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Spectroscopic Studies of Open-Shell Organic Cations in the Gas Phase*

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Abstract

The spectroscopic investigations of the radiative decay of open-shell organic cations in the gas phase are reviewed. The studies carried out were focused on the detection of emission spectra, which were discovered for around hundred such cations. The emission spectra enabled the vibrational frequencies of several of the totally symmetric fundamentals of these cations in their ground states to be inferred and the lifetimes in the excited electronic state to be directly measured. Detailed studies of the relaxation channels and of the rate constants were based on the determined lifetimes, as well as on ancillary data forthcoming from other techniques, such as when fragmentation pathways are also accessible. The knowledge thus acquired on the relaxation behaviour of electronically excited open-shell cations under isolated conditions is discussed.

Introduction

In this article the spectroscopic studies of open-shell organic cations in the gaseous phase which have been carried out in Basel in the past five years will be reviewed. These investigations have been centered on the detection of the radiative decay of the electronically excited cations. In many cases where emission spectra could be obtained, the vibrational frequencies of several of the totally symmetric modes for the respective cations in their ground states could be determined and their lifetimes in the lowest vibrational levels of the excited electronic state could be directly measured. As a consequence of these results, information forthcoming from other techniques probing the cationic decay e.g. via fragment ions, has been used to provide a more detailed insight into the fate of electronically excited open-shell cations under isolated conditions.

The search for the emission spectra of organic cations was commenced in 1974. At that time, the emission spectra of the following six triatomic cations, as well as of diacetylene cation, (and of their isotopes) were known.

CO_2^+	$\tilde{B}\,^2\Sigma_u^+, \tilde{A}\,^2\Pi_u \rightarrow \tilde{X}\,^2\Pi_g$	[1]
CS_2^+	$\tilde{B}\,^2\Sigma_u^+, \tilde{A}\,^2\Pi_u \rightarrow \tilde{X}\,^2\Pi_g$	[2]
COS^+	$\tilde{A}\,^2\Pi \rightarrow \tilde{X}\,^2\Pi$	[3]
N_2O^+	$\tilde{A}\,^2\Sigma^+ \rightarrow \tilde{X}\,^2\Pi$	[4]
H_2S^+	$\tilde{A}\,^2A_1 \rightarrow \tilde{X}\,^2B_1$	[5]
H_2O^+	$\tilde{A}\,^2A_1 \rightarrow \tilde{X}\,^2B_1$	[6]
$H\text{-}(C\equiv C)_2\text{-}H^+$	$\tilde{A}\,^2\Pi_u \rightarrow \tilde{X}\,^2\Pi_g$	[7]

The given references are of some of the high resolution studies and for further references two reviews on this topic should be consulted [8, 9].

The energy location of the doublet states of cations, which can be sufficiently populated in a dipole allowed process, became quite generally available only with the advent of photoelectron spectroscopy [10]. In fact, the identification of the band systems attributed to H_2O^+ and H_2S^+ were aided by the photoelectron spectroscopic measurements. From the photoelectron spectrum one could predict where the $\tilde{A} \rightarrow \tilde{X}$ electronic transition of the open-shell cation of interest would be expected and from the shape and structure of the photoelectron bands, whether it was likely that the radiative decay could be detected. Thus, in 1971, *Turner* and coworkers observed a "broad" fluorescence band when hexafluorobenzene gas was irradiated with the He(Iα), 21.22 eV, photon resonance line [11]. The wavelength region of this band (max $\approx$ 475 nm) corresponded to the energy gap between the first two bands in the photoelectron spectrum of hexafluorobenzene and was thus attributed to the $\tilde{A} \rightarrow \tilde{X}$ transition of this cation.

The approach which we adopted in Basel was to systematically search for the emission spectra of polyatomic cations using low energy (20–40 eV) electron impact excitation and by utilising the data on the cationic states obtained by photoelectron spectroscopy. Information on the fragmentation processes was sometimes available from a variety of techniques ranging from fragment ion appearance potentials measurements [12] to studies of state selected cations using photoelectron-photoion coincidence [13] and photodissociation [14] spectroscopies.

The crossed electron beam-sample apparatus which was constructed is shown schematically in fig. 1 [15]. An electron beam was chosen for the excitation for intensity reasons compared to photon sources, and the low electron energy in order to profit from the favour-

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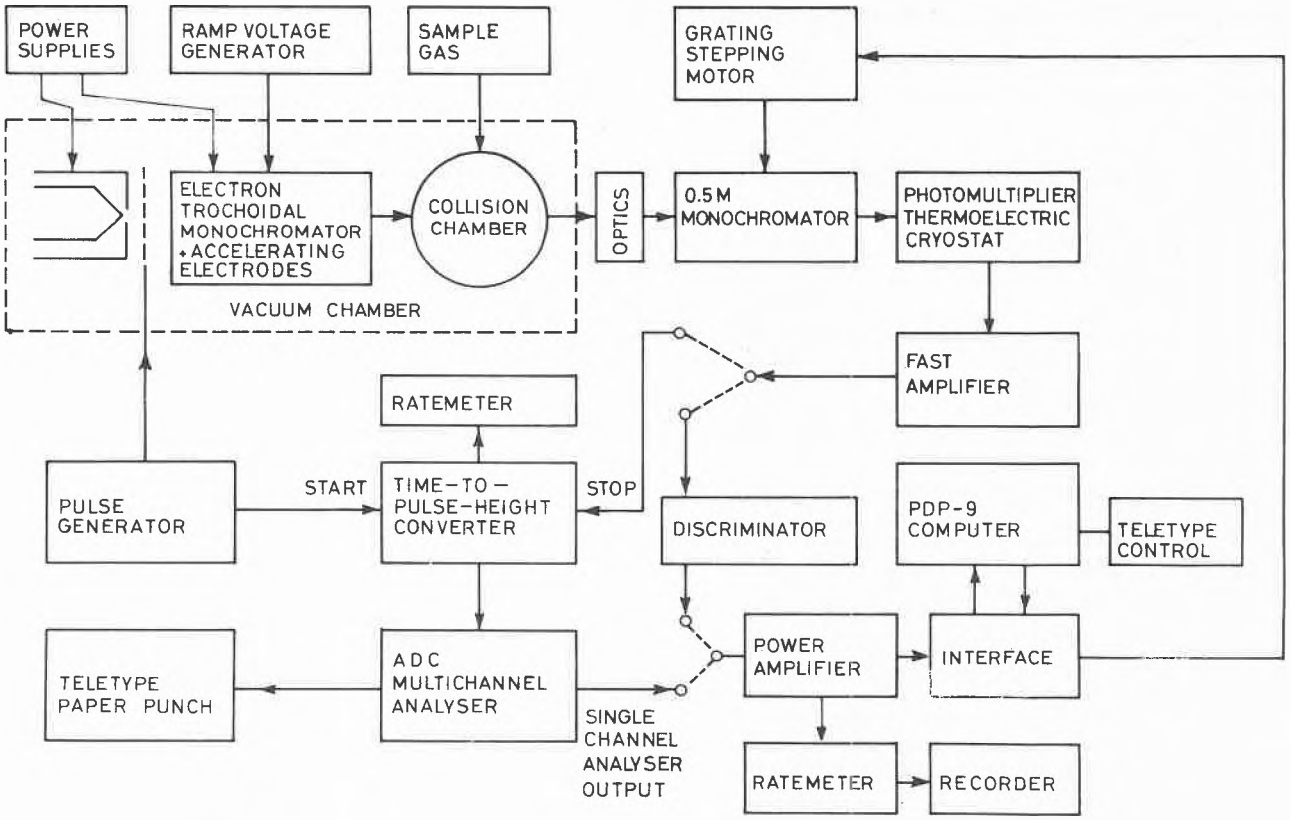

Fig. 1: Block diagram of the apparatus used for the investigations of radiative decay of cations in the gaseous phase.

able ionisation cross-section at energies ≈ 10–20 eV above the threshold and to minimize the fragment ion emissions. The latter are present concurrently as a result of the non-specificity of the electron impact processes.

Furthermore, it was desirable to record the excitation functions of selected emission bands to obtain the thresholds. These can be used in the identification; for example in the case of cations, by comparison with the ionisation energy required to form the cation in the excited state measured by photoelectron spectroscopy. Thus, in one of the modes of operation (cf. fig. 1), the incident electron energy is scanned. The other mode is a pulsed one, which is achieved by gating the electron beam, typically at frequencies up to 500 kHz, to produce electron pulses 20–70 ns wide and with a time resolution of ≈ 6 ns. This enabled us to measure lifetimes of selected vibrational levels in the excited electronic state of the cation (following the assignment of the emission bands) and also to record emission spectra in a chosen time interval following the excitation ("time-resolved spectra").

1. Emission spectra

As a result of such investigations [16], the emission spectra of around hundred polyatomic open-shell cations have been discovered, recorded and in many cases vibrationally analysed. In table 1 are collected most of these cations, their detected emission band systems, and the references to the reported studies.

In fig. 2 are shown two emission spectra of "small" cations i. e. of dicyanoacetylene and of dicyanodiacetylene. These spectra have been recorded in the indicated time intervals with the apparatus of fig. 1 operating in the pulsed mode. In these time resolved spectra the emission bands of the cyanogen radical ($A\,^2\Pi \rightarrow X\,^2\Sigma^+$) are suppressed, as otherwise they tend to obscure the emission bands of the parent cations. Both of these spectra may be of astrophysical interest in view of the detection of monocyanopolyacetylenes, $H{-}(C{\equiv}C)_n{-}CN$, n = 1–4, in the interstellar medium via their microwave transitions [39]. On the other hand, for the corresponding dicyano derivatives lacking the necessary microwave transitions, these optical transitions (cf. fig. 2) may be used as the probe. In addition, the $\tilde{A}\,^2\Pi \rightarrow \tilde{X}\,^2\Pi$ emission system of cyanodiacetylene cation has also been recently detected [26]. The primary information extracted from the emission spectra, recorded with optical resolutions (fwhm) 0.1 to 0.5 nm, are vibrational frequencies for the cationic ground states. By and large, the bands which are strongly excited in the spectra have been assigned to transitions from the zeroth vibrational level of the $\tilde{A}$ state to vibrational levels of the $\tilde{X}$ state which correspond to the excitation of the totally symmetric fundamentals, their overtones and combinations. Apart

Table 1: Polyatomic cations for which emission spectra have been detected and their measured lifetimes (τ) in the excited electronic state (zeroth vibrational level). The assumed symmetry is given.

Cation		Transition	τ (ns)	References
$Cl-C\equiv N^+$	$C_{\infty v}$		205 ± 20	[17]
			≥ 4400	
$Br-C\equiv N^+$			270 ± 30	[17]
		$\tilde{B}\ ^2\Pi \rightarrow \tilde{X}\ ^2\Pi$	≥ 3000	
$I-C\equiv N^+$		$\tilde{A}\ ^2\Sigma^+ \rightarrow \tilde{X}\ ^2\Pi$	300 ± 30	[17]
			≥ 1200	
$Cl-C\equiv C-H^+$	$C_{\infty v}$		17 ± 3[a]	[18]
		$\tilde{A}\ ^2\Pi \rightarrow \tilde{X}\ ^2\Pi$		
$Br-C\equiv C-H^+$			12 ± 3[a]	[18]
$I-C\equiv C-H^+$			15 ± 3[a]	[18]
$Cl-C\equiv C-Cl^+$	$D_{\infty h}$		13 ± 2[a]	[19]
$Br-C\equiv C-Br^+$			28 ± 3[a]	[19]
$I-C\equiv C-I^+$		$\tilde{A}\ ^2\Pi_g \rightarrow \tilde{X}\ ^2\Pi_u$	51 ± 5[a]	[19]
$H-(C\equiv C)_2H^+$			71 ± 3	[20]
$D-(C\equiv C)_2D^+$			78 ± 4	[20]
$Cl-(C\equiv C)_2H^+$	$C_{\infty v}$	$\tilde{A}\ ^2\Pi \rightarrow \tilde{X}\ ^2\Pi$	41 ± 2	[21]
$Br-(C\equiv C)_2H^+$			27 ± 3	[21]
$F-(C\equiv C)_2F^+$	$D_{\infty h}$		28 ± 3	[22]
$Cl-(C\equiv C)_2Cl^+$		$\tilde{A}\ ^2\Pi_u \rightarrow \tilde{X}\ ^2\Pi_g$	21 ± 3[a]	[23]
$Br-(C\equiv C)_2Br^+$			12 ± 2	[23]
$I-(C\equiv C)_2I^+$			≤ 6	[23]
$N\equiv C-C\equiv C-C\equiv N^+$	$D_{\infty h}$	$\tilde{A}\ ^2\Sigma_g^+ \rightarrow \tilde{X}\ ^2\Pi_u$	13 ± 2	[24]
cis-1,2-difluoroethylene$^+$	C_{2v}	$\tilde{A}\ ^2A_1 \rightarrow \tilde{X}\ ^2B_1$	320 ± 30	[25]
$H-(C\equiv C)_2-C\equiv N^+$	$C_{\infty v}$	$\tilde{A}\ ^2\Pi \rightarrow \tilde{X}\ ^2\Pi$	15 ± 2	[26]
$CH_3-C\equiv C-Cl^+$	C_{3v}	$\tilde{A}\ ^2E \rightarrow \tilde{X}\ ^2E$	19 ± 3[a]	[21]
$CH_3-C\equiv C-Br^+$			13 ± 3[a]	[21]
$H-(C\equiv C)_3H^+$	$D_{\infty h}$	$\tilde{A}\ ^2\Pi_g \rightarrow \tilde{X}\ ^2\Pi_u$	17 ± 2	[20]
$N\equiv C-(C\equiv C)_2C\equiv N^+$	$D_{\infty h}$	$\tilde{A}\ ^2\Pi_u \rightarrow \tilde{X}\ ^2\Pi_g$	≤ 6	[27]
$CH_3-(C\equiv C)_2H^+$	C_{3v}		48 ± 3	[28]
$CH_3-(C\equiv C)_2D^+$			46 ± 3	[28]
$CD_3-(C\equiv C)_2H^+$			51 ± 3	[28]
$CD_3-(C\equiv C)_2D^+$		$\tilde{A}\ ^2E \rightarrow \tilde{X}\ ^2E$	53 ± 3	[28]
$CH_3-(C\equiv C)_2Cl^+$			22 ± 2	[21]
$CH_3-(C\equiv C)_2Br^+$			10 ± 2	[21]
$CF_3-(C\equiv C)_2F^+$			30 ± 3	[22]
$H-(C\equiv C)_4H^+$	$D_{\infty h}$	$\tilde{A}\ ^2\Pi_u \rightarrow \tilde{X}\ ^2\Pi_g$	≤ 6	[20]
$CH_3-(C\equiv C)_2C\equiv N^+$	C_{3v}	$\tilde{A}\ ^2E \rightarrow \tilde{X}\ ^2E$	8 ± 2	[26]
$CH_3-(C\equiv C)_2CH_3^+$	D_{3d}		24 ± 2	[29]
$CH_3-(C\equiv C)_2CD_3^+$			28 ± 3	[28]
$CD_3-(C\equiv C)_2CD_3^+$		$\tilde{A}\ ^2E_u \rightarrow \tilde{X}\ ^2E_g$	32 ± 3	[28]
$CF_3-(C\equiv C)_2CF_3^+$			46 ± 2	[22]
$C_2H_5-(C\equiv C)_2H^+$	C_s	$\tilde{A}\ ^2A'' \rightarrow \tilde{X}\ ^2A''$	≤ 6	[29]
B-trifluoroborazine$^+$	D_{3h}	$\tilde{A}\ ^2A_2'' \rightarrow \tilde{X}\ ^2E''$	≤ 6	[30]
1,3-difluorobenzene$^+$			≤ 6	[31]
1,3,5-trifluorobenzene$^+$			58 ± 2	[31]
1,2,4-trifluorobenzene$^+$			10 ± 2	[31]
1,2,3,4-tetrafluorobenzene$^+$		$\tilde{B}(\pi^{-1}) \rightarrow \tilde{A}(\pi^{-1}), \tilde{X}(\pi^{-1})$	50 ± 2	[31]
1,2,3,5-tetrafluorobenzene$^+$			50 ± 2	[31]
1,2.4,5-tetrafluorobenzene$^+$			30 ± 2	[31]
Pentafluorobenzene$^+$			47 ± 2	[31]
Hexafluorobenzene$^+$			48 ± 2	[31]
1,3-dichlorobenzene$^+$			≤ 6	[32]
1,4-dichlorobenzene$^+$		$\tilde{B}(\pi^{-1}) \rightarrow \tilde{A}(\pi^{-1}), \tilde{X}(\pi^{-1})$	≤ 6	[32]
1,3,5-trichlorobenzene$^+$			22 ± 2	[32]

Cation		Transition	τ (ns)	References
1-chloro-3,5-difluorobenzene$^+$		$\tilde{B}(\pi^{-1}) \rightarrow \tilde{A}(\pi^{-1}), \tilde{X}(\pi^{-1})$	≤ 6	[33]
1-chloro-2,3,6-trifluorobenzene$^+$			21 ± 3	[33]
1-chloro-2,4,5-trifluorobenzene$^+$			≤ 6	[33]
1-chloro-2,3,4,5-tetrafluorobenzene$^+$			27 ± 2	[33]
1-chloro-2,3,5,6-tetrafluorobenzene$^+$			52 ± 2	[33]
1-chloro-pentafluorobenzene$^+$			43 ± 3	[33]
1,3-dichloro-2-fluorobenzene$^+$			14 ± 3	[33]
1,3-dichloro-4-fluorobenzene$^+$			8 ± 2	[33]
1,3-dichloro-5-fluorobenzene$^+$			8 ± 2	[33]
1,3-dichloro-2,4-difluorobenzene$^+$			29 ± 3	[33]
1,3-dichloro-2,5-difluorobenzene$^+$			38 ± 2	[33]
1,3-dichloro-2,4,6-trifluorobenzene$^+$			38 ± 3	[33]
1,4-dichloro-2-fluorobenzene$^+$			≤ 6	[33]
1,4-dichloro-2,5-difluorobenzene$^+$			≤ 6	[33]
1,3,5-trichloro-2-fluorobenzene$^+$			22 ± 2	[33]
1,3,5-trichloro-2,4,6-trifluorobenzene$^+$			34 ± 2	[33]
1,2,4,5-tetrachloro-3-fluorobenzene$^+$			–	[33]
1,3-dibromotetrafluorobenzene$^+$			≤ 6	[34]
1,4-dibromotetrafluorobenzene$^+$			≤ 6	[34]
1,3,5-tribromotrifluorobenzene$^+$			≤ 6	[34]
2,5-difluorophenol$^+$	C_s	$\tilde{B}(\pi^{-1}) \rightarrow \tilde{X}(\pi^{-1})$	13 ± 3	[35]
3,5-difluorophenol$^+$			36 ± 4	[35]
2,3,4-trifluorophenol$^+$			26 ± 3	[35]
2,4,5-trifluorophenol$^+$			≤ 6	[35]
2,3,5,6-tetrafluorophenol$^+$			41 ± 4	[35]
Pentafluorophenol$^+$			31 ± 3	[35]
t-1,3,5-hexatriene$^+$	C_{2h}	$\tilde{A}\,^2B_g \rightarrow \tilde{X}\,^2A_u$	17 ± 2	[36]
c-1,3,5-hexatriene$^+$	C_{2v}	$\tilde{A}\,^2A_2 \rightarrow \tilde{X}\,^2B_1$	≤ 6	[36]
C_2H_5–(C≡C)$_2$C≡N$^+$	C_s	$\tilde{A}\,^2A'' \rightarrow \tilde{X}\,^2A''$	≤ 6	[26]
all *trans* 1,3,5-heptatriene$^+$	C_s	$\tilde{A}\,^2A'' \rightarrow \tilde{X}\,^2A''$	9 ± 2	[37]
all *trans* 1,3,5,7-octatetraene$^+$	C_{2h}	$\tilde{A}\,^2A_u \rightarrow \tilde{X}\,^2B_g$	≤ 6	[38]
3,5-octadiyne$^+$	C_s	$\tilde{A}\,^2A'' \rightarrow \tilde{X}\,^2A''$	7 ± 2	[28]

[a] short-component lifetime (see text)

Table 2: Vibrational frequencies (cm^{-1}) of the totally stretching fundamentals, Σ^+ ($C_{\infty v}$), Σ_g^+ ($D_{\infty h}$) obtained from the emission spectra (± 10 cm^{-1}) for the cations of dicyanoacetylene, of dicyanodiacetylene and of cyanodiacetylene and comparison with the ground molecular state values.

	$\tilde{X}\,^2\Pi_u$ [24]	$X\,^1\Sigma_g^+$ [41]		$\tilde{X}\,^2\Pi_g$ [27]	$X\,^1\Sigma_g^+$ [42]		$\tilde{X}\,^2\Pi$ [26]	$X\,^1\Sigma^+$ [43]
ν_1(C≡N)	2210	2290	ν_1(C≡N)	2180	2235	ν_1(C–H)		3320
ν_2(C≡C)	1930	2119	ν_2(C≡C)	2100	2183	ν_2(C≡N)	2190	2330
ν_3(C–C)	570	629	ν_3(C–C)	1360	1288	ν_3(C≡C)		2250
			ν_4(C–C)	460	571	ν_4(C≡C)	2070	2190
						ν_5(C–C)	1220	1289
						ν_6(C–C)	630	642

from the few frequencies inferred from photoelectron spectra for organic polyatomic cations [10], from which good values are ± 40 cm^{-1} in accuracy, and in the case of a few species by photoionisation mass spectroscopy or from Rydberg series [40], the values obtained from the emission spectra have yielded the first sets of frequencies (± 10 cm^{-1}) of the totally symmetric fundamentals for the cations in their ground states. Of course, these data are limited to those cations whose radiative decay can be detected (table 1). For example, in the case of the two cations of concern in fig. 2, the frequencies of all the totally symmetric fundamentals have been obtained for the $\tilde{X}$ states, whereas for cyanodiacetylene cation only four of the seven Σ^+ fundamental frequencies are strongly excited in the emission spectrum. In table 2 the inferred vibrational data for these three cations are collected and are compared to the ground molecular state values. As is the situation for these species, in general, it has been found that the cationic frequencies seldom differ by more than 20% from the molecular values for the larger polyatomics.

As the size of the cations increases, so the emission spectra become more congested. This is illustrated by the spectra shown in fig. 3; nevertheless vibrational frequencies are still obtained and for these species not

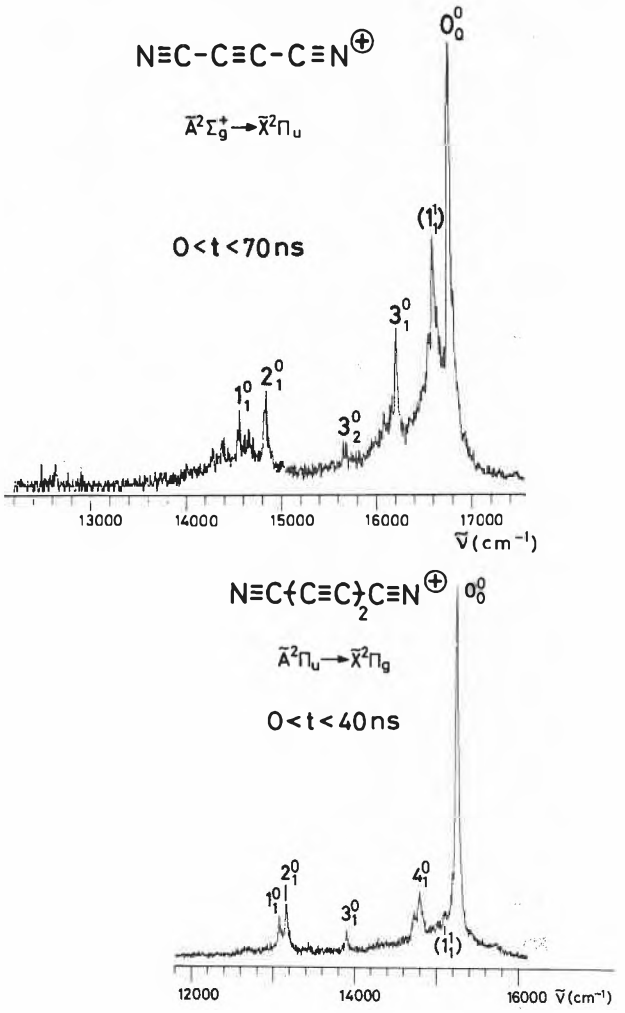

Fig. 2: Time-resolved emission spectra of dicyanoacetylene and dicyanodiacetylene cations recorded with optical resolutions of 0.4 nm and 0.8 nm respectively. The indicated time resolutions were chosen in order to suppress the overlapping A $^2\Pi \rightarrow$ X $^2\Sigma^+$ bands of the cyanogen radical.

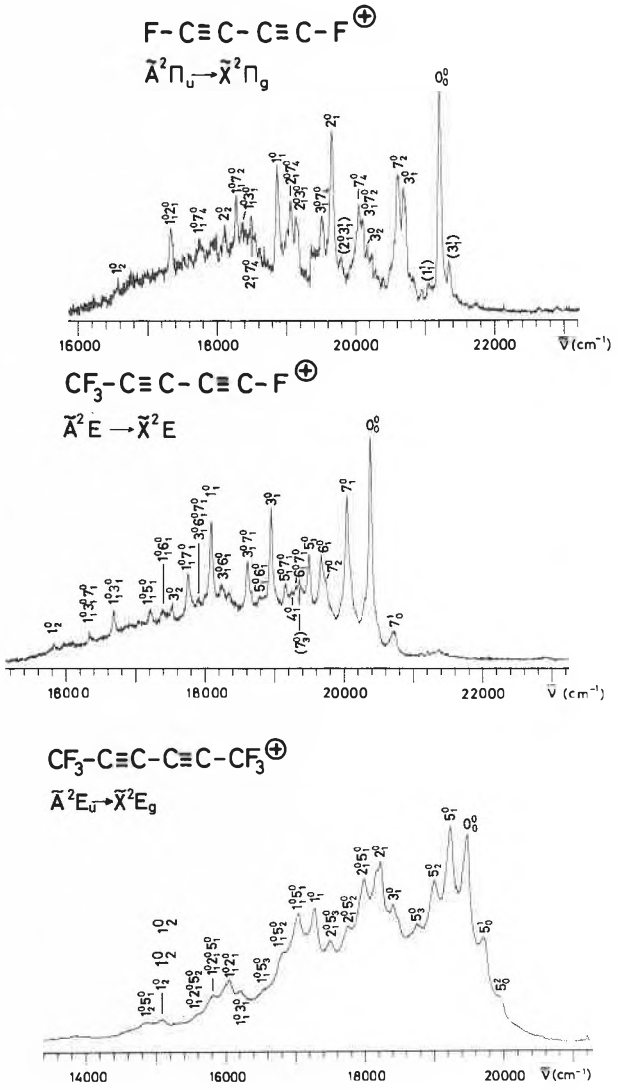

Fig. 3: Emission spectra of the cations of difluorodiacetylene, of perfluoropentadiyne-1,3 and of perfluorohexadiyne-2,4, recorded with optical resolutions of 0.5 nm, 0.5 nm and 0.16 nm respectively.

even the molecular values are as yet known. It is worth pointing out that the measurements of the emission spectra and lifetimes of these three cations were managed with sample amounts of merely 20–50 mg as a result of the on-line data acquisition and the sensitivity of the apparatus of fig. 1 [22].

The assignment of the bands in the emission spectra can often be substantiated, as is usual in spectroscopy, by the studies of the isotopic compounds. This is illustrated by the $\tilde{A}^2E \rightarrow \tilde{X}^2E$ emission band systems of 1,3-pentadiyne cation and of its deuterated derivatives (fig. 4).

In the case of even some of the halosubstituted benzene cations' spectra, two of which are shown in fig. 5 [32], a vibrational analysis has been carried out based on the fact that for such large species the cationic vibrational frequencies will be rather similar to the molecular values. In these recent studies the high resolution spectra were recorded either using a discharge source [44, 45] or by exciting the cationic transition with a laser [46, 47].

2. Lifetimes

Once the radiative decay of an excited electronic state has been detected, the lifetime (τ) of the species in this state can be directly measured. This yields the sum of the rate constants (k_T) of all the channels depleting the state of concern, i.e.

$$\frac{1}{\tau} = k_T = k_r + \Sigma\, k_{nr}$$

The summation refers to all the accessible non-radiative (k_{nr}) decay pathways. The latter are, in the case of the lowest excited electronic state of open-shell polyatomic cations, internal conversion to the cationic ground state, isomerisation and fragmentation. When the ra-

diative decay is not observed, the sensitivity of the apparatus puts a lower limit to the sum of the non-radiative rate constants. This turns out to be, $\Sigma k_{nr} \geq 10^{12}\ s^{-1}$.

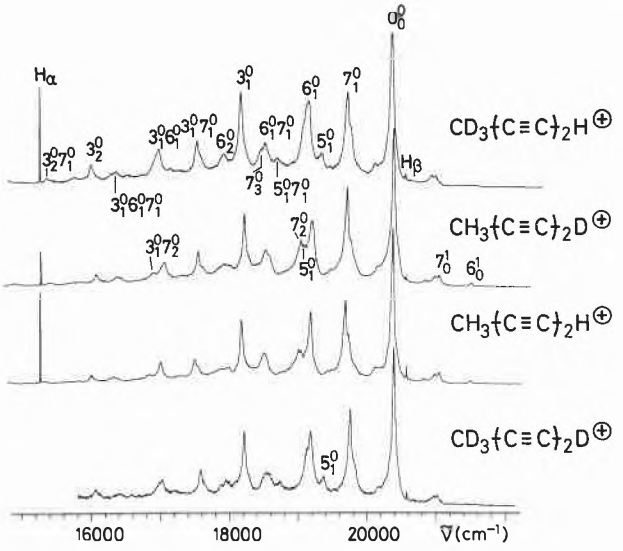

Fig. 4: Emission spectra of the cations of 1,3-pentadiynes; $\tilde{A}\,^2E \rightarrow \tilde{X}\,^2E$ band systems, recorded with optical resolutions of 0.16 nm. The vibrational numbering is that of the seven A_1 fundamentals.

The lifetimes of the cations listed in table 1 in the lowest vibrational levels of the $\tilde{A}$ (or $\tilde{B}$) electronic states have been measured. This was accomplished by gating the electron beam and by detecting single photons in delayed coincidence for emission bands selected by the monochromator (cf. fig. 1). The lifetimes were then extracted from the accumulated decay curves by a least-squares linear fit to a semi-logarithmic plot of the data. In table 1 the lifetimes measured in this manner of the cations in the zeroth vibrational level of the excited state are collected. The given error limits represent the reproducibility of the measurements rather than the statistical uncertainty of the data. The quality of the decay curves that could usually be obtained is illustrated by the ones shown in fig. 6. These data were obtained in about one hour using an optical band pass of 0.8 nm and sample gas pressures of $\leq 10^{-4}$ torr. In addition, when bands were observed in the emission spectra which lie to higher energy of the 0_0^0 bands, the lifetimes of vibrationally excited levels, to which the emission bands necessarily correspond, have been measured.

As the decay curves can be relatively easily obtained for several decades in amplitude, and can be followed for several microseconds, even weak long-lived components e.g. 1/100 in amplitude of the main-component, can be observed. The measurement of long-lived ions (microsecond time scale) is restricted by the thermal escape of the ions out of the observation zone, and as has been shown recently, by their escape due to

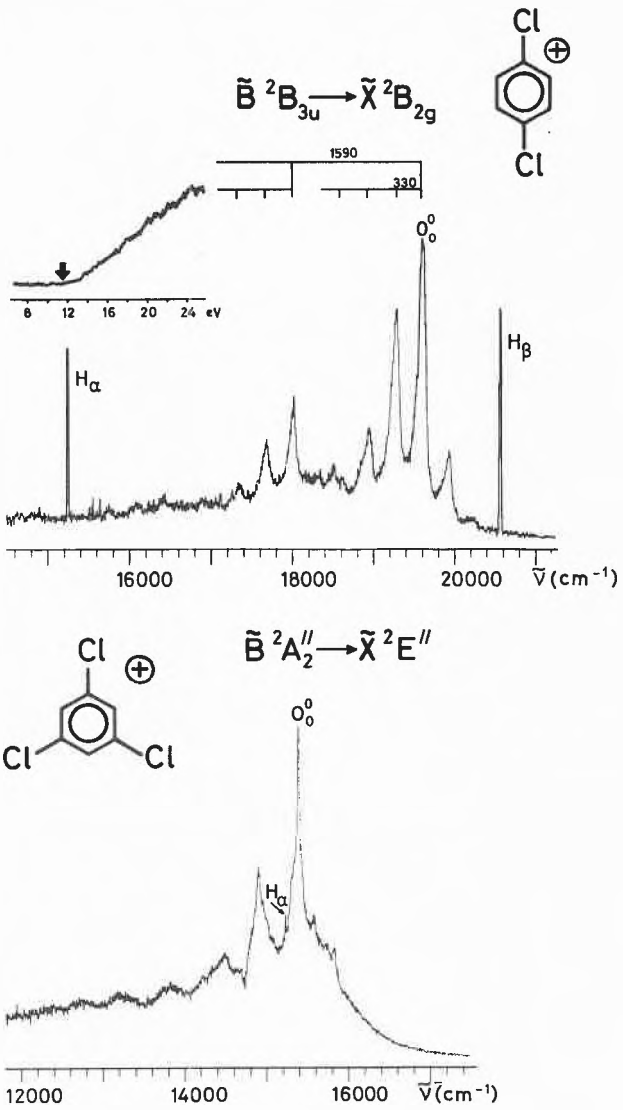

Fig. 5: Emission spectra of 1,4-dichlorobenzene and of 1,3,5-trichlorobenzene cations recorded with optical resolutions of 0.4 nm and 0.16 nm respectively. The excitation function of the 0_0^0 band of 1,4-dichlorobenzene cation is included as an inset.

electrostatic repulsion [48]. The consequence of these experimental limitations is that the inferred lifetimes which are $\geq 1\ \mu s$ are a lower limit. The problems and advantages of lifetime measurements by this technique are discussed in detail in connection with diatomic species in a recent comprehensive review [49].

3. Non-exponential decay

In the case of a few of the smallest polyatomic cations studied (table 1), non-exponential decays have been detected. The most striking are those of the monohaloacetylene cations, X–C≡C–H$^+$, X = Cl, Br, I, in their $\tilde{A}\,^2\Pi$ states for which the ratios of the amplitudes of the short and long components were found to be merely one order of magnitude (fig. 7) [18]. On the other hand for the dihaloacetylene cations X–C≡C–X$^+$

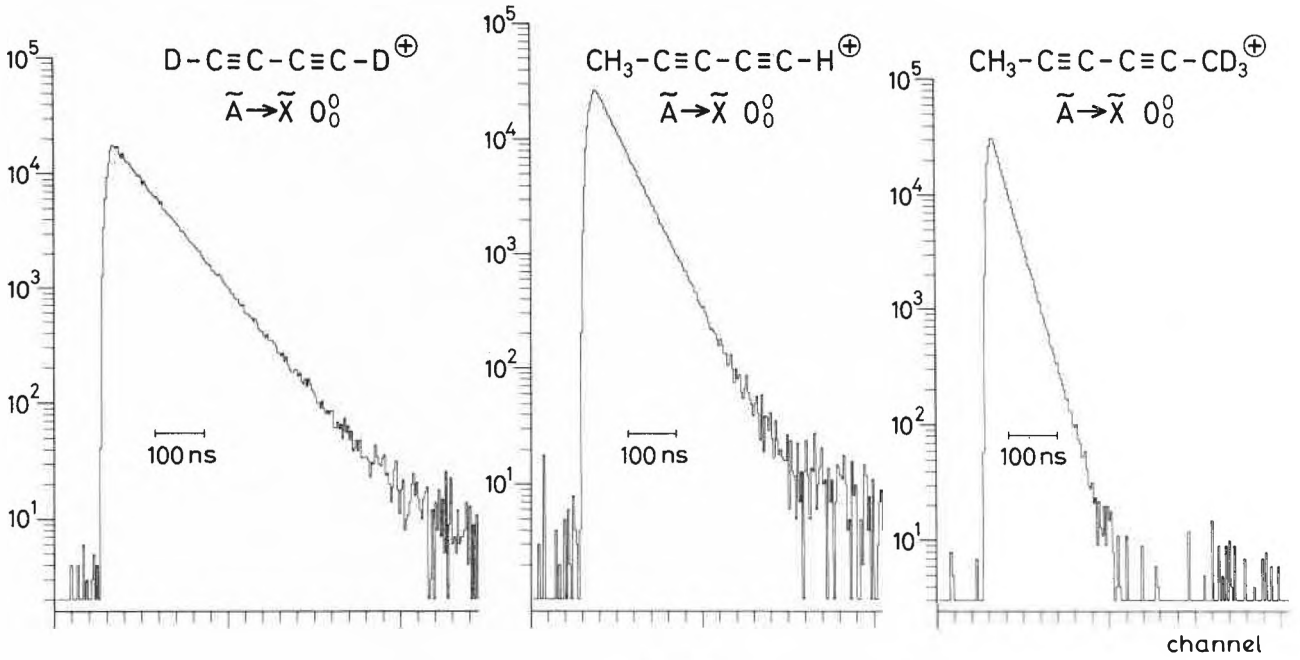

Fig. 6: Decay curves of the indicated cations accumulated for the $\tilde{A} \rightarrow \tilde{X}\ 0_0^0$ bands (0.8 nm band pass). The uniform background has been subtracted and the data are plotted on a semi-logarithmic scale.

X = Cl, Br, I, in their $\tilde{A}\ ^2\Pi_g$ states (fig. 7) [19] as well as for the cations of halo methylacetylenes, $CH_3{-}C{\equiv}C{-}X^+$, X = Cl, Br, [21] and of dihalodiacetylenes, $X{-}(C{\equiv}C)_2{-}X^+$, X = Cl, Br [23], long-lived components have also been detected, although their amplitudes are two orders of magnitude weaker than the dominant short-lived decays.

In order to demonstrate that the non-exponential curves show the genuine decay of these electronically excited cations, and are not, for example, the result of overlapping emission bands of fragments, two types of measurements were conducted. The first were the recording of time-resolved emission spectra in the time intervals corresponding to the short and long decay components. Such spectra are reproduced in fig. 8. In the spectra of chloroacetylene cation the intensities of the individual vibronic bands are very similar implying that the relative populations of the corresponding levels of the $\tilde{A}\ ^2\Pi$ state are to within $\approx 20\%$ the same during the chosen time intervals after their initial formation. The time-resolved spectra of dichloroacetylene cation again show similarities in that the prominent bands on the high energy side are still apparent. However, the low energy part of the long component spectrum becomes more congested. This is also evident, though to a smaller extent, in the chloroacetylene spectrum. This may reflect, for example, a slow redistribution of vibrational energy on the microsecond time scale. The second sort of investigations showed that the long decays are due to an ion. The decay curves, which were accumulated when an electric field was applied to the observation zone following the excitation to expel charged particles, showed that the long component was practically eliminated after about a microsecond. In addition, photoionisation fragment ion appearance potentials show that for the $\tilde{A}$ states of the halo- and dihaloacetylene cations fragmentation channels are not accessible [50]. Last, but not least, the decay curve of chloroacetylene cation has also been obtained using He(Iα) and Ne(I) photon excitation by detecting undispersed photons in coincidence with the parent mass ions [51]. This technique is described in detail elsewhere [52]. This confirms that the non-exponential decay is not an artefact of the electron beam excitation, and cascading from higher lying electronic states can also be excluded from all the results considered together.

An explanation proposed for the observed multi-component decay was that this represented a strong coupling of the radiative state, $\tilde{A}$, with the vibronic manifold of the ground cationic state [18]. The theory to rationalize such a behaviour in molecular systems has been classified as the "intermediate case" coupling scheme. The halo- and dihaloacetylene cations fit this category because the density of the vibrational levels of the ground state at the position of the $\tilde{A}$ state, is relatively small. The number of vibrational degrees of freedom is small and the $\tilde{A}$ states lie merely 2–3 eV above the lowest level of the $\tilde{X}$ states. Recently, the experimental data have been found to fit such a coupling model semi-quantitatively [51]. Apart from the

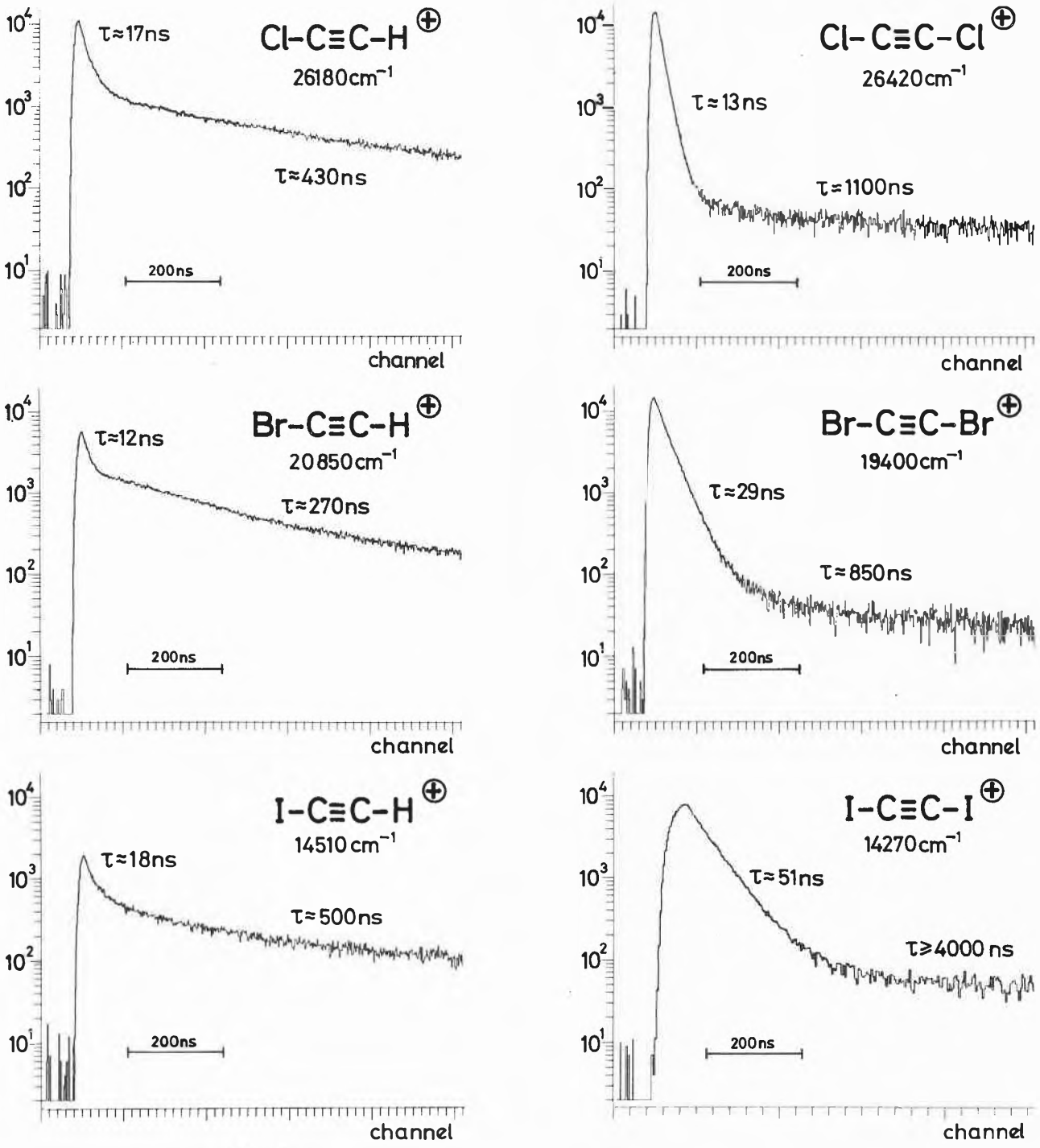

Fig. 7: Decay curves of the $\widetilde{A} \rightarrow \widetilde{X}$ bands of haloacetylene and of dihaloacetylene cations plotted on a semilogarithmic scale with background subtracted.

aforementioned cases, the decay curves obtained for the other cations listed in table 1 were reasonably exponential over at least two decades of signal.

4. Decay pathways

In order to evaluate quantitatively the partition between the radiative and non-radiative channels, the quantum yields of emission are requisite. These are, however, unavailable for polyatomic cations in the gaseous phase but can now be measured as a result of the development of new coincidence techniques. In the one, averaged quantum yields for the whole excited state populated in the photoionisation process are obtained when the undispersed photons are detected in coincidence with the parent mass cations [52]. Such studies on CO_2^+ ($\widetilde{A}$, $\widetilde{B}$) [53] and on the fluorinated

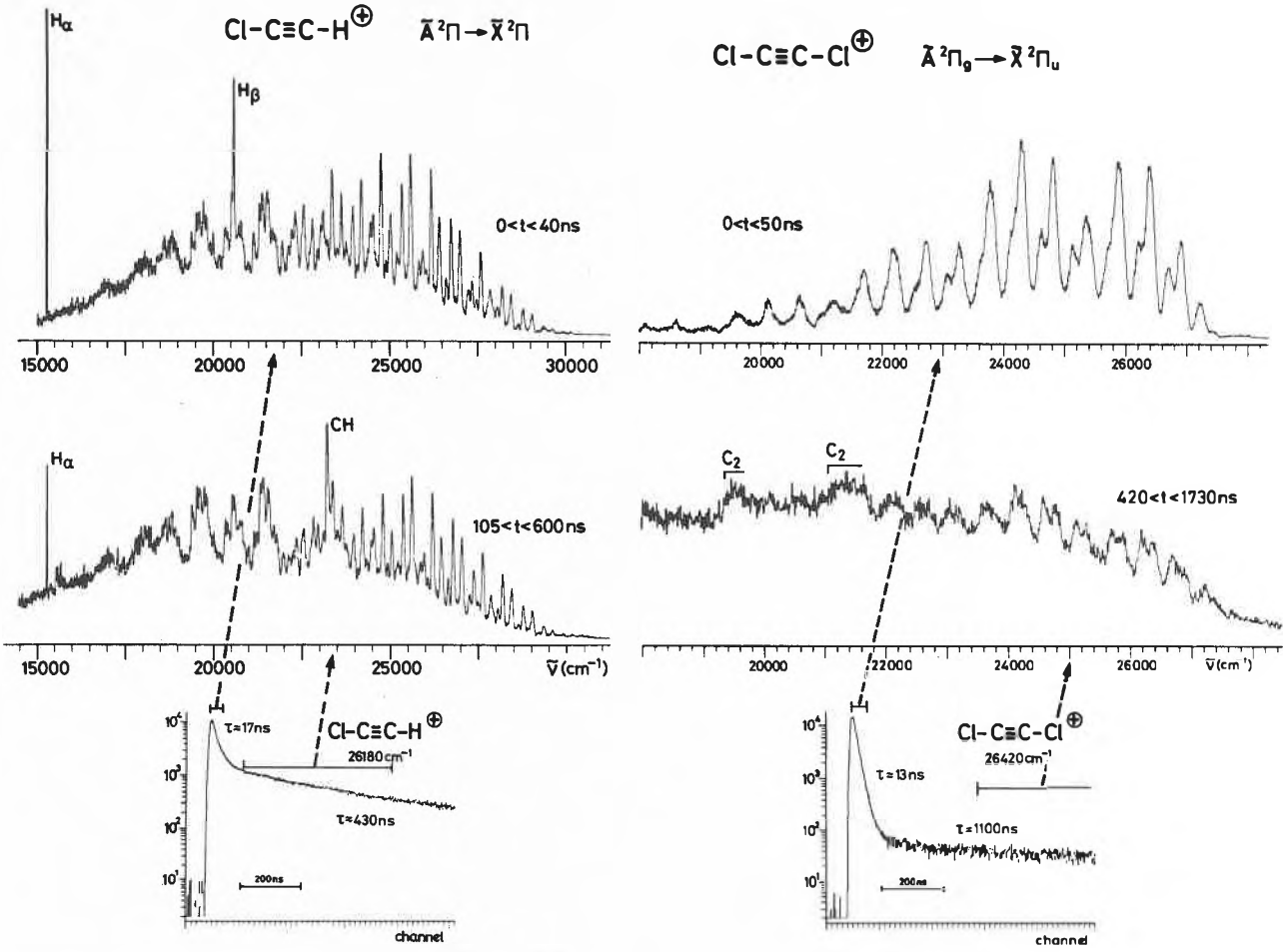

Fig. 8: Time-resolved emission spectra of the $\widetilde{A}\,^2\Pi_g \rightarrow \widetilde{X}\,^2\Pi_u$ band system of dichloroacetylene cation recorded with 0.8 nm resolution. The correspondence of the indicated time intervals to the decay curves is marked.

benzene cations [54] have been carried out. On the other hand when the coincidences between energy selected electrons and undispersed fluorescence photons are monitored [55], the lifetimes and quantum yields of the populated vibrational levels of the excited state of the cation can be obtained. The lifetimes of the fluorobenzene cations have been determined by this technique [56]. Also the quantum yields of vibrational levels of CO_2^+ ($\widetilde{A}\,^2\Pi_u$, $\widetilde{B}\,^2\Sigma_u^+$) [57] and N_2O^+ ($\widetilde{A}\,^2\Sigma^+$) [58] have so far been obtained using synchrotron radiation for the photoionisation process at thresholds and by detecting nominally zero-energy electrons.

One of the reasons for the lack of quantum yields for open-shell cations, is that, unlike the situation for molecular species, absorption spectra in the gas phase are not available. However, quite a few absorption spectra, and the extinction coefficients, of cations in low temperature freon matrices are known [59]. In one example so far, such absorption spectra have been obtained for two cations for which the gaseous phase radiative decay has been discovered; namely of *trans*- and *cis*-1,3,5-hexatriene cations (cf. table 1) [60]. In this instance the quantum yields of emission can be reasonably estimated from the integrated extinction coefficients of the $\widetilde{A} \leftarrow \widetilde{X}$ matrix spectra and from the measured "isolated state" lifetime via the $\widetilde{A} \rightarrow \widetilde{X}$ emission [36]. In the case of some other cations listed in table 1, order of magnitude estimates of the radiative quantum yields have been made by comparison of the integrated intensities of the emission systems within a series of cations, e.g. in refs. [20, 31].

Even though the radiative decay of around hundred open-shell organic cations in their lowest excited electronic states has been detected, with at least twice as many species emissions could not be detected. In fact, these investigated species had already been preselected on the basis of their photoelectron spectra. As yet, radiative decay from the $\widetilde{A}$ (or $\widetilde{B}$) cationic state was apparent only if the photoelectron band corresponding to the $\widetilde{A}$ (or $\widetilde{B}$) excited state showed vibrational fine structure. Conversely, unstructured photoelectron bands indicate, by the uncertainty principle, that the lifetime of the cation formed in that state is $\lesssim 10^{-12}$ s. Taking 10^7 s^{-1} for the typical $\widetilde{A} \rightarrow \widetilde{X}$ radiative rate (cf. table 1), the quantum yields of emission are thus expected to be less than 10^{-5} for these cations.

If vibrational fine structure is apparent on the photo-

electron band, but the radiative pathway is not detected, then the non-radiative decay is limited to the range $10^{11}-10^{12}$ s^{-1}. As examples, the photoelectron spectra of butadiene and of *trans*-1,3,5-hexatriene are reproduced in fig. 9 from ref. [61] where the second bands illustrate these differences.

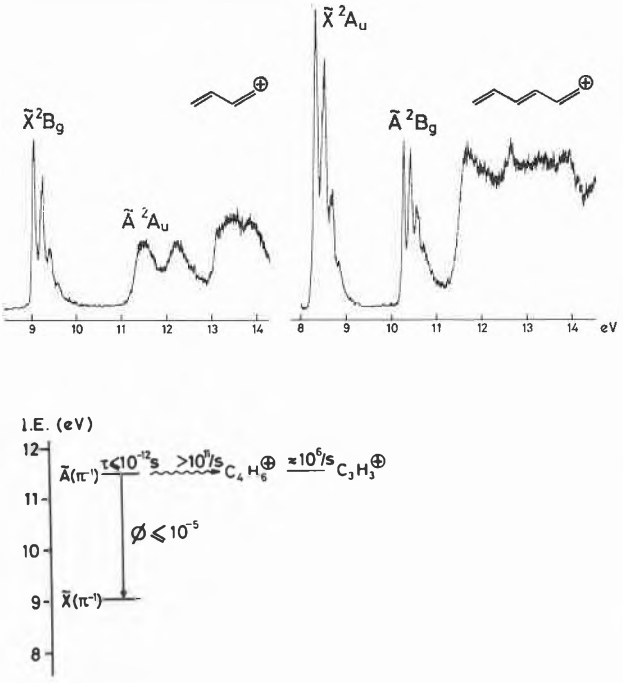

Fig. 9: He (Iα) photoelectron spectra of butadiene and of *trans*-1,3,5-hexatriene (redrawn from ref. [61]) and a schematic summary of the energetics and decay pathways of butadiene cation in the $\tilde{A}$ state. (For corresponding summary of the hexatriene cation see fig. 11.)

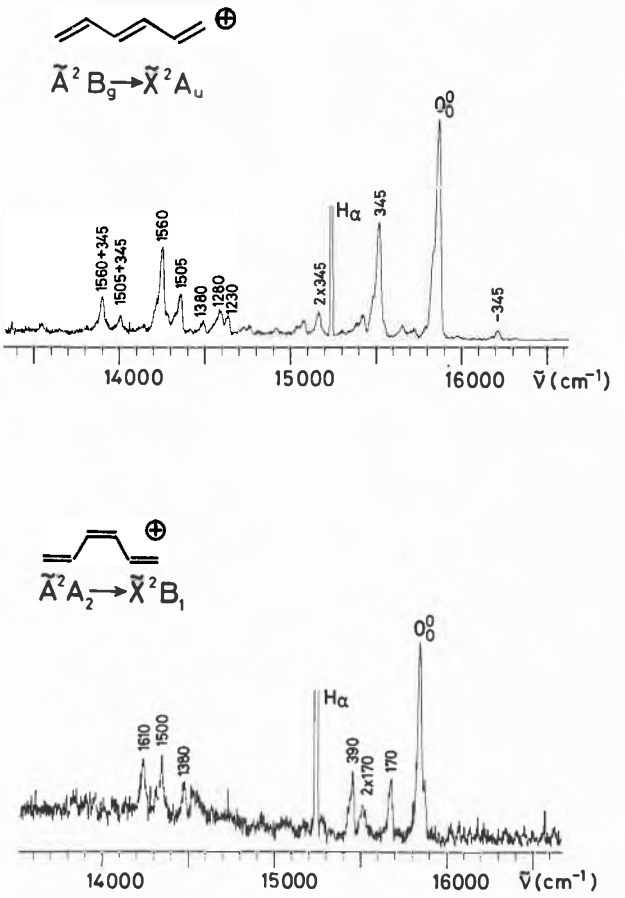

Fig. 10: Emission spectra of *trans*- and *cis*-1,3,5-hexatriene cations recorded with optical resolutions of 0.5 nm.

Butadiene cations produced in the first excited electronic state, $\tilde{A}\,^2A_u$, fragment, and near the threshold the rate has been found to be slow, 10^4-10^6 s^{-1} [62]. As expected in view of the appearance of the second photoelectron band, the $\tilde{A} \rightarrow \tilde{X}$ radiative decay was not detected. The implication of these observations is that for the lowest levels of the $\tilde{A}\,^2A_u$ state, the dominating non-radiative pathway is that of internal conversion, i.e. formation of vibrationally excited butadiene cation in its $\tilde{X}\,^2B_g$ state, and/or isomerisation. As the internal energy of butadiene cation is increased, however, the fragmentation rate rises rapidly [62].

The first excited states of *trans*- and *cis*-1,3,5-hexatriene cations, $\tilde{A}$, are longer lived ($\geq 10^{-12}$ s) as indicated by the fine structured second photoelectron bands (cf. fig. 9) [61], and in fact weak emission spectra, $\tilde{A} \rightarrow \tilde{X}$ transitions, of these two cations have been recorded [36, 37]. These are shown in fig. 10 where it is seen that the spectra are distinct; the 0_0^0 band of the *cis*-species lies ≈ 1.1 nm to the red of the *trans* cation, and the integrated emission intensity of the *trans* is found to be about twenty times larger than of the *cis* cation.

The quantum yield estimates from the lifetime measurements and from the integrated extinction coefficients of the matrix absorption spectra are about 7% and 0.3% for the zeroth vibrational level of the $\tilde{A}$ state of the *trans*- and *cis*-1,3,5 hexatriene cations respectively [37]. Thus, the radiative decay is a minor relaxation pathway. Because the non-radiative decay leads to fragment ions [63], the branching ratios (i. e. quantum yields to fragmentation) of the resultant cations were measured by photoelectron-photoion coincidence spectroscopy. The conclusions drawn from all the measurements on these two isomeric cations in the lowest vibrational level of their $\tilde{A}$ states are depicted schematically in fig. 11. It is postulated that there are two non-radiative channels which finally lead to the only accessible fragment ion, cyclic $C_6H_7^+$. The formation of the cyclic precursor from a linear $C_6H_8^+$ ion is then assumed to be slow thus explaining that the $C_6H_8^+$ branching ratios are larger than the evaluated emission quantum yields and that the ion sum curves are less than unity, on the time-scale of the coincidence measurements. In the case of the *cis* isomer, the non-radiative pathways leading to $C_6H_7^+$ are more efficient

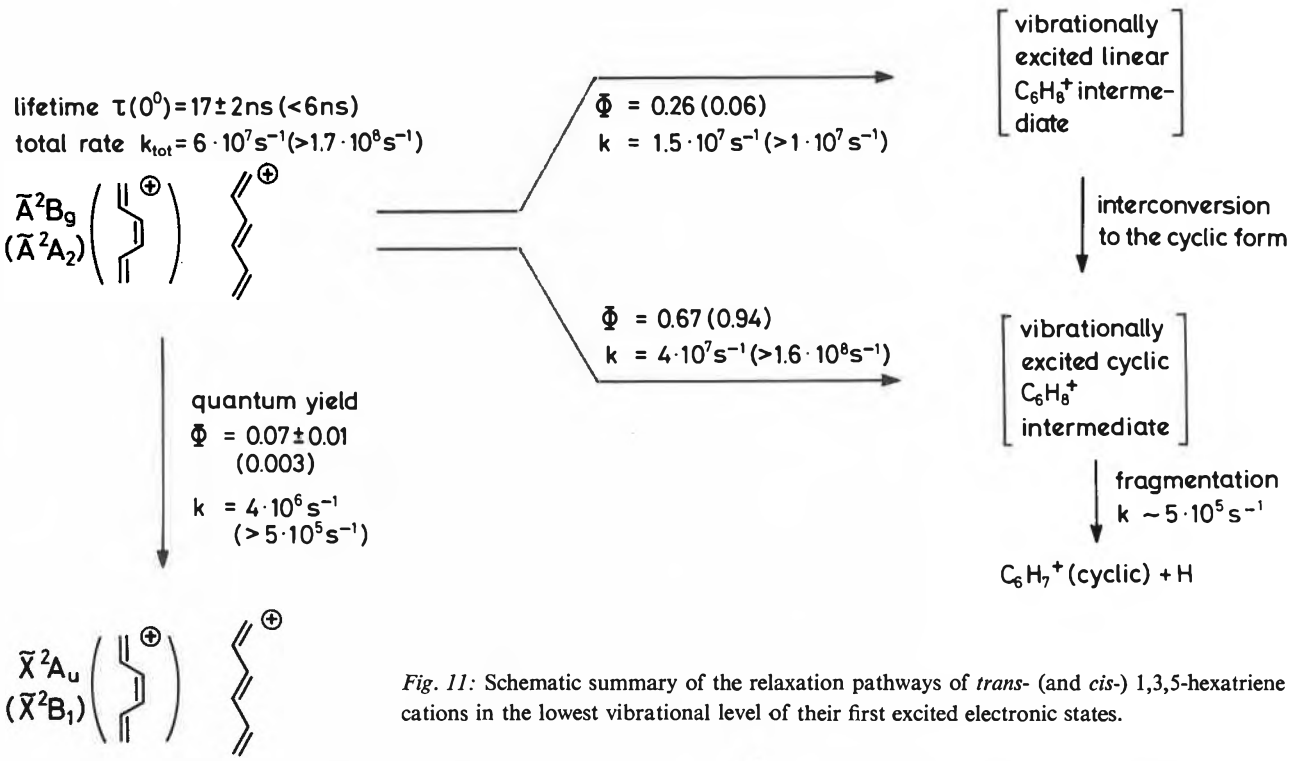

Fig. 11: Schematic summary of the relaxation pathways of *trans-* (and *cis-*) 1,3,5-hexatriene cations in the lowest vibrational level of their first excited electronic states.

(cf. fig. 11). This is consistent with the fact that the cyclisation of the *cis* species is easier than for the *trans* [37].

The decays of the $\tilde{A}$ states of the *trans-* and *cis-*1,3,5-hexatriene cations were found to be the first examples among open-shell organic cations whose radiative pathway is detected even though fragmentation is also evident. Such a behaviour had been noted earlier with N_2O^+ ($\tilde{A}\,^2\Sigma^+$) and COS^+ ($\tilde{A}\,^2\Pi$) [64] and recently with SO_2^+ ($\tilde{B}\,^2A_1$) [65]. Quite a few other cations have now been found to belong to this category and most of these are collected in table 3. For the listed cations emission spectra of the indicated electronic transitions have been recorded and the fragmentation pathways have been manifested at first from photon or electron impact fragment ion appearance potentials and later, in some cases, in more detail by photoelectron-photo-ion coincidence measurements [37, 66, 67].

Table 3: Open-shell polyatomic cations (M^+) for which the radiative (quantum yield $\geq 10^{-5}$) and fragmentation decay channels are both detected. Not all the fragmentation channels accessible, or all the isotopic derivatives studied (cf. table 3), are listed.

Fragment Ions	M^+	Emission	References
NO^+	N_2O^+	$\tilde{A}\,^2\Sigma^+ \rightarrow \tilde{X}\,^2\Pi$	[4]
CS^+	COS^+	$\tilde{A}\,^2\Pi \rightarrow \tilde{X}\,^2\Pi$	[64]
SO^+	SO_2^+	$\tilde{B}\,^2A_1 \rightarrow \tilde{X}\,^2A_1$	[65]
C_2HF^+	*c*-CHF=CHF$^+$	$\tilde{A}\,^2A_1 \rightarrow \tilde{X}\,^2B_1$	[25]
$C_3H_3^+$	$CH_3-C\equiv C-Cl^+$	$\tilde{A}\,^2E \rightarrow \tilde{X}\,^2E$	[21]
	$CH_3-C\equiv C-Br^+$		[21]
$C_5H_3^+$	$CH_3-(C\equiv C)_2Cl^+$		[21]
	$CH_3-(C\equiv C)_3Br^+$		[21]
	$CH_3-(C\equiv C)_2H^+$		[28]
$C_6H_5^+$, $C_6H_4^+$	$CH_3-(C\equiv C)_2CH_3^+$	$\tilde{A}\,^2E_u \rightarrow \tilde{X}\,^2E_g$	[29]
$C_4H_4^+$	$C_2H_5-(C\equiv C)_2H^+$	$\tilde{A}\,^2A'' \rightarrow \tilde{X}\,^2A''$	[29]
$C_6H_7^+$	*t*-1,3,5-hexatriene$^+$	$\tilde{A}\,^2B_g \rightarrow \tilde{X}\,^2A_u$	[36]
	c-1,3,5-hexatriene$^+$	$\tilde{A}\,^2A_2 \rightarrow \tilde{X}\,^2B_1$	[36]
$C_7H_{10}^+$, $C_7H_9^+$ $C_6H_7^+$, $C_6H_6^+$	all *t*-1,3,5-heptatriene$^+$	$\tilde{A}\,^2A'' \rightarrow \tilde{X}\,^2A''$	[37]
$C_8H_9^+$, $C_7H_7^+$	all *t*-1,3,5,7-octatetraene$^+$	$\tilde{A}\,^2A_u \rightarrow \tilde{X}\,^2B_g$	[38]
$C_7H_7^+$	$C_2H_5-(C\equiv C)_2C_2H_5^+$	$\tilde{A}\,^2A'' \rightarrow \tilde{X}\,^2A''$	[28]

Table 4: Radiative (k_r) and non-radiative (k_{nr}) rates for the depletion of the lowest vibrational level of the $\tilde{A}$ state of the alkyl substituted diacetylene cations, evaluated from the measured lifetimes [28] and by equating the parent cation branching ratios [66] with the quantum yield of emissions.

Radical Cation	State	Lifetime (ns)	Branching Ratio (M^+)	$k_r(s^{-1}) \cdot 10^7$	$k_{nr}(s^{-1}) \cdot 10^7$
$CH_3-C\equiv C-C\equiv C-H^+$	$\tilde{A}\,^2E$ 0°	48 ± 3	0.76 ± .06	1.6	0.5
$CH_3-C\equiv C-C\equiv C-D^+$	$\tilde{A}\,^2E$ 0°	46 ± 3	0.73 ± .01	1.6	0.6
$CD_3-C\equiv C-C\equiv C-H^+$	$\tilde{A}\,^2E$ 0°	51 ± 3	0.79 ± .06	1.5	0.4
$CD_3-C\equiv C-C\equiv C-D^+$	$\tilde{A}\,^2E$ 0°	53 ± 3	0.82 ± .01	1.5	0.3
$C_2H_5-C\equiv C-C\equiv C-H^+$	$\tilde{A}\,^2A''$ 0°	≤ 6	0.007 ± .002		
$CH_3-C\equiv C-C\equiv C-CH_3^+$	$\tilde{A}\,^2E_u$ 0°	24 ± 2	0.60 ± .05	2.5	1.7
$CH_3-C\equiv C-C\equiv C-CD_3^+$	$\tilde{A}\,^2E_u$ 0°	28 ± 3			
$CD_3-C\equiv C-C\equiv C-CD_3^+$	$\tilde{A}\,^2E_u$ 0°	32 ± 3	0.81 ± .07	2.5	1.1
$C_2H_5-C\equiv C-C\equiv C-C_2H_5^+$	$\tilde{A}\,^2A''$ 0°	7 ± 2			

As the non-radiative decay of the cations given in table 3 leads to fragment ions, techniques relying on ion as well as photon detection can be employed to probe the relaxation pattern. This was illustrated above for the hexatriene cations. Corresponding measurements have also been carried out for the alkyl-substituted diacetylene cations (table 3) [28, 66]. Thus, from the measured lifetimes of the lowest vibrational levels of their $\tilde{A}$ states [28] and by equating the parent cation branching ratios [66] with the quantum yields of emission, the radiative and non-radiative rates can be inferred. The results of these studies are collected in table 4. It should be noted, however, that the parent ion branching ratios yield only an upper limit for the emission quantum yield because, although the internal energy of the cations initially formed is defined, the structure (electronic or geometric) of the mass selected ions is not.

5. Current research

The discoveries and studies of the radiative relaxation of open-shell organic cations in the gaseous phase, which have been briefly reviewed in this article, have opened up the possibilities of detailed spectroscopic studies. The knowledge and findings acquired during the past five years were prerequisite for the development of new techniques and apparata for these investigations, which have now been undertaken in Basel. On the spectroscopic side these are aimed at obtaining more accurate vibrational frequencies and in some cases rotational details for the cations. To this end, two approaches are employed. In the one high resolution emission spectra can now be recorded with a new crossed electron-sample beam apparatus based on the principles outlined in fig. 1, which optical resolutions down to $\approx$ 0.004 nm. In the other, corresponding spectroscopic data are being obtained for the $\tilde{A}$ (or $\tilde{B}$) excited electronic states by means of laser induced fluorescence of the cations. This technique, which was first demonstrated for N_2^+ [68], has been successfully pursued in the studies of some of the larger cations [46, 47, 69] whose emissions were discovered in our earlier studies. The cations are generated by Penning ionisation using rare gas metastables, and the excitation spectra are recorded using a tunable dye laser [70]. High resolution measurements of electronically excited cations are thus attainable.

A further conclusion reached from the radiative decay studies was that the determination of quantum yields of emission of selected vibrational levels was essential. Therefore, an apparatus has been constructed based on the principle of detection coincidences between energy selected photoelectrons and undispersed fluorescence photons [55]. As discussed in an earlier paragraph, the coincidence curves yield the quantum yields and the cascade-free lifetimes of selected vibrational levels populated in the photoionisation process.

With the development and application of these techniques, detailed spectroscopic and relaxation rate studies of open-shell cations in the gaseous phase are in progress.

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