Double photoionization of molecular hydrogen

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The cross section for two-electron photoionization of the hydrogen molecule by high-energy photons is predicted in the nonrelativistic dipole approximation to be 2.25% of the cross section for single photoionization.

The double photoionization (DPI) of helium by high-energy photons has been the subject of several experimental [1–4] and theoretical investigations [5–8]. Questions remain that have not been fully answered. In this work, we draw attention to another experimentally accessible system, molecular hydrogen. The observable signature of the DPI in molecular hydrogen is the release of two protons of equal and opposite momentum. We recently proposed a simple analytic method for the determination of the asymptotic behavior of the double-to-single ionization rate for the helium isoelectronic sequence which, for the case of He, compared favorably with the observed trend [1,6]. Here, we describe the extension of this method to H_2.

Dujardin *et al.* [9], in a pioneering experiment, have measured the photoionization rate for double-electron escape from H_2 using photoion-photoion coincidence mass spectroscopy for photon energies in the range of 47.5–140 eV. The two-electron ionization of H_2 results in a Coulomb explosion in which the protons are ejected with a momentum distribution determined by the vibrational wave function of the initial state [9,10]. (The DPI of H_2 from the ground vibrational state by a vertical dipole transition requires 51.4 eV.) Further refinement in mass spectrometry allowed Kossmann *et al.* [11] to measure the angle-resolved DPI rate in the range of energies from threshold to 110 eV. A theoretical discussion of H_2 double ionization has been given by Le Rouzo [12,13] who used the correlated ground-state wave function of H_2 of Hagstrom and Shull [14] and a final-state wave function given by a symmetrized product of continuum Coulomb wave functions to calculate the DPI cross section.

In this work, we demonstrate that at large photon frequencies, the double-to-single ionization rate stabilizes at

about 2.25%, compared to 1.67% for helium; see Ref. [15]. Only transitions in which the final state of H_2^+ has σ symmetry participate in the photoionization process in the limit of high energies. For the π states the cross sections fall off more rapidly with energy than those of σ states, and have vanishing leading coefficients. Hence we may write the high-energy limit in a form [6]

$$\mathcal{R} = \frac{C}{\sum_{nl} C(nl\sigma)} - 1 , \tag{1}$$

where the summation is over all the single ionization channels in which the final state is the $nl\sigma$ state of H_2^+ and C is the sum of $c(nl\sigma)$ for single and double ionization channels given by

$$C = \sum_{nl} C(nl\sigma) + \sum_{l} \int_0^\infty d\epsilon' C(\epsilon' l\sigma) . \tag{2}$$

If now $\Psi(\mathbf{r}_1,\mathbf{r}_2)$ is the electronic wave function of H_2 evaluated at the equilibrium internuclear distance of $R_e = 1.4$ a.u., and $\psi_{nl\sigma}(\mathbf{r}_1)$ are the electronic wave functions of H_2^+ also at $R = R_e$, $C(nl\sigma)$ can be written

$$C(nl\sigma) = N|\langle \Psi(\mathbf{r}_1,\mathbf{r}_2)|\delta(\mathbf{r}_{2a}) + \delta(\mathbf{r}_{2b})|\psi_{nl\sigma}(\mathbf{r}_1)\rangle|^2 , \tag{3a}$$

where N is a constant irrelevant to our calculation, and $\mathbf{r}_{2a}$ and $\mathbf{r}_{2b}$ are, respectively, the position vectors from electron 2 to centers a and b. A sum rule [6,16] yields

$$C(nl\sigma) = N\langle \Psi(\mathbf{r}_1,\mathbf{r}_2)|\delta(\mathbf{r}_{2a}) + \delta(\mathbf{r}_{2b})|\Psi(\mathbf{r}_1,\mathbf{r}_2)\rangle . \tag{3b}$$

The coefficients in Eqs. (3) are conveniently evaluated in prolate spheroidal coordinates (λ,μ,ϕ) for each electron. For the H_2 wave function we adopt the correlated wave function of James and Coolidge [17],

$$\Psi(\lambda_1,\mu_1,\lambda_2,\mu_2,r_{12}) = \frac{1}{2\pi} e^{-3/4(\lambda_1+\lambda_2)} \sum_{m,i,j,k,p} D_{mijkp} [\lambda_1^m \lambda_2^i \mu_1^j \mu_2^k u^p + \lambda_1^i \lambda_2^m \mu_1^k \mu_2^j u^p] , \tag{4}$$

where the interelectronic coordinate is explicitly inserted as $u = 2r_{12}/R$. The sum $(j+k)$ is restricted to be *even* due to the symmetry of the H_2 wave function under the exchange of nuclei. The optimized parameters are listed in Ref. [17] for the equilibrium nuclear position of

$R_e = 1.4$ a.u. giving the dissociation energy of $D_e = 4.698$ eV. For the H_2^+ wave functions, we employed the tabulated forms of Bates, Ledsham, and Stewart [18] as

$$\psi_{nl\sigma}(\lambda_1,\mu_1) = N_{nl\sigma}\Lambda(\lambda_1)M(\mu_1) , \tag{5a}$$

where

$$\Lambda(\lambda)=(\lambda+1)^s e^{-p\lambda}\sum_i g_i \left[\frac{\lambda-1}{\lambda+1}\right]^i \tag{5b}$$

and

$$M(\mu)=\sum_j f_j P_j(\mu) . \tag{5c}$$

The energy-dependent parameters s and p, and the coefficients g_i and f_j, are listed in Tables I through III of Ref. [18]. The normalization factor $N_{nl\sigma}$ was evaluated numerically. $P_k(x)$ are the Legendre polynomials of argument x subject to the restriction that the sum in (5c) occurs over even (odd) values of j for gerade (ungerade) symmetries of the hydrogen positive ion. Because the integrands in Eqs. (3) contain δ-function operators, $C(nl\sigma)$ and C are reduced to two-dimensional integrals over λ_1 and μ_1, while λ_2 and μ_2 are fixed at their limiting values of 1 and 1 or -1, respectively,

Moving electron 2 from center a to center b amounts to an exchange of nuclei, and since the ground state of H_2 is a symmetric state, only the *gerade* states of H_2^+ can have nonvanishing matrix elements. Table I compares the values of $C(nl\sigma)/C$ for H_2 and its united-atom limit, He [6]. The values given for $ns\sigma_g$ for $n\geq4$ are estimates based on an n^3 fall off of the asymptotic oscillator strength. The values for H_2 and He agree closely for high Rydberg states because the Rydberg electrons in H_2 see essentially two nearby protons. There is also a small con-

TABLE I. The ratio of single to double ionization of H_2 and He.

$nl\sigma$	$C(nl\sigma)/C$	$C(ns)/C$
$1s\sigma_g$	0.9308	0.9294
$2s\sigma_g$	0.0397	0.0445
$3d\sigma_g$	3.0×10^{-6}	
$3s\sigma_g$	0.0036	0.0055
$4s\sigma_g$	0.0015	0.0018
$5s\sigma_g$	0.0008	0.0008
$6s\sigma_g$	0.0005	0.0005
$n\geq7$	0.0011	0.0011
$\mathscr{R}$ (%)	2.25	1.67

tribution of the $3d\sigma_g$ state of H_2^+ to the DPI rate, whereas the $3d$ contribution for helium is zero.

We calculate the ratio $\mathscr{R}$ for H_2 to be 2.25% as compared with the helium $R=0$ limit of 1.67%. At the highest experimental photon energy of 110 eV [11,19], far from the asymptotic regime, the measured ratio is approximately 3.8%.

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