JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

Registered in U. S. Patent Office. © Copyright, 1970, by the American Chemical Society

VOLUME 92, NUMBER 25 DECEMBER 16, 1970

Physical and Inorganic Chemistry

Theoretical Study of Photoionization Cross Sections for π-Electron Systems

L. L. Lohr, Jr.,* and M. B. Robin

*Contribution from the Department of Chemistry, University of Michigan,
Ann Arbor, Michigan 48104, and Bell Telephone Laboratories,
Murray Hill, New Jersey 07974.* *Received January 15, 1970*

Abstract: Cross sections for the photoionization of π electrons in gaseous planar hydrocarbons are calculated by a method combining plane waves for the photoelectrons and Hückel-type molecular orbitals formed from Gaussian basis functions for the bound electrons. Comparisons are made between the cross sections for different molecular orbitals in the same molecule and for different molecules, showing the dependence upon the symmetry of the molecular orbitals and the size of the molecule. In particular, it is found that increasing the number of nodes in a molecular orbital tends to reduce the photoionization efficiency of that orbital, while increasing the size of the molecule does not necessarily lead to an increased cross section. In general, the cross sections for an all-trans polyene are smaller than for the corresponding cis and cyclic polyenes. A method is outlined in which plane waves are orthogonalized to occupied molecular orbitals, thus incorporating many features of a rigorous treatment and permitting meaningful calculation of photoelectron angular distributions.

Recently the information available from studying the photoionization of gaseous molecules has been increased by the use of techniques for analyzing the kinetic energy of the ejected electrons. These studies are referred to as photoelectron spectroscopy.[1] A typical spectrum consists of a series of bands often showing vibrational fine structure. If an orbital description of the electronic structure of the molecule is assumed, these bands correspond to ionizations from successively lower lying molecular orbitals, the spectrum terminating when there are no further levels from which electrons can be ejected by the fixed-energy incident photons. While much effort has been devoted to the interpretation[2] of energies in photoelectron spectra, little information has been extracted from the corresponding intensities. These are best described as cross sections, which have the dimensions of area and are a measure of the probability of photoionization occurring at a given photon energy from a given molecular orbital. It is well known that spectroscopic intensities are difficult to calculate accurately. Nevertheless, it is hoped that cross sections that are semiquantitatively correct may be of use as an aid in making photoelectron spectral assignments.

There have been a large number of theoretical studies of photoionization cross sections in atoms and small molecules. Both exact and approximate calculations for the hydrogen atom have been described by Bethe and Salpeter,[3] while treatments of the hydrogen molecule-ion have been given by Bates, Öpik, and Poots[4] and by Cohen and Fano.[5] Cross sections for the hydrogen molecule have been calculated by Flannery and Öpik,[6]

---

* Alfred P. Sloan Research Fellow. Address correspondence to this author at the University of Michigan.

(1) For example, see D. W. Turner, *Proc. Roy. Soc., Ser. A*, **307**, 15 (1968); A. J. Blake and J. H. Carver, *J. Chem. Phys.*, **47**, 1038 (1967).

(2) For example, see A. D. Baker, C. R. Brundle, and D. W. Turner, *Int. J. Mass Spectrom. Ion Phys.*, **1**, 443 (1968); H. Basch, M. B. Robin, N. A. Kuebler, C. Baker, and D. W. Turner, *J. Chem. Phys.*, **51**, 52 (1969).

(3) H. A. Bethe and E. E. Salpeter, "Quantum Mechanics of One- and Two-Electron Atoms," Academic Press, New York, N. Y., 1957, pp 295–322.

(4) D. R. Bates, U. Öpik, and G. Poots, *Proc. Phys. Soc. London, Sect. A*, **66**, 74 (1953).

(5) H. D. Cohen and U. Fano, *Phys. Rev.*, **150**, 30 (1966).

while Marr[7] has reviewed studies on many-electron atoms and molecules. More recently Johnson and Rice[8] have reported results for benzene applicable to the vicinity of the ionization threshold. Angular distributions for molecular photoionization have been discussed by Cooper and Zare[9] and by Tully, Berry, and Dalton.[10] Kaplan and Markin[11,12] have treated hydrogen, ethylene, butadiene, and benzene, emphasizing interference phenomena of the type discussed by Cohen and Fano.

The method outlined in the next section is based upon the use of plane waves to describe the ejected electron. This approximation, also used by Basu[13] and by Kaplan and Markin,[11,12] ignores the influence of the positively charged molecular frame on the wave functions and density of states for the photoelectron. Thus it is invalid in the vicinity of threshold, although the approximation is good for sufficiently high-electron kinetic energy or for photodetachment of molecular anions. Since there are no experimental values of the photoionization cross sections of π electrons in planar hydrocarbons 10–30 eV or more above threshold, we emphasize instead the comparisons of both the cross sections for different molecules and for the different orbitals within a molecule. If future experiments should prove that even the relative cross sections computed here are worthless, then it will be necessary to turn to orthogonalized plane-wave calculations as outlined in the last section, or perhaps to an even better procedure.

Theoretical Method

The quantum-mechanical expression for the photoionization cross section σ is related to the Golden Rule rate, obtained from time-dependent perturbation theory.[14] We first review the derivation of σ from the rate

$$w = (2\pi/\hbar)|H_{\mathrm{ab}}'|^2\rho(E) \qquad (1)$$

where H_{ab}' is the interaction energy of the initial state $\langle \mathrm{a}|$ and final state $|\mathrm{b}\rangle$ due to the presence of the radiation field and $\rho(E)$ is the density of final states with energy in the vicinity of E_{b}. If the interaction is treated in the electric-dipole approximation, equivalent to the neglect of photon momentum and valid for low photon energies

$$w = \frac{2\pi e^2 A_0^2}{\hbar m^2 c^2}|\mathbf{u}\cdot\langle \mathrm{a}|\sum_n \mathbf{p}_n|\mathrm{b}\rangle|^2\rho(E) \qquad (2)$$

where A_0 is the magnitude of the vector potential, $\mathbf{u}$ is a unit vector in the polarization direction, and $\mathbf{p}_n$ is the linear momentum operator for the nth electron. The number rate is converted[14] to a cross section by multiplying by the photon energy $\hbar\omega$ and equating the result to the product of the cross section σ and the magnitude $\omega^2 A_0^2/2\pi c$ of the Poynting vector. If the expression for σ is divided by 4π, the result is the differential cross section for producing photoelectrons in the solid angle $\mathrm{d}\Omega$

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \frac{\pi e^2}{m^2 c\omega}|\mathbf{u}\cdot\langle \mathrm{a}|\sum_n \mathbf{p}_n|\mathrm{b}\rangle|^2\rho(E) \qquad (3)$$

If the ground state $\langle \mathrm{a}|$ is a determinant of doubly occupied molecular orbitals (MO's) and the excited state $|\mathrm{b}\rangle$ is a spin singlet constructed by the promotion of one electron from the jth MO to an unbound orbital $|\mathrm{k}\rangle$, with no change in the shape of the other MO's, then

$$\langle \mathrm{a}|\sum_n \mathbf{p}_n|\mathrm{b}\rangle = 2^{1/2}\langle \mathrm{j}|\mathbf{p}|\mathrm{k}\rangle \qquad (4)$$

The functions $|\mathrm{k}\rangle$ for the ejected electron are assumed to be plane waves (PW's) normalized in a cubic box of length L

$$\mathrm{PW}(\mathbf{k}) = L^{-3/2}\exp(i\mathbf{k}\cdot\mathbf{r}) \qquad (5)$$

The accompanying density of states is

$$\rho(E) = mkL^3/2\pi^2\hbar^2 \qquad (6)$$

yielding

$$\frac{\mathrm{d}\sigma_j}{\mathrm{d}\Omega} = \frac{e^2kL^3}{\pi mc\hbar^2\omega}|\mathbf{u}\cdot\langle \mathrm{j}|\mathbf{p}|\mathrm{PW}(\mathbf{k})\rangle|^2 \qquad (7)$$

where the subscript j on $\mathrm{d}\sigma/\mathrm{d}\Omega$ denotes the MO from which ionization occurs. Since the PW is an eigenfunction of $\mathbf{p}$ with eigenvalue $\hbar\mathbf{k}$

$$\frac{\mathrm{d}\sigma_j}{\mathrm{d}\Omega} = \frac{e^2kL^3}{\pi mc\omega}(\mathbf{u}\cdot\mathbf{k})^2|\langle \mathrm{j}|\mathrm{PW}(\mathbf{k})\rangle|^2 \qquad (8)$$

a result indentical with that given by Kaplan and Markin.[11,12]

Each MO $\langle \mathrm{j}|$ is a linear combination of atomic orbitals (AO's) $\langle \Phi_l|$

$$\langle \mathrm{j}| = \sum_l C_{lj}\langle \Phi_l| \qquad (9)$$

In contrast to Kaplan and Markin who used Slater-type basis functions, we take each AO to be a superposition of Gaussian basis functions, so that a carbon $2\mathrm{p}_z$ AO is written

$$\langle \Phi_l| = \sum_s A_s N(\alpha_s) z \exp[-\alpha_s(\mathbf{r} - \mathbf{R}_l)^2] \qquad (10)$$

where each A_s is the coefficient of a Gaussian function with normalization constant $N(\alpha) = 2\alpha^{1/2}(2\alpha/\pi)^{3/4}$. The vector $\mathbf{R}_l$ denotes the position of the lth carbon atom in the molecular xy plane (the atom index is identical with the AO index). The overlap of an AO with a PW is readily evaluated in Cartesian coordinates and is

$$\langle \Phi_l|\mathrm{PW}(\mathbf{k})\rangle = ik_z(2\pi)^{3/4}L^{-3/2} \times \exp(i\mathbf{k}\cdot\mathbf{R}_l)\sum_s A_s\alpha_s^{-5/4}\exp(-k^2/4\alpha_s) \qquad (11)$$

Substitution of eq 11 into eq 8 yields

$$\frac{\mathrm{d}\sigma_j}{\mathrm{d}\Omega} = \frac{e^2k^5\cos^2\theta_{ku}\cos^2\theta_{kz}(2\pi)^{3/2}}{\pi mc\omega}\left[\sum_s A_s\alpha_s^{-5/4} \times \exp(-k^2/4\alpha_s)\right]^2 \times \left[\sum_l C_{lj}^2 + 2\sum_{l>m} C_{lj}C_{mj}\cos(\mathbf{k}\cdot\Delta\mathbf{R}_{lm})\right] \qquad (12)$$

where $\Delta\mathbf{R}_{lm} = \mathbf{R}_l - \mathbf{R}_m$.

---

(6) M. R. Flannery and U. Öpik, *Proc. Phys. Soc. London*, **86**, 491 (1965).

(7) G. V. Marr, "Photoionization Processes in Gases," Academic Press, New York, N. Y., 1967.

(8) P. M. Johnson and S. A. Rice, *J. Chem. Phys.*, **49**, 2734 (1968).

(9) J. Cooper and R. N. Zare, *ibid.*, **48**, 942 (1968); **49**, 4252 (1968).

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

(11) I. G. Kaplan and A. P. Markin, *Opt. Spectrosc. (USSR)*, **24**, 475 (1968); **25**, 275 (1968) [*Opt. Spektrosk.*, **24**, 884 (1968); **25**, 493 (1968)].

(12) I. G. Kaplan and A. P. Markin, *Sov. Phys. Dokl.*, **14**, 36 (1969) [*Dokl. Akad. Nauk SSSR*, **184**, 66 (1969)].

(13) S. Basu, *Theor. Chim. Acta*, **3**, 238 (1965).

(14) For example, see E. Merzbacher, "Quantum Mechanics," Wiley, New York, N. Y., 1961, pp 439–481.

This equation, in which L does not appear, assumes that all AO's are the same except for their $\mathbf{R}_l$. It gives the differential cross section in terms of the orientation of the electron wave vector $\mathbf{k}$ to the molecular axes xyz and of the orientation of $\mathbf{k}$ to the electric polarization direction $\mathbf{u}$. As derived it is specific to photoionization from π MO's that are constructed from Gaussian $2p_z$ AO's.

Typical photoelectron spectrometers employ unpolarized light and detect electrons with velocities in a direction normal to the propagation of the light, so that $\mathbf{k}$ lies in the plane of the polarization $\mathbf{u}$. Thus eq 12 must be averaged over polarization directions, as well as over all orientations of the molecular axes with respect to laboratory axes to make the result applicable to a gaseous sample. We obtain

$$\left(\frac{d\sigma_j}{d\Omega}\right)_{\perp} = \frac{2^{1/2}\pi^{1/2}e^2k^5}{3mc\omega}\left[\sum_s A_s\alpha_s^{-5/4}\exp(-k^2/4\alpha_s)\right]^2 \times \left\{\sum_l C_{lj}^2 + 2\sum_{l>m} C_{lj}C_{mj}[j_0(k\Delta R_{lm}) + j_2(k\Delta R_{lm})]\right\} \quad (13)$$

where j_0 and j_2 are spherical Bessel functions, each with an argument that is the product of the scalars k and ΔR_{lm}. Although eq 13 is not for the total cross section,[15] it is specific to the geometry described, which corresponds to the maximum in the angular distribution obtained in the plane-wave approximation. (The subscript $\perp$ in $d\sigma/d\Omega$ denotes this restriction.) In obtaining this equation the factor $\cos^2\theta_{ku}$ in eq 12 averages to $^1/_2$ since $\mathbf{k}$ lies in the plane of $\mathbf{u}$. The $\cos^2\theta_{ku}$ factor means that our plane-wave approximation cannot yield a spherical term[9,10] in the angular distribution. Since such a spherical term is important in the photodetachment cross sections for 2p electrons in atomic anions,[9] we conclude that the PW approximation is totally inadequate for describing angular distributions for π ionizations. However, it is hoped that polarization averages are adequately described, as is the case[3] for the 2p state of the H atom.

The information required for the evaluation of eq 13 is of four types: (1) coordinates of carbon atoms to yield internuclear distance ΔR_{lm}, (2) a set of coefficients A_s and exponents α_s to define a $2p_z$ AO by eq 10, (3) a set of coefficients C_{lj} for each occupied MO, (4) an ionization potential IP_j for each MO, such that the magnitude of $\mathbf{k}$ for the photoelectron from the jth MO is

$$k_j = [(2m/\hbar^2)(h\omega - IP_j)]^{1/2} \quad (14)$$

We have written a computer program to evaluate eq 13 as a function of the photon energy $\hbar\omega$ using these four types of information as input. In the polyenes, we have taken single and double bond distances as 1.47 and 1.37 Å, respectively, with C–C–C angles of 120°. All cyclic systems were presumed to be regular polygons 1.40 Å on a side, and to be planar, even though it is known that this is not true for certain of them. Two carbon $2p_z$ AO's were available to us (Table I). One, a four-term Gaussian sum, gives a total energy in ethylene very nearly that given using a Slater orbital basis.[16] The second, a seven-term Gaussian, is thought to be of double-ζ quality.[17] The coefficients of the AO's in the MO's are generated internally by diagonalizing the conventional π-electron Hückel matrix with all β's equal and the overlap set equal to zero. Alternatively, coefficients obtained from molecular SCF calculations could be read in, but we have not done this as yet. One advantage of the latter option would be that each MO would have an associated IP *via* Koopmans' theorem. At present we must provide IP's as additional parameters, chosing either values from photoelectron spectra[18–20] or what are thought to be reasonable estimates.

Table I. Four-Term and Seven-Term Gaussian Carbon $2p\pi$ Atomic Orbitals[a]

Four-term[b]		Seven-term[c]	
A_s	α_s	A_s	α_s
0.0230551	12.8302	0.00876	25.3655
0.1568288	2.56604	0.05464	5.77636
0.4871830	0.646359	0.18365	1.78730
0.5498280	0.166252	0.35652	0.655774
		0.41977	0.252790
		0.21158	0.096693
		0.00869	0.027189

[a] See eq 10. [b] See ref 16. [c] See ref 17.

Though the cross sections have been calculated from threshold to 1500-eV incident photon energy, we report here the differential cross sections for only three photon energies: 21.21, 40.82, and 1486 eV. The first two of these are the He I and He II resonance lines which are widely used in valence-shell photoelectron spectroscopy. The Al Kα X-ray line has an energy of 1486 eV, and is used both for inner shell and valence shell spectroscopy.

Results and Discussion

The first series of compounds studied, the straight-chain trans polyenes and polyene anions, illustrate several of the points we wish to make. First, as regards the choice of $2p_z$ AO, calculations on several of the smaller polyenes using both the four-term and seven-term AO's showed that 21- and 41-eV cross sections calculated with the latter AO were very nearly 10% smaller in all cases. Since we are concerned only with the relative values of the cross sections, the results obtained with the four-term orbital are quoted throughout. Typical cross section *vs.* photon energy curves are shown in Figure 1, and all polyene results are tabulated in Table II. Since the cross sections vary so little at 1486 eV, they have not been calculated for every molecule in Tables II–IV.

Our calculated cross sections for all molecules are maximal very near the He I resonance line (21 eV). However, the rise to the maximum is much too slow, for the onset of ionization in neutral molecules is known to be much more of a step function.[21] The discrepancy arises from the PW density of states and from the nonorthogonality of the molecular and for free-electron waves. This seems less severe for the molecular anions, as our curves closely resemble that for H^-.[3]

---

(15) By contrast the expressions of Kaplan and Markin in ref 11 and 12 that correspond to our eq 13 are for the total cross section. (In addition they use Slater rather than Gaussian basis functions.) Their final expressions are larger than ours by a factor of $8\pi/3$, since we divided by 4π in averaging over orientations of molecular axes with respect to $\mathbf{k}$ and since our cylindrical average over polarization is $^1/_2$ instead of the spherical average of $^1/_3$.

(16) C. J. Hornback, private communication.

(17) C. Salez and A. Veillard, *Theor. Chim. Acta*, **11**, 441 (1968).

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

(19) V. Cermak, *Collect. Czech. Chem. Commun.*, **33**, 2739 (1968).

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

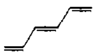
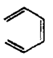
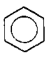
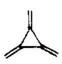
(21) See, for example, the ethylene results of W. A. Chupka, J. Berkowitz, and K. M. A. Refaey, *ibid.*, **50**, 1938 (1969).

Table II. Differential Cross Sections Computed for the MO's of Polyenes and Polyene Anions[a]

Molecule	Orbital	IP	$(d\sigma/d\Omega)_\perp$ at 21 eV[b]	41 eV[b]	1486 eV[c]
Methyl$^-$	$1a_2''$	12.5[d]	5.089	2.911	
Ethylene	$1b_{2u}$	10.53	9.626	3.349	5.144
Allyl$^-$	$1a_2$	8.5	6.646	2.876	
	$1b_2$	9.5	11.197	3.131	
Butadiene	$1b_g$	9.03	8.977	2.955	
	$1a_u$	11.30	11.453	3.173	
Pentadienyl$^-$	$2b_2$	8.5	6.789	2.758	5.136
	$1a_2$	9.5	9.937	2.952	5.152
	$1b_2$	10.5	12.057	3.058	5.169
Hexatriene	$2a_u$	8.26	8.795	2.882	
	$1b_g$	11.0	10.292	3.149	
	$1a_u$	14.0	10.168	3.537	
Heptatrienyl$^-$	$2a_2$	8.5	6.891	2.766	5.136
	$2b_2$	9.5	9.184	2.950	5.149
	$1a_2$	10.5	11.041	3.077	5.165
	$1b_2$	11.5	12.155	3.179	5.180
Octatetraene	$2b_g$	9.0	8.229	2.952	
	$2a_u$	10.0	9.857	3.041	
	$1b_g$	11.0	11.300	3.148	
	$1a_u$	12.0	12.045	3.247	
Nonatetraenyl$^-$	$3b_2$	8.5	6.937	2.776	5.136
	$2a_2$	9.5	8.697	2.945	5.149
	$2b_2$	10.5	10.249	3.082	5.129
	$1a_2$	11.5	11.380	3.200	5.174
	$1b_2$	12.5	11.841	3.311	5.188
Decapentaene	$3a_u$	8.5	8.250	2.904	
	$2b_g$	9.5	9.484	2.988	
	$2a_u$	10.5	10.736	3.098	
	$1b_g$	11.5	11.613	3.204	
	$1a_u$	12.5	11.903	3.311	

[a] All molecules in the all-trans configuration. [b] $\times 10^{-19}$ cm^2. [c] $\times 10^{-24}$ cm^2. [d] The IP's for this and other anions were chosen artificially high in order to compare cross sections with those of the neutrals. All cross sections are for doubly occupied MO's.

Table III. Differential Cross Sections Computed for the Isomeric Hexatrienes

Molecule	Orbital	IP	$(d\sigma/d\Omega)_\perp$ at 21 eV[a]	41 eV[a]
	$2a_u$	8.26	8.795	2.882
	$1b_g$	11.0	10.292	3.149
	$1a_u$	14.0	10.168	3.537
Same, but bonds 30% longer	$2a_u$	8.26	8.278	2.447
	$1b_g$	11.0	8.408	2.593
	$1a_u$	14.0	7.756	2.842
Same, but bonds 60% longer	$2a_u$	8.26	7.383	2.586
	$1b_g$	11.0	7.036	2.530
	$1a_u$	14.0	6.112	2.652
	$2b_2$	8.26	10.691	2.830
	$1a_2$	11.0	8.402	3.138
	$1b_2$	14.0	11.308	3.379
	$1e_{1u}$[b]	9.5	9.780	3.013
	$1a_{1g}$	11.3	13.465	3.145
	$1e$[b]	9.0	9.310	2.865
	$1a_1$	11.0	13.567	3.335
	$2a_u$	9.0	5.785	2.896
	$1b_g$	10.0	10.615	2.871
	$1a_u$	11.0	15.698	3.138
	$1e$[b,c]	9.0	8.859	2.728
	$1a_1$	11.0	16.217	3.313

[a] $\times 10^{-19}$ cm^2. [b] Values for doubly degenerate orbitals are for individual components. [c] A hypothetical planar triangular array of six carbon atoms.

Table IV. Differential Cross Sections Computed for the MO's of Cyclic Polyenes

Molecule	Orbitals	IP	$(d\sigma/d\Omega)_\perp$ at 21 eV[a,b]
Cyclopropenium$^+$	a_2''	10.5	12.830
Cyclobutadiene	e_g	9.5	5.016
	a_{2u}	10.5	14.418
Cyclopentadienide$^-$	e_1''	9.5	7.456
	a_2''	11.0	14.478
Benzene	e_{1g}	9.5	9.780
	a_{2u}	11.3	13.748
Cyclooctatetraene	e_{2u}	8.5	6.630
	e_{1g}	9.5	12.365
	a_{2u}	10.5	11.715

[a] Values for doubly degenerate orbitals are for individual components. [b] $\times 10^{-19}$ cm^2.

One notes in Table II that the cross-section differences among various orbitals are maximal at 21 eV, become much less obvious at 41 eV, and practically disappear at 1486 eV. Percentagewise, the largest is about 100%, 10%, and 1% larger than the smallest, at the three respective energies. Being the smallest species in our set, it is not surprising that the methyl anion CH_3^- has the lowest calculated cross section at 21 eV. Ethylene has very nearly twice the cross section of CH_3^- at 21 eV, but from this point on there is a rapid convergence of the cross section for the deepest (highest IP) π orbital, with that of decapentaene being only 1.23 times as large as that of ethylene. Moreover, in a given molecule, the cross sections decrease monotonically as one goes up the π-electron ladder, spanning a range of less than a factor of 2 from top to bottom. The relative constancy of the cross sections from the deepest π orbitals of the molecules from butadiene to decapentaene is quite unexpected, for one usually correlates increasing molecular size with rapidly increasing oscillator strength.[22] Nonetheless, the calculations predict a cross section of $8.5 \pm 3 \times 10^{-19}$ cm^2 for ionization out of any π orbital of any polyene. In fact, if we consider only the first π-electron ionization process in the polyene series, the largest cross section at both 21 and 41 eV is that of ethylene, though once again the ratio of extreme values is less than 2.

Figure 1 illustrates a feature which has been observed experimentally in the past, *i.e.*, the crossing of pairs of cross-section curves. Thus in both methane[23] and xenon difluoride[24] it has been found that the more intense partner in a certain pair of bands at one excitation energy is the less intense partner at another energy.

Another feature of interest is the Bessel function factor in eq 13, which imposes a damped sine-wave-like modulation upon the cross-section curve in the case of a diatomic molecule. This is interpretable as an interference effect between the out-going electron wave and the molecular core taken as an array of points. In ethylene, the period of modulation is about 300 eV, and fails to produce any noticeable oscillation of the cross-section curve.

In order to emphasize more strongly the dependence of the ionization cross sections on geometry, we have tabulated the cross sections for various isomeric C_6 π-electron hydrocarbons in Table III. Considering the deepest π-electron MO in this set of molecules (only

---

(22) W. C. Price, "Molecular Spectroscopy," P. Hepple, Ed., Institute of Petroleum, Elsevier, London, 1969, p 221.

(23) C. R. Brundle, M. B. Robin, and H. Basch, *J. Chem. Phys.*, **53**, 2196 (1970).

(24) C. R. Brundle, M. B. Robin, and G. R. Jones, *ibid.*, **52**, 3383 (1970).

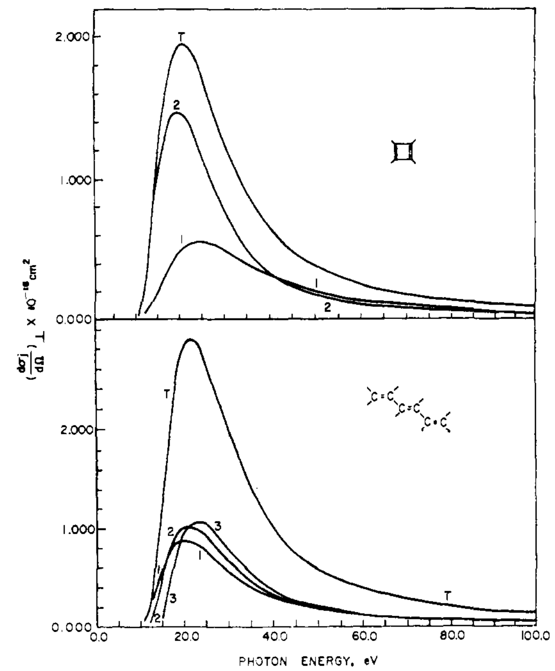


Figure 1. Differential photoelectron cross sections calculated for the occupied π MO's of cyclobutadiene (upper) and *trans,trans*-hexatriene-1,3,5 (lower). The curve marked T was obtained by adding the numbered curves. The curves (upper) marked 1 and 2 are for the e_g and a_{2u} orbitals, respectively (Table IV). The curves (lower) marked 1, 2, and 3 are for the $2a_u$, $1b_g$, and $1a_u$ orbitals, respectively (Table III).

a few of which really exist), the trend is immediately clear. The largest dimension in one direction is of little concern. Instead, what matters most is that the molecule be maximally condensed, *i.e.*, that every sp^2 carbon atom have as many other sp^2 carbon atoms bonded to it as possible. Moreover, since there is a near constancy of the sum of the cross sections from the occupied MO's of a molecule within a group of molecules of a given number of carbon atoms, the most highly condensed molecule will have the largest spread of cross sections among its orbitals.

The rationale behind this behavior is found in the nature of the Bessel function factor in eq 13, which is plotted *vs.* its argument $k\Delta R_{lm}$ in Figure 2. At a fixed value of the outgoing electron wave vector k, evaluation of eq 13 requires that the Bessel functions be summed over all pairs of internuclear distances ΔR_{lm}. For the ejection of a 10-eV electron, one sees from Figure 2 that an adjacent pair (labeled 1,2) contributes four times as much to the cross section than does a 1,3 pair, while 1,4 pairs actually come in with a negative sign and act to decrease the cross section. Thus, it is clear that the molecule with the maximum number of carbon–carbon 1,2 bonds (or distances) will have the maximum cross section for its all-in-phase MO.

Returning to the polyene series, the number of carbon–carbon 1,2 pairs increases as the chain length goes up, but the $C_{jl}C_{jm}$ multipliers necessarily decrease for normalized MO's, and apparently in such a way as to give a maximum cross section at heptatrienyl anion, and a decrease from there to decapentaene.

The cross section from the deepest π MO of an all-trans polyene will probably be smaller than that of the all-cis isomer since the end-to-end contribution will be larger for the latter (Table III). Also, if we leave all other factors constant, but increase all bond distances by, say, 30 or 60%, then all cross sections fall since the argument $k\Delta R_{lm}$ increases and $j_0(k\Delta R_{lm}) + j_2(k\Delta R_{lm})$ decreases. For the higher π-electron MO's, one cannot give any rule with 100% certainty, but it does appear in general that the more nodal surfaces introduced between the AO's, the more negative values of $C_{jl}C_{jm}$ at 1,2 and 1,3 distances appear, and thus diminish the cross sections. However, the facts that the C_{jm}'s differ for each orbital and that certain of the Bessel functions are negative when the corresponding $C_{jl}C_{jm}$'s are also negative can conspire to vitiate this generality for the higher MO's. It is clear, however, that in contrast to the deepest MO, the cross sections for the corresponding higher MO's in the series of polyenes increase monotonically (except for the second MO of hexatriene) as the chain length increases.

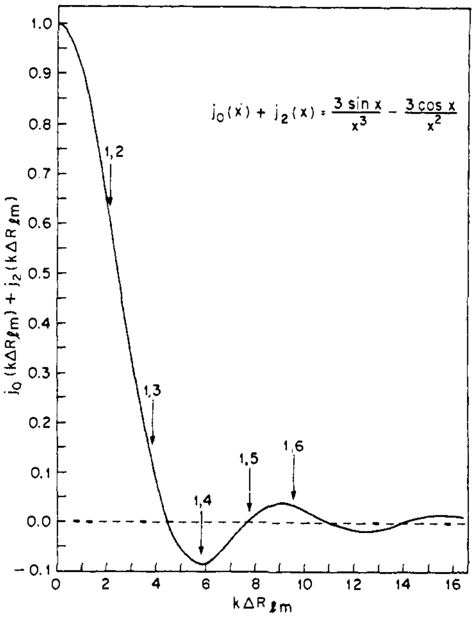


Figure 2. Plot of the Bessel function factor of eq 13 *vs.* its argument. The arrows give the value of the function for various pairs of atoms in the case of a photoelectron ejected with 10-eV energy from *trans,trans*-hexatriene (k = 1.63 Å^{-1}).

For the deepest π MO's of a set of molecules for which all $C_{jl}C_{jm}$ are necessarily positive, one can order the cross sections by considering simultaneously how condensed the molecular structure is and how dilute the π-electron density is at each atom. We define a cross-section index, Φ, equal to the number of 1,2 adjacencies in a molecule, divided by the number of sp^2 carbon atoms contained in the molecule. As seen from Figure 3, assembled from a random selection of entries in Tables II–IV, there is a trend apparent in the relationship between the cross section calculated for the in-phase orbital and the cross-section index, Φ, with those molecules of largest Φ being among those with the largest cross sections.

Since the Φ index is equal to 1 for all cyclic systems, one expects only a slight change in cross section on going from the smallest to the largest rings. The differential cross sections for the cyclic polyenes are displayed in Table IV, and, as expected, those of the lowest MO's are almost uniformly larger than those of the corresponding straight-chain polyenes. The inversion

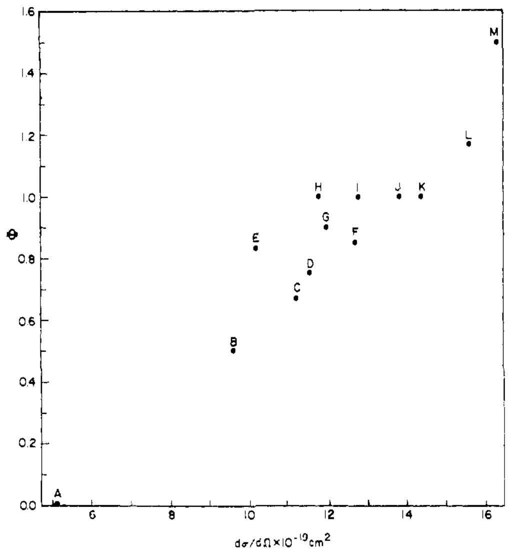


Figure 3. Correlation of the cross-section index, Φ, with the calculated differential cross section: (A) methyl anion, (B) ethylene, (C) allyl anion, (D) butadiene, (E) hexatriene, (F) 3-methylene-1,4-pentadiene, (G) decapentaene, (H) cyclooctatetraene, (I) cyclopropenium cation, (J) benzene, (K) cyclobutadiene, (L) 1,4-dehydrobenzene (next-to-last entry in Table III), (M) planar array of six carbon atoms (last entry in Table III). Values of Φ are $(n - 1)/n$ for a chain of n atoms, unity for single ring of any size, and greater than unity for fused rings. Cross sections here are for 21-eV light.

of levels which appears in hexatriene occurs in the ring compounds at cyclooctatetraene, and the maximum cross section, which occurs at heptatrienyl anion in the chains, falls at cyclopentadienide anion in the rings.

Though there are many more planar molecules for which cross sections can be calculated it does not seem worthwhile to proceed any further without either an experimental check of the relative cross sections computed already and/or some refinement of the theory, such as the orthogonalization procedure briefly described in the next section.

Use of Orthogonalized Plane Waves

The reduction in eq 4 of the many-electron matrix element of the linear momentum operator to a single one-electron matrix element is valid only if the orbital $|k\rangle$ is orthogonal to each of the occupied MO's in the ground-state $\langle a|$. This condition is in general not satisfied when $|k\rangle$ is a plane wave. Taking into account the nonorthogonality of $|k\rangle$ to each of the occupied MO's in $\langle a|$, but invoking the orthogonality of these MO's to one another, the correct expression replacing eq 4 is

$$\langle a|\sum_n \mathbf{p}_n|b\rangle = 2^{1/2}\left[\langle j|\mathbf{p}|k\rangle - \sum_l \langle j|\mathbf{p}|l\rangle\langle l|k\rangle\right] \qquad (15)$$

where $|l\rangle$ is one of the doubly occupied MO's and $\langle l|k\rangle$ is the overlap integral of $\langle l|$ with the plane wave $|k\rangle$. Terms diagonal in $|l\rangle$ would in general be present if the dipole length operator were used instead, but vanish for the linear momentum operator.

The result in eq 15 can also be obtained by the Schmidt orthogonalization of $|k\rangle$ to all MO's $|l\rangle$

$$|k'\rangle = |k\rangle - \sum_l \langle l|k|l\rangle \qquad (16)$$

Substitution of eq 16 into the now-valid eq 4 yields eq 15. While the function $|k'\rangle$ is not normalized, the normalization constant

$$N = \left[1 - \sum_l \langle l|k\rangle\langle k|l\rangle\right]^{-1/2} \qquad (17)$$

approaches unity as the size of the box within which the PW's are normalized (eq 5) becomes infinite, since the overlap $\langle l|k\rangle$ becomes negligible compared to unity. This same consideration also applies in the direct derivation of eq 15.

The equivalence of using orthogonalized plane waves (OPW's) to correctly evaluating the many-electron matrix elements when one orbital is not orthogonal to the rest removes a degree of arbitrariness in the selection of MO's for a Schmidt orthogonalization. Equation 15 contains linear momentum matrix elements between different occupied MO's, but none involving unoccupied MO's such as the π^* MO in ethylene. It would be possible to extend the method to include such orbitals, but we do not propose to do so at present. The use of the OPW procedure for a many-electron atom or molecule can be viewed as simply being the correct use of PW's since their nonorthogonality to occupied orbitals is not ignored.

Retaining the PW density of states given in eq 6, a result similar to eq 7 is obtained, but with $|k'\rangle$ replacing $|k\rangle$. Since $|k'\rangle$ is not an eigenfunction of $\mathbf{p}$, eq 8 no longer holds. As a result the differential cross section contains in general a spherical term, that is, a term independent of the angle between $\mathbf{k}$ and the electric polarization $\mathbf{u}$. Thus

$$\frac{d\sigma}{d\Omega} = \alpha + \beta \cos^2 \theta_{ku} \qquad (18)$$

where the coefficient α is zero in the simple PW approximation. In terms of eq 18, $(d\sigma/d\Omega)_\perp$ for unpolarized light is simply $\alpha + (\beta/2)$.

We have begun a study of cross sections using the OPW procedure described above. One of the objectives is a comparison of results with those reported here in order to establish the validity of the simpler PW method, particularly for relative values of the cross sections for photon energies at least 10 eV above the ionization threshold. These studies will be the subject of a future communication.

Some preliminary OPW results for ethylene using simple "diatomic" MO's constructed from carbon Gaussian AO's indicate that the cross-terms obtained when eq 15 is multiplied by its complex conjugate are negative, thus reducing the value of the cross section for ionization from the π_u (z) MO by roughly a factor of 2 for 21-eV light. The occupied σ_g^+ MO's constructed from C(1s), C(2s), and C(2p$_\sigma$) AO's contribute to the cross section, but the occupied xy component of the π_g MO cannot, nor can any MO's of odd parity. For photon energies less than 20 eV the principal contribution to $(d\sigma/d\Omega)_\perp$ is from the α term in eq 18, with β becoming negative for photon energies below 18 eV. However the quantity $\alpha + (\beta/2)$ must remain positive for all photon energies. Although the OPW cross section is zero at threshold[25] because of the PW density of states, the α term rises from zero with an initially infinite slope, reaching a maximum only 2 eV above threshold (photon energy 12.5 eV). This behavior, resulting from contributions to α that are proportioned to k rather than to k^5 as in the PW expression for $\beta/2$ in eq 13, produces two maxima in the dependence of $(d\sigma/d\Omega)_\perp$ on photon energy. The high-energy maximum is similar to those in Figure 1, but shifted about 5 eV to higher energy and reduced in height as described above. The question remains as to whether the OPW procedure[26] will confirm the chemical trends found in the PW cross sections.

Acknowledgment. Several discussions with Drs. A. Overhauser, H. Basch, and C. R. Brundle are gratefully acknowledged. Dr. Brundle and Mr. N. A. Kuebler have kindly informed us of their preliminary experimental measurements. Most especially, we thank Mr. Robert Kornegay for programming the calculations reported here.

---

(25) By contrast, the exact cross section for the photoionization of the H atom (ref 3) is a maximum at threshold. An improved procedure might be the combination of OPW matrix elements with the density of states appropriate to the H atom continuum.

(26) For an OPW study of anthracene applied to the photoconductivity of the crystal, see R. D. Sharma, *J. Chem. Phys.*, **46**, 2841 (1967).

ω-Type Calculations on π-Electron Systems with Inclusion of Overlap Charges. I. Ionization Potentials of Some Alternant Hydrocarbons

B. Krishna and S. P. Gupta*

Contribution from the Department of Chemistry, University of Allahabad, Allahabad-2, India.
Received February 16, 1970

Abstract: ω-Type calculations have been performed on π-electron systems with inclusion of overlap charges. Ionization potentials of some alternant hydrocarbons have been calculated and the results obtained compared with those obtained from the SCF–MO method and with experimental values.

In recent years much attention has been paid to the Hückel equation.[1] A simple argument shows that the coulomb integral $H_{\mu\mu}$ for a carbon atom μ in a π lattice for which the electron density q_μ is not unity cannot be treated as a parameter. If $q_\mu < 1$, the net positive charge $(1 - q_\mu)$ means that the screening "seen" by any one electron is reduced and the coulombic attraction to the nucleus is increased. $H_{\mu\mu}$ for such a carbon should have a more negative value. Conversely, a carbon with a net negative charge should have a less negative value of $H_{\mu\mu}$. Wheland and Mann[2] proposed that the value of $H_{\mu\mu}$ should be linearly related to the charge. Their proposal may be formulated as

$$H_{\mu\mu} = \alpha_0 + (1 - q_\mu)\omega \tag{1}$$

$$H_{\mu\nu} = \beta_{\mu\nu} \tag{2}$$

in which α_0 and ω are treated as empirical parameters whose value may be chosen so as to give best agreement with experimental results. The resonance integral $\beta_{\mu\nu}$ is supposed to be zero unless μ and ν are directly bonded; for all directly bonded μ,ν, it is given a constant value.

Thus the dependence of the coulomb integral upon the net charge of an atom introduces some electron repulsion within the framework of the simple LCAO method.[3] The use of this method in the literature is still rather limited, but it has been shown to lead to improved calculated dipole moments for hydrocarbons[2,4] and greatly improved energy values for organic cations.[3,5] The ω technique also involves an iterative procedure like the SCF equation. In the first iteration the Hückel charge distributions are used as a first approximation. However, in a semiempirical treatment, the iterative procedure is generally omitted.

Inclusion of Overlap Charges in the ω Technique (IOC ω Technique)

All investigators who have used the ω technique have neglected the overlap charges in their calculations. Therefore, according to Harris,[6] if we include the overlap, take the net charge on atom μ as that resulting when all overlap charges are divided equally among the atoms involved, and use the Wolfsberg–Helmholtz[7] form for $H_{\mu\nu}$, we have

$$H_{\mu\mu} = \alpha_0 + \omega[1 - {}^1/_2\sum_\sigma(p_{\mu\sigma}S_{\mu\sigma} + p_{\sigma\mu}S_{\sigma\mu})] \tag{3}$$

$$H_{\mu\nu} = {}^1/_2KS_{\mu\nu}(H_{\mu\mu} + H_{\nu\nu}) \tag{4}$$

where K is a dimensionless constant and $p_{\mu\sigma}$ is defined as

$$p_{\mu\sigma} = 2\sum_i^{\text{occ}} c_{i\mu}c_{i\sigma} \tag{5}$$

---

* Address correspondence to this author.

(1) (a) L. C. Cusachs and J. W. Reynolds, *J. Chem. Phys.*, **43**, 160 (1965); (b) R. Rein, N. Fukuda, H. Win, G. A. Clarke, and F. E. Harris, *ibid.*, **45**, 4743 (1966).

(2) G. W. Wheland and D. E. Mann, *ibid.*, **17**, 264 (1949).

(3) A. Streitwieser, Jr., *J. Amer. Chem. Soc.*, **82**, 4123 (1960).

(4) G. Berthier and A. Pullman, *C. R. Acad. Sci.*, **229**, 761 (1949).

(5) (a) N. Muller, L. W. Pickett, and R. S. Mulliken, *J. Amer. Chem. Soc.*, **76**, 4770 (1954); (b) N. Muller and R. S. Mulliken, *ibid.*, **80**, 3489 (1958); (c) A. Streitwieser, Jr., and P. N. Nair, *Tetrahedron*, **5**, 149 (1959).

(6) F. E. Harris, *J. Chem. Phys.*, **48**, 4027 (1968).

(7) M. Wolfsberg and L. Helmholtz, *ibid.*, **20**, 837 (1952).