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Abstract

Full Text

Physics

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On Interference Phenomena in the Photoionization of Molecules

(Presented by Academician V. A. Fock on 29 IV 1968)

There are extremely few works devoted to calculating photoionization cross sections of molecules. In the published works ($^{1-5}$) the total photoionization cross sections are calculated, but nowhere is the dependence of the cross section on the angle of emission of the photoelectron analyzed.

We have carried out a calculation of the photoeffect on the molecule H_2, from the results of which it follows that, in the case of photoionization of molecules, an effect qualitatively new in comparison with atoms appears, namely: for an oriented molecule the dependence of the cross section on the angle of emission of the photoelectron has an oscillatory character, and the number of maxima and minima depends on the product of the internuclear distance R_0 and the wave vector $\mathbf{q}$ of the ejected electron.

In the work of Cohen and Fano (^{5}) the presence in the photoionization cross section of the H_2^+ ion of a term oscillating with increasing qR_0 is noted. However, these oscillations are damped, since the oscillating term is preceded by a factor $\sim 1/q^7$. As will be shown below, the oscillations appear distinctly in the dependence of the cross section on the angle of emission of the photoelectron.

As the wave function of the ejected electron we used a plane wave normalized to volume:

$$v_q = \frac{1}{\sqrt{V}} e^{i\mathbf{qr}}. \tag{1}$$

The plane-wave approximation is valid for energies of the ejected electron considerably exceeding the ionization potential, when the electron may be regarded as free. This corresponds to small wavelengths of the incident radiation. Therefore, all multipoles were taken into account in the transition operator. In the first approximation of perturbation theory with respect to the interaction with the electromagnetic-wave field, the nonrelativistic expression for the differential photoionization cross section into the element of solid angle $d\Omega_q$ has the form*

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$$d\sigma = \frac{Ve^2 q}{2\pi\hbar^2 m_e c^2 k}\left|\mathbf{u}\left\langle \Phi_q \left| \sum_\nu e^{i\mathbf{k}\mathbf{r}_\nu}\hat{\mathbf{p}}_\nu \right| \Phi_0 \right\rangle\right|^2 d\Omega_q, \qquad (2)$$

where $\mathbf{k}$ is the wave vector of the incident radiation; $\mathbf{u}$ is the direction of polarization; e, m_e are the charge and mass of the electron; c is the speed of light; $\mathbf{p}_\nu$ is the momentum operator of the ν-th electron of the molecule; Φ_0, Φ_q are the coordinate electronic wave functions of the initial and final states of the system.

The following coordinate functions, corresponding to the singlet spin state, were taken:

$$\Phi_0 = N_1\{[\varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2)] + \mu[\varphi_a(1)\varphi_a(2) + \varphi_b(1)\varphi_b(2)]\}, \qquad (3)$$

$$\Phi_q = N_2\{[\varphi_a(1) + \varphi_b(1)]v_q(2) + v_q(1)[\varphi_a(2) + \varphi_b(2)]\}. \qquad (4)$$

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* The expression for the cross section (2) has been summed over all vibrational states. In the Born-Oppenheimer approximation, summation over vibrational states leads to a factor equal to 1; see (^{6}).

N_1, N_2 are normalization factors. The function Φ_0, describing the ground state of the H_2 molecule, takes into account the contributions of both covalent and ionic structures. At the equilibrium distance between the nuclei $R_0 = 1.431$ at. units, $\mu = 0.2644$ (7). For $\mu = 0$ the function (3) becomes the Heitler–London function, and for $\mu = 1$ the molecular-orbital-method function. Φ_q describes the final state of the system, corresponding–

Fig. 1. Curves of the dependence of the differential photoionization cross section of the H_2 molecule on the angle of ejection of the photoelectron in the plane of the vectors $\mathbf{k}$ and $\mathbf{u}$, for $E_\phi = 75$ eV (a and b), 500 eV (v and g), and 100 eV (d and e)

–to the ejection of an electron with momentum $\hbar\mathbf{q}$ and the formation of the ion H_2^+ in the ground electronic state; the ionization potential of this transition is $I_1 = 15.43$ eV. φ_a, φ_b denote Slater $1s$-orbitals centered on atoms a and b, respectively. The value of the effective Slater charge was taken to be $\alpha = 1.1937$ (7).

Let us denote the operator in the matrix element (2) by

$$F = \sum_{\nu=1}^{2} f_\nu = \sum_{\nu=1}^{2} e^{i\mathbf{k}\mathbf{r}_\nu}\hat{p}_\nu.$$

Substitution of the functions (3)–(4) into the matrix element brings it to the form

Fig. 2

Figure 1: Fig. 2

$$\begin{aligned}\langle \Phi_q | F | \Phi_0 \rangle = 2N_1N_2\{&(1+\mu)\langle \varphi_a | f | \varphi_a \rangle (\langle v_q | \varphi_a \rangle + \langle v_q | \varphi_b \rangle) \\ &+ (1-\mu)\langle \varphi_a | f | \varphi_b \rangle (\langle v_q | \varphi_a \rangle - \langle v_q | \varphi_b \rangle) \\ &+ (1+\mu)(1+\chi)(\langle v_q | f | \varphi_a \rangle + \langle v_q | f | \varphi_b \rangle)\};\end{aligned} \tag{5}$$

here χ denotes the overlap integral of the Slater orbitals, $\chi = \langle \varphi_a | \varphi_b \rangle$. It can be shown that the matrix element $\langle \varphi_a | f | \varphi_a \rangle \sim k$, and therefore $\mathbf{u}\langle \varphi_a | f | \varphi_a \rangle = 0$. The matrix element $\langle \varphi_a | f | \varphi_b \rangle$, which is a three-center integral, is reduced to a single integral by means of the integral transformation proposed by Bonham et al. (8). Substituting the squared modulus of (5) into formula (2), in the general case we arrive at a rather cumbersome expression. For specific particular cases this

the expression is simplified. Thus, in the case where the photon wave vector $\mathbf{k}$ is directed along the molecular axis, the expression for the differential photoionization cross section takes the form

$$\begin{aligned} d\sigma = \frac{2^6 a^5 e^2 (1+\mu^2)(1+\chi)}{m_e c^2 \left[(1+\mu^2)(1+\chi^2) + 4\mu\chi\right]} \, \frac{q^3 \sin^2\theta_q \cos^2\varphi_q}{k\left(a^2 + |\mathbf{k} - \mathbf{q}|^2\right)^4} \times \\ \times \left[1 + \cos\left(kR_0 - qR_0\cos\theta_q\right)\right] d\Omega_q; \end{aligned} \tag{6}$$

the angle θ_q is measured from the vector $\mathbf{k}$. The cross section contains an oscillating factor, the period of the oscillations being determined by the value qR_0. The same oscillating terms enter the cross section for other polarization directions as well.

Fig. 2

Figure 1 gives the dependence of the cross section on the photoelectron emission angle for three values of the photon energy and for two different polarizations. As is seen from the graphs, the number of maxima increases with increasing photon energy. In this case, for $\mathbf{u} \perp \mathbf{R}_0$, the probability of photoelectron emission in the direction $\mathbf{u}$ ($\theta_q = 90^\circ$) is maximal; for $\mathbf{u} \parallel \mathbf{R}_0$, the probability of emission in the direction $\mathbf{u}$, depending on the photon energy, may be either maximal or minimal. An analogous oscillatory pattern is also obtained when calculating the differential photoionization cross sections of π-electrons in conjugated and aromatic hydrocarbons, see (^{9}).

This pattern is qualitatively equivalent to that obtained from the interference of two coherent waves emitted from different centers. If two plane coherent waves $e^{i\mathbf{qr}}$ are emitted from centers a and b (see Fig. 2), then in the direction

θ their phase shift will be determined by the factor $q\Delta r = qR_0 \cos\theta$. Maxima will be observed for values of θ for which an integral number of de Broglie wavelengths $\lambda_e = 2\pi/q$ fits into the path difference Δr. At small photon energies the photoelectron wavelength λ_e is greater than the distance between the nuclei R_0, and the conditions for the appearance of additional maxima are not fulfilled; this explains the occurrence of the oscillatory pattern only at sufficiently high energy of the incident photon. Consequently, the wave properties of electrons underlie the phenomena obtained.

The qualitative analogy of the effect obtained with the interference of two waves emitted from the positions of the nuclei is supported by the form of the electron-density distribution along the axis passing through the nuclei. The probability distribution of the coordinates of one of the electrons in the ground state of the H_2 molecule is equal to the diagonal element of the density matrix determined by the coordinate wave function (3)

$$\rho(1) = \int |\Phi_0(1,2)|^2 dV_2. \tag{7}$$

Figure 3 gives the values of $\rho(1)$, taken along the straight line passing through the nuclei. The probability of finding an electron near the nuclei is maximal. Therefore, for an interference pattern to appear, the two-centeredness (or multicenteredness) in the electron-density distribution is essential. Otherwise, interference phenomena would have to appear both for a spherical distribution of the electron cloud and in the case of an oriented p-electron cloud of an atom. The latter, however, does not occur.*

When the differential cross section is averaged over the orientations of the molecule in space, the interference effect disappears. The total cross section of ionization is obtained by integrating the averaged differential cross section over all photoelectron emission angles and depends on the electronic state into which the molecular ion passes.

Table 1 gives the total photoeffect cross sections for the molecule H_2. Two cases have been calculated: a) the ion H_2^+ is formed in the ground electronic state with coordinate wave function $\sim (\varphi_a + \varphi_b)$, the cross section is denoted σ^+; b) the ion H_2^+ is formed in a repulsive electronic state with coordinate wave function $\sim (\varphi_a - \varphi_b)$, the ionization potential $I_2 = 32.94$ eV (^{1}), the cross section is denoted σ^-.

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* We note that in the case of an atom with a fixed direction of the electron cloud, the differential cross section as a function of the photoelectron emission angle may have several maxima. However, these maxima are associated with the shape of the electron cloud and do not depend on the de Broglie wavelength of the ejected electron.

From Table 1 it is seen that, as the photon energy increases, the probability of formation of the ion $H_2{}^+$ in an excited state at first decreases and at $E_\phi = 300$ eV is less than 0.1 of the probability of formation of $H_2{}^+$ in the ground state, but with further increase of E_ϕ the decrease ceases and the ratio σ^-/σ^+ begins to oscillate.

Fig. 3. Distribution of the electron density in the ground state of the H_2 molecule along the axis connecting the nuclei (a_0 is the Bohr radius)

For experimental observation of the interference phenomena occurring in the photoionization of molecules, two conditions must be fulfilled: rigid orientation of the molecule in space and selection of photoelectrons by energy. The latter condition is necessary for separating electrons emitted in processes occurring with formation of the ion in different electronic states, since the interference patterns obtained in these processes are different. One way of orienting molecules is to freeze them in solid solutions. In the case of a periodic structure (a molecular crystal), it is not difficult to show that the interference pattern obtained from an isolated molecule must have superimposed on it the interference pattern from the crystal lattice.

Table 1*

E_ϕ, eV	80	100	300	500	1000	1500	2000	3000	4000	5000
σ^-	0.192	0.086	0.0228	0.0853	0.0443	0.0441	0.0538	0.0540	0.0635	0.0617
σ^+	0.037	0.015	0.0324	0.0435	0.0534	0.0874	0.0630	0.0766	0.0725	0.0711
σ^-/σ^+	0.194	0.181	0.086	0.067	0.079	0.065	0.078	0.065	0.072	0.065

* The cross sections were calculated with the value $\mu = 0.2644$ in wave function (3) and are given in units of 10^{-18} cm^2.

In conclusion, we consider it our pleasant duty to express our gratitude to the participants of the seminar of the Department of Theoretical Physics of the Faculty of Physics of Leningrad University for discussion of the questions touched upon in this article.

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