

Radiative and fragmentation decay of the cations of *trans*-1,3,5-hexatriene and of all *trans*-1,3,5-heptatriene in the $\tilde{A}(\pi-1)$ states, studied by emission and photoelectron-photoion coincidence spectroscopy

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Radiative and fragmentation decay of the cations of *trans*- and *cis*-1,3,5-hexatriene and of all *trans*-1,3,5-heptatriene in the $\tilde{A}(\pi^{-1})$ states, studied by emission and photoelectron-photoion coincidence spectroscopy

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Gas phase emission spectra of the cations of *trans*- and *cis*-1,3,5-hexatriene and of all *trans*-1,3,5-heptatriene have been obtained using ≈ 25 eV electron impact as excitation. The band systems have been assigned as the $\tilde{A}(\pi^{-1}) \rightarrow \tilde{X}(\pi^{-1})$ electronic transitions according to the interpretation of their photoelectron spectra. An analysis of the emission bands yields several vibrational frequencies of the totally symmetric fundamentals for these cations in their ground states. These are compared to the frequencies obtained from the matrix absorption and photodissociation spectra of these cations for the \tilde{A} states, and from the photoelectron spectra. The title cations in the \tilde{A} states decay by radiative and fragmentation pathways, which are both detected. The fragmentation decays have been studied by photoelectron-photoion coincidence technique using He(I α) photon radiation. In the case of the 1,3,5-hexatriene cations, $C_6H_8^+$ and $C_6H_7^+$ ions are detected on formation of the \tilde{A} states, whereas for the all *trans*-1,3,5-heptatriene cation, in addition to the molecular ion, $C_7H_9^+$, $C_6H_7^+$, and $C_6H_6^+$ fragment ions are also observed. Quantum yields of emission from the lowest vibrational level of the \tilde{A} state of *trans*- and *cis*-1,3,5-hexatriene cations have been estimated as 7% and 0.3%, respectively, from the lifetime and relative emission intensity measurements, and the integrated extinction coefficients of the matrix absorption spectra. In order to explain the much larger branching ratios for the parent ions, and the $\approx 20\%$ deviation of the sum curves from unity obtained in the coincidence measurements, it is postulated that there are two nonradiative pathways for the lowest levels of the \tilde{A} states. One leads to cyclic $C_6H_7^+$ fragment ions via a cyclic $C_6H_8^+$ precursor, whereas the other decay is to a linear vibrationally excited $C_6H_8^+$ ion which cyclizes only slowly, at a rate $< 10^4$ s $^{-1}$. In the case of all *trans*-1,3,5-heptatriene cation the parent ion branching ratio (2.8%) is probably not much greater than the emission quantum yield.

I. INTRODUCTION

The detection of the emission spectra ($\tilde{A} \rightarrow \tilde{X}$) of *trans*- and *cis*-1,3,5-hexatriene cations provided the first examples of polyatomic organic cations where the radiative decay is apparent even though fragment ions are also observed on formation of these cations in a specific state.¹ The earlier measurements of the fragment ion appearance potentials by electron impact² showed, on comparison with the He(I α) photoelectron spectra of *trans*- and *cis*-1,3,5-hexatriene,³ that for their cations excited to the \tilde{A} states, a fragmentation decay pathway is energetically accessible. This was demonstrated directly by the report of the $\tilde{A} \rightarrow \tilde{X}$ photodissociation spectrum of a mixture of *trans*- and *cis*-1,3,5-hexatriene cations using an ion cyclotron resonance spectrometer.⁴ In a further such study higher resolution was employed, and it was concluded by comparison with the emission spectral data, that predominantly the spectrum of the *cis* cation isomer had been measured.⁵ Even more pertinent to the present article has been the measurement of the absorption spectra ($\tilde{A} \rightarrow \tilde{X}$) of *trans*- and *cis*-hexatriene cations in a freon matrix at 77 K because the extinction coefficients of the band systems have been also determined.⁶

In our preliminary communication the emission spectrum of *trans*-1,3,5-hexatriene cation was presented but

in case of the *cis* isomer, only the 0_0^0 band of the $\tilde{A} \rightarrow \tilde{X}$ transition was detected.¹ The emission band system of the latter cation has in the meantime been obtained and is presented in this article as well as the corresponding emission spectrum of the cation of all *trans*-1,3,5-heptatriene. From the assignment of the bands in these spectra, vibrational frequencies of some of the totally symmetric fundamentals are obtained for the \tilde{X} and \tilde{A} states, which are supplemented by the frequencies obtained from the photodissociation, matrix absorption, and photoelectron spectra.

In order to investigate the relaxation pathways of these cations in the $\tilde{A}(\pi^{-1})$ states under isolated conditions, techniques relying on photon as well as fragment ion detection can be implemented.⁷ Thus, as a result of the radiative decay, the lifetimes have been measured and the relative emission intensities for the \tilde{A} states estimated. Furthermore, the quantum yields of emission can, for once, be evaluated from the absorption cross sections of the matrix spectra.⁸ On the other hand, the quantum yields to fragmentation (known as branching ratios) have been obtained by means of the photoelectron-photoion coincidence measurements.⁸ In the latter approach, the cations are generated by photoionization using the He(I α) resonance line and by energy selecting the ejected electrons the internal energy of the cations is defined.⁹ As the resultant ions are then detected in coincidence with the electrons, branching ratios for the parent and fragment ions are obtained. Thus the data forthcoming from the various techniques applied to study

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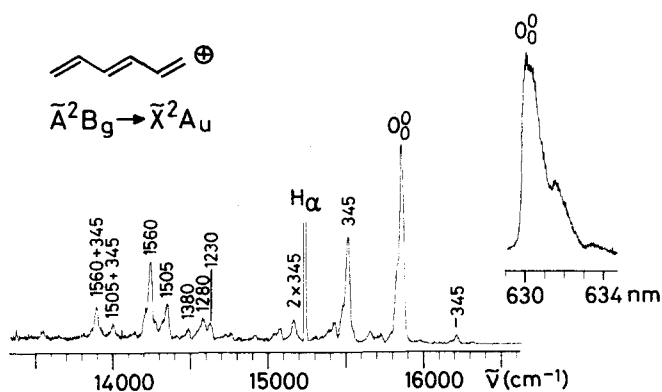


FIG. 1. Emission spectrum of *trans*-1,3,5-hexatriene cation: $\tilde{A}^2B_g \rightarrow \tilde{X}^2A_u$ band system, recorded with an optical resolution of 0.5 nm. The inset shows the 0_0^0 band (wavelength scale) recorded with 0.24 nm (FWHM).

the hexatriene cation provide a quantitative insight into the relaxation decay pathways.

II. EXPERIMENTAL

The emission spectra were obtained with the electron-sample crossed beam apparatus and detection system which have been described elsewhere.¹⁰ The spectra shown in Figs. 1, 2, and 3 were dispersed with optical resolutions of 0.3–0.5 nm (FWHM) following impact by a ≈ 25 eV electron beam on the samples at pressures $\leq 5 \times 10^{-3}$ Torr. The spectra were recorded on line with a PDP/9 computer and have been corrected for the instrumental optical transmission function. The 0_0^0 emission bands were, in addition, separately recorded with 0.24 nm resolution and calibrated to ± 0.01 nm using the H_α fragment emission line. The decay curves of the 0_0^0 bands were accumulated by gating the electron beam, typically at 100 kHz, and counting single photons in delayed coincidence.

The first two bands in the photoelectron spectra of *trans*- and *cis*-1,3,5-hexatriene and of all *trans*-1,3,5-heptatriene (Fig. 4) were remeasured by preretarding the photoelectrons to ≈ 5 eV following He(I α) 21.22 eV

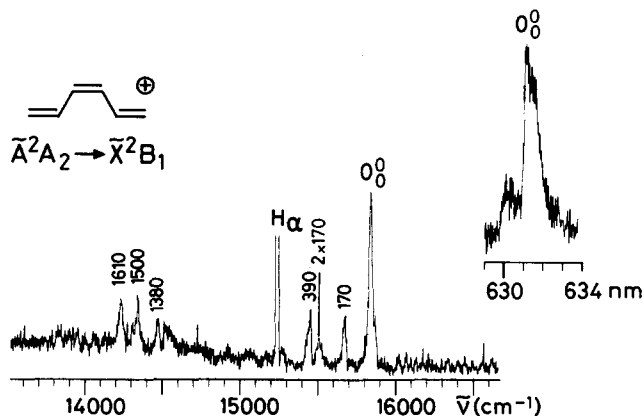


FIG. 2. Emission spectrum of *cis*-1,3,5-hexatriene cation: $\tilde{A}^2A_2 \rightarrow \tilde{X}^2B_1$ band system, recorded with an optical resolution of 0.5 nm. The inset shows the 0_0^0 (wavelength scale) recorded with 0.24 nm (FWHM).

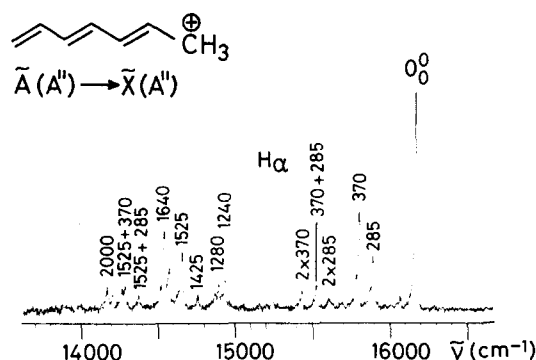


FIG. 3. Emission spectrum of all *trans*-1,3,5-heptatriene cation: $\tilde{A}^2A'' \rightarrow \tilde{X}^2A''$ band, recorded with an optical resolution of 0.3 nm.

photoionization. The electrons were transmitted through a $\pi/\sqrt{2}$ (5 cm radius) cylindrical sector analyzer, yielding a half-width of ≈ 20 meV for 5 eV electrons.

The photoelectron-photoion-coincidence technique and the corresponding apparatus used in the present study were described in detail in Ref. 11 and therefore only a brief review will be given here.

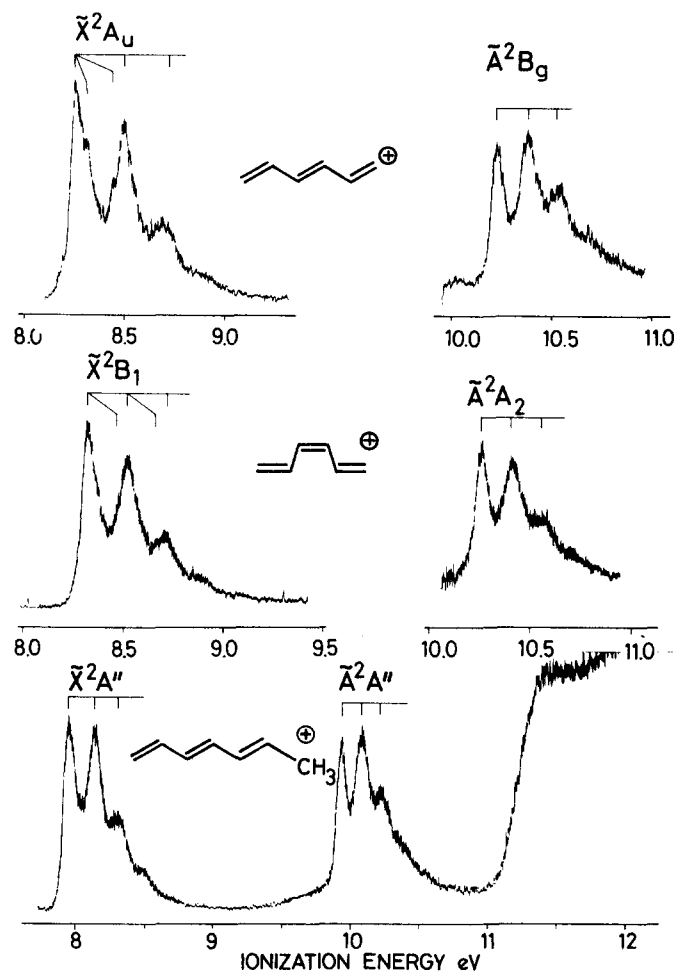
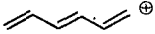

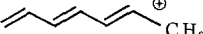


FIG. 4. He (58.4 nm) excited photoelectron spectra of the first two bands of (a) *trans*-1,3,5-hexatriene, (b) *cis*-1,3,5-hexatriene, and (c) all *trans*-1,3,5-heptatriene recorded with a constant half-width band pass.

TABLE I. Band maxima of the 0_0^0 bands of the $\tilde{A} \rightarrow \tilde{X}$ electronic transition in the emission, photodissociation, and matrix absorption spectra, and the adiabatic ionization energies leading to the \tilde{X} and \tilde{A} states of the cations of *trans*- and *cis*-1,3,5-hexatriene and of all *trans*-1,3,5-heptatriene.

Cation	0_0^0 (cm ⁻¹)			Ionization energies (eV) ^a		(cm ⁻¹) IE (\tilde{A}) - IE (\tilde{X})
	Emission ^b	Photodissociation ^c	Absorption ^d	\tilde{X}	\tilde{A}	
	15 868 ± 5		15 576	8.30	10.26	15 810 ± 160
	15 840 ± 5	15 828 ± 25	15 267	8.31	10.27	15 810 ± 160
	16 170 ± 5			7.96	9.96	16 050 ± 160

^a±0.02 eV.

^bThis work.

^cReference 5.

^dReference 6, errors not given.

A collimated beam of He(I α) radiation intersects in the ionization source a sample gas jet. The formed photoelectrons and photoions are accelerated in opposite directions by a weak electrostatic field of about 4.5 V/cm. The resolving power of the 10 cm radius $\pi/\sqrt{2}$ cylindrical condenser energy analyzer was adjusted to give a FWHM of 120 mV for the Xe $2P_{3/2}$ peak. By means of ion optics, the photoions are focused into the quadrupole mass spectrometer which provides unity mass resolution over the whole accessible mass range, i.e., up to $m/z = 511$. The ion collection efficiency f_i was ≈ 0.25 . The breakdown curves were corrected for the contributions of the ^{13}C isotope signals and a number of nonideal features as described in Ref. 11. No significant amounts of impurities have been detected in the PI-MS.

The high polymerization tendency of 1,3,5-hexatriene raised special problems with respect to the long time needed for the coincidence measurements (≈ 3 weeks for each isomer). In the course of an earlier coincidence study on another sample of the same compound, it was found that, especially, the presence of dimerized hexatriene ($\text{C}_{12}\text{H}_{16}$) can strongly distort the coincidence measurements of the monomers. The reason is that this species, volatile enough to be present in the gas phase, also yields photoelectrons between 10 and 11 eV, and fragments into $\text{C}_6\text{H}_8^+ + \text{C}_6\text{H}_8$ within the same energy range. Hence, in the present study, the absence of this dimer had been ascertained before, during and after the measurements.

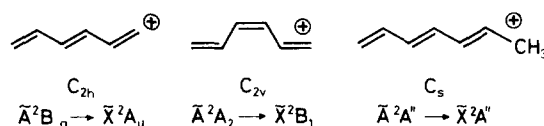
The samples of the trienes used throughout these studies were separated by gas chromatography from which it was estimated that the *trans*-1,3,5-hexatriene contained not more than 3% of the *cis*-isomer. It was also then assumed that the *cis* sample did not contain more than 3% of the *trans* species.

III. RESULTS AND DISCUSSION

A. Assignment of the emission spectra

The three emission band systems which have been detected lie in the spectral region between 14 000 and 17 000 cm⁻¹ and are similar in appearance (Fig. 3). These band systems are assigned to the $\tilde{A}(\pi^-) \rightarrow \tilde{X}(\pi^-)$ electronic transitions of the respective triene cation

on the basis of the photoelectron spectroscopic data and the ancillary measurements as discussed in the earlier communication.¹ The symmetries of the \tilde{X} and \tilde{A} states of these cations have been deduced earlier in the assignment of the photoelectron spectra³ which showed that these states are generated by ejection of electrons from π molecular orbitals. Thus, adopting the indicated symmetry point groups, the electronic transitions of the emission band systems are



The most intense bands in the emission spectra, lying near 16 000 cm⁻¹ (Figs. 1–3), are assigned to the 0_0^0 transition of these systems as their position corresponds to the difference in the adiabatic ionization energies leading to the \tilde{X} and \tilde{A} cationic states. The respective data are collected in Table I. Whereas the differences in the $\tilde{A} \rightarrow \tilde{X}$ adiabatic ionization energies are not much larger than the given error limits (± 0.02 eV), the size and the direction agree with the trends in the wavelengths of the band maxima of the 0_0^0 bands in the emission spectra. The latter bands were internally calibrated to ± 5 cm⁻¹ using the H_α emission lines. In the insets of Figs. 1 and 2 the recording of these bands with a higher resolution are shown.

In Table I are also compared the 0_0^0 band transition energies obtained from the photodissociation⁵ and from the matrix absorption spectra⁶ ($\tilde{A} \leftarrow \tilde{X}$), with the emission data for *trans*- and *cis*-1,3,5-hexatriene cations. Within the uncertainty limits given for each measurement the values agree, apart from the usual solvent shift in the matrix relative to the gas phase. Of the three spectroscopic studies of the $\tilde{A} \leftarrow \tilde{X}$ transition of the 1,3,5-hexatriene cations the emission spectra (Figs. 1 and 2) show the best resolved vibrational structure.

The prominent peaks lying to lower energies of the 0_0^0 bands in the emission spectra have been assigned to vibrational excitation in the ground states of these cations. In the case of *trans*-1,3,5-hexatriene and -heptatriene cations the one peak at higher energy of the 0_0^0 band corresponds to vibrational excitation in the \tilde{A}

TABLE II. Vibrational frequencies (cm^{-1}) of the totally symmetric fundamentals (under the given symmetry) for the ground and first excited states of the triene cation inferred from the emission (Em), photodissociation (P-D), absorption (Abs), and photoelectron (PE) spectra.

Cation	State	\tilde{X}			\tilde{A}		
		Em (± 10)	PE (± 80)	P-D	Em	PE	Abs
<i>trans</i> -1, 3, 5-hexatriene ^{a,b}		1560	1600				1636
		1505					
		1380					
		1280	1300				
		1230					
(C_{2h})		345			345	1130	1090
							345
<i>cis</i> -1, 3, 5-hexatriene		1610	1570				
		1500					
		1380					
(C_{2v})			(1200)		1200		
		390		350 \pm 25		1060 \pm 15	1040
		170				350 \pm 10	
all <i>trans</i> -1, 3, 5-heptatriene		2000					
		1640					
		1525	1530				
		1425					
		(1300)					
(C_s)		1280					
		1240			1230		
		370					
		285					

^aMolecular ground state frequencies (cm^{-1}) of the 13 a_g fundamentals of *trans*-1, 3, 5-hexatriene are 3085, 3039, 3039, 2989, 1623, 1573, 1394, 1280, 1238, 1187, 897, 444, 347 cm^{-1} [E. M. Popov and G. A. Kogan, Opt. Spectrosc. 17, 362 (1964)].

^bFrequencies (cm^{-1}) of some of the fundamentals of *trans*-1, 3, 5-hexatriene cation have, in the meantime, been also inferred from laser induced fluorescence studies in a neon matrix (Ref. 17). These are 1622, 1513, 1376, 1293, 1239, 1115, 951, 442, and 350 for the \tilde{X}^2A_g state and 1486, 1434, 1378, 1245, 1071, 443, and 343 for the \tilde{A}^2B_g cationic state.

states. In Table II the inferred vibrational frequencies are collected, and included are the frequencies obtained from the photodissociation and matrix absorption spectra. The latter spectra yield the vibrational frequencies for the \tilde{A} states, and one frequency for the \tilde{X} state from the hot bands, and thus complement the emission data for which the reverse situation holds. In the He(I α) photoelectron spectra the fine structure discernible on the first two bands is interpreted as indicated in the Fig. 4 and this corresponds to the excitation of the vibrations whose frequencies are also given in Table II. Only in the case of *trans*-1, 3, 5-hexatriene has a normal coordinate analysis been carried out and the frequencies of

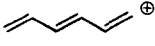
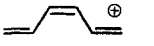
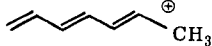
the thirteen totally symmetric A_g (under C_{2h} symmetry classification) fundamentals are given in the footnote of Table II.

B. Coincidence results

1. *cis/trans*-1,3,5-hexatriene

The results of the photoelectron (PE)–photoion-coincidence measurements for the first excited electronic states of *cis*-(\tilde{A}^2A_2) and *trans*-(\tilde{A}^2B_g) 1, 3, 5-hexatriene cation are presented in Fig. 5. The main features of the high resolution PE bands (cf. Fig. 4) are also discernible under coincidence conditions, as shown on the

TABLE III. Relative emission ($\tilde{A} \rightarrow \tilde{X}$) intensities, and the lifetimes and the parent ion branching ratios for the lowest vibrational level of the \tilde{A} states of *trans*- and *cis*-1, 3, 5-hexatriene and all *trans*-1, 3, 5-heptatriene cations.

Cation			
Emission intensity (rel.) ^a	100	≈ 5	≈ 12
Lifetime $\tilde{A}(0^0)$ (ns)	17 \pm 2	< 6	9 \pm 2
Branching ratio (M^+)	0.33 \pm 0.01	0.064 \pm 0.009	0.028 \pm 0.003

^aFor an estimation of the errors for these measurements, see text.

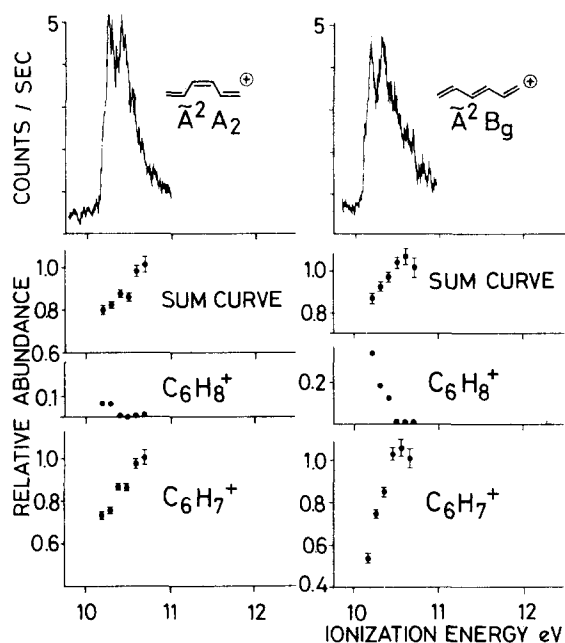


FIG. 5. Photoelectron bands recorded under coincidence conditions and the breakdown curves for the parent ($C_6H_8^+$) and the only observed fragment ion ($C_6H_7^+$), as well as the corresponding sum curves, for *cis*- and *trans*-1,3,5-hexatriene cations.

top of Fig. 5. The $C_6H_8^+$ molecular ion breakdown curves reveal that for both isomers, within the time scale of the coincidence experiment, part of the molecular ions initially generated in the low energy range of the first excited electronic state are stable, even though the lowest fragmentation threshold corresponding to $C_6H_8^+ \rightarrow C_6H_7^+ + H$ lies at 9.96 ± 0.15 eV², i.e., below the adiabatic ionization energy of the \bar{A} state. By comparison with the estimated value for the quantum yield of emission (*vide infra*), it appears that only part of these long living parent ions have decayed by emission of fluorescence. A possible rationalization of this behavior is given in Sec. III B.

The appearance energies (AEs) of all the important fragment ions produced from excited 1,3,5-hexatriene cations have been measured in an electron impact (EI) study.² From these data it can be inferred that besides the formation of $C_6H_7^+$ only the fragmentation into $C_6H_6^+ + H_2$ can occur below 11 eV, because the AEs of all the other fragment ions are larger than, or equal to, 12.25 eV. For this reason we also measured the breakdown curve for the $C_6H_6^+$ fragment ion between 10 and 11 eV. However, formation of $C_6H_6^+$ ions was not observed. Therefore, in agreement with the photodissociation experiments⁵ we conclude that $C_6H_7^+$ is the only observed fragment ion in this energy range.

The obviously different behavior of the two isomers below 10.5 eV can be summarized as follows. The relative amount of parent ions which survive the experimental time-of-flight (38 μ s) necessary to reach the ion detector is much larger in the case of the *trans* isomer. Furthermore, the energy span where stable parent ions have been detected is about 0.1 eV larger for the *trans* isomer. The significant deviation of the sum

curve from unity at the beginning of the band indicates the loss of metastable parent ions¹² fragmenting outside the ionization source. From the amount ($\approx 20\%$) of lost metastables at 10.2 eV the rate constant for the formation of $C_6H_7^+$ fragments is estimated to be about 5×10^5 s⁻¹, in both cases. The presence of such metastable parent ions is compatible with the low excess energy above the experimental fragmentation threshold and the observation of metastable transitions leading to $C_6H_7^+$ as observed in the EI study for 1,3- and 1,4-cyclohexadiene.²

Above 10.5 eV, the coincidence data for the two isomers, within the error limits of the counting statistics, are identical. The unity value of the fragment ion branching ratio, and consequently also of the sum curve, show that molecular ions initially formed above 10.5 eV are fully dissociated by "fast" ($k > 5 \times 10^6$ s⁻¹) decays into $C_6H_7^+$ fragment ions.

In Table IV, are collected the He(I α) photoionization (PI) mass spectra of *cis*- and *trans*-1,3,5-hexatriene, together with the 50 eV EI mass spectrum obtained for an unspecified isomeric mixture.² The PI-mass spectra of *cis*- and *trans*-1,3,5-hexatriene are identical with the exception of the slightly different parent ion intensity which reflects the distinct behavior of the two isomers in the \bar{A} state.

2. 1,3,5-all-trans-heptatriene

The strongly reduced polymerization tendency of this compound compared to the hexatrienes allowed us to carry out extended coincidence measurements. On the other hand most of the ancillary information forthcoming from the various techniques applied to the hexatrienes is unavailable for all *trans*-1,3,5-heptatriene cation. In order to test if the latter radical cation upon excitation to its \bar{A} state decays dissociatively, as well as radiatively, we were looking for an accessible frag-

TABLE IV. Mass spectral data of 1,3,5-hexatriene.

<i>m/z</i>	PI(HeI α) ^a		50 eV EI ^b isomeric mixture
	<i>cis</i>	<i>trans</i>	
81	3.5	3.5	
80	55	58	55.9
79	100	100	100
78	8	8	8.6
77	55	55	47.6
66	<1	<1	
65	7.5	7.5	13.2
64	<1	<1	
63	1	1	5.6
54	2	2.5	7.1
53	6.5	7	21.4
52	9	10	32.2
51	4.5	4.5	43.8
50	0.5	1	29.5
41	5.5	6	
40	2	2	
39	11	15	82.3
27	4	5	

^aThis work.

^bReference 2.

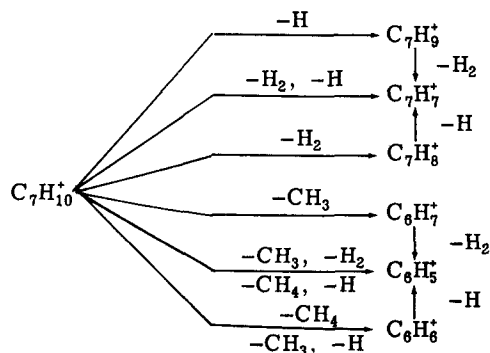
TABLE V. Mass spectral data of all-*trans*-1,3,5 hepta-triene.

m/z	PI(HeI α) ^a	EI-70 (eV) ^b	AE-EI (eV) ^c	AE-CO (eV) ^d
95	3.5	4		
94	44	47		
93	13	12	10.20	
92	3	3		12.4
91	15	20	11.90	12.2
80	6.5	6.5		
79	100	100	9.3	
78	8	9		
77	61	53		12.3
67	4	3		
66	7	8		
65	9	13		
63	1	6		
56	1.5	1		
55	4	4		
54	7	5		
53	18	11		
52	5	6		
51	6.5	12		
50	1	6		
43	3	1		
42	2	1		
41	15	12		
40	7	8		
39	17	33		
29	4	2		

^aThis work.^b10 μ A emission current, Hitachi-Perkin-Elmer RMU-7D, from Ref. 13.^c ± 0.2 eV, from Ref. 13.^d ± 0.15 eV, this work, coincidence measurements.

mentation pathway. Thermochemical considerations and an independent EI measurement of the lowest fragmentation thresholds¹³ indicated that the dissociation into $C_6H_7^+ + CH_3$ is energetically accessible below the adiabatic IE of the A state. In order to quantify this behavior the present coincidence study was undertaken.

The He(I α) PI mass spectrum is given in Table V in comparison with a 70 eV EI mass spectrum.¹³ In Table V are also collected the relevant AEs deduced from the EI measurements and/or this coincidence study. Breakdown curves were measured for the parent ion and the product ions of the following fragmentation reactions:



3. Sum curve [Fig. 6(b)]

The sum of the breakdown curves should be unity at all energies as long as all fragmentation channels are

considered and provided that there is no discrimination against fragment ions of high initial kinetic energy and that all fragments are produced within the ionization source. The relatively low value of the sum curve in the energy range of the higher excited electronic states, i. e., ≈ 11.3 –16 eV, is because in the present study only a few of the various fragments appearing in the mass spectrum have been investigated. On the other hand the EI data¹³ showed that between 10 and 10.6 eV only the three investigated fragmentations yielding $C_7H_9^+$, $C_6H_7^+$, and $C_6H_8^+$ occur. Therefore, the deviation of the sum curve in this energy range must be ascribed to discrimination effects against these ions due to high kinetic energy and/or low formation rates.

4. $C_7H_{10}^+$ (molecular ion) [Fig. 6(c)]

That the fragmentation of the parent ion is incomplete upon excitation to the low energy range of the first excited electronic state, is evidenced by the nonzero branching ratio for the molecular ion at these energies. The parent ion branching ratio is determined to be $(2.8 \pm 0.3)\%$ at 10 eV.

5. $C_7H_9^+$ [Fig. 7(a)]

The EI AE for this fragment ion is 10.3 ± 0.2 eV.¹³ The breakdown curve shows that this ion is already produced at 10 eV. The EI value coincides with the break in the curve between 10.2 and 10.3 eV. This break which

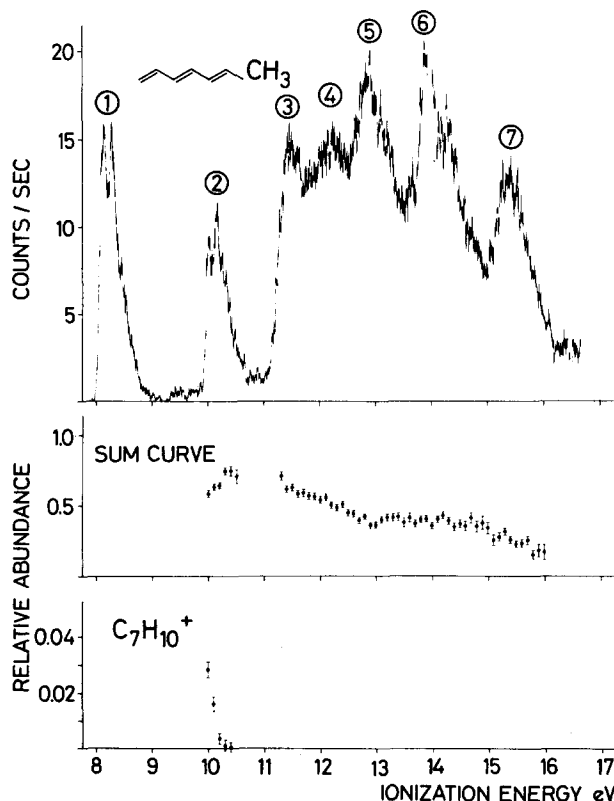


FIG. 6. PE spectrum obtained under coincidence conditions (a), the sum curve of all investigated individual breakdown curves (b), and the parent ion breakdown curve (c) of all *trans*-1,3,5-heptatriene. Numbering of the PE bands was adopted from Ref. 3.

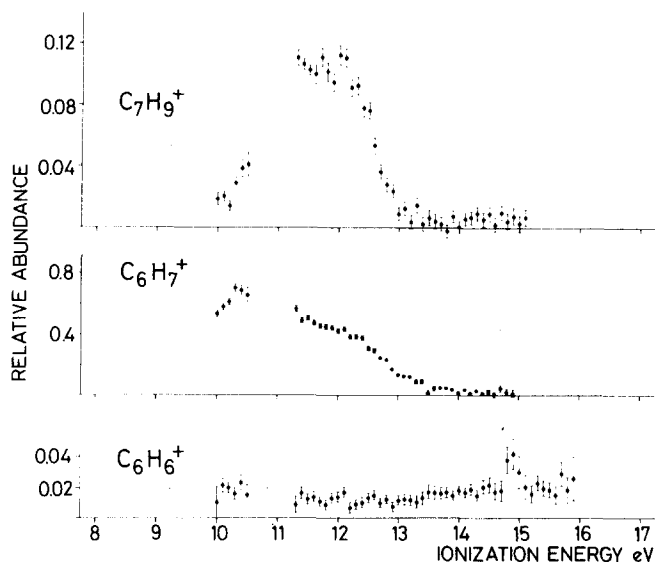


FIG. 7. Breakdown curves for the (a) $C_7H_9^+$, (b) $C_6H_7^+$, and (c) $C_6H_6^+$ fragment ions of all-*trans*-1,3,5-heptatriene cation.

also appears in the $C_6H_7^+$ breakdown curve at the same ionization energy suggests a change of the fragmentation process. Note that at the same ionization energy the parent ion breakdown curve falls to the baseline. The $C_7H_9^+$ breakdown curve then rises towards the high energy end of the \bar{A} state. Between 11.3 and about 12 eV it shows a plateau and after a strong decrease it reaches the noise level at about 13 eV.

6. $C_6H_7^+$ [Fig. 7(b)]

Dissociation into $C_6H_7^+$ constitutes the lowest fragmentation threshold for excited 1,3,5-all-*trans*-heptatriene cation. By adopting the heat of formation (913 kJ mol^{-1}) determined for this fragment from the dissociation of 1,3,5-hexatriene² one calculates an AE of $\approx 9.60 \text{ eV}$. In comparison the experimental EI AP is $9.3 \pm 0.2 \text{ eV}$.¹³ The large value of the $C_6H_7^+$ breakdown curve shows that this is the dominant fragmentation pathway in the energy range of the first excited electronic state. The break between 10.2 and 10.3 eV was already mentioned above. In the energy span of the higher excited electronic states the curve decreases with a change of slope around 12.5 eV and reaches the baseline at about 14 eV. It should be noted that the signal of this ion forms the base peak in the mass spectra (cf. Table V).

7. $C_6H_6^+$ [Fig. 7(c)]

A very weak but significant value (1%–2%) for the breakdown curve of this ion is observed within the whole energy range considered. The breakdown curve shows that this fragmentation is the third dissociation channel which competes with the radiative decay. The AE is located below 10 eV and cannot be measured by the coincidence method. The curve is essentially flat except for the few points around 15 eV which are most probably caused by improper corrections for scattered electrons.

The following three fragment ions are not formed within the energy range of the \bar{A} state.

8. $C_7H_8^+$ [Fig. 8(a)]

The breakdown curve for this ion nowhere exceeds a value of 2%. From the first linearly increasing part one extrapolates an AE of $12.4 \pm 0.15 \text{ eV}$. The increase around 15 eV indicates a new reaction path yielding $C_7H_8^+$ ions.

9. $C_7H_7^+$ [Fig. 8(b)]

The AE deduced from the breakdown curve of this ion is $12.2 \pm 0.15 \text{ eV}$. This energy corresponds roughly to the beginning of the decrease in the $C_7H_9^+$ breakdown curve [cf. Fig. 7(a)]. Therefore, most of the $C_7H_7^+$ ions seem to be produced by a secondary process, i.e., $C_7H_9^+ \rightarrow C_7H_7^+ + H_2$, and the structure of these $C_7H_7^+$ cannot be inferred directly by thermochemical considerations. At higher ionization energies (13.5–16 eV) the curve is essentially flat.

10. $C_6H_5^+$ [Fig. 8(c)]

Linear extrapolation of the rising part of the $C_6H_5^+$ breakdown curve yields an AP of $12.3 \pm 0.15 \text{ eV}$. By comparison with the $C_6H_7^+$ breakdown curve [cf. Fig. 7(b)] one can conclude that again a secondary process ($C_6H_7^+ \rightarrow C_6H_5^+ + H_2$) yields the dominant part of the $C_6H_5^+$ fragments. Above 14 eV the curve starts to decrease and it finally reaches a value of ≈ 0.1 at 16 eV.

C. Competition of radiative and nonradiative pathways

The lifetimes of the three triene cations in the zeroth vibrational level of the \bar{A} states were determined by a least-squares linear fit to a semilogarithmic plot of the recorded decay curves. The lifetimes are summarized in Table III where the error limits given refer to the reproducibility of such measurements. The \bar{A} (0^0) lifetime for *cis*-1,3,5-hexatriene cation, found to be $< 6 \text{ ns}$, is only an upper limit as this corresponds to the time resolution of the apparatus. Due to the weakness of the emission systems, decay curve measurements were carried out only for the 0_0^0 bands.

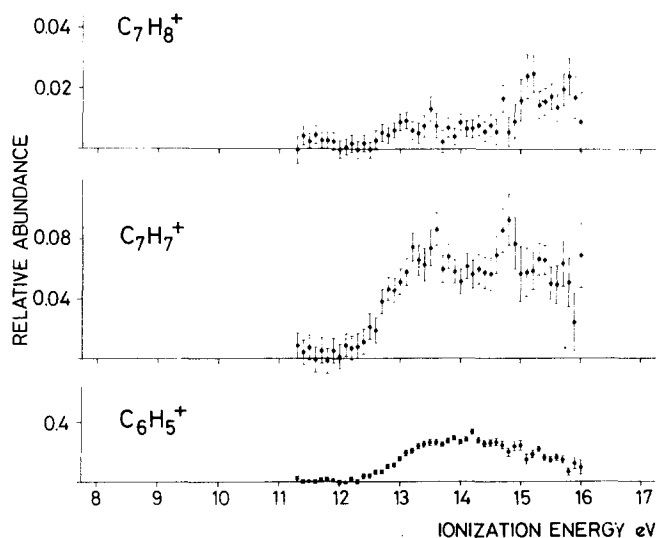


FIG. 8. Breakdown curves for the (a) $C_7H_8^+$, (b) $C_7H_7^+$, and (c) $C_6H_5^+$ fragment ions of all-*trans*-1,3,5-heptatriene cation.

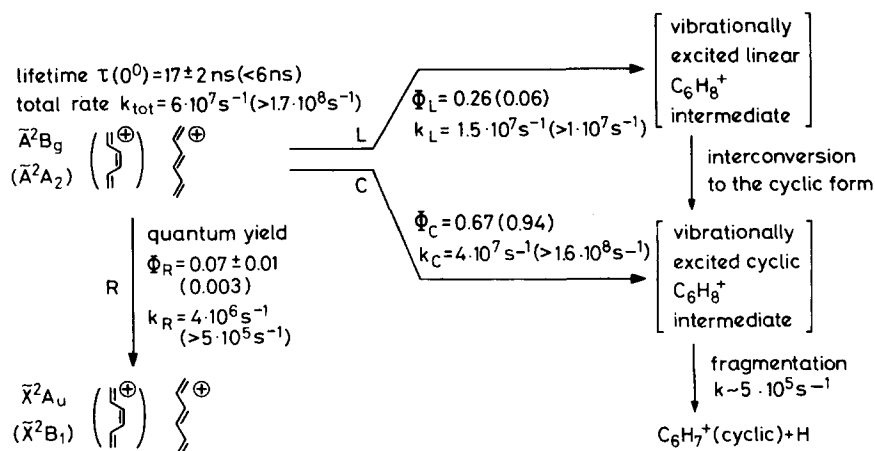


FIG. 9. Summary of the decay behavior of *cis*- and *trans*-1,3,5-hexatriene cations upon excitation to the zeroth vibrational level of the first excited electronic state. Numbers and symbols in brackets refer to the *cis* isomer.

In Table III are also given relative intensities of the emission band systems. These were determined by recording the emission spectra using the same excitation conditions and sample pressures, thus assuming that the response of the Penning gauge is not too different for these three trienes. The spectra were then corrected with the optical transmission function of the apparatus, the background and the H_α fragment line were subtracted, and then integrated over the whole emission system. These measurements were in each case repeated several times. In addition, for the *trans*- and *cis*-1,3,5-hexatriene cations, the emission intensities were also obtained by normalizing the integrals with respect to the intensity of the fragment H_α emission line instead of the Penning gauge reading. The same ratios were obtained in both methods and it is estimated that the ratios given in Table III should be correct to within a factor of 2.

In order to discuss the rates of the decay pathways of the electronically excited cations, in addition to the lifetimes, the quantum yields of the individual channels must be known. The measured lifetimes (Table III) yield the sum of the radiative and nonradiative rate constants, and the quantum yields of parent and fragment ions are obtained from the breakdown curve as described in Section III B. Moreover, the quantum yields of emission can be evaluated from the extinction coefficients of the absorption spectra ($\tilde{A} - \tilde{X}$) obtained for *trans*- and *cis*-1,3,5-hexatriene cations in matrices.⁶ For this reason the latter species are as yet unique among organic cations in that absorption as well as emission spectra have been observed. The integrated extinction coefficients can be converted into lifetimes,¹⁴ which yield a natural radiative lifetime of 250 ns for the zeroth level of the \tilde{A} state of *trans*-1,3,5-hexatriene cation. As the measured zeroth level lifetime has been determined to be 17 ± 3 ns, a quantum yield of emission of $(7 \pm 1)\%$ is implied. A value of this magnitude is also consistent with the "apparent" oscillator strength of ≈ 0.02 (cf. $f \approx 0.0247$ from the absorption spectrum⁶), derived from the photodissociation $\tilde{A} - \tilde{X}$ cross section.⁵ The latter, however, yields a lower limit for the oscillator strength as the dissociation may not be complete (cf. discussion in Sec. III B).

The lifetime of *cis*-1,3,5-hexatriene cation in the

$\tilde{A}(0^0)$ state was found to be too short to be measured (< 6 ns). In order to estimate the quantum yield of emission the ratio of the emission intensity relative to that of the *trans*-isomer cation (Table III) can be used, especially since the extinction coefficients of the matrix absorption spectra of the two isomers appear to be about the same.⁶ The emission quantum yield of the zeroth vibrational level of the \tilde{A} state is then estimated as $\approx 3 \times 10^{-3}$. Assuming the same radiative rate for the *cis* isomer cations ($\tilde{A} - \tilde{X}$) as for the *trans* (4×10^6 s⁻¹), the nonradiative rates are 5.5×10^7 s⁻¹ and 1.2×10^9 s⁻¹ for the *trans* and *cis* species, respectively.

In view of the above inferences, some comments are appropriate regarding the interpretation of the photodissociation spectra of the 1,3,5-hexatriene cations. Although the *cis* cation in the \tilde{A} state dissociates with a higher quantum yield ($\approx 93\%$) than does the *trans* species ($\approx 67\%$), the latter cation does not relax predominantly by a radiative pathway as was postulated.⁵ In fact, the radiative pathways for *trans* and *cis* are minor, as the corresponding quantum yields are merely $\approx 7\%$ and 0.3% , respectively. Thus, it is unlikely that the *trans* cations are suppressed in the photodissociation spectrum relative to the *cis* cations for these reasons. Furthermore, in view of the emission spectra, isomerization from the zeroth level of the \tilde{A} state of one isomer to the other in the \tilde{A} state is unlikely. In the inset of Fig. 2, the region of the 0_0^0 band of *cis*-1,3,5-hexatriene cation $\tilde{A} - \tilde{X}$ transition is shown. Although, part of the weaker band lying at the high energy base of the 0_0^0 peak (at $15\,870$ cm⁻¹) could correspond to the 0_0^0 band of the *trans* cation emission, this could be at most, $\approx 1\%$, because the intensity of the *trans* emission is about 20 times stronger than of the *cis* cation.

The values for the quantum yield of emission are considerably smaller than the branching ratios for the parent ions (Table III) as obtained from the coincidence measurements, within the uncertainties of the counting statistics and the limited electron energy resolution (cf. Fig. 5). Thus, the presence of excited molecular ions with unusually long lifetimes ($\approx 10^{-4}$ s) must be taken into account for the low energy range of the \tilde{A} state. However, we want to point out that the geometric and electronic structure of the detected parent and fragment ions cannot be identified by the coincidence measurement and

therefore the following rationalization is only one reasonable model which accounts for the entirety of the various observations.

The lowest fragmentation process has been attributed to the formation of a cyclic $C_6H_7^+$ fragment ion requiring the hexatriene cation to form a ring.² On the other hand internal conversion to the ground state manifold of a linear $C_6H_8^+$ ion is also possible. Thus, as depicted in Fig. 9, there are three accessible decay channels for the hexatriene cations upon excitation in the low energy part of their \tilde{A} states. The radiative decay (R) to the ground state, internal conversion to a vibrationally excited cyclic $C_6H_8^+$ ion (C) which acts as the precursor to the only accessible fragment ion ($C_6H_7^+$) (postulated to be cyclic²) and internal conversion to a vibrationally excited linear $C_6H_8^+$ ion (L). For the latter a fragmentation channel into a linear $C_6H_7^+$ is energetically not accessible. The existence of long-lived molecular ions can then be ascribed to this excited linear $C_6H_8^+$ intermediate provided that its interconversion rate to the cyclic isomer is less than 10^4 s^{-1} . These considerations suggest that the distinct behavior of the two isomers in the low energy range of the first excited electronic state must be attributed to different cyclization rates. Whereas cyclization of *cis*-1,3,5-hexatriene cation involves rotation around the carbon-carbon single bonds, rotation around carbon-carbon double bonds must instead occur for the *trans* isomer.

In the case of all *trans*-1,3,5-heptatriene cation the parent ion branching ratio $[(2.8 \pm 0.3)\%]$ at 10 eV again seems to be too large compared to the quantum yield of emission indicated from the relative emission intensities (Table III). However, the discrepancy is much smaller than in the case of the 1,3,5-hexatrienes and is not even very significant in view of the error limits. Therefore, in the absence of a better estimate of the quantum yield of emission the parent ion branching ratio at 10 eV is assumed to be a good upper limit for the quantum yield of emission.

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