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Double photoionization of H_2: An experimental test of electronic-correlation models in molecules

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The double-photoionization cross sections of molecular hydrogen (H_2) and molecular deuterium (D_2) were measured by using the photoion-photoion coincidence method for photon energies ranging from the threshold energy around 50 eV up to, respectively, 140 and 98 eV. The comparison with the recent *ab initio* calculations of Le Rouzo [J. Phys. B **19**, L677 (1986)] indicates that an important part of the double-photoionization process is accounted for by a rigorous description of the electron-electron interaction in the initial state. As a by-product of this work, it was also concluded that double photoionization of hydrogen can be considered as a vertical process and that Franck-Condon approximations are quite valid to calculate the kinetic energy of the resulting $H^+ + H^+$ fragments.

I. INTRODUCTION

Double photoionization consists in the absorption of a *single* photon by an atom or a molecule followed by the ejection of *two* electrons. The interaction of a photon with each electron is independent from the others so that double photoionization is a forbidden process unless the electron-electron interactions are taken into account.

Such processes have been experimentally shown to occur in various atoms[1-8] and molecules.[9-18] Species with only two electrons (He,H_2) are of particular interest since, in such cases, there is no complication, neither experimentally nor theoretically, with the remaining electrons. The double photoionization of molecular hydrogen has never been studied so far, although the case of helium has given rise to numerous experimental[1,4,5,19] and theoretical works[20-26] in the past 20 years.

The experimental data on the double photoionization of helium, as obtained from the literature,[1,4,5,19] consist in the measurement of the total double-photoionization cross section for photon energies ranging from the threshold energy at 79 eV up to about 200 eV.

From a theoretical point of view the double-photoionization cross section can be expressed[20] as a sum of electronic matrix elements which account for the dipole transition from the initial state of the two bounded electrons to the final state of the two outgoing electrons. Within this model, the key point in the understanding of the double-photoionization processes is to be able to correctly represent the electronic correlations in the initial and final states of the two electrons. This was clearly demonstrated in the case of helium by Byron and Joachain.[20] They calculated the double-photoionization cross section of He by representing the two ejected electrons with a symmetrized product of uncorrelated Coulomb wave functions, focusing their attention on the representation of the two bounded electrons in the initial state ψ_i. A Hartree-Fock representation of ψ_i, which is known to poorly account for the electronic correlations, was shown to be strongly inadequate, whereas a well-correlated wave function ψ_i of the Hylleraas type was found by Byron and Joachain to give cross-section values in much better agreement with the experimental results. The complicated problem of considering the Coulomb interaction between the two outgoing electrons was investigated by Tiwary,[26] on the basis of the Altick representation.[27,28] Tiwary pointed out that the electronic correlations in the final state seem to play an important role both at high photon energies and at low photon energies near the threshold energy of double photoionization. His calculations also indicate that in the high-photon-energy region the electron-electron Coulomb interaction mainly acts at long distances, whereas the Coulomb interaction at short distances probably dominates for photon energies in the vicinity of the double-photoionization threshold energy. Another interesting way of taking into account the electronic correlations both in the initial and final states is the many-body perturbation theory as applied to the study of double photonization of helium by Carter and Kelly.[25]

At this point it seems, however, that the comparison of experimental with theoretical double-photoionization cross sections of helium is not sufficient to completely test the validity of different models. Additional experimental data on the kinetic energies and angular momenta of the two outgoing electrons would be useful. Also interesting is to extend the double-photoionization studies to another system with only two electrons, i.e., to molecular hydrogen. Although this latter species is a little bit more complicated, due to its molecular symmetry, it is simple enough to allow some new insights into the double-photoionization processes.

We report the first measurement of the double-photoionization cross section σ^{2+} of H_2. The cross section $\sigma^{2+}(E)$ was measured by using the photoion-photoion coincidence (PIPICO) method for photon energies E in the range 47.5—140 eV. We will discuss these results in connection with the recent theoretical work of Le Rouzo[29] on the double photoionization of hydrogen.

II. EXPERIMENTAL PROCEDURE

The ejection of the two electrons from a hydrogen molecule leads to the formation of a $H_2{}^{2+}$ species which turns out to be a pair of energetic protons due to the Coulomb repulsion.

The measurement of the double-photoionization cross section can thus be achieved by counting the number of pairs of protons produced as a function of the photon energy. For that purpose we used the recently developed photoion-photoion coincidence method[11] in which the two protons are detected with a single detector and the difference $\Delta t = t_{H^+} - t_{H^+}$ between their times of flight is measured by delayed coincidences. The experimental setup is identical to that previously described in detail in Ref. 11 and is schematically represented in Fig. 1.

Synchrotron radiation from ACO (Orsay's storage ring), dispersed by a grazing-incidence monochromator,[30] was used as a photon source of variable energy in the 47.5–140 eV range. In order to check that the second-order and stray-light components have negligible effects, the experiments were repeated with two different gratings having 450 and 1200 lines/mm and blazed, respectively, at 35 and 125 eV.

Most of the experiments were carried out with H_2 (L'air Liquide product, 99.9% purity), and some of them were repeated with D_2 (L'air Liquide product, 99.9% purity). One expects, *a priori*, that molecular hydrogen and deuterium have the same double photoionization cross sections. However, as will be seen in the following, some of the experimental correction factors depend on the mass of the detected ions. The comparison of results obtained with H_2 and D_2 is thus a test of the validity of our measurements. The pressure in the photoionization region is estimated to be about 10^{-3} torr. We believe that at such a low pressure ion-molecule collisional effects are negligible. This was checked by varying the pressure between 10^{-4} and 10^{-3} torr without any noticeable change in the results.

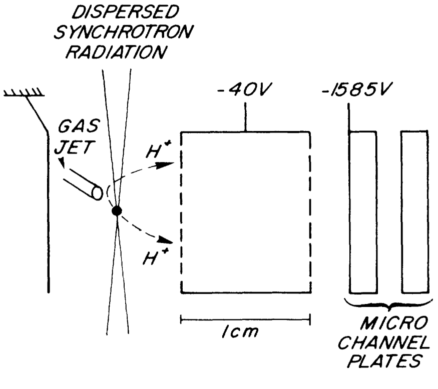

FIG. 1. Schematic diagram of the photoion-photoion coincidence PIPICO experiment.

TABLE I. Equilibrium distance in the $X\,{}^1\Sigma_g^+$ state, the thermodynamic and vertical double-ionization energies of H_2 and D_2.

	r_{H-H} (Å) (Ref. 31)[a]	Energy (eV) of the $H^+ + H^+$ limit (Refs. 31,32)[b]	Vertical energy (eV) of double ionization[b]
H_2	0.741 44	31.668	51.089
D_2	0.741 52	31.752	51.171

[a] Equilibrium distance in the $X\,{}^1\Sigma_g^+$ state.
[b] Energies are relative to the $X\,{}^1\Sigma_g^+(v=0)$ state.

A. Kinetic energy distribution of the fragments

As shown in Fig. 2, the double photoionization of hydrogen can be represented by a transition from the ${}^1\Sigma_g^+(v=0)$ ground state of neutral H_2 to the Coulomb repulsive curve of $H_2{}^{2+}$ of which the dissociation limit corresponds to the formation of $H^+ + H^+$. Some of the data related to the potential energy curves of H_2 and D_2 are summarized in Table I. It seems, *a priori*, reasonable to assume that double photoionization corresponds to a vertical transition, i.e., that the ejection of the two electrons is much more rapid than the separation of the two protons. In such a case the kinetic energy distribution of the two H^+ is predicted to be determined, within the Franck-Condon approximation, by the vibrational overlap integral for a transition from the $X\,{}^1\Sigma_g^+(v=0)$ ground state of H_2 to the Coulomb repulsive state of $H_2{}^{2+}$. The theoretical kinetic energy distribution, as calculated by

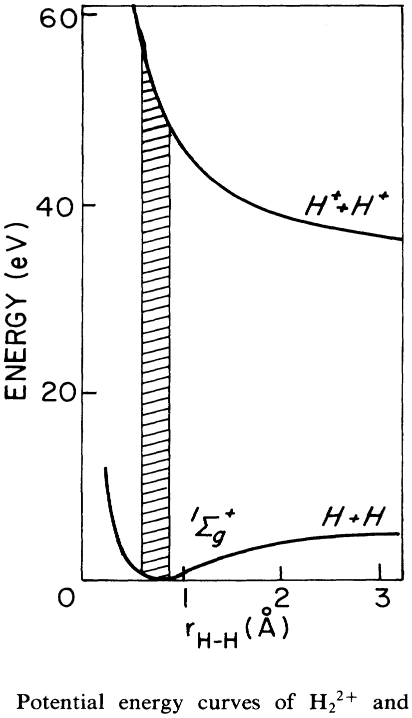

FIG. 2. Potential energy curves of $H_2{}^{2+}$ and the $X\,{}^1\Sigma_g^+$ ground state of H_2.

McCulloh,[33] is shown in Fig. 3. The validity of the Franck-Condon approximations was checked by several authors who measured the kinetic energy distribution of the two protons when producing double ionization of H_2 by electron impact[34,35] or ion impact.[36,37] In our experiment, where double ionization is produced by photon impact, the kinetic energy distribution of the fragments can be obtained by comparing the experimental photoion-photoion coincidence curve with those simulated with various kinetic energy distributions. This method was previously used in the case of CO_2,[15] NH_3,[17] HCl,[38] and HI,[38] and is illustrated in the case of H_2 in Fig. 4. Throughout the photon energy range that we investigated, the PIPICO curves have approximately the same shape as that recorded at a 70-eV photon energy which is shown in Fig. 4(a) as an example. The PIPICO curves recorded at photon energies near the double-photoionization threshold ($h\nu < 58$ eV) probably have different shapes due to the different kinetic energy distributions that we expect to obtain at these energies. However, the low intensity of double photoionization near the threshold energy prevented us from observing such changes of the PIPICO curves. The simulated PIPICO curves in Figs. 4(b)—4(d) were obtained by using the procedure of Ref. 12 and by considering the kinetic energy of the $H^+ + H^+$ fragments is distributed respectively over the curve of Fig. 3 [Fig. 4(b)], a Gaussian function centered at 18.8 eV with a full width at half maximum (FWHM) of 3 eV [Fig. 4(c)] and a Gaussian function centered at 18.8 eV with a FWHM of 12 eV [Fig. 4(d)].

From the curves in Fig. 4 we see that the kinetic energy distribution of Fig. 3, as calculated by McCulloh,[33] is quite compatible with that obtained in our experiments [Fig. 4(a)]. Other kinetic energy distributions such as those used to simulate the PIPICO curves in Figs. 4(c) and 4(d) clearly disagree with our results.

We conclude that double photoionization of hydrogen can be considered as a vertical process and that the Franck-Condon approximations are quite valid to calculate the kinetic energy of the $H^+ + H^+$ fragments.

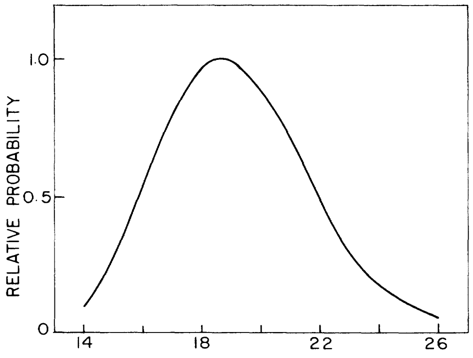

FIG. 3. Theoretical kinetic energy distribution of the two protons issued from the double photoionization of H_2 as calculated by McCulloh (Ref. 33).

B. Double-photoionization cross sections

Considering the $H_2 + h\nu \rightarrow H^+ + H^+$ process, the total number N_c of detected photoion-photoion coincidences can be expressed by

$$N_c = A\sigma^{2+}(E) f_{H^+} f_{H^+} d(H^+,H^+) \ . \quad (1)$$

$\sigma^{2+}(E)$ is the double-photoionization cross section at the photon energy E and f_{H^+} is the detection efficiency of H^+ ions. We will see in the following that the ion detection efficiency depends on the mass of the ions and also on the high voltage of the multichannel plates. The $d(H^+,H^+)$ factor is the proportion of created pairs of protons which can reach the ion detector. We see indeed in Fig. 4(a) that the PIPICO curve is depressed at low Δt values. This corresponds to pairs of protons which are emitted perpendicularly to the direction of acceleration and which cannot reach the ion detector due to the angular discrimination of the various parts of the time-of-flight detector. The coefficient A in Eq. (1) is a function of the time of accumulation, the density of molecules, the

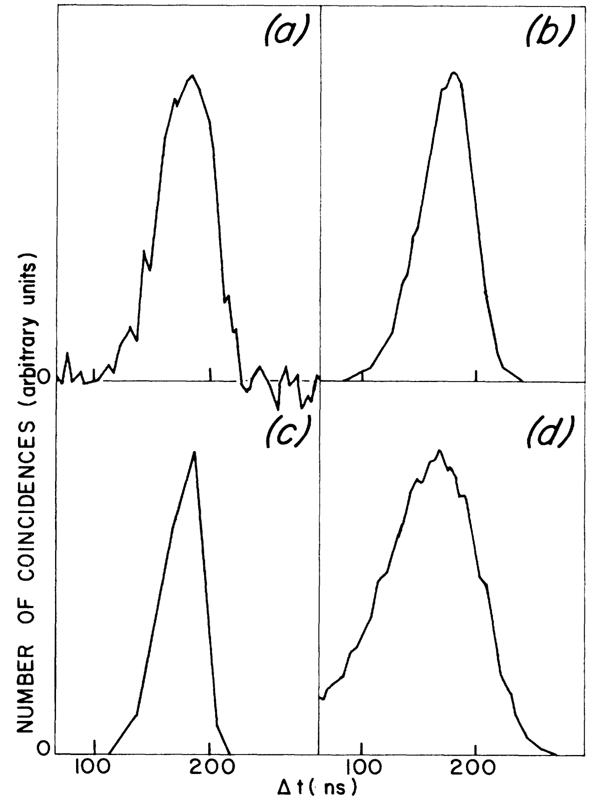

FIG. 4. Comparison of experimental with simulated PIPICO curves. (a) Experimental PIPICO curve recorded at a photon energy of 70 eV. (b) Simulated PIPICO curve obtained for the distribution of kinetic energy given in Fig. 3. (c) Simulated PIPICO curve obtained for a Gaussian distribution of the kinetic energy centered at 18.8 eV with a FWHM of 3 eV. (d) Simulated PIPICO curve obtained for a Gaussian distribution of the kinetic energy centered at 18.8 eV with a FWHM of 12 eV.

photon flux, and the volume of the ionization region.

The total number of detected ions N_i, as counted during the same time of accumulation without any coincidence, can be expressed by

$$N_i = A[2\sigma^{2+}(E) f_{\mathrm{H}^+} d_2(\mathrm{H}^+) + \sigma^{+}_{\mathrm{H}_2^+}(E) f_{\mathrm{H}_2^+} + \sigma^{+}_{\mathrm{H}^+}(E) f_{\mathrm{H}^+} d_1(\mathrm{H}^+)] \ . \tag{2}$$

$\sigma^{+}_{\mathrm{H}_2^+}(E)$ and $\sigma^{+}_{\mathrm{H}^+}(E)$ are the single-ionization cross sections for the formation of, respectively, the stable and dissociative states of $\mathrm{H}_2{}^+$ at the photon energy E, $f_{\mathrm{H}_2^+}$ is the ion detection efficiency of $\mathrm{H}_2{}^+$, and $d_1(\mathrm{H}^+)$ and $d_2(\mathrm{H}^+)$ are the proportions of protons issued respectively from single dissociative ionization and double ionization which can reach the ion detector. Equation (2) was obtained by assuming that the proportion of $\mathrm{H}_2{}^+$ ions produced which can reach the detector is unity because of their zero initial kinetic energy. We emphasize that the $d(\mathrm{H}^+,\mathrm{H}^+)$ and $d_2(\mathrm{H}^+)$ factors have different values since they are related to coincidence and noncoincidence detection, respectively.

By considering that $\sigma^{2+}(E) < \sigma^{+}_{\mathrm{H}_2^+}(E)$, $\sigma^{+}_{\mathrm{H}^+}(E) < \sigma^{+}_{\mathrm{H}_2^+}(E)$, and that $2 f_{\mathrm{H}^+} d_2(\mathrm{H}^+)$ and $f_{\mathrm{H}^+} d_1(\mathrm{H}^+)$ are approximately equal to $f_{\mathrm{H}_2^+}$, one obtains an approximated expression of N_i as a function of the absorption cross section $\sigma_{\mathrm{abs}}(E)$ at the photon energy E:

$$N_i = A \sigma_{\mathrm{abs}}(E) f_{\mathrm{H}_2^+} \ , \tag{3}$$

with $\sigma_{\mathrm{abs}}(E) = \sigma^{+}_{\mathrm{H}_2^+}(E) + \sigma^{+}_{\mathrm{H}^+}(E) + \sigma^{2+}(E)$, by assuming that at high photon energies the photoionization efficiency is unity.

The validity of these approximations can be checked, for example, at a photon energy of 60 eV. We will see in Sec. III that at this energy $\sigma_{\mathrm{abs}} \simeq 0.25$ Mb and $\sigma^{2+} \simeq 0.45 \times 10^{-2}$ Mb. From the results of Backx *et al.*,[39] we deduced that $\sigma^{+}_{\mathrm{H}^+}$ (60 eV)$\simeq$0.035 Mb and $\sigma^{+}_{\mathrm{H}_2^+}$(60 eV)$\simeq$0.21 Mb. Furthermore, the $d_1(\mathrm{H}^+)$ and $d_2(\mathrm{H}^+)$ factors can be obtained by simulating the ion trajectories (see method in Ref. 12) and by assuming that the kinetic energy distributions are those given, respectively, by McCulloh[33] and Landau *et al.*[40] By this method we obtain $d_1(\mathrm{H}^+) = 0.6$ and $d_2(\mathrm{H}^+) = 0.2$. We will see in the following that f_{H^+} and $f_{\mathrm{H}_2^+}$ are equal, respectively, to 0.21 and 0.15 in our experimental conditions. It follows that the value of N_i in expression (3) is the same as that in (2) with an uncertainty of about 2% which will be found to be negligible as compared to the experimental uncertainties.

From relations (1) and (3) one thus obtains

$$\frac{N_c}{N_i} = \frac{\sigma^{2+}(E) f_{\mathrm{H}^+} f_{\mathrm{H}^+} d(\mathrm{H}^+,\mathrm{H}^+)}{\sigma_{\mathrm{abs}}(E) f_{\mathrm{H}_2^+}} \ . \tag{4}$$

The number of coincidences N_c is obtained by integrating the experimental PIPICO curve over all the Δt values, whereas N_i is directly measured during the same experimental time with a counter. The determination of $\sigma^{2+}(E)$ from relation (4) thus requires the knowledge of f_{H^+}, $f_{\mathrm{H}_2^+}$, and $d(\mathrm{H}^+,\mathrm{H}^+)$ by assuming that $\sigma_{\mathrm{abs}}(E)$ is known from the literature (see Sec. III).

1. Determination of $d(\mathrm{H}^+,\mathrm{H}^+)$

The discrimination factor $d(\mathrm{H}^+,\mathrm{H}^+)$ can easily be obtained from the simulated PIPICO curve of Fig. 4(b) as being equal to the total number of coincidences relative to the number of trajectories used in the simulation. This factor depends on the kinetic energy distribution of the protons. At high photon energies ($h\nu \geq 58$ eV), the shape of the kinetic energy distribution does not vary with $h\nu$ and is identical to that in Fig. 3, whereas for photon energies between 47 and 58 eV, it varies with $h\nu$ according to the distribution of the Franck-Condon factors. The $d(\mathrm{H}^+,\mathrm{H}^+)$ factor was thus estimated to be equal to 0.093 for $h\nu \geq 58$ eV and to increase up to 0.13 at 47 eV. In the case of deuterium we used the kinetic energy distribution calculated by Fournier *et al.*[37] The $d(\mathrm{D}^+,\mathrm{D}^+)$ values that we obtained are very similar to that of $d(\mathrm{H}^+,\mathrm{H}^+)$.

2. Determination of f_{H^+}, f_{D^+}, $f_{\mathrm{H}_2^+}$, *and* $f_{\mathrm{D}_2^+}$

The determination of the absolute values of the detection efficiency of the ion detector is essential in the measurement of the double-photoionization cross sections. We thus will explain in detail how we got these values.

In our experiment, a negative high voltage varying from 1585 to about 3000 V is directly applied to the entrance of the multichannel plates used as an ion detector. It follows that ions are strongly accelerated prior to detection so that we will assume in the following that the detection efficiency may depend on the mass of the ions, and on the high voltage, but is independent of the initial kinetic energy of these species.

It is well known[41] that the detection efficiency reaches an asymptotic value at high values of the acceleration field and that this asymptotic value is independent of the mass of the ions. We also observed such a trend by measuring the total count of ions as a function of the high voltage. The ion count reached an asymptotic value for voltage higher than about 2500 V. We thus assumed that the detection efficiency has the same value $f_{\max}$, whatever the ion produced, provided that the high voltage of the ion detector is higher than 2500 V. The $f_{\max}$ value was obtained from a separate experiment on SO_2. The double-photoionization cross section of SO_2 was previously determined by Dujardin *et al.*[11] who measured the ion-detection efficiency of using a threshold photoelectron-photoion coincidence method. By using their double-photoionization cross-section data and by repeating the PIPICO experiment on SO_2 with the present ion detector we obtained $f_{\max} = 0.33$. In the case of hydrogen it was unfortunately not possible to work with a very high voltage in the ion detector. We chose a potential of 1585 V in order to decrease the false coincidence background due to the noise of the ion detector which occurs at low Δt values. By counting the relative number of ions detected with a 2500- and a 1585-V voltage on the ionic detector, we obtained the mean value of the detection efficiency over the various ions produced. At a photon energy of 65 eV these values at 1585 V were, respectively, 0.16 and 0.12 with hydrogen and deuterium. The abundances of the parent and fragment ions produced by photoionization of H_2 and D_2 at 65 eV are known from the work of Backx *et al.*[39] The detection efficiency for each ion could then be obtained by assuming that $f_{H_2^+}=f_{D^+}$ and that $f_{H^+}/f_{H_2^+}=f_{D^+}/f_{D_2^+}$, which yields the following values:

$$f_{H^+}=0.21,\ f_{H_2^+}=f_{D^+}=0.15,\ f_{D_2^+}=0.11\ .$$

The uncertainties on the detection efficiencies are estimated to be about 10%.

To end this section we note that PIPICO experiments were repeated for two different positions of the time-of-flight axis at 90° from each other in the plane perpendicular to the synchrotron beam direction. The absence of variation of the measured double-photoionization cross section led us to conclude that anisotropy effects were negligible in our experiment.

III. RESULTS AND DISCUSSION

The $\sigma^{2+}/\sigma_{\text{abs}}$ ratio of the double-photoionization cross section to the photoabsorption cross section was obtained for hydrogen in the 47.5—140-eV photon energy range and for deuterium in the 50—98-eV energy range by using the relation (4) developed in Sec. II.

The results are shown in Tables II and III and in Figs. 5 and 6. The uncertainties on the $\sigma^{2+}/\sigma_{\text{abs}}$ values are estimated to be about 50%, due to the uncertainties on the measurement of N_c/N_i ($\simeq$20%) plus those on the ion-detection efficiencies ($\simeq$30%). First of all, we remark that the results are quite similar to those of hydrogen and with deuterium, which is a test of consistency since no difference is, *a priori*, expected to occur between the electronic part of the double-photoionization cross sections of these two compounds.

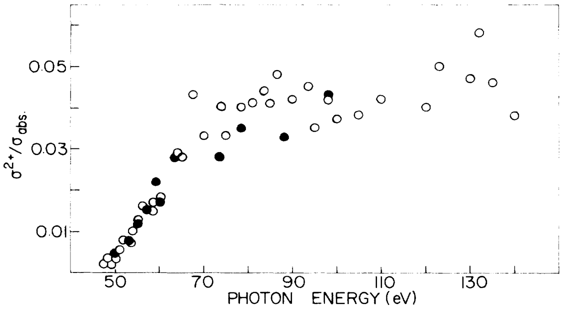

FIG. 5. Ratio of the double-photoionization to the photoabsorption cross sections as a function of the photon energy. ○ shows results obtained for hydrogen; ● shows results obtained for deuterium.

TABLE II. Relative and absolute values of the double-photoionization cross section (σ^{2+}) of hydrogen as a function of the photon energy. σ_{abs} is the total photoabsorption cross section.

Photon energy (eV)	$\sigma^{2+}/\sigma_{\text{abs}}$	σ^{2+} (10^{-20} cm^2)
47.5	0.0019	0.11
48	0.0029	0.16
48.5	0.0019	0.10
49	0.0018	0.095
49.5	0.0024	0.12
50	0.0027	0.13
51	0.0056	0.26
52	0.0074	0.31
53	0.0072	0.29
54	0.010	0.37
55	0.013	0.46
56	0.0158	0.52
57	0.0154	0.47
58	0.147	0.41
59	0.017	0.45
60	0.0178	0.45
64	0.029	0.61
65	0.028	0.56
67.5	0.043	0.77
70	0.033	0.53
74	0.040	0.54
75	0.033	0.41
78.5	0.040	0.44
81	0.041	0.41
83.5	0.044	0.40
85	0.041	0.35
86.5	0.048	0.38
90	0.042	0.29
93.5	0.045	0.27
95	0.035	0.19
98	0.042	0.21
100	0.037	0.17
105	0.038	0.15
110	0.042	0.15
120	0.040	0.12
123	0.050	0.13
130	0.047	0.11
132	0.058	0.12
135	0.046	0.09
140	0.038	0.07

We see from Fig. 6 that the threshold energy for double photoionization of H_2 is well below the vertical energy at 51.1 eV (see Table I). As is shown in Fig. 2, this reflects the strongly repulsive part of the $H^+ + H^+$ Coulomb curve near the equilibrium geometry of the neutral H_2 molecule.

The $\sigma^{2+}/\sigma_{\text{abs}}$ ratio reaches an asymptotic value of about 4% for photon energies higher than 80 eV. The only value in the literature which can be compared with this measurement is that of Brehm and De Frênes[35] who used electron impact on H_2 to obtain a maximum value of the $\sigma^{2+}/\sigma_{\text{abs}}$ ratio of about 6×10^{-3} which is almost 10 times smaller than our asymptotic value. This difference is most probably due to an underestimation of this ratio by Brehm and De Frênes rather than to a significant change when going from photon impact to electron impact.

It is noticeable that the behavior of $\sigma^{2+}/\sigma_{\text{abs}}$ as a func-

TABLE III. Ratio of the double-photoionization to the photoabsorption cross sections of deuterium as a function of the photon energy.

Photon energy (eV)	$\sigma^{2+}/\sigma_{\text{abs}}$
50	0.0042
53	0.0074
55	0.012
57	0.0152
59	0.022
60	0.017
63.5	0.028
73.5	0.028
78.5	0.035
88	0.033
98	0.043

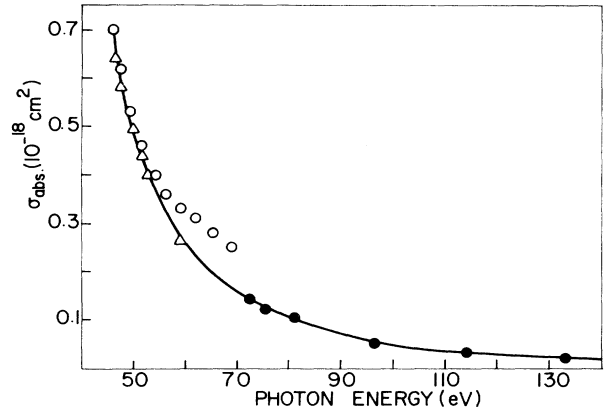

FIG. 7. Photoabsorption cross section of hydrogen. △ are results of Samson and Cairns (Ref. 42). ○ are results of Lee *et al.* (Ref. 43). ● are results of Alaverdov and Podolyak (Ref. 44). The solid curve was drawn by hand to fit the experimental values.

tion of the photon energy as shown in Fig. 5 is similar to that obtained with helium by Holland *et al.*[5] We note in particular that the asymptotic value is about the same in both these cases.

In order to deduce the absolute values of σ^{2+} we used the values of the absorption cross section σ_{abs} which are represented by the solid curve in Fig. 7. This curve was drawn by hand to fit the experimental results of Samson and Cairns,[42] Lee *et al.*,[43] and Alaverdov and Podolyak.[44] The resulting values of σ^{2+} are shown in Table II and in Figs. 8 and 9. We note that σ^{2+} increases almost linearly for photon energies between 50 and 60 eV, reaches a maximum value of about 0.7×10^{-20} cm^2 at 65 eV, and then decreases at higher photon energies. Relative error bars are 20%, whereas the absolute values have total uncertainties of about 70%.

Also shown in Fig. 8 are the results of the recent theoretical study of Le Rouzo.[29] The *ab initio* calculation of the double-photoionization cross section of H_2 was performed at the fixed equilibrium geometry of the neutral molecule in its electronic ground state. This calculation is thus not believed to be able to reproduce the variation of the cross section near the double-photoionization threshold energy where the vibration of the molecule has a strong influence. We expect, however, this influence to be negligible at higher photon energies ($h\nu\geq 55$ eV). The basic idea of the work of Le Rouzo[29] was to calculate the double-photoionization cross section, within the electric dipole approximation, by using a very well correlated wave function ψ_i of the initial state of neutral H_2 as optimized by Hagström and Shull,[45] whereas he chose for the final state a symmetrized product of uncorrelated Coulomb wave functions as was done by Byron and Joachain[20] in the case of helium. Within this model the double-ionization process is considered to be due to electron-correlation effects, which is markedly different from the case of double ionization by electron or ion im-

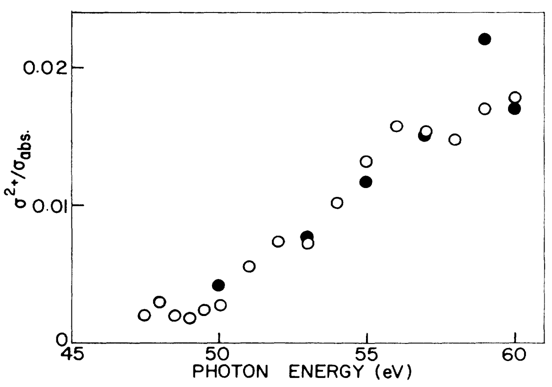

FIG. 6. Ratio of the double-photoionization to the photoabsorption cross sections as a function of the photon energy. ○ shows results obtained for hydrogen; ● shows results obtained for deuterium.

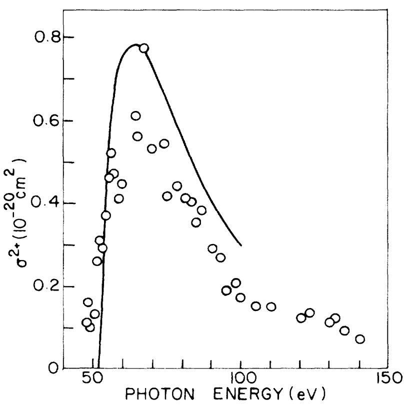

FIG. 8. Double-photoionization cross section of hydrogen as a function of the photon energy. ○ are experimental results from this work. The solid curve represents the calculated values of Le Rouzo (Ref. 29).

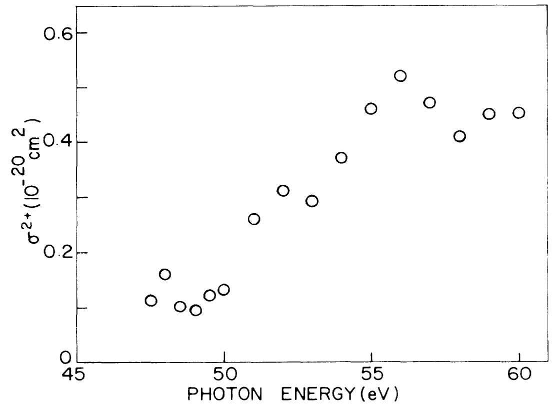

FIG. 9. Double-photoionization cross section of hydrogen as a function of the photon energy.

pact where the shakeoff and double-collision processes are considered to be dominant.[46–49]

The agreement between the experimental and calculated values of the double-photoionization cross section is excellent (see Fig. 8) as long as we consider the variation of this quantity as a function of the photon energy. The absolute values of the experimental and calculated cross sections are also in reasonable agreement.

The energy dependence of the double-photoionization cross section, as shown in Fig. 8, has to be analyzed differently whether we consider the increasing part above the threshold or the decreasing behavior at high photon energies. According to the theory of Wannier[50] the threshold law for double photoionization is mainly governed by interactions outside the "reaction zone." It follows, in particular, that the long-range terms in $1/R$ and $R^{-3/2}$ (R is the distance between the two outgoing electrons) in the interaction potential are dominant as compared to the angular-momentum-dependent terms in $L(L+1)/R^2$. The increasing part of the σ^{2+} curve and its maximum at about 65 eV has thus a specific meaning, although it looks like the threshold behavior of the simple-ionization cross section of numerous atoms and molecules of which a typical example is the $4d$ ionization of xenon.[51] In this latter case the energy dependence of the photoionization cross section is more likely considered to be determined by potential barrier effects due to the $L(L+1)/R^2$ term in the potential energy.[51] At higher photon energies the threshold law for double photoionization is no more valid and the decreasing of the σ^{2+} curve (Fig. 8) may be ascribed, like in the case of the single-ionization cross section (Fig. 7), to a lowering of the overlap of the initial and final electronic wave functions in the reaction zone due to the high kinetic energy of the ejected electrons.

To end this part, we remark that from both the experimental and theoretical results of Fig. 8, there seems to exist no structure in the σ^{2+} curve such as those mentioned by Masuoka,[52] on the basis of the photoion spectrum of H^+ produced from photon impact on H_2. We note in particular, from the calculations of Le Rouzo,[29] that the partial cross sections corresponding to pairs of electrons in the final state with different angular momenta, i.e., s,p and p,d pairs of electrons, have a maximum at about the same photon energy. This makes unlikely the existence of structures in the σ^{2+} curve.

IV. CONCLUSION

Studying the double photoionization of H_2 and D_2 has been shown to be possible by using the photoion-photoion coincidence method. The comparison of the experimental values of the double-photoionization cross section with those recently calculated by Le Rouzo indicates that the main features of the double-photoionization process can be understood within the "wave-function" model, which accounts for the electron-correlation effects in terms of a well-correlated initial wave function. There exists, however, at the present time, some limitations to a better understanding of these processes. On the experimental side it seems to be difficult to obtain the absolute values of the double-photoionization cross sections with a much better precision than in the present work ($\simeq$70%), mainly due to the difficulty of getting accurate values of the single-photoionization cross section and of the efficiency of the ion detector. On the theoretical side it would be necessary, in order to obtain a complete description, to express the final-state wave function of the two outgoing electrons by taking into account both the symmetry of the molecule and the electron-correlation effects, which also turns out to be a difficult task.

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