Open-Shell Organic Cations: Spectroscopic Studies by means of Their Radiative Decay in the Gas Phase

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More and more studies on molecular ions are being undertaken in view of the chemical role they play in terrestrial and extraterrestrial environments.[1] Spectroscopic characterization of such ions is thus of prime importance. Their spectra can be used not only to identify them but also to provide information on the physical conditions of their surroundings. Examples of this include the spectroscopic investigations of ions in interstellar space, in comets, in plasmas, or in the elucidation of the energy transfer in collision and fragmentation reactions.[1]

Open-shell, or radical, organic cations $(M^+ {}^2\tilde{J})^2$ constitute an extensive set among these species. They are produced by ejection of electrons in ionization processes from closed-shell organic molecules in their ground states $(M \, {}^1X)$. Such cations were and are of course the object of many studies by mass spectroscopic methods, albeit the internal energy, or the state is in general not specified. On the other hand, with the advent of photoelectron spectroscopy[3] a general means of locating the doublet cationic states $({}^2\tilde{X}$ (ground), ${}^2\tilde{A}$ (first excited), ${}^2\tilde{B} \ldots {}^2\tilde{J} \ldots)$ became available. It should, nevertheless, be remembered that these states, and their labeling, refer only to the states populated directly in the photoionization process and thus do not encompass all the possible doublet cationic states.[4]

However, for higher resolution spectroscopic investigations and in order to follow the fate and dynamics of the generated cations, other techniques dependent on the emission, or absorption, of photons have to be involved. Emission spectroscopy has been the most successful approach in the past and has contributed a great deal toward our understanding of the electronic and geometric structure of molecules[5] and radicals.[6] For a handful of open-shell triatomic cations, analysis of rotational structure in the optical emission spectra also played a crucial role.[7] The only emission spectrum of a polyatomic organic cation known until the last decade, and which in fact had been rotationally analyzed, was that of diacetylene cation.[8]

This situation has changed in the last 10 years, primarily because one could predict from photoelectron spectroscopic data the wavelength region where the ${}^2\tilde{A}$ (or ${}^2\tilde{B}) \rightarrow {}^2\tilde{X}$ electronic transitions of organic cations are to be expected. Furthermore, the appearance of vibrational fine structure on the photoelectron bands, implying an excited-state lifetime of $\geq 10^{-12}$ s, as well as the relative positions of the bands, strongly suggested

Table I
Main Classes of Open-Shell Organic Cations Which Decay Radiatively from Their Lowest ($^2\tilde{A}$ or $^2\tilde{B}$) Excited Electronic States[a]

$XC \equiv N^+$, X = Cl, Br, I
$XC \equiv CH^+$, X = Cl, Br, I
$XC \equiv CX^+$, X = Cl, Br, I
$X(C \equiv C)_2 H^+$, X = Cl, Br, I, CN, CH_3, C_2H_5
$X(C \equiv C)_2 X^+$, X = Cl, Br, I, CN, F, CF_3, C_2H_5
$CH_3 C \equiv CX^+$, X = Cl, Br, CN
$CH_3(C \equiv C)_2 X^+$, X = Cl, Br, CN, CH_3
$H(C \equiv C)_n H^+$, n = 2, 3, 4
$H(CH=CH)_n H^+$, n = 3, 4
fluorobenzenes(+), chlorobenzenes(+)
chlorofluorobenzenes(+), bromofluorobenzenes(+)
fluorophenols(+)

[a] A more detailed list including the references to the individual studies has been given.[12,13]

whether radiative decay would be likely.

Armed with such knowledge the emission system of hexafluorobenzene cation was observed. This showed up as a broad fluorescence band when hexafluorobenzene gas was photoionized with the He Iα resonance line.[9] Subsequent, higher resolution measurements using a low-energy electron beam for the preparation of the electronically excited cations[10] revealed that this emission system is actually rich in vibrational structure.[11]

These experiments by means of electron impact excitation were aimed at obtaining the emission spectra of organic radical cations. The species were selected according to their photoelectron spectra as well as ancillary information on their stability provided by tech-

(1) See various series on ion studies such as P. Ausloos, Ed., "Kinetics of Ion-Molecule Reactions", Plenum Press, New York, 1979; M. T. Bowers, Ed., "Gas Phase Ion Chemistry", Vol. I and II, Academic Press, New York, 1979; J. L. Franklin, Ed., "Ion-Molecule Reactions", Vol. 1 and 2, Butterworths, London, 1972.

(2) The energy sequence of molecular states located spectroscopically is conventionally designated as X, A, B ... and a, b, ... for singlet and triplet multiplicity, respectively (see ref 5). For cationic states a tilde is introduced. Usually the multiplicity is given as a superscript to the symmetry of the appropriate state, e.g., B^1A_g, and thus in this script in the general discussion these are indicated as ^1X, ^3a or $^2\tilde{X}$, $^4\tilde{a}$, etc.

(3) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley-Interscience, London, 1970, and references therein.

(4) R. Zahradnik and P. Carsky, Top. Curr. Chem., 43, 1 (1973).

(5) G. Herzberg, "Molecular Spectra and Molecular Structure", Vol. I, Van Nostrand, New York, 1950; Vol. III, 1966.

(6) G. Herzberg: "The Spectra and Structure of Simple Free Radicals", Cornell University Press, Ithaca, NY, 1971.

(7) G. Herzberg, Q. Rev., Chem. Soc., 25, 201 (1971); S. Leach in "The Spectroscopy of the Excited State", NATO Advanced Study Institute, Plenum Press, New York 1976.

(8) J. H. Callomon, Proc. R. Soc. London, Ser. A, 244, 220 (1958).

(9) J. Daintith, R. Dinsdale, J. P. Maier, D. A. Sweigart, and D. W. Turner In "Molecular Spectroscopy", Institute of Petroleum, London, 1972.

(10) M. Allan, E. Kloster-Jensen, and J. P. Maier, J. Chem. Soc., Faraday Trans. 2, 73, 1406 (1977).

(11) M. Allan and J. P. Maier, Chem. Phys. Lett., 34, 442 (1975).

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niques monitoring fragmentation processes.[12] By this means, the emission spectra of over a hundred open-shell organic cations were obtained and assigned to their $^2\tilde{A}$ (or $^2\tilde{B}$) → $^2\tilde{X}$ electronic transitions.[12,13] In Table I the main classes of these cations are summarized.

A consequence of the detection of the radiative channel of relaxation was that besides emission spectroscopy, techniques based on laser-induced fluorescence[14] and photoelectron-photon coincidence[15] could be applied to probe deeper into the structure and relaxation dynamics of such cations.

One of the aims of these spectroscopic studies is to measure the vibrational frequencies of the organic cations. Usually, a few of these are available from photoelectron spectroscopy,[3] and in some cases from photoionization mass spectroscopy,[16] but only with limited accuracy. On the other hand, emission and laser-induced excitation spectra provide the vibrational frequencies of many of the totally symmetric fundamentals for the cationic ground, $^2\tilde{X}$, and excited, $^2\tilde{A}$ or $^2\tilde{B}$, electronic states respectively. These have been deduced for many of the organic radical cations decaying radiatively.

As far as the relaxation dynamics are concerned, the lifetimes and fluorescence quantum yields of state-selected cations are required. Lifetimes can be obtained by means of the techniques of emission or laser-induced fluorescence spectroscopy but the corresponding fluorescence quantum yields can at present only be determined absolutely by photoelectron-photon coincidence measurements (vide infra).

In connection with these measurements, it is appropriate to point out that there are advantages in the study of nonradiative relaxation processes for open-shell organic cations rather than for their molecular species. These are due to the respective sequences of electronic states.[4] Whereas for closed-shell species the lowest state of higher multiplicity ($^3T_1$) always lies below the first excited singlet state ($^1S_1$ arising from the same configuration), in the case of most open-shell cations the lowest excited state is the doublet state that can be reached in the ionization process (i.e., $^2\tilde{A}$).[2] The lowest quartet state ($^4\tilde{a}$) corresponds to a different electronic configuration and thus lies to higher energies at the same geometries. Consequently, more often than not, only coupling of the prepared state ($^2\tilde{A}$) with high vibrational levels of the ground state ($^2\tilde{X}$) need be considered as an alternative decay mechanism to the radiative one.

Emission Spectroscopy

The essential aspect of the electron-impact excitation of the emission spectra of open-shell cations is depicted in Figure 1. The molecular species in its ground state (M ^1X) is ionized by an electron beam of energy E_i resulting, among other processes, in the various doublet states of the cation (M$^+$ $^2\tilde{J}$) which are accessible ac-

(12) See J. P. Maier, in "Kinetics of Ion-Molecule Reactions", P. Ausloos, Ed., Plenum, New York, 1979, p 437; J. P. Maier, *Chimia* **34** 219 (1980); and J. P. Maier, *Angew. Chem., Int. Ed. Engl.*, **20**, 638 (1981), for more detailed reviews of this field.

(13) J. P. Maier, O. Marthaler, L. Misev, and F. Thommen in "Molecular Ions", J. Berkowitz, Ed., Plenum Press, New York, 1982.

(14) P. C. Engelking and A. L. Smith, *Chem. Phys. Lett.*, **36**, 22 (1975).

(15) M. Bloch and D. W. Turner, *Chem. Phys. Lett.*, **30**, 344 (1975).

(16) M. R. Robin "Higher Excited States of Polyatomic Molecules", Vol. 1 and 2, Academic Press, London, 1975.
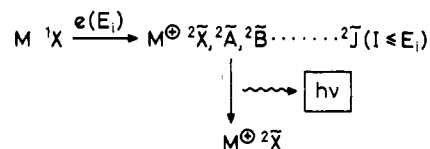
Figure 1. Schematic representation of the approach used to excite emission spectra of open-shell organic cations by controlled electron impact.
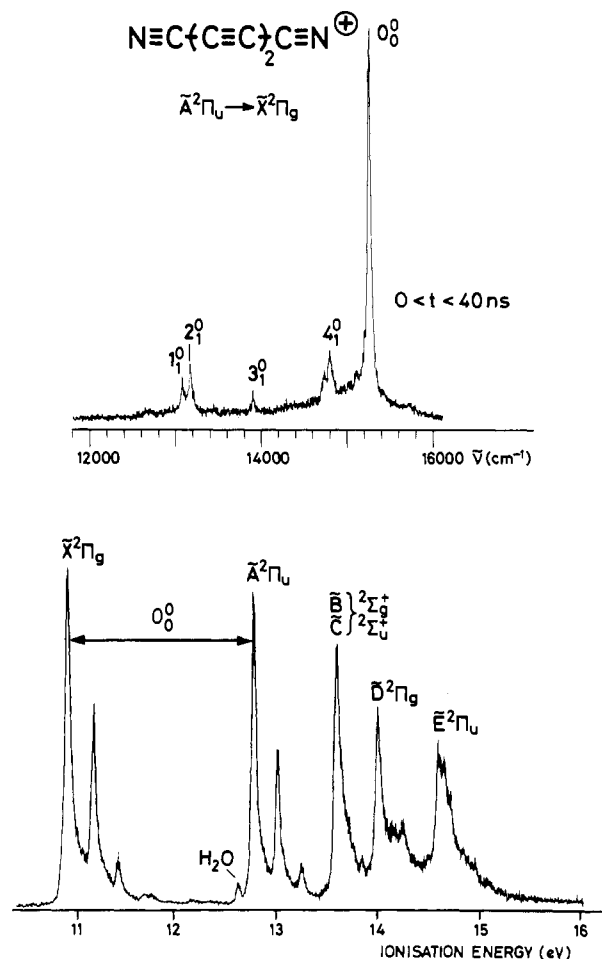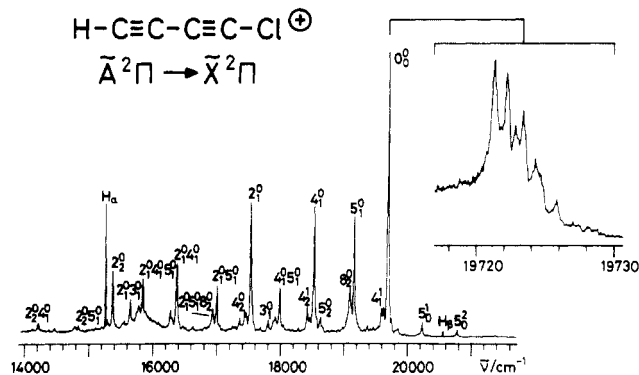

Figure 2. Emission spectrum of dicyanodiacetylene cation (top) and the He Iα photoelectron spectrum (bottom). The $\tilde{A}^2\Pi_u$ → $\tilde{X}^2\Pi_g$ emission band system was recorded under time-resolved conditions ($0 < t < 40$ ns) with an optical resolution of 0.8 nm. The assigned vibrational structure corresponds to the excitation of the four Σ_g^+ fundamentals.

cording to the selection rules and energy restrictions. Any resulting photons emitted, as shown in the example of Figure 1 for the $^2\tilde{A}$ → $^2\tilde{X}$ cationic transition, are then wavelength dispersed and detected by a single photon counting technique. The actual apparatus operates in a crossed-beam arrangement whereby the sample is introduced as an effusive beam.[10]

In practice the electron energy is usually tuned to around 20–40 eV because the ionization cross sections are reasonable and yet fragment emissions (e.g., from C_2, CH, CN) are not overwhelming. The latter result from inelastic processes due to the nonspecificity of the electron-impact excitation. However, it is possible to separate superimposed band systems if the emitting species differ appreciably in their lifetimes. This is illustrated by the time-resolved emission spectrum shown in Figure 2. The band system of interest, $\tilde{A}^2\Pi_u$ → $\tilde{X}^2\Pi_g$, of dicyanodiacetylene cation is overlapped by

Figure 3. Emission spectrum of chlorodiacetylene cation ($\tilde{A}^2\Pi \rightarrow \tilde{X}^2\Pi$) recorded with 0.16-nm bandwidth. The inset (top right) was obtained with 0.008-nm resolution.

Figure 4. Decay curves for the $^2\tilde{A}$ states of 1,3-pentadiyne and of chloroacetylene cations plotted on a semilogarithmic scale (without background). These were obtained, for a selected emission band, by detecting photons in delayed coincidence with reference to the gated exciting electron beam.

the red system ($A^2\Pi \rightarrow X^2\Sigma^+$) of the cyanogen radical.[17] However, as the latter lifetime is several microseconds compared to a few nanoseconds for the cation, time discrimination is efficient and the otherwise dominant CN bands are effectively attenuated.

The assignment of the band system to an electronic transition of the cation follows by comparison with the photoelectron spectroscopic measurement. Such data are shown in the bottom part of Figure 2. The comparison is several-fold. The separation of the first two band systems in the photoelectron spectrum corresponds to the wavelength range of the emission band system, and actually the 0_0^0 band position is usually located to within ± 0.02 eV by the difference of the adiabatic ionization energies. The excitation function (i.e., emission intensity as function of the electron excitation energy) can be recorded for, say, the 0_0^0 emission band, and the threshold corresponds, within the error limits, to the adiabatic ionization energy of the $^2\tilde{A}$ state. Furthermore, the excitation function for cationic states is characteristically different from that of excited neutral or fragment species. By this means the emission spectra of the organic radical cations (cf. Table I) have been found and identified.[12]

The emission spectra, such as shown in Figures 2 and 3, provide the vibrational frequencies of mainly the totally symmetric fundamentals, though excitation of degenerate modes by two quanta (possessing a totally symmetric component) is also sometimes observed. In the smaller, or high symmetry, radical cations the vibrational frequencies of all, or the majority, of the totally symmetric modes have been inferred for their ground state. This is apparent from the emission spectra of the cations of dicyanodiacetylene[17] (Figure 2) and chlorodiacetylene[18] (Figure 3) which have four Σ_g^+ and five Σ^+ fundamentals, respectively. On the other hand, in the largest, or low symmetry, species, although vibrational frequencies are still obtained, the assignment to specific modes is more problematic due to the large choice possible. Also, the emission spectra are usually more congested.

The prominent bands in the emission spectra have been assigned to transitions which originate from the zeroth vibrational level of the excited state (cf. Figures 2, 3). However higher resolution recordings of these
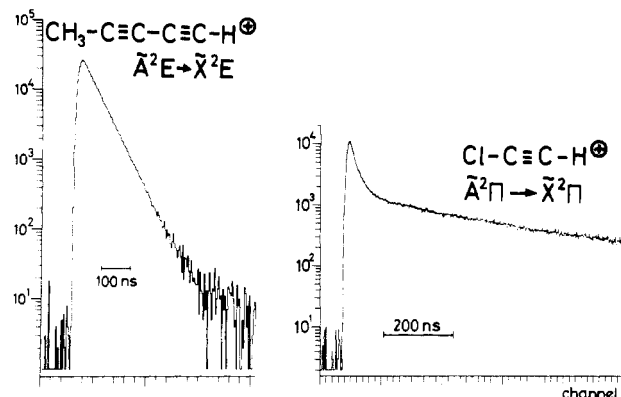
bands (e.g., as shown as insert in Figure 3)[19] reveal that they are composed of several peaks which can be attributed to the sequence transitions. As only a few weak bands are apparent to higher energy of the 0_0^0 bands, the intensity of the transitions from vibrationally excited levels is concentrated in the sequence bands which flank each of the prominent bands. In the highest resolution recordings for some of the smaller linear cations, such as of chloroacetylene, rotational structure has also been resolved.[13]

Another inference that can be drawn from the detection, or lack, of the radiative decay is the symmetry of the excited state involved in the transition, by consideration of the dipole selection rules and the information available on the symmetry of the cationic ground state. The latter can usually be unambiguously deduced from photoelectron spectroscopic[20] and theoretical studies.[4] Thus, for example, the symmetry of the $^2\tilde{A}$ state of dicyanoacetylene cation has been shown to be $^2\Pi_g$ in view of the emission, photoelectron, and theoretical data.[21] On the other hand the lack of detectable radiative decay from electronically excited benzene cation[11] in addition to other experimental observations,[22] leads one to conclude that the adiabatic ionization energy of the $^2E_{2g}$ state (i.e., $\tilde{A}$) is less than that of the $^2A_{2u}$ (i.e., $\tilde{B}$) state.

One of the first steps in studies of the relaxation behavior of electronically excited radical cations under collision-free conditions is measurement of their lifetimes. This can be accomplished by pulsing the electron gun and by accumulating a decay curve using the single photon delayed coincidence approach. The excited-state level is selected by tuning the monochromator to an appropriate emission band; in practice these measurements are usually restricted to the zeroth and the lowest excited levels of the excited state. A typical decay curve, obtained for 1,3-pentadiyne cation,[23] is shown in Figure 4 as a semilogarithmic plot.

(17) E. Kloster-Jensen, J. P. Maier, O. Marthaler, and M. Mohraz, *J. Chem. Phys.*, 71, 3125 (1979).

(18) J. P. Maier, O. Marthaler, and E. Kloster-Jensen, *J. Electron Spectrosc. Relat. Phenom.* 18, 251 (1980).

(19) J. P. Maier, O. Marthaler, L. Misev, and F. Thommen, *Faraday Discuss. Chem. Soc.*, 71, 1981.

(20) See E. Heilbronner and J. P. Maier in "Electron Spectroscopy: Theory, Techniques and Applications", C. R. Brundle and A. D. Baker, Eds., Academic Press, New York, 1977, for a discussion of this aspect.

(21) J. P. Maier, L. Misev, and F. Thommen, *J. Phys. Chem.*, 86, in press, and references therein.

(22) B. S. Freiser and J. L. Beauchamp, *Chem. Phys. Lett.*, 35, 35 (1975).

(23) J. P. Maier, O. Marthaler, and E. Kloster-Jensen, *J. Chem. Phys.*, 72, 701 (1980).
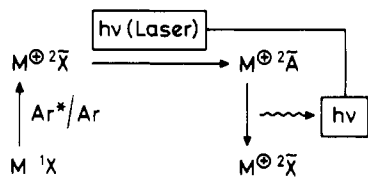
Spectroscopy of Open-Shell Cations

Figure 5. Schematic summary of the essential features of the technique used to obtain laser-induced excitation spectra of open-shell organic cations.

It has been found that the typical radiative lifetimes of the larger organic cations in their $^2\tilde{A}$ (or $^2\tilde{B}$) electronic states are around 100 ns.[12] These correspond in all cases to dipole-allowed transitions, and the energy gap between the ground and the emitting excited electronic state is in the 2–3-eV range. However, in the case of the halocyanide[24] and haloacetylene[10] cations in their $\tilde{B}^2\Pi$ and $\tilde{A}^2\Pi$ states, respectively, pronounced nonexponential decay curves are obtained. One such curve for chloroacetylene cation is reproduced also in Figure 4. This relaxation behavior was consequently studied by time-resolving the emission spectra[10] and also by the photoion–photon coincidence measurements.[25]

These cations provide good examples of "intermediate case" decay within the hierarchy of nonradiative transition theory.[26] They fall into this category because the radiative state ($^2\tilde{A}$) is coupled only with the manifold of vibrational states of the ground cationic state whose density is still relatively small (10^3–10^4 levels/cm^{-1}). The nonexponential behavior could be semiquantitatively rationalized within the proposed theoretical framework.[25]

Laser-Induced Excitation Spectroscopy

The technique of laser-induced fluorescence has been demonstrated to be a powerful tool for spectroscopic and dynamic studies of molecular systems.[27] In the case of open-shell cations, however, it is only in the recent years that such techniques have been applied. The difficulty lies with the fact that the cations, like radicals, have to be generated prior to laser excitation. It requires about 8–12-eV energy to produce most of the open-shell organic cations listed in Table I in their ground states. On the other hand, the advantage lies in the fact that merely 2–3 eV of energy are required to reach their $^2\tilde{A}$ (or $^2\tilde{B}$) states, which is ideal for tunable dye lasers.

A successful approach has been to produce the cations by Penning ionization using rare gas metastables.[14,28] The generated cations are furthermore thermalized in their ground states by collisions with the rare gas carrier. The electronic transition (e.g., $^2\tilde{A} \leftarrow {}^2\tilde{X}\ 0^0$) can then be pumped by the laser excitation, and when the resulting fluorescence is monitored, the excitation spectrum is obtained. The essential aspects of this technique are summarized in Figure 5. This provides the means to follow the absorption process of a cation in the gas phase. This method was in fact first

(24) M. Allan and J. P. Maier, *Chem. Phys. Lett.*, 41, 231 (1976).
(25) G. Dujardin, S. Leach, G. Taieb, J. P. Maier, and W. M. Gelbart, *J. Chem. Phys.*, 73, 4987 (1980).
(26) See S. Leach, G. Dujardin, and G. Taieb, *J. Chim. Phys. Phys.-Chim. Biol.*, 77, 705 (1980), for a discussion on ions.
(27) R. N. Zare and P. J. Dagdigian, *Science* (*Washington, D. C.*) 185, 739 (1974); J. L. Kinsey, *Annu. Rev. Phys. Chem.*, 28, 349 (1977), and references therein.
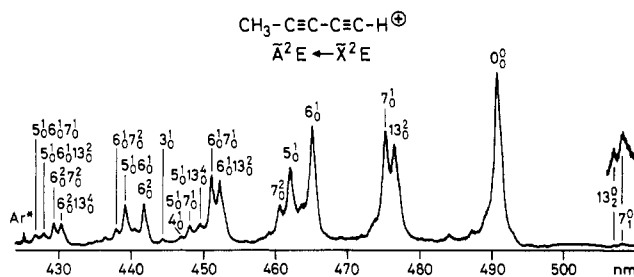(28) T. A. Miller and V. E. Bondybey, *J. Chim. Phys. Phys.-Chim. Biol.*, 77, 695 (1980), and references therein.

Figure 6. Laser induced excitation spectrum of the $\tilde{A}^2E \leftarrow \tilde{X}^2E$ transition of 1,3-pentadiyne cation recorded with a bandwidth of 0.02 nm. A vibrational assignment of the stronger bands is mainly among the seven A_1 fundamentals.
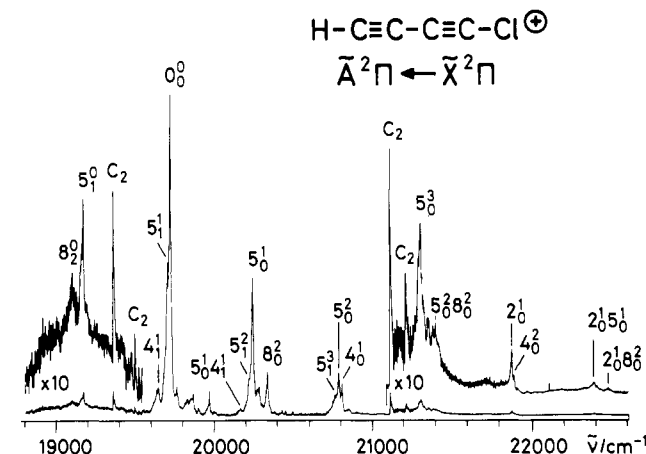
Figure 7. Laser-induced excitation spectrum of the $\tilde{A}^2\Pi \leftarrow \tilde{X}^2\Pi$ transition of chlorodiacetylene cation (0.02-nm band-pass). The vibrational assignment of some of the bands is indicated.

applied to the molecular cation N_2^+[14] and subsequently to some of the organic cations which have been found to decay radiatively (cf. Table I).[28]

In Figure 6 is shown the laser-induced excitation spectrum of 1,3-pentadiyne cation, $\tilde{A}^2E \leftarrow \tilde{X}^2E$.[29] As in the case of the emission spectra, the various bands can be vibrationally assigned. This is indicated in the example given, for which the ν_1 to ν_7 fundamentals are totally symmetric, A_1, under C_{3v} symmetry classification. From such spectra the vibrational frequencies of many of the totally symmetric fundamentals are inferred for the cations in their excited electronic state ($^2\tilde{A}$ or $^2\tilde{B}$)[29] and complement the $^2\tilde{X}$ state values deduced from the emission spectra.[23]

For a further illustration of this aspect, the laser-induced excitation spectrum of chlorodiacetylene cation ($\tilde{A}^2\Pi \leftarrow \tilde{X}^2\Pi$) is shown in Figure 7[19] and should be compared with the emission spectrum ($\tilde{A}^2\Pi \rightarrow \tilde{X}^2\Pi$)[18] shown in Figure 3. In both spectra, excitation of six of the seven Σ^+ fundamentals is apparent either in the $\tilde{X}^2\Pi$ (Figure 3) or $\tilde{A}^2\Pi$ (Figure 7) states. On the whole it has been found that for these and for most of the organic cations studied, the vibrational frequencies in their $^2\tilde{X}$ and $^2\tilde{A}$ (or $^2\tilde{B}$) states do not differ by more than 10–15% from molecular ground-state values.

Higher resolution recordings have also been achieved (≥ 0.002 nm) by incorporation of an intracavity etalon. In the example of chlorodiacetylene, substructure can be resolved for each of the peaks (Figure 7), such as shown for the 0^0_0 band in Figure 3. This corresponds to the transitions of the two spin–orbit components (i.e.,

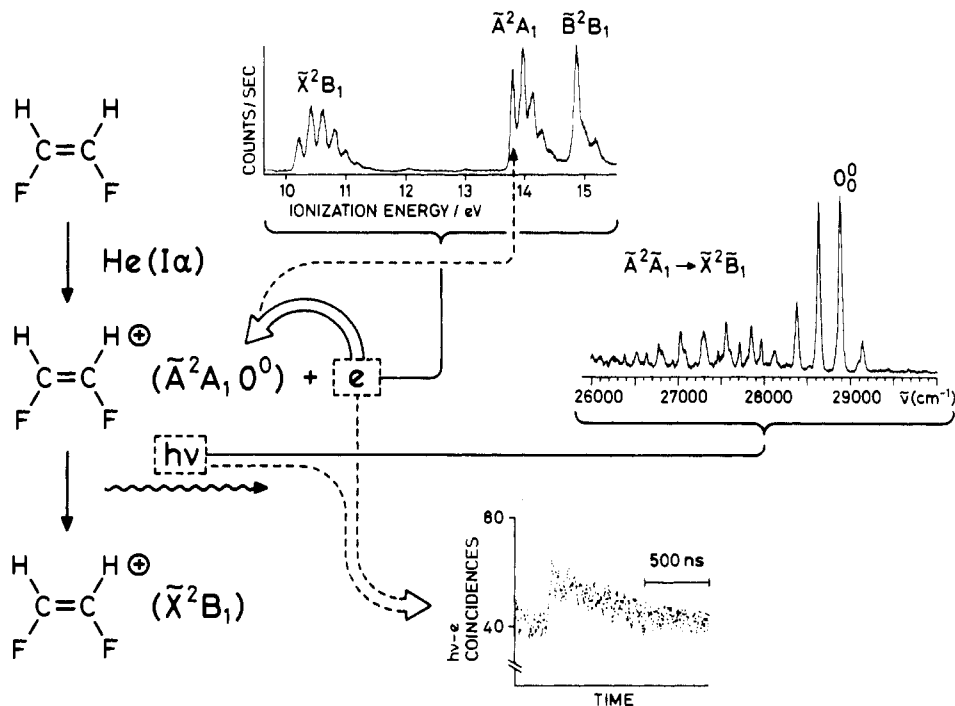(29) J. P. Maier and L. Misev, *Chem. Phys.*, 51, 311 (1980).

Figure 8. Summary of the principles of the photoelectron–photon coincidence method illustrated for *cis*-1,2-difluoroethylene cation. The spectra shown are the photoelectron (top), emission (middle right), and the photoelectron–photon coincidence curve (bottom).

$^2\Pi_{3/2} \rightarrow {}^2\Pi_{3/2}$ and $^2\Pi_{1/2} \rightarrow {}^2\Pi_{1/2}$) as well as to sequence bands. In some of the smaller linear species, such as diacetylene cation, the rotational structure can be clearly resolved.[30] A further important application of this technique is the measurement of lifetimes of the excited cations in selected vibrational, and in some cases rotational, states.

Photoelectron–Photon Coincidence Spectroscopy

The goal of measurements by means of the photoelectron–photon coincidence technique is the determination of fluorescence quantum yields, $\phi_F(v')$, and lifetimes, $\tau(v')$, of state-selected cations. The technique as such was first used to obtain lifetimes of some diatomic and triatomic cations using He $I\alpha$ as the photoionization source.[15] Subsequently, an alternative approach was adopted, namely the use of a tunable photoionization source (synchrotron radiation) and detection of zero energy photoelectrons.[31]

The principles and essential features of the coincidence technique[32] are illustrated in Figure 8 for *cis*-1,2-difluoroethylene. The cations are generated by He $I\alpha$, 21.22 eV, photoionization, and the level ($^2\tilde{A}(v')$) is defined by the energy of the ejected photoelectrons. The latter are registered as well as those events arising from the detection of wavelength undispersed photons which may be emitted from the well-defined ionization region. If the excited cation decays radiatively (cf. Figure 8), then true photoelectron–photon coincidences will be detected. This is manifested by a decay curve superimposed on a uniform background of random coincidences as shown for *cis*-1,2-difluoroethylene.[33] Conversely, the detection of such a curve proves that,

(30) J. P. Maier and L. Misev, unpublished results.
(31) E. W. Schlag, R. Frey, B. Gotchev, W. B. Peatman, and H. Pollak, *Chem. Phys. Lett.*, 51, 406 (1977).
(32) J. P. Maier and F. Thommen, *Chem. Phys.*, 51, 319 (1980).
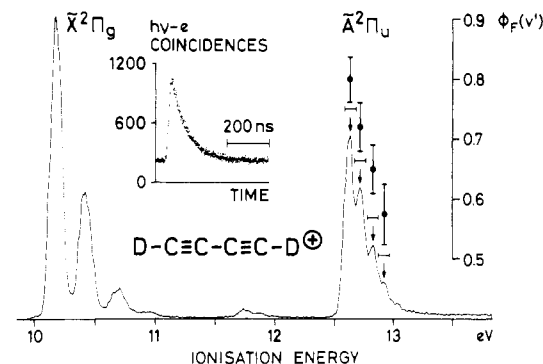(33) J. P. Maier and F. Thommen, *J. Chem. Soc., Faraday Trans. 2*, 77, 845 (1981).

Figure 9. Photoelectron–photon coincidence curve (inset) for the $\tilde{A}^2\Pi_u$ 0^0 level of dideuteriodiacetylene cation accumulated in about a day. Above the He $I\alpha$ photoelectron spectrum are plotted the determined fluorescence quantum yields at the selected internal energies.

upon formation of the cation with the defined internal energy, photons (200 < λ < 900 nm being the wavelength region monitored) are emitted from this, or any subsequently formed, isoenergetic, species or fragments. In the present application to cations whose emission spectra have been identified, there is no ambiguity.

For evaluation of fluorescence quantum yields, the rate of detection of true electrons, N_e, has to be measured (i.e., electron count rate compensated, if necessary, for scattered electrons) as well as the rate of true coincidences, N_T, which is inferred from the coincidence curve. It can be shown that $N_T/N_e = f_{h\nu}(\lambda)\phi_F(v')$. The overall transmission efficiency for the collection of photons, $f_{h\nu}(\lambda)$, is determined as a function of wavelength using internal standards,[32] i.e., for diatomic and triatomic cations for which $\phi_F(0^0) = 1.0$. The $\phi_F(v')$ values of an organic cation can thus be obtained as well as the lifetimes which are extracted from the decay curves in the usual manner. However, so that a 5% accuracy for the $\phi_F(v')$ and $\tau(v')$ values can be attained, accumulation times of about a day are required.

As an example, coincidence results for dideuteriodiacetylene cation[34] are presented in Figure 9. The He Iα photoelectron spectrum recorded under the measurement conditions is shown, and the arrows marked above the second band, associated with the $\tilde{A}^2\Pi_u$ cationic state, indicate the internal energies selected. These correspond to the maxima of the vibrational peaks due to the excitation of the ν_3 (C–C stretching) Σ_g^+ fundamental. The bars attached to the arrows (Figure 9) show the band pass for electrons, implying that in effect "energy slices" of about 800 cm^{-1} within the $\tilde{A}^2\Pi_u$ state are sampled. The determined $\phi_F(v')$ values are plotted at the appropriate location in Figure 9.

The $\phi_F(v')$ and $\tau(v')$ data enable one to obtain the rate constants of the radiative, $k_r(v')$, and nonradiative, $k_{nr}(v')$, pathways depleting the energy-selected level, i.e., $k_r(v') = \phi_F(v')/\tau(v')$ and $k_{nr}(v') = [1 - \phi_F(v')]/\tau(v')$. Thus their dependence on excess internal energy/vibrational excitation can be followed. In the case of dideuteriodiacetylene cation, these data show that $\phi_F(v') < 1$ and the $k_{nr}(v')$ rate increases approximately exponentially with excess energy.[34] Similar observations were found as a result of the corresponding measurements for fluorinated benzenes[35] and for alkyl-substituted diacetylene cations.[36]

These results are in accord with the theoretical models, in the statistical limit, of radiationless decay.[37] The nonradiative pathway is that of internal conversion, $^2\tilde{A} \rightsquigarrow {}^2\tilde{X}$, and because for these cations the density $\rho(\tilde{X})$ of the $^2\tilde{X}$ state vibrational levels isoenergetic with the $^2\tilde{A}$ state is sufficiently high, the relationship $\tau << \hbar\rho(\tilde{X})$ for irreversible decay is satisfied.

It has also been found that for about a dozen organic cations decaying radiatively the nonradiative pathway leads to fragmentation.[12] Thus the relaxation dynamics can be probed by using techniques relying on fragment ion as well as photon detection. cis-1,2-Difluoroethylene cation also belongs to this category. Following its preparation in the $\tilde{A}^2A$ 0^0 state, either a fluorescence photon[38] ($^2\tilde{A} \rightarrow {}^2\tilde{X}$) or C_2HF^+ fragment ion[39] is produced. Consequently the $\phi_F(0^0)$ and $\tau(0^0)$ values have been obtained from the photoelectron–photon coincidence measurements[33] (cf. Figure 8), and the parent and fragment ion branching ratio (BR (0^0) $C_2H_2F_2^+$; C_2HF^+),[39] by the photoelectron–photoion coincidence technique.[40] The results obtained are summarized schematically in Figure 10.

It is seen that the BR (0^0) of the parent ions is about three times larger than $\phi_F(0^0)$. This suggests that the $C_2H_2F_2^+$ cations undergo a slow fragmentation, as is indeed the evidence from other mass spectroscopic investigations.[39,41] This can furthermore be put on a quantitative basis by using the available data. The $k_r(0^0)$ and $k_{nr}(0^0)$ data are inferred directly from the

Figure 10. Schematic summary of the relaxation pathways and of their inferred rate constants for cis-1,2-difluoroethylene cation after its formation in the lowest vibrational level of the $\tilde{A}^2A_1$ state.

$\phi_F(0^0)$ and $\tau(0^0)$ values. On the other hand, the slowest step in the pathway leading to fragmentation, k_f, is deduced from the BR (0^0) and $\phi_F(0^0)$ values as well as from the time-of-flight of the $C_2H_2F_2^+$ ions in the mass analyzer. This turns out to be about 2 orders of magnitude slower than the nonradiative rate, competing directly with the radiative process (cf. Figure 10). This nonradiative process is assumed to be internal conversion (and/or isomerization), and the highly vibrationally excited cation has then ample time to rearrange prior to fragmentation to C_2HF^+ and HF, as has been suggested.[41] A similar mechanism fits the data for the corresponding decay of alkyl-substituted diacetylene[35] and hexatriene cations.[42]

Concluding Remarks

The examples of the studies on open-shell cations presented above show how the application of complementary techniques can provide detailed insight into their spectroscopic structure and their relaxation behavior under collision-free conditions. The emission and laser-induced excitation spectra provide sets of vibrational frequencies for the cations in their ground and lowest excited electronic states. In the smaller cations further spectral characterization is provided by the rotational structure. These techniques also enable the lifetimes of the cations in excited state levels to be determined. The fluorescence quantum yields obtainable from the photoelectron–photon coincidence data enable the relaxation behavior to be put on a quantitative level. An aim is to establish clearly the links between the spectroscopic and decay features of such ions.

Undoubtedly the energy and time resolution of the techniques described will be further improved in the future. Double resonance techniques, in which the radiative decay is used as the sensitive probe, can also be envisaged. These developments should on the one hand lead to finer spectroscopic and hence structural information on open-shell cations and on the other hand provide a means of following state to state processes as in the study of ion–molecule reactions.

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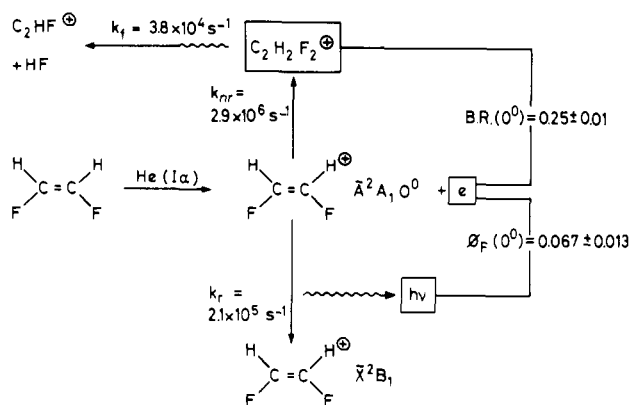(41) H. W. Jochims, W. Lohr, and H. Baumgärtel, *Nouv. J. Chim.*, **3**, 109 (1979).

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