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Interpretation of Photoelectron Spectra of Halomethanes

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Theoretical studies of the electronic structure of chloromethanes ($CH_{4-n}Cl_n$, where $n=1\sim4$) were carried out by the CNDO/2 method. The resulting Koopmans' theorem ionization energies were generally in good agreement with the experimental data available, and somewhat different assignments from those previously reported were obtained for the nonbonding orbitals. A "sum rule" was employed for interpreting the photoelectron bands of three series of di- and poly-halomethanes (chloro-, bromo-, and iodo-methanes) in terms of some localized molecular orbitals. Reasonable assignments were derived for the photoelectron spectra of all these halomethanes and the resulting assignments for the chloromethanes were in good accord with those obtained from the CNDO/2 calculation.

The high resolution photoelectron (PE) spectra of all the halomethanes $CH_{4-n}X_n$ ($n=1\sim4$; X=F, Cl, Br, and I) except CI_4 have been reported by Turner *et al.*,[1] Potts *et al.*,[2] and Ragle *et al.*,[3] and interpreted by them in terms of molecular orbital (MO) structures on experimental basis. A theoretical calculation of ionization energy (IE) for chloro- and bromomethanes has been carried out by Dixon *et al.*,[4] with a pseudo one-electron hamiltonian. The PE spectra and electronic structures[1-3] of methyl halides are simple and their outer orbital structures are well understood. For di- and poly-halomethanes, however, the PE spectra are more complicated and some partly conflicting results have been reported for spectral assignment by different workers.[1,2,4] Assignments of the experimental IE's of these compounds to their MO's still seem to remain unresolved, especially for outer electronic structures associated with the nonbonding orbitals of halogen atoms.

Theoretical studies on the electronic structures of fluoromethanes have been carried out with the semi-empirical CNDO/2 method by Davis[5] and Pullen *et al.*,[6] and with the GTO calculation by Brundle *et al.*[7] For other halomethanes, however, no CNDO calculations have been published yet.

We have undertaken a study of a series of chloromethanes using the CNDO/2 method. Furthermore, since Kimura *et al.*[8] recently proposed a sum rule with which the PE spectra of various alkyl monohalides from the methyl to the *n*-butyl can be interpreted in terms of several localized MO's, we employed this method to various polyhalomethanes.

CNDO/2 Calculations of Chloromethanes

The semi-empirical CNDO/2 method treating all the valence electrons in a molecule has been proposed by Pople *et al.*,[9] and extended by Santry and Segal.[10a] to various molecules containing the elements sodium through chlorine. We used this method in calculating IE's of the chloromethanes, taking 1s(H), 2s(C), 2p(C), 3s(Cl), and 3p(Cl) orbitals into account and assuming Koopmans' theorem.

We employed different sets of parameter values for C and H atoms as follows. (1) Values originally used by Pople *et al.*,[9] (2) values given by Del Bene and

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[1] D. W. Turner, C. Baker, A. G. Baker, and C. R. Brundle. "Molecular Photoelectron Spectroscopy," Wiley-Interscience, New York, 1970.

[2] A. W. Potts, H. J. Lempka, D. G. Streets, and W. C. Price, F. R. S., *Phil. Trans. Roy. Soc. Lond.*, **A. 268**, 59 (1970).

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

[4] R. N. Dixon, J. N. Murrell, and B. Narayana, *Mol. Phys.*, **20**, 611 (1971).

[5] D. W. Davis, *Chem. Phys. Lett.*, **2**, 173 (1968).

[6] B. P. Pullen, T. A. Carlson, W. E. Moddeman, G. K. Schweitzer, W. E. Bull, and F. A. Grimm, *J. Chem. Phys.*, **53**, 768 (1970).

[7] C. R. Brundle, M. B. Robin, and H. Basch, *ibid.*, **53**, 2196 (1970).

[8] K. Kimura, S. Katsumata, Y. Achiba, H. Matsumoto, and S. Nagakura, This Bulletin, **46**, 373 (1973).

[9] a) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S 129 (1965); b) J. A. Pople and G. A. Segal, *ibid.*, **43**, S 136 (1965); *ibid.*, **44**, 3289 (1966).

[10] a) D. P. Santry and G. A. Segal, *ibid.*, **47**, 158 (1967); b) D. P. Santry, *J. Amer. Chem. Soc.*, **90**, 3309 (1968). When his parameter values were used, we employed $\gamma_{Cl}=15.01$ eV reported by H. G. Benson and A. Hudson, *Theoret. Chim. Acta*, **23**, 259 (1971).

Jaffé,[11] and (3) as for (2) except that $\beta_C = -14.0$ eV was used; For Cl atom: (a) values given by Santry and Segal,[10a] (b) values used by Santry,[10b] and (c) as for (a) except that $\beta_{Cl} = -20.0$ eV was used. A value of 14.28 eV was used for γ_{Cl}, evaluated by the approximate formula.[10a] Resonance integrals were approximated by $\beta_{AB} = {}^1/_2\, K(\beta_A + \beta_B)$ where K was made to 0.75 when both A and B are Cl atom and 1.0 otherwise, since it has been pointed out by Santry and Segal[10a] that better results can be obtained by introducing such constants for K.

SCF conditions were that the energy of the lowest unoccupied MO and those of the highest and second highest occupied MO's converge within 5×10^{-4} eV. Bond lengths used for CH_3Cl,[12a] CH_2Cl_2,[12b] $CHCl_3$,[12c] and CCl_4[12d] were taken from literature. The calculation was carried out on an electronic computer FACOM 230-60 in Hokkaido University, using a program kindly offered by Dr. M. Tsuda.

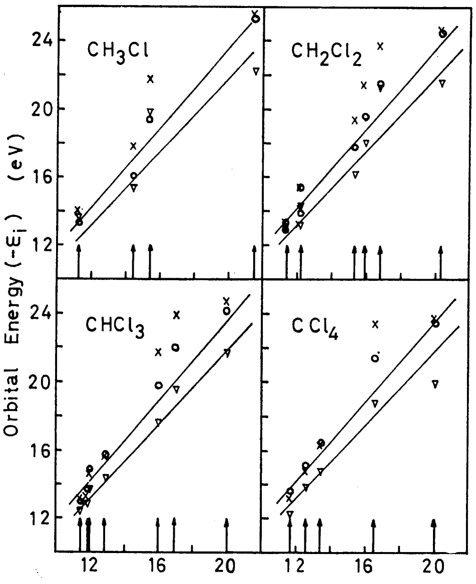

Fig. 1. Plots of the IE's calculated with different sets of parameter values against experimental values. The results obtained with parameter values (3) and (c) are indicated by ○, those of (1) and (a) by X, and those of (2) and (b) by ▽. The positions of experimental IE's are shown with an arrow. Two straight lines with k=0.85 (upper) and 0.92 (lower) are shown in each of the chloromethanes.

The IE's calculated with the different sets of parameter values are plotted in Fig. 1 against the corresponding experimental values. Two straight lines with k=0.85 and 0.92 are drawn to show a measure for adjusting the theoretical results. It is recognized from theoretical calculations available that the calculated IE's based on Koopmans' theorem are high compared with the experimental ones, so that much better agreement with experiment is obtained if Koopmans' theorem values are empirically reduced by a constant factor[13] or reduced by 4 eV.[14] This was done using a factor of k=0.85 or 0.92, as shown in Fig. 1.

Table 1. Comparison of theoretical and experimental results on ionization energies (eV) and orbital assignments

	CNDO/2		Ref. 2 Exptl		Ref. 4
CH_3Cl	11.40 (e)	n(Cl)	11.31 (I_1)	e	e
	13.75 (a_1)	σ(C–Cl)	14.42 (I_2)	a_1	
	16.56 (e)	$\pi(CH_3)$	15.40 (I_3)	e	
	21.59 (a_1)	3s(Cl)	21.5 (I_4)	a_1	
CH_2Cl_2	11.05 (b_1)	n(Cl)	11.40 (I_1,I_2)	b_2,a_2	b_2,b_1
	11.42 (a_1)	n(Cl)			
	11.89 (b_2)	n(Cl)	12.22 (I_3,I_4)	a_1,b_1	a_2,a_1
	13.15 (a_2)	n(Cl)			
	15.22 (b_2)	σ(C–Cl)	15.30 (I_5)	b_2	
	16.74 (a_1)	σ(C–Cl)	15.94 (I_6)	a_1	
	18.37 (b_1)	$\pi(CH_2)$	16.77 (I_7)	b_1	
	20.83 (a_1)	3s(Cl)	20.30 (I_8)	a_1	
$CHCl_3$	11.04 (a_1)	n(Cl)	11.48 (I_1)	a_2	a_2
	11.70 (e′)	n(Cl)	11.91 (I_2)	a_1	e″
	12.71 (a_2)	n(Cl)	12.01 (I_3)	e′	a_1
	13.49 (e″)	n(Cl)	12.85 (I_4)	e″	e′
	16.95 (e′)	σ(C–Cl)	15.99 (I_5)	e′	
	18.80 (a_1)	σ(C–Cl)	16.96 (I_6)	a_1	
	20.55 (a_1)	3s(Cl)	19.80 (I_7)	a_1	
CCl_4	11.63 (t_2)	n(Cl)	11.69 (I_1)	t_1	t_1
	12.93 (t_1)	n(Cl)	12.62 (I_2)	t_2	t_2
	14.11 (e)	n(Cl)	13.44 (I_3)	e	e
	18.27 (t_2)	σ(C–Cl)	16.58 (I_4)	t_2	
	20.10 (a_1)	σ(C–Cl)	20.00 (I_5)	a_1	
	24.39 (t_2)	3s(Cl)			

a) Values of (3) and (c) and a factor of 0.85 for k were used.

The best sets of theoretical results obtained with the values of (3) and (c) are given in Table 1, corresponding to the data indicated by circles in Fig. 1.

Partial and Total sums of Orbital Energies of Halomethanes

In the region below about 17 eV, the PE bands of CH_3X, CH_2X_2, CHX_3, and CX_4 (X=Cl, Br, and I) are considered to be essentially due to ionization of electrons from the localized MO's such as n(X), σ(C–X), $\pi(CH_3)$, and $\pi(CH_2)$. This was supported by the present CNDO/2 calculation for a series of chloromethanes, and in this section we will deal with their IE's from a different standpoint.

If the MO's giving rise to the PE bands in the range 11—17 eV interact very little with inner orbitals such as 2s(C) and ns(X), the total sums of the orbital energies should be almost unchanged considering mutual interactions among the localized MO's. Therefore, we considered that on the basis of Koopmans' theorem the IE's should be interpreted in terms of interactions

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[11] J. Del Bene and H. H. Jaffé, *J. Chem. Phys.*, **48**, 1807 (1968).

[12] a) L. S. Bartell and L. O. Brockway, *ibid.*, **23**, 1860 (1955); b) R. J. Myers and W. D. Gwinn, *ibid.*, **20**, 1420 (1952); c) S. N. Ghosh, R. Trambarulo, and W. Gordy, *ibid.*, **20**, 605 (1952); d) L. S. Bartell, L. O. Brockway, and R. H. Schwendeman, *ibid.*, **23**, 1854 (1955).

[13] For instance, see Ref. 7.

[14] For instance, see Ref. 5.

TABLE 2. COMPARISON OF CALCULATED AND EXPERIMENTAL SUMS (IN eV)

	Partial sum					
	e		a_1		Total sum	
	Calcd [n+π]	Exptl (I_1+I_3)	Calcd [σ]	Exptl (I_2)	Calcd [2n+σ+2π]	Exptl
CH_3Cl	27.08	27.19[a)]	14.42[b)]	14.42	68.58	68.80
CH_3Br	26.13	26.18[a)]	13.49[b)]	13.49	65.75	65.85
CH_3I	25.01	24.93[a)]	12.50[b)]	12.50	62.52	62.36

	Partial sum									
	b_1		a_1		a_2		b_2		Total sum	
	Calcd [n+π]	Exptl (I_1+I_7)	Calcd [n+σ]	Exptl (I_2+I_6)	Calcd [n]	Exptl (I_4)	Calcd [n+σ]	Exptl (I_3+I_5)	Calcd [4n+2σ+π]	Exptl
CH_2Cl_2	27.08	28.17	27.20	27.34	12.78	12.22	27.20	27.52	94.26	95.25
CH_2Br_2	26.13	26.86	25.32	25.57	11.83	11.28	25.32	25.40	88.60	89.11
CH_2I_2	25.01	24.92	23.21	23.43	10.71	10.56	23.21	22.96	82.14	81.87

	Partial sum									
	a_1		e′		a_2		e″		Total sum	
	Calcd [n+σ]	Exptl (I_1+I_6)	Calcd [n+σ]	Exptl (I_2+I_5)	Calcd [n]	Exptl (I_3)	Calcd [n]	Exptl (I_4)	Calcd [6n+3σ]	Exptl
$CHCl_3$	27.20	28.44	27.20	27.90	12.78	12.01	12.78	12.85	119.94	121.95
$CHBr_3$	25.32	26.28	25.32	25.59	11.83	11.28	11.83	11.80	111.45	112.34
CHI_3	23.21	23.75	23.21	22.65	10.71	10.29	10.71	10.50	101.76	100.34

	Partial sum							
	t_2		t_1		e		Total sum	
	Calcd [n+σ]	Exptl (I_1+I_4)	Calcd [n]	Exptl (I_2)	Calcd [n]	Exptl (I_3)	Calcd [8n+3σ]	Exptl
CCl_4	27.20	28.27	12.78	12.62	12.78	13.44	145.50	149.55
CBr_4	25.32	25.69	11.83	11.17	11.83	12.17	135.11	134.92

a) Values in Ref. 3 were used, numerical values for the Jahn-Teller splittings of the third bands not being reported in Ref. 2.

b) Taken from experimental I_2 values (see also Table 3).

TABLE 3. EMPIRICAL ORBITAL ENERGIES USED FOR THE LOCALIZED MO'S (IN eV), THE NEGATIVE SIGN BEING OMITTED

n(X)[a)]:	12.78 (Cl), 11.83_5 (Br), 10.71_5 (I)
σ(C–X)[b)]:	14.42 (Cl), 13.49 (Br), 12.50 (I)
π(CH_3)[c)]:	14.3
π(CH_2)[d)]:	14.3

a) Taken from the mean positions of the first PE bands of HX (Ref. 17).

b) Taken from the second IE's of CH_3X (Ref. 2).

c) Obtained from Eq. (1).

d) Assumed to be equal to the value for π(CH_3).

among several localized MO's in unperturbed states.

Calculations of the theoretical partial sums are given in Table 2. They were carried out on the basis of the present CNDO/2 assignments by using the formulas given in brackets in which letters n, π, and σ denote parameter values. The parameter values are given in Table 3. Since electrons in the nonbonding orbital of HX and those in the σ(C–X) bonding orbitals of CH_3X are essentially in unperturbed states, the first photoelectron band of HX and the second band of CH_3X are considered to give good standards as unperturbed-state orbital energies. For π(CH_3) the orbital energy in its unperturbed state can be estimated by simply considering that the first and third bands of CH_3X arise from the interaction of the π(CH_3) and n(X) orbitals. Taking the centers of the Jahn-Teller splittings for the third IE's of CH_3X, we obtained an average value of −14.3 eV for the orbital energy of n(CH_3) from the relation

$$\{-I_1(\mathrm{HX})\}_{\mathrm{av}} + \varepsilon^0\{\pi(\mathrm{CH_3})\} = \{-I_1(\mathrm{CH_3X})\}_{\mathrm{av}} + \{-I_3(\mathrm{CH_3X})\}_{\mathrm{av}} \quad (1)$$

using available IE values. (I_1 values for HX were taken from Ref. 2, and I_1 and I_3 for CH_3X from Ref. 3 since the Jahn-Teller splittings are reported in Ref. 3).

The experimental partial sums (Table 2) were obtained by taking sums over the appropriate I_i's shown in parentheses also on the basis of the CNDO/2 assignments.

The partial sums are taken over the IE's in each symmetry species and the total sums are taken over all under consideration.

In calculating the partial and total sums for bromomethanes and iodomethanes, orbital orderings were assumed to be the same as those of chloromethanes.

Discussion

CNDO/2 Results. From the present calculation it was found that the resulting MO orders are almost independent of the different sets of parameter values with a few exceptions. The best set of calculated IE's is generally in good agreement with the corresponding experimental values (Table 1).

The PE spectrum of CH_3Cl has been reported by several workers,[1-3] the outer electronic structure being interpreted in terms of the orbital structure of $(e)^4(a_1)^2(e)^4$ which was earlier predicted by Mulliken.[15] Our result supports his assignment. Potts *et al.*[2] have observed a PE band at 21.5 eV and ascribed this to a_1(2s, C). However, we found the 21.5 eV band to be ascribed to a_1(3s, Cl) rather than a_1(2s, C). From the resulting wavefunctions it was found that $3p\pi$(Cl) orbital contributes to the highest occupied MO by 68% with mixing of the $\pi(CH_3)$ orbital, and that the contributions of $3p\sigma$(Cl) and 2p(C) orbitals to the second inner MO are 43 and 46%, respectively. This indicates that the second MO of CH_3Cl is essentially due to σ(C–Cl) bonding.

For CH_2Cl_2, the electronic structure of $(a_2)^2(b_2)^2(a_1)^2(b_1)^2$ was derived for the chlorine nonbonding orbitals (Table 1). The PE spectrum of this compound in the 11—13 eV region consists of two sharp bands (11.40 and 12.22 eV) with nearly equal areas.[2] The spectral appearance indicates that these bands correspond to accidentally degenerate orbitals (in CH_2Br_2 and CH_2I_2 the nonbonding bands have been observed separately[1,2]). The a_2 orbital is strictly nonbonding, being located at the fourth. The order of the nonbonding orbitals obtained here partly differs from that assigned by Potts *et al.*[2] and Dixon *et al.*,[4] while in the inner orbitals the CNDO/2 assignments are in agreement with those proposed by Potts *et al.*[2] However, it is recognized that from a CNDO/2 calculation it is difficult to determine the order of two levels close to each other within about 0.5 eV. It is considered from a symmetry consideration of orbitals that the order of $n(a_1)$ and $n(b_2)$ in CH_2Cl_2 might be reverse and consequentely the assignment by Dixon *et al.*[4] is better.

The nonbonding orbital structure of $CHCl_3$ is expressed by $(e'')^4(a_2)^2(e')^4(a_1)^2$. This orbital assignment differs partly from that reported by other workers.[1,2,4] In CCl_4 the present calculation indicates $(e)^4(t_1)^6(t_2)^6$ for the nonbonding orbital structure, the order of the t_1 and t_2 orbitals being opposite to that reported,[2] and in disagreement with the prediction deduced from the consideration of spin-orbit splittings.[4]

When the parameter values of Santry[10b] are used for Cl, some minor changes occur in the orbital ordering; opposite orders are obtained between the b_1 and b_2 orbitals ascribed to the nonbonding orbitals of CH_2Cl_2 and also between the e′ and a_1 orbitals ascribed to the nonbonding orbitals of $CHCl_3$. It should be mentioned that the resulting MO orderings of the halomethanes depend on the selection of parameter values for Cl atom [(a) and (b)], but independent of those for C and H atoms [(1)—(3)]. The values of (3) and (c) are considerably close to those of (1) and (a) respectively, so that no different orderings occur. In the present work, (3) and (c) were used only for modifying the resulting IE values, giving the better results. From the shape of the spectrum of $CHCl_3$, it is reasonable to consider that the degenerate orbitals are ascribed to the second band rather than the first band. Thus we conclude that, as far as Cl parameter values are concerned, those proposed by Santry and Segal[10a] give better results than those used later by Santry.[10b]

Using the parameter values of (3) and (c), we also calculated total charge densities on the C, H, and Cl atoms of the chloromethanes, and obtained the following values: 4.08 (C), 0.95 (H), and 7.04 (Cl) for CH_3Cl; 3.70 (C), 1.04 (H), and 7.10 (Cl) for CH_2Cl_2; 3.45 (C), 1.11 (H), and 7.14 (Cl) for $CHCl_3$; 3.31 (C) and 7.17 (Cl) for CCl_4.

Partial and Total Orbital-Energy Sums. Good agreements were generally obtained for the total sums in all the halomethanes studied, indicating that the selection of the empirical orbital energies (Table 2) is appropriate. The total sum is independent of orbital assignment in the case of CH_2X_2, whereas in the molecules with the degenerate orbitals it depends on their orbital ordering. The partial sums of course depend always on orbital assignments. We tested various possible assignments and found that the CNDO/2 assignments given in Table 1 are also the best in terms of standard deviations calculated over all the partial sums for each series of CH_2X_2, CHX_3, and CX_4 (where X is Cl, Br, and I) except CI_4 whose PE data are not available.

In calculating the experimental partial sums with an appropriate combination of I_i, in addition to a numerical comparison of experimental and theoretical partial sums the magnitudes of interaction should be also taken into consideration. If there are two nondegenerate localized MO's interacting with each other, the interaction should shift the upper level upwards and the lower level downwards. In CH_2Cl_2, the n and σ levels belonging to a_1 interact with each other to give I_2 (11.40 eV) and I_6 (15.94 eV), causing shifts of 1.38 and 1.52 eV. The n and σ levels belonging to b_2 interact to give I_3 (12.22 eV) and I_6 (15.30 eV), causing shifts of 0.56 and 0.88 eV. Thus, it should be pointed out that the shifts as well as the parameter values we used for n and σ are appropriate. Rigorously speaking, n (or σ) levels in polyhalomethanes should split to some extent to give different orbital energies in different symmetry species because of mutual interactions among equivalent n (or σ). However, there are no remarkable discrepancies between calculated and experimental partial sums when no interactions are considered (Table 2).

If n (or σ) orbitals are split to a large extent by their linear combinations according to orbital symmetry, no good agreement can be obtained between the calculated and experimental partial sums. Taking partial sums over MO's, for instance, in a_1+b_2 and b_1+a_2 in CH_2X_2, better results should be obtained than those in a_1, a_2, b_1, and b_2 separately, where nonbonding

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[15] R. S. Mulliken, *Phys. Rev.*, **47**, 413 (1935).

orbitals belonging to a_1 and b_2 are symmetric and those belonging to b_1 and a_2 are antisymmetric with respect to the CCl_2 plane. Similar situations also occur in CHX_3 and CX_4. Taking a lower symmetry than the original molecular symmetry, such mutual interactions among n (or σ) can be cancelled in partial sums.

It is interesting to note that the a_2 orbital of CH_2X_2, the a_2 and e″ orbitals of CHX_3, and the t_1 and e orbitals of CX_4 are strictly nonbonding and that the corresponding IE's are in agreement with the n(X) parameter values within about 0.8 eV.

It seems reasonable that the a_2 orbital is completely nonbonding so that its IE is higher than those of other nonbonding orbitals interacting with the σ and π orbitals. The same situation occurs also in CHX_3 and CX_4, *viz.*, the a_2 and e″ orbitals in CHX_3 and the t_1 and e orbitals in CX_4 are lower than other nonbonding orbitals which interact with the σ and π orbitals. The present CNDO/2 calculation supports this view.

It should be mentioned that the sums of the experimental orbital energies can be interpreted in terms of simple model in which only a few localized MO's are taken into account for each of the halomethanes.

Potts *et al.*[2] have also reported PE data for BCl_3, BBr_3, BI_3 as well as their orbital assignments. Applying the sum rule to these compounds, we obtained values of about −125, −115, and −102 eV, respectively, for total sums, considerably close to the total sums obtained for $CHCl_3$, $CHBr_3$, and CHI_3 (−122, −112, and −100 eV, respectively). This indicates that the orbital energy of σ(B–X) is very close to that of σ(C–X) for each halogen.

Finally, let us consider total sums for fluoromethanes. Adopting the assignments proposed by Potts *et al.*,[2] the total experimental sums of CH_3F, CH_2F_2, CHF_3, and CF_4 are −60.72, −78.52, −93.60, and −128.40 eV, respectively,[16] while the corresponding calculated total sums are −60.20, −78.49, −96.46, and −138.10 eV, omitting the σ(C–F) orbital and using an empirical value of −16.05 eV for the nonbonding F orbital which is deduced from the first IE of HF[17] by use of Koopmans' theorem. Thus agreement between the experimental and calculated sums is surprisingly good except for CF_4, where a discrepancy of about 10 eV cannot easily be explained.

Although no unambiguous assignment can be concluded, the sum rule should be very helpful for spectral assignments, especially for analyzing an overlapping band.

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[16] We used the following values taken from the data of Potts *et al.* (see Ref. 2). CH_3F: 13.04(e), 17.06(e); CH_2F_2: 13.29, 15.25, 15.40, 15.58, 18.97; CHF_3: 14.80, 15.50, 16.16(e), 17.25(e); CF_4: 16.23(t), 17.47(t), 18.50(e).

[17] H. J. Lempka, T. R. Passmore, and W. C. Price, *Proc. Roy. Soc., A*, **304**, 53 (1968).