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FAST TRACK COMMUNICATION

Two-photon double ionization of the hydrogen molecule

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Abstract
Cross sections for the removal of both electrons of the hydrogen molecule by two photons are presented at 30 eV photon energy using the time-dependent close-coupling method. Our approach allows detailed information about the dynamics of the ionization process to be extracted, including angular distributions for the outgoing electrons. Analysis of our calculations reveals some similarities to the analogous process of two-photon double ionization of helium, but also uncovers some purely molecular effects. For example, we find that the differential cross sections vary with the kinetic energy released to the outgoing protons if the molecule is parallel to the polarization direction, but do not vary if the molecule is perpendicular to the polarization direction.

(Some figures in this article are in colour only in the electronic version)

Few-photon multiple ionization processes in light atoms and molecules are currently a timely and exciting field of study in atomic collision physics. The advent of free-electron lasers (FELs) such as at the FLASH facility in Germany, which provide intense photon sources over wide energy ranges, coupled with the latest experimental techniques, such as COLTRIMS spectroscopy, allow maximal extraction of information about the ionization dynamics [1]. Anticipating these exciting experimental advances, much theoretical effort has recently been placed in calculating cross sections for the two-photon double ionization of helium [2–11]. Although even the magnitude of the two-photon double ionization cross section has been under intense debate, it appears that fully converged non-perturbative methods are coming to some agreement [10] near the only available experimental data point [12] for the total cross section. Also, several of these methods allow the calculation of fully differential cross sections for this process [4, 7, 9]. In addition, the role of sequential versus non-sequential ionization for the two-electron escape is currently under scrutiny [10].

There has been also recent progress in the study of the single-photon double ionization of H_2, in which experimental measurements of fully differential cross sections [13, 14] have recently been confirmed by the latest theoretical techniques [15–18]. These theoretical and experimental studies have uncovered ionization dynamics unique to molecules, such as dependence of the electron angular distributions on the orientation of the molecule with respect to the polarization direction, and on the kinetic energy released to the protons. These single-photon studies are complemented by intense efforts in examining the strong-field (multiphoton) ionization of molecules (see [19] for a review). Experimental work in this field has recently focused, for example, on short-pulse laser ionization of H_2 and control of the Coulomb explosion after multiphoton ionization [20]. These techniques have been used to propose a 'molecular clock' [21] which can distinguish recollision processes from non-sequential processes in strong-field ionization. Such work is complemented by calculations of these (one-electron) multi-photon processes in H_2^+ and H_2, some of which has been able to include the nuclear vibrational motion in the calculations so that dissociative processes may be investigated in tandem with experiment [22].

In this communication, we demonstrate that the time-dependent close-coupling method is capable of combining the first two fields described, in the study of two-photon double ionization of H_2. Two-photon ionization is of interest as it probes final-state correlations in the H_2 system of a gerade symmetry, unlike single-photon ionization which can only

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result in final ungerade states. We emphasize that we are not exploring the well-studied strong-field ionization of H_2, in which multiphoton ionization by 10 or more photons is common. Rather, we focus on few-photon processes and on the correlated electron dynamics which results when two electrons are instantaneously ejected from H_2 by two photons. We present the total and triple differential cross sections (TDCS) for this process at a photon energy of 30 eV. We employ the 'fixed-nuclei' approximation, which assumes that both electrons are doubly ionized from the molecule before the nuclei begin to move apart, which is a very good approximation due to the large mass differences between the protons and electrons, and when the electrons are ejected with sufficient energy so that they move quickly away from the nuclei. If the length of the incoming laser pulse is long, it may be necessary to relax the fixed-nuclei approximation, since there is the possibility that the molecule could stretch between absorption of the two photons. However, for now we focus on the short pulse case where both photons are absorbed instantaneously and so our assumption that the nuclei do not move is valid. Thus we focus solely on the electron dynamics of the double ionization into this gerade final state. Since there are no other theoretical or experimental works with which to compare our cross sections, we compare and contrast our results to equivalent two-photon double ionization cross sections for helium. We also examine the TDCS as a function of internuclear separation (which is equivalent to a dependence on the kinetic energy release to the outgoing protons).

The time-dependent Schrödinger equation for a two-electron molecule in a strong time-varying laser field may be written as

$$\mathrm{i}\frac{\partial \psi(\vec{r}_1, \vec{r}_2, t)}{\partial t} = (H_{\mathrm{mol}} + H_{\mathrm{rad}})\psi(\vec{r}_1, \vec{r}_2, t), \qquad (1)$$

where H_{mol} is the molecular Hamiltonian and H_{rad} represents the interaction of the electromagnetic field (which has frequency ω and intensity I) with the molecule. We expand the time-dependent wavefunction for a given MS symmetry in products of rotation functions

$$\psi(\vec{r}_1, \vec{r}_2, t) = \sum_{m_1, m_2} \frac{P^M_{m_1 m_2}(r_1, \theta_1, r_2, \theta_2, t)}{r_1 r_2 \sqrt{\sin\theta_1}\sqrt{\sin\theta_2}} \Phi_{m_1}(\phi_1)\Phi_{m_2}(\phi_2), \qquad (2)$$

where $\Phi_m(\phi) = \frac{\mathrm{e}^{\mathrm{i}m\phi}}{\sqrt{2\pi}}$ and $M = m_1 + m_2$ is the projection of total electronic angular momentum onto the z-axis. Substitution of equation (2) into equation (1), and an application of the variational principle yields a set of time-dependent close-coupled partial differential equations which are given by

$$\begin{aligned}
\mathrm{i}\frac{\partial P^M_{m_1 m_2}(r_1, \theta_1, r_2, \theta_2, t)}{\partial t}
&= T_{m_1 m_2}(r_1, \theta_1, r_2, \theta_2) P^M_{m_1 m_2}(r_1, \theta_1, r_2, \theta_2, t) \\
&\quad + \sum_{m_1', m_2'} V^M_{m_1 m_2, m_1' m_2'}(r_1, \theta_1, r_2, \theta_2) P^M_{m_1' m_2'}(r_1, \theta_1, r_2, \theta_2, t) \\
&\quad + \sum_{M''} \sum_{m_1'', m_2''} W^{MM''}_{m_1 m_2, m_1'' m_2''}(r_1, \theta_1, r_2, \theta_2, t) \\
&\quad \times P^{M''}_{m_1'' m_2''}(r_1, \theta_1, r_2, \theta_2, t).
\end{aligned} \qquad (3)$$

Expressions for the kinetic energy, one-electron potential and two-electron potential terms may be found in [23]. The $W^{MM''}_{m_1 m_2, m_1'' m_2''}$ term represents the interaction of the electromagnetic field with the molecule.

The exact lattice eigenfunction for the H_2 ground state is obtained as previously, by relaxation of the Schrödinger equation in imaginary time [23]. By using seven terms in the expansion over rotation functions, the relaxation procedure results in a fully correlated initial state of H_2 on the lattice. We solve the time-dependent close-coupling equations using lattice techniques to obtain a discrete representation of the reduced wavefunctions and all operators on a four-dimensional radial and angular grid. A 384 × 384 × 32 × 32 point lattice is employed with a uniform mesh spacing of 0.15 au in both r_1 and r_2 and a mesh spacing of 0.03125π in both θ_1 and θ_2. For the linear polarization calculation, seven coupled channels were again employed in the real time propagation to the final $M = 0$ symmetry. For the circular polarization calculation, 14 coupled channels were employed in the real time propagation to the final M symmetries. The boundary condition at $t = 0$ for the reduced wavefunction is simply $P^M_{m_1 m_2}(r_1, \theta_1, r_2, \theta_2, t = 0) = P^{M_0}_{m_1 m_2}(r_1, \theta_1, r_2, \theta_2, \tau\ (=\mathrm{i}t) \rightarrow \infty)$, where $P^{M_0}_{m_1 m_2}$ is the reduced wavefunction for ψ_0, the ground state of H_2.

The total cross section for two-photon double ionization for a given M symmetry can be written, following [4], as

$$\sigma(2\gamma, 2e) = \left(\frac{\omega}{I}\right)^2 \frac{\mathcal{P}_{kk}}{T}, \qquad (4)$$

where $\mathcal{P}_{kk}$ is the probability for double ionization, and T is the effective pulse duration. For the $M = 0$ case the contamination of the final time-dependent wavefunction by the initial state $P^{M_0}_{m_1 m_2}(r_1, \theta_1, r_2, \theta_2, \tau \rightarrow \infty)$ must be removed, which is accomplished by subtracting the overlap of the initial state with the final state. Equation (3) is usually propagated for ten laser cycles where the pulse has constant amplitude and is ramped on and off smoothly over one laser period. We note that changing the shape of the pulse (e.g. to a sine-squared pulse) can affect the total ionization cross section somewhat, but not the angular distributions [7].

For a fixed internuclear separation, two-photon double ionization of H_2 results in a fixed amount of energy available to be shared between the two electrons. In considering TDCS from this process, various choices are available to us, depending on the polarization of the field, and on the orientation of the molecule with respect to the field. For example, if linear polarized light is used, and the molecule is parallel to the polarization direction, only $\Delta M = 0$ transitions are possible (a: $^1\Sigma_{\mathrm{g}} \rightarrow {}^1\Sigma_{\mathrm{u}} \rightarrow {}^1\Sigma_{\mathrm{g}}$). If linear polarized light is used but the molecule is perpendicular to the polarization direction, $\Delta M = \pm 1$ transitions are possible (b: $^1\Sigma_{\mathrm{g}} \rightarrow {}^1\Pi_{\mathrm{u}} \rightarrow {}^1\Delta_{\mathrm{g}}$ and $^1\Sigma_{\mathrm{g}} \rightarrow {}^1\Pi_{\mathrm{u}} \rightarrow {}^1\Sigma_{\mathrm{g}}$). Also, if (right) circularly polarized light is used only $\Delta M = +1$ transitions are possible (c: $^1\Sigma_{\mathrm{g}} \rightarrow {}^1\Pi_{\mathrm{u}} \rightarrow {}^1\Delta_{\mathrm{g}}$). If the molecule is oriented at an arbitrary direction with respect to the polarization direction, then contributions from all possible final states must be considered when computing a TDCS. However, it is unclear at present if such distributions could be measured, given the strong tendency for molecules to quickly

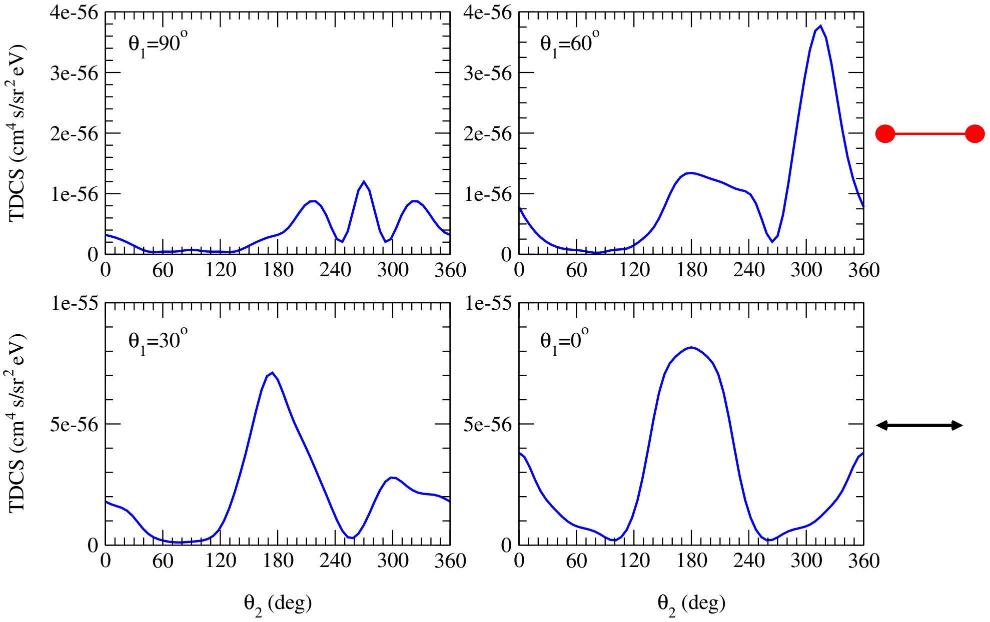

Figure 1. TDCS for the two-photon double ionization of H_2 at 30 eV photon energy, for equal energy sharing between the outgoing electrons, and for various values of θ_1, using linearly polarized light with the molecule oriented along the polarization axis.

align along the polarization direction in intense fields [24]. We also do not consider possibilities where the molecule can change its orientation during the two-photon absorption process, which could lead to exotic final states such as Π_g as previously discussed [25], as the time scales are such that this possibility is unlikely.

The TDCS for H_2 can be written for all of these cases as

$$\frac{d^3\sigma}{d\alpha\, d\Omega_1\, d\Omega_2} = \left(\frac{\omega}{I}\right)^2 \frac{1}{T}\int dk_1 \int dk_2\, \delta\left(\tan\alpha - \frac{k_2}{k_1}\right)|\mathcal{M}|^2, \qquad (5)$$

where Ω_1 and Ω_2 are the solid angles in which the outgoing electrons are ejected (with $\Omega \equiv (\theta, \phi)$). The amplitude $\mathcal{M}$ is given by

$$\mathcal{M} = \sum_{M} \sum_{l_1 l_2} \sum_{m_1 m_2} (-i)^{l_1+l_2}\, e^{i(\sigma_{l_1}+\sigma_{l_2})} \times P^{M}_{l_1 m_1 l_2 m_2}(k_1, k_2, T) Y_{l_1 m_1}(\hat{k}_1) Y_{l_2 m_2}(\hat{k}_2) \delta_{m_1+m_2,M}, \qquad (6)$$

where in this equation σ_l is the Coulomb phase, $Y_{lm}(\hat{k})$ represents a spherical harmonic and $P^{M}_{l_1 m_1 l_2 m_2}$ is the momentum-space amplitude at the final time T, obtained from the final time radial wavefunction. In equation (6) all orbital angular momenta up to $l = 6$ are retained. For cases (a) and (c), the sum over M contains only one term. For case (b) the sum contains three terms: $M = 0$, $M = +2$ and $M = -2$. All the calculations presented here were made at a photon energy of 30 eV, which results in between 6 and 10 eV to be shared between the outgoing electrons, depending on the internuclear separation. We note that, for two-photon ionization, the sum over angular momenta must be chosen so that only the terms which result in an even (*gerade*) parity need be retained. For one-photon ionization, only terms which result in an odd (*ungerade*) parity should be retained.

As a check on our equations, computer programs and convergence parameters, we first performed calculations for a photon energy of 76 eV and for $R = 1.4$ au (where R is the molecular internuclear separation). In this case, by extracting the one-photon double ionization probabilities, we are able to check our calculations against our previous work using a different time-dependent technique [18]. For both the total cross section and TDCS, good agreement is found with our previous work [18], which was shown to be in excellent agreement with time-independent calculations [16] and experiment [14].

Subsequently, we calculated the double ionization of H_2 at a photon energy of 30 eV, which requires two photons to doubly ionize. 30 eV was chosen as it is energetically removed from any excited states of H_2^+ so that we probe only the direct two-photon process. The total two-photon double ionization cross section for H_2 at this energy, for the equilibrium internuclear separation of $R = 1.4$ au, from $\Delta M = \pm 1$ transitions is 4.7×10^{-52} cm^4 s (into final $M = 0, 2, -2$ states), and 1.7×10^{-53} cm^4 s from $\Delta M = 0$ transitions (into a final $M = 0$ state). The much lower probability of the H_2 doubly ionizing via $M = 0 \rightarrow 0$ transitions is also observed in single-photon double ionization, where ionizing into a $M = 1$ final state is around 5–10 times more probable, depending on the photon energy. We note that the two-photon double ionization cross section at 30 eV photon energy is of the same magnitude as the two-photon double ionization cross sections for helium at similar excess energies [4, 7, 10].

We now turn to the TDCS for two-photon double ionization of H_2 at its equilibrium internuclear separation. In figure 1 we present angular distributions for equal energy sharing between the outgoing electrons, for various values of θ_1, the emission angle of one of the electrons, for double

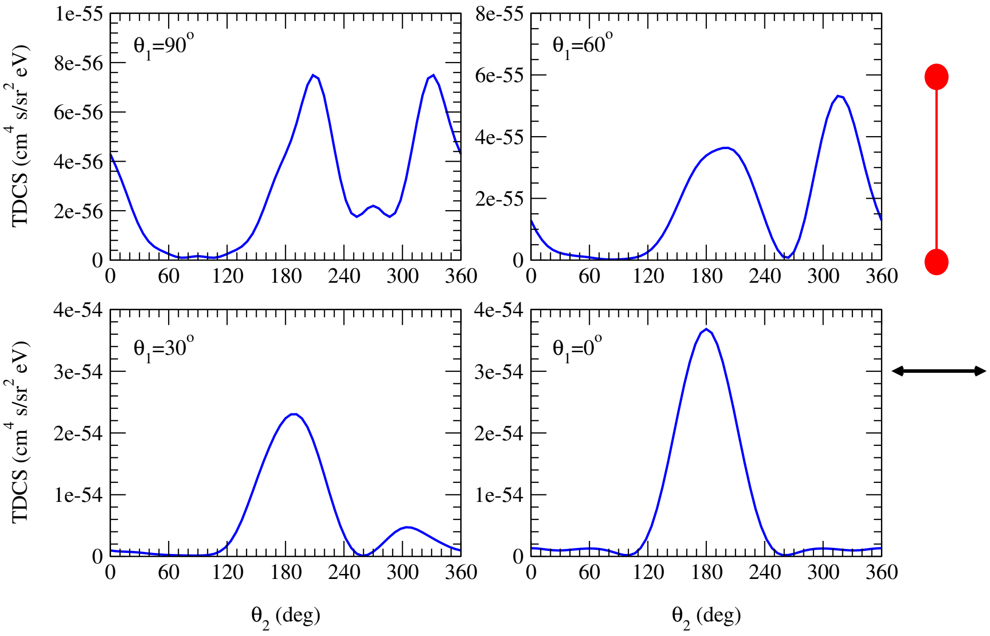

Figure 2. TDCS for the two-photon double ionization of H_2 at 30 eV photon energy, for equal energy sharing between the outgoing electrons, and for various values of θ_1, using linearly polarized light with the molecule oriented perpendicular to the polarization axis.

ionization by linearly polarized light when the molecule is aligned along the polarization axis. Most of the cross section is in the backward direction, with strong peaks where the electrons are at 180° to each other, i.e. back-to-back emission. This contrasts strongly with similar distributions for single-photon double ionization [18], where selection rules (for equal energy sharing) dictate zero cross section in the backward direction. In the two-photon case no such selection rule exists, so the electrons try to leave the molecule as far apart from each other as possible. There is little cross section in the forward direction due to electron repulsion. Extra structure in the TDCS on top of the main back-to-back trend most likely arises due to the interplay of the coupled angular momenta of the outgoing electrons, which will be influenced by the electron energies and angles of ejection.

In figure 2 we present similar angular distributions where in this case the cross sections are computed for orientations of the molecule perpendicular to the polarization axis (i.e. into final $M = 0, 2, -2$ states). Again, most of the cross section is in the backward direction relative to the ejection angle of the first electron. These two-photon angular distributions for H_2 are qualitatively similar to those for helium [4]. For this perpendicular orientation, we see that the double ionization is more ‘atom-like’, which was also found in single-photon double ionization studies [18]. In both figures 1 and 2 we observe a similar pattern found for helium in the magnitude of the distributions: as the ejection angle of the first electron is decreased from 90° towards 0°, the cross section increases in magnitude by around a factor of ten. Since this occurs when the molecule is parallel or perpendicular to the polarization axis, this does not seem to be strongly dependent on the positions of the nuclei with respect to the directions of the ejected electrons. We also note that, if circular polarized light is used, the shapes of the differential cross sections will be very similar to those in figure 2, since this transition also leads to a final $M = 2$ state.

In figure 3 we now turn to the dependence of these angular distributions on the internuclear separation (R) of the molecule. In single-photon double ionization studies, these distributions have been shown to be sensitive to R, or equivalently, to the kinetic energy release (KER) to the outgoing protons (which is directly proportional to R) [13, 17]. Figure 3 shows the TDCS for equal energy sharing, when the first electron is ejected at 30° with respect to the polarization direction, for three values of R around the equilibrium separation. The left panels show the cross sections when the molecule is parallel to the polarization direction and the right panels show the cross section when the molecule is perpendicular to the polarization direction. The ‘perpendicular’ cross sections display little dependence on R (i.e. on the KER). The cross sections have a very similar shape for all R and the ratio of the two peaks at $\theta_2 = 180°$ and at $\theta_2 = 300°$ is very similar at each R. The magnitude of the cross section changes slightly as R is increased, which reflects the changing total two-photon double ionization cross section.

However, for the ‘parallel’ case, the TDCS are different as R is changed. Although the overall cross section shapes are similar, the position of the main peak in the cross section around 180° shifts as R is varied. Also, the ratio of the two main peaks in the cross section decreases rapidly as R is increased. We can also detect some smaller extra features in the cross section for $R = 1.6$ au at around $\theta_2 = 150°$, which is not evident at smaller R. The parallel cross section also decreases rapidly in magnitude as R is increased; at $R = 1.2$ au the TDCS is ten times smaller than the cross section for the perpendicular transition, whereas at $R = 1.6$ the parallel cross section is

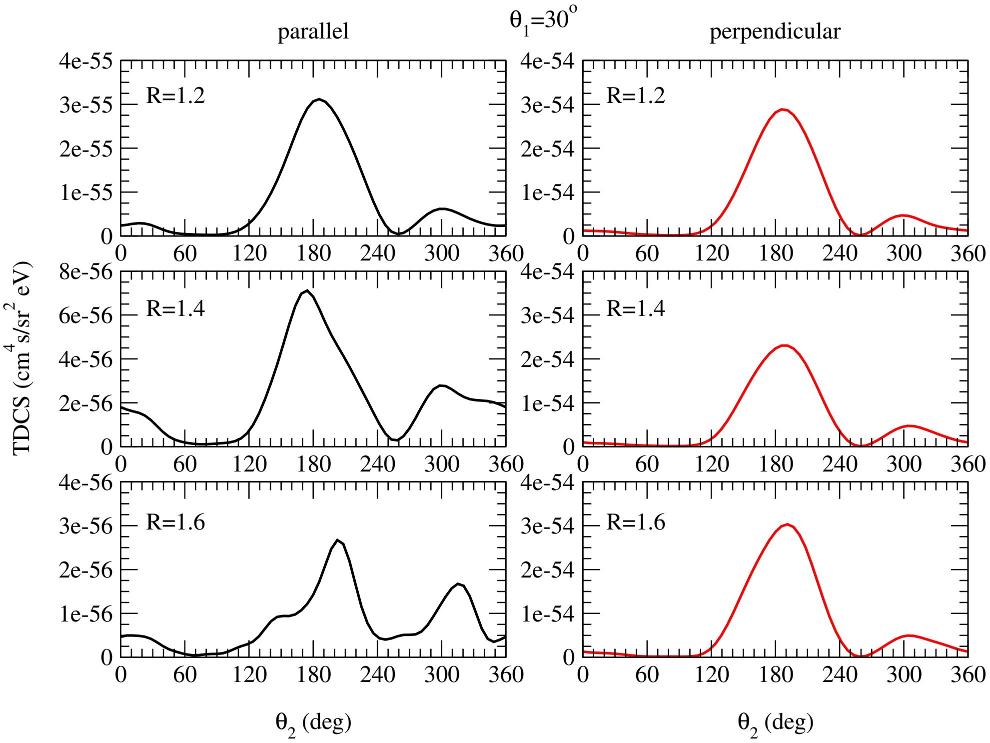

Figure 3. TDCS for the two-photon double ionization of H_2 at 30 eV photon energy, for equal energy sharing between the outgoing electrons, for $\theta_1 = 30°$, and for various internuclear separations, R, as indicated. The left panels show the TDCS when the molecule is parallel to the polarization direction and the right panels show the TDCS when the molecule is perpendicular to the polarization direction.

100 times smaller. The total two-photon double ionization cross sections follow a similar trend. The smaller magnitude of the parallel cross section may also make it more sensitive to interference effects as the electrons leave the molecule along the internuclear axis, which could be the source of some of the extra structure observed in the left-hand panels of figure 3. Also, doubly excited states of H_2 may influence the structure of the differential cross sections, especially the so-called $Q_1\,{}^1\Sigma_u^+$ doubly excited states [26], which lie around 30 eV above the H_2 ground state, depending on the internuclear separation. These results show that the two-photon ‘parallel’ transition has a clear KER dependence, unlike the two-photon ‘perpendicular’ transition. Such a phenomenon has no analogue in two-photon double ionization of atoms. It is hoped that these results can stimulate experimental measurements of such cross sections, although the small magnitude of these cross sections will make measurements a challenge.

In conclusion, we have presented the first cross sections, to our knowledge, for two-photon double ionization of the hydrogen molecule. We find cross sections that show some similarities to the two-photon double ionization of helium, especially when the molecule is oriented perpendicular to the polarization axis, where the cross sections show a more ‘atom-like’ behavior. We also present cross sections for transitions corresponding to aligned molecules with respect to the polarization axis, which display novel molecular effects.

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References

[1] Moshammer R *et al* 2007 *Phys. Rev. Lett.* **98** 203001
[2] Pindzola M S and Robicheaux F 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** L823
[3] Nikolopoulos L A A and Lambropoulos P 2001 *J. Phys. B: At. Mol. Opt. Phys.* **34** 545
[4] Colgan J and Pindzola M S 2002 *Phys. Rev. Lett.* **88** 173002
[5] Feng L and van der Hart H W 2003 *J. Phys. B: At. Mol. Opt. Phys.* **36** L1
[6] Piraux B *et al* 2003 *Eur. Phys. J.* D **26** 7
[7] Hu S X, Colgan J and Collins L A 2005 *J. Phys. B: At. Mol. Opt. Phys.* **38** L35
[8] Foumouo E *et al* 2006 *Phys. Rev.* A **74** 063409
[9] Ivanov I A and Kheifets A S 2007 *Phys. Rev.* A **75** 033411
[10] Horner D A *et al* 2007 *Phys. Rev.* A **76** 030701
[11] Nikolopoulos L A A and Lambropoulos P 2007 *J. Phys. B: At. Mol. Opt. Phys.* **40** 1347
[12] Hasegawa H *et al* 2005 *Phys. Rev.* A **71** 023407
[13] Weber T *et al* 2004 *Phys. Rev. Lett.* **92** 163001
Weber T *et al* 2004 *Nature* **431** 437
[14] Gisselbrecht M *et al* 2006 *Phys. Rev. Lett.* **96** 153002

[15] Vanroose W *et al* 2005 *Science* **310** 1787
[16] Vanroose W *et al* 2006 *Phys. Rev.* A **74** 052702
[17] Horner D A *et al* 2007 *Phys. Rev. Lett.* **98** 073001
[18] Colgan J, Pindzola M S and Robicheaux F 2007 *Phys. Rev. Lett.* **98** 153001
[19] Bandrauk A D 1994 *Molecules in Laser Fields* (New York: Dekker)
[20] Alnaser A S *et al* 2004 *Phys. Rev. Lett.* **93** 183202
[21] Niikura H *et al* 2002 *Nature* **417** 917
[22] Staudte A *et al* 2007 *Phys. Rev. Lett.* **98** 073003
[23] Colgan J *et al* 2004 *J. Phys. B: At. Mol. Opt. Phys.* **37** L377
[24] Posthumus J *et al* 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** L553
[25] Nikolopoulos L A A *et al* 2007 *Phys. Rev.* A **76** 033402
[26] Martín F 1999 *J. Phys. B: At. Mol. Opt. Phys.* **32** R197