CHEMISTRY LETTERS, pp. 785-790, 1974. Published by the Chemical Society of Japan

PHOTOELECTRON SPECTRA OF TETRACYANOETHYLENE (TCNE) AND TETRACYANOQUINODIMETHANE (TCNQ)

Isao IKEMOTO*, Kuniko SAMIZO*, Takashi FUJIKAWA*, Kikujiro ISHII**,
Toshiaki OHTA* and Haruo KURODA*
* Department of Chemistry, Faculty of Science, The University of Tokyo,
Hongo, Tokyo, 113
** The Institute for Solid State Physics, The University of Tokyo,
Roppongi, Tokyo, 106

The photoelectron spectra of TCNE and TCNQ in the gaseous state were measured by stimulating with He I resonance line. The first ionization potential is determined to be 11.77 eV for TCNE and 9.61 eV for TCNQ. The interpretations of the observed photoelectron spectra are carried out with the aids of the photoelectron spectroscopic data of the related compounds and the results of CNDO/2 calculation.

Tetracyanoethylene (TCNE) and tetracyanoquinodimethane (TCNQ) are very strong electron acceptors, which form solid charge-transfer complexes or radical salts with a wide variety of electron donors. Extensive investigations have been carried out on the electronic structures and physical properties of these solids. In particular, a great interest has been recently stimulated in the radical salts of TCNQ by the finding of the high conductive behavior of the tetrathiafulvalinium (TTF) salt of TCNQ[1).

For understanding the electronic properties of these complexes, it is of fundamental significance to know the ionization potentials of the valence electron levels of TCNE and TCNQ. However no experimental results have been hitherto reported of the photoelectron spectra of these molecules in gaseous state, although the solid-state photoelectron spectrum of TCNQ solid was recently reported by Grobman et al[2).

Both TCNE and TCNQ were commercially obtained and purified by recrystallization and sublimation. Their gas-phase photoelectron spectra, stimulated by He I resonance line (21.21 eV), were obtained with a Perkin-Elmer PS 18 spectrometer. Samples were heated (47°C for TCNE and 155°C for TCNQ) in the spectrometer so as to give a vapor pressure sufficient for the measurement of photoelectron spectrum since both TCNE and TCNQ are a solid of low vapor pressure at the room temperature. The calibration of ionization potential was carried out by introducing Ar and Xe gases into the ionization chamber of the spectrometer, simultaneously with the sample vapor.

As shown in Fig. 1, the photoelectron spectrum of TCNE exhibits the first band with sharp

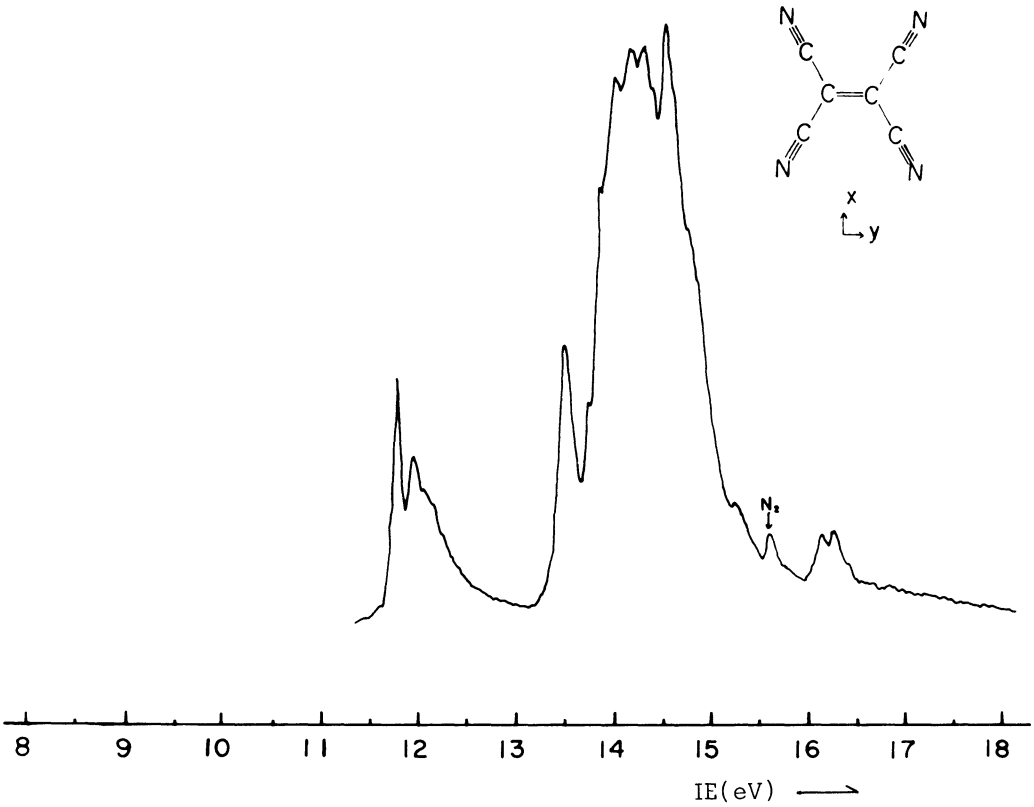

Fig. 1 Photoelectron Spectrum of TCNE

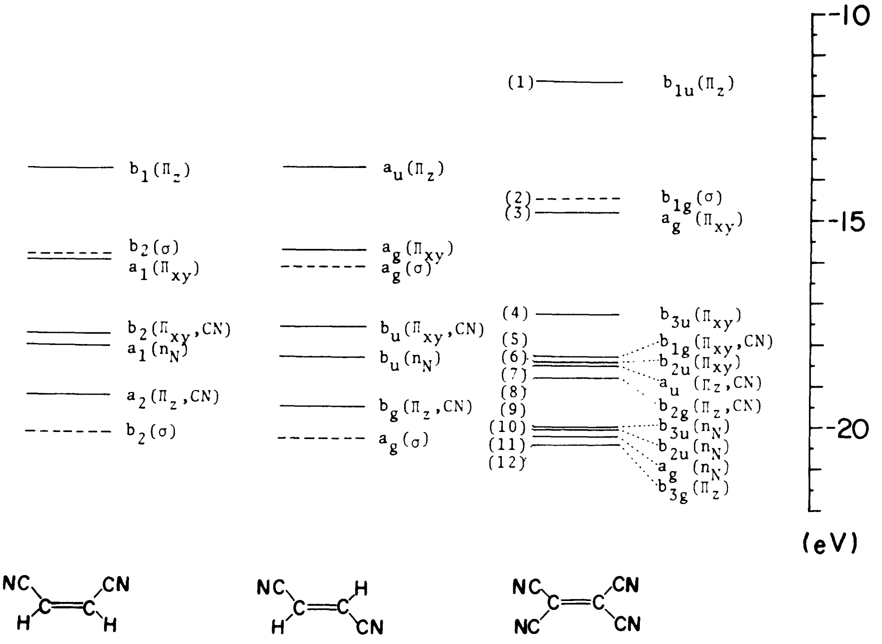

Fig. 2 CNDO/2 molecular orbitals of maleonitrile, fumaronitrile and TCNE

peaks at 11.77, 11.96 and 12.05 eV. The next sharp band is found at 13.49 eV, which is followed with a broad band composed of several peaks (13.7 - 15.6 eV).

The CNDO/2 calculation predicts that the highest occupied molecular orbital of TCNE is a delocalized π_z orbital (b_{1u}) with a node at the middle of each C-C single bond. This orbital is well separated in energy from the next occupied molecular orbital (see Fig. 2). Therefore, we can safely attribute the first photoelectron band to the ionization of the above orbital. In this band, the second and third peaks are separated from the first one by ca. 1530 and 2260 cm^{-1} respectively. These values nearly correspond to the vibrational frequency of the C=C and C≡N stretching modes of TCNE which are 1573 and 2262 cm^{-1} respectively[3]. Thus the above peaks can be attributed to the structure associated with these vibrational modes.

In order to interpret the photoelectron spectrum in the 12 - 16 eV region, it is worth-while to compare TCNE with related cyano-compounds. The photoelectron spectra of fumaronitrile and maleonitrile were reported by Bock and Stafast[4], who interpreted the spectra with the aids of the extended Hückel calculations and the analysis of the vibrational structures. The CNDO/2 orbitals of these molecules are illustrated in Fig. 2. It should be noted that, both in fumaronitrile and maleonitrile, there are three molecular orbitals localized on the C≡N groups, which are π_{xy} (in plane), π_z (out of plane) and n_N (lone pair on nitrogen) orbitals. Although Bock and Stafast considered that there are two n_N orbitals with a very small energy difference, the CNDO/2 calculation gives only one orbital that is definitely of n_N character. If we disregard this discrepancy, we can say that the orbital scheme shown in Fig. 2 is mostly in accord with the interpretations of the photoelectron spectra given by the above authors as regards the nature of molecular orbital responsible for each photoelectron band. Seemingly the photoelectron band associated with the highest σ orbital predicted by the CNDO/2 calculation is not observable. The observed ionization energies of the molecular orbitals localized on the C≡N groups are listed in Table 1. According to the CNDO/2 calculation of TCNE, there are six orbitals localized on the C≡N groups, corresponding to the ones described above, which are a π_{xy} orbital (5), two π_z orbitals (7 and 8), and three n_N orbitals (9, 10 and 11). These orbitals are again predicted to be in the energy region nearly same as in the cases of the dicyanoethylenes, although the order of π_z (C≡N) and n_N orbitals is reversed in the case of TCNE. Therefore, we can attribute the bands in the 13.7 - 15.6 eV region of the photoelectron spectrum of TCNE to the ionization of the orbitals localized on the C≡N groups. Assuming the orbital sequence predicted by the CNDO/2 calculation, we will tentatively assign the 14.50 eV peak to the ionization of the n_N orbitals, and the 14.14 and 14.27 eV peaks to the ionization of the π_z (C≡N) orbitals. The peaks in the 13.7 - 14.0 eV region are likely to be associated with the π_{xy} orbitals, 4 - 6.

The sharp peak at 13.49 eV is a little separated from the bands mentioned above. The possible

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Table 1. Ionization potentials of the orbitals localized on C≡N groups (eV)

	π_{xy} (in plane)	n_N (lone pair on N atom)	π_z (out of plane)
fumaronitrile	13.10	13.44	13.67
maleonitrile	13.35	13.5	(~13.5)

orbital would be either the π_{xy} (a_g) orbital 3 or the σ(b_{1g}) orbital 2. Since a σ orbital usually gives a broad band, we will attribute the 13.49 eV peak to the ionization of the π_{xy} (a_g) orbital 3.

The photoelectron spectrum of TCNQ shows five bands (Fig. 3). The first one is sharp and exhibits peaks at 9.61, 9.78 and 9.87 eV. As in the case of TCNE, the second and third peaks in this photoelectron band can be attributed to the vibrational structures. Their separations from the first peak, ca. 1370 and 2020 cm^{-1}, nearly correspond to the vibrational frequencies of the C=C and C≡N stretching modes, which are 1540 and 2228 cm^{-1} respectively for neutral TCNQ molecule[5] We can safely assign this band to the ionization of the highest occupied π orbital, which is predicted to be π_z (b_{1u}) by the CNDO/2 calculation.

As shown in Table 2, the orbital scheme of TCNQ is more complicated than TCNE. But, again, there are six orbitals mainly localized on the C≡N groups, which are a π_{xy} orbital (9), two π_z orbitals (11 and 12) and three n_N orbitals (13,14 and 15). Among the five photoelectron bands of TCNQ, the third one in the 12 - 14 eV region most closely resembles the 13.7 - 15.6 eV band of TCNE as regards the band shape and ionization potential. Thus we will attribute this band to the ionization of the orbitals localized on the C≡N groups. From the comparison with the CNDO/2

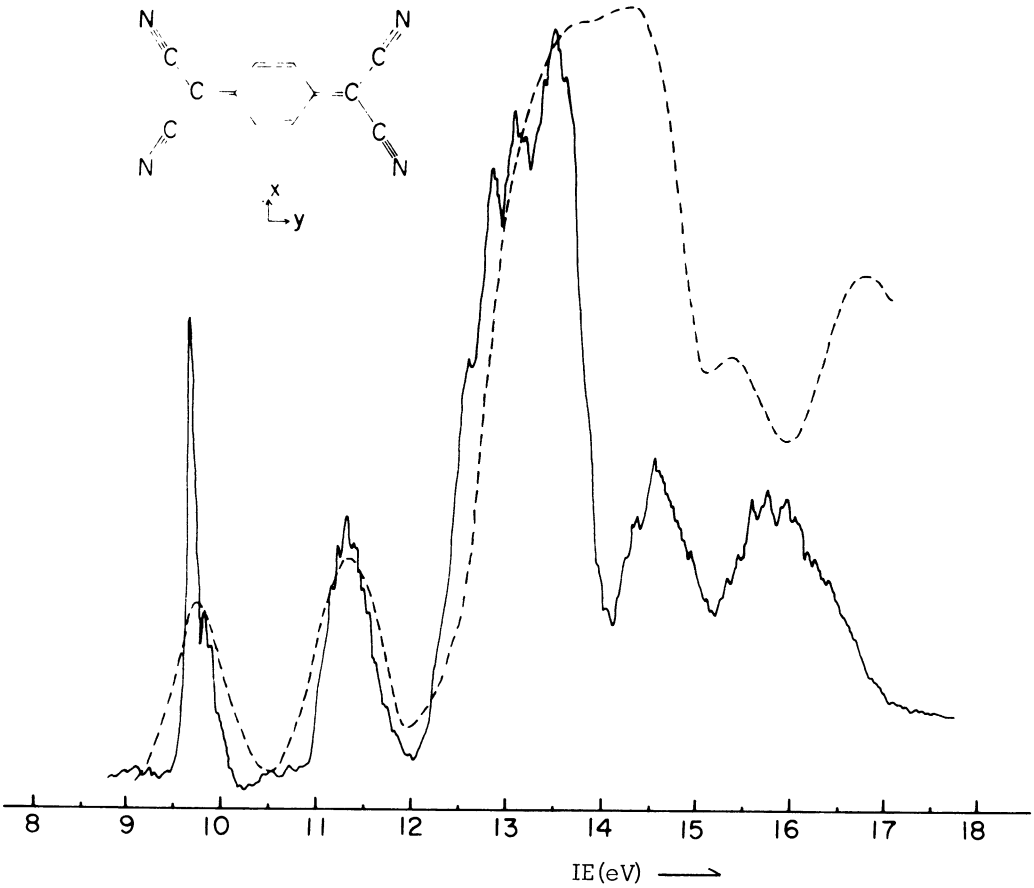

Fig. 3 Photoelectron Spectra of TCNQ: gas phase spectrum (solid line) and solid phase spectrum (broken line)

orbitals, we will tentatively assign the peaks around 13.38 eV to the n_N orbitals, the 12.90 eV peak to the π_z (C≡N) orbitals, and the 12.68 eV peak to the π_{xy} orbitals 9 and 10. The 12.41 eV peak is likely to be associated with the π_{xy} orbital 8. Then we have to consider that the second photoelectron band in the 11 - 12 eV region is due to the ionizations of the orbitals 4,6 and 7. Possibly the bands associated with the σ orbitals 2,3 and 5, are hidden under the π bands. We may attribute the fourth band (14 - 15 eV) to the orbitals 16 - 19, and the fifth one (15 - 18 eV) to the orbitals 20 - 22. The assignments described above are summarized in the last column of Table 2.

Table 2. Molecular orbitals of TCNQ

CNDO/2 calculation

	symmetry	orbital type	orbital energy (eV)	observed ionization energy (eV)
(1)	b_{1u}	π_z	-9.95	9.61 9.78 9.87
(2)	b_{1g}	σ	-13.89	
(3)	a_g	σ	-14.71	
(4)	b_{3g}	π_z	-15.31	11-12
(5)	b_{3u}	σ	-15.86	
(6)	b_{2u}	π_{xy}	-15.88	
(7)	b_{2g}	π_z (ring)	-16.05	
(8)	b_{1g}	π_{xy}	-16.94	(12.41)
(9)	b_{3u}	π_{xy} (C≡N)	-17.91	12.68
(10)	a_g	π_{xy}	-18.05	
(11)	a_u	π_z (C≡N)	-18.38	12.90
(12)	b_{2g}	π_z (C≡N)	-18.40	
(13)	b_{1g}	n_N	-18.50	13.30 13.38 13.53
(14)	b_{2u}	n_N	-18.84	
(15)	a_g	n_N	-19.04	
(16)	b_{3u}	σ	-20.29	14-15
(17)	b_{1u}	π_z	-20.70	
(18)	b_{2u}	σ	-20.94	
(19)	b_{3u}	σ	-20.98	
(20)	b_{2u}	σ	-23.25	15-18
(21)	b_{1g}	σ	-23.76	
(22)	b_{3g}	π_z	-23.85	
(23)	b_{1u}	π_z	-26.5	
(24)	b_{3u}	σ	-28.7	

In Fig. 3, we have reproduced the photoelectron spectrum of the TCNQ solid reported by Grobman et al.$^{2)}$, the energy scale of which has been shifted so that the maxima of its first and second bands coincide with those of the gas-phase spectrum. It should be noted that the two spectra show a very good agreement in the region below 14 eV, except the presence of a broadening of about 0.5 eV. However, a marked disagreement is found in the higher energy region. This discrepancy is quite interesting but further experimental studies seem to be necessary before discussing its origin.

In the photoelectron spectrum of the TCNQ solid, the first band is located at 2.9 eV from the Fermi level. If we assume that the Fermi level is located at 5.0 eV from the vaccum level$^{2)}$, the first ionization potential of the TCNQ solid is estimated as 7.9 eV. This is smaller by 1.7 eV than the first ionization potential of the free molecule. This solid-state shift can be attributed to the polarization energy term.

The intrinsic energy gap in a molecular crystal can be estimated by the following relation:

$$\epsilon = I - A - (P_e + P_h)$$

where I and A are the ionization potential and electron affinity of the molecule, and P_e and P_h are the polarization energies associated with the conduction electron and positive hole respectively. Substituting the values, $I = 9.6$ eV, $A = 2.8$ eV$^{6)}$ and $P_e = P_h = 1.7$ eV into the above equation, we obtain 3.4 eV as the intrinsic energy gap. It has been reported that the TCNQ crystal exhibits a considerably high photoconductive sensitivity in the visible region$^{7)}$. However, the energy gap estimated above suggests that such a photoconduction must be of extrinsic nature.

The authors are grateful to Dr. J.N.A. Ridyard of Perkin-Elmer Ltd. for taking the photoelectron spectra of TCNE and TCNQ.

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(Received May 14, 1974)