

A MODIFIED PLANE WAVE MODEL FOR CALCULATING UV PHOTO-IONIZATION CROSS-SECTIONS

M J M BEERLAGE* and D FEIL**

Chemical Physics Laboratory, Twente University of Technology, Enschede (The Netherlands)

(Received 14 March 1977)

ABSTRACT

Photoionization cross-sections are calculated for a number of molecules, using a plane wave method. Agreement with experimental data is considerably improved with respect to common plane wave results if the energy of the photoelectron is assumed to equal the incident photon energy.

INTRODUCTION

Recently the calculation of photoionization cross-sections of large molecules has become feasible owing to the development of the plane wave theory by Ellison¹ and, independently, by Schweig and Thiel^{2, 3} and Dewar et al.⁴ The theory in which the photoelectron is described as a plane wave accounts for interference effects, caused by the extension in space of the molecular wavefunction, which may be very important in the ultraviolet region³, where the wavelength of the photoelectron corresponds to molecular dimensions. It has been tested for several small and medium size molecules, e.g. methane, water⁵, carbon disulphide, cyanic acid⁶, ammonia, phosphine⁷, cyclopropane and oxirane⁸. Although occasionally the theory does not agree with experiments, it is successfully used in several cases, either to identify photoionization bands or to affirm previous identifications. It turns out that a slight modification of the theory improves the results considerably.

THEORY

To calculate the differential photoionization cross-section $d\sigma^n$ of the n^{th} molecular orbital (MO) of a molecule one usually assumes the validity of (a) the

* Present address: FOM Institute for Atomic Molecular Physics, Amsterdam, WGM

** Author to whom correspondence should be directed

Born approximation in time-dependent perturbation theory, (b) the Born–Oppenheimer approximation, (c) the orbital approximation, (d) the dipole approximation, (e) the frozen orbital approximation, (f) the selection rule of spin conservation

A discussion of these approximations is given in ref 3 Under these conditions¹⁻³

$$d\sigma^n = \frac{8\pi^2 e^2 k}{\hbar^2 m \omega c} |\mathbf{u} \cdot \mathbf{P}_{fn}|^2 d\Omega \quad (1)$$

where e and m are respectively the charge and mass of an electron, \hbar is Dirac's constant, c the velocity of light, ω its circular frequency, k the wavenumber of the photoelectron and \mathbf{u} the unit vector of polarization Photoelectrons in the direction of $d\Omega$ are considered The transition moment vector \mathbf{P}_{fn} is given by

$$\mathbf{P}_{fn} = \langle \psi_f | \mathbf{p} | \psi_n \rangle \quad (2)$$

where $|\psi_n\rangle$ and $|\psi_f\rangle$ are the wavefunctions of the photoelectron in initial and final state respectively, and \mathbf{p} is the (linear) momentum operator of the electron A further approximation—the essence of plane wave theory—consists of the assumption

$$|\psi_f\rangle = |e^{i\mathbf{k}\cdot\mathbf{r}}\rangle \quad (3)$$

i.e. $|\psi_f\rangle$ is represented by a plane wave, the wavenumber k of which is given by Einstein's relation

$$\frac{\hbar^2 k^2}{2m} = \hbar\omega - IP_n \quad (4)$$

IP_n is the ionization potential of the n^{th} MO Finally the wavefunction $|\psi_n\rangle$ is chosen to be a linear combination of atomic orbitals $|\chi_p\rangle$

$$|\psi_n\rangle = \sum_p |\chi_p\rangle c_{pn} \quad (5)$$

In the experimental situation we have a large collection of randomly oriented molecules, ionized by an unpolarized beam Therefore eqn (1) must be averaged over all orientations of the molecule and all polarization directions of the beam Inserting eqns (2), (3) and (5) the averaged cross-section $d\sigma^n$ may be written as¹⁻³

$$\overline{d\sigma^n} = C \frac{k}{\omega} \left[\sum_p Q_p^n + \sum_{p < q} Q_{pq}^n \right] d\Omega \quad (6)$$

where k and ω have their usual meaning, C is a constant, incorporating all experiment-independent quantities, Q_p^n denotes the one center contribution from AO $|\chi_p\rangle$, whereas the two center terms Q_{pq}^n are interference contributions from AO's $|\chi_p\rangle$ and $|\chi_q\rangle$ Explicit formulae of the Q terms are given in ref 2 Here it suffices to say, that both one- and two-center terms depend on photoelectron wavenumber and atomic-

orbital parameters, whereas the two center terms also depend on length and direction of the distance vector between the atomic centers of $|\chi_p\rangle$ and $|\chi_q\rangle$

The major deficiencies of the plane wave theory are the neglect of electrostatic interaction between cation and photoelectron and the neglect of orthogonalization of the plane wave to the molecular orbitals of the molecule Rabalais et al ⁵ showed that, off threshold, the errors resulting from the second omission are relatively small The effects of the first omission are more serious In fact the theory is only "valid" for the deionization of anions and for high energy photoionization^{3 9} In those cases the electron, classically, moves away from its origin with a uniform velocity and is described, quantum mechanically, by a plane wave, having a definite k -value, corresponding to the classical velocity In an UV photoionization process the electron, classically, moves away from its origin with decreasing velocity In asymptotic regions, where again its velocity is constant, it is described correctly by a plane wave, with a wavenumber k , given by Einstein's relation (4) As may be seen from eqn (2) we are only interested in the behaviour of photoelectrons near the (ionized) molecule, since only there does $|\psi_n\rangle$ have an appreciable value If we adhere to a plane wave description of the UV photoionization process we should therefore use a plane wave with a wavenumber corresponding to the velocity of the electron near the molecule, i.e. we should take a wavenumber k' , higher than the asymptotic one, k , given by eqn (4) Analogous to eqn (4) we define the value k' by

$$\frac{\hbar^2 k'^2}{2m} = \hbar\omega - IP_n + \beta \frac{\hbar^2}{2m} \quad (7)$$

or equivalently

$$k' = (k^2 + \beta)^{\frac{1}{2}} \quad (8)$$

where eqn (4) is used The parameter β accounts for the electrostatic interaction effects

RESULTS

The importance of the parameter β is illustrated in Fig 1 In this figure calculated photoionization cross-sections of the four highest MO's of tetrafluoropyrimidine are shown Both He(I) and He(II) cross-sections are given in arbitrary units Values obtained with $\beta = 0$ correspond to the results of the simple plane wave theory Molecular wavefunctions, used in these calculations, were obtained by the MIEHM method¹⁰ (Modified Iterative Extended Huckel Method) Experimental ionization potentials were used¹¹ Although in this case experimental data on cross-sections were rather unreliable the results suggest that an electrostatic potential close to the ionization potentials involved (ranging from ca 10 to 14 eV) should be introduced This leads us to perform cross-section calculations based on

$$\frac{\hbar^2 k^2}{2m} = \hbar\omega \quad (9)$$

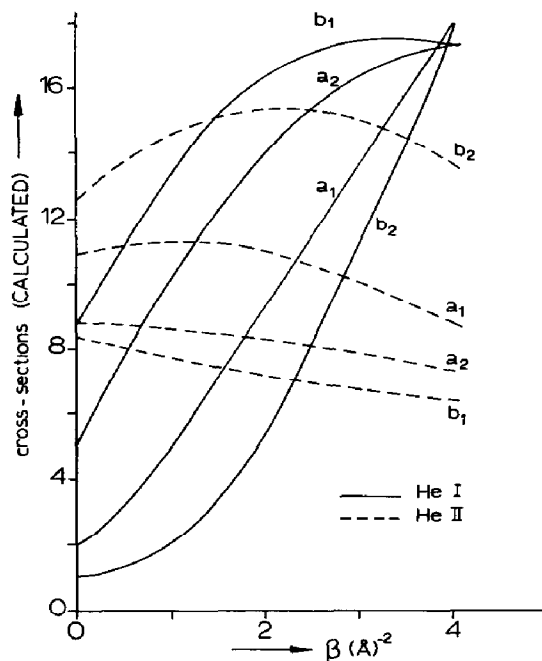


Figure 1 Calculated photoionization cross-sections of tetrafluoropyrimidine

Use of eqn (9) instead of (4) implies that the kinetic energy of the photoelectron in the neighbourhood of the molecule is assumed to be equal to the photon energy transferred to it. The difference in potential energy in the molecular region and at infinity accounts for the increased wavenumber.

Results are summarized in Table 1. He(I) and He(II) photoionization cross-sections have been calculated both in the plane wave (PW) approximation, based on eqns (4) and (6), and in the modified plane wave (MPW) approximation, based on eqns (6) and (9). Molecular wavefunctions were obtained from CNDO/2 and MIEHM calculations. Experimental structures and (vertical) ionization potentials were used. Molecules were selected according to three criteria:

a) Experimental data on photoionization cross-sections and orbital symmetries should be available from literature, references are given in the last column of Table 1.

b) Molecules should be planar and contain atoms from hydrogen up to fluorine only, due to the limitations of our computing programme.

c) There should be at least two ionization potentials below 16.5 eV when He(I) photoionization is considered. This rather arbitrary limit is set for two reasons: (1) Near threshold the effects of nonorthogonalization of the photoelectron to the occupied molecular orbitals may become important⁵. (2) Usually photoionization cross-sections are obtained from photoelectron spectra by dividing the area of each band by the corresponding electron kinetic energy. In that way only the first order effect of the apparatus is taken into account^{1,2}. At low electron kinetic energy unknown higher order effects may become important.

TABLE 1

RELATIVE PHOTOIONIZATION CROSS-SECTIONS

Molecule	Orbital Symmetry	IP vert exp	Experi- mental value	Theoretical values PW			Theoretical values MPW				
				CNDO 2	MIEHM Average	Average	CNDO 2	MIEHM Aver.	Aver.		
He (I)	1 HF	π	16 06	100	38	64	51	100	100	100	100
		σ	16 48	57	100	100	100	83	73	78	
2 (CN) ₂		π_g	13 36	93	74	90	82	86	100	93	93
		σ_u	14 49	61	10	18	14	46	65	56	56
		σ_g	14 86	27	10	25	18	26	31	28	28
		π_u	15 55	100	100	100	100	100	96	98	98
		π	11 60	79	86	100	93	88	100	94	94
		σ	13 54	51	9	16	13	37	47	42	42
3 C ₂ H ₂ CN		π	14 03	100	100	96	98	100	93	96	96
		π_u	11 81	41	76	77	76	51	54	52	52
		$\pi_g +$	13 89	100	75	100	99	100	100	100	100
		π_u	14 95	54	100	77	89	62	49	56	56
		a_2	8 88	100	100	100	100	100	100	100	100
		b_1	10 31	84	61	50	56	74	72	73	73
5 Furan		a_2	8 88	100	100	100	100	100	100	100	100
		b_1	10 31	84	61	50	56	74	72	73	73
6 Pyrrole		a_2	8 21	100	100	100	100	100	100	100	100
		b_1	9 20	89	68	69	68	83	86	85	85
He (II)	7 N ₂	σ_g	15 60	58	34	41	38	56	68	62	62
		π_u	16 98	100	100	100	100	100	100	100	100
		σ_u	18 78	25	46	60	53	25	34	29	29
	8 CO	σ	14 01	38	37	47	42	44	61	53	53
		π	16 91	100	100	100	100	100	100	100	100
	9 H ₂ O	σ	19 72	58	43	56	49	36	34	35	35
b_1		12 62	92	75	90	83	100	100	100	100	
a_1		14 74	100	83	90	91	98	97	97	97	
b_2		18 51	94	100	96	98	99	83	91	91	
10 Furan	a_2	8 88	77	100	100	100	100	98	91	95	
	b_1	10 31	100	88	90	89	100	100	100	100	
11 Pyrrole	a_2	8 21	71	100	99	100	100	95	90	92	
	b_1	9 20	100	97	100	98	100	100	100	100	

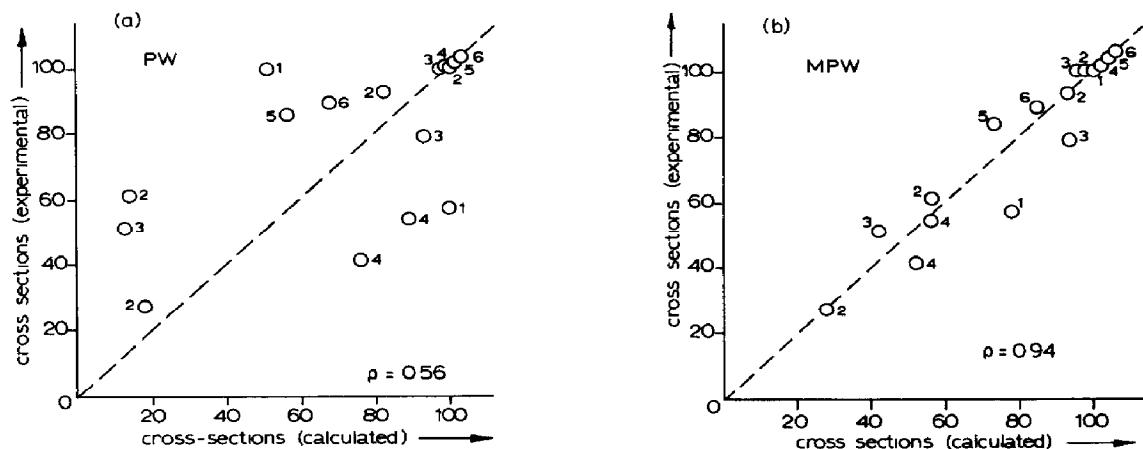


Figure 2 Correlation of experimental He (I) photoionization cross-sections versus PW (2(a)) and MPW (2(b)) calculations (numbers refer to compounds in Table 1)

TABLE 2

CORRELATION COEFFICIENTS

Correlated to	Theoretical values PW			Theoretical Values MPW			Number of Points	Light source
	CNDO2	MIEHM	Average	CNDO2	MIEHM	Average		
Experimental values	0.51	0.48	0.56	0.92	0.94	0.94	16	He (I)
Theoretical values MIEHM	0.80	0.82	0.81	0.92	0.88	0.91	13	He (II)
Theoretical values CNDO2	0.95	1.00		0.94	1.00		16	He (I)
Theoretical values MIEHM	0.97	1.00		0.96	1.00		13	He (II)

Besides CNDO/2 and MIEHM results, the arithmetical averages of these are given in Table 1. The correspondence of experimental to calculated (average) results in the He(I) case is illustrated by Fig 2(a) (PW) and Fig 2(b) (MPW). Table 2 gives the correlation of experimental with theoretical data (first two rows) as well as the correlation of CNDO/2 with MIEHM results (last two rows).

DISCUSSION

A comparison of PW with MPW results immediately reveals the superiority of the MPW model, especially in the He(I) case. In the He(II) case the differences between MPW and PW results are rather small. This is obvious since MPW and PW models become equal in the limit of high photon energy.

Results obtained from a CNDO/2 description of the molecules are in very

good agreement with calculations based on MIEHM MO's. This independence of molecular description was found before^{5, 7}

Finally it should be noted that absolute values calculated by the MPW method are in all cases higher by a factor between 2 and 15 with respect to PW values. Since absolute PW values are usually too low by a factor between 2 and 10⁶, the absolute values found by the MPW method will probably correspond to absolute experimental values.

NOTE

After finishing the calculations, the work of Hilton et al¹⁶ came to our attention. These authors use a spherical square well to represent the potential of the photoelectron.

REFERENCES

- 1 F O Ellison, *J Chem Phys*, 61 (1974) 507
- 2 W Thiel and A Schweig, *Chem Phys Lett*, 12 (1971) 49
- 3 A Schweig and W Thiel, *J Chem Phys*, 60 (1974) 951
- 4 M J S Dewar, A Komornicki, W Thiel and A Schweig, *Chem Phys Lett*, 31 (1975) 286
- 5 J W Rabalais, T P Debies, J L Berkosky, J J Huang and F O Ellison, *J Chem Phys*, 61 (1974) 516
- 6 W Thiel and A Schweig, *Chem Phys Lett*, 16 (1972) 409
- 7 A Schweig and W Thiel, *J Electron Spectrosc Relat Phenom*, 3 (1974) 27
- 8 A Schweig and W Thiel, *Chem Phys Lett*, 21 (1973) 541
- 9 L L Lohr, in D A Shirley (Ed), *Electron Spectroscopy*, North-Holland, Amsterdam, 1972, p 245
- 10 J Spanget Larsen, *J Electron Spectrosc Relat Phenom*, 2 (1973) 33
- 11 D M W van den Ham, D van der Meer and D Feil, *J Electron Spectrosc Relat Phenom*, 3 (1974) 479
- 12 O Klemperer, *Electron Optics*, Cambridge University Press, London, 1953, p 414
- 13 D C Frost, C A McDowell and D A Vroom, *J Chem Phys*, 46 (1967) 4255
- 14 D W Turner, C Baker, A D Baker and C R Brundle, *Molecular Photoelectron Spectroscopy*, Wiley-Interscience, New York, 1970
- 15 C Baker and D W Turner, *Proc Roy Soc, Ser A*, 308 (1968) 19
- 16 P R Hilton, S Nordholm and N S Huch, *Chem Phys*, 15 (1976) 345