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Interference in the Photo-Ionization of Molecules

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Initial observations by Samson of the far-uv photoabsorption by molecules suggest that the spectrum of photoelectrons emerging from a multicenter molecular field is modulated by interferences. This effect is discussed in terms of Huygens' approach and of a partial-wave analysis with a Born-approximation calculation. It is compared with processes of diffraction by molecules. It appears related to the onset of photoionizing transitions to states of increasing orbital momenta which occurs at increasing photon energies.

1. INTRODUCTION

RECENTLY, Samson has obtained photoabsorption cross sections for a few simple molecules, notably N_2 and O_2, up to photon energies of ~ 60 eV.[1] As seen in Fig. 1, these spectra show some structures below 30 eV ($\lambda > 400$ Å) that are presumably due to detailed properties of valence orbitals, and at higher energies they show the general decrease of absorption which is expected on the basis of qualitative theory and of experiments on comparable single atoms. They also show some undulations, superposed on the down trend in the 30–60-eV range. These undulations, which may be described as "shoulders," are reminiscent of interference effects and appear foreign to the atomic spectra observed and interpreted in recent years.[2]

Interference (or diffraction) phenomena should in fact occur when electrons are released within a multicenter molecular field. From Huygens' point of view one may, for example, regard the two atoms of N_2 or of O_2 as essentially independent absorbers of light which constitute, in turn, separate sources of photoelectrons. Superposition of the emissions from these two sources produces an interference pattern whose properties should depend periodically on the ratio of the internuclear distance to the photoelectron wavelength. This interference may modulate the cross section for photoabsorption by the whole molecule in accordance with its periodicity. Since the internuclear distance is larger in O_2 than in N_2, corresponding interference effects should occur in O_2 at longer photoelectron wavelengths, that is—other circumstances being equal—at lower photon energies, than in N_2. This expectation agrees with the relative position of the shoulders in Fig. 1.

This remark encouraged us to explore the theory of interference in photo-ionization somewhat systematically even though only semiquantitatively. Our main objective is to call attention to the phenomena to be expected, to the relevant circumstances, and to their connection with other phenomena of molecular interference or diffraction. The results provide a tentative, but by no means cogent, interpretation of the shoulders in the N_2 and O_2 spectra and some guidance for examining other spectra, experimentally and theoretically, from the same point of view.

2. THRESHOLD EFFECT OF CENTRIFUGAL BARRIERS

Huygens' approach to interference effects has afforded us initial guidance, but does not lend itself readily to more detailed analysis. Since the interference of electron emission by different atoms leads anyhow to the production of standing waves between and around the nuclei, we shall consider directly the standing-wave patterns which characterize alternative final states of photoelectrons, without further reference to Huygens' approach. The analysis will be confined to diatomic molecules, for the sake of simplicity.

Photoelectrons from diatomic molecules may be assigned to various sets of continuum states with real wave functions. These sets can be classified by quantum number pairs (l,λ), such that $l(l+1)$ corresponds to the square of the orbital angular momentum in the united-atom limit and λ^2 to the square of its component along the internuclear axis. Such wave functions have λ nodal planes through the internuclear axis and $l-\lambda$ hyperboloid-like nodal surfaces that cross this axis between the nuclei. Continuum states with successive values of $l-\lambda$ may be said to involve emissions from the two

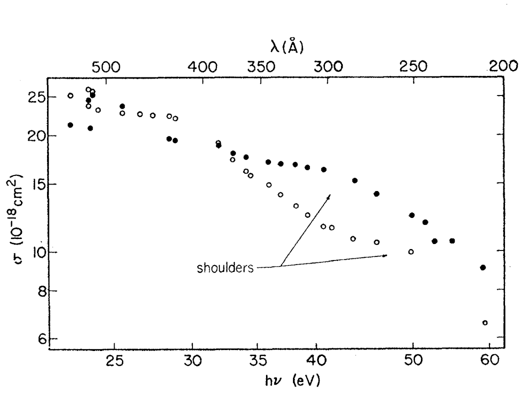

FIG. 1. Logarithmic plot of experimental photoabsorption cross sections (Ref. 1). ● O_2; ○ N_2.

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[1] J. A. R. Samson and R. B. Cairns, J. Opt. Soc. Am. **55**, 1035 (1965).

[2] J. W. Cooper, Phys. Rev. Letters **13**, 762 (1964); U. Fano, Science **153**, 522 (1966) and references therein.

atoms which interfere to form successively larger numbers of standing waves between the nuclei.

The familiar selection rule $\Delta l = \pm 1$ of single-atom optical transitions does not apply to molecules (with nonzero internuclear distance) because angular momentum can be transferred to rotational motion; parity conservation is fulfilled by any *odd* value of Δl for homonuclear diatomic molecules. True enough, transitions to states with large l are quite unlikely in the usual frequency range of spectroscopy, but for a reason other than orbital-momentum conservation. An electron in an excited or ionized state with high l is kept away from the region of the ground state by the centrifugal force; that is, its wave function has a negligible overlap with that of the ground state. *This situation changes for states in the far continuum*, whose energy permits the electron to overcome the centrifugal barrier and approach the nuclei. The change takes place at higher and higher energies for higher and higher values of l.

Therefore, it is suggested that photoabsorption by transitions to states with increasing l becomes appreciable in succession at increasing photon energies. A related phenomenon occurs in atoms, where transitions from inner d orbitals to f states do not set in with appreciable strength until the photon energy exceeds the "absorption edge" by an amount sufficient to overcome the centrifugal barrier.[2]

The energy required for the onset of transitions to continuum states of given l can be estimated by considering the sign of the kinetic energy of an electron at various distances r from the center of a molecular ion. This energy is represented by

$$k^2 + 2Z_{\text{eff}}/r - l(l+1)/r^2, \tag{1}$$

where k^2 is the energy of the photoelectron in rydbergs, Z_{eff} is an effective charge of the ion, and r is in atomic units (0.53 Å). The last term represents the centrifugal barrier. The onset of absorption should occur for values of k^2 which cause (1) to vanish for values of r comparable to the internuclear distance R, that is, for $(kR)^2 \sim l(l+1) - 2Z_{\text{eff}}R$. Since the k^2 values thus determined depend quadratically upon l, successive values of l correspond to well separated photoabsorption thresholds for each molecule. The value $l=3$ is of particular relevance to the photon energy range ~30–60 eV for moderately small molecules. In Table I we list some sample values of threshold photon energies and wavelengths for the onset of specified photo-ionizing transitions. Each of these photon energies equals the critical photoelectron energy k^2, estimated as described above taking simply $Z_{\text{eff}}=1$, plus the binding energy in the initial state.

The threshold values for the $3\sigma_g \to kf$ transitions in N_2 and O_2 approximate the position of shoulders at ~280 and 330 Å in the respective curves of Fig. 1 to an extent that appears better than consistent with our crude model. However, we regard this interpretation of the shoulders as most tentative.

3. BORN CALCULATION

To obtain additional insight, we have calculated the photoabsorption of H_2^+ in the Born approximation in the following manner, which brings out the connection with Huygens' approach automatically. The position of the single electron is indicated by $\mathbf{r}$, $\mathbf{r}_a$, and $\mathbf{r}_b$ with reference to the center of the molecule and to its two nuclei, respectively, so that

$$\mathbf{r} = \mathbf{r}_a + \tfrac{1}{2}\mathbf{R} = \mathbf{r}_b - \tfrac{1}{2}\mathbf{R}, \tag{2}$$

where $\mathbf{R}$ is the internuclear distance. The ground-state electron wave function is represented by

$$[u(r_a)+u(r_b)]/(2+2S)^{1/2},$$
$$u(r) = Z^{*3/2}\pi^{-1/2}\exp(-Z^*r), \quad Z^*=1.24,^3 \quad S\approx 0.46. \tag{3}$$

As a final-state wave function we take a free-field spherical wave[4] about the molecular center

$$(\mathbf{r}\,|\,klm) = (2k/\pi)^{1/2} j_l(kr) Y_{lm}(\hat{r}), \tag{4}$$

where $(2k/\pi)^{1/2}j_l$ is a spherical Bessel function normalized per unit range of the final-state energy $\frac{1}{2}k^2$.[4] The photoabsorption cross section is, then,

$$\sigma_l = 0.29(k^2+k_0^2)\tfrac{1}{3}\sum_m |(klm|\mathbf{r}|u_a) + (klm|\mathbf{r}|u_b)|^2/(2+2S), \tag{5}$$

where $\frac{1}{2}k_0^2$ is the binding energy (~1.1 a.u.).

The term $\pm\frac{1}{2}\mathbf{R}$ in the representation (2) of the dipole operator $\mathbf{r}$ transforms the $1\sigma_g$ ground-state wave function (3) into $2^{-1/2}[u(r_a)-u(r_b)]$, which represents roughly the $1\sigma_u$ wave function. This function should be approximately orthogonal to the true continuum states inasmuch as they are approximate eigenfunctions of the same Schrödinger equation. Accordingly we disregard the $\pm\frac{1}{2}\mathbf{R}$ terms and replace r by r_a or r_b in the two matrix elements of (5), respectively. (This argument is admittedly quite crude; we use it only because we are interested in the gross features of our phenomenon.)

TABLE I. Approximate thresholds for some transitions.

Transition	$h\nu$ (eV)	λ (Å)
	H_2, $R=1.42$ a.u.	
$1\sigma_g \to kf$	76	160
	N_2, $R=2.07$ a.u.	
$3\sigma_g \to kf$	41	300
$1\pi_u \to kg$	66	185
	O_2, $R=2.28$ a.u.	
$1\pi_g \to kf$	31	400
$3\sigma_g \to kf$	38	325
$1\pi_u \to kg$	58	210

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[3] C. A. Coulson, Trans. Faraday Soc. 33, 1479 (1937).

[4] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press Inc., New York. 1957), p. 23.

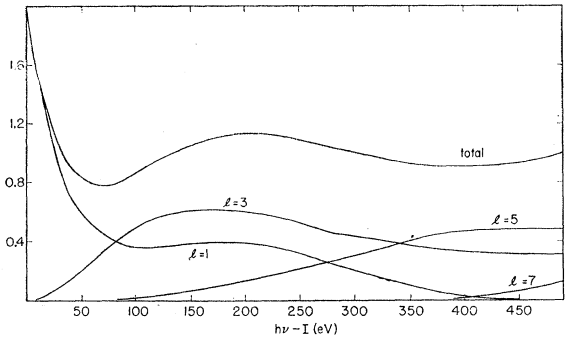

FIG. 2. Plot of the factor in brackets in Eq. (12) and contributions to it by different final states. $R=2$ a.u.

We can reduce further the matrix elements (5) to their well-known form for a hydrogen-like atom by expanding the spherical wave (4) into similar waves centered on either atom, e.g.,

$$(\mathbf{r}|klm)=\sum\nolimits_{l_a}(\mathbf{r}_a|kl_am)T_{l_al}{}^{(m)}(\tfrac{1}{2}kR)\,,\tag{6}$$

where the coefficients T are given by Danos and Maximon,[5] and we refer m to the axis $\mathbf{R}$. Thus we have

$$(klm|\mathbf{r}_a|u_a)=T_{1l}{}^{(m)}(\tfrac{1}{2}kR)\quad(k1m|\mathbf{r}_a|u_a)\,,\tag{7}$$

with $l_a=1$ owing to the $\Delta l=1$ selection rule for atoms. The matrix element on the right of (7) is the same for atom b as for a and can be factored out of the $|\ \ |^2$ in (5), after which it is also independent of m. Thereby (3) becomes

$$\begin{aligned}\sigma_l=0.29(k^2+k_0{}^2)^2(k10|z|u)^2\tfrac{1}{3}\sum\nolimits_m|T_{l1}{}^{(m)}(kR/2)&\\ +T_{l1}{}^{(m)}(-kR/2)|^2/(2+2S)&\\ =\sigma_H(Z^*)\tfrac{1}{3}\sum\nolimits_m[T_{l1}{}^{(m)}(kR/2)]^2&\\ \times[1+(-1)^{l-1}]^2/(2+2S)\,,&\end{aligned}\tag{8}$$

where

$$\sigma_H=47Z^{*5}k^3(k_0{}^2+k^2)/(Z^{*2}+k^2)^6\tag{9}$$

is the cross section for a hydrogen-like atom of atomic number Z^* adjusted for the difference of binding energies, in atomic units, and Eq. (7′) of Ref. 5 has been taken into account. Notice that the "odd l" parity requirement has emerged here.

Taking the value of $T_{l1}{}^{(m)}(\frac{1}{2}kR)$ from (15) of Ref. 5 and utilizing (10.1.19) of Ref. 6, we find

$$\begin{aligned}&\tfrac{1}{3}\sum\nolimits_m[T_{l1}{}^{(m)}(x)]^2\\ &\quad=(2l+1)\{l(l+1)j_l{}^2(x)/x^2+[j_{l+1}(x)-lj_l(x)/x]^2\}\\ &\quad=lj_{l-1}{}^2(x)+(l+1)j_{l+1}{}^2(x)\,,\end{aligned}\tag{10}$$

$$\sigma_l=\sigma_H(Z^*)[lj_{l-1}{}^2(\tfrac{1}{2}kR)+(l+1)j_{l+1}{}^2(\tfrac{1}{2}kR)]2/(1+S)\,,\quad l\text{ odd}\,,\tag{11}$$

and $\sigma_l=0$ for l even. Summation over odd l reduces to a sum over $(2l+1)j_l{}^2$ for even l and yields the total cross section

$$\sigma=\sum\nolimits_l\sigma_l=\sigma_H(Z^*)[1+(\sin kR)/kR]/(1+S)\,.\tag{12}$$

Figure 2 shows the factor in brackets of (12), as well as the separate contributions of several terms from (11). Multiplication of the factor in brackets by the rapidly decreasing factor $\sigma_H(Z^*,k^2)$ obscures its oscillations to visual inspection. Therefore, we do not show this product. However, we expect the qualitative features of our result to apply to all diatomic molecules. Accordingly, factors similar to those shown in Fig. 2 should appear in more realistic calculations. The detection of shoulders in Fig. 1 is favored by the circumstance that atomic cross sections σ_{N} and σ_{O} decrease less rapidly than σ_H with increasing photon energy.

The photon energy at which $l=3$ becomes important in Fig. 2 is substantially higher than one would expect for $H_2{}^+$ by scaling the plots of Fig. 1 in accordance with the relevant values of kR. However, our Born calculation and the discussion following Eq. (1) utilize unrealistically low values of k^2 for any given photon energy, because they do not consider the distortion of the final-state wave function by the nuclear attraction. [Adjustment of Z_{eff} in (1) would correct this error.]

4. DISCUSSION

To establish the effect considered in this paper in a manner appropriate for comparison with experimental data, calculations should be performed with final-state wave functions substantially better than those for free particles. The $H_2{}^+$ calculations by Bates *et al.*[7] would presumably display the effect realistically if extended beyond their highest photon energy of 30 eV; at this energy $\sigma(l=3)$ is beginning to rise but is still only one-twelfth of $\sigma(l=1)$.

By treating the particular example of $H_2{}^+$ in Sec. 3, we have sidestepped a circumstance which arises in homonuclear molecules with valence electrons in states of different parity. As shown in the table of Sec. 2, photoelectrons ejected from the $1\pi_u$ and $1\pi_g$ orbitals, which occur in O_2, must end in states with even and odd l, respectively. Photo-ionization of π orbitals will then exhibit twice as many maxima in a given interval of kR, as have been indicated in the $H_2{}^+$ example of Fig. 2. These two sets of maxima will also be shifted relative to one another by the difference in ionization potential of the bound orbitals. A detailed analysis of this aspect of the problem is required to interpret experimental spectra dependably.

The main point of these initial considerations, which has been illustrated by the Born calculation and should have general validity, concerns the analysis of the cross section into contributions from final states with successively higher l values. Each contribution sets in at an

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[5] M. Danos and L. C. Maximon, J. Math. Phys. **6**, 766 (1965).

[6] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (U. S. Department of Commerce, National Bureau of Standards, Washington, D. C., 1964).

[7] D. R. Bates, U. Öpik, and G. Poots, Proc. Phys. Soc. (London) **66**, 1113 (1953).

appropriate energy, yields a maximum of the factor that modulates the cross section, and thereafter recedes at higher energies with oscillatory character. The sum of all contributions will be modulated with a periodicity akin to that of $\sin kR$ in Fig. 2 if all valence-electron orbitals have the same parity. If the photoelectrons arise from states of both parities, the modulation will have shorter steps, akin to that of the $\sin 2kR$, but its successive humps may have alternating magnitude. For heteronuclear diatomic molecules, parity considerations have only approximate relevance, if any, and the modulation will proceed at a rate akin to $\sin 2kR$. [If Eq. (11) were assumed to apply to even, as well as to odd, values of l, the sum (12) would yield no modulation at all instead of a $\sin 2kR$ modulation. However, the total loss of modulation would be an artifact of the lowest Born approximation.]

For inner-shell photo-ionization processes this modulation factor $\sin 2kR$ may be produced by a mechanism suggested by Kronig[8] long ago. His model involved the photo-ionization of the K shell of one atom of a heteronuclear diatomic molecule; the outgoing electron then interferes with the wave scattered by the other atom. It has been known (see, e.g., Shiraiwa *et al.*[9]) that a $\sin 2kR$ modulation factor follows from the Kronig approach. This approach may also be applied to homonuclear molecules in which the resonance frequency of the exchange process, $X^+(K\text{-hole})-X(\text{g.s.}) \leftrightarrow X(\text{g.s.})-X^+(K\text{-hole})$, is small as compared to the frequency of decay by x-ray emission or Auger process. Otherwise the photo-ionization of a homonuclear molecule must be considered through a molecular-orbital approach as in the present paper.

Finally we may indicate how the phenomena discussed here fit in with other well-known diffraction properties of two-center systems. The two-center modulation factor $1+(\sin kR)/kR$ appears in the literature as early as Rayleigh's calculation of the acoustic power radiated by a pair of point sources.[10] The same factor appears in the formulas for elastic coherent scattering of x rays, electrons, or neutrons by a diatomic molecule.[11] The variable k indicates, in general, the magnitude of the wave vector that represents the momentum transfer between the radiation and the molecule; its value is often indicated by $4\pi \sin\frac{1}{2}\theta/\lambda$ in elastic processes. Photoionization of a homonuclear diatomic molecule may be regarded as a generalized scattering process with different input and output channels; the photon in the input channel contributes a negligible momentum so that k pertains to the motion of the output electron with respect to the molecule. However, under the typical conditions of the Kronig approach, only one of the atoms acts as the effective source of the photoelectrons and the diffraction occurs in a second stage of the process, when the electron leaves the molecule; the relevant momentum transfer is now indicated by $2k$.

In each of the processes mentioned in the preceding paragraph, the two centers are normally regarded as point-like, i.e., as independent of one another, so that the internuclear distance R is the only geometrical parameter of the molecule relevant to the interference. The partial-wave analysis considered in this paper permits one on the one hand to work out more accurate and realistic calculations, as may be required in less schematic problems, and on the other hand to show how, under schematic conditions, the contributions of the partial waves add up to yield an analytical modulating function of the single variable kR.

It should be understood, of course, that the various schematized approaches considered above are intended only to guide one in the analysis of experimental data and perhaps in the development of approximation methods to solve the exact quantum-mechanical problem. However, any consistent and workable solution of this problem should reproduce the relevant interference effects whether or not it utilizes an approximation designed to anticipate them.

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[8] R. de L. Kronig, Z. Physik **75**, 468 (1932). H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon Press, Oxford, England, 1952), p. 201.

[9] T. Shiraiwa, T. Ishimura, and M. Sawada, J. Phys. Soc. Japan **13**, 847 (1958).

[10] Lord Rayleigh, Phil. Mag. **6**, 289 (1903).

[11] For example, W. J. Moore, *Physical Chemistry* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1955), 2nd ed., pp. 236–239.