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Assignments in Photoelectron Spectroscopy Using the CNDO/2 Method

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In the photoelectron spectra of molecules vibrational fine structure often accompanies the observed ionization potentials (IPs). For non-diatomic molecules it is difficult to make vibrational assignments because the frequencies of the ion often differ greatly from those of the neutral molecule. In order to make both the vibrational assignments and the assignments of the IPs to molecular orbitals (MOs) using Koopmans' theorem CNDO/2 MO calculations have been carried out. Within the framework of this method a quantity ΔE_{AB} has been calculated which is the change in potential energy between an atom-pair A–B for a particular MO on ionization. Application to some diatomic molecules has shown that this quantity reflects the changes in vibrational frequencies on ionization. The IP–MO assignments are made such that removal of an electron from a particular MO is in accord with the observed vibrational fine-structure; attempting to make these assignments on the basis of the calculated MO ordering alone has been shown to be very unsatisfactory.

Photoelektronenspektren von Molekülen zeigen neben den Ionisierungspotentialen oft noch eine Schwingungsfeinstruktur, deren Zuordnung bei nicht-zweiatomigen Molekülen wegen der starken Frequenzverschiebungen vom Molekül zum Ion Schwierigkeiten macht. Um sowohl Schwingungs- als auch Ionisierungs-Zuordnungen vornehmen zu können, wurden Rechnungen mit dem CNDO/2-Verfahren durchgeführt. Dabei stützt man sich auf die Änderung der potentiellen Energie zwischen dem Atompaar AB in bezug auf ein bestimmtes MO bei Ionisierung (ΔE_{AB}). Die Anwendung auf zweiatomige Moleküle zeigt, daß diese Größe tatsächlich die Änderung der Schwingungsfrequenzen wiedergibt, und die Zuweisungen des IP werden so vorgenommen, daß die Entfernung eines Elektrons aus einem MO im Einklang mit der Schwingungsfeinstruktur ist. Dagegen erweist sich die einfache Zuweisung auf Grund der MO-Reihenfolge als schlechter.

1. Introduction

A proper approach to the calculation of IPs of molecules (and atoms, for that matter) involves the calculation of the total electronic energies of the ground state and of the ionized states. Such calculations, which should also include a realistic account of electron-correlation and possibly a relativistic correction [1], are generally impracticable. Consequently, a less rigorous approach must be sought. Koopmans' theorem [2] is a convenient and often used approximation. This theorem results in a direct equality between the observed IP and $-\varepsilon_i$, where ε_i is the energy of the ith MO. Various correction terms have been used in application of the theorem [3]. In this work such correction terms have not been applied since it has been demonstrated [4] that their neglect may be approximately compensated for in the application of semi-empirical MO theory (as used in this work) in the choice of the semi-empirical parameter-values.

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The advent of photoelectron spectroscopy (pes) [5] meant that IPs could be determined unambiguously. Apart from the direct observation of ionization high-resolution vacuum ultra-violet pes has a real strength in that the vibrational structure of the ions is also observed. Thus, assignment would be aided substantially if comparison could be made between the vibrations accompanying the IP and those predicted to be excited when an electron is removed from a particular MO. The problem is simply stated: How can one predict which vibrations are excited? The postulate of Koopmans' theorem is that the MOs remain unchanged on ionization. This is equivalent to assuming that the bonding between any pair of atoms in the ion is the same as that before ionization *minus* the contribution from the removed electron. Since the result of Koopmans' theorem is to be assumed it is only fair to assume the postulate. So, when an electron is removed from a MO which is bonding between atoms A and B then *if* the vibration ν_{AB} is observed it should occur at a lower frequency than in the neutral molecule, and *vice versa*; the magnitude of the change in bonding should reflect the change in the frequency of ν_{AB}. This is a severe approximation for a non-diatomic molecule – the validity of its adoption is discussed at the end of this paper. But, even yet, the question of whether or not a particular vibration *will* be observed has not been answered. The information on the vibrational states in the ion is carried by the departing electrons, but the ion is not properly formed until the electron is outside the influence of the ion. The manner in which the departing electron acquires this information is not clear. Is it possible for there to be a change in bonding between an atom-pair on ionization, giving rise to a change in vibrational frequency, without the departing electrons relaying the information? Are there selection rules, and, if there are, what are they? In the present work attempts have not been made to answer these questions. The present calculations are meant to be used not in predicting spectra but as an aid to their interpretation. For example, in a molecule A–B–C let us suppose that removal of an electron from a particular MO gives a decrease in bonding between A and B and an increase in that between B and C. If a single vibrational series is observed with frequency lower than ν_{AB} or ν_{BC} in the neutral molecule then ν_{AB} is taken as the observed vibration. Of course, it is too much to expect that all assignments may be made in this clear-cut fashion.

It only remains now to obtain a theoretical measure of the change in bonding between all atom-pairs on ionization from each MO. This will be discussed in the next section together with an outline of the MO method adopted. From symmetry it is clear that anti-symmetric vibrations are not considered in the present approach, in keeping with experiment where only symmetric vibrations are observed.

2. Theory

The MO *Method*

The MO Method used was that devised by Pople *et al.* [6] and is known as CNDO/2 (Complete Neglect of Differential Overlap-version 2). An earlier method CNDO/1 is also relevant here [7]. Some familiarity with the symbols used in this now standard method will be assumed.

The integral-values evaluated by Sichel and Whitehead [8] (hereinafter S–W) resulted in far better agreement with experimental IPs [9] and binding energies than those used in the original work. The evaluation procedure adopted in the present work differs only for the average of the electron-interaction terms on atom A, γ_{AA} – the present approach is simpler. While 1st and 2nd row elements were included in the re-parameterization only the former will be discussed since only these atoms occur in the molecules under consideration.

It can be readily shown for Slater orbitals [13] that $\gamma_{AA} = \gamma_{ss} - 12F^2/700$, where F^2 is 8.6 eV for fluorine and is less for the other 1st row elements. γ_{ss} may be calculated from $\gamma_{ss} = I_s - A_s$, where I_s and A_s are the IP and electron affinity, respectively, of the 2s orbital, the experimental values being taken from the valence state data of Hinze and Jaffé [12]. The approximation is made that $\gamma_{AA} = I_s - A_s$. For the 2-centre Coulomb-integral γ_{AB} the Mataga [14] expression has been adopted, where $\gamma_{AB} = 1/(R_{AB} + 2/(\gamma_{AA} + \gamma_{BB}))$.

The U_μ parameters were evaluated in exactly the same manner as that adopted by Pople and Segal [7], except that the more recent data of Hinze and Jaffé were used.

S–W obtained values for β_A^0 by adjusting to give agreement with the experimental binding energies [15] for the binary hydrides AH_n, and such a procedure was used in the present work. They used the approximation that $1/R_{AB}$ be replaced by γ_{AB} in evaluating the core-core repulsion. The rationale for this step was that by this means the electrostatic interaction in a homopolar molecule is zero. But this is not a necessary requisite. Further, this means that for the $^3\Sigma_u^+$ state of H_2 the binding energy is zero, but it was in order to make this state repulsive (in agreement with more sophisticated calculations) that the CNDO/2 approximation of replacing V_{AB} by $Z_B \gamma_{AB}$ was adopted (V_{AB} is the interaction between the core of B and a valence electron on A). However, there is no doubting the truth of their observation that such an approximation was necessary to obtain sensible values for β_A^0. Thus, resignedly, this approximation was adopted in the present work. The formulae required for calculation of the atomic energies and the binding energies are given in the work by S–W and so will not be reproduced here.

The β_A^0 values for the 1st row atoms are given in Table 1. The experimental and calculated values of the binding energies of C_2H_4, N_2 and F_2 are given in Table 2.

Table 1. Values of the β_A^0 parameters (eV)

A	H	Li	Be	B	C	N	O	F
$-\beta_A^0$	5.4	0.9	4.3	6.1	8.8	8.9	13.9	15.5

Table 2. Experimental and calculated binding energies of C_2H_4, N_2 and F_2 (eV)

Binding energies	C_2H_4	N_2	F_2
Calculated	24.32	8.66	1.89
Experimental	24.36	9.90	1.65

Interatomic Bonding

In the literature there are numerous concepts for use in discussing the extent of bonding between atom-pairs in a molecule. More specifically, what is required is the contribution from each MO to the interatomic bonding. The concept of overlap populations in the population analysis theory of Mulliken [17] is appealing. Mulliken's theory and the CNDO/2 theory give rise to the same expression for covalent bond strength (momentarily neglecting electrostatic interaction) although the concept of overlap populations has no meaning in the latter method. In Mulliken's theory overlap integrals occur in the expression for covalent bond strength from lack of orthogonality between the basis functions, whereas in the CNDO/2 theory they occur only because of the approximation adopted for $\beta_{\mu\nu}$. Attempting to use the population analysis formulae in CNDO/2 theory would give, among other discrepancies, a non-integer number of electrons in the molecule! It is not known how clear is the relation between covalent bond strength and overlap population when Coulombic interaction is explicitly included in the expression for ε_i. Such inclusion need not necessarily invalidate the concept of overlap populations, but in the absence of this knowledge, and because CNDO/2 theory neglects overlap in the evaluation of the MOs, another, and very simple, approach has been adopted. In the CNDO/2 method the electronic energy may be partitioned into one- and two-centre contributions [6], the latter being given below.

$$E_{\mathrm{AB}} = \sum_{\mu}^{\mathrm{A}} \sum_{\nu}^{\mathrm{B}} \left(P_{\mu\nu}(\beta_{\mathrm{A}}^{0} + \beta_{\mathrm{B}}^{0})\, S_{\mu\nu} + \left[(P_{\mathrm{AA}} - Z_{\mathrm{A}})(P_{\mathrm{BB}} - Z_{\mathrm{B}}) - \frac{1}{2} P_{\mu\nu}^{2} \right] \gamma_{\mathrm{AB}} \right).$$

On removing an electron from the ith MO we have

$$\Delta E_{\mathrm{AB}} = E_{\mathrm{AB}} - E_{\mathrm{AB}}^{+} = \sum_{\mu}^{\mathrm{A}} \sum_{\nu}^{\mathrm{B}} \big(p_{\mu\nu}^{i}(\beta_{\mathrm{A}}^{0} + \beta_{\mathrm{B}}^{0})\, S_{\mu\nu} + [(P_{\mathrm{AA}} - Z_{\mathrm{A}})\, p_{\nu\nu}^{i} + (P_{\mathrm{BB}} - Z_{\mathrm{B}})\, p_{\mu\mu}^{i} - P_{\mu\nu} p_{\mu\nu}^{i}]\, \gamma_{\mathrm{AB}} \big)$$

where $p_{\mu\nu}^{i}$ is the Coulson partial bond-order [16, 18]. This represents the change in potential energy, and hence the change in bonding, between atoms A and B when an electron is removed from the ith MO.

The correlation between ΔE_{AB} and ν_{AB} is not direct since the same value of ΔE_{AB} for two unlike bonds, C–H and C–C say, is unlikely to result in the same changes, fractional or absolute, in ν_{CH} and ν_{CC}. However, as will be demonstrated, ΔE_{AB} may be used successfully, and this is helped by some assignments made by other means e.g. isotopic substitution [19].

It is worth noting that in an investigation of bond length changes on ionization of tetrachloroethylene Coulson and Luz [20] considered in detail, although in a different manner to that adopted here, changes in both bond orders and Coulombic electrostatic forces. They also considered repulsive exchange forces, but concluded that the necessary more complete MOs would destroy the simple picture being sought.

The values calculated for ΔE_{AB} for H_2, N_2, HF, H_2O and C_2H_4 are given in Table 3, together with the pes results and the proposed assignments.

Table 3. Experimental and calculated IPs (eV), and the proposed assignments for H_2, N_2, HF, H_2O and C_2H_4

Compound	IP (calc.)	IP (expt.) (vertical)	$-\Delta E_{AB}$			ν_{AB}				Assignment (orbital symmetry)
$H_2(D_{\infty h})$	14.68	15.98 [23]	7.5			0.27 [23]				$\sigma_g(^2\Sigma_g^+)$
						(0.53)				
$N_2(D_{\infty h})$	14.34	15.59 [23]	4.0			0.27 [24]				$\sigma_g(^2\Sigma_g^+)$
	14.22	16.96	5.7			0.23				$\pi_u(^2\Pi_u)$
	24.19	18.78	−1.6			0.30				$\sigma_u(^2\Sigma_u^+)$
	31.16					(0.29)				
$HF(C_{\infty v})$	16.43	16.04 [25]	2.9			0.37 [25]				$\pi\ (^2\Pi_i)$
	16.78	19.90	6.6			0.17				$\sigma\ (^2\Sigma^+)$
	36.29					(0.50)				
			OH	HH		OH	HH			
$H_2O(C_{2v})$	15.86	12.61 [19]	1.5	0.0		0.40	0.17 [19]			b_1
	14.70	14.73	2.8	1.0			0.12			a_1
	15.36	18.55	4.1	−0.2		0.37	0.20			b_2
	33.59					(0.45)	(0.20)			
			CH	CC	HH	CH	CC	HH	$2\nu_4$	
$C_2H_4(D_{2h})$	10.64	10.51 [26]	0.1	4.9	0.0		0.15	0.17	0.05 [26]	b_{1u}
	11.85	12.74	0.9	3.5	0.1	0.36	0.16		0.10	a_g
	11.18	14.6	1.6	−1.0	−0.1	0.21	0.21			b_{1g}
	15.03	15.7	1.8	1.4	−0.1	0.15				b_{2u}
	19.60	~19								b_{3u}
	26.29					(0.37)	(0.20)	(0.17)	(0.10)	

3. Results

All energies are given in electron volts (eV). The vibrational energies of both the neutral molecules (in parentheses in Table 3) and the ions are of the $0 \rightarrow 1$ transitions for the diatomics and are an average over the bands for H_2O and C_2H_4.

4. Discussion

H_2 Obviously, the 1st IP arises from a strongly bonding orbital.

N_2 The assignments for N_2 have been very well established previously. The agreement between the vibrational spacings in the pe spectrum and those in the electronic spectra of the ions [24] is excellent, as is that between the calculated and observed Franck-Condon factors for the 3rd band [23]. The numerical agreement between the calculated and observed IPs is almost non-existent, a not uncommon feature in calculations on N_2 [1, 8]. Since the calculated IP at 24.19 eV is quite definitely the 3rd, the assignment of the observed 18.78 eV IP to $^2\Sigma_u^+$ is reasonable. Excellent confirmation is given by the slightly anti-bonding nature of the σ_u orbital. For the 1st and 2nd IPs we have from experiment that the 2nd arises from a strongly bonding MO and the 1st from a less strongly bonding one. This suggests the assignments shown, where the ordering of the two IPs has been inverted, in agreement with those proposed in the work cited above.

In an *ab-initio* calculation Scherr [27] correctly predicted the ordering of the IPs, but in an overlap population analysis he predicted the ordering to be weakly anti-bonding, strongly bonding and strongly anti-bonding. This poor agreement with experiment is possibly due to neglect of Coulombic forces in the derivation of the expression for the overlap populations. As pointed out by Mulliken [17], "... the major contributions even for homopolar bond energies may come from Coulomb-energy terms". In the present calculations the Coulombic term constistutes approximately one half of ΔE_{NN} for the 1st MO.

HF In view of the closeness of the predicted IPs it is impossible to attempt assignment on the basis of the ordering alone. Inspection of the ΔE_{HF} values makes it quite clear that the ordering of states is $^2\Pi_i$, $^2\Sigma^+$, the 1st being associated with the fluorine lone pairs and the 2nd with the strongly bonding σ orbital. This is the accepted assignment [25].

H_2O There is little doubt as to the assignment of the 1st IP to the weakly bonding b_1 MO. For the 2nd IP the presence of the scissors vibration, denoted ν_{HH}, at a greatly reduced frequency is strikingly confirmed; the value of $\Delta E_{OH} = -2.8$ eV is not bothersome because, as emphasised previously, a large value of ΔE_{AB} need not be indicative of a strongly allowed vibration. The assignment of the third IP to b_2 seems reasonable because of the strongly bonding OH and essentially non-bonding HH character.

C_2H_4 For the 1st IP the occurence of ν_{CC} at a lower frequency than in the neutral molecule is consistent with the present calculations. The associated MO is the C–C π-orbital. On removing an electron the planar constraint of the molecule is largely lifted, and it might be expected that the CH_2 twist (ν_4) be excited – the $2\nu_4$ sequence is well known in the Rydberg spectrum [28]. And, indeed, a vibrational spacing of 430 cm^{-1} is observed which is in excellent agreement with $2\nu_4(0 \rightarrow 1) = 472\ cm^{-1}$ obtained from the Rydberg spectrum. Excitation of the scissors vibration, denoted ν_{HH}, at a virtually unchanged frequency is also possible, in agreement with the suggestion of Baker *et al.* [26]. For the 2nd IP it is expected that if ν_{CC} and ν_{CH} are excited the former will have a frequency just a little above the value observed in the 1st IP and the latter a frequency lower than that of the neutral molecule. This is in agreement with the proposed assignment. So far, the assignments for the 1st and 2nd IPs are in agreement with those proposed by Baker *et al.* However, they have assigned the observed spacing of 0.10 eV to the ν_{HH} vibration. It is not felt that $\Delta E_{HH} = -0.1$ eV is likely to give a decrease in ν_{HH} of 0.07 eV. For lack of any other evidence it is tentatively suggested that the 0.10 eV spacing arises from $2\nu_4$. For the 3rd IP we might have a substantial decrease in ν_{CH}, and an increase in ν_{CC}, and a very small increase in ν_{HH}. The required change in ν_{HH} is far too large to be associated with $\Delta E_{HH} = 0.1$ eV (compare with the 2nd IP). However, the possibility is not discounted of ν_{CC} and ν_{CH} both being excited at approximately the same frequency; this would certainly account for the observed broadness of the bands. For 4th IP Baker *et al.* have suggested assignments to ν_{CH} or ν_{HH}, whereas Branton *et al.* [29] have suggested assignments to ν_{CC} and ν_{HH}. On the basis of the present calculations ν_{CH} seems to be the most reasonable assignment. It is interesting that there is a good linearity between ΔE_{CH} and ν_{CH} for the 2nd, 3rd and 4th bands, but hardly significant since the appropriate plot fails to go through the origin, unlike the equally good linear plot between ΔE_{CC} and ν_{CC}. For the 5th IP the resolution is insufficient for vibrational analysis. The only comment is that the value of ~ 19 eV is very close to the calculated value of 19.60 eV for the b_{3u} MO.

For all 5 IPs the predicted ordering is only incorrect in the reversal of the a_g and b_{1g} MOs, and in view of the closeness of the calculated values this is not regarded as a serious discrepancy. In a survey of MO calculations Baker *et al.* [26] showed this reversal to be generally the case, with the exception of the results of Berthod [30].

5. Conclusion

It is believed that the general usefulness of the parameter ΔE_{AB} has been demonstrated, and that its application to other molecules will be informative. However, there are weaknesses in the approach, and it will be just as well to point them out here.

It would be more systematic to calculate the changes in vibrational frequency on ionization via a properly constructed force-field. This would circumvent the difficulty in the present work of there being no explicit relationship between the calculated ΔE_{AB} and the experimental ν_{AB}. But a compromise has to be reached between the intrinsic accuracy of the MO theory and the subsequent rigorousness used in the treatment of the results. It is strongly felt that the simplistic concept of ΔE_{AB} as a parameter for pes is consistent with the inherent inaccuracy of the CNDO/2 theory. The procedure of retaining invariancy *via* a series of extremely crude approximations is completely contrary to the proper means of approaching invariancy by including greater numbers of integrals. Cook *et al.* [31] carried out *ab initio* calculations on H_2O and CH_4 and then repeated them neglecting those integrals not included in the CNDO/2 theory. The basis functions were Löwdin orthogonalized orbitals [32], and it would be anticipated that if CNDO/2 type approximations were to work they would work best with such basis functions. The agreement between the two sets of calculations was poor. This does not look promising for the normal CNDO/2 application where Slater orbitals are assumed orthogonal. And yet, applications of the CNDO/2 method have been anything but completely unsuccessful. Like all semi-empirical MO methods the success of the CNDO/2 method lies in the manner of evaluating the integrals. Provided that the demands made of the method are not too great it can be used meaningfully, and it is hoped that this has been done in the present work.

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