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Spectroscopic Structure of Open-shell Polyatomic Cations

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1 Introduction

Ions are transient species which have attracted increasing attention in the last decade. This is because they are known to occur in comets, interstellar space, planetary atmospheres, plasmas, and flames, where their presence has led to many suggestions concerning their involvement in chemical reactions. For example, the formation of hydrocarbons in dark interstellar clouds has been modelled by ion-molecule schemes.[1] In addition, technological developments have allowed the design and implementation of sensitive methods for the spectroscopic characterization of such reactive species, which are invariably produced in small concentrations.

The focus of attention of this review is on the approaches to characterize open-shell cations of polyatomic molecules spectroscopically by means of their electronic transitions. Such data on diatomic species have provided the foundations of modern spectroscopic theories,[2] and the advent of high resolution lasers and Doppler-free techniques[3] has led to further refinements and developments. Many diatomic, and a few triatomic, ions can be readily produced in discharge sources with sufficient densities for detection by classical emission and absorption methods;[4] with polyatomic ions, however, their generation and the environment for their study is more demanding and crucial. Consequently such investigations have required specially designed approaches.[5] This last area has been the centre of our research activity over the past decade and will be considered presently and illustrated by examples showing the sort of information on ions which can be obtained.

There are also several other approaches used to study the spectroscopy of ions which are not discussed here. In particular, the advances in i.r. lasers, and in the means of detection of ions by modulation methods, have led to many successful measurements of vibrational transitions of closed-shell cations,[6] and recently of some open-shell polyatomic cations[7] and anions.[8] A few simple cations have also

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[1] G. Winnewisser, *Top. Curr. Chem.*, 1981, **99**, 39.

[2] G. Herzberg, 'Spectra of Diatomic Molecules', van Nostrand, New York, 1950.

[3] See for example, G. Duxbury, *Chem. Soc. Rev.*, 1983, **12**, 453.

[4] G. Herzberg, *Quart. Rev., Chem. Soc.*, 1971, **25**, 201; G. Herzberg, *Proc. Indian Nat. Sci. Acad.*, 1985, **A51**, 495.

[5] J. P. Maier, *Acc. Chem. Res.*, 1982, **15**, 18.

[6] C. S. Gudeman and R. J. Saykally, *Annu. Rev. Phys. Chem.*, 1984, **35**, 387.

[7] M. W. Crofton, M.-F. Jagod, B. D. Rehfuss, and T. Oka, *J. Chem. Phys.*, 1987, **86**, 3755.

[8] M. Polak, M. Gruebele, and R. J. Saykally, *J. Am. Chem. Soc.*, 1987, **109**, 2884; M. Gruebele, M. Polak, and R. J. Saykally, *J. Chem. Phys.*, 1987, **86**, 6631.

been characterized by microwave spectroscopy.[9]

Other methods have utilized mass-selected ion-beams in conjunction with laser excitation both in the visible[10] and i.r. regions.[11] A further area of activity is in obtaining information on the structures of ions by indirect means, such as those using photodissociation,[12] ion–molecule or collisional processes on mass-selected ion beams produced in conventional[13] as well as laser evaporation and supersonic expansion sources.[14] Some ion geometries have been determined by the Coulomb explosion approaches.[15]

As far as polyatomic cations of stable molecules (as well as of some semi-stable species) are concerned, photoelectron spectroscopy has provided a great deal of information on the energy location of the electronic states of their ions, and some on the vibrational structure in the lowest states.[16] The limitation of the method has been the resolution, typically 160 cm^{-1}, though it has recently been shown that it is possible to reduce this to a few cm^{-1} in favourable cases.[17] Consequently the methods which we have applied are based on the detection of photons, because their energy can be determined much more accurately.[5] A further improvement came about with the incorporation of lasers, with the associated inherent resolution and intensity advantages.[18]

The spectral characterization of open-shell cations discussed here is the result of studies of the emission spectra from electron excitation of effusive and supersonic free jets, of the laser excitation spectra with Penning ionization, and of absorption measurements on ions isolated in 5 K neon matrices.[19] It goes without saying that the concomitant application of such techniques has enabled information to be extracted which by one method alone would not have been possible. Thus with these methods the ions are prepared with rotational and vibrational temperatures ranging from ≈ 5 K to 300 K, using different projectiles to generate the ions. The analysis of the respective spectra yields the term values of the electronic transitions, vibrational frequencies, and, in favourable cases, the rotational constants and hence geometries of the ions in the ground and lowest excited electronic states.

Related to the above are the studies of the radiative and non-radiative relaxation pathways of state selected ions. These aspects are not considered here and have been the object of other reviews based on the techniques used for such investi-

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[9] R. C. Woods, *J. Mol. Struct.*, 1983, **97**, 195.

[10] A. Carrington, *Proc. R. Soc. London A*, 1979, **367**, 433.

[11] A. Carrington and T. P. Softley in 'Molecular Ions: Spectroscopy, Structure and Chemistry', ed. T. A. Miller and V. E. Bondybey, North-Holland, Amsterdam, 1983, p. 49.

[12] R. C. Dunbar in 'Gas-Phase Ion Chemistry', Vol. 3, 'Ions and Light', ed. M. T. Bowers, Academic Press, New York, 1984, p. 129.

[13] 'Ionic Processes in the Gas Phase', ed. M. A. Almoster-Ferreira, D. Reidel, Dordrecht, 1984.

[14] R. E. Smalley, *Laser Chem.*, 1983, **2**, 167.

[15] E. P. Kanter, Z. Vager, G. Both, and D. Zajfman, *J. Chem. Phys.*, 1986, **85**, 7487, and references therein.

[16] D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, 'Molecular Photoelectron Spectroscopy', Wiley-Interscience, New York, 1970.

[17] K. Müller-Dethlefs, M. Sander, and E. W. Schlag, *Z. Naturforsch., Teil A*, 1984, **39**, 1089.

[18] T. A. Miller and V. E. Bondybey, *J. Chim. Phys. Phys.-Chim. Biol.*, 1980, **77**, 695.

[19] J. P. Maier, *J. El. Spectrosc. Rel. Phenom.*, 1986, **40**, 203; J. P. Maier, *J. Chem. Soc., Faraday Trans. 2*, 1987, **83**, 49.

gations; photoelectron–photon,[20] photoion–photon,[21] or photoelectron–ion[22] coincidence measurements yielding lifetimes, fluorescence quantum yields, and fragmentation branching ratios.

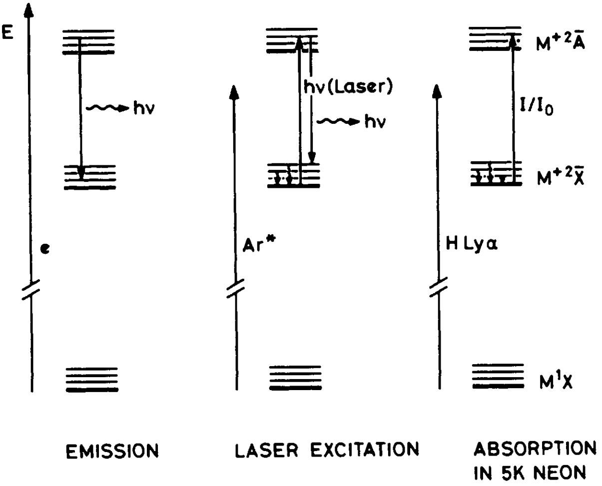

Figure 1 *Essential aspects of the emission, laser excitation, and matrix absorption approaches for the vibrational characterization of cations. The ions are prepared in the three methods by* $\approx$200 eV *electron impact, by Penning ionization* (Ar, He *metastables*) *and by photoionization* [H(Ly α) *or* Ne(I)]. *The latter two processes are followed by collisional relaxation* (*wavy lines*) *prior to wavelength selected photon absorption*

2 Vibrational Characterization

The principal features of the three approaches used for vibrationally characterizing open-shell cations of polyatomics in their ground ($\tilde{X}$) and lowest excited ($\tilde{A}$, $\tilde{B}$...) electronic states are depicted in Figure 1. The three methods rely on the detection of the dipole allowed electronic transition between the ionic states; in the case of the emission and laser excitation experiments, the emitted photons are monitored, whereas in the matrix the absorption is measured directly. The ions are initially generated by different means in the three approaches. In the emission method the ionization takes place by electron impact on an effusive or supersonic beam containing the molecular precursor; in the laser excitation technique Penning ionization with He or Ar metastables and collisional relaxation is employed; and for the absorption measurements, molecules embedded in a 5 K neon matrix are photoionized with either H(Ly α) or Ne(I) radiation.

The emission spectra yield vibrational information mainly on the ionic ground state ($\tilde{X}$) and, usually, to a lesser extent on the excited ($\tilde{A}$) state. On the other hand,

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[20] J. P. Maier and F. Thommen, in 'Gas-Phase Ion Chemistry', Vol. 3, 'Ions and Light', ed. M. T. Bowers, Academic Press, London, 1984, p. 357.

[21] S. Leach, *J. Mol. Struct.*, 1986, **141**, 43.

[22] T. Baer, *Adv. Chem. Phys.*, 1986, **64**, 111.

the laser excitation and absorption spectra probe the excited states because the population of the ions is concentrated in the lowest vibrational level of the ground state ($\tilde{X}$) prior to the interaction with the electromagnetic radiation.

A. Emission Spectroscopy.—This was the first approach used to look for the emission spectra from electronically excited polyatomic ions.[23] In the initial experiments an effusive beam of the sample was ionized/excited by a collimated electron beam (typically 20—200 eV, several mA current), in a perpendicular arrangement; the resulting fluorescence was dispersed by a monochromator and detected by single photon counting electronics. The optical resolution usually attainable for studies of the vibrational structure of the electronic transitions was $\approx$0.01 nm, and this could be improved in a few cases by a factor of two. The strengths of this approach are the sensitivity and especially the ability to scan large wavelength regions (200—900 nm) easily. The results obtained in such studies[24] have laid the foundation stone for the application of higher resolution laser, and of technically more demanding approaches such as photoelectron–photon coincidence measurements.[20] Though the approach has by and large outlived its usefulness, it is still occasionally used to obtain the initial information on the optical transitions of ions of, for example, semi-stable molecules[25] (*vide infra*) and, recently, of the type XF_4^+ (X = C,[26] Si,[27] Ge[28]) using similar or related experimental arrangements.

The emission spectra of over one hundred open-shell polyatomic cations have been observed. These are listed in Table 1, or their structural moiety is indicated (*e.g.* fluoro-benzene cations). The symmetries of the electronic transitions are also given and the references to the original and subsequent studies on these ions are to be found in several compilations.[24,29,30] In two of these the lifetimes of the ions in their excited electronic states are also listed.[24,29] In a further review, the fluorescence quantum yields, and radiative and non-radiative rate constants of many of the ions are given and their relaxation behaviour is discussed.[20]

An important improvement in the quality of the emission spectra and the amount of information which could be extracted came about with the introduction of the molecular precursors into the ionization region in the form of a supersonic free jet.[31] Usually seeded helium jets were employed: the molecular precursor at a pressure of 1—10 mbar was premixed with $\approx$ 1 bar of He and expanded through a 50—100 μm orifice. As a result of the expansion the internal degrees were cooled

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[23] J. P. Maier, in 'Kinetics of Ion-Molecule Reactions', ed. P. Ausloos, Plenum Press, New York, 1979, p. 437.

[24] J. P. Maier, *Chimia*, 1980, **34**, 219.

[25] J. P. Maier, *Philos. Trans. R. Soc. London A*, 1988, **324**, 209.

[26] J. F. M. Aarts, S. M. Mason and R. P. Tuckett, *Mol. Phys.*, 1987, **60**, 761.

[27] J. F. M. Aarts, *Chem. Phys.*, 1986, **101**, 105; S. M. Mason and R. P. Tuckett, *Mol. Phys.*, 1987, **60**, 771.

[28] H. Van Lonkhuyzen and J. F. M. Aarts, *Chem. Phys. Lett.*, 1987, **140**, 434.

[29] J. P. Maier, O. Marthaler, L. Misev, and F. Thommen, in 'Molecular Ions', ed. J. Berkowitz and K.-O. Groeneveld, Plenum Press, London 1983, p. 125.

[30] T. A. Miller and V. E. Bondybey, *Appl. Spectrosc. Rev.*, 1982, **18**, 105; T. A. Miller, *Annu. Rev. Phys. Chem.*, 1982, **33**, 257.

[31] D. Klapstein, J. P. Maier, and L. Misev, in 'Molecular Ions: Spectroscopy, Structure and Chemistry', ed. T. A. Miller and V. E. Bondybey, North-Holland, New York, 1983, p. 175.

Table 1 *Polyatomic cations for which emission spectra have been detected in the gas phase. (Not all the isotopic derivatives studied are listed.) A literature survey of all the studies of these cations by means of the indicated electronic transitions is to be found in several reviews*[24,29,30]

Cation	*Transition*	
CO_2^+	$\tilde{B}^2\Sigma_u^+ - \tilde{X}^2\Pi_g$ ($D_{\infty h}$)	
	$\tilde{A}^2\Pi_u - \tilde{X}^2\Pi_g$	
CS_2^+	$\tilde{B}^2\Sigma_u^+ - \tilde{X}^2\Pi_g$ ($D_{\infty h}$)	
	$\tilde{A}^2\Pi_u - \tilde{X}^2\Pi_g$	
N_2O^+	$\tilde{A}^2\Sigma - \tilde{X}^2\Pi$ ($C_{\infty v}$)	
OCS^+	$\tilde{A}^2\Pi - \tilde{X}^2\Pi$ ($C_{\infty v}$)	
H_2O^+	$\tilde{A}^2A_1 - \tilde{X}^2B_1$ (C_{2v})	
H_2S^+	$\tilde{A}^2A_1 - \tilde{X}^2B_1$ (C_{2v})	
XCN^+	$\tilde{B}^2\Pi - \tilde{X}^2\Pi$ ($C_{\infty v}$)	X = Cl, Br, I
	$\tilde{A}^2\Sigma^+ - \tilde{X}^2\Pi$	
XCP^+	$\tilde{A}^2\Sigma^+ - \tilde{X}^2\Pi$ ($C_{\infty v}$)	X = H, D, F
XBS^+	$\tilde{A}^2\Sigma^+ - \tilde{X}^2\Pi$ ($C_{\infty v}$)	X = H, D, F, Cl
$XC{\equiv}CH^+$	$\tilde{A}^2\Pi - \tilde{X}^2\Pi$ ($C_{\infty v}$)	X = Cl, Br, I
$XC{\equiv}CX^+$	$\tilde{A}^2\Pi_g - \tilde{X}^2\Pi_u$ ($D_{\infty v}$)	X = Cl, Br, I
$ClC{\equiv}CBr^+$	$\tilde{A}^2\Pi - \tilde{X}^2\Pi$ ($C_{\infty v}$)	
RF_4^+	$\tilde{D}^2A_1 - \tilde{C}^2T_2$ (T_d)	R = C, Si, Ge
$X(C{\equiv}C)_2X^+$	$\tilde{A}^2\Pi_g - \tilde{X}^2\Pi_u$ ($D_{\infty h}$)	X = H, D, F, Cl, Br, I
$N{\equiv}CC{\equiv}CC{\equiv}N$	$\tilde{A}^2\Pi_g - \tilde{X}^2\Pi_u$ ($D_{\infty h}$)	
cis-1,2-difluoroethylene$^+$	$\tilde{A}^2A_1 - \tilde{X}^2B_1$ (C_{2v})	
$H(CC)_2C{\equiv}N^+$	$\tilde{A}^2\Pi - \tilde{X}^2\Pi$ ($C_{\infty v}$)	
CH_3CP^+	$\tilde{A}^2A_1 - \tilde{X}^2E$ (C_{3v})	
$CH_3C{\equiv}CX^+$	$\tilde{A}^2E - \tilde{X}^2E$ (C_{3v})	X = Cl, Br
$H(C{\equiv}C)_3H^+$	$\tilde{A}^2\Pi_g - \tilde{X}^2\Pi_u$ ($D_{\infty h}$)	
$N{\equiv}C(C{\equiv}C)_2C{\equiv}N^+$	$\tilde{A}^2\Pi_u - \tilde{X}^2\Pi_g$ ($D_{\infty h}$)	
$CH_3(C{\equiv}C)_2X^+$	$\tilde{A}^2E - \tilde{X}^2E$ (C_{3v})	X = H, D, F, Cl, Br
$CF_3(C{\equiv}C)_2F^+$		
$H(C{\equiv}C)_2F^+$	$\tilde{A}^2E - \tilde{X}^2E$ (C_{3v})	
$CH_3(C{\equiv}C)_2C{\equiv}N^+$	$\tilde{A}^2\Pi_u - \tilde{X}^2\Pi_g$ ($D_{\infty h}$)	
$R(C{\equiv}C)_2R^+$	$\tilde{A}^2E - \tilde{X}^2E$ (C_{3v})	R = CH_3, CD_3, CF_3
$Et(C{\equiv}C)_2X^+$	$\tilde{A}^2E_u - \tilde{X}^2E_g$ (D_{3d})	X = H, CN, Et
trans-1,3,5-Hexatriene$^+$	$\tilde{A}^2A'' - \tilde{X}^2A''$ (C_s)	
cis-1,3,5-Hexatriene$^+$	$\tilde{A}^2B_g - \tilde{X}^2A_u$ (C_{2h})	
trans-1,3,5-Heptatriene$^+$	$\tilde{A}^2A_2 - \tilde{X}^2B_1$ (C_{2v})	
trans-1,3,5,7-Octatetraene$^+$	$\tilde{A}^2A'' - \tilde{X}^2A''$ (C_s)	
$Bu^t(C{\equiv}C)_4Bu^{t+}$	$\tilde{A}^2A_u - \tilde{X}^2B_g$ (C_{2h})	
	$\tilde{A}^2A'' - \tilde{X}^2A''$ (C_s)	
Benzenoid Cations		
$C_6F_6^+$	$\tilde{B}^2A_{2u} - \tilde{X}^2E_{1g}$ (D_{6h})	
1,3,5-$C_6H_3X_3^+$	$\tilde{B}^2A_2 - \tilde{X}^2E''$ (D_{3h})	X = F, Cl
1,3,5-$C_6F_3X_3^+$	$\tilde{B}^2A_2 - \tilde{X}^2E''$ (D_{3h})	X = Cl, Br
1,3,5-$C_6F_3(CH_3)_3^+$	$\tilde{B}^2A_1 - \tilde{X}^2E''$ (C_{3v})	
Fluorobenzenes$^+$	$\tilde{B}(\pi^{-1}) - \tilde{X}(\pi^{-1})$ (C_s)	
Chlorobenzenes$^+$		
Bromofluorobenzenes$^+$		
Fluorophenols$^+$		
Chloroalkylbenzenes$^+$		
$C_6F_5X^+$		
X = CF_3, CH_3, CN, CHO, NO, NH_2		

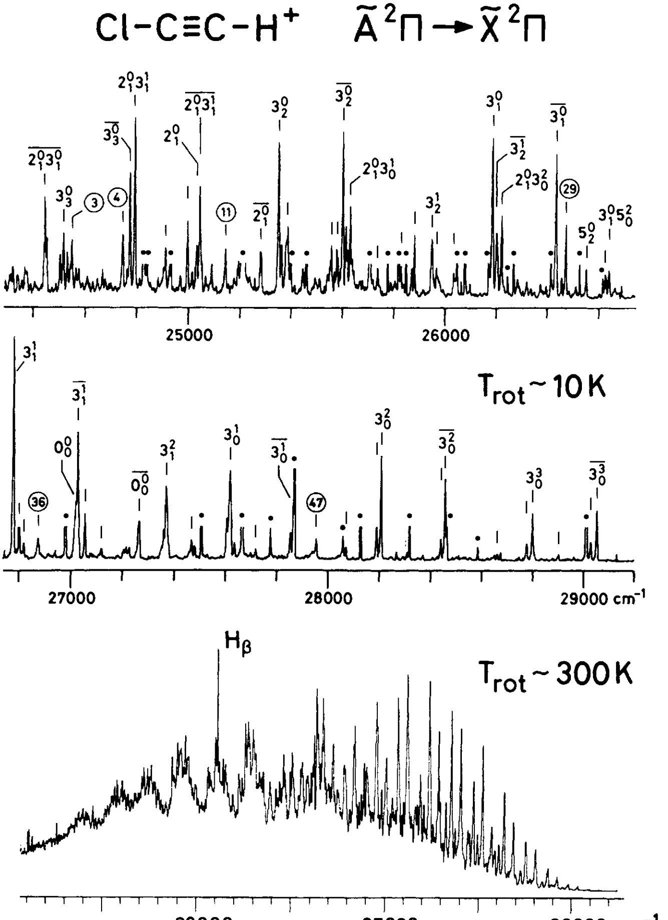

Figure 2 *Emission spectrum.* $\tilde{A}^2\Pi \longrightarrow \tilde{X}^2\Pi$ *of chloroacetylene cation excited by* ≈ 200 eV *electron impact on a seeded* He *supersonic free jet (top—*$T_{\text{rot}} \approx$ 10 K; 0.03 nm *resolution) or on an effusive beam (bottom—*$T_{\text{rot}} \approx$ 300 K, 0.16 nm fwhm). *The bars above the vibrational assignments refer to the* $\Omega = 1/2$ *component; the dots refer to atomic lines*

($T_{\text{rot}} \approx$ 5—10 K) and, following electron impact ionization, one obtained emission spectra of rotationally cold ($T_{\text{rot}} \approx$ 5—10 K) ions.

In Figure 2 is shown such an emission spectrum, the $\tilde{A}^2\Pi \longrightarrow \tilde{X}^2\Pi$ transition of chloroacetylene cation, recorded in a supersonic free jet[32] (top) and with an effusive beam[33] (bottom). The improvements are self-evident. As a result of the reduction in the inhomogeneous broadening of the bands at rotational temperature 5—10 K,

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[32] D. Klapstein, R. Kuhn, and J. P. Maier, *Chem. Phys.*, 1984, **86**, 285.

[33] M. Allan, E. Kloster-Jensen, and J. P. Maier, *J. Chem. Soc., Faraday Trans. 2*, 1977, **73**, 1406.

Table 2 *Fundamental vibrational frequencies* (cm^{-1}) *of chloroacetylene cation inferred from the emission*[32] *and laser excitation*[34] *spectra. The molecular values are from ref. 36*

			Σ^+		Π	
Species	*State*	v_1	v_2	v_3	v_4	v_5
^{35}Cl-C≡C-H	$X^1\Sigma^+$	3 340	2 110	756	604	326
^{35}Cl-C≡C-H$^+$	$\tilde{X}^2\Pi_{3/2}$	3 146	1 984.5	836.8	595	235
	$\tilde{A}^2\Pi_{3/2}$	3 230.7	2 063.8	595.7		224
^{35}Cl-C≡C-D	$X^1\Sigma^+$	2 612	1 980	742	472	312
^{35}Cl-C≡C-D$^+$	$\tilde{X}^2\Pi_{3/2}$	2 475	1 882.9	817.0	476	
	$\tilde{A}^2\Pi_{3/2}$	2 561.2	1 919.7	587.2		216

Uncertainty in values is ± 0.2 cm^{-1} for figures quoted to one decimal place, all others ± 1 cm^{-1}

vibrational frequencies can be inferred to within 1 cm^{-1} (and sometimes to even less), as opposed to ± 10 cm^{-1} at an ambient temperature of ≈ 300 K. Furthermore, sequence and combination bands, obscured by the broadened profiles at the higher temperatures, become apparent. Important for the vibrational assignment in the case of the spectrum of chloroacetylene cation (Fig. 2) is the resolution of the bands of the naturally occurring isotopic species ^{35}Cl–C≡C–H$^+$ and ^{37}Cl–C≡C–H (in the intensity ratio 3:1), and the identification of the bands belonging to $\Omega = 3/2$ and 1/2 sub-components.

Although the chloroacetylene cation in the $\tilde{X}^2\Pi$ and $\tilde{A}^2\Pi$ states is linear,[34] there is a large difference in the C—Cl distance in these two states as well as in the molecular ground state ($X^1\Sigma^+$) values.[35] The C—C distance changes less and the C–H distance variation is small. The result of this is that the emission spectrum is congested with transitions involving many vibrational levels in both the $\tilde{A}^2\Pi$ and $\tilde{X}^2\Pi$ ionic states; the v_3(C–Cl stretch) vibration of Σ^+ symmetry is especially prominent (*cf.* Figure 2).[32] The vibrational frequencies of all the five fundamentals ($3 \cdot \Sigma^+, 2 \cdot \Pi$) in the $\tilde{X}^2\Pi$ state are obtained from the analysis of the emission spectra of Cl–C≡C–H$^+$ and Cl–C≡C–D$^+$, as well as their v_3 frequency in the $\tilde{A}^2\Pi$ state. The fundamentals are listed in Table 2 (for the ^{35}Cl derivative) together with the molecular values.[36]

The detection of the emission spectra has also proved fruitful in the vibrational characterization of ions of unstable molecular species. The spectroscopic studies of the latter neutral species have been the subject of a review in this journal.[37] Armed with the knowledge of the photoelectron spectra of the semi-stable molecules, and with the methods used for their preparation in the microwave studies, the emission spectra of the cations of the phospha-alkynes, XCP$^+$ (X = H, D,[38] F,[39] CH$_3$[40])

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[34] M. A. King, J. P. Maier, and M. Ochsner, *J. Chem. Phys.*, 1985, **83**, 3181.

[35] E. Heilbronner, K. A. Muszkat, and J. Schäublin, *Helv. Chim. Acta*, 1971, **54**, 58.

[36] G. R. Hunt and M. K. Wilson, *J. Chem. Phys.*, 1961, **34**, 1301.

[37] H. W. Kroto, *Chem. Soc. Rev.*, 1982, **11**, 435.

[38] M. A. King, D. Klapstein, H. W. Kroto, J. P. Maier, O. Marthaler, and J. F. Nixon, *Chem. Phys. Lett.*, 1981, **82**, 543; M. A. King, R. Kuhn, and J. P. Maier, *Mol. Phys.*, 1987, **60**, 867.

[39] M. A. King, D. Klapstein, H. W. Kroto, R. Kuhn, J. P. Maier, and J. F. Nixon, *J. Chem. Phys.*, 1984, **80**, 2332.

[40] J. Lecoultre, M. A. King, R. Kuhn, and J. P. Maier, *Chem. Phys. Lett.*, 1985, **120**, 524.

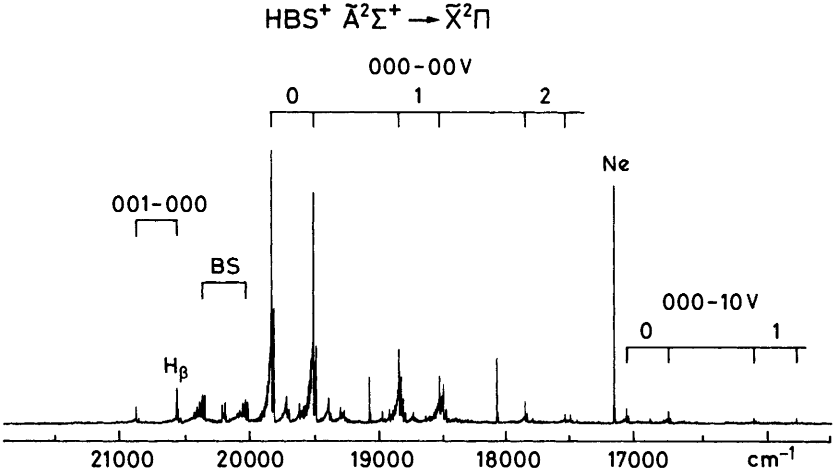

Figure 3 *The* $\tilde{A}^2\Sigma^+ \longrightarrow \tilde{X}^2\Pi$ *emission spectrum of thioborine cation* (0.033 nm fwhm) *obtained by passing* H_2S *over* B *chips at* ≈ 1 000 °C *and* ≈ 200 eV *electron beam ionization. The assignment of the main progressions*—v_1(B—H), v_3(B—S)—*is indicated*

and of the sulphidoborons, XBS^+ (X = H, D,[41] F, Cl[42]) were recorded. In all these cases the observed band systems are due to their $\tilde{A}^2\Sigma^+ \longrightarrow \tilde{X}^2\Pi$ electronic transitions ($\tilde{A}^2A_1 \longrightarrow \tilde{X}^2E$ for CH_3CP^+). The analysis of the vibronic structure has enabled their fundamental frequencies, spin–orbit constants as well as Renner–Teller and Fermi resonance parameters in the $\tilde{X}^2\Pi$ state, which complicate the pattern, to be inferred.

In Figure 3 is shown the $\tilde{A}^2\Sigma^+ \longrightarrow \tilde{X}^2\Pi$ emission spectrum of HBS^+ obtained by passing H_2S over B at ≈ 1 000 °C and ionization of the products by a ≈ 200 eV electron beam with the apparatus described.[41] The essential modification to the instrument was the incorporation of an oven near to the ionization region, in much the same way as in studies of the semi-stable molecules by photoelectron spectroscopy.[37]

In the spectrum (Figure 3) two sub-band systems are apparent as a result of the spin–orbit splitting in the cationic ground state ($A''_0 \approx -323$ cm^{-1}). The rotational profiles show a strong Q-branch, and a weaker P-branch, maximum component. The vibronic pattern is complicated by the overlap of the isotopic bands of $H^{11}B^{32}S^+$ and $H^{10}B^{32}S^+$ (the bands due to the ^{34}S modification are not clearly discernible). The two main progressions involve the two Σ^+ modes, v_1(B—H str.) and v_3(B—S str.), whereas the weaker bands are due to the excitation of the degenerate, v_2, mode associated with which are further splittings and intensity changes because of Renner–Teller and Fermi resonance interactions. The observed pattern can be reproduced by the usual parameters which mimic such effects.

The emission spectrum thus yields the frequencies of the three fundamentals in

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[41] M. A. King, D. Klapstein, R. Kuhn, J. P. Maier, and H. W. Kroto, *Mol. Phys.*, 1985, **56**, 871.
[42] M. A. King, R. Kuhn, and J. P. Maier, *J. Phys. Chem.*, 1986, **90**, 6460.

Table 3 *Fundamental vibrational frequencies* (cm^{-1}) *and spin-orbit splittings,* $A_{0,\mathrm{eff.}}$ (cm^{-1}) *of the phosphaethyne and sulphidoboron cations obtained from their emission spectra. The values given are for the most abundant isotopic derivative*

Cation	*State*	v_1	v_2	v_3	$A_{0,\mathrm{eff.}}$	*Ref.*
HCP^+	$\tilde{X}^2\Pi_{3/2}$	3 125.1(4)	642(1)	1 167.1(4)	−146.97(3)	38
	$^2\Pi_{1/2}$	3 124.9(4)		1 159.9(4)		
	$\tilde{A}^2\Sigma^+$	2 985.6(4)	706(1)	1 275.4(4)		
DCP^+	$\tilde{X}^2\Pi_{3/2}$	2 356.5(4)	499(1)	1 112.4(4)	−146.71(1)	38
	$^2\Pi_{1/2}$	2 356.6(4)		1 113.4(4)		
	$\tilde{A}^2\Sigma^+$	2 274.4(4)	552(1)	1 218.1(4)		
FCP^+	$\tilde{X}^2\Pi$	1 729(2)		765(1)	−190.2(6)	39
	$\tilde{A}^2\Sigma^+$	1 866(2)		817(2)		
HBS^+	$\tilde{X}^2\Pi_{3/2}$	2 746.8(4)	659(1)	975.9(4)	−322.6(4)	41
	$^2\Pi_{1/2}$	2 747.1(4)		≈991		
	$\tilde{A}^2\Sigma^+$	2 214.8(4)	550(1)	1 050.9(4)		
DBS^+	$\tilde{X}^2\Pi_{3/2}$	2 071.1(4)		937.4(4)	−322.2(4)	41
	$^2\Pi_{1/2}$	2 074.2(4)		≈993		
	$\tilde{A}^2\Sigma^+$	1 706.6(4)		1 011.1(4)		
FBS^+	$\tilde{X}^2\Pi_{3/2}$	1 721(2)	339(2)	637(2)	−339(2)	42
	$^2\Pi_{1/2}$	1 718(2)		633(2)		
	$\tilde{A}^2\Sigma^+$	1 718(2)		691(2)		
$ClBS^+$	$\tilde{X}^2\Pi$	1 347.8(8)		508.9(8)	−383(1)	42
	$\tilde{A}^2\Sigma^+$	1 390.6(8)		516.0(8)		

the $\tilde{X}^2\pi$ state and the two stretching modes in the $\tilde{A}^2\Sigma^+$ state (Table 3). These values have been obtained for the four isotopic derivatives, $H^{11}B^{32}S^+$, $H^{10}B^{32}S^+$, $D^{11}B^{32}S^+$, and $D^{10}B^{32}S^+$.[41]

In Table 3 are summarized the vibrational frequencies, and spin–orbit constants, determined from the emission spectra of all the XCP^+ and XBS^+ species studied. It can be seen that this approach has led to a fairly extensive vibrational characterization of these ions. With such information in hand, higher resolution studies using both visible and i.r. lasers, are now feasible.

B. Laser Excitation Spectroscopy.—As indicated in Figure 1, the laser excitation spectra lead primarily to a vibrational characterization of the ions in the excited electronic states. Thus it yields spectroscopic data which are complementary to those obtained from the emission spectra. The reason for this lies in the means of preparation of the ions in the two methods and is illustrated by two examples: the electronic transition of bromocyanoacetylene and of chloracetylene cations.

In Figure 4 are shown the spectra of the $\tilde{A}^2\Pi$—$\tilde{X}^2\Pi$ transition of $Br{-}C{\equiv}C{-}C{\equiv}N^+$ recorded in emission in a supersonic free jet (top trace) and as a laser excitation spectrum (bottom) at a reduced ambient temperature (100—150 K).[43] As is seen the emission and excitation spectra provide, almost exclusively, the vibrational characterization of the ion in the $\tilde{X}^2\Pi$ and $\tilde{A}^2\Pi$ states respectively. The explanation is straightforward. In the laser excitation approach the ions are prepared by

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[43] R. Kuhn, J. P. Maier, L. Misev, and T. Wyttenbach, *J. El. Spectrosc. Rel. Phenom.*, 1986, **41**, 265.

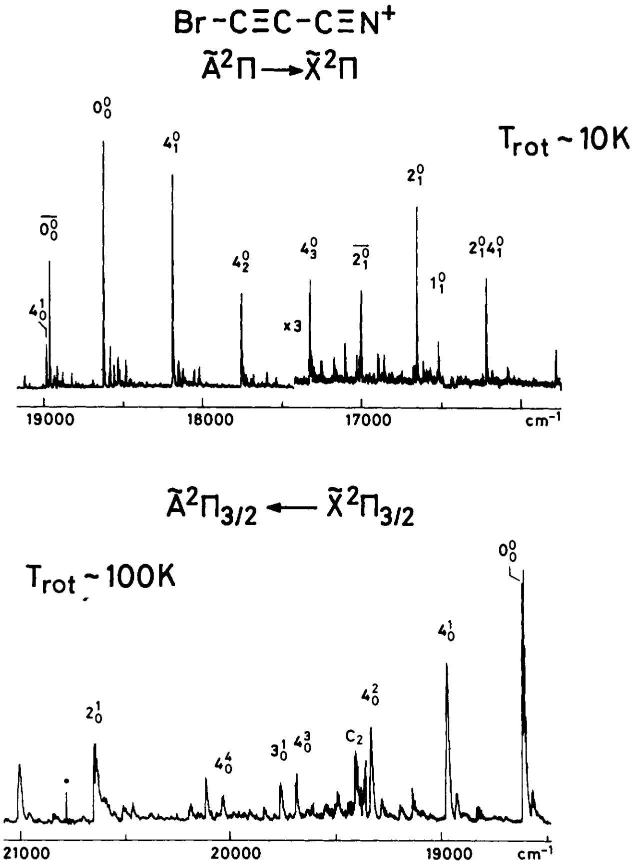

Figure 4 *The $\tilde{A}^2\Pi$—$\tilde{X}^2\Pi$ electronic transition of bromocyanoacetylene cation recorded in emission* (*top*—$T_{rot} \approx 10$ K, 0.05 nm fwhm) *and as laser excitation spectrum* (*bottom*—$T_{rot} \approx 100$ K, 0.02 nm fwhm). *The emission spectrum shows both $\Omega = 3/2$ and $1/2$* (*denoted with bar above the assignment*) *components, the excitation spectrum only $\Omega = 3/2$*

Penning ionization (with Ar or He metastables) and are subsequently collisionally relaxed by the excess of the rare gas atoms, which have been cooled by a liquid nitrogen environment. Thus the population of the ions is concentrated in the lowest vibrational level of the $\tilde{X}^2\Pi$ state and levels lying up to ≈ 500 cm^{-1} above may be populated to a few percent. The $^2\Pi_{1/2}$ component is also completely quenched as the spin–orbit splitting in the ground state of the ion is ≈ -900 cm^{-1}. The excitation spectrum is consequently relatively simple (Figure 4). The laser photons induce transitions from the lowest level (Σ^+ vibrational symmetry) of the $\tilde{X}^2\Pi_{3/2}$ state to the symmetry and Franck–Condon allowed levels of the $\tilde{A}^2\Pi_{3/2}$ state. As can be seen the v_4(C—Br str.) mode is particularly strongly excited; in addition the excitations of the v_2(C≡C str.), v_3(C–C str.); and of the degenerate modes v_6 and v_7 in double quanta are observed. A more complicated laser excitation spectrum would be obtained using ions produced under collision-free conditions.

The emission spectrum of bromocyanoacetylene cations cooled rotationally to 5—10 K (Figure 4) shows that the vibrational excitation is mainly in the $\tilde{X}^2\Pi$ state. Only the v_4 vibration, and those of the low frequency degenerate modes v_6 and v_7, which appear as sequence transitions to the red of each main band, are excited by one or two quanta in the $\tilde{A}^2\Pi$ state. Transitions between the $^2\Pi_{1/2}$—$^2\Pi_{1/2}$ components (denoted with a bar in the figure) are also seen because in the electron impact ionization of the molecular species in the $X^1\Sigma^+$ state both $\Omega = 3/2$ and $1/2$ components are populated. The $\tilde{A}^2\Pi \longleftarrow X^1\Sigma^+$ ionization process is fairly vertical (linearity is retained and all the internuclear distances are expected to be a little elongated) and only a few excited vibrational levels in the $\tilde{A}^2\Pi$ state are significantly populated because of the Franck–Condon factors.[44] In the $\tilde{A}^2\Pi \longrightarrow \tilde{X}^2\Pi$ emission, various levels in the $\tilde{X}^2\Pi$ state are accessed, those involving the v_4(C–Br str.) mode are prominent as in the excitation spectrum. This is expected because the main geometrical change on passing from the $\tilde{A}^2\Pi$ state is a decrease in the C–Br distance, which is readily predicted from the molecular orbital description of the electronic structure.[44] This is also reflected in the v_4 fundamental frequency changes: $X^1\Sigma^+$—419, $\tilde{X}^2\Pi_{3/2}$—438, $\tilde{A}^2\Pi_{3/2}$—359 cm^{-1}.[43] Thus in considering the vibrational activity in the emission spectrum, the transition probabilities involve three electronic states, $X^1\Sigma^+ \longrightarrow \tilde{A}^2\Pi \longrightarrow \tilde{X}^2\Pi$, whereas in the laser excitation spectrum only the two ionic states need to be considered.

The analysis of the emission and excitation spectra of bromocyanoacetylene cation yields the vibrational frequencies, to within ± 1—2 cm^{-1}, for most of the seven fundamentals in the $\tilde{X}^2\Pi$ and $\tilde{A}^2\Pi$ states. Such combined studies have been carried out for many of the ions listed in Table 1; tables of the ionic vibrational frequencies are to be found in the original references.

In the case of the $\tilde{A}^2\Pi$—$\tilde{X}^2\Pi$ transition of chloroacetylene cation, the emission spectrum[32] (Figure 2) also provided extensive information on the $\tilde{A}^2\Pi$ state. This is because the large geometry change on ionization to this state (C–Cl distance increase of ≈ 0.13 Å)[45] results in the population of a larger part of the upper state surface than with bromocyanoacetylene cation. The laser excitation spectrum, however, is again simple[34] (Figure 5) for the same reasons as discussed above. The vibronic structure is dominated by the excitation of the v'_3 mode in progression and combination series with the v_1(C–H) and v_2(C≡C) Σ_g^+ modes. Though the emission spectrum (Figure 2) also shows the v'_3 progression, the v'_1 and v'_2 modes are discernible only weakly, reflecting the small Franck–Condon factors to these levels in the $\tilde{A}^2\Pi$—$X^1\Sigma^+$ ionization step. The frequency values obtained by the emission and laser excitation approaches in conjunction are used for the completion of Table 2.

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[44] G. Bieri, E. Heilbronner, V. Hornung, E. Kloster-Jensen, J. P. Maier, F. Thommen, and W. von Niessen, *Chem. Phys.*, 1979, **36**, 1.

[45] P. Botschwina, P. Sebald, and J. P. Maier, *Chem. Phys. Lett.*, 1985, **114**, 353.

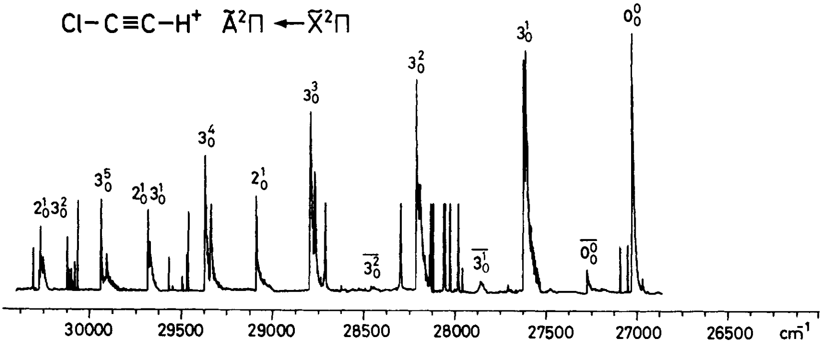

Figure 5 *Laser excitation spectrum of the* $\tilde{A}^2\Pi \longleftarrow \tilde{X}^2\Pi$ *transition of chloroacetylene cation* (0.005 nm fwhm). *The ions were prepared by Penning ionization with argon metastables and were collisionally relaxed to* $T_{\mathrm{rot}} \approx 100$ K. *The* $\Omega = 1/2$ *component bands are identified by the bar above the vibrational assignment; the sharp lines are atomic*

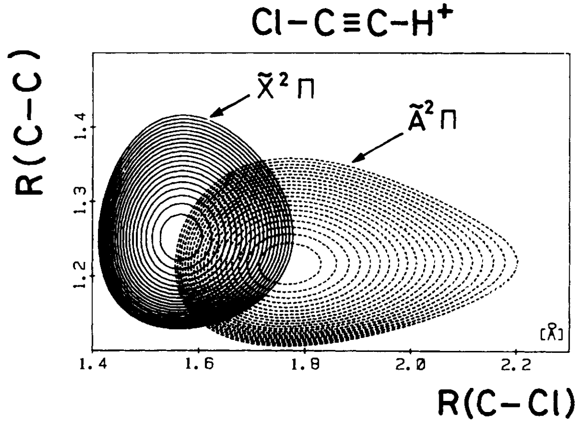

Figure 6 *Potential energy contour lines* (*in* 300 cm^{-1} *intervals*) *of chloroacetylene cation in its ground and first excited state obtained from* ab initio *calculations and some experimental data*[45]

In Figure 6 is reproduced a potential energy plot for the $\tilde{X}^2\Pi$ and $\tilde{A}^2\Pi$ states of chloroacetylene cation.[45] The ion is linear in the two states—this is proved from a rotational analysis of the $\tilde{A}^2\Pi$—$\tilde{X}^2\Pi$ transition[34]—and the C–Cl and C–C distances are the two coordinates. The C–H bond lengths are fixed. The potential energy functions were obtained from *ab initio* calculations, with some experimental data (v_2, v_3 frequencies and the rotational constants) as optimization parameters.

The relative positions of the surfaces show the reason for the extensive excitation of the v_2 mode in the emission and excitation spectra. On $\tilde{A}^2\Pi \longleftarrow X^1\Sigma^+$ ionization, the C–Cl and C–C distances increase by 0.13 Å and 0.05 Å, and in the $\tilde{A}^2\Pi \longrightarrow \tilde{X}^2\Pi$ transition the changes are a decrease of 0.20 Å (C–Cl) and an increase of 0.03 Å (C–C). The changes in the C–H distances are small (calculated to be less than 0.01 Å). The distance changes have also a marked and corresponding effect on the totally symmetric stretching vibrational frequencies (Table 2) because they are essentially localized: v_1(C–H), v_2(C–C), v_3(C–Cl). Thus the fundamental values are in the order $v_2(\tilde{X}^2\Pi) < v_2(\tilde{A}^2\Pi) < v_2(X^1\Sigma^+)$ and $v_3(\tilde{A}^2\Pi) < v_3(X^1\Sigma^+) < v_3(\tilde{X}^2\Pi)$, which reflect directly the described bond length changes (*cf.* Figure 6). On the basis of the v_1 frequencies one would expect the C–H distance to be slightly longer in the $\tilde{X}^2\Pi$ compared to the $\tilde{A}^2\Pi$ state. This is borne out by the calculations.[45]

Thus it is seen that the vibrational characterization of the ionic states leads to a detailed insight into the description of the electronic structure. The treatment could be taken further by construction of the force field based on the frequency data available for the various isotopes [^{35,37}Cl–C≡C–H(D)].

C. Absorption Spectroscopy in Neon Matrices.—In order to characterize ions which do not relax in their excited electronic states by emission of photons, and which are not therefore amenable to study by the methods discussed above, other approaches are required. Two such successful ones are based on direct absorption measurements either of vibrational–vibrational or electronic transitions. The former approach utilizes i.r. lasers and modulation techniques and has been applied to a variety of (mainly closed-shell) ions which can be produced in discharge sources in the gas phase.[6]

The second approach relies on the measurement of the absorption spectra of ions embedded in rare gas matrices.[46] Only a few studies have been carried out in the i.r.,[47] but the electronic transitions of many large unsaturated organic cations and anions have been observed in freon and some in argon matrices.[48] In such investigations the energy positions of the transitions were of interest; information on vibrational frequencies is rather limited. The latter is, however, exactly the focus of our studies, especially for the smaller open-shell cations.

The scheme for the generation of the ions in a neon matrix is depicted as part of Figure 1. The molecular precursors are deposited in a low concentration (typically in ratio 1 : 5 000) in a 5 K neon matrix and the ions to be studied are produced by photoionization with either a LiF windowed H(Ly α), or an open Ne(I) photon source. Because only 1 in 10^5—10^6 of the molecules present in the matrix are ionized, it is necessary to enhance the sensitivity of the absorption measurement. This is achieved by passing the light along the matrix, through its thin side, in a waveguide manner.[49] The path length is thus increased ≈200 fold. As the matrix is deposited on a rhodium-coated copper substrate, the differences in the refractive indices of the adjacent media ensure efficient total internal reflection of the light. The enhancement is sufficient for the absorption spectra of ions to be recorded using standard light sources and modulation techniques.

The first ions to be studied by this method were those of the fluorinated

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[46] V. E. Bondybey, T. A. Miller, and J. H. English, *J. Chem. Phys.*, 1980, **72**, 2193.

[47] L. Andrews, *Annu. Rev. Phys. Chem.*, 1979, **30**, 79.

[48] T. Shida, E. Haselbach. and T. Bally, *Acc. Chem. Res.*, 1984, **17**, 180.

[49] R. Rossetti and L. E. Brus, *Rev. Sci. Instrum.*, 1980, **51**, 467.

benzenes;[46,50] we have used this technique to characterize the ions of substituted (poly-) acetylenes. The vibrational information obtained relates to their excited electronic states since in the 5 K matrix the population is in the lowest vibrational level of the cationic ground state (*cf.* Figure 1).

Most of the earlier studies of the electronic spectra of ions in neon matrices, whether by direct absorption or by laser excitation spectroscopy, were concerned with comparing the inferred vibrational frequencies with the gas phase values for the ions known to fluoresce. The general conclusion is that, for polyatomic cations, the gas and neon matrix frequencies rarely differ by more than 5—10 cm^{-1}. The frequency of the electronic transition itself is significantly shifted owing to the difference in the interactions of the ground and excited state of the ion with the neon matrix. For the polyenes and aromatic cations, where the electronic transitions are of the $\pi^{-1} \longleftarrow \pi^{-1}$ type, a red shift of 100—200 cm^{-1} in the neon matrix is common. Recently, a detailed comparison of the vibrational frequencies of hexafluorobenzene cation in the matrix and gas phase have been discussed.[51] References to the matrix studies can be found in two reviews.[30]

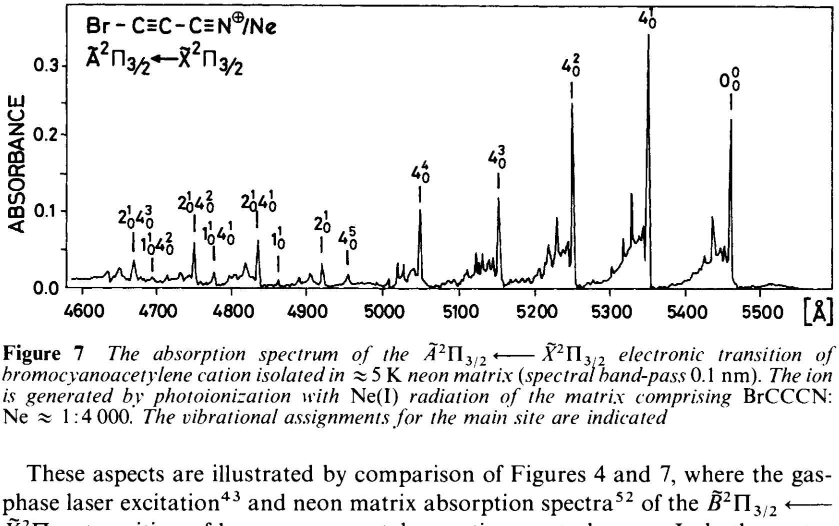

Figure 7 *The absorption spectrum of the* $\tilde{A}^2\Pi_{3/2} \longleftarrow \tilde{X}^2\Pi_{3/2}$ *electronic transition of bromocyanoacetylene cation isolated in* ≈ 5 K *neon matrix* (*spectral band-pass* 0.1 nm). *The ion is generated by photoionization with* Ne(I) *radiation of the matrix comprising* BrCCCN: Ne ≈ 1:4 000. *The vibrational assignments for the main site are indicated*

These aspects are illustrated by comparison of Figures 4 and 7, where the gas-phase laser excitation[43] and neon matrix absorption spectra[52] of the $\tilde{B}^2\Pi_{3/2} \longleftarrow \tilde{X}^2\Pi_{3/2}$ transition of bromocyanoacetylene cation are to be seen. In both spectra only the $\Omega = 3/2$ component is observed because of the reduced temperature of the ions initially prepared (≈ 100—150 K and 5 K respectively).

The vibrational pattern is similar in both spectra; in the matrix several sharp sites are apparent and the assignment is given for the main site. The bands are actually narrower in the matrix because sequence transitions involving the low frequency

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[50] V. E. Bondybey and T. A. Miller in 'Molecular Ions: Spectroscopy, Structure and Chemistry', ed. T. A. Miller and V. E. Bondybey, North-Holland, Amsterdam, 1983, p. 125.

[51] Y.-C. Hsu, R. A. Kennedy, T. A. Miller, L. A. Heimbrook, and V. E. Bondybey, *Mol. Phys.*, 1987, **61**, 225.

[52] S. Leutwyler, J. P. Maier, and U. Spittel, *J. Chem. Soc., Faraday Trans. 2*, 1985, **81**, 1565.

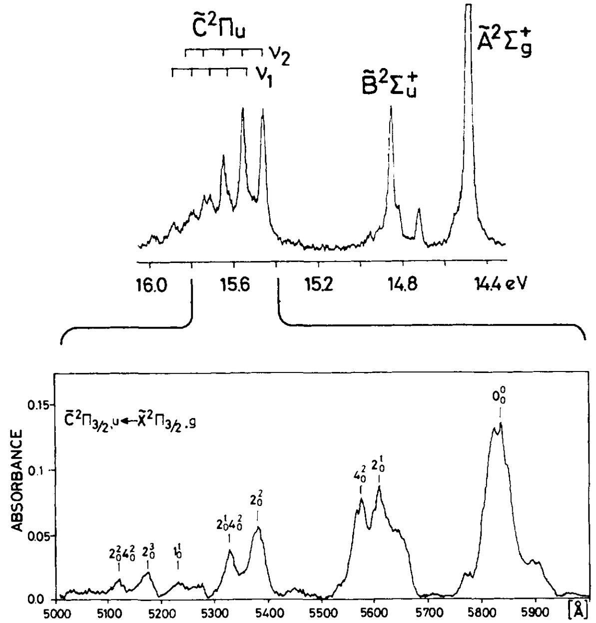

Figure 8 *The excited electronic states of cyanogen cation revealed by* He(Iα) *photoelectron spectroscopy* (*top*—≈ 80 cm^{-1} *resolution and by the absorption spectrum in a* 5 K *neon matrix* (*bottom*—4 cm^{-1} *optical band-pass*)
(Top spectrum redrawn by permission from ref. 16)

degenerate modes (ν_6, ν_7) are absent; at the higher vibrational temperature (100—150 K) of the gas phase excitation spectrum, they are discernible to the red of each progression and combination peak. In the latter spectrum there is also broadening and red-shading due to the rotational structure (Figure 4); lowering the rotational temperature to 5—10 K in a seeded supersonic free jet, leads to the narrow bands observed in the emission spectrum[43] (Figure 4, top).

In both spectra the prominent excitation is of the ν_4(C–Br str.) mode because of the considerable increase in C–Br distance during the $\tilde{B}^2\Pi \longleftarrow \tilde{X}^2\Pi$ transition. The frequencies of the four Σ^+ stretching modes, ν_1 to ν_4, can be inferred (with ± 4 cm^{-1} uncertainty) from the matrix spectrum; from the gas phase excitation spectrum (Figure 4), ν_2—ν_4 and ν_6, ν_7 fundamentals have been deduced. The complementary nature of the measurements is evident: when a particular mode is not easily located in the excitation spectrum, it may be discernible in the matrix absorption spectrum, and *vice versa*.

The matrix absorption technique has recently been used to obtain vibrational information on simple, fundamental, cations for which the only spectroscopic data available came by photoelectron spectroscopy, albeit at low resolution (100—200 cm^{-1}). Cyanogen cation is one such species and the photoelectron spectrum (top trace, Figure 8) yielded the ionization energies of the one-electron accessible doublet states and a few vibrational frequencies to within ±80 cm^{-1}.[53] Higher resolution data are obtained for the $\tilde{C}^2\Pi$ state of NCCN$^+$ by measurement of the $\tilde{C}^2\Pi_{3/2} \longleftarrow \tilde{X}^2\Pi_{3/2}$ absorption spectrum in a 5 K neon matrix (bottom trace Figure 8).[54] Although the bands are not as sharp as can be the case in the matrix (*cf.* Figure 7), owing to strong electron–phonon coupling and indistinct sites, the fundamental frequencies of this ion in the $\tilde{C}^2\Pi_{3/2}$ state can be deduced to ± 10 cm^{-1} for the $v_1' = 2\,020$ and $v_2' = 740$ cm^{-1} totally symmetric (Σ_g^+) stretching modes. The photoelectron spectrum yielded the values (±80 cm^{-1}) of 2 020 and 710 cm^{-1} respectively.[53] Similar studies of the absorption spectra of cyanoacetylene and methylcyanoacetylene cations in neon matrices have improved our knowledge of the vibrational frequencies of these ions in their excited electronic states.[54]

The observed frequency of the origin band of the electronic transition in the matrix can be used to make a good estimate for the expected location of the transition in the gas phase for more detailed studies using a method such as two-photon absorption of mass-selected ion beams.[55]

The above mentioned studies were an intermediate step towards one of the present goals—the spectral characterization of ions known only in mass-spectroscopic measurements, such as isomers and fragment ions. To this end, the ions are first studied in absorption in neon matrices, and then armed with the absorption data, higher resolution gas-phase laser methods are subsequently applied.

The first success in this direction has been the detection of the $\tilde{B}^4\Sigma_u^- \longleftarrow \tilde{X}^4\Sigma_g^-$ absorption spectrum of C_2^+ in a neon matrix.[56] The ion C_2^+ is invariably involved in the chemical reaction schemes in interstellar clouds, in plasmas, and in flames leading to the formation of hydrocarbons and clusters. It has also been recently detected in the comets Halley and Giacobini–Zinner by *in situ* mass-spectrometric sampling.[57] However, spectroscopic information on C_2^+ is scarce. A rotationally resolved gas-phase absorption spectrum, of $^2\Sigma^-$–$^2\Pi$ symmetry, has been attributed to C_2^+,[58] but this assignment has been questioned in two theoretical studies.[59] There also exists a low resolution measurement of electronic transitions of C_2^+ by translational energy-loss spectroscopy, where broad bands were observed[60] and assigned by comparison with calculations.

C_2^+ was produced by a two-step process: acetylene or chloroacetylene was embedded in low concentration in a 5 K neon matrix, C_2 was generated by photolysis with a Xe (147 nm) or H(Ly α) (121.6 nm) source, and C_2^+ by subsequent ionization with Ne(I) (73.6 nm) radiation. The absorption spectrum reproduced in

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[53] C. Baker and D. W. Turner, *Proc. R. Soc. London A*, 1968, **308**, 19.

[54] J. Fulara, S. Leutwyler, J. P. Maier, and U. Spittel, *J. Phys. Chem.*, 1985, **89**, 3190.

[55] P. O. Danis, T. Wyttenbach, and J. P. Maier, *J. Chem. Phys.*, 1988, **88**, 3451.

[56] D. Forney, H. Althaus, and J. P. Maier, *J. Phys. Chem.*, 1987, 1987, **91**, 6458.

[57] D. Krankowsky, P. Lämmerzahl, I. Herrwerth, J. Woweries, P. Eberhardt, U. Dolder, U. Herrmann, W. Schulte, J. J. Berthelier, J. M. Illiano, R. R. Hodges, and J. H. Hoffman, *Nature*, 1986, **321**, 326; M. A. Coplan, K. W. Ogilvie, M. F. A'Hearn, P. Bochsler, and J. Geiss, *J. Geophys. Res.*, 1987, **92**, 39.

[58] H. Meinel, *Can. J. Phys.*, 1972, **50**, 158.

[59] C. Petrongolo, P. J. Bruna, S. D. Peyerimhoff, and R. J. Buenker, *J. Chem. Phys.*, 1981, **74**, 4594; P. Rosmus, H.-J. Werner, E.-A. Reinsch, and M. Larsson, *J. El. Spectrosc. Rel. Phenom.*, 1986, **41**, 289.

[60] A. O'Keefe, R. Derai, and M. T. Bowers, *Chem. Phys.*, 1984, **91**, 161.

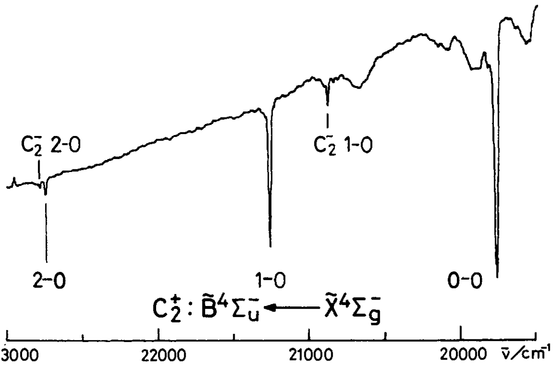

Figure 9 *The* $\tilde{B}^4\Sigma_u^- \longleftarrow \tilde{X}^4\Sigma_g^-$ *absorption spectrum of* C_2^+ *in a* 5 K *neon matrix.* C_2^+ *was produced from* ClCCH *deposited in the matrix by* Xe(I) (147 nm) *photolysis followed by* Ne(I) (73.6 nm) *photoionization.* C_2^- *is concomitantly formed and two of its* $\tilde{B}^2\Sigma_u^+ \longleftarrow \tilde{X}^2\Sigma_g^+$ *absorption bands are labelled*

Figure 9[56] is identified as the $\tilde{B}^4\Sigma_u^- \longleftarrow \tilde{X}^4\Sigma_g^-$ transition of C_2^+ on the basis of chemical evidence (using different precursors), isotopic shifts (using ^{13}C, D derivatives), and by comparison with the calculated term values and vibrational frequencies.[59] The agreement with the latter is excellent. Based on the matrix data this transition was found in the gas phase by the laser excitation approach, and the rotational structure proves the correctness of the assignment.[61] These experiments on C_2^+ pave the way for characterization of other fragment ions in the matrix and gas phase.

3 Rotational Characterization

In the case of the linear open-shell cations, predominantly those of tri- and tetra-atomics, it has proved possible to resolve the rotational structure in their electronic transitions.[25] Most of such studies have used the laser excitation approach; however, emission spectroscopy using electron excitation has proved valuable in two areas outlined in the next section. As far as triatomic cations are concerned, rotational analyses of the emission spectra, and some absorption spectra obtained by classical techniques, have been carried out in the past for CO_2^+, CS_2^+ ($\tilde{B}^2\Sigma_u^+$, $\tilde{A}^2\Pi_u$—$\tilde{X}^2\Pi_g$), N_2O^+($\tilde{A}^2\Sigma^+$—$\tilde{X}^2\Pi$), H_2O^+, H_2S^+ ($\tilde{A}^2A_1$—$\tilde{X}^2B_1$) and of some of their isotopic derivatives[62] and for diacetylene cation.[63]

A. Emission Spectroscopy.—The spectral characterization of the ions of unstable precursors, XCP^+, XBS^+ (X = H, D, F, Cl), has so far only been possible in emission (*cf.* Figure 3). However, in two of the studies, the attainable resolution ($\approx$ 0.005 nm) was sufficient to resolve the rotational structure in the emission band

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[61] M. Rösslein, M. Wyttenbach, and J. P. Maier, *J. Chem. Phys.*, 1987, **87**, 6770.

[62] See S. Leach, in 'Spectroscopy of the Excited State', ed. B. di Bartolo, Plenum Press, New York, 1976, p. 369; R. J. Saykally and R. C. Woods, *Annu. Rev. Phys. Chem.*, 1981, **32**, 403, for references therein.

[63] J. H. Callomon, *Can. J. Phys.*, 1956, **34**, 1046.

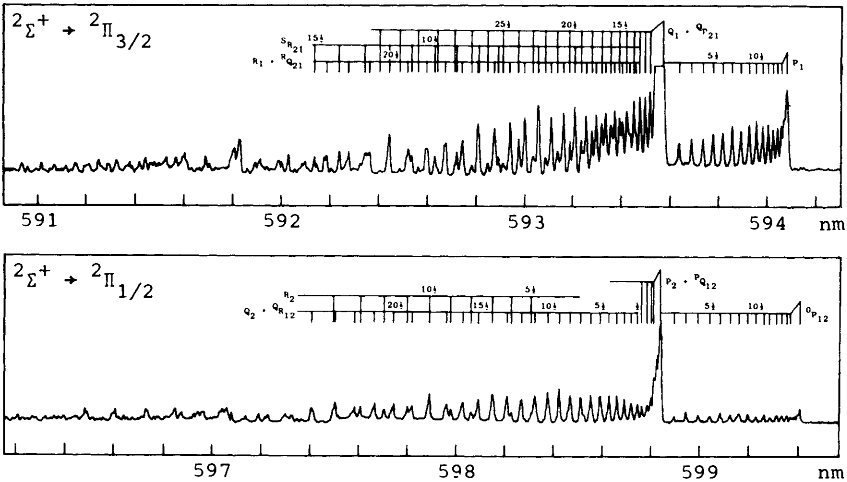

Figure 10 *Rotational structure of the origin band in the* $\tilde{A}^2\Sigma^+ \longrightarrow \tilde{X}^2\Pi$ *emission spectrum of deuterophosphaethyne cation* (0.008 nm fwhm). *The spectrum was obtained by* ≈ 40 eV *electron impact on an effusive source of the molecular precursor*

Table 4 *Rotational constants* (cm^{-1}) *of the polyatomic cations inferred recently from their laser excitation (LE) or emission (E) electronic spectra.*[a] *The constant for the most abundant naturally occurring isotope is given. References to the constants of the earlier studied triatomic cations*[b] *are to be found in two reviews*[62]

Cation	$B_{eff,0}$ $\tilde{X}^2\Pi_{3/2}$	$^2\Pi_{3/2}$	*Ref.*		
OCS^+	0.194 66(8)	0.186 89(8)	($\tilde{A}$)	LE	73
$ClCN^+$	0.204 433 (50)	0.176 60(13)	($\tilde{B}$)	LE	74
$^{79}BrCN^+$	0.141 612 (44)	0.127 474 (45)	($\tilde{B}$)	LE	75
$ClCCH^+$	0.194 647 (49)	0.170 881 (48)	($\tilde{A}$)	LE	34
$^{79}BrCCH^+$	0.137 794 (37)	0.121 351 (36)	($\tilde{A}$)	LE	69
$ICCH^+$	0.109 59(7)	0.096 69(7)	($\tilde{A}$)	LE	72
	B_0 $\tilde{X}^2\Pi$	$\tilde{A}$			
HCP^+	0.622 4(16)	0.669 0(17)	($^2\Sigma^+$)	E	64
HBS^+	0.576 0(2)	0.614 8(2)	($^2\Sigma^+$)	E	65[c]
$H(CC)_2H^+$	0.146 90(4)	0.140 09(4)	($^2\Pi$)	LE	70

[a] Values in brackets correspond to one standard deviation. [b] CO_2^+, CS_2^+, N_2O^+, H_2O^+, H_2S^+. [c] In the given reference, these constants were incorrectly attributed to states of BS

systems. These were the $\tilde{A}^2\Sigma^+ \longrightarrow \tilde{X}^2\Pi$ transitions of HCP^+, DCP^+,[64] HBS^+, and DBS^+.[41] Such a recording for DCP^+ is reproduced in Figure 10 where the assignment of the rotational lines is indicated. From the analysis the rotational constants for HCP^+, DCP^+ were derived[64] and these are to be found in Table 4.

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[64] M. A. King, D. Klapstein, H. W. Kroto, J. P. Maier, and J. F. Nixon, *J. Mol. Spectrosc.*, 1982, **80**, 23.

The values given there for HBS^+ were not determined in our studies, because the rotational constants were already available in the literature;[65] they were, however, incorrectly attributed to two electronic states of BS of $^2\Sigma^+$ and $^2\Pi$ symmetry. The vibrational and isotopic (DBS^+) analyses of the emission spectra showed conclusively that the reported band system and constants are of the $\tilde{A}^2\Sigma^+$ and $\tilde{X}^2\Pi$ states of HBS^+.[41] Higher resolution studies of the ions XCP^+, XBS^+ await the application of the laser excitation technique, but are hampered by the difficulties of preparing such species in sufficient quantities.

The second area where the emission technique, in combination with supersonic free jets, has proved successful is in the study of the rotational structure in the electronic transition of di- and tri-atomic ions at low temperatures. Thus the rotational pattern of vibronic bands of the $\tilde{A}^2A_1 \longrightarrow \tilde{X}^2B_1$ transition of H_2O^+ was investigated[66] under the temperature conditions encountered in extra-terrestrial environments, such as in comets, where this fluorescence has been detected.[67] The 'desired' rotational temperature is tuned by choice of the expansion conditions and is determined by comparison with measurements of the rotational distribution of transitions such as $\tilde{B}^2\Sigma_u^+—\tilde{X}^2\Sigma_g^+$ of N_2^+, or $\tilde{A}^2\Sigma^+—\tilde{X}^2\Pi$ of N_2O^+.

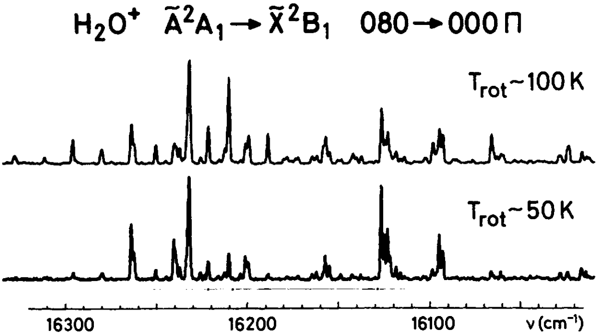

Figure 11 *The rotational structure of the* 080—000 Π *sub-band in the* $\tilde{A}\ ^2A_1 \longrightarrow \tilde{X}^2B_1$ *emission spectrum of* H_2O^+ *at two reduced rotational temperatures, obtained by* ≈200 eV *electron impact on a seeded helium supersonic free jet* (0.045 nm *resolution*). *The chosen temperatures are typical of comet tails*

In Figure 11 is shown the rotational structure of the 8—0 Π sub-band within the $\tilde{A}^2A_1 \longrightarrow \tilde{X}^2B_1$ emission system of H_2O^+ at rotational temperatures of ≈ 50 K (bottom trace) and ≈ 100 K (top). The temperatures were actually evaluated from the pattern of the Σ components of the 8—0 transitions, for reasons which are discussed in the original study.[66] The temperatures of 50 and 100 K were chosen because these correspond to comet tail measurements of these bands at particular heliocentric distances. Some such cometary spectra can be found in reference 68.

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[65] J. K. McDonald and K. K. Innes, *J. Mol. Spectrosc.*, 1969, **29**, 251.

[66] S. Leutwyler, D. Klapstein, and J. P. Maier, *Chem. Phys.*, 1983, **74**, 441.

[67] P. A. Wehinger, S. Wyckoff, G. H. Herbig, G. Herzberg, and H. Lew. *Astrophys. J.*, 1974, **190**, L43.

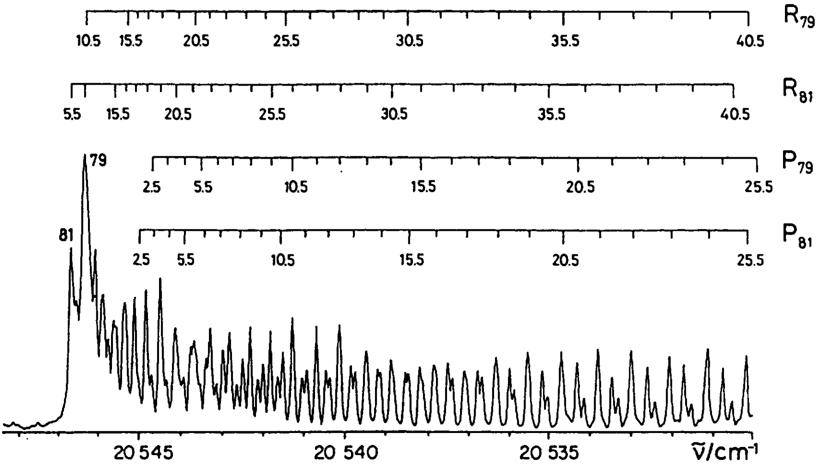

Figure 12 *Rotationally resolved origin band* (0.0008 nm fwhm) *in the* $\tilde{A}^2\Pi_{3/2}$ *laser excitation spectrum of deuterobromoacetylene cation. The ions are produced by Penning ionization and collisional relaxation* ($T_{\rm rot} \approx$ 100 K). *The* 79 *and* 81 *labels identify the two equally abundant bromine isotopic derivatives*

Prior to the experimental observations at the reduced rotational temperatures, the line intensities were determined using the known rotational constants of H_2O^+ and calculated line strengths of the $^2A_1$—$^2B_1$ transitions.[68] As our study showed,[66] however, there are considerable differences between the predicted and observed spectra, probably due to uncertainties in the calculated line strengths. One may now instead use the experimental data (Figure 11) in a direct comparison with the cometary spectra for temperature and other determinations. This example illustrates how the techniques can be used to provide information on physicochemical parameters of inaccessible environments. Related applications in the laboratory can be envisaged for plasma and flame-characterizations using ions which are often present in such media.

B. Laser Excitation Spectroscopy.—The laser excitation approach lends itself favourably to studies of the rotational structure of electronic transitions because, unlike the situation with the emission approach where the intensity limits the useable resolution of the monochromator, narrowing the laser band-width with an intracavity etalon does not cause deterioration in the signal-to-noise ratio of the experiment.

In Figure 12 is shown the rotationally resolved origin band in the $\tilde{A}^2\Pi_{3/2} \longleftarrow \tilde{X}^2\Pi_{3/2}$ excitation spectrum of deuterobromoacetylene cation recorded with 0.03 cm^{-1} laser band pass.[69] The ions were produced by Penning ionization with argon

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[68] S. Wyckoff and P. A. Wehinger, *Astrophys. J.*, 1976, **204**, 616.

[69] M. A. King, J. P. Maier, L. Misev, and M. Ochsner, *Can. J. Phys.*, 1984, **62**, 1437.

metastables and were collisionally relaxed and thus only the $\Omega = 3/2$ sub-component bands were detected because the spin–orbit splitting in the ground cation state is $\approx -1\,000\ \mathrm{cm}^{-1}$.[33] The rotational and vibrational temperature of the ions is estimated as 100—150 K.

The rotational structure is composed of two overlapping R and two P branches due to the two naturally occuring isotopic forms, ^{79}Br–C≡C–D$^+$ and ^{81}Br–C≡C–D$^+$. The head is in the R branch and the band is red-shaded (*i.e.* $B' < B''$); the Q-branch is too weak to be detected at the temperature of the measurement but should, however, become apparent by lowering the temperature to below about 20 K (as has been demonstrated on the $\tilde{A}^2\Pi$—$\tilde{X}^2\Pi$ transition of diacetylene cation conducted in a supersonic free jet[70]). The assignment of the lines in the respective branches is indicated in Figure 12.

Such recordings have been made on a number of bands of the v_3'(C–Br str.) progression for both HCCBr$^+$ and DCCBr$^+$. The rotational analyses show that the ions are linear in the $\tilde{X}^2\Pi$ and $\tilde{A}^2\Pi$ states. The rotational and related constants were obtained by fitting the observed line positions to the differences of the eigenvalues of lower and upper state effective Hamiltonian matrices. The actual expression used for each state

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

is derived from the diatomic matrix elements[71] and second order perturbation correction for the $\Omega = 1/2$ sub-component which is not sampled in the experiment.[69] The $B_{\mathrm{eff..0}}$ values are given in Table 4 for the most abundant isotopic variants of bromoacetylene cation, as well as for chloro-[34] and iodo-acetylene[72] cations where corresponding measurements and analyses have been completed.

A complete r_s structure of the halogenoacetylene ions in the ground and first excited electronic states is not yet available as only the terminal atoms were isotopically substituted (*i.e.* either H/D or ^{79,81}Br, ^{35,37}Cl). However, the data obtained show, for example for HCCBr$^+$, that the average H—Br distances are 3.94 and 4.07 Å in the $\tilde{X}^2\Pi$ and $\tilde{A}^2\Pi$ states respectively, as compared with 4.05 Å for the neutral molecule.[69] As has been discussed for the chloroacetylene ion earlier, the dominant reason for the difference in the H • • • X distance in the two states is the change in the C—X distance (*cf.* Figure 6).

Apart from the halogenoacetylene cations, the laser excitation approach has been used to obtain the rotational structure of the origin bands in the $\tilde{A}^2\Pi_{3/2}$—$\tilde{X}^2\Pi_{3/2}$ transition of OCS$^+$,[73] and of the $\tilde{A}^2\Pi^{\Omega}\tilde{X}^2\Pi$ one of H(CC)$_2$H$^+$ and D(CC)$_2$D$^+$.[70] Most recently the $\tilde{B}^2\Pi$—$\tilde{X}^2\Pi$ band systems of chloro-[74] and bromo-cyanide[75] cations have been rotationally analysed (*cf.* Table 4).

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[70] R. Kuhn, J. P. Maier, and M. Ochsner, *Mol. Phys.*, 1986, **59**, 441.

[71] R. N. Zare, A. L. Schmeltekopf, W. J. Harrop, and D. L. Albritton, *J. Mol. Spectrosc.*, 1973, **46**, 37.

[72] J. P. Maier and M. Ochsner, *J. Chem. Soc., Faraday Trans. 2*, 1985, **81**, 1587.

[73] M. Ochsner, M. Tsuji, and J. P. Maier, *Chem. Phys. Lett.*, 1985, **115**, 373.

[74] F. G. Celii, M. Rösslein, M. A. Hanratty, and J. P. Maier, *Mol. Phys.*, 1988, **62**, 1435.

[75] M. A. Hanratty, M. Rösslein, F. G. Celli, T. Wyttenbach, and J. P. Maier, *Mol. Phys.*, 1988, in press.

4 Outlook

Concurrent with the spectral characterization of open-shell cations by the methods described above has been the development of other approaches for probing such ions at higher resolution and of the different detection schemes required for other ions. In the former category belongs stimulated emission pumping. This technique has proved useful for the spectroscopic studies of stable molecules in highly excited vibrational levels of the ground state manifold.[76] We have recently shown, with experiments on diacetylene cation, that this is also a viable and attractive approach for the study of reactive species produced in small concentrations, such as open-shell cations.[77]

The method, which depends on the fluorescence of the ions in the excited electronic state, uses two laser wavelengths. One is used to transfer the population from the ground to the excited state, whereas the second laser stimulates the transitions to the chosen level of the ground state. Detection is by measuring changes in the fluorescence intensity from the excited state.

One of the features of interest of the stimulated emission pumping method is that it opens the way for the study of vibrational levels of the ions in their ground states at higher resolution than is attainable with the emission approach using a monochromator. Furthermore, as the transitions to the ground state manifold are driven by the laser, many more vibrational levels become accessible. Thus precise vibrational frequencies of the levels, and for the smaller ions the rotational constants, can be determined. The double resonance nature of the measurement is often useful in assignment clarifications. It is envisaged that the method could also be used for the preparation of ions in selected vibrational levels for subsequent ion–molecule reactions, in a similar way to that demonstrated for molecules.[78]

The major effort using the matrix absorption and laser excitation techniques is at present directed towards spectral characterization of ions known so far only by mass spectrometry. The first step in this direction has been the identification of the $\tilde{B}^4\Sigma_u$—$\tilde{X}^4\Sigma_g^-$ transition of C_2^+ in absorption in a 5 K neon matrix.[56] Based on this observation the corresponding laser excitation spectrum of C_2^+ in the gas-phase was found and rotationally analysed.[61] The use of the matrix and gas-phase techniques in tandem is clearly advantageous for the characterization of other simple fragment ions.

Another approach with this aim, but also for ions which do not decay radiatively, is centred on a mass-selected ion beam in conjunction with laser excitation. Several groups have successfully employed such an approach where, with the exception of a few studies which used charge-transfer reactions to monitor the electronic transition,[79] the detection relied on the predissociation of the excited state.[80] The approach we have been pursuing is more general: the electronic transition of a mass-

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[76] C. E. Hamilton, J. L. Kinsey, and R. W. Field, *Annu. Rev. Phys. Chem.*, 1986, **37**, 493.

[77] F. G. Celii, J. P. Maier, and M. Ochsner, *J. Chem. Phys.*, 1986, **85**, 6230.

[78] S. H. Kable and A. E. W. Knight, *J. Chem. Phys.*, 1987, **86**, 4709.

[79] A. Carrington, D. R. J. Milverton, and P. J. Sarre, *Mol. Phys.*, 1978, **35**, 1505.

[80] See for example S. P. Goss, R. G. McLoughlin, and J. D. Morrison, *Int. J. Mass Spectrom. Ion Phys.*, 1985, **64**, 213.

selected ion beam is induced by one laser wavelength and a second laser colour then produces a daughter ion. The latter is detected as the first laser wavelength is scanned to record the spectrum of the chosen ion. The apparatus is a triple quadrupole system with a high pressure source to produce collisionally relaxed ions for the mass selection. The feasibility of this method has now been demonstrated on the $\tilde{C}\,^2\Sigma_g^+ \longleftarrow \tilde{B}\,^2\Sigma_u^+ \dashleftarrow \tilde{X}\,^2\Pi_g$ transitions of CS_2^+—the $\tilde{C}\,^2\Sigma_g^+$ state leads to the production of S^+ ions which are monitored—and on analogous transitions of N_2O^+ and $CO_2{}^+$.[55] This paves the way for the spectral characterization of a variety of ions which can be generated by fragmentation and ion molecule reactions.

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