Photoelectron Angular Distribution Measurements for Some Aliphatic Alcohols, Amines, and Halides

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The angular distributions for the He I photoelectron spectra of some aliphatic alcohols, amines, and halides were measured in order to reexamine the assignments of the so-called p-type photoelectron spectral bands in the He I region of these molecules. The second band of methanol and the third band of ethanol were assigned to the in-plane n orbitals localized mainly on the oxygen atom. Furthermore, it was found that the angular distributions of photoelectrons were useful for the conformational analysis of molecules and that the sum of β values was conserved for these compounds.

The photoelectron differential cross-section ($d\sigma/d\Omega$) for an unpolarized light and an ensemble of randomly oriented molecules or atoms is given by

$$d\sigma/d\Omega \propto 1 + 0.5\beta(1.5\sin^2\theta - 1) \qquad (1)$$

where β is an asymmetry parameter, and θ is the angle between the direction of an ejected photoelectron and that of an incoming photon.[1,2] The β value depends on the kinetic energy of the photoelectron and the character of the molecular orbital from which the photoelectron is ejected. Therefore, the β value is expected to be useful for the interpretation of photoelectron spectra. Actually, using the β values, we solved the problems of the photoelectron spectral band assignments of benzene[3] and pyridine[4] about which there had been disputes.

He I/II photoelectron spectra have been studied by a number of workers with methanol and ethanol[5-11] and also with methylamine and ethylamine.[5,9,11] However, studies of the assignments of all the bands in the He I region are few. Katsumata and coworkers[11] proposed the assignments of all the p-type bands in the He I region of these alcohols and amines on the basis of the sum rule.[12] As for methanol, Robin and Kuebler[10] assigned all the photoelectron spectral bands with the aid of an *ab initio* MO calculation.

Many photoelectron spectral studies have been made with alkyl halides.[8,12-19] Kimura and coworkers[12] studied systematically the photoelectron spectra of alkyl halides covering the higher alkyl chlorides, bromides, and iodides, and assigned all the p-type bands in the He I region with the aid of the sum rule.

In the present study, the photoelectron angular distributions have been measured for aliphatic amines, alcohols, and halides, and the band assignments have been reexamined from the standpoint of the photoelectron angular distributions. The correlation between the β value and the character of the orbital from which the photoelectron is ejected, and the existence of the sum rule for the β values are discussed.

Experimental

The details of a photoelectron spectrometer used for the angular distribution measurements in the present study were described in a previous paper.[3] The β values were obtained according to formula (1) using the intensities measured at two angles, $\theta=45°$ and 90°. The measurements were carried out at room temperature, and the vapor pressure of the samples was kept at 4×10^{-4} Torr.

Results and Discussion

Aliphatic Alcohols and Amines. The photoelectron spectra of methanol and ethanol are shown in Fig. 1, and those of methylamine and ethylamine in Fig. 2. The vertical ionization potentials (I_v) and the β values of methanol and ethanol are summarized in Table 1 together with the band assignments. It is known that ethanol and ethylamine take the *trans* and *gauche* forms in the gaseous state, the *trans* form being predominant for both compounds.[20,21]

The first band of methanol or ethanol is assigned to the out-of-plane n orbital (a″n′(O)) which is localized mainly on the oxygen atom.[6-8,10,11] As is seen in Table 1, the β values of these orbitals are nearly equal to each other. The second band of methanol was ascribed to the a′π(CH$_3$) orbital by Katsumata and coworkers[11] from the sum rule. However, from the comparative consideration of the second bands of methanol, water, and dimethyl ether, it is derived

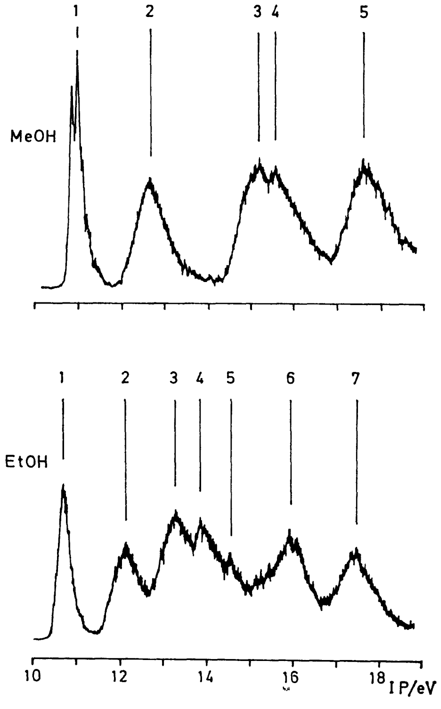

Fig. 1. Photoelectron spectra of methanol and ethanol.

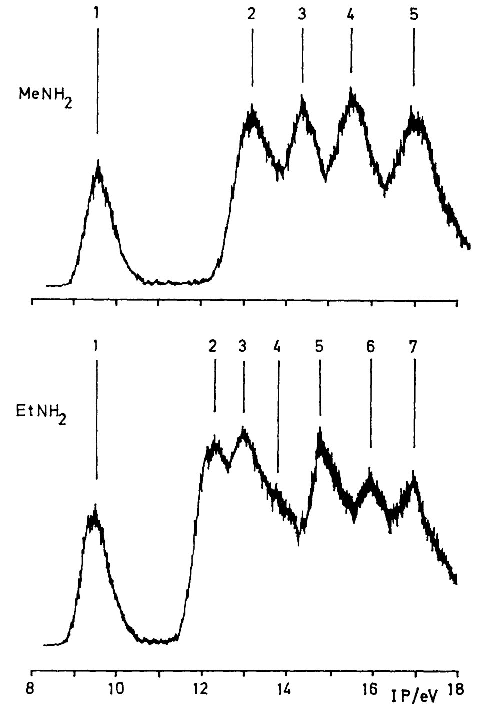

Fig. 2. Photoelectron spectra of methylamine and ethylamine.

that the band is assigned to the in-plane n orbital (a'n(O)) localized mainly on the oxygen atom. The second bands of water[13] and dimethyl ether[22] are assigned to the in-plane n(O) orbitals experimentally. The *ab initio* MO calculations of water[23] and dimethyl ether[24] also support the assignment. The β values and the ionization potentials of the second bands of water, methanol, and dimethyl ether are shown in Table 2. We can see from this table that the β value and ionization potential of the second band of methanol are intermediate between the corresponding values of water[25] and dimethyl ether. This shows that the second band of methanol is also assigned to the in-plane n(O) orbital. The MO calculation[26] is consistent with this assignment. The third, fourth, and fifth bands of methanol are assigned to the a'σ(CO), a''π'(CH$_3$), and a'π(CH$_3$) orbitals, respectively, with the aid of the MO calculation.[26] As described later, these assignments are reasonable from the consideration of the β values and are consistent with Robin and Kuebler's result.[10]

As is seen in Table 1, the β values of the second and third bands of ethanol are 0.30 and 0.56, respectively. On the other hand, the β value of the a'σ(CC) orbital of ethylamine is <0.37 (see the later discussion), and that of the in-plane n(O) orbital is 0.45 for methanol and 0.64 for dimethyl ether (Table 2). Therefore, the second band of ethanol should be assigned to the a'σ(CC) orbital, and the third band to the in-plane n(O) orbital.

The fourth, fifth, and sixth bands of ethanol were assigned by Katsumata *et al.*[11] to the a'σ(CO), a''π^-(C$_2$H$_5$), and a''π^+(C$_2$H$_5$) orbitals. These assignments are supported by the observed β values. Since the MO calculation of methanol[26] suggests that the energy of the a'π(CH$_3$) orbital is higher than that of the a'σ(OH) orbital, the seventh band of ethanol is preferably assigned to the a'π(CH$_3$) orbital.

The band positions, β values, and assignments of the photoelectron spectra of methylamine and ethylamine are given in Table 3. The observed bands are assigned by considering the β values, the sum rule, and the MO's calculated with methylamine.[27]

According to the assignments given in Table 3, the β values of the pseudo π orbitals of the methyl group of methanol correspond to those of methylamine. This is also the case for the pseudo π orbitals of the ethyl groups of ethanol and ethylamine. The β value of the third band of ethylamine (a'σ(CC)) is 0.46 at the band maximum. This value, however, may conceivably be higher than the real value because this band is largely overlapped by the second band with the larger β value. The observed β value shows the energy dependence; 0.46 at 13.08 eV, 0.39 at

TABLE 1. VERTICAL IONIZATION POTENTIALS (I_v IN eV), β VALUES, AND BAND ASSIGNMENTS OF ALKANOLS

	Band[a)]	1	2	3	4	5	6	7
MeOH	I_v	10.95	12.65	15.17	15.53	17.57		
	β[b)]	0.50±0.05	0.45±0.04	0.70±0.03	0.62±0.03	0.46±0.03		
	Assign. (sum rule)[c)]	a''n'(O)	a'π(CH$_3$)	a'σ(CO)	a''π'(CH$_3$)	a'σ(OH)		
	Assign. (this work)	a''n'(O)	a'n(O)	a'σ(CO)	a''π'(CH$_3$)	a'π(CH$_3$)		
EtOH	I_v	10.64	12.16	13.28	13.85	14.55	15.96	17.45
	β[b)]	0.44±0.03	0.30±0.03	0.56±0.03	0.64±0.04	0.57±0.03	0.69±0.05	0.68±0.05
	Assign. (sum rule)[c)]							
	trans	a''n'(O)	a'σ(CC)	a'π(CH$_3$)	a'σ(CO)	a''π^-(C$_2$H$_5$)[e)]	a''π^+(C$_2$H$_5$)[e)]	a'σ(OH)
	gauche[d)]	$\underline{\mathrm{n}'(\mathrm{O})}$	π^-(C$_2$H$_5$)	$\underline{\sigma(\mathrm{CC})}$	$\underline{\pi(\mathrm{CH}_3)}$	π^+(C$_2$H$_5$)	$\underline{\sigma(\mathrm{CO})}$	σ(OH)
	Assign. (this work)	a''n'(O)	a'σ(CC)	a'n(O)	a'σ(CO)	a''π^-(C$_2$H$_5$)	a''π^+(C$_2$H$_5$)	a'π(CH$_3$)

a) These numbers correspond to those shown in Fig. 1. b) The error of the β value denotes the mean square error. c) Ref. 11. d) The underlined orbitals of the *gauche* form are a'' like out-of-plane orbitals because ethanol has no symmetry in the *gauche* form. e) The π^+ and π^- denote the bonding and antibonding types of combinations of the methyl pseudo π and methylene pseudo π orbitals, respectively.

13.18 eV, and 0.37 at 13.28 eV. The band overlap decreases with increasing *IP*. This means that the real β value of the third band of ethylamine is smaller than 0.37 and corresponds well to the β value of the $a'\sigma(CC)$ band of ethanol (0.3). Thus, the present band assignments of alcohols and amines given in Tables 1 and 3 are supported by the consistency of the β values determined for the corresponding bands.

TABLE 2. IONIZATION POTENTIALS (I IN eV) AND β VALUES OF THE SECOND BANDS OF WATER, METHANOL, AND DIMETHYL ETHER

	H_2O[a]	MeOH	Me_2O
I	13.7	12.65	11.94
β[b]	0.3±0.1	0.45±0.04	0.64±0.03

a) Ref. 25. b) See footnote b) for Table 1.

From the above-mentioned consistency of β values, we can discuss the conformation of ethylamine as an example. On the assumption of the *gauche* form as the predominant conformation, the second band of ethylamine is assigned to the $\sigma(CC)$ orbital (see Table 3) and its β value may be expected to be ~0.3, being inconsistent with the observed value, 0.54. This seems to support the *trans* form as the predominant conformation.

From the comparison of the band assignments made by the present authors with those made by Katsumata *et al.* with the aid of the sum rule, we can see that

TABLE 3. VERTICAL IONIZATION POTENTIALS (I_V IN eV), β VALUES, AND BAND ASSIGNMENTS OF ALKYLAMINES

	Band[a]	1	2	3	4	5	6	7
$MeNH_2$	I_V	9.58	13.18	14.32	15.46	16.83		
	β[b]	0.84±0.05	0.43±0.04	0.55±0.03	0.58±0.02	0.71±0.03		
	Assign. (sum rule)[c]	$a'n(N)$	$a''\pi'(CH_3)$	$a'\sigma(CN)$	$a'\pi(CH_3)$	$a''\pi(NH_2)$		
	Assign. (this work)	$a'n(N)$	$a''\pi'(CH_3)$	$a'\sigma(CN)$	$a'\pi(CH_3)$	$a''\pi(NH_2)$		
$EtNH_2$	I_V	9.50	12.27	12.98	13.8	14.80	15.81	16.75
	β[b]	0.93±0.04	0.54±0.03	0.46±0.03	0.55±0.02	0.53±0.03	0.62±0.03	0.62±0.03
	Assign. (sum rule)[c]							
	trans	$a'n(N)$	$a''\pi^-(C_2H_5)$	$a'\sigma(CC)$	$a'\pi(CH_3)$	$a'\sigma(CN)$	$a''\pi^+(C_2H_5)$	$a''\pi(NH_2)$
	gauche[d]	$n(N)$	$\underline{\sigma(CC)}$	$\underline{\pi(CH_3)}$	$\pi^-(C_2H_5)$	$\underline{\sigma(CN)}$	$\pi^+(C_2H_5)$	$\pi(NH_2)$
	Assign. (this work)	$a'n(N)$	$a''\pi^-(C_2H_5)$	$a'\sigma(CC)$	$a'\pi(CH_3)$	$a'\sigma(CN)$	$a''\pi^+(C_2H_5)$	$a''\pi(NH_2)$

a) These numbers correspond to those shown in Fig. 2. b) See footnote b) for Table 1. c) Ref. 11. d) The underlined orbitals of the *gauche* form are a″ like out-of-plane orbitals because ethylamine has no symmetry in the *gauche* form.

TABLE 4. VERTICAL IONIZATION POTENTIALS (I_V IN eV), β VALUES AND BAND ASSIGNMENTS OF ALKYL HALIDES

	Band[a]	1	2	3	4	5	6	7
MeCl	I_V	11.29		14.46	15.48	16.10		
	β[b]	1.13±0.02		0.46±0.03	0.75±0.03	0.75±0.03		
	Assign.[c]	$n(Cl)$		$\sigma(CCl)$	$\pi(CH_3)$	$\pi(CH_3)$		
EtCl	I_V	11.01		12.99	13.45	14.46	15.64	16.32
	β[b]	1.04±0.05		0.61±0.04	0.54±0.04	0.44±0.07	0.66±0.03	0.76±0.03
	Assign.[d]	$n(Cl)$		$\sigma(CCl)$	$\sigma(CC)$	$\pi^-(C_2H_5)$	$\pi(CH_3)$	$\pi^+(C_2H_5)$
MeBr	I_V	10.53	10.85	13.47	15.13	15.79		
	β[b]	1.32±0.04	1.39±0.03	0.46±0.03	0.79±0.05	0.80±0.05		
	Assign.[c]	$n(Br)$	$n(Br)$	$\sigma(CBr)$	$\pi(CH_3)$	$\pi(CH_3)$		
EtBr	I_V	10.29	10.60	12.47	13.11	14.17	15.33	16.26
	β[b]	1.33±0.03	1.24±0.04	0.56±0.06	0.53±0.04	0.50±0.05	0.69±0.04	0.77±0.04
	Assign.[d]	$n(Br)$	$n(Br)$	$\sigma(CBr)$	$\sigma(CC)$	$\pi^-(C_2H_5)$	$\pi(CH_3)$	$\pi^+(C_2H_5)$
MeI	I_V	9.53	10.16	12.49	14.66	15.43		
	β[b]	1.60±0.03	1.56±0.03	0.66±0.02	0.82±0.04	0.87±0.03		
	Assign.[c]	$n(I)$	$n(I)$	$\sigma(CI)$	$\pi(CH_3)$	$\pi(CH_3)$		
EtI	I_V	9.33	9.92	11.60	12.98	13.89	15.00	15.97
	β[b]	1.50±0.03	1.49±0.04	0.69±0.02	0.58±0.04	0.51±0.04	0.76±0.02	0.87±0.02
	Assign.[d]	$n(I)$	$n(I)$	$\sigma(CI)$	$\sigma(CC)$	$\pi^-(C_2H_5)$	$\pi(CH_3)$	$\pi^+(C_2H_5)$

a) These numbers correspond to those shown in Figs. 3 and 4. b) See footnote b) for Table 1. c) Refs. 12—15, 19. d) Ref. 12.

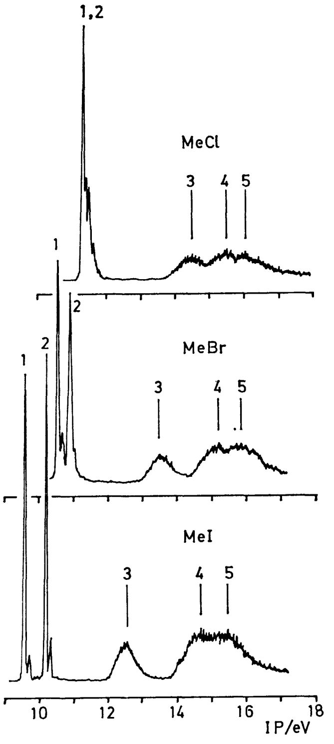

Fig. 3. Photoelectron spectra of methyl chloride, bromide, and iodide.

the agreement is satisfactory for amines but some discrepancies due to the unreasonable assignments based on the sum rule are found for alcohols. This may be caused by the inadequate choice of parameters of the sum rule for the localized orbitals concerning the oxygen atom.

Alkyl Halides. The photoelectron spectra of methyl chloride, bromide, and iodide are shown in Fig. 3, and those of ethyl chloride, bromide, and iodide are in Fig. 4. The I_v's and the β values of these compounds are summarized in Table 4 together with the assignments made so far by other authors.[12-15,19] The β values of methyl halides were reported by Carlson and coworkers[25], and their values are consistent with ours. As is seen in Table 4, the consistency of β values among the related molecules is satisfied for the n(Cl), n(Br), n(I), σ(CCl), σ(CBr), and σ(CI) orbitals. This is also the case for the σ(CC) orbitals and the pseudo π orbitals of methyl and ethyl groups. These reasonable correspondences of the β values support the former assignments. The first and second bands of the bromides and iodides are caused by the spin-orbit splitting, and the fourth and fifth bands of the methyl halides are by the Jahn-Teller effect. The β values change scarcely by the splittings for the compounds.

Sum of β Values. The sums of the β values ($\sum\beta$) of all the p-type bands are shown in Table 5 for the alcohols, amines, and halides. The difference between the sum for methyl and ethyl derivatives ($\Delta\sum\beta$, see Table 5) is regarded to be the sum of the β values of the σ(CC) and $\pi(CH_2)$ orbitals. We can see from Table 5 that the values for the alcohols and the amines correspond well to each other. The values for the halides correspond well to one another and are equal to those for the alcohols and amines within the limits of experimental error as shown in Table 5. These results indicate that the sum of the β values is conserved for these molecules.

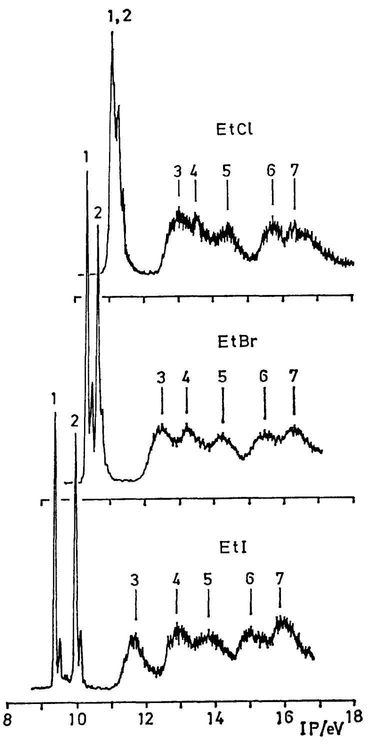

Fig. 4. Photoelectron spectra of ethyl chloride, bromide, and iodide.

Table 5. Sums of β values and their differences for aliphatic alcohols, amines, and halides

Compounds	$\sum\beta^{a)}$	$\Delta\sum\beta^{b)}$
MeOH	2.73±0.08	1.15±0.13
EtOH	3.88±0.10	
$MeNH_2$	3.11±0.08	1.14±0.11
$EtNH_2$	4.25±0.08	
MeCl	4.22±0.06	0.87±0.14
EtCl	5.09±0.12	
MeBr	4.76±0.09	0.86±0.15
EtBr	5.62±0.12	
MeI	5.51±0.07	0.89±0.11
EtI	6.40±0.08	

a), b) The errors for $\sum\beta$ and $\Delta\sum\beta$ denote mean square errors.

Finally, the β values of various orbitals of the molecules under consideration are summarized in Table 6. We can see from this table that a fluctuation of the β value from one molecule to another is small for the respective orbitals under consideration except for the $\pi(CH_3)$ orbital. Particularly the consistency of the β values is satisfied for the respective n orbitals.

From the above discussion, it is concluded that the photoelectron spectral bands can be assigned effectively with the aid of photoelectron angular distributions.

Table 6. β values of various orbitals of aliphatic alcohols, amines, and halides

	n (Cl)	n (Br)	n (I)	n′ (O)	n (O)	n (N)	σ (CCl)	σ (CBr)	σ (CI)	σ (CC)	σ (CO)	σ (CN)	π (Me)	π^- (Et)	π^+ (Et)	π (NH_2)
MeOH				0.50	0.45						0.70		0.62 0.46			
EtOH				0.44	0.56					0.30	0.64		0.68	0.57	0.69	
$MeNH_2$						0.84						0.55	0.43 0.58			0.71
$EtNH_2$						0.93				0.46		0.53	0.55	0.54	0.62	0.62
MeCl	1.13						0.46						0.75 0.75			
EtCl	1.04						0.61			0.54			0.66	0.44	0.76	
MeBr		1.32 1.39						0.46					0.79 0.80			
EtBr		1.33 1.24						0.56		0.53			0.69	0.50	0.77	
MeI			1.60 1.56						0.66				0.82 0.87			
EtI			1.50 1.49						0.69	0.58			0.76	0.51	0.87	
Range of β[a]	1.04 | 1.13	1.24 | 1.39	1.49 | 1.60	0.44 | 0.50	0.45 | 0.56	0.84 | 0.93	0.46 | 0.61	0.46 | 0.56	0.66 | 0.69	0.30 | 0.58	0.64 | 0.70	0.53 | 0.55	0.43 | 0.87	0.44 | 0.57	0.62 | 0.87	0.62 | 0.71

a) The minimum and maximum values are shown.

References

1) J. C. Tully, R. S. Berry, and B. J. Dalton, *Phys. Rev.*, **176**, 95 (1968).

2) J. W. McGowan, D. A. Vroom, and A. R. Comeaux, *J. Chem. Phys.*, **51**, 5626 (1969).

3) T. Kobayashi and S. Nagakura, *J. Electron Spectrosc. Relat. Phenom.*, **7**, 187 (1975).

4) C. Utsunomiya, T. Kobayashi, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **51**, 3482 (1978).

5) M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.*, **1964**, 4434.

6) M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc., B*, **1967**, 373.

7) M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **50**, 654 (1969).

8) A. D. Baker, D. Betteridge, N. R. Kemp, and R. E. Kirby, *Anal. Chem.*, **43**, 375 (1971).

9) A. W. Potts, T. A. Williams, and W. C. Price, *Faraday Discuss. Chem. Soc.*, No. 54, 104 (1972).

10) M. B. Robin and N. A. Kuebler, *J. Electron Spectrosc. Relat. Phenom.*, **1**, 13 (1972/73).

11) S. Katsumata, T. Iwai, and K. Kimura, *Bull. Chem. Soc. Jpn.*, **46**, 3391 (1973).

12) K. Kimura, S. Katsumata, Y. Achiba, H. Matsumoto, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **46**, 373 (1973).

13) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, London (1970).

14) J. L. Ragle, I. A. Stenhouse, D. C. Frost, and C. A. McDowell, *J. Chem. Phys.*, **53**, 178 (1970).

15) A. W. Potts, H. J. Lempka, D. G. Streets, and W. C. Price, *Phil. Trans. R. Soc. London, Ser. A*, **268**, 58 (1970).

16) J. A. Hashmall and E. Heilbronner, *Angew. Chem. Int. Ed.*, **9**, 305 (1970).

17) A. D. Baker, D. Betteridge, N. R. Kemp, and R. E. Kirby, *Int. J. Mass Spectrom. Ion Phys.*, **4**, 90 (1970).

18) F. Brogli and E. Heilbronner, *Helv. Chim. Acta*, **54**, 1424 (1971).

19) L. Karlsson, R. Jadrny, L. Mattsson, F. T. Chau, and K. Siegbahn, *Phys. Scr.*, **16**, 225 (1977).

20) J. Michielsen-Effinger, *Ann. Soc. Sci. Bruxelles, Ser. 1*, **78**, 223 (1964).

21) M. Tsuboi, K. Tamagake, A. Y. Hirakawa, J. Yamaguchi, H. Nakagawa, A. S. Manocha, E. C. Tuazon, and W. G. Fately, *J. Chem. Phys.*, **63**, 5177 (1975).

22) S. Cradock and R. A. Whiteford, *J. Chem. Soc., Faraday Trans. 2*, **68**, 281 (1972).

23) R. M. Pitzer and D. P. Merrifield, *J. Chem. Phys.*, **52**, 4782 (1970).

24) W. J. Hehre, cited in W. L. Jorgensen and L. Salem, "The Organic Chemist's Book of Orbitals," Academic Press, New York (1973), p. 167.

25) T. A. Carlson, G. E. McGuire, A. E. Jonas, K. L. Cheng, C. P. Anderson, C. C. Lu, and B. P. Pullen, "Electron Spectroscopy," ed by D. A. Shirley, North-Holland, Amsterdam (1971), p. 207.

26) W. H. Fink and L. C. Allen, *J. Chem. Phys.*, **46**, 2261 (1967).

27) W. H. Fink and L. C. Allen, *J. Chem. Phys.*, **46**, 2276 (1967).