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Internuclear separation dependence of the angular distributions from photoionization of H_2^+

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Abstract

Recent experimental and theoretical works examining the double photoionization of H₂ have uncovered surprising changes in the resulting fully differential cross sections as the kinetic energy released to the outgoing protons is varied. In this work, a complementary study is made of the angular distributions arising from the photoionization of H₂⁺ at various internuclear separations *R*. Different internuclear separations correspond to different amounts of kinetic energy released to the exploding protons. We find that the angular distributions for the $\sigma_g \rightarrow \pi_u$ transition in H₂⁺ are relatively insensitive to changes in *R*, but that the angular distributions for the $\sigma_g \rightarrow \sigma_u$ transition display dramatic variations with *R*. We investigate the underlying mechanisms of these phenomena, and explore the implications of these findings for the double photoionization of H₂.

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

1. Introduction

The double photoionization (DPI) of H₂ has recently been an intense and fruitful field of study by both theory [1-3]and experiment [4-6] in exploring the roles of electron correlation and of the non-spherical (molecular) Coulombic potential on the double ionization process. Recent advances in experimental technology have enabled coincidence detection of all four outgoing particles, which, along with knowledge of the polarization state, allows all information about the double ionization process to be recorded. The detection of the proton momenta also allows the alignment of the molecule with respect to the polarization direction to be uncovered at the moment of double ionization. Furthermore, an analysis of the protons' kinetic energy enables the internuclear separation of the molecule at the moment of double ionization to be inferred. Such work has uncovered interesting physics; specifically, that the differential cross sections for the DPI of H₂ can depend strongly on the internuclear separation (R) at the moment of double ionization, for certain molecular orientations. The

reasons for this phenomenon have been further explored using the exterior complex-scaling (ECS) approach [7] and by a very recent joint theoretical (using time-dependent close-coupling theory) and experimental analysis [8]. The latter work found that only the Σ_u component of the fully differential cross section (FDCS) was sensitive to changes in *R*, whereas the Π_u component was relatively insensitive to changes in *R*. Molecular orientations which resulted in the Σ_u and Π_u components having approximately equal magnitudes show most sensitivity to variations in *R*. Furthermore, the cross terms resulting from a coherent addition of these two components can often determine the change in shape of the FDCS as *R* is varied.

Further analysis discussed in [8] uncovered possible reasons for the sensitivity of the Σ_u component of the FDCS to changes in *R*. Photoionization of H₂⁺ was investigated, and it was found that in this process, in which electron correlation plays no role, the σ_u component of the angular distributions were sensitive to changes in *R*, whereas the π_u component was fairly insensitive. The similarities between photoionization of



Figure 1. Angular distributions for the photoionization of H_2^+ as a function of the internuclear separation, *R*, for a photon energy of 65 eV, for molecular orientations aligned parallel to the polarization axis (i.e. a final σ_u state).

 H_2^+ and DPI of H_2 were discussed. In this paper, we present a full exploration of the photoionization of H_2^+ as a function of the molecular internuclear separation. This process has been studied for many years, due in part to its importance in astrophysics, starting with the analytic approach of Bates *et al* [9]. In this work, we find it convenient and efficient to use a time-dependent technique [10] to follow the photoionization process to a final state from which total cross sections and angular distributions may be easily computed.

2. Theory

Our time-dependent technique used to compute the total cross sections and angular distributions for photoionization of H_2^+ has previously been described in detail [10, 11]. The angular differential cross section (in the molecular, or body-fixed frame) as defined in [11] can be written for the special case where the polarization axis lies along the molecule as

$$\frac{\mathrm{d}\sigma_{\mathrm{PI}}^{m=0}}{\mathrm{d}\theta\,\mathrm{d}\phi} = \frac{\omega}{I}\frac{1}{T}\int\mathrm{d}k\left|\sum_{l}(-\mathrm{i})^{l}\,\mathrm{e}^{\mathrm{i}\sigma_{l}}P_{l}^{m=0}(k,\,T,\,R)Y_{l0}(\theta,\,\phi)\right|^{2},\tag{1}$$

and for the case where the molecule and polarization axes are perpendicular as

$$\frac{\mathrm{d}\sigma_{\mathrm{Pl}}^{m=\pm 1}}{\mathrm{d}\theta\,\mathrm{d}\phi} = \frac{\omega}{I}\frac{1}{T}\int\mathrm{d}k\left|\sum_{l}(-\mathrm{i})^{l}\,\mathrm{e}^{\mathrm{i}\sigma_{l}}\left\{P_{l}^{m=1}(k,\,T,\,R)Y_{l1}(\theta,\,\phi)\right.\right|^{2}$$

$$+ P_l^{m=-1}(k, T, R) Y_{l-1}(\theta, \phi) \Big\} \bigg| .$$
 (2)

In these expressions σ_l is the Coulomb phase shift and ω and *I* are the field frequency and intensity respectively. These expressions are special cases of the expressions for the generalized angular distributions found in [12] for the

(homonuclear) H₂⁺ molecule subjected to linearly polarized light. The functions $P_l^m(k, T, R)$ are the result of a timedependent propagation of the electronic wavefunction under the influence of the molecular and electromagnetic field Hamiltonians to a time T, where k is the momentum of the outgoing electron. Two possible *m* final states, m = 0 (σ_u) or $m = \pm 1$ (π_u) can result from photoionization from the H_2^+ ground state, and the sum over l only contains odd contributions due to parity considerations of photoionization from an even ground state. Time-dependent calculations must be carried out for each m final state. In this study we are interested in photoionization of H₂⁺ at various internuclear separations R. Time-dependent calculations must also be carried out for each R, where the initial H_2^+ ground state is fixed at a given R. The ground state of H_2^+ is found by diagonalization of the molecular Hamiltonian defined in [10]. Angular distributions are presented in the following section at parallel and perpendicular orientations of the molecule with respect to the polarization axis, and in all cases the angle $\phi = 0^{\circ}$. These cases correspond to pure $\sigma_g \rightarrow \sigma_u$ and pure $\sigma_g \rightarrow \pi_u$ transitions, respectively.

3. Results and discussion

Angular distributions for photoionization of H_2^+ at a photon energy of 65 eV, leaving the ion in a final σ_u or in a final π_u state are shown in figures 1 and 2 respectively for nine *R* values from 0.0 to 2.4 au, encompassing the H_2^+ equilibrium separation of 2.0 au. All angular distributions in this paper are presented with θ defined with respect to the molecular axis, and with $\phi = 0^\circ$. The distributions leaving the ion in a final σ_u state are independent of ϕ , and the distributions leaving the ion in a final π_u state vary in magnitude as ϕ moves from 0 to 2π , but have the same shape as the distributions shown here. A 65 eV photon ionizes a photoelectron with 10 eV



Figure 2. Angular distributions for the photoionization of H⁺₂ as a function of the internuclear separation, *R*, for a photon energy of 65 eV, for molecular orientations aligned perpendicular to the polarization axis (i.e. a final π_u state).

when R = 0.0 au and a photoelectron with around 37 eV at the largest R of 2.4 au. The most obvious trend in these figures is the dramatic change in the shape of the angular distribution for photoionization into a final σ_u state at around R = 1.4 au. The angular distribution develops more structure, with small peaks evident at around 60° and 120° , which persist at all R greater than 1.4 au. No such change in structure is observed in the angular distributions for photoionization into a final π_u state, in which the shape retains its 'bell-curve' nature at all R, with the exception of the largest R considered (2.4 au), where some small extra structure can be observed. We also note that the magnitude of the cross section drops dramatically for photoionization into the final σ_u state at intermediate R, before increasing at the largest R, whereas the magnitude of the cross section for the final π_u state decreases smoothly with R. This trend is shown in figure 3, which shows the total photoionization cross section as a function of R at the same photon energy. The photoionization cross sections into final σ_u and π_u states are identical in the limit as R approaches zero, which of course corresponds to photoionization of He⁺. We note here that in figure 3 we plot the 'raw' σ_u and π_u contributions to the total H₂⁺ photoionization cross section. The total cross section, averaged over all molecular orientations, is given by $(\sigma_{\rm PI}^{m=0} + 2\sigma_{\rm PI}^{m=1})/3$. The shapes of the angular distributions differ at R = 0.0 for final σ_u and π_u states as these correspond to photoionization of He⁺ into final p_0 and p_1 states of the photoelectron, respectively.

Photoionization at a fixed photon energy results in ejected electrons with differing energies as R varies, with photoionization at the largest R resulting in the most energetic electrons. In order to show that the trends presented in figures 1 and 2 are not 'kinematic' in origin, in figures 4 and 5 we show similar angular distributions, but this time at a fixed ejected electron energy of 10 eV. Very similar trends to figures 1 and 2 are found, with the dramatic variation in the



Figure 3. Total photoionization cross section for H_2^+ as a function of the internuclear separation, *R*, for a photon energy of 65 eV, for molecular orientations aligned parallel to the polarization axis (σ_u final state; black solid line) and perpendicular to the polarization axis (π_u final state; red dotted line).

final σ_u angular distribution occurring at around R = 1.6 au in this case. Furthermore, the total cross section again shows a minimum at intermediate R for final σ_u states, whereas the total cross section into final π_u states is very slowly decreasing with R.

In figures 4 and 5 we also show the relative partial wave contributions to the angular distributions at each R. The (red) dashed lines show inclusion of up to the p partial wave in the sum in equation (1), and the (green) dotted lines show inclusion of up to the f wave in the sum. The full calculations (black solid lines) included up to l = 7. This analysis reveals the reason for the sensitivity of the angular distributions of the final σ_u state. At low R both final states are dominated by the p component (at R = 0.0, the He⁺ case, the p component is the sole contribution), but for the



Figure 4. Angular distributions for the photoionization of H_2^+ as a function of the internuclear separation, *R*, for an outgoing electron energy of 10 eV, for molecular orientations aligned parallel to the polarization axis (i.e. a final σ_u state). The red dashed line and green dotted lines give the angular distributions when partial wave contributions up to only l = 1 and l = 3, respectively, are included. The full calculations (black solid lines) include partial wave contributions up to l = 7.



Figure 5. Angular distributions for the photoionization of H_2^+ as a function of the internuclear separation, *R*, for an outgoing electron energy of 10 eV, for molecular orientations aligned perpendicular to the polarization axis (i.e. a final π_u state). The red dashed line and green dotted lines give the angular distributions when partial wave contributions up to only l = 1 and l = 3, respectively, are included. The full calculations (black solid lines) include partial wave contributions up to l = 7.

 σ_u case, as *R* approaches 1.6 au, the *p* component decreases in the σ_u case and is almost zero at R = 1.8 au. Thus, at these internuclear separations, the cross section decreases significantly, and the shape is dominated by the *f* component, which gives rise to the extra structure observed in the angular distribution. For the π_u case, the *p* component dominates at all *R*, with the *f* component only making a noticeable contribution at the highest *R* considered. Returning to figure 2, the extra structure observed in the π_u angular distribution for R = 2.4 au can now be understood as arising from the greater influence of the *f* component for this geometry. In this case, however, this trend is enhanced by a 'kinematic' effect, since at R = 2.4 au the higher photoelectron energy of 37 eV favours the *f* component compared with the 10 eV photoelectron for R = 0.0 au.

The reason for the sensitivity of the total cross section and angular distribution of photoionization into a final σ_u state is now clear; it is caused by the sudden decrease of photoionization into the *p* component, so that the shape and magnitude of the cross section is dominated by the *f* component. No such decrease is found in photoionization into a final π_u state. In fact, this finding was also reached more than 50 years ago by Bates *et al* [13], who were among the first to study H₂⁺ photoionization using an analytic method based on an expansion of the H₂⁺ wavefunction in elliptic coordinates [9]. The study of [13] focused on photoionization where the ejected electron has almost zero energy, but found, just like in figure 4, that the cross section exhibits a minimum, which for this photoelectron energy, occurred near R = 2 au. Bates *et al* attributed this minimum to an essentially complete cancellation between the positive and negative portions of the $1s\sigma_g \rightarrow kp\sigma_u$ integrand in this coordinate system. In the 10 eV photoelectron case, the minimum in the cross section occurs at R = 1.8 au, indicating that the position of the minimum moves towards smaller internuclear separations as the photoelectron energy increases, due to the first radial node of the $kp\sigma_u$ state moving inward as its energy increases.

This cancellation in the dipole matrix element is closely analogous to a Cooper minimum, which has been discussed in detail for many molecular systems [14], including H₂ [15]. In the H_2^+ case under investigation in this paper, we see a zero in the dipole matrix element at a given photoelectron energy and at a given value of the internuclear separation, and only for the $1s\sigma_g \rightarrow kp\sigma_u$ transition. The cancellation is, however, almost complete for a single-partial cross section (in this case, $kp\sigma_u$). Moreover, as Bates *et al* note, such a cancellation will occur along a line in (ϵ_e, R) space, i.e. the minimum in the cross section will occur for different photoelectron energies at different *R* values. The transition into a final $kp\pi_u$ state shows no such minimum since the integrand is dominated by positive contributions. Also, Bates *et al* pointed out that the $1s\sigma_g$ and $kp\pi_u$ wavefunctions overlap to a considerable extent, which causes the larger cross section into the final $kp\pi_u$ state. Since the f component of both the σ and π states is more diffuse, no cancellation occurs, and the magnitude of the transition into the $kf\sigma_u$ and $kf\pi_u$ states are similar. We note that the β_{ion} parameter for photoionization of H_2^+ at R = 2.0 au is -0.44, and that the largest magnitude of the β_{ion} occurs at R = 1.4 au, where it is -0.93. We also point out that the σ electronic states which show the strong sensitivity to changes in R, lie on or near the internuclear axis, while the π states, which are less sensitive to changes in R are concentrated in the plane between the nuclei. Such geometric considerations may help us to ascribe a physical reason for the quite different behaviours of the $\sigma_g \rightarrow \sigma_u$ and $\sigma_g \rightarrow \pi_u$ transitions.

3.1. Implications for the double photoionization of H_2

Having analysed the photoionization of H_2^+ as a function of Rand uncovered the reasons for the R dependence of the angular distributions of the final σ_u state, it is worthwhile considering the similar trends observed for DPI of H_2 . Although it is tempting to state that the reasons for the R dependence of the fully differential cross sections of H_2 are the same as the reasons for similar trends in H_2^+ , we must be cautious, since DPI of H_2 is a much more complicated process than single photoionization of H_2^+ . In particular, the shapes of the differential cross sections from DPI of H_2 are often dominated by the electron correlations between the outgoing electrons. However, these electrons move in a very similar (molecular)

Table 1. Contributions to the total double photoionization cross section for H₂, at a photon energy of 76 eV, from final Σ_u and Π_u states, respectively. All cross sections are given in kb. In this table, the total DPI cross section is given by the sum of the Σ_u and Π_u contributions, i.e. the orientation average factor is included (1 kb = 1.0×10^{-21} cm²).

<i>R</i> (au)	Σ_u	Π_u	$\beta_{\rm ion}$
0.8	1.10	4.42	-0.40
1.0	0.50	4.00	-0.67
1.2	0.20	3.25	-0.83
1.4	0.19	2.58	-0.80
1.6	0.34	2.04	-0.57
1.8	0.53	1.63	-0.26

potential to the potential which is seen by the outgoing electron in H_2^+ photoionization. The question then becomes, to what extent does the potential in which the outgoing electrons move modify the differential cross sections in DPI of H₂? This issue quickly becomes complicated to analyse in terms of partial waves as was done for photoionization of H_2^+ , since for DPI of H₂ the orbital angular momenta of the two outgoing electrons must be added vectorially, and because this expansion also determines the degree of electron correlation present in the problem [8]. However, as discussed in [8], by limiting the number of $l_1 l_2$ angular momenta retained in full time-dependent close-coupling calculations, we find that low angular momenta dominate the Π_u amplitude in DPI of H₂, whereas larger angular momenta expansions are required to fully converge the Σ_u amplitude. Further evidence that the analogy between photoionization of H₂⁺ and DPI of H₂ is justified is also found by noting that the shape of the total DPI cross section for H₂ into final Σ_u and Π_u states, which is presented in table I for selected internuclear separations, follows a similar trend to figure 3. The Π_u contribution decreases steadily with increasing R, whereas the Σ_u contribution displays a shallow minimum around R =1.4 au. The β_{ion} parameter for DPI of H₂ (also listed) has a similar trend to that for photoionization of H_2^+ . Finally, we note in passing that the angular distributions for photoionization of H₂⁺ are peaked along the direction of the polarization vector, for both symmetries, resulting in a positive β_e for the electron. This is quite distinct from the DPI of H₂ (or He) case, where selection rules (for equal energy) prevent the electrons from leaving 'back-to-back', and Coulomb repulsion prevents them from leaving in the same direction. As a consequence, they cannot both be emitted along the polarization direction, resulting in a near-zero or negative β_e .

4. Conclusions

In summary, we have analysed the photoionization of H_2^+ as a function of internuclear separation. We find that the surprising variations of the angular distributions with *R* have a relatively simple origin, which was also known more than 50 years ago. The variations are due to a strong cancellation in the dipole matrix element for the $\sigma_g \rightarrow \sigma_u$ transition, for a given photoelectron energy and a given internuclear separation, and is analogous to the well-known Cooper minimum. It seems plausible that similar effects are responsible for the variation

of the differential cross sections from double photoionization of H_2 with R, a phenomenon of much interest in recent years.

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Note added in proof. We note the recent appearance of an article on photoionization partial cross sections of H_2^+ , which is fully consistent with our study [16]. This paper was published after submission of our manuscript.

References

- Vanroose W, Martín F, Rescigno T N and McCurdy C W 2005 Science 310 1787–9
- [2] Vanroose W, Horner D A, Martín F, Rescigno T N and McCurdy C W 2006 Phys. Rev. A 74 052702
- [3] Colgan J, Pindzola M S and Robicheaux F 2007 Phys. Rev. Lett. 98 153001

- [4] Weber T et al 2004 Phys. Rev. Lett. 92 163001
- [5] Weber T *et al* 2004 *Nature* 431 437–41
 Weber T *et al* 2006 *Nature* 443 1014
- [6] Gisselbrecht M, Lavollée M, Huetz A, Bolognesi P, Avaldi L, Seccombe D P and Reddish T J 2006 *Phys. Rev. Lett.* 96 153002
- [7] Horner D A, Vanroose W, Rescigno T N, Martín F and McCurdy C W 2007 Phys. Rev. Lett. 98 073001
- [8] Reddish T J, Colgan J, Bolognesi P, Avaldi L, Gisselbrecht M, Lavollée M, Pindzola M S and Huetz A 2008 Phys. Rev. Lett. submitted
- [9] Bates D R, Ledsham K and Stewart A L 1953 Proc. R. Soc. Lond. A 246 215–40
- [10] Colgan J, Pindzola M S and Robicheaux F 2003 Phys. Rev. A 68 063413
- [11] Foster M, Colgan J, Al-Hagan O, Peacher J L, Madison D H and Pindzola M S 2007 Phys. Rev. A 75 062707
- [12] Lebech M, Houver J C, Dowek D and Lucchese R R 2006 Phys. Rev. Lett. 96 073001
- [13] Bates D R, Öpik U and Poots G 1953 Proc. Phys. Soc. A 66 1113–23
- [14] Carlson T A, Krause M O, Svensson W A, Gerard P, Grimm F A, Whitley T A and Pullen B P 1986 Z. Phys. D 2 309–18
- [15] Semenov S K and Cherepkov N A 2003 J. Phys. B: At. Mol. Opt. Phys. 36 1409–22
- [16] Della Picca R, Fainstein P D, Martiarena M L and Dubois A 2008 Phys. Rev. A 77 022702