208. (all-*E*)-1,3,5,7-Octatetraene: Electron-Energy-Loss and Electron-Transmission Spectra

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Summary

Electron-energy-loss and electron-transmission spectra of (all-*E*)-1,3,5,7-octatetraene were recorded with a trochoidal electron spectrometer. The energy-loss spectra reveal two triplet states at 1.73 and 3.25 eV (0,0-transitions), the UV-active 1^1B_u state at 4.40 eV, and a higher-lying singlet state at 6.04 eV. The 2^1A_g state recently reported to be the lowest excited singlet state in this polyene, could not be observed. This failure is probably due to a small excitation cross section under the scattering conditions used and the presence of the second triplet state in the pertinent energy region. The electron-transmission spectrum revealed three resonances (*i.e.* short-lived anion states) at 1.5, 2.5, and 4.15 eV.

Introduction. – Until recently, the electronic structure of the polyene and its change on photon impact were thought to be rather simple and well-understood in the framework of approximate MO models. In particular, the nature of the lowest-lying excited singlet state was commonly assumed to be 1^1B_u (in C_{2h}-symmetry) – originating from HOMO→LUMO electron promotion.

Recent reports have shown, however, that the lowest excited state in larger polyenes is not the above-mentioned 'traditional' 1^1B_u [1] but the 2^1A_g state. Although, in a simple orbital configuration picture the 2^1A_g configuration lies *above* the 1^1B_u configuration, it is lowered by interaction with higher-lying configurations of the same symmetry to such an extent that the resulting state order is reversed. The extensive literature on this subject has recently been reviewed by *Hudson et al.* [2]. The 'reversed' ordering is supported by theory and by various experiments in glassy matrices, including the comparison between the first absorption and the first fluorescence band. In addition, direct observation of the electric-dipole-forbidden $2^1A_g \leftarrow 1^1A_g$ transition could be achieved by two-photon spectroscopy [3].

Despite this firm evidence in the condensed phase, the low-lying 2^1A_g state has never been observed in the isolated molecule in the gas phase. In the latter, no gap was observed between absorption and fluorescence spectra; the few weak bands observed below the $1^1B_u \leftarrow 1^1A_g$ transition were attributed to hot bands [4].

In view of these conflicting facts, *McDiarmid* [5] recently suggested that the theoretical predictions might be misleading since the calculation procedures did not include diffuse orbitals in the basis set, which are required for the correct description of the energetic order of the 1^1B_u and 1^1A_g states.

Electron-energy-loss (EEL) spectroscopy has proven to be a powerful method for observing dipole- (and/or spin-) forbidden transitions in the gas phase [6]. The present (slightly modified) version of this method has demonstrated its capability to detect both spin-forbidden transitions (*e.g.* in benzene [7]) and dipole-forbidden singlet-singlet transitions (*e.g.* to the $^1E_{1g}$ state of benzene [7] and to the $a\ ^1\Pi_g$ state of the N_2-molecule [8]). The present paper deals with an EEL study of (all-*E*)-1,3,5,7-octatetraene (**4**), aimed at the observation of its debated 2^1A_g state. We also considered the triplet energies of **4** as well as the energies of its radical anion ($\mathbf{4}^{\bar{\cdot}}$).

Experimental. – The trochoidal electron spectrometer and the calibration procedures used were described in [7]. An electron beam with a narrow energy spread collides with a gaseous sample. In the electron transmission (ETS) mode, the total unscattered electron current transmitted through the collision chamber is collected. In the EEL mode, electrons inelastically scattered at 0° and – after one reflection – at 180° are energy-analysed by two trochoidal analysers arranged in series. The spectrometer was employed to record the EEL spectra with constant residual energy E_r. The ordinates of all *Figures* show scattered current in arbitrary units, except in *Fig. 3*. Compound **4** was prepared as described in [9] and its purity was checked by GC and UV-photoelectron spectroscopy.

Results and Discussion. – *Fig. 1* shows the EEL spectra obtained with residual energies of 0.5 and 20 eV; the results are summarized in *Table 1*. The $E_r = 20$ eV spectrum is to a large extent identical to the UV-absorption spectrum [3]: the strongest transition $1^1B_u \leftarrow 1^1A_g$ is found at 4.40 eV in agreement with the value of 4.404 eV from optical spectroscopy [3]. The energy of the 2^1A_g state of the isolated molecule has been extrapolated from the condensed phase data to lie at 3.7 eV [4] [9]. In our experiments, only very weak bands (about one permille of the maximum of the $1^1B_u \leftarrow 1^1A_g$ transition intensity) are observed in this energy region. Similar transitions were also found in the UV spectrum and their assignment to hot bands was considered probable in [4]. The intensity of these weak bands in the present experiment rises rapidly with temperature in the 50–200° range, which supports their former assignment to hot bands. However, the assignment to the transition $2^1A_g \leftarrow 1^1A_g$ sought in this paper cannot be firmly excluded.

In the higher energy region of 5.5–6.5 eV the $E_r = 20$ eV spectrum agrees with the UV spectrum as far as band positions are concerned, but a progression of three vibronic bands starting at 6.04 eV is more pronounced compared to the UV spectrum [4]. This result is not surprising since the residual electron energy of 20 eV is still too low for the dipole-selection rule limit of electron scattering to be reached.

At $E_r = 0.5$ eV, two additional bands appear at low energies (1.73 and 3.25 eV; 0,0-transitions) as well as a very weak band at 5.85 eV. The trends found for the three lowest transitions in the electron impact spectra along the series butadiene (**2**), (*E*)-hexatriene (**3**) [2] [6], and octatetraene (**4**) indicate, that the two low-energy transitions

Table 1. *Excited State Energies* (eV), *0,0-Transitions* (band maxima in parenthesis)

Energy	1.73 (2.1)	3.25 (3.55)	4.40 (4.40)	6.04 (6.04)
Assignment	1^3B_u	(2^3B_u)[a]	1^1B_u	(2^1B_u)[b]

[a] Could also be the 1^3A_g state. [b] Tentative assignment.

lead to triplet states of **4**. Thus, the separation of the 1st and 3rd band (singlet-triplet splitting) is 2.7, 2.5, and 2.3 eV, and the separation of the 1st and 2nd band (triplet-triplet splitting) is 1.8, 1.5, and 1.4 eV for these three polyenes (band maxima), respectively, suggesting that the two lowest-energy transitions are of the same nature in all three polyenes. In hexatriene both transitions were convincingly shown to lead to triplet states (measurement of angular dependence [10]) which were assigned as 1^3B_u and 1^3A_g [11]. A comparison with the results of a recent PPP calculation [12] *(Fig. 1)* suggests, however, that an alternative assignment of the second state as 2^3B_u should also be considered. Indeed, the transition to the 1^3A_g state, which is both spin- and dipole-forbidden, could have low intensity, and be hidden under one of the other triplet transitions. In the EEL spectra of benzene the spin- and symmetry-forbidden transitions also appear with lower intensity than transitions which are only spin-forbidden [6].

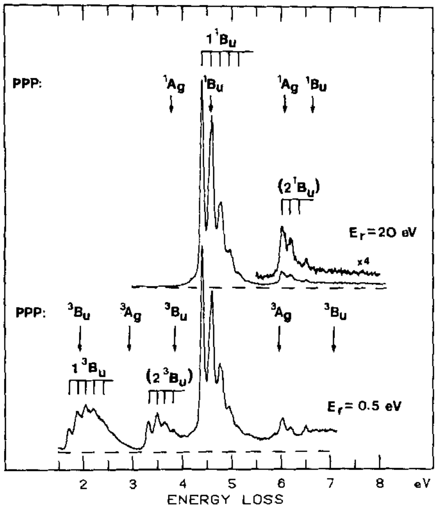

Fig. 1. *EEL spectra of* **4** *recorded with constant residual energies given on the right.* The results of a recent PPP calculation [12] are indicated by vertical arrows.

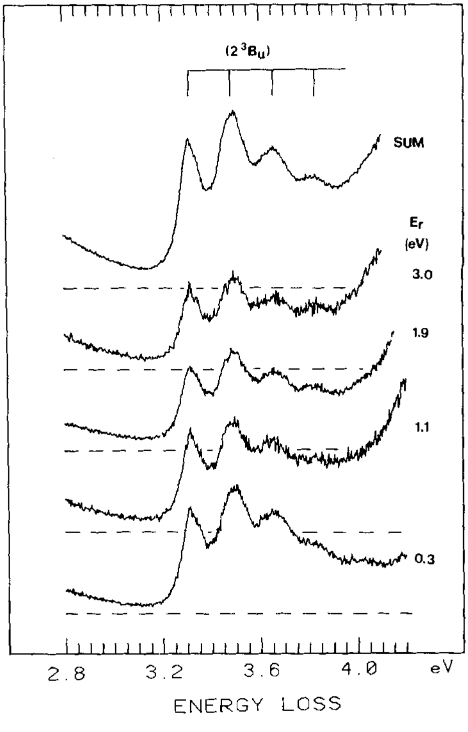

Fig. 2. *A series of EEL spectra of* **4** *in the energy region where the* 2^1A_g *state is expected.* The residual energies used are given on the right.

To investigate the possibility that the discussed 2^1A_g state is excited only within a narrow range of residual energies, we recorded a number of spectra with different E_r in the range 0.03–5 eV in the pertinent energy-loss region. Several of those spectra are shown in *Fig. 2*. No evidence of an additional state was found. The digitally obtained sum of all the spectra is also shown; it provides only a low-noise spectrum of the second triplet of **4**.

The electron-transmission spectrum (ETS) of **4** was also recorded and is shown in *Fig. 3*. Four prominent bands are observed in the spectrum and their positions determined from the inflection points in the derivative of the transmitted current using the convention described in [13] *(Table 2)*.

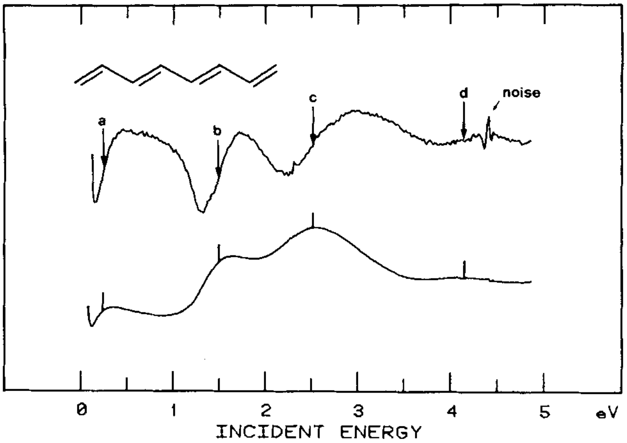

Fig. 3. *The ET spectrum of* **4**. The lower curve is the scattering cross section *shifted by an arbitrary amount along the ordinate*, the upper curve the derivative of the transmitted current. The bands are indicated by vertical bars and arrows and labeled a–d.

Table 2. *Band Positions in the ET-Spectrum of* **4** (eV)

Band	*a*	*b*	*c*	*d*
Assignment	see text	^2B_g	^2A_u	^2B_g
Energy	–0.25	–1.50	–2.52	–4.16

An important question concerns band a which at first sight would indicate **4** possessing a vertical negative EA of –0.25 eV. Two points speak against such an assignment:

- Previous ET studies for **3** did suggest that already this triene has a bound ground state ^2B_g for its anion $\mathbf{3}^{\cdot-}$ [14] [15].
- The above conclusion is supported by theoretical calculations of the HAM/3-type [16].

In view of these points for $\mathbf{3}^{\cdot-}$, it seems unreasonable to propose a non-bound ground state for $\mathbf{4}^{\cdot-}$ and other explanations than a π^*-resonance for the appearance of band a must be considered. As can be seen in *Fig. 3*, lower curve, this feature can be viewed as a drop in the scattering cross section at energies below 0.4 eV. Such a decrease occurs also in other molecules, *e.g.* N_2, below 0.5 eV [17], where it is definitely not due to a π^*-resonance. Furthermore, a minimum in the scattering cross section at low energies, called the *Ramsauer-Townsend* minimum [18], is known for the heavier rare gases and for some molecules, and is also not caused by a resonance. Finally, the

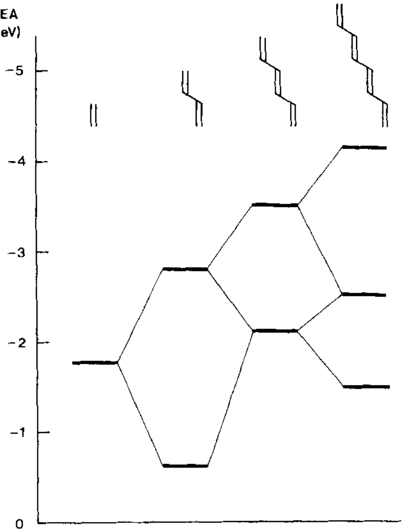

Fig. 4. *Diagram of the experimental vertical negative EA's of ethylene* (**1**), *butadiene* (**2**), *(*E*)-1,3,5-hexatriene* (**3**), *and (all-*E*)-1,3,5,7-octatetraene* (**4**)

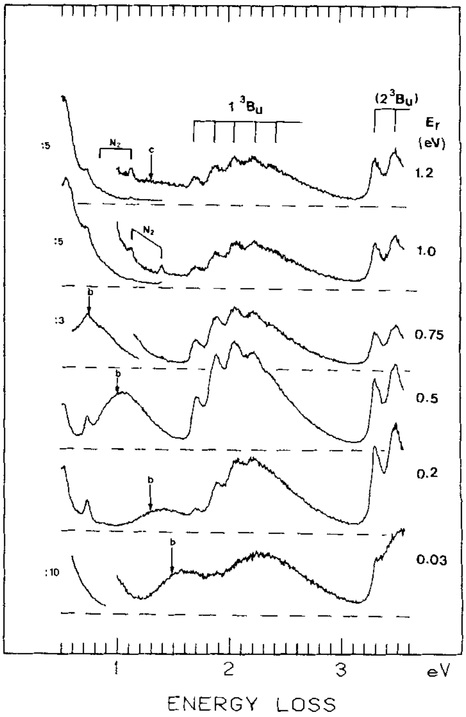

Fig. 5. *EEL spectra of* **4** *illustrating resonant near threshold vibrational excitation.* The residual energies are given on the right. The incident energies corresponding to resonances are indicated by vertical arrows and the label of the respective resonance (b or c).

energy region below 0.5 eV in ETS is notorious for experimental artifacts caused by variations in scattered electron rejection efficiency with energy. We exercized great care to avoid such artifacts, but the possibility of them being the cause of band a cannot be completely excluded.

Fig. 4 compares the present ETS energies of bands b, c and d of **4** with the known experimental negative EA's of ethylene (**1**), butadiene (**2**) [19], and (all-*E*)-hexatriene

Table 3. *The Mean of the Vertical j-th π-Ionization Energy and π*-Electron Affinity* (($\mathrm{IE_j} + \mathrm{EA_j})/2$) *for Linear Polyenes with n Double Bonds*

j	n = 1	n = 2	n = 3	n = 4
1	4.36	4.20	–	–
2		4.33	4.06	4.06
3			4.18	4.19
4				(4.02)[a]

[a] $\mathrm{IE_4}$ is not known with certainty because of interfering σ-bands in the PE spectrum.

(**3**) [14] from previous ET-measurements. These bands may be safely assigned to excited states of $\mathbf{4}^{\overline{\cdot}}$ as this results in a systematic trend for the EA's of this homologous series. Furthermore, it has been shown that in a conjugated alternant unstrained hydrocarbon the arithmetic means $(IE_j + EA_j)/2$ of the first and higher ionization energies IE_j, and the first and higher electron affinities EA_j are nearly constant for all j's, as would be expected from the pairing theorem [20]. These mean values are also nearly constant in a series of related compounds [20]. For the linear polyenes, they are calculated using the known IE's [21] [22], see *Table 3*. All the values are close to 4 eV and only weak systematic trends are found: *i*) they drop as the number of double bonds increases, and *ii*) they increase with raising j.

The three ETS bands b, c and d are paired with the three π-IE's, and their description involves the higher virtual π^*-orbitals $\pi^*_6(b_g)$, $\pi^*_7(a_u)$, and $\pi^*_8(b_g)$. As shown recently [23], the excited states of linear polyene ions cannot be described in terms of single configurations, their correct description requiring extensive configurational mixing. The picture of an electron being captured in a single π^*-MO may thus also be oversimplified for the excited states of $\mathbf{4}^{\overline{\cdot}}$ discussed above, since doubly excited configurations may also play a decisive role in their description. Theoretical calculations treating this aspect of polyene radical anions are, however, lacking.

In the EEL spectra of **4** *(Fig. 5)* an additional band is found with low residual energies below the lowest electronically excited state. This band differs from a band due to an electronically excited state by its shift on the energy-loss scale as the residual energy is increased. It is not found at a fixed energy loss but at a fixed incident energy. This indicates that the band is caused by the excitation of high vibrational levels of the electronic ground state of **4**, *via* initial formation of the first excited state (resonance b) of the anion $\mathbf{4}^{\overline{\cdot}}$ and subsequent loss of e^- of lower kinetic energy. Such excitation of high vibrational levels was recently found in several polyatomic molecules [24]. The presence of this effect in **4** further supports the assumption that this interesting phenomenon found in electron-scattering experiments is not limited to a particular type of molecule, but may occur quite generally.

Conclusions. – The electronic excitation of molecules by electron impact may be divided into two prevailing mechanisms. The first is by nonresonant scattering and is dominant for residual electron energies of several tens to several hundreds of eV. Triplet states are not markedly excited with these high electron energies. The excitation may be understood in terms of dipole- and higher multipole-transitions depending on the momentum transfer. It has been recently discussed in general and also specifically for **4** on an elementary level [2].

The experiment described here works with slow electrons. The dominant mechanism is resonant excitation where a short-lived excited state of the anion decays into an excited state of the neutral molecule, and thus serves as a relay in inducing a spin- or dipole-forbidden transition. The triplet states are prominent in the spectrum under these conditions. An example is the excitation of triplet states in benzene from threshold to several eV above (that is E_r in the range 0–8 eV) [7].

The cause of the failure to detect the 2^1A_g state in the present experiment is the apparently low excitation cross section together with the fact that the pertinent energy-loss region is obscured by the second triplet state.

Thus the detection of the 2^1A_g state might still be possible with high impact energies and small scattering angles, where the triplet state will not be excited. Unfortunately, our experimental setup does not allow studies at different scattering angles and high impact energies.

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