Unexpected Behavior of Double Photoionization in H_2

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(Received 14 July 1989)

For the first time and in contrast to a recent experiment, a pronounced nonspherical angular distribution for the fragment ions following double photoionization of H_2 has been observed. In addition, the accompanying cross section has turned out to be surprisingly small in comparison to the prediction of a recent theoretical investigation. Both observations suggest that the dynamics of double photoionization for the simplest two-center two-electron system remains an open problem.

PACS numbers: 33.80.Eh

Direct double photoionization is a clear manifestation of electron correlation, since the photon operator is a one-particle operator and therefore not able to excite —in the framework of independent particles— more than one electron. Consequently, experimental and theoretical investigations of many-electron processes are of general importance for the proper treatment of atoms and molecules. For the double-photoionization cross section of the rare-gas atoms helium, neon, and argon reliable experimental data exist, against which different theoretical treatments could be compared; experimental and theoretical data are now in gratifying agreement. For molecules, direct double photoionization has attracted increasing attention in recent years by several exploratory experimental studies and first attempts at a theoretical description. H_2 is the simplest molecular two-electron system and serves as a model for more complicated species. In addition to this general aspect, photoprocesses in H_2 allow comparison with the atomic counterpart helium elucidating the influence of the molecular structure. Of special interest is the complete fragmentation of H_2 caused by double photoionization since it yields to four particles in the continuum correlated by pure Coulomb interaction only. Because of these properties, the double photoionization in H_2 is ideally suited for probing quite different concepts.

For the energies of interest, the photon operator is well described in the dipole approximation, and this results in only two transition amplitudes, D_Σ and D_Π, from the molecular ground state of H_2 to the double-ionization continuum which belong to photoionization with molecular orientation along (Σ) or perpendicular (Π) to the electric vector of the light. Within the axial-recoil model[1] which applies well in the present case, the photoionization cross section σ^{++} for the ejection of both electrons of H_2 equals the dissociation cross section $\sigma(H^+, H^+)$ of the fragment ions. Therefore, one has[2]

$$\sigma(H^+,H^+) = \tfrac{4}{3}\pi^2 \alpha h\nu (D_\Sigma + 2D_\Pi) . \quad (1)$$

The angular distribution parameter β_m of the fragment ions is given by[2]

$$\beta_m = 2(D_\Sigma^2 - D_\Pi^2)/(D_\Sigma^2 + 2D_\Pi^2) . \quad (2)$$

In a pioneering work, Dujardin *et al.*[3] measured the double-photoionization cross section of H_2 from threshold to 140-eV photon energy, and the results were found to be in reasonable agreement with the recent calculation of Le Rouzo[4,5] based on the "wave-function approach" developed for helium originally.[6] However, two objections must be made. First, the accuracy of the experimental data is only within 70%. Second, the stated agreement refers to the calculation in the velocity formulation for the dipole matrix element; the length-form calculation yields results which are higher by approximately a factor of 1.8. Even though arguments are given that the length-form calculation should be less reliable, we remark that in the corresponding case of double photoionization in helium, for reasons still awaiting clarification, from threshold up to the maximum of the cross section the length-form results of the wave-function approach of Byron and Joachain[6] lie close to the experimental data which also agree with improved theoretical calculations.[7,8] On this ground, experimental $\sigma(H^+,H^+)$ values close to the theoretical length-form results should be expected in the near threshold region.

In this Letter we report a measurement of the direct-double-photoionization cross section of H_2 in the photon energy range between 52 and 110 eV. Our data are in agreement with the experimental values of Dujardin *et al.*,[3] but—because of the smaller uncertainty—they expose a discrepancy with the calculated values: very pronounced against the length-form but also significantly with respect to the velocity-form results. In addition, we present the first experiment on the angular distribution of the charged photofragments following direct double photoionization. Although Dujardin *et al.*[3] found that anisotropy effects were negligible in their experiment, probably because their setup delivers nearly unpolarized light, we get for decreasing photon energy increasing negative values for the angular distribution parameter β_m (down to -0.75). Guided by extended studies of two-electron processes in helium around the threshold for double photoionization,[9–15] we propose that the dynamics of two-electron excitations in molecules is dictated within a large threshold region by the presence of high orbital angular momenta. This might be needed in

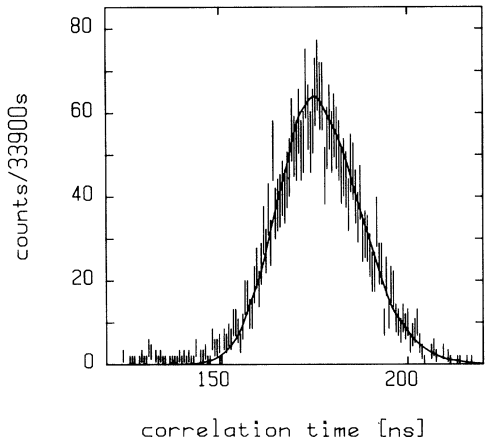

FIG. 1. Photoion-photoion coincidences at 80-eV photon energy for dissociation of H_2. Experimental data, points with error bars; Monte Carlo simulation, solid line. The time scale shown covers the range of electronically allowed correlation times which is larger than all possible flight-time differences of correlated ion fragments (solid line).

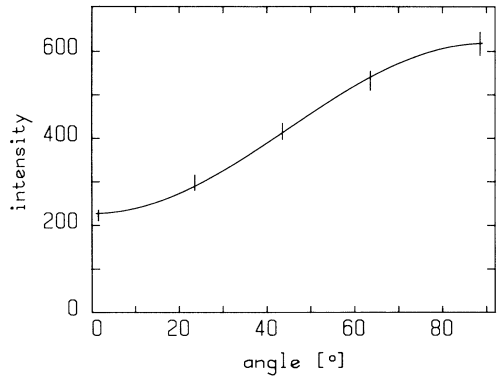

FIG. 2. Angle-dependent photoion-photoion coincidence intensities for H_2 at 80-eV photon energy. Experimental data, points with error bars; fit according to Eq. (3) with $P_1 = 0.778(3)$ and $\lambda = -1.4(1.0)$, solid line. The angle is given with respect to the major axis of the polarization ellipse of the light.

improved calculations of the cross section and might play a role also for the explanation of the observed negative β_m values.

For the investigation of the double photoionization in H_2, photoion-photoion coincidences (PIPICO)[16,17] were collected by means of a time-of-flight analyzer operating with pulsed electric fields, synchronized in the present work to the pulsed time structure[18] of the electron storage ring Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung (BESSY), Berlin, and adapted for the necessary angle-resolved measurement. The performance of our time-of-flight analyzer and the necessary determination of its transmission and detection efficiency are described in detail for the case of single and double ionization of H_2 caused by electron impact.[19] The angle-resolved true coincidence count rate $N_t(\Phi)$ follows from[1,2,20]

$$N_t(\Phi) \sim \sigma(H^+,H^+)\{1+\tfrac{1}{4}\beta_m[1+3P_1\cos(2\Phi-2\lambda)]\}\,, \tag{3}$$

with Φ being the angle between the ion analyzer and the plane of the electron storage ring, λ the angle between the major axis of the polarization ellipse and this plane, and P_1 the degree of linear polarization with respect to the major and minor axis of the polarization ellipse. Computer calculations considering the angle dependence have shown that Eq. (3) also applies for the accepted solid angle of our analyzer. The quantities P_1 and λ of the monochromatized synchrotron light were measured by means of angle-resolved photoelectron spectrometry.[21]

Figure 1 shows the coincidence yield at 80-eV photon energy summed over five angles in order to improve the counting statistics. It can be seen that the experimental data (points with error bars) are described very well by a Monte Carlo simulation[19] (solid line) which considers the performance of our ion analyzer, the thermal velocity distribution, and the distribution of dissociation energies of H_2.[22] The small amount of coincidences at around 130 ns is due to false coincidences and will be subtracted from the measured total coincidence count rate. In Fig. 2 the angle-dependent PIPICO signals at 80-eV photon energy are shown together with a fit according to Eq. (3). The resulting β_m value is plotted together with further data at other photon energies in Fig. 3. By lowering the photon energy towards the threshold region, the β_m values decrease towards $\beta_m = -0.75$. This value implies that in the threshold region the D_Π amplitude dominates the double-photoionization process; i.e., the fragment ions fly apart during their Coulomb explosion preferentially perpendicular to the electric vector of the light. For the following discussion it is essential to emphasize that for double ionization in H_2—in contrast to atoms—a quite extended threshold region exists (cf. Fig. 3). Therefore, it is reasonable to assume that threshold effects take place over a much wider energy range, above (double-ionization continuum) and below (doubly excited states and excited states of H_2^+) the threshold energy. In this context, the slightly negative β_m values for photofragments of the first excited state of H_2^+ corroborate our result.[2]

For the two-electron ejection the dominant D_Π amplitude can contain contributions from many asymptotic orbital angular momentum l and l', but the sum of their projection quantum numbers must add to 1. A prediction of the resulting angular distribution parameter β_e of the emitted electrons is not possible since the strength and the interference of the individual l,l' contributions are not known. However, at this point one might specu-

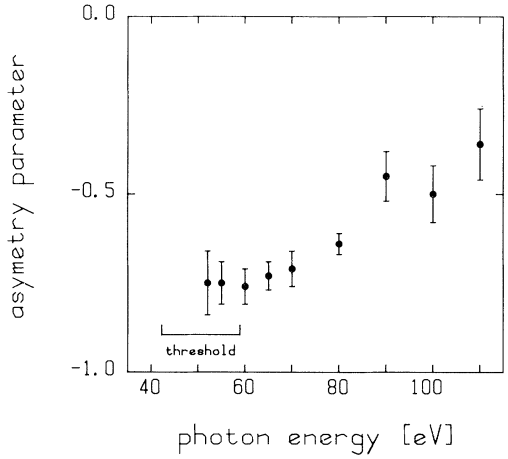

FIG. 3. Angular distribution parameter β_m of fragment ions following double photoionization in H_2. Values with smaller error bars come from measurements at five angles; for the other values three angle settings were taken. The nuclear motion in the molecular ground state causes for the double-ionization transitions an extended threshold range which is also indicated.

late that the requirement of Π symmetry allows comparison to the double photoionization in helium where around threshold high orbital angular momenta are present and lead to the prediction $\beta_e = -1$. Transferring β_e values close to -1 also to the case of H_2 one ends up with negative β_m and β_e values. In this situation the electrons and the fragment ions would fly apart preferentially perpendicular to the electric vector of the light. Whether the electronic and interprotonic axis are nearly orthogonal to each other as proposed for the threshold region of the four-particle breakup[23] cannot be answered here.

Absolute values for the $\sigma(H^+,H^+)$ cross section were obtained in the same manner as described in detail for the case of electron impact.[19] Briefly, a simultaneous measurement of coincident H^+ ions, $I(H^+,H^+)$, and H_2^+ ions, $I(H_2^+)$, and information on the transmission τ and detection efficiencies ϵ provided the cross-section ratio $\sigma(H^+,H^+)/\sigma(H_2^+)$:

$$\frac{\sigma(H^+,H^+)}{\sigma(H_2^+)} = \frac{I(H^+,H^+)}{\gamma I(H_2^+)} \frac{\tau(H_2^+)}{\tau(H^+,H^+)} \frac{1}{g^k} \frac{\epsilon(H_2^+)}{\epsilon(H^+)} \frac{1}{\epsilon(H^+)}, \quad (4)$$

where γ corrects for stray light contributions from the monochromator at high photon energies (the low coincidence rates prevented the use of suitable absorption foils which reduce the stray light; stray light was found to be important for the H_2^+ signal above 80-eV energy).[24] The factor g^k accounts for the ion transmission through the gold meshes of the analyzer. With the help of known data for $\sigma(H_2^+)$[24] absolute values of $\sigma(H^+,H^+)$ were established. They are shown in Fig. 4 together with other data. We ascribe to our values an uncertainty of 32% representing the mean of a linear and quadratic error combination of the individual contributions listed in the caption of Fig. 4. It can be seen that there is close agreement with the experimental data of Dujardin *et al.*[3] which are subject to an uncertainty of 70%.

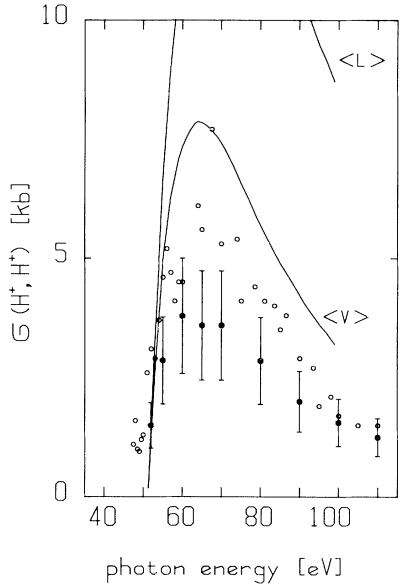

FIG. 4. Compilation of $\sigma(H^+,H^+)$ cross-section data for double photoionization in H_2. Present work, full circles with 32% error bars; the error contains [compare Eq. (4)] 3% counting statistics, 10% for $\sigma(H_2^+)$ which includes the error on γ, 1% for $\tau(H_2^+)$, 3.3% for $\tau(H^+,H^+)$, 4% for g^5, 6.5% for $\epsilon(H_2^+)/\epsilon(H^+)$, and 16% for $\epsilon(H^+)$. Open circles, experimental values of Dujardin *et al.* (Ref. 3). Solid lines, theoretical data of Le Rouzo (Refs. 4 and 5) for the length ($\langle L \rangle$) and velocity ($\langle V \rangle$) formulation, respectively.

Comparing our $\sigma(H^+,H^+)$ values with the calculation, it can be recognized (cf. Fig. 4) that the velocity-form and (even more pronounced) the length-form results are substantially higher. Only if the cross sections are multiplied by 0.3 or 0.5, respectively, the shape and magnitude of our cross section are well reproduced. We are unable to resolve this issue. We would only like to comment on three observations. First, in addition to the required proper theoretical treatment for the correlated motion of the two continuum electrons in the molecular two-center problem,[5] our result for the angular distribution parameter indicates that high asymptotic orbital angular momenta also might play an important role in the calculation of $\sigma(H^+,H^+)$, probably over an appreciable energy range up to 60-eV photon energy which is close to

the maximum of the $\sigma(H^+,H^+)$ cross section. Second, when comparing our $\sigma(H^+,H^+)$ and $\sigma(H_2{}^+)$ [24] values with the corresponding photoionization cross-section data of helium, a striking difference of the shapes of $\sigma(H_2{}^+)$ and $\sigma(He^+)$ appears; on the other hand, the ratios $\sigma(H^+,H^+)/\sigma(H_2{}^+)$ and $\sigma(He^{++})/\sigma(He^+)$ are quite similar. Third, looking at the corresponding data for electron impact,[19] the two-electron systems H_2 and He behave even more similarly: Up to 3.0-keV impact energy, the single-ionization cross sections have nearly the same shape, with $\sigma_e(H_2{}^+)$ being approximately larger than $\sigma_e(He^+)$ by a factor of 2. As in the case of photoionization the ratios $\sigma_e(H^+,H^+)/\sigma_e(H_2{}^+)$ and $\sigma_e(He^{++})/\sigma_e(He^+)$ are quite similar.

Although our observations for the angular distributions in the four-particle breakup of H_2 and for the single- and double-ionization cross section in H_2 and He caused by photon or electron impact give a quite consistent picture, the underlying mechanisms for our specific results still await clarification from the theoretical point of view. Therefore, the dynamics of double photoionization in the simplest molecular two-electron system remains an open problem.

It is a pleasure to thank the members of BESSY, especially W. Braun, for excellent research facilities and J. S. Briggs, J. Dehmerr, G. Dujardin, and H. Le Rouzo for helpful comments on the manuscript. This work has been funded by the German Federal Minister for Research and Technology (BMFT) under Contract No. 05 372 AA.

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