PHOTO-IONIZATION CROSS SECTIONS OF HYDROGEN MOLECULE IN THE AMO–LCAO APPROXIMATION*

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Photo-ionization cross sections of the hydrogen molecule have been calculated using AMO–LCAO approximation. Calculated results of the cross section have been compared with the experimentally determined cross sections as well as with other similar calculations. Some remarkable conclusions have been drawn.

INTRODUCTION

The current interest in the study of photo-ionization of atoms and molecules has been exponentially enhanced because of the recent development of the photo-electron spectroscopy and its bearance on the atomic structure of the matter (Price *et al.* 1972). The nature of the photoelectron spectrum particularly its intensity pattern has a direct correlation with the photo-ionization cross section and, thus, it gives the information regarding the electronic structure of the atoms and molecules. Furthermore, the knowledge of the photo-ionization process becomes an essential tool for understanding the interesting features of astrophysics, atmospheric physics and physics of the auroral zone. In atmosphere, particularly in ionosphere, the production of electrons is mainly caused by the solar radiation.

For studying the photoionization of diatomic molecules experimentally, an appreciable amount of progress has been made during the last two decades. Whereas, the theoretical work for calculating the cross sections for ionization, as compared to atom (Marr 1967) is quite limited. This is, mainly because of the lack of suitable wavefunctions for the bound and free electronic states. Calculations have appeared for H_2^+ (Bates *et al.* 1953) where the *Schroedinger Equation* can be written down and solved accurately for the electronic motion. For many electron systems it is necessary to find suitable approximate electronic eigen functions. This has been achieved for H_2 (Flannery and Opik 1965), methane (Dalgarno 1952) and more recently for the electrons of ethylene, butadiene, and benzene (Kaplan and Markin 1968a, 1968b). The results obtained by Kaplan and Markin (1968b) for various molecules were encouraging in their agreement with the experimentally determined cross sections. This method, of course because of choosing the final state wavefunctions as plane wavefunctions associated with the ejected electron, is supposed to give more

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reliability in the cross sections in the energy region away from the ionization threshold.

The calculation of the photo-ionization cross sections of H_2 molecule reported in this paper is an application of the Kaplan and Markin's method and it is observed that the results obtained are in fair agreement with the experimentally determined cross sections of Cook and Metzger (1964).

Method of Calculation and Result

As derived by Kaplan and Markin (1968a) the expression for the differential photoionization cross sections of an arbitrary molecule can be represented in the following equation,

$$d\sigma = \frac{8\pi^2 e^2}{\hbar^2 \mu \omega c} \sum_m q_m \mid u < \nu_{q_m} \mid \hat{p} \mid \varphi_m > \mid^2 d_n \qquad (1)$$

where e and μ are the charge and mass of the electron; ω is the frequency of the ejected electron; u is the direction of its polarization; c is the velocity of light; p is the momentum operator of the molecular electron; q_m and $\nu q_m = (2\pi)^{-3/2} \times exp.\ (i\ q_m r)$ are the wavevector and wavefunction of the ejected electron φ_m is the molecular wavefunction. The sum over m includes all one electron states from which ionization is possible. In deriving the above equation the exchange between the knocked-out electron and the electron of the ion is disregarded.

This equation holds good when molecular wavefunctions derived by the molecular orbital method are used. In the case when molecular orbitals in the form of linear combinations of the atmoic orbitals are used in the AMO–LCAO approximation, we have the following form :

$$\varphi_m = \sum_{a,\rho} C^m{}_{a,\rho}\ \Phi_{a,\rho} \qquad (2)$$

where $C^m{}_{a,\rho}$ are the coefficients of the m^{th} molecular orbital; $\Phi_{a,\rho}$ is the atomic function assigned to a nucleus; ρ is the type of the atomic orbital with molecular wavefunction as (2). The equation for the differential photoionization cross section takes the form

$$d\sigma = \frac{8\pi^2 e^2}{\hbar \mu \omega c} \sum_m q_m \mid u\ C^m{}_{a,\rho} < \nu_{q_m} \mid \hat{p} \mid \Phi_{a,\rho} > \mid^2 d\Omega \qquad (3)$$

Thus the problem of calculating the differential photoionization cross section is reduced to an evaluation of the double-centred integrals entering into the above equation.

With 1s-orbital for H_2 molecule taking in the form

$$\Phi_{a,\,1s} = \frac{\alpha^{3/2}{}_{a,\,1s}}{\sqrt{\pi}}\ e^{-\alpha_{a,\,1s} r_a}$$

Evaluation of the integrals entering into matrix element (3) was carried out with the following results :

$$< \nu_{q_m} \mid \hat{p} \mid \Phi_{a,\,1s} > = \frac{4\hbar\ \alpha^{5/2}{}_{a,\,1s}\ q_m\ e^{-i(q_m R_a)}}{\sqrt{2\pi}(\alpha^2{}_{a,\,1s} + q_m^2)^2} \qquad (4)$$

In order to calculate the total cross section it is necessary to substitute these integrals into the integration over the solid angle *dr*. First it is necessary to average equation (3) over all orientation of the molecule in space. This leads to the disappearance of the dependence of the cross sections on the direction of the polarization vector u and to the appearance of an additional factor of 1/3. The form of the total photo-ionization cross section of ls elections is

$$\bar{\sigma} = \frac{2^8 \pi e^2}{3\mu\omega c} \sum_m q^3{}_m \sum_{a,\,p} C^m{}_{a,1s}\; C^m{}_{b,1s}\; \frac{\alpha_{a,1s}^{5/2}\; \alpha_{b,1s}^{5/2}\; J_0(q_m R_{ab})}{(\alpha_{a,1s}{}^2 + q_m{}^2)^2 (\alpha_{b\cdot 1s}{}^2 + q_m{}^2)^2} \qquad .. \qquad (5)$$

where $J_0\,(q_m\, R_{ab})$ is the spherical Bessel function of Zeroth order, $Rab = |\, Ra - Rb\,|$ For H_2 molecule, $m=1$, $\alpha_{a,\,1s} = \alpha_{b,\,1s} = 1.24$

$$q_1 = q,\; C^1{}_{a,\,1s}{}^1 = C^1{}_{b,\,1s} = \frac{1}{\sqrt{2(1+s)}}$$

S is the overlap integral of ls orbitals for H_2 molecule with the equilibrium internuclear distance $1.4a_0$. The value of the overlap integral with $\alpha = 1.24$ and at the equilibrium internuclear distance is 0.463. Substituting all these into the cross section expression given above it can be written in a simple form

$$\bar{\sigma}(H_2) = \frac{2^8 \times 0.668\; q^3\; J_0(qR_0)}{\mu\omega c(1.5376 + q^2)^4} \qquad .. \qquad .. \qquad (6)$$

where R_0 is the equilibrium internuclear distance. Calculations of the photoionization cross sections have been made with the incident photon of wavelength 804 Å

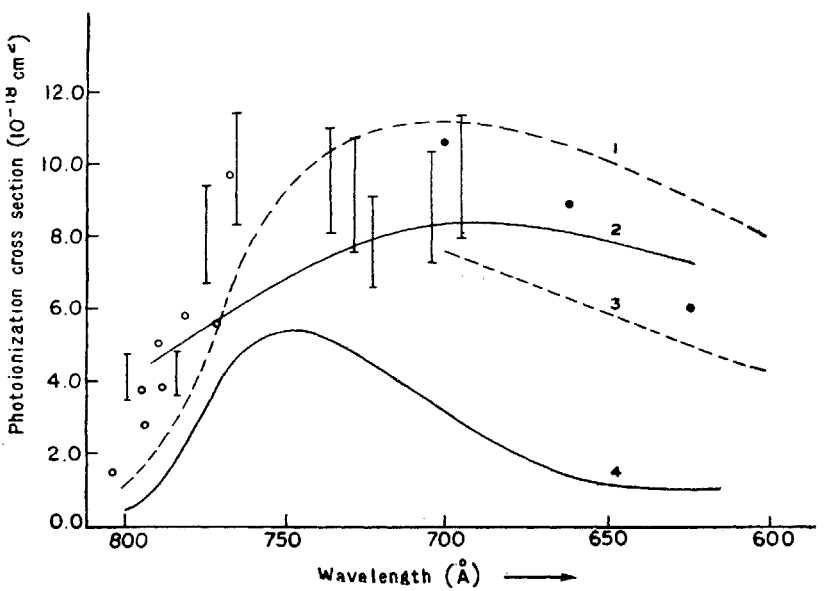

FIG. 1. Photo-ionization cross section of H_2. Experimental : O. Cook and Mitzger (1964); Lassettre and Jones (1964); I. Wainfan *et al.* (1955); Theoretical : 1—Flannery and Opik (1965); 2—present calculation; 3—Khare (1968); 4—Shaw and Berry (1972).

(threshold value) up to the wavelength 600 Å. Photoionization cross sections so calculated are displayed in Fig. 1, wherein experimental results of Cock and Metzger (1964). Wainfan *et al.* (1955) and Lassettre and Jones (1964) and theoretical calculations of Flannery and Opik (1965), Shaw and Berry (1972) and of Khare (1968) are also plotted for the sake of comparison.

Discussion

Peak position in the present curve is more flattened than the other cross section curves and lies comparatively at somewhat higher photon energy. The cross sections reported by Khare (1968) are qualitatively in good agreement with that of the Flannery and Opik though somewhat less in magnitude. Though the overall agreement between the various observed cross sections, especially the Wainfan *et al.* (1955) results and that of the presently calculated values is reasonably good, the threshold behaviour, as indicated by Lassettre and Jones (1964) experimental results, is better explained by the Flannery and Opik's (1965) calculated cross sections. However, as all of the experimentally determined cross sections are incomplete in so far as covering up of the sufficient energy range of the impacting photon is concerned, any generalization about the photoionization process made only on the basis of an agreement found in a certain region is liable to be immature and untenable.

As is seen from the equation (6) the cross sections contain an oscillating factor. However, the presence in Eq. (6) of a factor that decreases rapidly with increasing q damps the oscillation. Of course, the oscillations are not damped for the dependence of the differential cross section on the angle of escape of the photoelectron. Such oscillations are the result of interference of photoelectrons emitted from two centres. The transition moment depends upon the spread and nodal character of the wavefunction of the initial state and the wavelength and phase of the photoelectron (i.e., the final state). The simplest fact that this illustrates is the face-off of the photoionization cross section with higher energy (shorter wavelength) photoelectron. It can be appreciated that the cross section appropriate to any orbital will vary with the dimensions and nodal character of this orbital and the wavelength of the photoelectron. As a rough generalization it might be expected that the photoionization cross section would minimize when the photoelectron is not less than the orbital dimension. This would explain experimental observations that near the threshold of ionization the cross sections of molecular orbitals built from p atomic orbitals are greater than those arising from s-orbitals. This situation is reversed for high photoelectron energies where because of the smaller radial spread of s-orbitals, the transition moment integral maximizes with shorter wavelength photoelectrons. The study of the variation of the relative intensities of the photoelectron spectra of different orbitals with varying irradiating wavelengths is clearly going to yield much information on the nature of orbital wavefunctions.

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