Complete Photo-fragmentation of the Deuterium Molecule

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Abstract

All properties of molecules from binding and excitation energies to their geometry, and bond length are determined by the highly correlated initial state wavefunction of the electrons and nuclei. Perhaps surprisingly, one promising way to reveal the details of these correlations is to study the break-up these systems into their constituents. For instance this can be done by photon absorption [ref], collision with a charged particle or exposure to a strong laser pulse [ref]. If the exciting interaction is sufficiently understood, one can use the fragmentation process as a tool to learn about the bound initial state [Moshammer, Levin]. However, often the interaction and the fragment motions pose formidable challenges to quantum theory [McCurdy, Weber, Briggs]

Here we report results from the four particle coincident measurement of the momenta of both nuclei and both electrons from the single photon induced fragmentation of the deuterium molecule. We show that the correlated motion of the electrons is strongly dependent on the inter-nuclear separation in the molecular ground state at the instant of photon absorption.

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Text

Small systems of Coulomb interacting particles such as the Helium atom or the Hydrogen molecule have been paradigms for quantum theory since its early days. However, despite 80 years of theoretical attention, near exact calculations for such systems are only available for bound states. On the experimental side, the tests of these calculations are largely based upon level energies or single particle momentum distributions [ref]. Very promising and challenging new classes of experiments are those which achieve a complete description of the outcome following the excitation of the ground state to an unbound continuum. The momenta, i.e. the vectors, of all the fragments of an atom or molecule break-up can be measured in coincidence with high precision using state-of-theart imaging and timing techniques [ref]. Thus in contrast to bound states, the squared, multidimensional, momentum-space, continuum wave-function can now be measured completely. These asymptotic many-particle momentum distributions are determined by the interaction process that caused the fragmentation, and the bound initial state from which it emerged as well as final state interactions between the outgoing particles. Thus it is useful to the experimentalist to keep the interaction process as simple as possible and find a geometry in which final state interactions are negligible or constant. Therefore, in the present study we used the absorption of a single photon to completely break up the deuterium molecule by depositing a well defined energy and angular momentum into the system, i.e:

 $hv + D_2 \rightarrow 2 e^- + 2 d^+$

(To uncover the correlation effects we have chosen a special non-coplanar geometry we will introduce later.)

Due to their heavy masses, the velocities of the nuclei are much smaller (by a factor of $\sim 1/60$) than those of the electrons; hence the initial motion of the nuclei in the continuum

can be assumed to be as it was in the ground state at the instant of the electronic transition (Born Oppenheimer approximation). Once the electrons have left the system, the motion of the nuclei is governed by their Coulomb repulsion; they accelerate and potential converts to kinetic energy. Therefore, classically, the inter-nuclear distance at the instant of photo absorption corresponds to a unique Kinetic Energy Release (KER). Quantum mechanically one maps the nuclear vibrational wave-function (via the reflection approximation) onto the Coulomb potential to yield a KER spectrum. By reversing this process a measured KER spectrum can be converted to the squared nuclear vibrational wave-function. Thus the coincident measurement of the momenta of the electrons and the ions give one access to not only the molecular orientation but also to the important internal coordinate, the inter-nuclear separation ΔR at the instant of fragmentation. Therefore by selecting the measured events that occur within a fixed sub-region in the KER spectrum, one samples molecules for which the corresponding inter-nuclear distance is defined much more precisely than the full extent of the initial nuclear wavefunction. This is an important experimental grip on a parameter decisive in determining the initial electronic wave-function; in this report we show how the electronic continuum momentum distribution depends on the inter-nuclear separation in the molecule and its orientation with respect to the photon polarization.

The validity and high sensitivity of the mapping of the ground state distribution of internuclear distances to the KER is demonstrated in figure 1. The red line shows the nuclear wave-function obtained when approximating a D_2 potential curve by a harmonic oscillator with the correct vibration frequency and equilibrium distance, while the black curve shows the calculation with a more refined wave-function obtained from a much more accurate Morse potential. Clearly the experimental KER spectrum is a sensitive measure of the nuclear component of the total molecular wave-function.

Multi-particle coincidence experiments, such as reported here, have become possible with the advent of modern micro-channel plate multiplier based imaging techniques combined with high resolution time-of-flight measurements. Our utilization of these is manifested in what has been termed COLTRIMS (COLd Target Recoil Ion Momentum Spectroscopy) [doerner2000pr, ullrich03rpp, weber00nature, schulz02nature]. In brief, inside our momentum spectrometer, a supersonic D₂-gas jet was crossed with the linear polarized photon beam from beamline 7.013 of the Advanced Light Source at Lawrence Berkeley National Laboratory (D_2 provides a higher target density than a comparable H_2 gas jet and data less contaminated by random coincidences from background H₂O). The electrons and ions created in the intersection of the photons with the jet are guided by a combination of homogeneous electric and parallel magnetic fields onto two 80 mm diameter channel plate detectors (one for the electrons, one for the ions) equipped with delay-line position readout anodes (see www.Roentdek.com). The detectors can register multiple coincident events ("hits"). For each particle, the position of impact and the timeof-flight to the detector is registered in event-mode. From these values and the geometry and fields, the momentum vectors of all particles from each fragmentation event can be calculated. For a part of the experiment the electric fields were pulsed; they were low during the short flight time of the electrons, then switched high to project the ions onto their detector. This procedure provided better resolution for the electron momenta without sacrificing collection efficiency for the slower moving ions

In figure 2 we illustrate the dependence of the coincident electron angular distribution on the molecular orientation represented by the (green) barbell. In the figure the molecular axis, the light polarization axis (aligned horizontally) and one of the electrons are fixed to one plane. An equal energy sharing between the outgoing electrons has been selected. The momentum vector of the second electron is fixed perpendicular to that plane pointing towards the observer as indicated by the circled (red) cross. This geometry is chosen because here the distribution is determined mainly by the molecular effect on the correlated wave function and the influence of angular momentum and parity selection rules. By keeping the angle between the two electrons constant at 90° everywhere in the plane of the figure, we expect minimal influence of the electron-electron interaction in the final state. For other geometries, e.g. where all particles and polarization are coplanar, we find that the angular distributions are almost completely dominated by the interplay between the electron-electron repulsion and the selection rules [ref].

An *atomic* photo-ionization cross section can be described by $d\sigma/d\theta = A + B \cos^2(\theta)$ where θ is the angle of the electron with respect to the polarization axis (this is the dipole approximation result valid at low photon energies). The symmetry axis would necessarily be the axis of the polarization of the photon, which caused the electronic transition. In contrast, figure 2 for the molecular case shows a strong dependence of the electron angular distribution on the molecular orientation demonstrating the importance of this new reference axis. While the light field attempts to drive electrons toward a dipole pattern keyed to its polarization axis, the two-body Coulomb potential of the molecule fixed-in-space seems to favor electrons escaping perpendicular to its axis. Furthermore the distribution is not describable by a pure dipole shape; it shows additional small lobes (see fig. 2b+c) indicating that higher angular momentum components are present. The interplay of these effects yields the observed distributions. A possible reason for the preferred emission perpendicular to the molecular axis could be the ground state electron momentum distributions in the molecule, neglecting any electron-electron repulsion in the final state. Since in configuration space the electronic wave function is elongated along the inter-nuclear axis the momentum space wave function, i.e. the Fourier transform, peaks perpendicular to the molecular axis. The photo-ionization probes the momentum space wave function; indeed, the photo-ionization matrix element in the high energy limits corresponds to the Fourier transform of the initial state. On the other hand, a description of the ionization process in terms of diffraction of an initial outgoing electron wave (again, neglecting the electron-electron interaction) by the two centers of the potential can yield similar complex angular distribution patterns. From this one might expect that these emission patterns of the Photo Double Ionization (PDI) shown in fig 2, can be described by the single ionization of a D_2^+ -Ion. Despite these seemingly reasonable qualitative ideas, we show in the following that nature requires something else.

A key result of our experiment is shown in figure 3 for a fixed molecular orientation of $55 \text{ deg} \pm 24$ with respect to the polarization vector. This is the same geometry as in figure 2, but here the plots are made for selected regions in the KER spectrum as show in the small insets on the right of each panel. As shown in Fig. 1, this corresponds directly to a selection of the inter-nuclear separation and this is represented by the varying length of

the (green) barbell. Surprisingly for the largest separation, where the influence of the two body nuclear Coulomb field of the fixed molecule is supposed to be strongest, the angular distribution resembles a helium-like dipole pattern, i.e. mainly aligned along the polarization axis (see fig. 3a). For the smallest inter-nuclear separation (fig 3c) two effects are seen: The emission pattern is essentially orthogonal to the molecular axis and the distribution has changed from a dipole to a four-lobe pattern, indicating higher angular momentum components involved. Although not shown here, this behavior is also observed for other electron energy sharing ratios. What is the physical origin of these observations? First, we exclude interference from on a simple two center diffraction, since here the wavelengths of the electrons are 4-6 times the inter-nuclear separation hence precluding observation of a minimum. Second, whereas a multiple scattering of the photoelectron wave at the two centers could lead to a variation of the angular distributions, as is predicted and observed for K-shell ionization of the CO molecule for instance [ref], calculations on H₂ show that this effect, as a function of the inter-nuclear separation ΔR , is negligible [ref = ?]. This is because the protons (deuterons) are relatively weak scattering centers and the long wavelength of the photoelectrons would require long paths within the molecular potential. A remaining possibility might be found in the initial state electronic wave function. However, here one would expect, in the limit of a vanishing inter-nuclear separation a He-like pattern, whereas we observe stronger molecular behavior at our smallest ΔR .

A calculation based on an appropriate two-electron initial state is included in fig. 3b for the intermediate case corresponding to the most probable equilibrium distance of 1.4 a.u. The experimental data show a mixture of patterns similar to the dipole distribution of fig. 3a and the four lobe structure of fig. 3c. A simple model [ref] in which a pair of photo ionization amplitudes f_{Σ} and f_{Π} is introduced for the light polarization parallel (Σ) and perpendicular (Π) to the molecular axis ionizing the molecule is shown as the (blue) solid line. To evaluate the amplitudes f_{Σ} and f_{Π} we used a single-center expansion of the H₂ ground state (wave-function by Joy and Parr [ref]), and a convergent close-coupling (CCC) expansion of the final two-electron state in the field of a point-like charge Z = 2. This theory, neglecting two-center electron-nuclei interaction in the final state, yields only the dipole pattern. The difference between this result and the observations reveals the complex diffraction of the outgoing electron wave from a highly correlated two electron initial state.

In conclusion we see a highly structured and strong dependency of the electronic angular distribution on the molecular orientation which can be rudimental understand by the Heisenberg uncertainty, multiple scattering or a single center expansion combined with a CCC-calculation. These makeshifts break down while examine the emission pattern as a function of the internuclear distance of the molecule at the instant of photon absorption. The angular distributions, apparently highly influenced by an appropriate initial state wave function, diffraction and electron-electron correlation, show fully unexpected behaviors which are not understood yet. We emphasize that the present investigation represents an exquisitely sensitive and direct test of the initial state wavefunction and its correlation effects! An intricate calculation to describe the results found in this experiment is highly desirable: The complete understanding of the break-up of this

fundamental molecule represents the first step of the discovery of the dynamics of many particles systems, which will have an enormous impact on the world of chemistry.

Figure captions

Fig1.eps:

Determination of the internuclear distance ΔR in the ground state nuclear wave function of D₂ by measuring the Kinetic Energy Release KER after double ionization with linear polarized light of 75.5 eV. The ground state wave function is mirrored at the repulsive d + d potential curve onto the KER: The red curves show the reflection approximation starting with a harmonic oscillator potential, the black curves base on a description with a Morse potential. The open triangles represent the experimental data points.

Fig2.eps:

Angular distribution of one electron (black dots) in the plane of the molecular axis (green barbell) and the electric field vector of the linear polarized light ε (see double headed arrow aligned horizontally) for a photon energy of 75.5 eV. The second electron is pointing out of the plane orthogonally towards the observer marked as the (red) circled cross. Both electrons have an energy of 12.25 eV each. The dashed lines show a fit with spherical harmonics ($l \in [1,4]$, $m \in [0,1]$).

Same as fig2, but here the molecular axis is fixed as indicated while the Kinetic Energy Release KER varies as shown in the insets to the right. High kinetic energy release corresponds to small internuclear distances ΔR at the instant of photon absorption and vice versa as described in fig.1. The dashed lines show a fit with spherical harmonics ($l \in [1,4]$, $m \in [0,1]$). The (blue) solid line represents the result from a single center expansion of the molecular ground state and a convergent close-coupling (CCC) expansion of the final two-electron continuum.