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Electron Energy-Loss Spectrum of Methanol. Observation of Singlet-Triplet Transitions at Low Incident Energy

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The electron energy-loss spectrum of methanol was measured at incident electron energies from 100 to threshold +2 eV. There were several intense bands assignable to the Rydberg transitions. Three singlet-triplet transitions were observed at 5.7 - 7.0, 7.3 - 7.6 and 8.8 - 9.5 eV at low incident electron energies.

The electron energy-loss spectroscopy is a useful technique to obtain highly-excited levels and optically forbidden levels.[1)] Although synchrotron radiation has also been used to obtain higher excited states, the electron energy-loss spectroscopy is the most versatile method for investigations on triplet states. There are a wealth of results on diatomic and triatomic molecules; however, little have been measured on complicated organic molecules. Methanol is a simple organic molecule and its electron energy-loss spectra have been measured at high incident electron energies,[2,3)] but no spectrum has been reported at a low electron energy.

An electron energy-loss spectrometer has been designed and constructed. its details will be published elsewhere[4)] and only several salient features are described below. A stainless-steel chamber is evacuated with two turbomolecular pumps: a 550 l/s pump (Shimadzu TMP550)

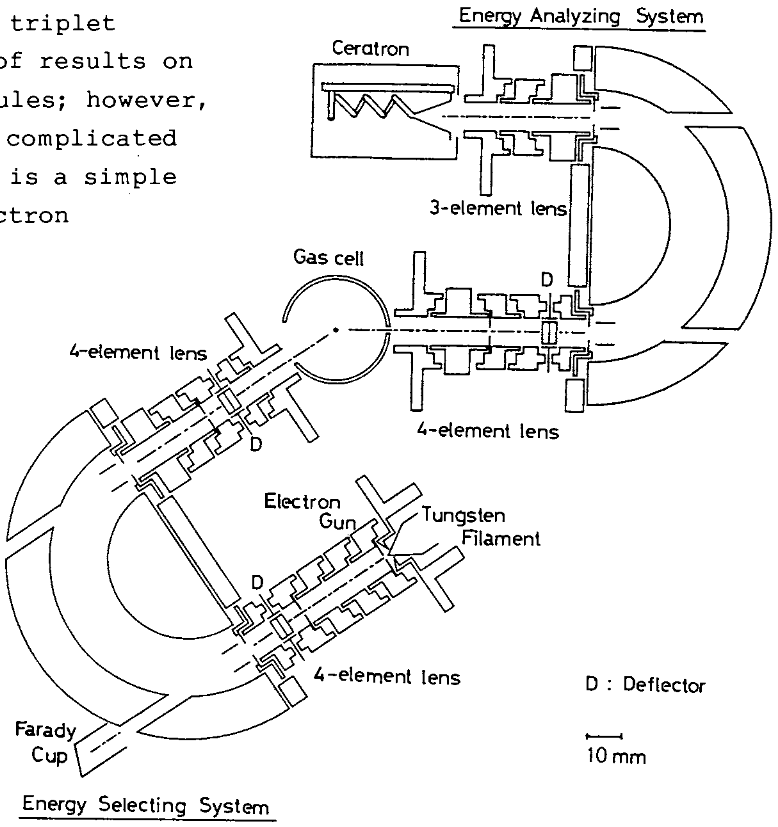

Fig. 1. The electron energy-loss spectrometer. Gun, selector, gas cell, analyzer and detector.

for the main chamber and a 160 l/s pump (Osaka Vacuum TF160) for the sample compartment. The base pressure was about 5×10^{-5} Pa, and the operating pressure was about 1×10^{-3} Pa. It has two oxygen-free copper hemispherical analyzers; the diameter of the electron path is 90 mm. Its energy resolution was 60 meV as measured by the half-width of the 1s - 2p line of He. The observation angle can be varied from 0° to 110°. Electrons are detected with a Ceratron detector (Murata EMS-6081B) and counted by a pulse counter (ORTEC 9315).

Typical spectra of methanol measured at a high and a low incident electron energies are shown in Fig. 2. The spectrum taken at 51 eV agrees with the one taken by previous authors.2,3) The spectra were almost identical at electron energies of 50 - 100 eV.

The spectrum taken at 51 eV has several intense bands and they can be assigned to Rydberg transitions.2) The 2a"-3s transition at around 6.7 eV is broad and weak. Tsubomura et al. observed a broad absorption band at 7.1 eV and assigned it to the n-σ^* transition.5) Thus, a valence and a Rydberg transitions may be overlapped at this region. The 2a"-3p transitions are sharp and have some vibrational structure. The 2a"-3d, 2a"-4p, 7a'-3p, 1a"-3s and 5a'-3s transitions were clearly observed. An improved virtual orbital calculation was used to estimate vertical excitation energies and agreed with experimental results.6)

The spectrum showed some changes when the electron energy was lowered and the observation angle was enlarged. The band which appears only at a low incident electron energy and at a large observation angle can be assigned to a singlet-triplet transition.1) Many such transitions have been assigned for diatomic and triatomic molecules; however, no such investigations have been carried out on methanol.

Three bands as indicated by arrows in Fig. 2 (b) and (c) appeared at a lower electron energy and at a larger scattering angle; they lie at 5.7 - 7.0, 7.3 - 7.6 (shoulder) and 8.8 - 9.5 eV.

The band at 5.7 - 7 eV became relatively stronger and shifted to the lower loss energy by about 0.3 eV than the 2a"-3s transition observed at 51 eV. Thus, a singlet-triplet transition overlapped with the 2a"-3s(^{1}A") band. The vertical excitation energy of the singlet-singlet transition of 2a"-3s(^{1}A") was calculated to be 6.72 eV and that of the singlet-triplet transition of 2a"-3s(^{3}A") was calculated to be 6.23 eV; the calculated singlet-triplet separation is 0.49 eV.6) These calculated values agreed with the experimental results. A single-triplet band was also found at 6.5 eV by a trapped electron and a double retarding potential difference methods.7)

The shoulder at 7.3 - 7.6 eV can be assigned to the 2a"-3p(^{3}A) singlet-triplet transition, since the difference of the calculated energies6) between the singlet-singlet and the singlet-triplet transitions of 2a"-3p is 0.1 - 0.2 eV.

The band at 8.8 - 9.5 can be assigned either to the 2a"-4p(^{3}A) singlet-triplet transition or to the 7a'-3p(^{3}A) singlet-triplet transition; the difference of the calculated energies6) between the singlet-singlet and the singlet-triplet transitions of 7a'-3p is 0.1 - 0.5 eV.

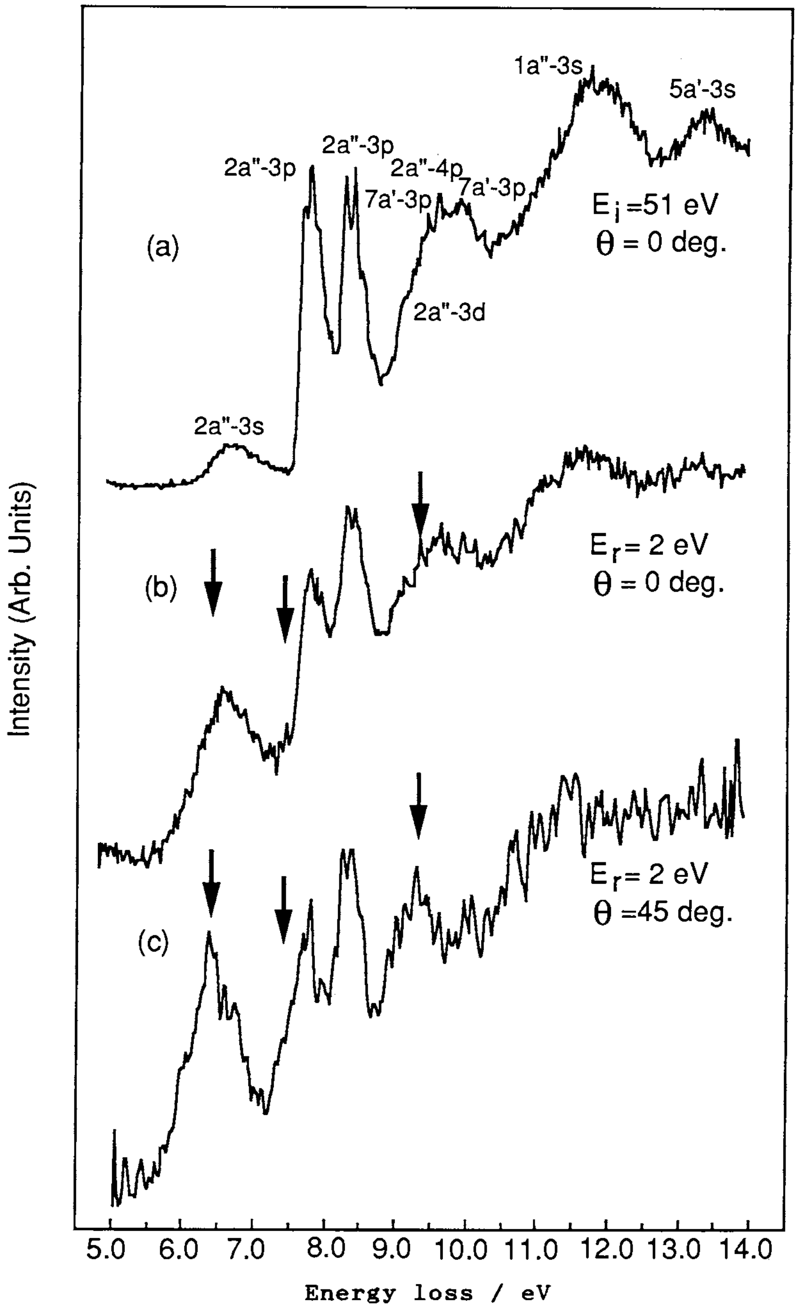

Fig. 2. The electron energy-loss spectra of methanol.
Bands assignable to a singlet-triplet transition are indicated by arrows.
(a) measured at a high incident electron energy (E_i) and at 0°, keeping the incident electron energy at 51 eV.
(b) measured at a low incident energy and at 0°, keeping the collected electron energy (E_r) constant at 2 eV as the incident energy was varied.
(c) measured at a low incident energy and at 45°, keeping the collected electron energy (E_r) constant at 2 eV as the incident energy was varied.

The electron energy-loss spectrum is useful for an understanding of the singlet-triplet transitions of organic molecules.

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References

1) S. Trajmar and D. C. Cartwright, "Excitation of Molecules by Electron Impact," in "Electron-Molecule Interactions and Their Applications," ed by L. G. Christophorou, Academic Press, Orlando (1984), Vol. 1, Chap. 2.
2) M. B. Robin and N. A. Kuebler, J. Electron Spectrosc. Relat. Phenom., 1, 13 (1972/73).
3) W-C. Tam and C. E. Brion, J. Electron Spectrosc. Relat. Phenom. 3, 263 (1974).
4) T. Yoshidome, E. Yamamoto, H. Kawazumi, and T. Ogawa, Eng. Sci. Rept. Kyushu Univ. 3, 297 (1989).
5) H. Tsubomura, K. Kimura, K. Kaya, J. Tanaka, and S. Nagakura, Bull. Chem. Soc. Jpn., 37, 417 (1964).
6) W. R. Wadt and W. A. Goddard III, Chem. Phys., 18, 1 (1976).
7) F. W. E. Knoop, H. H. Brongersma, and L. J. Oosterhoff, Chem. Phys. Lett., 13, 20 (1972).

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