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Excited Triplet States of Dimethyl Ether Studied by Electron Energy-Loss Spectroscopy

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Synopsis. The elecron energy-loss spectrum of dimethyl ether was measured at electron energies of 50, 20 and +2(residual energy) eV and at scattering angles of 0—90°. Six new bands were observed at about 6.4, 7.0, 7.5, 7.8, 8.2, 8.9 eV and assigned as the singlet-triplet and/or symmetry-forbidden transition.

Triplet states of organic molecules are important for understanding not only their electronic levels but also their chemical reactions, because such states may show a different reactivity due to spin multiplicity and longer lifetime. The electron energy-loss spectroscopy using a low energy electron beam and a large scattering angle is a unique and useful technique to determine triplet states.[1,2] However, such spectra of complicated organic molecules have scarcely been measured.[2,3] Those of methanol have recently been investigated.[4]

The vacuum UV[5] and photoelectron[6,7] spectra of dimethyl ether showed its excited and ionized states. The electron energy-loss spectrum using high energy electrons[7,8] exhibited its optically-allowed excited states in the 5—570 eV region. However, no information on triplet states has been obtained.

In the present paper, the electron energy-loss spectra of dimethyl ether in the electron energy region of 50—+2(residual energy) eV and at the scattering angle of 0—90° are described together with assignments of the observed bands.

Experimental

The experimental apparatus has been described in detail elsewhere.[3] The collision chamber is 45 cm in diameter and is evacuated with two turbomolecular pumps. The base pressure was about 5X10^{-7} Torr at the wall of the collision chamber (1 Torr=133.322 Pa).

The electron energy-loss spectrometer consists of two hemispherical energy analyzers (Copper: 90 mm in mean diameter), four sets of electrostatic electron lenses, a sample compartment, an electron gun, and a Ceratron detector (Murata, EMS-6081B). The electron energy resolution of the spectrometer was 0.06 eV.

The spectrum was measured at a constant incident electron energy for an incident electron energy above 20 eV. However, the incident electron energy was scanned synchronously with the energy loss for a near-threshold measurement so that the residual energy of scattering electrons was constant (2 eV) throughout a spectrum. A singlet-triplet transition would appear clearly with this technique due to its relatively large cross section near threshold. The dimethyl ether was guaranteed grade (Tokyo Kasei) and was used without any further purification.

Results

The electron energy-loss spectra of dimethyl ether at incident electron energies of 50 and 20 eV are shown in Figs. 1 and 2. The spectra near threshold was measured at the constant residual energy mode (+2 eV) and at scattering angles of 23, 45, 68 and 90°, and are

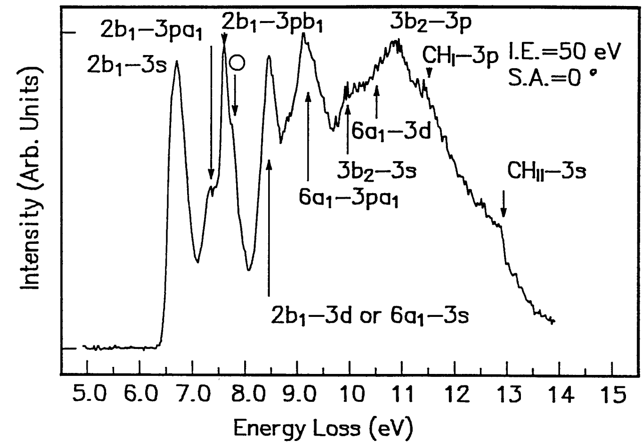

Fig. 1. Electron energy-loss spectrum of dimethyl ether measured at 50 eV and at 0°.

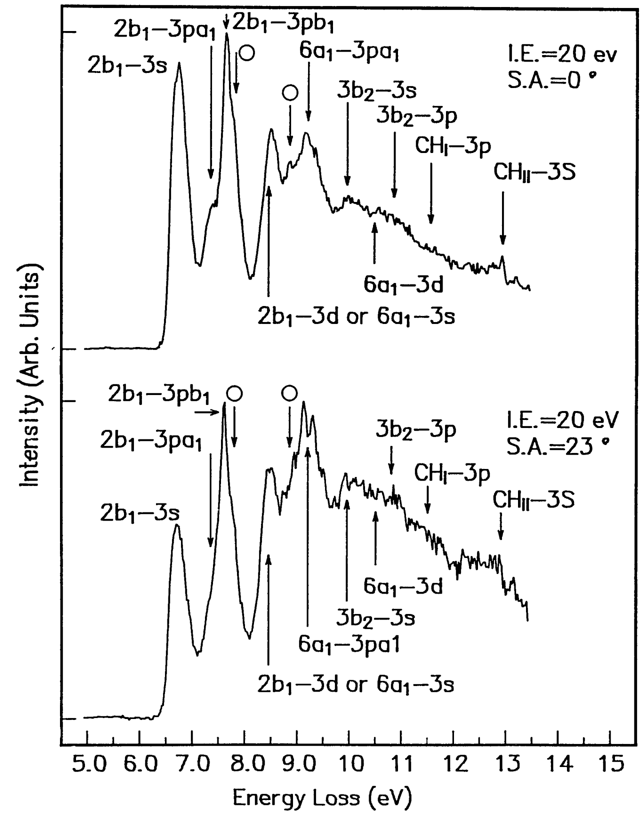

Fig. 2. Electron energy-loss spectra of dimethyl ether measured at 20 eV and at (a) 0° and (b) 23°. The new bands observed in the present study are indicated with O at the top of an arrow on (a).

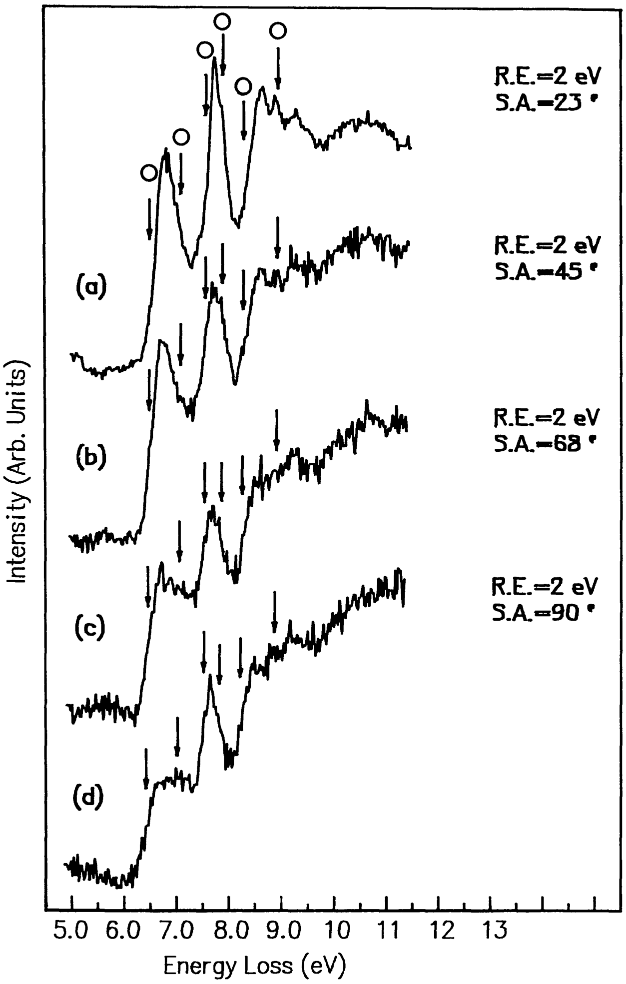

Fig. 3. Electron energy-loss spectra of dimethyl ether measured at a residual energy of 2 eV and at (a) 23°, (b) 45°, (c) 68° and (d) 90°. The new bands observed in the present study are indicated with O at the top of an arrow at 23°.

shown in Fig. 3. The signal-to-noise ratio was rather poor in Fig. 3, because the signals were weak at a low incident electron energy and at a large scattering angle. The spectra change successively from high-energy to low-energy and from small-angle to large-angle measurements.

The spectrum at 50 eV agrees qualitatively with that at 100 eV obtained previously.⁷⁾ They observed ten bands in the region of 6—13 eV and found changes in the relative intensity when the electron energy was decreased from 100 to 50 eV. They assigned these bands on the basis of term values and photoelectron spectroscopy; their assignments are also shown in Fig. 1.

When we compare spectra shown in Figs. 1, 2 and 3, we can find six new bands, as indicated by a circle (O) at the top of an arrow. Most of them are relatively more intense at lower electron energies and at large scattering angles. Their approximate locations are 6.4, 7.0, 7.5, 7.8, 8.2, and 8.9 eV. The observed results are summarized in Table 1, together with those by previous authors.

Discussion

Dimethyl ether has C_{2v} symmetry. Its electronic states is:⁷⁾

$(1a_1)^2(2a_1)^4(1b_2)^2$ (CH bonding)^{12} $(3b_2)^2(6a_1)^2(2b_1)^2$, where $(3b_2)$ and $(6a_1)$ are orbitals for the skeletal bonds and $(2b_1)$ is the nπ orbital of the oxygen atom.

The first band at 6.75 eV in Fig. 1 was assigned to the $2b_1$–$3sa_1$ transition.⁷⁾ This feature shifts to lower energy and becomes broader by decreasing the incident energy and by increasing the scattering angle. By subtracting the feature in Fig. 1 from that in Fig. 3, we can conclude that a new band appears at about 6.4 eV. Its intensity behavior indicates that this band is a singlet–triplet transition. The energy of the $2b_1$–$3sa_1$($^3A_1$) transition was calculated to be 6.31 eV.⁹⁾ Thus,

Table 4. Electronic Excited States of Dimethyl Ether (6—13 eV)ᵃ⁾

Transition	Symmetry	Vertical excitation energy		
		Present work	Previous work⁸⁾	Theoretical calculation¹⁰⁾
$2b_1 \rightarrow 3sa_1$	$^1B_1$	6.75	6.67	6.76
	$^3B_1$	6.4		6.31
$2b_1 \rightarrow 3pa_1$	$^1B_1$	7.37	7.34	7.38
	$^3B_1$	7.0		7.01
$2b_1 \rightarrow 3pb_1$	$^1A_1$	7.65	7.63	7.79
	$^3A_1$	7.5		7.72
$2b_1 \rightarrow 3pb_2$	$^1A_2$	7.8		7.89
	$^3A_2$			7.84
$2b_1 \rightarrow 3d$ or $6a_1 \rightarrow 3sa_1$	(S)	8.50	8.46	8.71
	(T)	8.2		8.39
$2b_1 \rightarrow 3d$	Sym-forbid.	8.9		
$6a_1 \rightarrow 3pa_1$	$^1A_1$	9.17	9.20	9.43
	$^3A_1$	8.9?		9.03
$3b_2 \rightarrow 3sa_1$	$^1B_1$	9.9	9.95	
$6a_1 \rightarrow 3d$	(S)	10.5	10.48	
$3b_2 \rightarrow 3p$	(S)	10.8	10.84	
$CH_1 \rightarrow 3p$	(S)	11.5	11.58	
$CH_2 \rightarrow 3s$	(S)	12.9	12.92	

a) The new bands observed and assigned in the present study are underlined.

we can assign this band to the $2b_1$–$3sa_1(^3A_1)$ transition.

The two bands at 7.37 and 7.65 eV in Fig. 1 were assigned to the $2b_1$–$3pa_1$ (in-plane) and $2b_1$–$3pb_1$ (out-of-plane) transitions,[7,9] respectively. The spectrum changes substantially at an incident energy of +2 eV. The relative increase of the signal at about 7.0 eV indicates an appearance of a new band, which can be assigned to the $2b_1$–$3pa_1(^3B_1)$ transition, because the observed singlet–triplet separation of about 0.37 eV agrees with the calculated value[9] of 0.37 eV. A weak band at 7.5 eV can similarly be assigned to the $2b_1$–$3pb_1(^3A_1)$ transition. The transition to $3pb_2$ would be weak due to symmetry forbidden character. There is a shoulder at 7.8 eV in Fig. 1, which was assigned to a vibrational structure of the $2b_1$–$3pb_1$ transition;[5] however, its energy and scattering angle dependence is different from that transition, and this shoulder could be assigned to the weak $2b_1$–$3pb_2(^1A_2)$ transition, which was calculated to lie at 7.89 eV.[9]

The band at 8.50 eV in Fig. 1 was assigned either to the $2b_1$–3d transition or to the $6a_1$–3s transition.[7,9] A weak feature at 8.2 eV in Fig. 3 can be assigned to the singlet–triplet transition of either of term; the calculated singlet–triplet separation for the latter transition is 0.32 eV, which corresponds well with the observed one.

A sharp feature appears at 8.9 eV at +2 eV. This feature appears faintly in the spectrum even at 50 eV. Thus this band can be assigned as an overlap of a symmetry-forbidden and a spin-forbidden transitions. The former would be of $2b_1$–3d character. The latter would be the singlet–triplet transition corresponding to the $6a_1$–$3pa_1(^1A_1)$ transition at 9.17 eV, because the calculated separation[9] is 0.40 eV.

The band around 9 eV has four features, which can be assigned as its vibrational structure, because the electron energy dependence of their intensity is identical.

The results are summarized in Table 1.

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