Complete Photo-induced Breakup of the H_2 Molecule as a Probe of Molecular Electron Correlation

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Abstract

Despite decades of progress in quantum mechanics, electron correlation effects are still only partially understood. Experiments in which both electrons are ejected from an oriented hydrogen molecule by absorption of a single photon have recently demonstrated a puzzling phenomenon: The ejection pattern of the electrons depends sensitively on the bond distance between the two nuclei as they vibrate in their ground state. Here we report a complete numerical solution of the Schrödinger equation for the double photoionization of H_2. The results suggest that the distribution of photoelectrons emitted from aligned molecules reflects electron correlation effects that are purely molecular in origin.

Chemical physics has long sought deeper insight into correlation effects, because they lie at the heart of understanding atomic and molecular structure. Because quantum mechanics does not offer an analytic solution of the wave function for any physical system with three or more charged particles, electron correlation is a challenge to model mathematically even in the simplest atomic and molecular systems. Processes that put two electrons into the continuum, particularly near the ionization threshold, can offer unique insight into the nature of electron correlation. In particular, complete breakup of a hydrogen molecule after the absorption of only one photon, $h\nu + H_2 \rightarrow p + p + e^- + e^-$, is a pure manifestation of the correlated motion of all the particles in the system, because the energy of a single photon must be shared by all the outgoing particles. Recent imaging techniques have allowed the simultaneous observation of the charged particles that emerge in the breakup of atoms and molecules after a collision with photons or other particles (*1-4*). Such detailed data (*5*) offer substantial insight into the nature of electronic correlation. However, a precise quantum theoretical treatment is needed to unambiguously unravel the possible origins of the effects observed (*6*). We report such a complete computational treatment of molecular double ionization.

In double photoionization two electrons are emitted from an atom or a molecule after absorption of a single photon. The observed pattern of electron ejection is a reflection of the competition between the effects of electron-nuclear attraction, electron-electron repulsion and the acceleration of the electrons by the electric field in the direction of its polarization. To the degree that the electron ejection pattern is different when the two electrons are in a chemical bond (in the H_2 molecule versus in the helium atom) these experiments can probe the nature of correlation in that bond. Are the observed angular patterns simply a manifestation of the intrinsic molecular symmetries

of the initial and final states, or do they reveal more specific information about the dynamics of the ejection process? The variation of the two-electron ejection pattern with respect to initial orientation and internuclear distance of the molecule – either in precise calculations or in experiments – allows us to investigate these questions.

In the experiments recently reported by Weber *et al.* (*5*), linearly polarized 75.5 eV synchrotron radiation was used to study single-photon induced fragmentation of molecular deuterium (*7*). By measuring the final momenta of both nuclei and the ejected electrons in coincidence, they were able to relate the angular pattern of the ejected electrons to a particular internuclear separation in the molecular ground state at the instant of photon absorption. Weber *et al.* demonstrated experimentally that this essentially classical interpretation of nuclear motion (consistent with the "reflection principle" for photodissociation spectra (*8*)) is valid for the conditions of their experiment. For certain geometries they found marked differences in the angular patterns of ejection of the electrons with small changes in the nuclear momenta, and they speculated that this effect was the signature of changes in electron correlation with bond distance. It is not surprising of course that electron correlation in a molecule should change with bond distance. However, Weber *et al.* asserted that small changes in bond distance result in major changes in the angular distributions of the ejected electrons.

There is, however, a complication. The two electrons are ejected suddenly from the vibrating molecule with the nuclei a particular distance apart. A Coulomb explosion follows, and the nuclei separate with a kinetic energy determined by the potential energy of their repulsion at that distance. Therefore, observing the process at different internuclear distances changes the kinetic energy available to be shared by the outgoing electrons. Could the recently observed changes in the ejection pattern of the electrons

with internuclear distance be due to this purely kinematic effect, or do they really reflect changes in electron correlation? This question could not be answered by the experiment because it was performed with a single photon energy. Precise solutions of the Schrödinger equation are required to unambiguously resolve this issue and thereby test the assertion that large changes in the ejection pattern are the signature of changes in electron correlation with bond distance.

The calculation we report here required a major extension, described in the supplementary material (*9*), of the methods that only recently solved such problems for isolated atoms (*6, 10, 11*). Only the first steps towards a precise solution of the molecular problem, based on a numerical solution of the full Schrödinger equation with no appeal to models, had previously been taken with the use of any methods (*12, 13*), and those efforts produced only the total ionization probability and not the angular patterns of the ejected electrons. The only assumption we have made here is that the nuclei do not move during the time required to eject the two electrons. This simplification is consistent with the familiar Born-Oppenheimer approximation, which is valid for electrons moving much faster than the nuclei, as is the case in the current experiments on D_2 and for the same process in H_2.

One of the clearest molecular effects that can be observed both by experiment and by our current theory is manifested in the angular pattern of two ejected electrons or triple differential cross section (TDCS), so called because it depends on the directions of the two ejected electrons and their energy sharing. We have calculated the TDCS for double photoionization of the helium atom at 24.5 eV excess energy (Fig. 1A) using the methods we developed earlier for atomic problems (*10*). We chose 24.5 eV excess energy to facilitate comparison with the results for molecular hydrogen. For the case

shown, one electron goes out along the direction of the polarization vector of the incident photon with 90% of the available energy, and the cross section is plotted as a function of the direction of the other electron. The resulting distribution for an atom must have cylindrical symmetry about the common axis of the polarization and the direction of the fixed electron. In contrast, when the H_2 molecule, oriented perpendicular to the polarization direction, is doubly ionized with the same excess energy, our calculations show that the cylindrical geometry of the atomic case (Fig. 1A) becomes flattened along the direction of the molecular axis (Fig. 1B).

This molecular effect has been observed experimentally (Fig. 1C) (*14, 15*). The experimental data were collected in a manner that corresponds to making two cuts of the three-dimensional distribution shown in Fig. 1B, and they reveal a widening of the distribution when the cut is parallel to the molecule. The detailed comparison of theory with the existing experiments is complicated by the finite resolution of the experiment in both angle and energy. The experiment accepts all events with "fixed" electron angles $\pm 20^0$, "swept" electron angles $\pm 17.5^0$, molecular angles $\pm 25^0$, "fixed" electron energies $^3 80$ of that available, and a range of proton kinetic energies of ~1 eV. The calculated data in Fig. 1C also give some indication of the major changes that occur in the TDCS with relatively small changes in the energy sharing between the electrons. To determine the full implications of these experiments, we focused on the accurate theoretical description of this process without the complication of averaging over the experimental resolutions.

To see the effect on the angular dependence of varying the internuclear distance, we must choose an experimental geometry that is sensitive to that variation. As the molecule rotates between being parallel and perpendicular to the polarization direction,

the dipole-allowed transitions $^1S_g \rightarrow {}^1S_u$ (parallel) and $^1S_g \rightarrow {}^1P_u$ (perpendicular) contribute in varying proportion to the observed TDCS. The behavior of the TDCS for an angle between the molecule and polarization vector of 15^0 (Fig. 2) probes both those components visibly. Experimental data resolving the orientation of the molecule sufficiently to show the smaller ^1S_u component (a factor of 10 smaller (*12, 13*) than ^1P_u) unambiguously have yet to be published. In the existing experiments (*5,14,15*), differences in the observed cross section for various internuclear distances, with one electron ejected perpendicular to the plane formed by the molecular axis and polarization vector were attributed to changes in the electronic correlation of the initial state of the D_2 molecule (*5*).

To explore that effect uncomplicated by the finite resolutions of the experiment, we examined the TDCS at three internuclear distances: the equilibrium position of the nuclei and the inner and outer classical turning points of their vibrational motion in the ground vibrational state. The behavior of the TDCS (Fig. 2A) shows a marked variation with internuclear separation that is particularly notable when seen in complete three-dimensional views of the angular dependence of the second electron for a fixed ejection direction of the first. The differences are even larger than the experiment was able to reveal because of its finite angular and energy resolutions.

However, the variation shown in Fig. 2A does not establish that the effect on the cross section of varying internuclear distance is a result of changes in electron correlation. The electrons liberated by ionization at the inner vibrational turning point share 5.42 eV less energy than electrons released by ionization at the outer turning point, because the nuclei carry off different amounts of repulsion energy. The experiments (*5, 14, 15*) were performed at a photon energy 24.5 eV above the threshold for double

ionization of D_2 in its ground vibrational state. This variation with internuclear distance of kinetic energy shared by the outgoing electrons is more than 20% of that nominal value. Double photoionization cross sections of atoms are known to be sensitive to energy differences, and very sensitive to changes in energy sharing. Therefore, one must suspect that changes observed in the molecular TDCS with varying internuclear distances might only be due to the change in the effective energy transmitted to the outgoing electrons.

To investigate that question we examined the TDCS for the same three internuclear distances - but now calculated with different photon energies so that the outgoing electrons always shared 24.5 eV of energy (Fig. 2B). The resulting variations in the cross section with varying internuclear distance were both qualitatively and quantitatively similar to those observed when a single photon energy was used (Fig. 2A). This comparison therefore establishes that experiments observing the complete dynamics of the breakup process can measure changes in the effect of electron correlation that are purely molecular in character and vary with molecular geometry.

The three-dimensional representations of the TDCS seen in Figs. 1 and 2 can be viewed as variations on a theme already seen in the helium atom. There, the angular distribution of the plotted electron shows an apparent tendency to go out in the direction more or less opposite to that of the fixed electron (*10*). This pattern is modified in the case of equal energy sharing by selection rules (*16-18*) that place a zero in the angular distribution for back-to-back ejection of the electrons. The molecular cases in Fig. 2 show interesting modifications of the resulting simple two-lobed pattern seen in the case of the helium atom.

To see how the presence of the nuclei in the molecular case modifies the angular

distributions, we can examine how the TDCS changes when the orientation of the molecule is varied while keeping the direction of the fixed electron unchanged. Choosing the fixed electron along the polarization vector and with 90% of the available kinetic energy (as in Fig 1B) we compare the atomic distribution to that obtained for the molecule when it makes an angle of 30^0 (Fig. 3A), 60^0 (Fig. 3B), 75^0 (Fig. 3C) or 90^0 (Fig. 1B) with the polarization vector. This sequence suggests the effect of nuclear attraction on the slower outgoing electron for a set of cases for which no simple symmetry selection rules apply. At 30^0 the nuclei break the single lobe of the atomic pattern into two lobes, which change to have very different sizes by 60^0. The overall flattening of the distribution in the direction of the molecular axis is evident in all four figures.

A comparison of the angular distribution at 75^0 (Fig. 3C) with the more symmetric 90^0 pattern (Fig. 1B) shows how attraction to the nuclei tends to orient some parts of the ejection pattern along that axis, but the set of four patterns show that this effect is strongly modified by the forces of electron repulsion and the applied radiation field. At some geometries, such as the one shown in Fig. 3D, the presence of the nuclei alter the corresponding atomic ejection pattern even more. In this case the two lobes of the atomic angular distribution are broken into three lobes, and no simple model appears to explain the resulting TDCS.

This initial view of accurate calculations of the angular dependence of double photoionization of a molecule shows that experiments measuring the TDCS for different internuclear distances can reveal the signature of essentially molecular effects in electronic correlation. The wealth of information that can only be obtained from calculations and experiments on oriented molecules is highlighted by the fact that, when

averaged over molecular orientations, the TDCS patterns for molecular hydrogen are almost identical to those for helium (*19*). Detailed comparison of measurements on oriented molecules with accurate theory may form the basis for improving existing models (20-*22*) to show clearly how simple physical effects are manifested in the TDCS. However, some aspects of the angular distributions are the signatures of the essentially complicated physics of electron correlation, and may not be easy to model. Nonetheless, the present calculations indicate that there is promise that such analyses can be performed for double photoionization of other molecules to probe correlation in more complicated molecular cases. We expect that this class of experiment and theory will be used, for example, to study the difference between the correlation effects that dominate when two electrons are ionized from the same molecular orbital in a molecule like CO, as opposed to when those electrons are ionized from different shells leaving behind a different electronic state of the CO^{++} ion.

References and Notes

1. R. Dörner, *et al.*, *Phys. Rep.* **330**, 96 (2000).
2. J. H. D. Eland, M. Takahashi and Y.Hikosaka, *Faraday Discuss.* **115**, 119 (2000).
3. M. Lebech, J. C. Houver and D. Dowek, *Rev. Sci. Inst.* **73**, 1866 (2002).
4. M. Gisselbrecht, A. Huetz, M. Lavollée, T. J. Reddish and D. P. Seccombe, *Rev. Sci. Inst.* **76**, 013105 (2005).
5. T. Weber, *et al., Nature* **431**, 437(2004).
6. T. N. Rescigno, M. Baertschy, W. A. Isaacs and C. W. McCurdy, *Science* **286**, 2474 (1999).
7. The experiments in ref. 5 were performed on D_2 rather than H_2 but this has no bearing on the comparisons in Figs. 1 and 3, and it only changes the locations of the inner and outer turning points for the comparison in Fig. 2.
8. G. Herzberg, *Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules*, (Van Nostrand Reinholdt, New York, 1950), pp. 391-393.
9. The methods used are described as supplementary material at *Science* Online.
10. C. W. McCurdy, D. A. Horner, T. N. Rescigno and F. Martín, *Phys. Rev. A* **69** 032707 (2004).
11. C. W. McCurdy, M. Baertschy and T. N. Rescigno, *J. Phys. B* **37**, R137 (2004).
12. W. Vanroose, F. Martín, T. N. Rescigno and C. W. McCurdy, *Phys. Rev. A* **70**, 050703 (2004).
13. J. Colgan, M. S. Pindzola and F.Robicheaux, *J. Phys. B: At. Mol. Opt. Phys.* **37,** L377 (2004).
14. Th. Weber, thesis, Institut fuer Kernphysik Frankfurt/Germany, (2003), p.428-429 (available at http://hsb.uni-frankfurt.de/web/publications/diplom%5Fdoktor/.

15. Th. Weber, private communication.

16. M. Walter and J. S. Briggs, *Phys. Rev. Lett.* **85**, 1630 (2000).

17. L. Malegat, P. Selles and A. Huetz, *J. Phys. B* **30**, 251 (1997).

18. A. Huetz, P. Selles, D. Waymel and J. Mazeau, *J. Phys. B* **24**, 1917 (1991).

19. D. P. Seccombe, *et al.*, *J. Phys. B: At. Mol. Opt. Phys.* **35**, 3767 (2002).

20. M. Walter and J. Briggs, *J. Phys. B: At. Mol. Opt. Phys.* **32**, 2487 (1999).

21. A. S. Kheifets, *Phys. Rev. A* **71** 022704 (2005).

22. T. J. Reddish and J. M. Feagin, *J. Phys. B: At. Mol. Opt. Phys.* **32** 2473 (1999).

23. This work was supported by the US DOE Office of basic energy Sciences, Division of Chemical Sciences, the Misisterio de Educacion y Ciencia project BFM2003-00194 (Spain), and at the Lawrence Berkeley National Laboratory was performed under contract DE-AC02-05CH11231. W.V. is funded by the Belgian Science Policy Office through its action "return grants". We thank Th. Weber for sharing unpublished experimental data shown in Fig 1C, and D. A. Horner for assembling the data on helium double ionization.

Figures

Fig. 1 Angular distribution (TDCS) of ejected electrons with direction of one electron (red arrow, momentum k_1) with 90% of the available energy fixed along the polarization direction (green arrow). A manifestation of a purely molecular effect can be seen by comparing the angular distributions (TDCS) for (A) helium atom with (B) H_2 molecule with axis oriented perpendicular to the polarization. Comparison (C) with relative experimental measurements shows that two cuts of the distribution in (B) have been observed to verify this effect. The dashed curve in (C) shows how the TDCS changes when the fixed electron has 80% of the available energy.

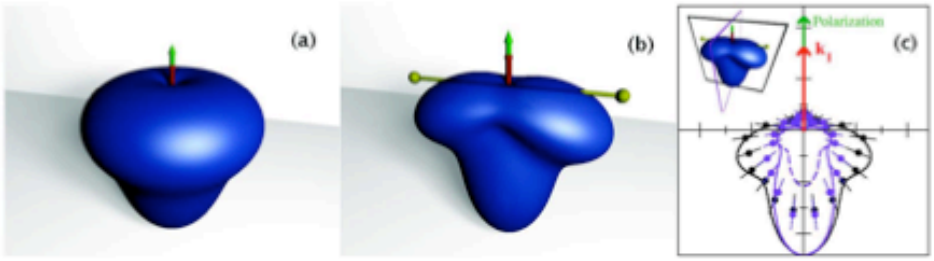


Fig. 2 Effect on the angular distribution for D_2 of varying the internuclear distance. (A) TDCS is shown with molecular axis (yellow) 15^0 from polarization vector (green arrow) and fixed electron (red arrow) leaving perpendicular to that plane with 50% of the available ejection energy. (Left) Inner vibrational turning point; (middle) equilibrium internuclear distance; (right) outer turning point. Background shows ground state potential curve (blue), ground state vibrational wave function (red) and energy (green line, with black dots indicating equilibrium, inner and outer turning points). (B) The effect on the angular distribution of varying internuclear distance is primarily due to changes in molecular electronic correlation. The angular distributions closely resemble those in (A) when the photon energy is varied, so as to produce the same amount of final kinetic energy to be shared by the outgoing electrons, regardless of the internuclear distance at which ionization occurs. Inset shows the corresponding atomic case (helium).

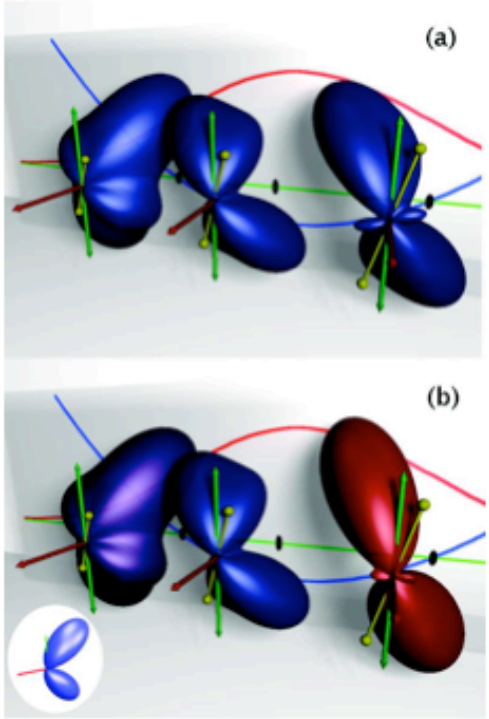
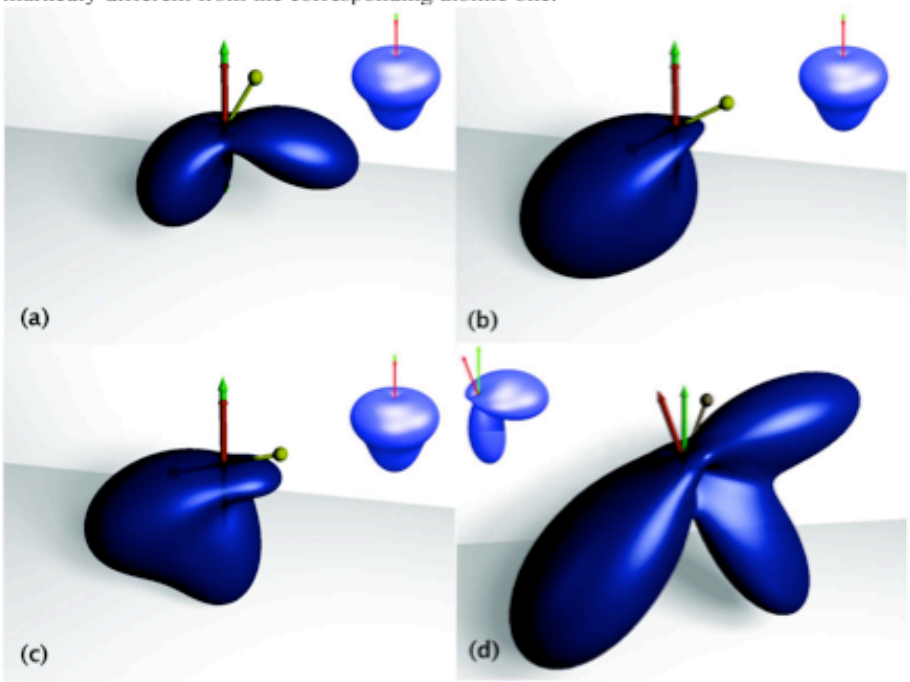


Fig. 3 Effects of molecular orientation on the angular distribution of ejected electrons. For the fixed electron ejected along the polarization direction with 90% of the kinetic energy, the molecule makes an angle with the polarization of (A) 30^0, (B) 60^0 and (C) 75^0, and splits the corresponding pattern for the helium atom (insets) into two lobes which vary in size and ultimately show a tendency to align along the molecular axis as in Fig 1B. The cross section in (A) is about one-fourth the magnitude of (B) and (C). (D) A case in which the molecule and fixed electron have 10% of the kinetic energy, both at 20^0 from the polarization vector but on opposite sides, yielding an ejection pattern markedly different from the corresponding atomic one.



We begin by writing the equation for the outgoing wave function, Ψ_{sc}, that describes the final electronic state after the absorption of a photon with polarization $\vec{\varepsilon}$ and frequency ω, by the molecule in an initial state of energy E_0, described by the wave function, Ψ_0.

$$\left(E_0 + \omega - H\right)\Psi_{sc} = \vec{\varepsilon} \cdot \vec{\mu}\, \Psi_0 \qquad \text{(S1)}$$

Here and elsewhere we use atomic units, and H is the electronic Hamiltonian. Applying the exterior complex scaling (ECS) transformation (*S1*) scales the radial coordinates of the electrons by a complex factor of unit modulus, $e^{i\eta}$, beyond some radius, R_0. Inside that radius the physical wave function, Ψ_{sc}, is unchanged by the transformation, but beyond R_0 it decays exponentially, allowing a simple numerical treatment of the equation. The amplitude for double ionization with outgoing electrons having momenta $\mathbf{k}_1$ and $\mathbf{k}_2$ is then extracted from a matrix element defined with integration over a finite volume within the scaling radius,

$$f(\mathbf{k}_1, \mathbf{k}_2) = \left\langle \phi^{(-)}_{\mathbf{k}_1} \phi^{(-)}_{\mathbf{k}_2} \middle| E - h_1 - h_2 \middle| \Psi_{sc} \right\rangle_{r_1, r_2 \le R_0}, \qquad \text{(S2)}$$

where the functions $\phi^{(-)}_{\mathbf{k}_i}$ are exact *molecular* continuum eigenfunctions of the one-electron Hamiltonian, h_i, for H_2^+. The TDCS, which is a function of the solid angles, Ω_1 and Ω_2, of the outgoing electrons and one of their energies, E_1, is then given by the simple relation, $d\sigma / dE_1 d\Omega_1 d\Omega_2 = 4\pi^2 k_1 k_2 \left| f(\mathbf{k}_1, \mathbf{k}_2) \right|^2 / \omega c$, where c is the speed of light. Numerical implementations of this method, including the one involving B-splines *(S2,S3)* used here, are described in detail elsewhere *(S1)*.

To solve Eq. (S1) we used a single center expansion including all contributions of products of spherical harmonics with angular momentum quantum numbers for the two

electrons, l_1, m_1 and l_2, m_2, having magnitudes up to five. To test the convergence of our numerical solution for the outgoing wave function, Ψ_{sc}, we compared the solutions of Eq. (S1) using the formally equivalent length and velocity forms of the dipole operator, μ. That comparison gave small but noticeable differences only for polarization parallel to the molecular axis (Σ_u contribution), for which the cross sections are nearly a factor of ten smaller than that for perpendicular polarization (Π_u) *(S4,S5)*. A further comparison of the results using the velocity form of the dipole operator including angular momenta, l_i, $|m_i| \leq 4$, with calculations including l_i, $|m_i| \leq 5$ showed essentially no differences, and we therefore conclude that the calculations using the velocity form have converged. To test the accuracy of the initial state we compared the results with maximum values of *l* equal to 6 and 8 and found no visible changes in any of the cross sections shown in the figures. The combined B-splines and spherical harmonics representation converts Eq. (1) into coupled linear equations. Using angular momenta up to five leads to 22 coupled pairs of angular momenta for the two electrons in Σ_u symmetry and 79000 unknowns, while in Π_u symmetry there are 35 coupled pairs of angular momenta and 126000 unknowns. The resulting linear systems are sparse and were solved with the help of iterative methods on cluster computers.

Supporting Online Material References

S1. C. W. McCurdy, M. Baertschy and T. N. Rescigno, *J. Phys. B At. Mol. Phys*. **37**, R137 (2004).

S2. C. W. McCurdy and F. Martín, *J. Phys. B: At. Mol. Opt. Phys.* **37**, 917 (2004). H.

S3. Bachau, E. Cormier, P. Decleva, J. E. Hansen and F. Martín, *Rep. Prog. Phys.* **64** 1815 (2001).

S4. W. Vanroose, F. Martín, T. N. Rescigno and C. W. McCurdy, *Phys. Rev. A* **70**, 050703 (2004).

S5. J. Colgan, M. S. Pindzola and F.Robicheaux, *J. Phys. B: At. Mol. Opt. Phys.* **37,** L377 (2004).

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Methods Section

Equations S1- S2

References S1-S5