

Emission spectra of the radical cations of difluorodiacetylene, perfluoropentadiyne-1,3, and perfluorohexadiyne-2,4 in the gas phase: $\pi \rightarrow \pi^*$ band systems and the lifetimes of the π^* states

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Emission spectra of the radical cations of difluorodiacetylene, perfluoropentadiyne-1,3, and perfluorohexadiyne-2,4 in the gas phase: $\tilde{A} \rightarrow \tilde{X}$ band systems and the lifetimes of the \tilde{A} states

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Emission spectra of the radical cations of difluorodiacetylene, perfluoropentadiyne-1,3, and perfluorohexadiyne-2,4 have been observed in the gas phase following excitation with low energy electrons. The band systems, which are detected in the 450–630 nm wavelength region, are assigned to the $\tilde{A}^2\Pi_u \rightarrow \tilde{X}^2\Pi_g$, $\tilde{A}^2E_u \rightarrow \tilde{X}^2E_g$, and $\tilde{A}^2E_u \rightarrow \tilde{X}^2E_g$ electronic transitions of these three cations, respectively, by reference to their photoelectron spectroscopic studies. The vibrational fine structure of the emission spectra is interpreted, and the frequencies of most of the totally symmetric modes in the ground state of these cations are inferred. The lifetimes of the lowest vibrational level of the \tilde{A} excited electronic states have been measured to be 28 ± 3 ns, 30 ± 3 ns, and 46 ± 2 ns for the cations of difluorodiacetylene, perfluoropentadiyne-1,3, and perfluorohexadiyne-2,4, respectively.

I. INTRODUCTION

The electronic states of the radical cations of difluorodiacetylene, perfluoropentadiyne-1,3, and perfluorohexadiyne-2,4 have recently been studied by He(I α) photoelectron spectroscopy. In the cases of the first two compounds, these studies¹ followed their successful preparation by means of a Tesla discharge through hexafluorobenzene.² The photoelectron measurements on perfluorohexadiyne-2,4,³ whose synthesis was described some time ago,⁴ have also been complemented by those dealing with the fragmentation behavior of the cation.⁵ In this contribution, we present and discuss the results of our investigations of these three radical cations by optical spectroscopy.

Using the technique we have applied hitherto in the study of the emission spectra of polyatomic radical cations of organic molecules in the gas phase,⁶ the $\tilde{A} \rightarrow \tilde{X}$ electronic transitions of the title cations have been detected following excitation by electron impact. Thus, the lifetimes of the \tilde{A} states of these cations could also be measured. This work extends our earlier studies of the radiative relaxation of electronically excited haloacetylenes,⁷ dihaloacetylenes,⁸ and dihalodiacetylene cations.⁹ In addition, perfluorohexadiyne-2,4 cation yields the emission spectrum of the second $C_6F_8^+$ isomer, following that of hexafluorobenzene cation,¹⁰ and its investigation was prompted by the results obtained on the decay of the \tilde{A} state of its hydrogen analog (2,4-hexadiyne cation), where radiative and fragmentation pathways compete and are both detected.¹¹

Vibrational frequencies for difluorodiacetylene, perfluoropentadiyne-1,3, and perfluorohexadiyne-2,4 have not been determined and only the few strong bands observed in the gas phase IR spectra have been reported.^{2,4} In this work, we can present, however, the vibrational

frequencies of most of the totally symmetric modes in the ground cationic states, which are inferred from the vibrational analysis of the emission spectra.

II. EXPERIMENTAL

The emission spectra (Figs. 1–3) were obtained with the apparatus whose design and operation have already been described.⁷ In brief, the gas sample is excited with electrons of ≈ 30 eV in energy in a crossed-beam arrangement and the emitted photons are dispersed by an 0.5 m monochromator and detected in a single-photon counting mode using an RCA C31034 photomultiplier. The data are recorded on line with a PDP/9 computer, which controls the wavelength scan, and are then corrected for the optical transmission function of the instrument. By means of this data acquisition and the sensitivity of the apparatus, it proved possible to obtain the emission spectra of the three perfluoro cations and to measure the lifetimes of the zeroth vibrational level of their first excited electronic states with sample amounts of merely 20–50 mg.

The samples were bled into the interaction region, at pressures of $\approx 10^{-5}$ Torr, from glass vessel containers kept at -130 , -100 , and -80°C for difluorodiacetylene, perfluoropentadiyne-1,3, and perfluorohexadiyne-2,4, respectively. For the former two species, the decay curves were accumulated for the 0_0^0 bands, by gating the electron beam in conjunction with the single photon coincidence technique, until the sample quantities were exhausted. In the case of perfluorohexadiyne-2,4, several measurements for the 0_0^0 band (Fig. 4) as well as for other bands in the emission spectrum could be carried out. The Ne(I) excited photoelectron spectrum of the latter compound was also measured with a resolving power of ≈ 200 . The samples of difluorodiacetylene and perfluoropentadiyne-1,3 were prepared via an electrodeless Tesla excited discharge through hexafluorobenzene as outlined by Bieri *et al.*² Perfluorohexadiyne-2,4 was synthesized in ≈ 100 mg amounts, starting with 1,1,2-trichloro-3,3,3-trifluoropropene, according to the prescription given by Norris and Finnegan.⁴

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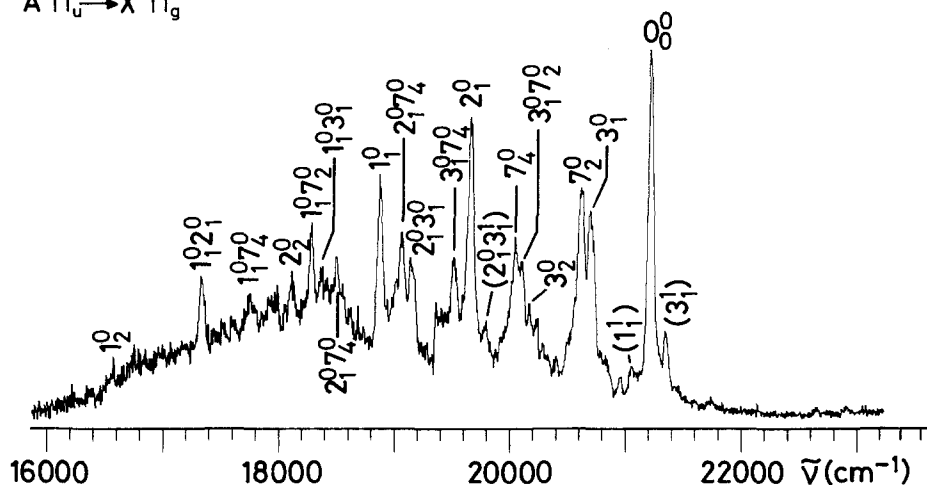
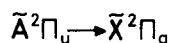
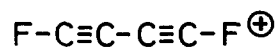


FIG. 1. Emission spectrum of difluorodiacetylene cation: $\tilde{A}^2\Pi_u \rightarrow \tilde{X}^2\Pi_g$ band system, recorded with optical resolution of 0.5 nm.

III. RESULTS AND DISCUSSION

A. Assignment

The emission band systems are found in the energy region 16 000–22 000 cm^{-1} (Figs. 1–3). They are readily assigned to the $\tilde{A} \rightarrow \tilde{X}$ electronic transitions of the radical cations of difluorodiacetylene, perfluoropentadiyne-1, 3, and perfluorohexadiyne-2, 4 on the basis of the photoelectron spectra of these species and in analogy to the previous works dealing with the emission spectra of diacetylene,^{12,13} haloacetylenes,^{7,8} halodiacetylenes,⁹ and dimethyldiacetylene cations.¹¹

Each emission spectrum lies in the energy region equivalent to the separation of the first two bands in the respective photoelectron spectrum and the most intense band at the high energy part of the emission spectrum (Figs. 1 and 2) corresponds to the predicted energy of the 0_0^0 transition of the $\tilde{A} \rightarrow \tilde{X}$ system from the photoelec-

tron data. In Table I, the results of the two sets of data are collected. By such a comparison, the 0_0^0 band of the emission spectrum of perfluorohexadiyne-2, 4 is also assigned (Fig. 3). From the photoelectron data, the ground \tilde{X} and the first excited \tilde{A} states of perfluorohexadiyne-2, 4 cation were inferred to have the symmetries 2E_g and 2E_u , respectively (under D_{3d} symmetry classification).³ In the case of difluorodiacetylene and perfluoropentadiyne-1, 3 cations, the ground and first excited electronic states were shown to have the symmetries $\tilde{X}^2\Pi_g$, $\tilde{A}^2\Pi_u$ (under $D_{\infty h}$ classification) and \tilde{X}^2E , \tilde{A}^2E (C_{3v}), respectively, from photoelectron spectroscopic studies.¹ Thus, the emission spectra shown in Figs. 1–3 are assigned to the band systems of the following electronic transitions:

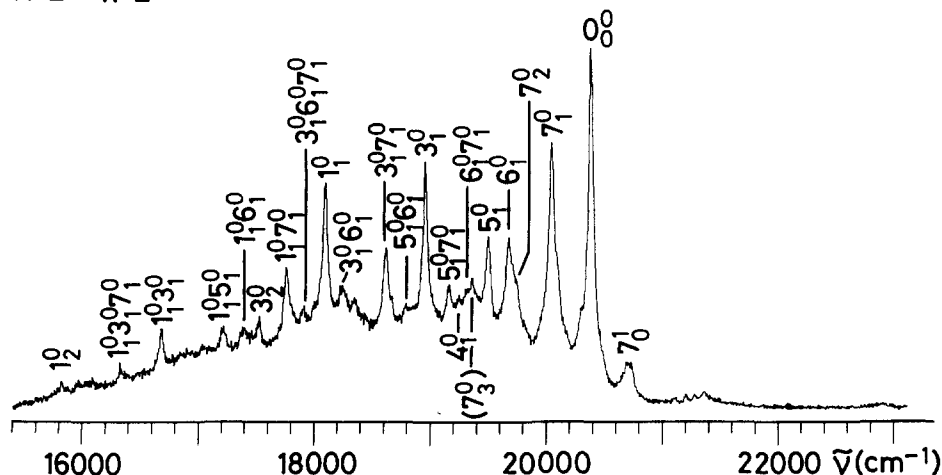
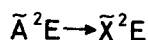
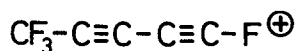
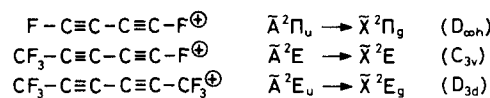


FIG. 2. Emission spectrum of perfluoropentadiyne-1, 3 cation: $\tilde{A}^2E \rightarrow \tilde{X}^2E$ band system, recorded with optical resolution of 0.5 nm.

TABLE II. Vibrational frequencies of totally symmetric fundamentals of the radical cations of difluorodiacetylene, perfluoropentadiyne-1,3, and perfluorohexadiyne-2,4 in their ground and first excited electronic states inferred from the emission and photoelectron spectra. A numbering and approximate description of the modes with the symmetry adopted is given, according to which the assigned bands in the emission spectra are labeled (Figs. 1-3).

		$\tilde{X}^2\Pi_g$		$\tilde{A}^2\Pi_u$	
F-C≡C-C≡C-F ⁺	($D_{\infty h}$)	Emission ^a	PES ^b	Emission	PES
Σ_g^+	ν_1 (C≡C stretch)	2320	2280		2290
	ν_2 (C-F stretch)	1550			1450
	ν_3 (C-C stretch)	520	480		520
	ν_7	300 ^c			
		\tilde{X}^2E		\tilde{A}^2E	
CF ₃ -C≡C-C≡C-F ⁺	(C_{3v})	Emission	PES	Emission	PES
A_1	ν_1 (C≡C stretch)	2280			
	ν_2 (C≡C a stretch)				
	ν_3 (C-C a stretch)	1440			
	ν_4 (C-F stretch)	1140	1160		1160
	ν_5 (C-F stretch)	880			
	ν_6 (C-C stretch)	710			760
	ν_7 (CF ₃ def)	340		340	
		\tilde{X}^2E_g		\tilde{A}^2E_u	
CF ₃ -C≡C-C≡C-CF ₃ ⁺	(D_{3d})	Emission	PES	Emission	PES
A_{1g}	ν_1 (C≡C stretch)	2200			
	ν_2 (C-F stretch)	1280	1280		
	ν_3 (C-C stretch)	1080			940
	ν_4 (C-C stretch)				
	ν_5 (CF ₃ def)	240		220	

^aValues ± 10 cm⁻¹.

^bValues ± 40 cm⁻¹.

^cDeduced from $2\nu_7 = 600$ cm⁻¹.

The excitation of the ν_1 (C≡C stretch) and ν_3 (C-C stretch) vibrations is also apparent on the first band in the photoelectron spectrum. On the second photoelectron band, the excitation of all three Σ_g^+ modes in the $\tilde{A}^2\Pi_u$ state is indicated¹⁴ and although the absolute values given in Table II are uncertain to ± 40 cm⁻¹, relative measurement of the spacings in the first two bands allows us to deduce that the 1_1^1 transition lies to the red of the 0_0^0 , whereas the 3_1^1 transition lies to the blue in the emission spectrum. A tentative assignment of bands in the vicinity of the 0_0^0 band which could correspond to these transitions is given in parentheses in Fig. 1.

As in the emission spectrum of diacetylene¹² cation, the intense bands lying near the 3_n^0 bands are attributed to the overtones of a degenerate vibration which possess a totally symmetric component. These are labeled as ν_7 purely by analogy with diacetylene. The choice of assignment between the ν_3 and ν_7 overtones was decided on the basis of the photoelectron data (Table II). The intensity of these bands arises presumably as in diacetylene cation, by Fermi resonance with the 3_n^0 transitions.^{12,15} The rotational analysis of the $\tilde{A}^2\Pi_u - \tilde{X}^2\Pi_g$ emission of diacetylene cation showed that in both these states the species is linear. From the similarity of the Franck-Condon features of the emission spectra and of the first two bands of the photoelectron spectra, difluorodiacetylene is also very probably linear in its ground and first excited cationic states.

There are seven vibrational modes of A_1 symmetry

for perfluoropentadiyne-1,3 under C_{3v} point group classification. In Table II, we propose a nomenclature for these modes and the assigned bands in the emission spectrum are labeled accordingly (Fig. 2). The labeling of the modes is based on comparison with the vibrational analyses for methyldiacetylene, halomethyldiacetylenes, and trifluoromethylacetylenes.¹⁸ In the ground cationic state, six of the totally symmetric modes are seen to be excited in the emission spectrum (cf. Fig. 2 and Table II), whereas only one is distinct in the photoelectron spectrum. The latter vibration, labeled ν_4 , is also observed on the second photoelectron band with the same frequency of 1160 ± 40 cm⁻¹. This vibration does not appear, however, to be strongly excited in the emission spectrum. The only vibrational frequency inferred for the \tilde{A}^2E state from the emission spectrum is for ν_7 (340 ± 10 cm⁻¹) as the intensity of the bands lying to the blue of the 0_0^0 band diminishes rapidly and the sequence bands are not resolved with this resolution.

Vibrational analysis for the ground molecular state of perfluorohexadiyne-2,4 are also not known and only the frequencies of the four strong bands observed in the ir spectrum have been reported.⁴ Thus, once more, the five totally symmetric A_{1g} modes (whose excitation is dipole forbidden in the IR spectrum) (D_{3d} symmetry assumed) are labeled as indicated in Table II. The bands in the emission spectrum (Fig. 3) are not as well separated as in the other two spectra (Figs. 1 and 2); however, the excitation of four of the A_{1g} vibrational modes

in the ground cationic state can be seen. The ν_2 vibration is also excited in the lowest photoionisation process,³ whereas the vibrational spacing apparent on the second photoelectron band corresponds to a frequency of $940 \pm 40 \text{ cm}^{-1}$. In the emission spectrum, the two bands on the higher energy side of the 0_0^0 band are attributed to the excitation of the ν_5 mode in the \tilde{A}^2E state of perfluorohexadiyne-2, 4 cation.

C. Lifetimes and decay processes of the \tilde{A} states

The lifetimes of the zeroth vibrational level of the \tilde{A} electronic states were inferred from the decay curves of the 0_0^0 bands by a least-squares linear fit to the semi-logarithmic plot. For the cations of difluorodiacetylene and perfluoropentadiyne-1, 3, these lifetimes were found to be 28 ± 3 and $30 \pm 3 \text{ ns}$, respectively, from only the two measurements possible (see "Experimental" section). In the case of perfluorohexadiyne-2, 4 cation emission, decay curves shown in Fig. 4 were measured for the 0_0^0 band, and for several bands lying to lower energy. The bands at higher energy of the 0_0^0 band, between $19\,600$ and $20\,000 \text{ cm}^{-1}$, were also used, and these necessarily correspond to vibrationally excited levels in the \tilde{A}^2E_u state. All the lifetimes extracted from these measurements were found to be the same within the reproducibility limits given as $46 \pm 2 \text{ ns}$. This is the same as the lifetime of the \tilde{A}^2A_{2u} state of its C_6F_6^+ isomers and hexafluorobenzene radical cation, which was measured to be $48 \pm 2 \text{ ns}$.¹⁰

The emission spectra of these two C_6F_6^+ isomers are, on the other hand, spectroscopically distinct and energetically separated. The $\tilde{A}^2A_{2u} - \tilde{X}^1E_{1g}$ band system of hexafluorobenzene cation lies between $16\,000$ and $22\,700 \text{ cm}^{-1}$ with the 0_0^0 transition located at $21\,600 \text{ cm}^{-1}$.¹⁰ Thus, from the emission spectrum shown in Fig. 3, one can see that no bands are observed which can be attributed to that of hexafluorobenzene cation. Furthermore, as the quantum yield of emission of the \tilde{A}^2A_{2u} state of hexafluorobenzene cation has been determined to be near unity,¹⁷ it follows from the lifetime measurements that this will probably also be the case for the \tilde{A}^2E_u state of perfluorohexadiyne-2, 4 cation. Fragmentation is not an accessible nonradiative channel for the latter cations with internal energies of $\approx 2.5 \text{ eV}$, which corresponds to the lowest vibrational levels in the \tilde{A}^2E_u state based on the fragment ion appearance potentials, the lowest being that of C_5F_4^+ at $14.2 \pm 0.2 \text{ eV}$.⁵

There is, however, an apparent loss of vibrational fine structure on the higher ionization energy portion of the second photoelectron band ($> 13.5 \text{ eV}$) which may be an indication that rapid predissociation is already setting in and thus the threshold for C_5F_4^+ ions may be lower than given. In fact, even if the photoelectron bands show distinct vibrational fine structure (lifetime $\geq 10^{-12} \text{ s}$), this is not a sufficient criterion to exclude fragmentation as one of the decay channels, as illustrated best

by the results obtained for the \tilde{A} states of the radical cations of hexadiyne-2, 4,¹¹ or of *trans*- and *cis*-1, 3, 5 hexatriene.¹⁸ For these electronically excited cations, fragmentation and emission are in competition as both the decay processes have been detected. Thus, due to the lack of fragmentation threshold and thermochemical data for the cations of difluorodiacetylene and perfluoropentadiyne-1, 3, the decay pathways accessible for their \tilde{A} states are not known.

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