191. Laser-Induced Fluorescence and Photoelectron-Photon Coincidence Studies of 3,5-Octadiyne Cation

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Summary

3,5-Octadiyne cation in its lowest excited state has been studied in the gas phase by laser-induced fluorescence and photoelectron-photon coincidence techniques. The excitation spectrum of the $\tilde{A}^2A'' \leftarrow \tilde{X}^2A''$ transition has been obtained and yields vibrational frequencies of some of the fundamentals for the excited cationic state. The fluorescence quantum yields and lifetimes at selected energies within the $\tilde{A}^2A''$ state have been determined from the coincidence measurements. This provides quantitative data for the discussion of the relaxation behaviour of such an excited open-shell cation.

Introduction. - 3,5-Octadiyne cation, $H_5C_2-C\equiv C-C\equiv C-C_2H_5^+$, is one of the largest open-shell cations found to relax radiatively when generated in its lowest excited electronic state [1]. This was revealed by its emission spectrum, excited by low energy electron impact, and assigned to the $\tilde{A}^2A'' \rightarrow \tilde{X}^2A''$ transition (under C_s-symmetry classification) [2]. The spectrum was studied in conjunction with the corresponding emission spectra of the related cations, $CH_3-C\equiv C-C\equiv C-R^+$ ($R = H, CH_3$), and these yielded the vibrational frequencies of the totally symmetric fundamentals in the cationic ground states, $^2\tilde{X}$. More recently, the excited states, $^2\tilde{A}$, of the latter cations could be investigated by means of two further techniques; laser-induced fluorescence [3] and photoelectron-photon coincidence spectroscopies [4]. In this article are presented the complementary results on 3,5-octadiyne cation obtained using these two methods. The *Scheme* shown on the following page summarizes the principles of these two techniques as applied to 3,5-octadiyne cation.

In the laser-induced fluorescence approach [5] (route ①) the cations are generated by *Penning* ionization with argon metastables (of energies 11.5 and 11.7 eV) and are also collisionally relaxed with the argon carrier gas (at about 1 Torr) which has been cooled to liquid nitrogen temperature [6]. The cations in the $^2\tilde{X}$ states are also consequently cooled to this temperature and they are then laser-excited to a specific level, v′, in the $^2\tilde{A}$ excited state. When the undispersed emitted photons are collected as function of the laser wavelength, the $^2\tilde{A} \leftarrow {}^2\tilde{X}$ absorption process can be followed and the excitation spectrum is obtained. The analysis of the

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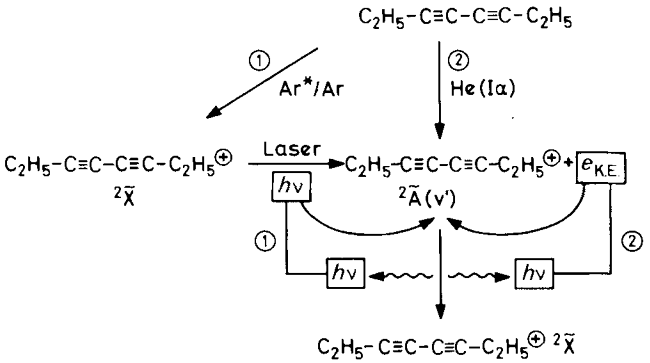
Scheme



spectral band structure yields the vibrational frequency data for the cation in the excited state.

The photoelectron-photon coincidence approach (route ②) relies on the energy of the ejected photoelectron, $e_{\mathrm{K.E.}}$, to define the selected level of the excited cation [7]. Emitted photons are then detected in delayed coincidence with the electrons. From the coincidence statistics the fluorescence quantum yield and lifetime of the cation with the chosen internal energy are determined [4]. These in turn allow the decay pathways of such an excited cation to be followed quantitatively as the radiative and non-radiative rate constants are directly obtained.

Experimental part. – The apparatus built for the laser-induced fluorescence measurements has been described [3]. One modification was that the glass vessel with tantalum electrodes for the d.c. discharge was itself surrounded by a vessel containing liquid nitrogen. The gas sample was mixed with the argon about 5 cm above the region where the laser beam passed. The latter was the output from a nitrogen-pumped dye laser operating at 30 Hz with a band-width of 0.02 nm. The fluorescence was detected with an S-20 photomultiplier and appropriate cut-off filters to reduce the stray light from the laser. The data were recorded on-line by means of a transient digitizer coupled to an *LSI* 11/23 microcomputer. For the measurements on 3,5-octadiyne cation three dye solutions were used and the spectrum shown *(Fig. 1)* was constructed by recording bands common to the dye ranges. The wavelength was calibrated using Ar and Ta atomic lines apparent in the spectrum *(Fig. 1)*.

The design and operation of the photoelectron-photon coincidence apparatus has also been given [4]. The measurements were carried out using He(Iα), 21.22 eV, radiation and thus the energy band-pass for electrons corresponding to the $\tilde{A}^2A''$ state of 3,5-octadiyne cation was ≈ 100 meV. Following the selection of the electron energy, the electron events and those arising from the detection of undispersed photons, were sampled in delayed coincidence. Typical accumulation periods to obtain data such as shown in *Figure 2* were about a day. In order to evaluate the fluorescence quantum yields, the rates of detection of true electrons, N_e, and of true coincidences, N_T, have to be measured [4]. The sample was introduced into the apparatus from a glass vessel held at ambient temperature and the pressure in the ionization region was $< 10^{-4}$ Torr.

Results and Discussion. – The laser-induced excitation spectrum of 3,5-octadiyne cation is shown in *Figure 1.* Bands associated with the $\tilde{A}^2A'' \leftarrow \tilde{X}^2A''$ transition of this cation are observed in the wavelength range 430–500 nm, and in *Table 1* the wavenumbers of the maxima of the distinct bands are collected. The determined position of the 0_0^0 band, 20079 ± 5 cm^{-1} is in accord with the value obtained previously, 20076 ± 4 cm^{-1}, from the emission spectrum [2].

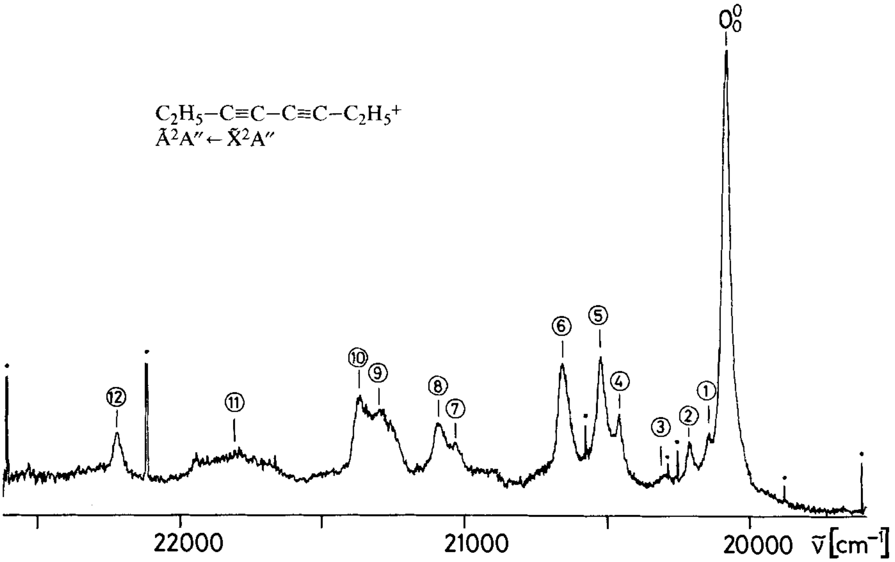


Fig. 1. *Laser-induced excitation spectrum of the $\tilde{A}^2A'' \leftarrow \tilde{X}^2A''$ transition of 3,5-octadiyne cation, cooled to liquid nitrogen temperature and recorded with optical resolution of 0.02 nm* (some of the atomic lines of Ar or Ta are marked with a dot)

Table 1. *Maxima of the prominent bands in the $\tilde{A}^2A'' \leftarrow \tilde{X}^2A''$ laser excitation spectrum of 3,5-octadiyne cation* (The numbers in the first column refer to the labelling of the bands in *Fig. 1*. Values ±5 cm^{-1}; those with * ±10 cm^{-1})

Label	$\tilde{\nu}$(cm^{-1})	$\Delta\tilde{\nu}$(cm^{-1})	Label	$\tilde{\nu}$(cm^{-1})	$\Delta\tilde{\nu}$(cm^{-1})
SL	20079	0	7	21031	952
1	20144	65	8	21090*	1011
2	20212	133	9	21296*	1217
3	20296*	217	10	21365	1286
4	20458	379	11	21788*	1709
5	20522	443	12	22217	2138
6	20656	577			

The vibrational frequencies which are inferred from the excitation spectrum are 2138, 1286, 1217, 577, 443 and 379 cm^{-1}. The uncertainty in these values is taken as ±10 cm^{-1} due to the inherent broadness of the bands in spite of the rotational cooling. The given frequencies correspond to the totally symmetric fundamentals of 3,5-octadiyne in the $\tilde{A}^2A''$ excited state. However, assignment to specific modes is not made in view of the large number of fundamentals in C_s-symmetry and in fact the molecular values are not known either. For comparison, the vibrational frequencies (±10 cm^{-1}) deduced for the cationic ground state from the emission spectrum were 2235, 1330, 540 and 470 cm^{-1} [2].

The photoelectron spectrum displayed in *Figure 2* was recorded under the coincidence conditions and the labels ① to ④ show the ionization energies selected for the measurements. These correspond to 'slices' of about 100 meV as represented

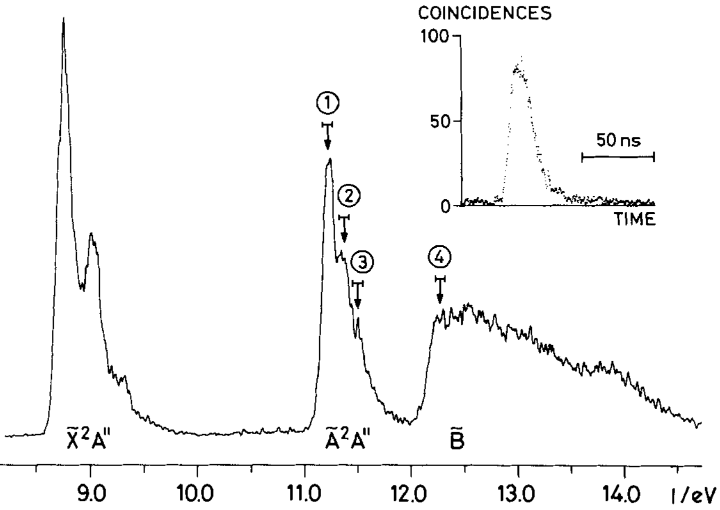


Fig. 2. *Photoelectron-photon coincidence curve for the lowest level (position ①) of the* $\tilde{A}^2A''$ *state of 3,5-octadiyne cation:* $N_e = 70$ *Hz,* $N_T = 0.05$ *Hz, accumulation time = 24 h. The He(Iα) photoelectron spectrum shows the internal energies (①–④) and resolution selected.*

Table 2. *Fluorescence quantum yields,* $\phi_F(v')$, *lifetimes* $\tau(v')$ *and radiative* k_r *and non-radiative* k_{nr} *rate constants of 3,5-octadiyne cation at selected ionization energies* I *within the* $\tilde{A}^2A''$ *state*

I/eV	Label	$\phi_F(v')$	$\tau(v')$/ns	$k_r/10^7$ s^{-1}	$k_{nr}/10^8$ s^{-1}
11.25	1	0.19 ± 0.02	8 ± 1	2.4 ± 0.4	1.0 ± 0.1
11.41	2	0.15 ± 0.02	7 ± 1	2.3 ± 0.4	1.2 ± 0.2
11.57	3	0.13 ± 0.01	6 ± 1	2.2 ± 0.4	1.5 ± 0.2

by the bars above the arrows. True photoelectron-photon coincidences were detected at the three locations within the $\tilde{A}^2A''$ state, whereas at ④, within the $\tilde{B}^2A'$ state, none were observed indicating that ϕ_F (④) $< 10^{-3}$. The $^2\tilde{B}$ state is formed by ejection of electrons from in-plane orbitals (*i.e.* σ^{-1}) whereas the $^2\tilde{X}$ and $^2\tilde{A}$ state result from the removal of electrons from the acetylenic π orbitals (*i.e.* π^{-1}-processes) [8].

The results of the photoelectron-photon coincidence measurements are presented in *Table 2.* The lifetimes, τ (v′), were extracted from the decay part of the true coincidence curve which is superimposed on a background of random coincidences. One such curve is shown as the inset of *Figure 2.* As can be seen, the fall part of the curve is almost of the same time scale as the rise part. The latter represents the overall time resolution of the apparatus and this depends on the kinetic energy of the selected photoelectrons. The lifetime determined for the 0^0 level of the $\tilde{A}^2A''$ state, 8 ± 1 ns, is in agreement with the value (7 ± 2 ns) obtained using pulsed electron beam excitation [2].

The fluorescence quantum yields, $\phi_F(v')$, were evaluated from the relationship $N_T/N_e = \phi_F(v') \cdot f_{h\nu}(\lambda)$, where $f_{h\nu}(\lambda)$ is the calibrated, absolute detection efficiency for photons [4]. N_T, the rate of true coincidences, is obtained from the coincidence curve and N_e by direct measurement of the electron count rate. The error limits of the $\phi_F(v')$ values given in *Table 2* include the variations between individual measurements. The $\phi_F(v')$ values are less than unity and decrease with increasing internal energy *(Table 2)*.

The coincidence data prove that the radiative relaxation depletes vibrational levels of 3,5-octadiyne cation up to ≈ 3000 cm^{-1} above the zero*th* level in the $\tilde{A}^2A''$ state. This is also evident from the excitation spectrum *(Fig. 1)* where the highest energy band detected corresponds to the excitation of a vibration in the $\tilde{A}^2A''$ state with ≈ 2140 cm^{-1}. Actually very weak bands have been detected up to vibrational energies of ≈ 5000 cm^{-1}. Detection of such higher levels is difficult however, because the intensity of an excitation band is dependent not only on the $\phi_F(v')$ value of the emitting level but also on the probability of initially populating the level in the absorption process from the cationic ground state. The combination of these two factors is that, for example band ⑫, in the excitation spectrum is almost an order of magnitude less intense than the 0_0^0 band *(Fig. 1)*.

The radiative, $k_r(v')$, and non-radiative, $k_{nr}(v')$ rate constants for the depletion of the selected levels of 3,5-octadiyne cation can be calculated according to the relationships $k_r(v') = \phi_F(v')/\tau(v')$ and $k_{nr}(v') = [1 - \phi_F(v')]/\tau(v')$. These values are given in the last two columns in *Table 2*. It is seen that, within the error limits, the $k_r(v')$ rate remains constant for the studied energies within the $\tilde{A}^2A''$ state but the $k_{nr}(v')$ rate increases with excess energy.

The radiationless decay of such a cation under collision-free conditions is characteristic of the statistical limit case [9]. For this cation, and as is usually the case for open-shell organic cations [1], the two competing pathways couple the $^2\tilde{A}$ and $^2\tilde{X}$ states either radiatively $^2\tilde{A} \rightarrow {}^2\tilde{X}$ or non-radiatively $^2\tilde{A} \rightsquigarrow {}^2\tilde{X}$ (*i.e.* internal conversion). Thus on the time scale of the experiment the decay to the dense ground state manifold is irreversible, leading to less than unity fluorescence quantum yields. A linear or exponential increase in the non-radiative rate with excess vibrational energy is also predicted [9].

One can also compare the series, $R-C\equiv C-C\equiv C-R^+$ with R = H, CH_3 and C_2H_5 for all of which the coincidence measurements of $\phi_F(v')$ and $\tau(v')$ have been undertaken [10] [11]. The $k_r(v')$ rate turns out to be about the same for all the three cations; in the range $1-3 \times 10^7$ s^{-1}. In contrast, the k_{nr} (0^0) rate increases from 4×10^6 s^{-1} for R = H [10] to 1×10^7 s^{-1} for R = CH_3 [11], to 1×10^8 s^{-1} for R = C_2H_5. However, only in the case of diacetylene cation in the $^2\tilde{A}$ state is a fragmentation pathway not accessible. On the other hand 2,4-hexadiyne and 3,5-octadiyne cations belong to about the dozen organic cations for which radiative decay $^2\tilde{A} \rightarrow {}^2\tilde{X}$ is apparent in spite of the fact that the $^2\tilde{A}$ excited state lies above observed fragment ion onsets [1]. The energy situation for 3,5-octadiyne cation in the $^2\tilde{A}$ state is that as least two fragmentation channels are open; loss of CH_3 or C_2H_5 group, *i.e.* $^2\tilde{A} \rightsquigarrow {}^2\tilde{X}^* \rightarrow C_6H_5^+$ or $C_7H_7^+$ [12]. This decay mechanism is suggested in analogy with 1,3-pentadiyne and 2,4-hexadiyne cations for which it could be shown directly that a fragmentation step is slower than the internal conversion rate [2] [11].

In conclusion, the presented studies of a large open-shell organic cation in the gas phase illustrate the spectroscopic and relaxation information that can be obtained from the laser-induced excitation spectra and photoelectron-photon coincidence data. The results are complementary and of mutual aid in their interpretation. Whereas in the one case the excited level is prepared at high resolution with the laser photons starting with the cation in the ground state, in the other approach state selection and the quantitative measurement relies on the ejected photoelectron from the molecular ground state.

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