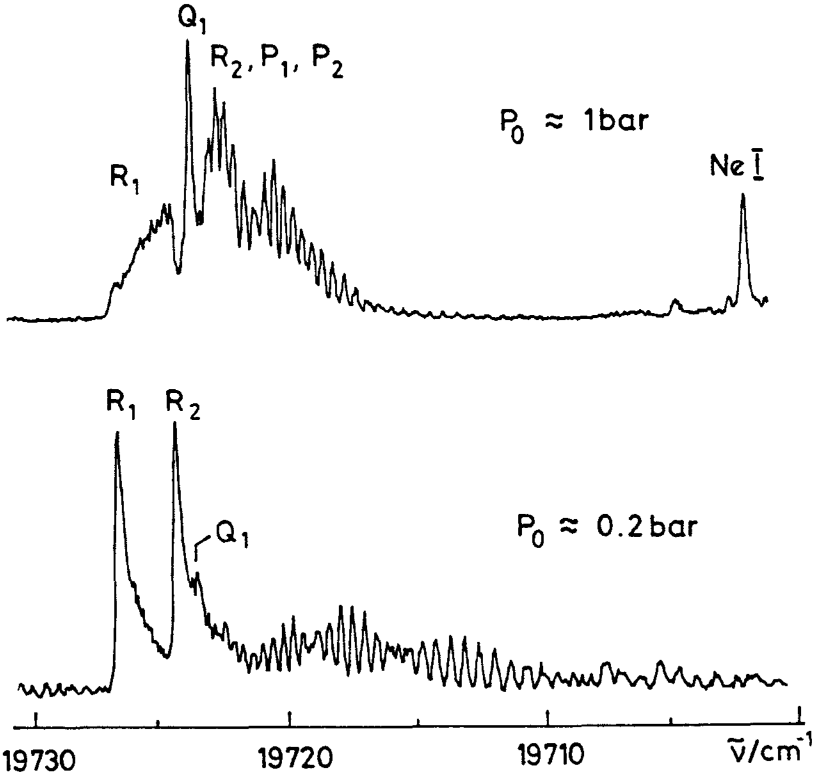


Figure 3. The discernible rotational structure in the emission spectrum of the $\tilde{A}\,^2\Pi_u \rightarrow \tilde{X}\,^2\Pi_g\,0_0^0$ transition of diacetylene cation at about 10 K (top trace) and about 100 K (bottom trace). The spectra were recorded with 0·25 cm^{-1} optical bandpass by means of 200 eV electron impact excitation of a seeded helium supersonic expansion at the shown backing pressure (Kuhn *et al.* 1986).

$A_0''(\mathrm{X} \equiv \mathrm{Cl}) = -276(2)\,\mathrm{cm}^{-1}$; $A_0''(\mathrm{X} \equiv \mathrm{Br}) = -1477(2)\,\mathrm{cm}^{-1}$) and the fit is to the expression

$$F_v(J) = \nu_0 + B_{\mathrm{eff},v}[(J+\tfrac{1}{2})^2 - 1] - D_{\mathrm{eff},v}[(J+\tfrac{1}{2})^2 - 2]^2.$$

In this, $B_{\mathrm{eff},v}$, $D_{\mathrm{eff},v}$ and ν_0 are treated as parameters. Although for the diacetylene cation the rotational constants B_0'' and B_0' are derived directly from the fits, for the halocyanide cations the mechanical values B_v are deduced from the fitted $B_{\mathrm{eff},v}$ values via the known spin–orbit constants A:

$$B_{\mathrm{eff},v} = B_v\left(1 + \frac{B_v}{A\Lambda}\right).$$

This pre-supposes Hund's case (a) coupling and Λ is the orbital angular momentum quantum number.

The geometry of the ions is subsequently determined from the B_0 values by the isotopic substitution method outlined at the beginning of section 2.1. The resulting r_s bond lengths of diacetylene, chlorocyanide and bromocyanide cations are summarized in table 1. The r_s distances of the halocyanide cations in the excited $^2\Pi$ electronic states could not be determined because of perturbations of the rotational levels in that state.

Table 1. The r_s bond lengths of chlorocyanide, bromocyanide and diacetylene molecules and cations.

		r_s(Cl–C) (Å)	r_s(C–N) (Å)	r_s(Cl–N) (Å)
ClCN†	X $^1\Sigma^+$	1·631	1·159	2·790
$ClCN^+$	$\tilde{X}$ $^2\Pi_{3/2}$	1·559(12)	1·215(12)	2·774(12)
		r_s(Br–C) (Å)	r_s(C–N) (Å)	r_s(Br–N) (Å)
BrCN†	X $^1\Sigma^+$	1·789	1·158	2·947
$BrCN^+$	$\tilde{X}$ $^2\Pi_{3/2}$	1·745(14)	1·195(16)	2·940(16)
		r_s(H–C) (Å)	r_s(C≡C) (Å)	r_s(C–C) (Å)
H–C≡C–C≡C–H§	X $^1\Sigma_g^+$	1·046	1·205	1·376
H–C≡C–C≡C–H^+	$\tilde{X}$ $^2\Pi_g$	1·046(10)	1·234(10)	1·346(10)
H–C≡C–C≡C–H^+	$\tilde{A}$ $^2\Pi_u$	1·045(10)	1·243(10)	1·410(10)

† Harmony *et al.* (1979); uncertainty, ±0·002–0·005 Å.

‡ The values in parentheses represent 2σ uncertainty.

§ Callomon and Stoicheff (1957); the r_s(C≡C) distance is assumed.

In table 1 the molecular geometries are also given. The changes in the bond lengths on ionization reflect the description of the electronic structure of these species. For example, the molecular ground-state configuration of diacetylene is

$$\ldots\pi_u^4\pi_g^4\,\mathrm{X}\ {}^1\Sigma_g^+$$

and the ground and first excited ionic states are well described by the single configurations

$$\ldots\pi_u^4\pi_g^3\tilde{\mathrm{X}}\ {}^2\Pi_g, \qquad \ldots\pi_u^3\pi_g^4\tilde{\mathrm{A}}\ {}^2\Pi_u.$$

According to this the C≡C bond lengths should increase on formation of either of these two ionic states (cf. table 1) because both π_g and π_u molecular orbitals are bonding in this region. In contrast, the C–C interatomic distance will increase in the $\tilde{A}$ $^2\Pi_u$ but decrease in the $\tilde{X}$ $^2\Pi_g$ state relative to the molecular values (Callomon and Stoicheff 1957) because the π_u and π_g molecular orbitals are antibonding and bonding respectively between the central carbon atoms. The C–H distances remain unchanged within the error limits at 1·046 Å.

A similar correlation between the bond-length changes in the molecule and ion exists for the halocyanide cations as can be quantitatively seen in table 1. Qualitatively this has already been discussed earlier in connection with the photoelectron spectra of these species (Heilbronner *et al.* 1970) and with the emission spectra of their ions (Fulara *et al.* 1985a).

2.3. *Partial* r_s *structures*

In the case of the haloacetylene cations, the rotational constants for the cations containing different combinations of naturally occurring isotopes of the halogens and substituted deuterium substitution, for example $^{35,37}ClCCH(D)^+$ (King *et al.* 1985) or

^{78,81}BrCCH(D)$^+$ (King *et al.* 1984), could be inferred from the analysis of their $\tilde{A}\ ^2\Pi_{3/2} \leftarrow \tilde{X}\ ^2\Pi_{3/2}$ laser excitation spectra. However, the ^{13}C substituted derivatives could not as yet be synthesized; although the resolution of i.r. and microwave techniques is sufficient to detect the natural abundance of ^{13}C components, constraints in resolution and Doppler broadening preclude this in the visible region. Thus only the distance of the chlorine or bromine atoms and of the hydrogen atom from the centre of mass of the haloacetylene cation could be calculated, as well as the overall distance between the terminal atoms.

3. Spectral characterization of C_2^+

A research direction still in its infancy concerns the development and application of methods for the spectral characterization of fragment ions. Our first such studies, in which we have dealt with electronic transitions of C_2^+, illustrate the obstacles encountered.

Problems in the investigations of the electronic transitions of fragment ions are their production, the ability to search a wide spectral region and the identification of any observed band system. Although high-resolution laser studies in the gas phase are the ultimate aim, our philosophy has been to locate the transition of interest by means of a low-resolution, but sensitive, technique and then armed with such information to look for the transition with laser methods. The low-resolution approach that we employed in the past was emission spectroscopy with effusive and supersonic beams and this paved the path for the higher-resolution laser excitation measurements. In the case of fragment ions this approach is generally not applicable because the species would need to be generated directly, in the excited electronic state, from their precursor. Instead the method that we have adopted is the detection of the electronic absorption spectrum of the ions embedded in the inert environment of a 5 K neon matrix (Bondybey *et al.* 1980, Leutwyler *et al.* 1983). Once the ions are produced, they can be kept trapped, and a broad spectral region (220–1200 nm in our case) can easily be scanned.

C_2^+ is deemed to be an important constituent in various terrestrial and interstellar environments. The former include flames and plasmas where C_2^+ is a building unit in clustering reactions when carbon is present (O'Keefe *et al.* 1986); in the latter belong comets and dark interstellar clouds where C_2^+ is supposed to participate in ion–molecule reactions, leading to the formation of more complex hydrocarbons (Winnewisser 1981). Spectroscopic information on C_2^+ is, however, almost non-existent; in one study (Meinel 1972) the reported tentative assignment of an electronic transition to C_2^+ is unlikely to be correct (but rather a transition between Rydberg states of C_2) and the only other study is a low-resolution translational energy loss spectrum on an ion beam of C_2^+ (O'Keefe *et al.* 1984). The latter investigation revealed several broad bands which were attributed to electronic transitions of C_2^+, between either the doublet or the quartet states. Therefore a spectroscopic search for the electronic transition of C_2^+ in its ground state $\tilde{X}\ ^4\Sigma_g$ was launched. There were in addition, two detailed configuration interaction calculations available (Petrongolo *et al.* 1981, Rosmus *et al.* 1986), which suggested the planning of the experiments.

3.1. *Absorption spectrum in a neon matrix*

Photolysis of many carbon-containing molecules constrained in a 5 K neon matrix leads to the appearance of the well known (from the gas phase) D $^1\Sigma_u^+ \leftarrow$ X $^1\Sigma_g^+$ and

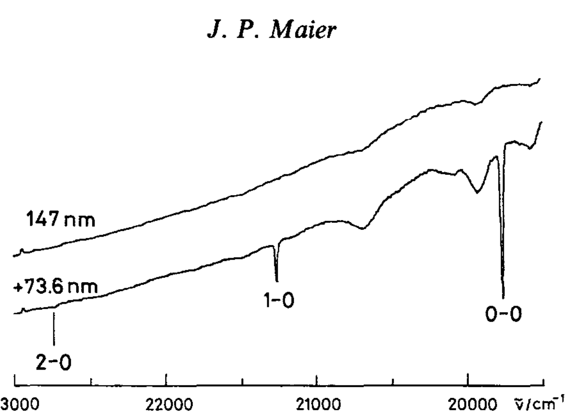


Figure 4. Absorption spectrum (0·1 nm resolution) observed when a 5 K neon matrix containing chloroacetylene in dilute concentration (about 1 : 4000) is irradiated with Xe I 147 nm (top trace) and subsequently with Ne I 73·6 nm photons (bottom) (Forney *et al.* 1987). The sharper peaks marked belong to the $\tilde{B}\,^4\Sigma_u^- \leftarrow \tilde{X}\,^4\Sigma_g^-$ absorption bands of C_2^+.

A $^1\Pi_u \leftarrow X\,^1\Sigma_g^+$ absorption band systems of C_2. Consequently, appropriate precursors were chosen to produce C_2 in good yield, followed by further irradiation, this time with ionizing photons to produce C_2^+.

The acetylenes XCCH and XCCX (X ≡ H, D, Cl, Br) proved suitable precursors for C_2 when embedded in a 5 K neon matrix in dilute concentrations (typically 1 : 4000) after Xe I 147 nm photolysis. The absorption spectra were measured by a waveguide technique (Rosetti and Brus 1980), whereby the light is passed along 2 cm of the matrix through its thin side (about 100 μm). This method has established itself as an attractive approach for matrix spectroscopy (Bondybey and Miller 1983); in the optical region a rhodium-coated (or aluminium-coated) copper substrate is used and an absorption enhancement of 200 compared with conventional methods is attained. We have been using this technique for a number of years to measure the absorption spectra of parent open-shell cations: first for cations known to fluoresce (Leutwyler *et al.* 1984) and subsequently those which do not (Fulara *et al.* 1985b).

In figure 4 are reproduced portions of the absorption spectrum after photolysis (top trace) and subsequent photo-ionization (bottom trace) with chloroacetylene as precursor (Forney *et al.* 1987). The relatively sharp prominent peaks apparent in the final spectrum (labelled 0–0, 1–0, 2–0) can be identified as part of the $\tilde{B}\,^4\Sigma_u^- – \tilde{X}\,^4\Sigma_g^-$ absorption system of C_2^+. This is based on

(1) chemical evidence (different precursors);
(2) spectroscopic evidence (isotopic shifts using $H^{13}C^{13}CH$ as the precursor);
(3) bleaching experiments (absorption signals of ionic species decrease on irradiation of matrix with visible light as result of recombination with liberated electrons) and
(4) comparison with theoretical calculations (T_{00} and vibrational frequency values, the latter of which (Rosmus *et al.* 1986) were in excellent agreement with the experimental data).

3.2. *Laser excitation spectrum in the gas phase*

Having located the origin band of the $\tilde{B}\,^4\Sigma_u^- – \tilde{X}\,^4\Sigma_g^-$ transition of C_2^+ in the neon matrix, it proved relatively straightforward to detect the system in the gas phase and to resolve the rotational structure by means of its laser excitation spectrum (Rösslein *et al.*

1987). To produce C_2^+, acetylene was reacted with helium metastable ions (and some He^+) generated in a d.c. discharge. The concomitantly formed C_2 results in the observation of the d ${}^2\Pi_g$–a ${}^2\Pi_u$ Swan system bands in the spectral region of interest; these, however, can be discriminated by using wavelength filtering for the detected fluorescence.

The observed rotational structure is characteristic of a ${}^4\Sigma_u^- - {}^4\Sigma_g^-$ transition of a homonuclear species with zero nuclear spin; the odd lines are missing (cf. bottom trace in figure 5). The corresponding spectrum obtained using $H^{13}C^{13}CH$ as the precursor yields the pattern shown as the upper trace in figure 5; there are no longer missing lines and the intensity ratio of the even- to odd-N lines is 3 : 1. This is consistent with the homonuclear species ${}^{13}C_2^+$ $(I=\frac{1}{2})$. Furthermore, recordings of the bands with resolution increased to about 0·04 cm^{-1} shows that the lines consist of several components. Many of the rotational lines appear perturbed but this has not yet been analysed. These observations, together with the knowledge from the theoretical calculations that the ground state of C_2^+ has ${}^4\Sigma_g^-$ symmetry, confirm the assignment as the $\tilde{B}\ {}^4\Sigma_u^-$–$\tilde{X}\ {}^4\Sigma_g^-$ band system.

All in all, vibronic transitions with v', $v'' \leqslant 2$ for ${}^{13}C_2^+$, were studied (Rösslein and Maier 1988) and the rotational, vibrational and related constants determined by standard procedures.

It is also interesting to follow the trends in equilibrium distance and vibrational frequency in the C_2 species shown in table 2. The electronic states are well described by the given single configuration and they differ by the successive addition of an electron to the π_u molecular orbital. Because the latter is bonding in the C–C region, the internuclear distance r_e decreases and the vibrational frequency ω_e increases with each further π_u electron.

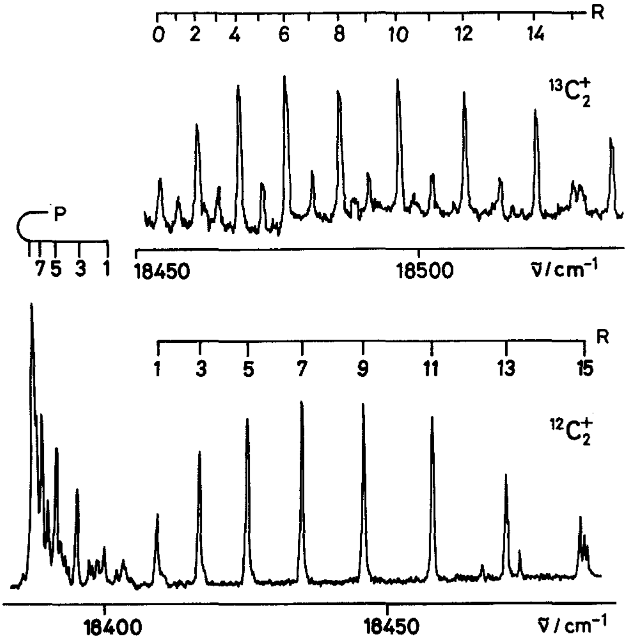


Figure 5. The rotational structure of the 0–1 band in the $\tilde{B}\ {}^4\Sigma_u^- \leftarrow \tilde{X}\ {}^4\Sigma_g^-$ laser excitation spectrum (0·3 cm^{-1} f.w.h.m.) of ${}^{12}C_2^+$ and ${}^{13}C_2^+$ in the gas phase (Rösslein *et al.* 1987).

Table 2. Trends in equilibrium distance and vibrational frequency.

Species	Configuration	State	r_e (Å)	ω_e (cm^{-1})
C_2^+	$\ldots\sigma_u^2\pi_u^2\sigma_g^1$	$\tilde{X}\ {}^4\Sigma_g^-$	1·4034	1351
C_2	$\ldots\sigma_u^2\pi_u^3\sigma_g^1$	a $^3\Pi_u$	1·3119	1641
C_2^-	$\ldots\sigma_u^2\pi_u^4\sigma_g^1$	$\tilde{X}\ {}^2\Sigma_g^-$	1·2682	1781

With the determined spectroscopic constants of C_2^+, one may be able to detect C_2^+ in comet tails by resonance fluorescence, in plasmas and flames by laser excitation of the fluorescence, and in diffuse interstellar clouds (if present) by absorption against starlight background. In order to be able to determine the abundance of C_2^+, the oscillator strength $f_{0-0} = 0{\cdot}023(3)$ has been determined from lifetime measurements (Rösslein and Maier 1988) in selected rovibronic levels of the excited state (e.g. $\tau(v' = 0) = 113(12)$ ns) and using the calculated Franck–Condon factors (Rosmus *et al.* 1986) for the $\tilde{B}\ {}^4\Sigma_u^- – \tilde{X}\ {}^4\Sigma_g^-$ transition.

3.3. *Stimulated emission pumping spectra*

The stimulated emission pumping technique has grown in popularity since its initial introduction to the study of highly excited vibrational levels of molecules (Hamilton *et al.* 1986). In the meantime, it has been used to study radicals (Xie *et al.* 1988) and molecules in supersonic free jets (Kable and Knight 1987). We showed sometime ago that one could also use the technique to probe ions prepared in a flow system at low concentrations (Celii *et al.* 1986). This approach has been applied to probe higher vibrational levels of C_2^+ in its ground state and the scheme is outlined with reference to the calculated (Rosmus *et al.* 1986) potential energy curves of C_2^+ reproduced in figure 6.

The essence of the technique is to transfer the population by laser absorption (pump) to a Franck–Condon-accessible level of the excited state ($v' = 2$ of $\tilde{B}\ {}^4\Sigma_u^-$ (figure 6)) and then to drive the transitions to vibrationally excited levels of the ground state ($v'' = 5$ of $\tilde{X}\ {}^4\Sigma_g^-$ (figure 6)), for which the Franck–Condon factors are small, by a second laser (dump). The dump process is monitored by measuring the decrease in the fluorescence from the excited-state level populated ($v' = 2$). The apparative layout and recording procedure have been given by Celii and Maier (1990).

In the case of the measurements on C_2^+ (which was prepared from acetylene by Penning ionization), it proved necessary to discriminate between the C_2 Swan bands excited concomitantly by the dump laser. Thus an optical chopper blocked every second pulse from the pump laser while the normalized difference of the fluorescence signals detected after each pulse was recorded. A few such spectra are shown in figure 7. The pump laser was tuned to a single rotational level (e.g. via *R*(*N*)) within the $v' = 2$; $\tilde{B}\ {}^4\Sigma_u^-$ manifold and thus, on scanning the dump laser two rotational lines, R(*N*) and P(*N* + 2) were observed. By varying *N* with the pump laser wavelength, the rotational structure of the $\tilde{B}\ {}^4\Sigma_u^- – \tilde{X}\ {}^4\Sigma_g^-$ 2–5 transition can be accumulated as is seen in figure 7. By this means, the $v = 4–6$ levels of the ground state of C_2^+ could be characterized; these data together with those for the $v = 0–3$ levels obtained from the laser excitation spectra enable the $\tilde{X}\ {}^4\Sigma_g^-$ potential surface to be reasonably well parametrized. The resulting spectroscopic constants are given in table 3.

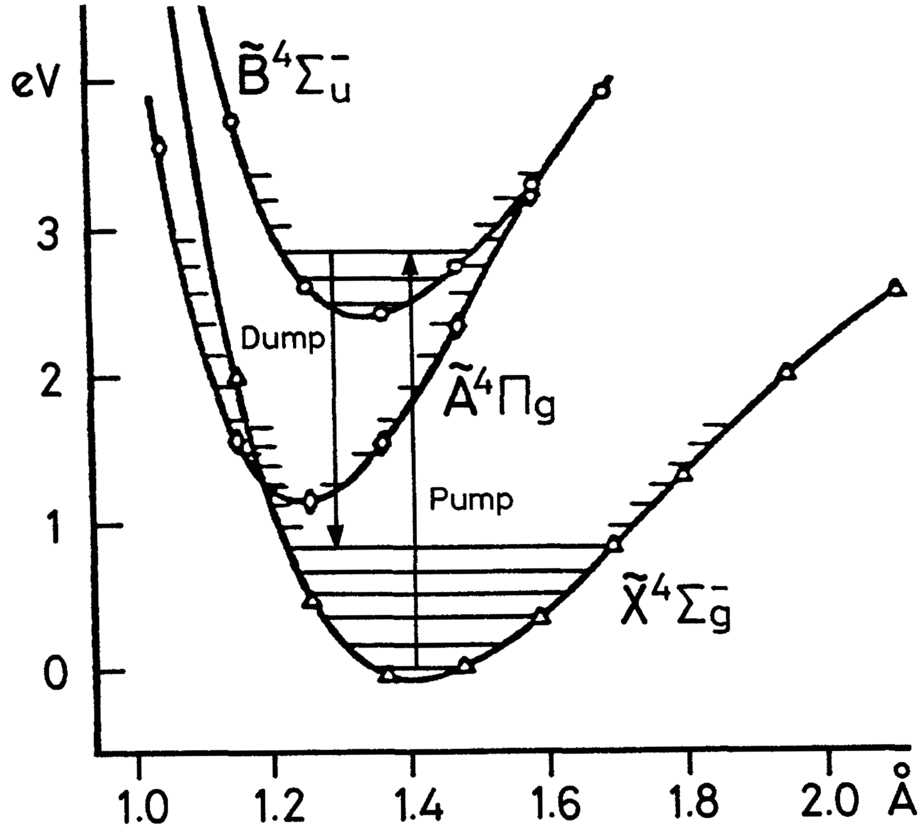


Figure 6. The principle of the stimulated emission pumping approach used to probe the higher vibrational levels of C_2^+ in the ground state. The means of studying the $v=5$ level of the $\tilde{X}\ ^4\Sigma_g^-$ manifold is depicted.

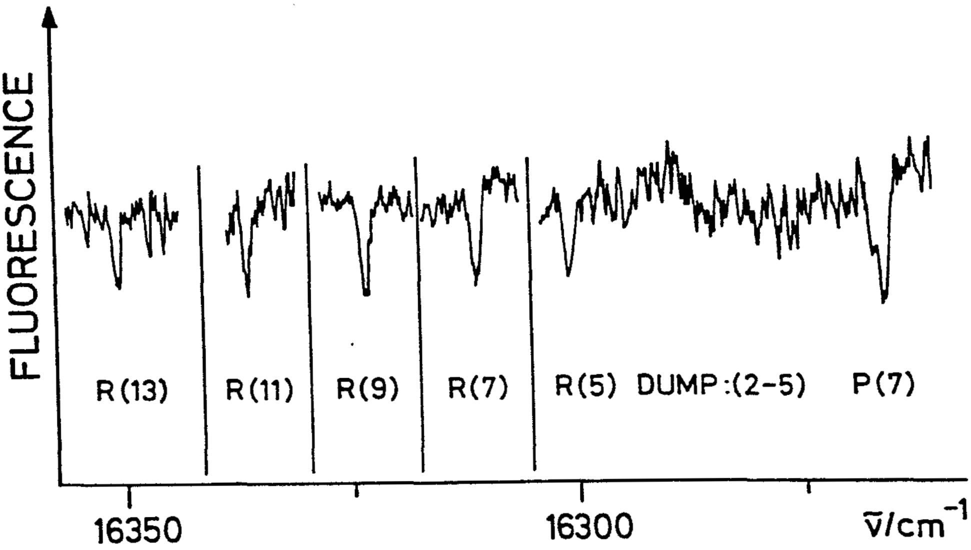


Figure 7. Part of the stimulated emission spectrum (0·3 cm^{-1} f.w.h.m.) of the $\tilde{B}\ ^4\Sigma_u^-$–$\tilde{X}\ ^4\Sigma_g^-$ 2–5 transition of C_2^+ (cf. figure 6) (Celii and Maier 1990). The spectrum is put together from individual recordings whereby two lines R(N) and P($N+2$) are observed for each selected line R(N) of the pump laser.

Table 3. Spectroscopic constants of $^{12}C_2^+$ in the ground state $\tilde{X}\,^4\Sigma_g^-$ and excited electronic state $\tilde{B}\,^4\Sigma_u^-$. D_e was assumed and held fixed during the spectral fits.

	$\tilde{X}\,^4\Sigma_g^-$	$\tilde{B}\,^4\Sigma_g^-$
T_e (cm^{-1})	0	19652·2 (4)
ω_e (cm^{-1})	1351·7 (2)	1508·1 (5)
$\omega_e x_e$ (cm^{-1})	12·18 (2)	12·69 (11)
B_e (cm^{-1})	1·4258 (3)	1·5465 (5)
α_e (cm^{-1})	0·01762 (8)	0·01704 (25)
D_e (cm^{-1})	$6{\cdot}3(5) \times 10^{-6}$	$6{\cdot}5(5) \times 10^{-6}$

4. Electronic absorption spectra mass-selected ions

Two major problems are encountered in the attempts to characterize ions spectroscopically. One is to know the wavelength region where the transitions are expected and the second is the identification of the species responsible for any newly observed band system. The first obstacle can be overcome by using low-resolution techniques which enable the band system to be located either by emission spectroscopy (cf. section 2), or by measurement of the absorption spectrum of the ion in a neon matrix (cf. section 3.1). In the latter case the matrix–gas shift has to be estimated by reference to several classes of ions for which both the matrix and the gas-phase data are available. Such spectral information is crucial for the successful subsequent application of higher-resolution techniques, using lasers. The second obstacle, the identification of the carrier, persists in the low-resolution approaches; in the case of open-shell cations of parent molecular species, the assignment was possible by comparison with the photoelectron spectra of these species, as well as using ancillary experimental data (Maier 1980). A general way to circumvent these difficulties is to carry out experiments on mass-selected ions in the gas phase. The price paid for this is that reduced ion densities preclude direct absorption measurements, and usually also the detection of the fluorescence. Thus indirect ways of monitoring the absorption have to be devised. In this section, the approach employed by us, two-photon dissociation spectroscopy on mass-selected ion beams, is illustrated by the first such examples.

The goal of these measurements is to record the electronic absorption spectrum between two bound states of an ion. This is achieved by encouraging a mass-selected ion to absorb two photons of different wavelengths λ_1 and λ_2 sequentially, whereby the second photon populates a pre-dissociative repulsive state. This is illustrated by the actually studied case of CS_2^+; figure 8 shows schematically the relevant potential energy curves. Thus the method resembles multiphoton ionization spectroscopy of molecules, with the difference that in the case of ion dissociation the final photon has to be resonant with an upper level whereas with the neutrals this is not a requisite as the final transition is to the ionization continuum.

The process involving the second photon λ_2 in figure 8 has been used in the past for the spectroscopic studies of mass-selected ions which have a bound ground state but a pre-dissociative excited state. The resulting one-photon pre-dissociation spectra rely on the situation that the pre-dissociation is slow enough that the spectroscopic structure is not smeared out. This has proved successful for N_2O^+ (Abed *et al.* 1983), SO_2^+ (McLoughlin and Morrison 1985), OCS^+ (Kakoschke *et al.* 1985) and alkyl halide cations (McLoughlin *et al.* 1985) among polyatomic ions. Another approach, which does not rely on the pre-dissociation of the excited state is to monitor the change in the rate of a particular reaction, or the observation of a new product ion (e.g. via charge

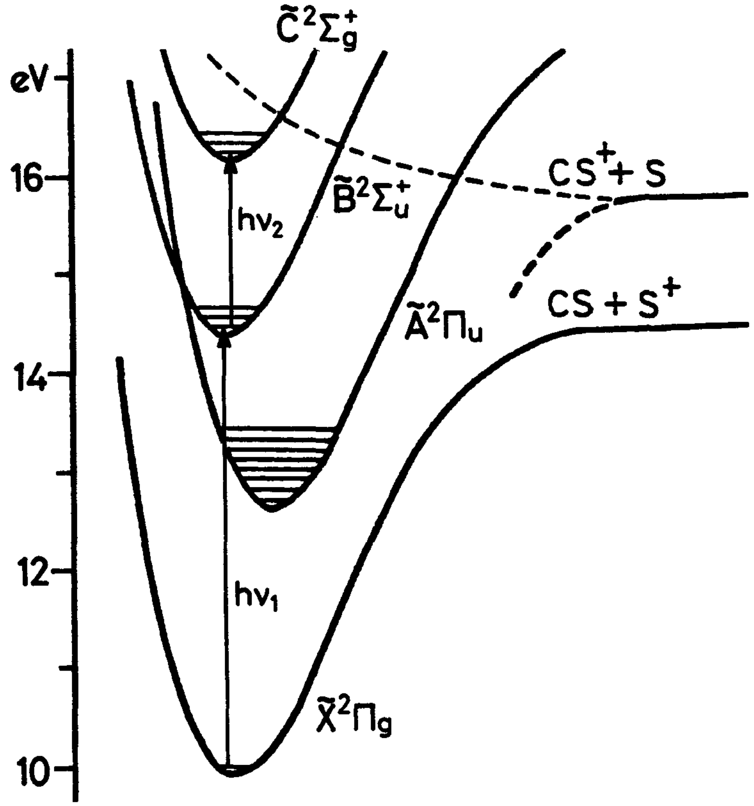


Figure 8. A qualitative plot of the potential energy curves of CS_2^+. In the measurements of the two-photon absorption spectra of the mass-selected CS_2^+ beam, either $h\nu_1$ (cf. figure 10) or $h\nu_2$ (cf. figure 11) is varied while the other wavelength is fixed.

exchange) when the ion is electronically excited (Carrington 1979). Also related are (1 + 1) photodissociation (Weinkauf *et al.* 1987), optical-i.r. absorption (Carrington *et al.* 1988) and i.r. multiphoton absorption (Okumura *et al.* 1986) experiments on ion beams in which the dissociation enhancement is monitored.

4.1. *Two-photon absorption spectroscopy*

Our approach involves the consecutive absorption of two photons of different wavelengths λ_1 and λ_2 of a mass-selected ion. Thus, with respect to the situation of CS_2^+ depicted in figure 8 the reaction sequence is

$$CS_2^+\ \tilde{X}\ {}^2\Pi_g \xrightarrow{\lambda_1} CS_2^+\ \tilde{B}\ {}^2\Sigma_u^+ \xrightarrow{\lambda_2} CS_2^+\ \tilde{C}\ {}^2\Sigma_g^+ \rightarrow S^+.$$

The bound–bound transition $\tilde{B}\ {}^2\Sigma_u^+ \leftarrow \tilde{X}\ {}^2\Pi_g$ is detected by scanning λ_1 while λ_2 is constant and the S^+ fragment ion intensity is monitored. If the $\tilde{C}\ {}^2\Sigma_g^+ \leftarrow \tilde{B}\ {}^2\Sigma_u^+$ transition is of interest, then λ_1 is fixed while λ_2 is varied.

The apparatus layout (Danis *et al.* 1989b) is shown schematically in figure 9. The ions are produced by electron impact ionization of a seeded helium supersonic free jet (pulsed) and are extracted into the first quadrupole Q_1 where the ion CS_2^+ is selected. They are then transmitted into the middle quadrupole Q_2 where an r.f. field only is

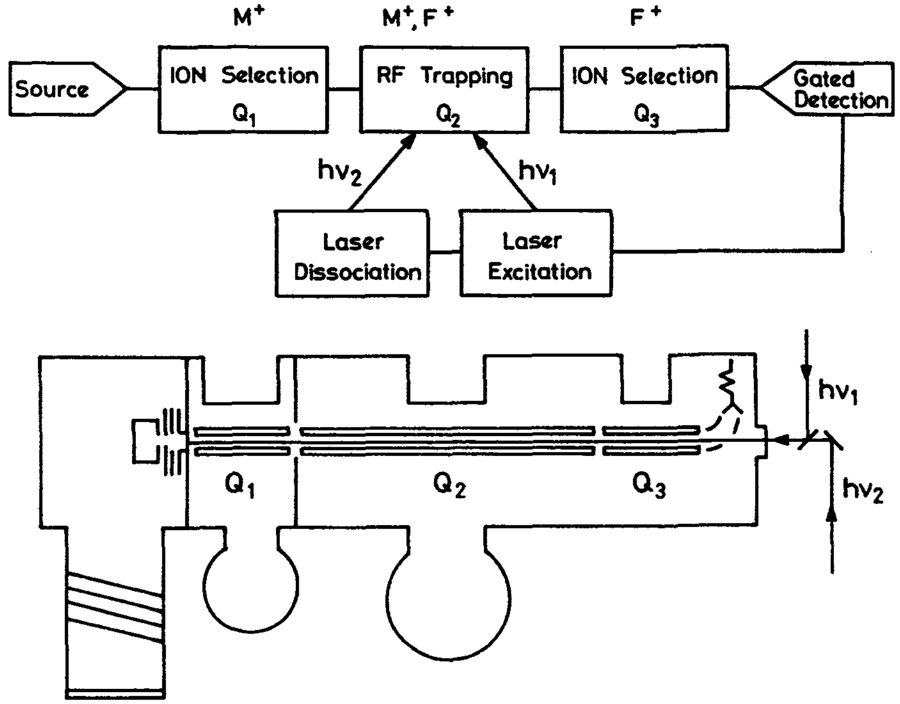


Figure 9. An outline of the apparatus arrangement used for the measurement of the electronic absorption spectra of mass-selected ions based on the two-colour-photon excitation scheme depicted in figure 8. The ion source is to the left; Q_1 and Q_3 are mass-selective quadrupole analysers whereas, in Q_2, ions within a broader mass range are constrained.

applied to constrain a range of ion masses. In this region 60 cm long, the ion encounters a counter-propagating photon packet (λ_1), from a pulsed dye laser, which transfers population to the excited electronic state (CS_2^+ $\tilde{B}$ $^2\Sigma_u^+$). Within about 30 ns, the second set of photons of wavelength λ_2 enters the Q_2 region and induces the transition (CS_2^+ $\tilde{C}$ $^2\Sigma_g^+ \leftarrow \tilde{B}$ $^2\Sigma_u^+$). The upper state then decays to produce the fragment ions (CS_2^+ $\tilde{C}$ $^2\Sigma_g^+ \rightarrow S^+ + CS$) which are also trapped in the field of Q_2. The third quadrupole Q_3 is set to transmit the generated fragment ion S^+. A gated electronic system follows the process as function of the laser wavelengths λ_1 and λ_2.

4.2. *Characterization of ground states of ions*

As outlined above, to study the ions in their ground state a bound–bound electronic transition is scanned (λ_1) while λ_2 is kept constant. In figure 10 is shown such a spectrum for the $\tilde{B}$ $^2\Sigma_u^+ \leftarrow \tilde{X}$ $^2\Pi_g$ transition of CS_2^+, which is rotationally resolved ($\lambda_1 \approx 0{\cdot}04\ \mathrm{cm}^{-1}$ bandwidth) (Danis *et al.* 1989b). This transition is well known from the emission spectrum of this ion (Callomon 1958) and the indicated assignments are taken from there; it illustrates the potential of the technique. The cumbersome feature is, however, that, when looking for a new transition, two laser wavelengths λ_1 and λ_2 have to be tuned. In the case of CS_2^+. λ_1 was known and thus only λ_2 had to be scanned until the S^+ fragments were produced.

In the absence of information on λ_1, that is the separation of the first two electronic states, the procedure could be to tune a single wavelength until the ions on absorption

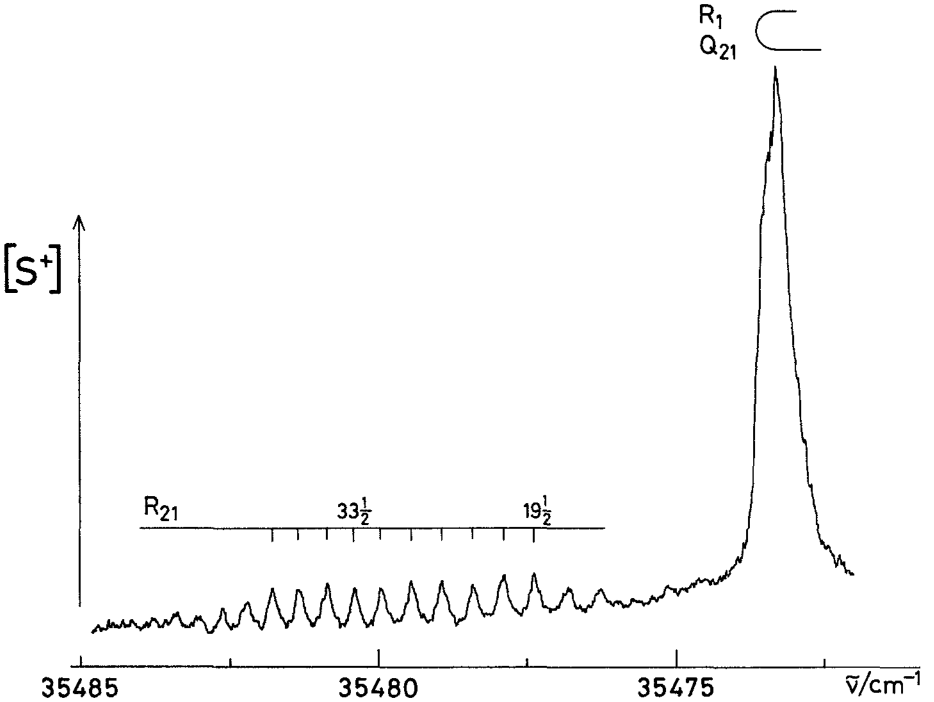


Figure 10. The rotational structure on the origin band of the $\tilde{B}\ ^2\Sigma_u^+ \leftarrow \tilde{X}\ ^2\Pi_g$ electronic transition of CS_2^+ recorded (0·04 cm^{-1} resolution) with a mass-selected ion beam (Danis *et al.* 1988b). The indicated transition was observed by measuring the intensity of the S^+ fragment ions while $h\nu_1$ was varied ($h\nu_2$ was fixed).

of one photon ($\lambda_3 \approx \lambda_1 + \lambda_2$) or alternatively two simultaneously ($2\lambda_3 \approx \lambda_1 + \lambda_2$) produce a fragment ion. Subsequently in a two-photon experiment, while λ_3 is kept constant, λ_1 is again scanned. When λ_1 coincides with a bound–bound transition, a decrease in the intensity of the fragment ion being detected is observed. Such measurements have in fact been demonstrated on mass-selected beams of N_2O^+ (Danis *et al.* 1988a).

4.3. *Characterization of higher excited states of ions*

Once a transition from the ground state to a bound low-lying excited state of the ion has been located in the manner described in the preceding section, the wavelength λ_2 of the second photon can be scanned to map out a higher-lying excited electronic state. If the lifetime of the ion in the latter predissociative state is long enough ($\tau > 10^{-13}\ s^{-1}$), vibrational and rotational structure can be observed and a spectroscopic characterization undertaken.

An example of this is provided by CS_2^+ (Evard *et al.* 1989). Upon excitation of the ion to the $\tilde{B}\ ^2\Sigma_u^+$ state (c.f. section 4.2), the $\tilde{C}\ ^2\Sigma_g^+$ can be mapped out using a further photon λ_2:

$$CS_2^+\ \tilde{X}\ ^2\Pi_g \xrightarrow{\lambda_1} \tilde{B}\ ^2\Sigma_u^+ \xrightarrow{\lambda_2} CS_2^+\ \tilde{C}\ ^2\Sigma_g^+ \rightarrow S^+ + CS.$$

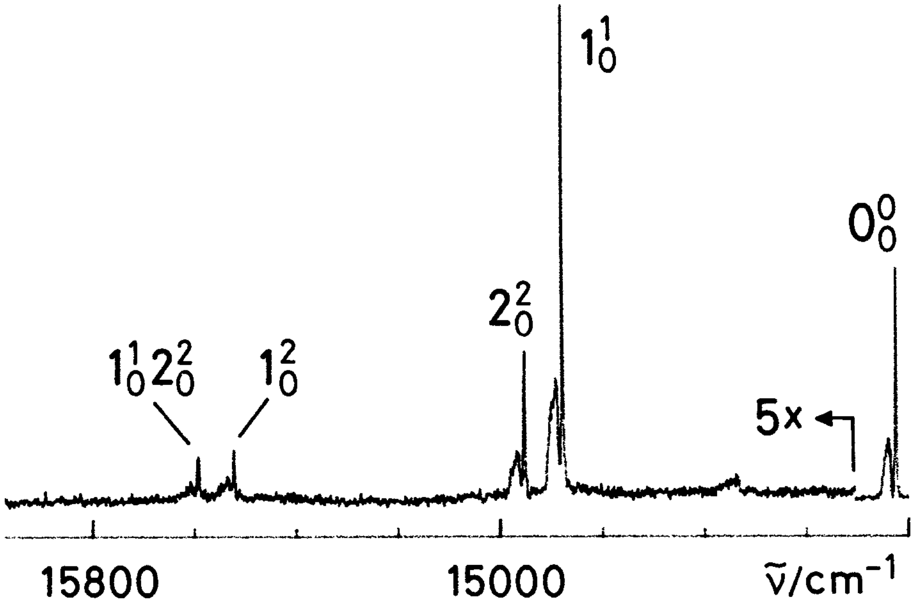


Figure 11. The vibrational structure of the $\tilde{C}\ ^2\Sigma_g^+ \leftarrow \tilde{B}\ ^2\Sigma_u^+$ transition of CS_2^+ recorded (0·6 cm^{-1} resolution) with a mass-selected ion beam (Evard *et al.* 1989). Keeping $h\nu_1$ fixed (tuned to the head of the $\tilde{B}\ ^2\Sigma_u^+ \leftarrow \tilde{X}\ ^2\Pi_g\ 0_0^0$ transition; cf. figure 10), $h\nu_2$ is scanned while the S^+ intensity is monitored.

Thus λ_1 is fixed and λ_2 scanned while the fragment ion S^+ is counted. The result of this experiment at low resolution (λ_1, $\lambda_2 \approx 0{\cdot}6\ \mathrm{cm}^{-1}$ bandwidth) is shown in figure 11. The wavelength λ_1 of the first set of photons is set to coincide with the Q_{21}, R_1 head (cf. figure 10) of the $\tilde{B}\ ^2\Sigma_u^+ \leftarrow \tilde{X}\ ^2\Pi_{g,3/2} 0_0^0$ transition and then λ_2 of the second set of photons is varied. The spectrum shows transitions from the vibrationless level in the $\tilde{B}\ ^2\Sigma_u^+$ state to levels in the $\tilde{C}\ ^2\Sigma_g^+$ state; the sharp prominent lines are the P heads and the broader components are the R-branch profiles. These observations enable the vibrational frequencies $\nu_1 = 653(1)\ \mathrm{cm}^{-1}$ and $2\nu_2 = 728(1)\ \mathrm{cm}^{-1}$ of CS_2^+ in the $\tilde{C}\ ^2\Sigma_u^+$ state to be inferred.

When the resolution of λ_2 is increased to 0·04 cm^{-1}, the rotational structure becomes resolved, and the width of the lines corresponds to the excited-state lifetime of 4×10^{-12} s. To exploit the advantages of the double-resonance nature of the approach, the λ_1 bandwidth is also narrowed to 0·04 cm^{-1} and individual rotational lines in the $\tilde{B}\ ^2\Sigma_u^+ \leftarrow \tilde{X}\ ^2\Pi_g\ 0_0^0$ transition are picked out. Say an R_{21} line is selected by λ_1; then, by scanning λ_2, two rotational lines E_2 and P_2 will be observed for the $\tilde{C}\ ^2\Sigma_g^+ - \tilde{B}\ ^2\Sigma_u^+$ transition (figure 12). By systematically changing J, the rotational structure can be mapped out. Such a series of experimentally observed rotational line pairs is seen in figure 13 (Evard *et al.* 1989). From a rotational analysis, the appropriate constants for the $\tilde{C}\ ^2\Sigma_g^+$ state of CS_2^+ are obtained, and the geometry is inferred. The ion remains linear with a C–S bond length of 1·538(2) Å. Analogous measurements on the $\tilde{C}\ ^2\Sigma_g^+ \leftarrow \tilde{B}\ ^2\Sigma_u^+$ transition of CO_2^+ have been carried out (Wyttenbach *et al.* 1989). In table 4 are collected the spectroscopically determined rotational constants and interatomic distances of CO_2^+ and CS_2^+ in their $\tilde{X}\ ^2\Pi_g$, $\tilde{A}\ ^2\Pi_u$, $\tilde{B}\ ^2\Sigma_u^+$ and $\tilde{C}\ ^2\Sigma_g^+$ states. These ions

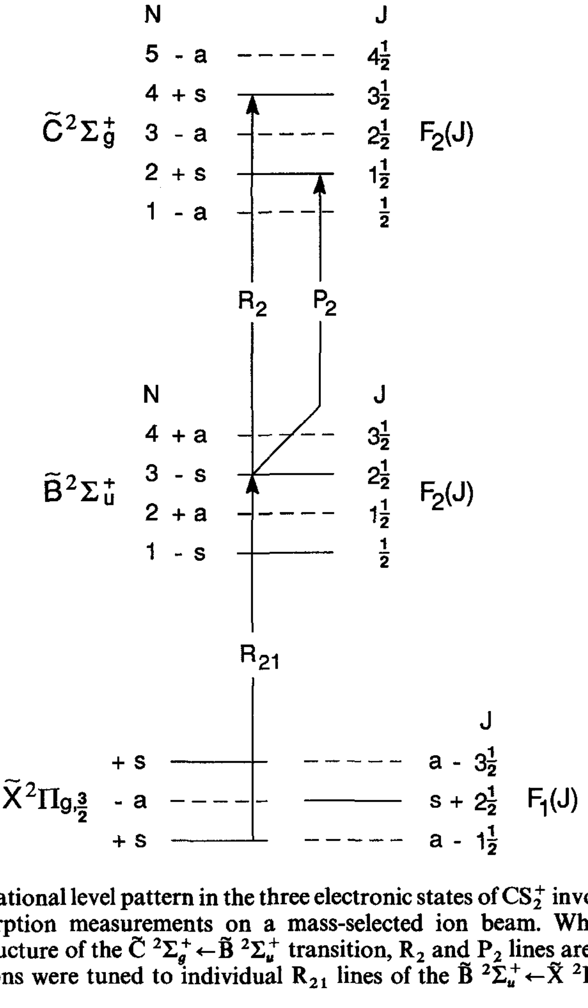


Figure 12. The rotational level pattern in the three electronic states of CS_2^+ involved in the two-photon absorption measurements on a mass-selected ion beam. When probing the rotational structure of the $\tilde{C}\,^2\Sigma_g^+ \leftarrow \tilde{B}\,^2\Sigma_u^+$ transition, R_2 and P_2 lines are observed when the $h\nu_1$ photons were tuned to individual R_{21} lines of the $\tilde{B}\,^2\Sigma_u^+ \leftarrow \tilde{X}\,^2\Pi_{g,3/2}$ transition (cf. figure 13).

are linear in all these states. The data for the $\tilde{X}$, $\tilde{A}$ and $\tilde{B}$ states are taken from earlier studies (referenced in the table) of the emission spectra of these ions.

The above example of CS_2^+, as well as our studies on CO_2^+ and N_2O^+, have demonstrated the potential of this approach. The main constraint of this method is the necessity of tuning two lasers to resonance, which in the case of ions hitherto completely spectroscopically uncharacterized (e.g. fragment ions) is a considerable challenge. Thus, at present, alternative ways of monitoring the absorption process between two bound states of an ion are being researched, by charge exchange and ion–molecule reactions. Such experiments have been used to detect electronic transitions of N_2^+, CO^+ (Kuo *et al.* 1986) and H_2O^+ (Carrington *et al.* 1978) and vibrational transitions in HD^+ (Wing *et al.* 1976).

Table 4. Rotational constants and bond lengths of CO_2^+ and CS_2^+.

State	CO_2^+			CS_2^+		
	B_0 (cm^{-1})	r_0 (Å)	Reference	B_0 (cm^{-1})	r_0 (Å)	Reference
$\tilde{X}\ ^2\Pi_g$	0·3803(1)	1·1769	Gauyacq (1979)	0·10909(6)	1·5641(4)	Callomon (1958)
$\tilde{A}\ ^2\Pi_u$	0·3497(1)	1·2274	Gauyacq (1979)	0·1011	1·615	Balfour (1976)
$\tilde{B}\ ^2\Sigma_u^+$	0·378(1)	1·1805	Gauyacq *et al.* (1975)	0·10776(5)	1·5542(4)	Callomon (1958)
$\tilde{C}\ ^2\Sigma_g^+$	0·395(1)	1·155(2)	Wyttenbach *et al.* (1989)	0·1112(2)	1·528(2)	Evard *et al.* (1989)

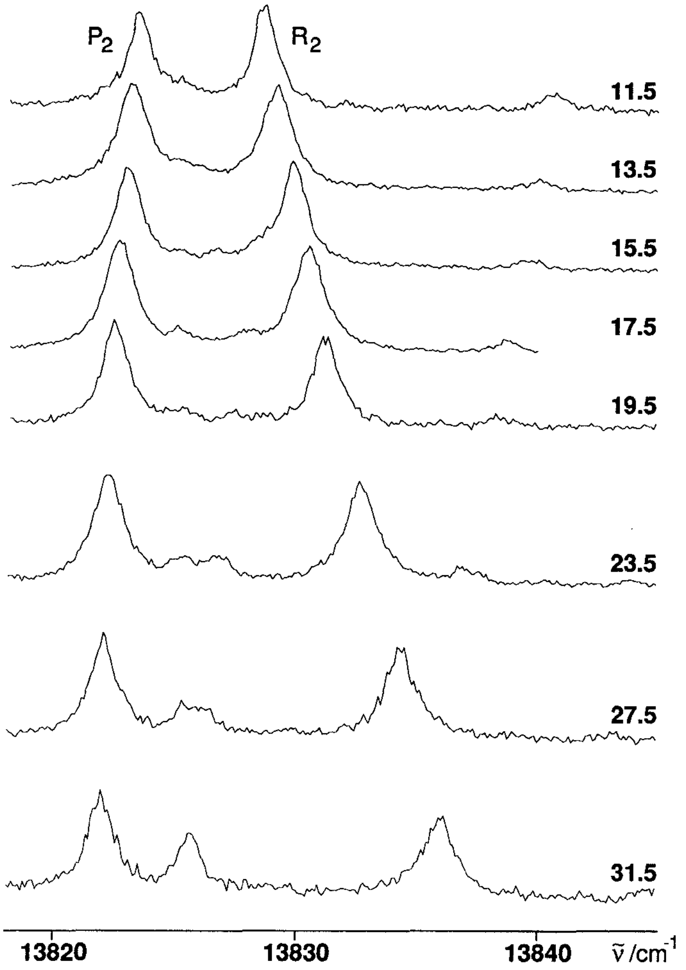


Figure 13. Rotational lines of the $\tilde{C}\,^2\Sigma_g^+ \leftarrow \tilde{B}\,^2\Sigma_u^+$ transition of CS_2^+ recorded with 0·04 cm^{-1} laser bandwidth using a mass-selected ion beam (Evard *et al.* 1989). The double-resonance nature of the experiment is indicated in figure 12.

5. Absorption spectroscopy of mass-selected ions in neon matrices

As is apparent from the discussion in the preceding section, mass selection in the gas phase does not lead to an easy way of studying a variety of ions if their spectroscopy is entirely unknown. It is clearly desirable to have low-resolution spectroscopic information available, to alleviate the problems of laser tuning and transition search. With this in mind we have devised an approach to obtain exactly such low-resolution data on mass-selected ions.

The essence of the technique is simply to mass-select the ion of interest in the gas phase, to co-deposit this with neon to produce a matrix at 5 K and to measure its electronic absorption spectrum.

The layout of the apparatus put together to test the feasibility of this approach (Forney *et al.* 1989a) is shown in figure 14. Ions are produced by electron impact in a low-pressure source and are then mass selected with a small quadrupole mass analyser. Typically an ion current of 10^{-8}–10^{-9} A and a kinetic energy of 50–350 eV is

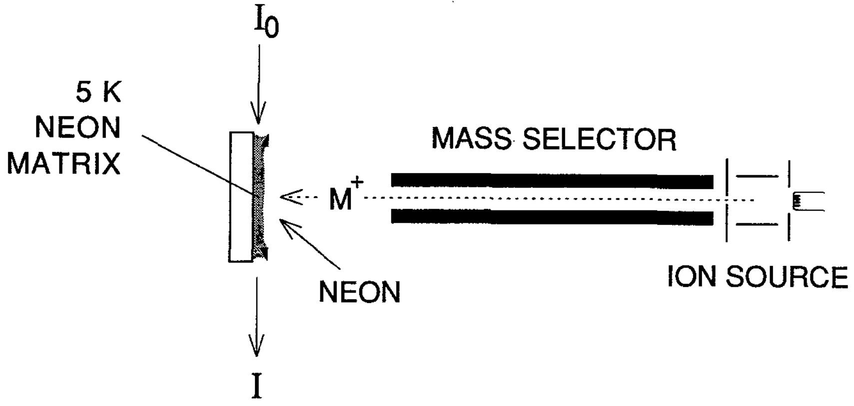


Figure 14. The apparatus layout for the measurement of the absorption spectra of mass-selected ions in 5 K neon matrices.

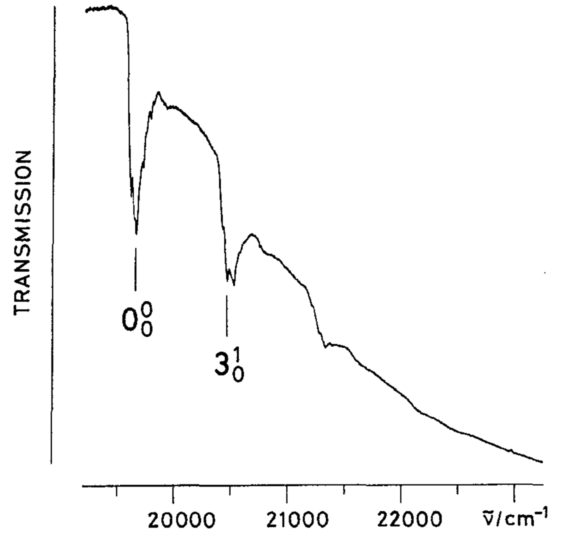


Figure 15. The $\tilde{A}\,^2\Pi_u \leftarrow \tilde{X}\,^2\Pi_g$ absorption bands of the diacetylene cation. The spectrum was recorded (with 0·1 nm resolution) after mass-selected $C_4H_2^+$ (about 150 eV; about 2×10^{-4} A) was co-deposited with neon over a period of about 2 h to form a matrix at 5 K (Forney *et al.* 1989b).

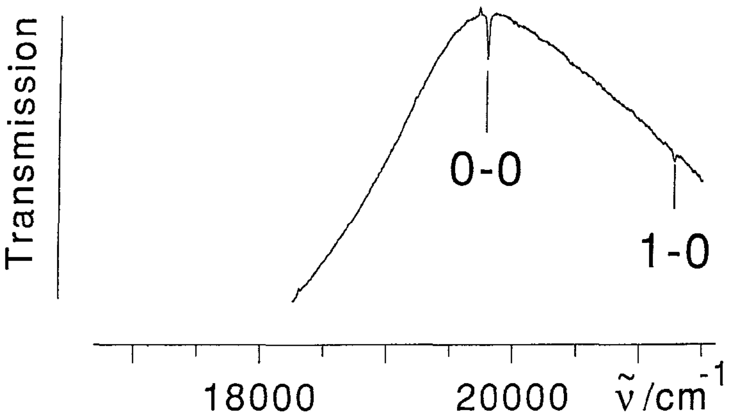


Figure 16. The $\tilde{B}\,^4\Sigma_u^- \leftarrow \tilde{X}\,^4\Sigma_g^-$ electronic absorption spectrum of C_2^+ (0·1 nm f.w.h.m.) measured after a mass-selected beam of C_2^+ (about 150 eV; about 5×10^{-4} A) was co-deposited with neon to form a 5 K matrix.

transmitted. The ion beam exiting from the quadrupole is co-deposited with neon gas on a rhodium-coated copper substrate held at 5 K. In about 2–3 h a matrix of about 150 μm thickness is grown. The absorption spectrum can then be measured in the 220–1200 nm region by passing the light parallel to the substrate through the thin side of the matrix (cf. section 3.1).

To test the method, matrices were grown with mass-selected parent ions such as N_2^+, CO_2^+, $C_2N_2^+$, $ClCCH^+$ and $H(CC)_2H^+$. In the latter case, using an ionic kinetic energy of about 150 eV, the resulting absorption spectrum, that of the $\tilde{A}\ {}^2\Pi_u \leftarrow \tilde{X}\ {}^2\Pi_g$ transition, is reproduced in figure 15 (Forney *et al.* 1989b). This electronic band system is known in the gas phase (cf. section 3.2) as well as in the neon matrix where its laser excitation spectrum has been measured (Bondybey and English 1979). In the spectral region scanned (220–1200 nm), only the known electronic absorption system of $H(CC)_2H^+$ is apparent. Similar observations apply to the other parent ions codeposited with neon. However, with certain ions such as $C_2N_2^+$, use of higher kinetic energy (e.g. 350 eV) leads to the observation of absorption systems of fragments (e.g. C_2^+ and CN).

As a further test, C_2^+ was mass-selected and co-deposited (kinetic energy, about 125 eV; current, 2×10^{-8} A), using acetylene as the precursor in the ionization source. The recently discovered $\tilde{B}\ {}^4\Sigma_u^- – \tilde{X}\ {}^4\Sigma_g^-$ electronic absorption system of C_2^+ is observed, and no other absorbers in the optical spectral region are detected (Forney *et al.* 1989b). The recorded spectrum (figure 16) should be compared with that shown in figure 4, obtained after a series of photochemical and ionization reactions.

These initial observations demonstrate the potential of the approach and, when various technical improvements are made and the method is fully developed, it should be applicable to all sorts of ions which can be produced in a mass spectrometer. Other established matrix techniques such as i.r. absorption and electron spin resonance could equally be applicable once the mass-selected ions are trapped in the neon. Armed with such spectroscopic knowledge, the search for the transitions in the gas phase can then easily be undertaken. It should also be pointed out that neutralization of the ions held in the matrix could lead to the corresponding studies of their mass-selected neutrals. Thus this approach may open up a general route for the spectroscopic characterization for mass-selected ions, radicals and their clusters in rare-gas matrices.

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