3036 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 3036—3040 (1973) [Vol. 46, No. 10

The Photoelectron Spectra of Alcohols, Mercaptans and Amines

Hitoshi Ogata, Hatsuki Onizuka, Yoshimasa Nihei, and Hitoshi Kamada
Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113

(Received December 19, 1972)

The HeI photoelectron spectra of aliphatic amines, alcohols and mercaptans were measured. These spectra, especially those of methylsubstituted compounds, were interpreted in terms of the orbital energies and corresponding eigenvectors calculated by the CNDO/2 and the INDO type self-consistent field molecular orbital techniques. Modification of CNDO/2 was also performed and the results are briefly discussed.

Photoelectron spectroscopy (pes) has become a powerful tool for the interpretation of the electronic structure of molecules and the corresponding ions, and widely used for studies of various molecular systems. The present paper is meant to make a contribution to the interpretation of the photoelectron (pe) spectra of some aliphatic alcohols, ROH, mercaptans, RSH, and amines, RNH_2. The CNDO/2[1] and the INDO[2] calculations have been performed on these molecules in order to interpret the pe spectra. We assume throughout the validity of Koopmans' theorem.[3] Since the calculations have been performed in the ground state geometries, the calculated ionization potentials will be compared with the experimental vertical values throughout.

Experimental

A Jasco Model PE-1 Photoelectron Spectrometer was used for measurements. The resonance line of He(584 Å) was emitted by means of DC glow discharge. A hemispherical electrostatic condenser with 100 mm diameter was used for electron energy analysis, a channel electron multiplier for detection and a pulse counting method for signal processing system. As low energy electrons are largely affected by terrestrial magnetic field and fluctuating magnetic field around the apparatus, they were eliminated by μ-metal shielding. In order to obtain ionization potentials from spectra, xenon gas is mixed into the sample gas as internal standards of ionization potential. We have measured the spectra of aliphatic amines, RNH_2, alcohols, ROH and mercaptans, RSH, where R=CH_3, C_2H_5, *n*-C_3H_7, *iso*-C_3H_7, *n*-C_4H_9, *iso*-C_4H_9, *sec*-C_4H_9 and *tert*-C_4H_9. The spectra were obtained in gas phase at room temperature. The compounds were obtained commercially, and further purification was not performed. Theoretical calculations were based on the CNDO/2 and the INDO method.

Results and Discussion

Alcohols. Figure 1 shows the pe spectra of eight aliphatic alcohols.[4] Each spectrum contains a relatively sharp and symmetrical peak in the lowest ionization potential (i.p.) region (termed as the first band) and a series of broad peaks in the higher i.p. region.

The first band of methanol shows fine structure ascribable to the vibration of the ion in the ground electronic state. It consists of at least three peaks, and the spacing is about 960 cm^{-1}. The intense band in the infrared absorption spectra of methanol located in 990 to 1050 cm^{-1} is complicated and may be related to CO stretching, OH bending and CH bending (CH rocking) modes. Fine structure observed in the pe spectra of methanol may be due to these vibrational modes of methanol ion.

Refaey and Chupka measured the photoionization total cross section of methanol and found six sharp peaks in the region of photon energy from 10.5 to 12.0 eV.[5] They concluded that these peaks might be due to vibration of methanol ion in the electronic ground state. They also stated that to ascertain this assignment it would be necessary to measure the pe spectra of CH_3OH.

Brehm *et al.* measured the pe spectra of methanol using Lyα line (12.08 eV) and He resonance line as light sources.[6] Their results show that both first

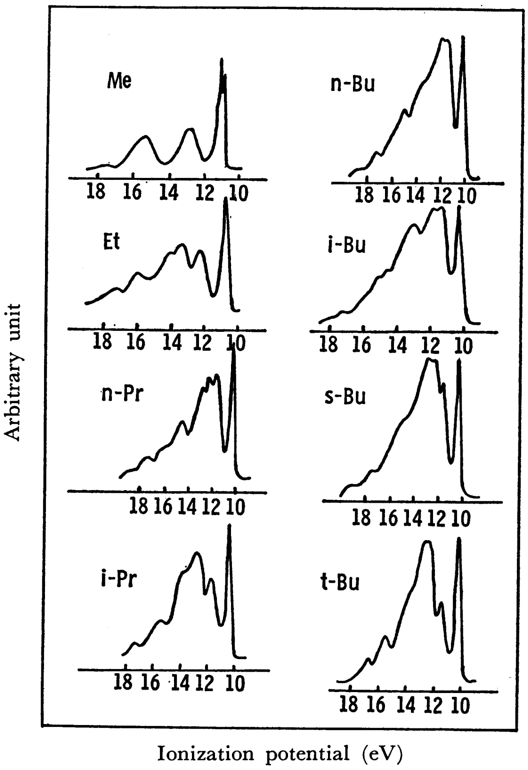

Fig. 1. The photoelectron spectra of alcohols.

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[1] J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3298 (1966).

[2] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *ibid.*, **47**, 2026 (1967).

[3] T. Koopmans, *Physica*, **1**, 104 (1934).

[4] Some of the spectra shown here have already been published. A. D. Baker, *Anal. Chem.*, **43**, 375 (1971).

[5] K. M. A. Refaey and W. A. Chupka, *J. Chem. Phys.*, **48**, 5205 (1968).

[6] B. Brehm, V. Fucks, and P. Kebarle, *Int. J. Mass Spectrom. Ion Phys.*, **6**, 279 (1971).

bands of methanol obtained by Lyα and He resonance line give similar fine structure, *i.e.*, there are only three peaks due to vibration of CH_3OH^+. Of the six peaks in the derivative curve of the total ionization cross section presented by Chupka, the envelope of three peaks located in the region from 10.8 to 11.2 eV bears a striking resemblance to that of the first band of the pe spectra. On the other hand, the remaining three peaks in the derivative curve which are in 11.3 to 11.6 eV cannot be found in the pe spectra. Accordingly, three of six peaks located in higher energy region reported by Chupka may be due to some other process than the direct ionization, presumably due to auto-ionization process.

It is interesting while the 0–0 peak is the most intense in the first pe band of water,[7] the 0–1 peak is the most intense in the case of methanol. This fact, perhaps, indicates that the character of the highest occupied molecular orbital (HOMO) of methanol is considerably different from that of water. In fact, this is ascertained by the calculated HOMO's: the HOMO of water is wholly composed of an oxygen 2p atomic orbital, but, as for methanol, only 62% of the HOMO is composed of an oxygen 2p atomic orbital.

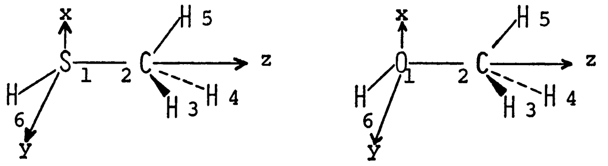

Fig. 2. Models employed for calculations.

Table 1. Calculated ionization potentials and eigenvectors[a)] of methanol

	Ionization potentials (eV)				
CNDO/2	22.87	21.93	19.25	16.16	15.28
MCNDO/2[b)]	21.63	20.23	18.13	14.84	13.00
INDO	22.32	21.97	18.67	15.16	14.24
Obsd	17.53	15.69	15.09	12.66	10.95
1OS	0.170		0.116	−0.197	
1OZ	0.118		−0.722	0.183	
1OX	0.582			−0.564	
1OY		0.606			−0.788
2CS					
2CZ	−0.144		0.545	−0.110	
2CX	0.519		0.199	0.426	
2CY		0.598			0.362
3HS	−0.223	0.370		0.244	0.352
4HS	−0.223	−0.370		0.244	−0.352
5HS	0.313		0.295	0.409	
6HS	−0.366		0.180	0.360	
MO Sym.	3a′	1a″	4a′	5a′	2a″

a) Eigenvectors are those calculated by CNDO/2.
b) Modified CNDO/2. See text for explanation.

Fig. 2 shows the models of methanol and methyl mercaptan used in theoretical calculations. Results for methanol obtained by the CNDO/2 and the INDO method are summarized in Table 1. In Table 1 1OZ, for example, indicates the $2p_z$ atomic orbital of an oxygen atom. Wave functions are approximated as a linear combination of atomic orbitals and the coefficients, C_{hi}, are given in Table 1. The calculated orbital energies are compared with observed vertical i.p.'s. The first band of the pe spectrum of methanol is thought to be due to the ionization from a "lone pair" orbital localized on an oxygen atom. This is ascertained by the fact that the first band of the pe spectrum is considerably sharp. But this "lone pair" orbital is not completely atomic: only 62% of this orbital is composed of an oxygen $2p_y$ atomic orbital. Relationship between band shapes of the photoelectron spectra which can be assigned to "lone pair" orbitals and the wave functions obtained from theoretical calculations has been considered in detail elsewhere.[8]

As for methanol, ethanol, 2-propanol, *sec*-butanol and *tert*-butanol, the well-defined second i.p.'s can be determined. But as for alcohols with straight chain alkyl group, the second band overlaps with higher ionization potential bands and the second i.p.'s cannot be determined. Figure 1 shows that the more the alkyl group is branched, the second ionization band is the more clearly isolated.

Table 1 shows that the nature of the 5a′ orbital of methanol is rather indistinct. This orbital consists of contribution of CH and OH bonding character. It is interesting that the second occupied orbitals of alcohols that have strongly electron-releasing branched alkyl groups, *i.e.*, *iso*-propanol, *tert*-butanol, have con-

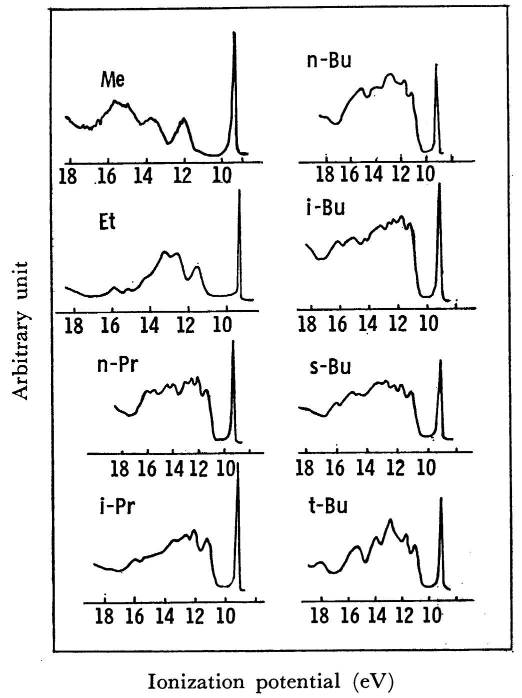

Fig. 3. The photoelectron spectra of mercaptans.

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[7] D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, London, New York, Sydney and Toronto (1970).

[8] H. Ogata, H. Onizuka, Y. Nihei, and H. Kamada, *Chem. Lett.*, **1972**, 895.

siderable CO bonding character. Though third i.p.'s cannot be given from pe spectra except for methanol and ethanol, calculations show that the third occupied orbitals consist of mainly CO bonding orbitals. In the case of methanol the fourth pe band is thought to be the ionization from CH_3 group.

Mercaptans. The pe spectra of eight aliphatic mercaptans are shown in Fig. 3. Calculated ionization potentials and the corresponding eigenvectors are given in Table 2. The first to the third vertical i.p.'s can be readily obtained from spectra and they are summarized in Table 3. Since an oxygen and a sulfur atoms belong to the same column of the periodic table, pe spectra of mercaptans might be expected to contain some of the characteristic features of the spectra of alcohols, *i.e.*, they would contain a sharp intense peak ascribable to a 3p "lone pair" electrons localized on the sulfur atom in the lowest i.p. region, and a series of broader bands in higher i.p. region. The i.p.'s of the "lone pair" electrons may be expected to be lower in mercaptans than in alcohols because a sulfur atom has 3p "lone pair" electrons. Comparison of Fig. 3 with Fig. 1 shows the validity of these predictions. Mercaptans give pe spectra composed of a sharp intense peak at the lowest i.p. region and a series of broader but well-resolved bands in higher i.p. region.

Table 2. Calculated ionization potentials and eigenvectors[a] of methyl mercaptan

	Ionization potentials (eV)				
CNDO/2	21.04	20.41	17.09	14.81	12.07
MCNDO/2[b]	19.14	19.03	15.01	12.16	9.97
INDO	20.03	19.84	16.20	13.37	11.30
Obsd		15.63	13.67	12.08	9.44
1SS	0.249			−0.369	
1SZ			−0.605	0.378	
1SX	0.426		−0.187	−0.578	
1SY		0.372			0.923
2CS					
2CZ	−0.190		0.544	−0.212	
2CX	0.591		0.251	0.267	
2CY		0.673			−0.236
3HS	−0.289	0.452		−0.186	−0.236
4HS	−0.289	−0.452		−0.186	0.192
5HS	0.381		0.359	0.243	
6HS	−0.229		0.319	0.376	
MO Sym.	3a′	1a″	4a′	5a′	2a″

a) Eigenvectors are those calculated by CNDO/2.
b) Modified CNDO/2. See text for explanation.

Table 3. The first to the third ionization potentials of mercaptans

	1st	2nd	3rd
CH_3SH	9.44	12.08	13.67
C_2H_5SH	9.29	11.59	12.61
n-C_3H_7SH	9.19	11.38	12.08
i-C_3H_7SH	9.14	11.19	12.15
n-C_4H_9SH	9.15	11.15	11.80
i-C_4H_9SH	9.12	11.14	11.69
s-C_4H_9SH	9.10	11.07	11.64
t-C_4H_9SH	9.03	11.01	11.67

Table 2 shows that the largest contribution to the HOMO is given by 1SY, and amounts to more than 80%. The first band of each mercaptan is assigned to the ionization from the "lone pair" orbital localized on a sulfur atom on the ground that this band is composed of single sharp peak and that calculations show the HOMO is non-bonding. That the first bands of mercaptans are sharp compared with those of alcohols and that though the first band of methanol contains vibrational fine structure, mercaptan shows no vibrational structure, are consistent with the difference between the degree of contribution of 1OY and 1SY to the HOMO.

When the comparison is made between methyl- and *tert*-butyl-substituted compounds, the contribution of 1NX and 1OY to the highest occupied orbital reduces from 51% to 32% for amines and from 62% to 36% for alcohols. On the contrary, the contribution of 1SY to it only reduces from 85% to 82%. This property is the marked characteristic of the "lone pair" orbital of aliphatic mercaptan. Of the eight alkyl-substituted amines, alcohols and mercaptans, methyl-substituted compounds have the highest i.p.'s and *tert*-butyl-substituted compounds have the lowest i.p.'s. Difference of ionization potentials of methyl and *tert*-butyl-substituted compounds is 0.40 eV for amine, 0.77 eV for alcohol and 0.41 eV for mercaptan. The first i.p.'s of amines, alcohols and mercaptans are given graphically in Fig. 4.

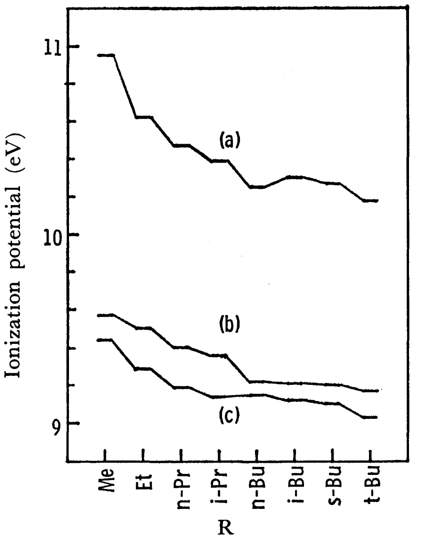

Fig. 4. The first adiabatic i.p.'s of (a) alcohols, (b) amines and (c) mercaptans.

Unlike alcohols, the second bands of mercaptans are all separated from the higher i.p. bands. The second occupied molecular orbital of methyl mercaptan is indistinct in character but has the feature that the electronic population is relatively high on the SH functional group of this molecule. The third vertical ionization potentials can be determined from spectra and calculations indicate that the third occupied molecular orbital of methyl mercaptan is rich in SC bonding character. As in the case of methanol, the fourth ionization band of methyl mercaptan is largely contributed to by CH_3 group.

Amines. The first i.p.'s of the aliphaticamines have been measured by photoionization[9] and by low resolution pes.[10] Recently, the i.p.'s of methylamine determined by the high resolution pe spectra and those predicted by the INDO type MO calculations have been reported by McDowell *et al.*[11]

The pe spectra of aliphatic amines are shown in Fig. 5. Since the lowest i.p. bands of amines are very broad and show no vibrational fine structure, it is difficult to determine the first adiabatic i.p.'s. But if the onsets of these bands are taken for the adiabatic i.p.'s, our values are in good agreement with those reported by Watanabe *et al.*[9] The first pe bands of amines can be assigned to the ionization from the so-called "lone pair" orbitals. That these bands are very broad compared with those of the first i.p. bands of alcohols and mercaptans is the characteristic feature of amines.[8] As in the case of alcohols, the second i.p.'s can be determined only for amines which have the strong electron-releasing alkyl group, *i.e.* *iso*-C_3H_7 and *tert*-C_4H_9. Calculated results for ethylamine are summarized in Table 4.

Although one center exchange integrals are neglected in CNDO/2, they are taken into account in the INDO method. It is supposed that the inclusion of one center exchange integrals most affects the energy level of an orbital which is localized. Tables 1, 2 and 4 show that the first i.p.'s calculated by INDO are, in all cases, lower than those calculated by CNDO/2 and the remaining i.p.'s obtained by INDO are somewhat lower but the two methods give essentially the same results.

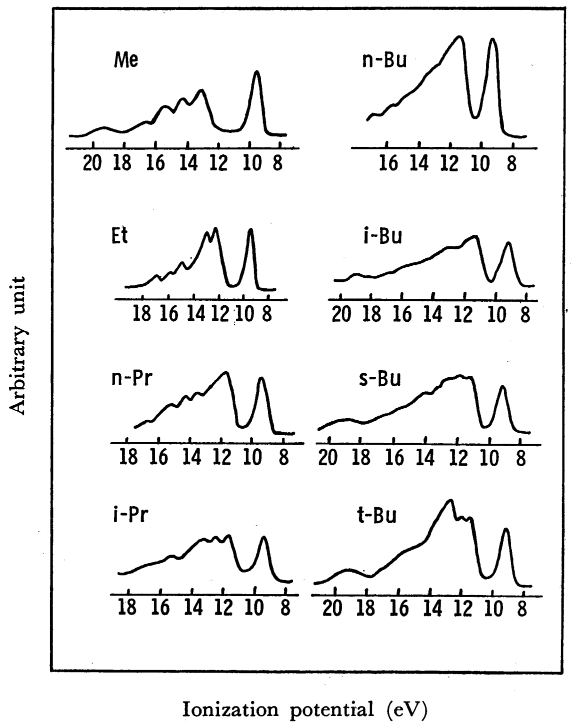

Fig. 5. The photoelectron spectra of amines.

Table 4. Calculated and observed i.p.'s of ethylamine (eV)

CNDO/2	13.69	14.95	16.08	18.70
MCNDO/2	11.87	14.19	15.22	17.80
INDO	12.20	14.83	15.88	18.49
Obsd	9.50	12.27	13.01	14.80
MO Sym.	a′	a″	a′	a′

Modification of the CNDO/2 method. Making a comparison between the observed i.p.'s and the calculated orbital energies by the use of Koopmans' theorem, the calculated values are too large as can be seen from Tables 1 and 2. In order to improve calculated orbital energies, some changes of approximations were introduced to the CNDO/2 method.

From the preliminary calculations, it became clear that the change in the coulombic repulsion integrals causes the parallel translation of the orbital energies and that the bonding parameters have relationship to the intervals of the orbital energies. Taking these facts into consideration, it is necessary first to investigate the parametrization of the electron repulsion integrals, γ_{AB}. These integrals calculated by using the Slater orbitals in the original CNDO/2 method are much larger compared with those semiempirically evaluated.[12] In the present modification, therefore, these integrals are calculated by Klopman's equation.[12] The next modification relates to bonding parameters. In the CNDO/2 approximation, $\beta_A{}^0$ is treated as a parameter characteristic of atom A. In our modification, the following approximations were introduced:

$$\beta^0{}_{AB} = (1/2)K(z_A'+z_B')$$

where z_A' is the effective nuclear charge of atom A, and K is a constant determined for each row.

Figure 6 shows the variation of orbital energies of

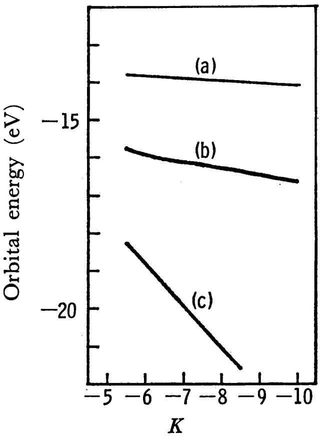

Fig. 6. Orbital energies of water *vs.* parameter *K*. (a) $1b_1$, (b) $3a_1$ and (c) $1b_2$ orbitals.

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[9] K. Watanabe and J. R. Mottl, *J. Chem. Phys.*, **26**, 1773 (1957).

[10] M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.*, **1964**, 4434.

[11] A. B. Cornford, D. C. Frost, F. G. Herring, and C. A. McDowell, *Can. J. Chem.*, **49**, 1135 (1971).

[12] G. Klopman, *J. Amer. Chem. Soc.*, **87**, 3300 (1965).

H_2O. The observed difference between the first and the second i.p.'s is 2.1 eV and that between the second and the third ionization potential is 3.7 eV. The value of -6.5 was adopted for K so as to fill these conditions. The same procedure has been performed for the determination of K of the third-row atoms and the value of -2.3 was obtained citing H_2S as instance.

Results for methanol, methyl mercaptan and ethylamine are given in Tables 1, 2 and 4, respectively. Ionization potentials obtained by these modifications are still larger compared with the observed values but considerable improvement was obtained. It should be noted that the CNDO/2, INDO and the modified CNDO/2 calculations lead to the same ordering of the molecular orbital energy levels.

The authors wish to thank Mr. H. Matsumoto for his continuous help in the measurements of the photoelectron spectra.