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Towards simultaneous imaging of ultrafast nuclear and electronic dynamics in small molecules

Saurabh Mhatre^{1,2}, Zack Dube³, André Staudte³, Stefanie Gräfe^{2,4} & Matthias Kübel¹✉

When a chemical bond is broken, the molecular structure undergoes a transformation. An ideal experiment should probe the change in the electronic and nuclear structure simultaneously. Here, we present a method for the simultaneous time-resolved imaging of nuclear and electron dynamics by combining Coulomb explosion imaging with strong-field photoelectron momentum imaging. We study the dissociative photoionization of H_2 and N_2O using time-resolved photoion-photoelectron coincidence spectroscopy. The measured delay-dependent kinetic energy release clearly reveals the ultrafast nuclear dynamics. The transient changes in the electronic structure of the dissociating H_2^+ molecular ion are studied by solving the three-dimensional Schrödinger equation in the fixed-nuclei approximation. A detailed comparison of the numerical results to those from a simple imaging model is conducted. The numerical results reflect the evolution in the electron density in the molecular ion as its bond is first stretched and then breaks apart. While these details remain unresolved in the H_2 experiment, we demonstrate the sensitivity of the photoelectron signal to the site of electron localization following bond cleavage for the case of N_2O . Our work shows opportunities and challenges on the track towards capturing simple gas-phase chemical dynamics in complete molecular movies.

Femtosecond and attosecond laser technology have made it possible to resolve the ultrafast phenomena on the molecular timescales^{1–4}. Owing to the substantial difference between timescales on which the electronic and nuclear motion occur, they are usually treated separately in the framework of the Born-Oppenheimer approximation. Although this treatment has proven helpful, it fails in situations where the energy separation of electronic states becomes small, implying slow electronic dynamics. This is the case in the vicinity of avoided crossings and conical intersections^{5,6}. However, the dynamics of nuclei and electrons are also intertwined even in relatively simple processes, such as bond stretching or bond breakage.

From the experimental side, the correlated motion of electrons and nuclei calls for suitable experimental techniques⁷. Significant progress has been made using, among others, time-resolved fluorescence⁸, transient absorption⁹, or high-harmonic^{10,11} spectroscopy. However, it is challenging to disentangle the contributions from different molecular processes when detecting only photons. A powerful approach is the use of multi-messenger techniques, such as the coincidence detection of electrons and nuclear fragments^{12–14}. In such experiments, one can, for example, measure the photoelectron spectra associated with different fragmentation channels^{12,15,16}, thus identifying the states involved.

Besides the scalar energy values of photoelectrons and ions, spatial resolution is of interest in order to obtain geometrical information about the molecular structure. Imaging of the nuclear geometry of a molecule can be achieved, for example, using Coulomb Explosion Imaging (CEI), where the momentum vectors of multiple ionic fragments from the breakup of a multiply-charged molecule are measured in coincidence^{17,18}. By combining CEI with pump-probe techniques, a series of snapshots visualizing the nuclear motion can be obtained, sometimes referred to as Molecular Movies. Examples include movies of molecular alignment^{19,20}, vibrational wave packet motion²¹, hydrogen migration^{22,23} and roaming dissociation^{24,25}. Recently, CEI was combined with coincident photoelectron momentum imaging to follow the ultrafast vibrational wavepacket of H_2^+ created by tunnelionization from H_2 ^{26,27}.

For probing the electronic structure, it is promising to turn to the electrons themselves. Using intense laser pulses, the recolliding electron wave packet²⁸ as a means to image molecular structure^{29–32} has received much attention. Laser-induced electron diffraction (LIED)³³ allows for measuring the internuclear distances in a molecule if the deBroglie wavelength of the recolliding electron is comparable to the relevant bond

¹Institute of Optics and Quantum Electronics, Friedrich Schiller University, 07743 Jena, Germany. ²Institute for Physical Chemistry, Friedrich Schiller University, 07743 Jena, Germany. ³Joint Attosecond Science Laboratory, National Research Council of Canada, Ottawa, Canada. ⁴Fraunhofer Institute of Applied Optics and Precision Engineering, 07745 Jena, Germany. ✉email: matthias.kuebel@uni-jena.de

lengths^{31,34–37}. Moreover, the re-scattered wave packet interferes with the unscattered electrons, leading to a holographic interference pattern^{38–40}. This hologram contains information on the rescattering potential⁴¹, and the ionization dynamics^{42–45}.

In the absence of recollision, the momentum distribution arising from strong-field ionization also contains structural information^{30,46–50}. It was shown in Ref.³⁰ that the photoelectron momentum distribution (PMD) in the plane perpendicular to the laser polarization resembles the projected valence electron density of the highest occupied molecular orbital, or more specifically, the Dyson orbital. Murray et al. showed that orbital imaging by laser-induced tunnel ionization could be understood within a partial Fourier-transform (PFT) method^{46,47}. Recently, this method was successfully used to reproduce and interpret time-resolved measurements of an electronic wavepacket in the argon cation⁵¹. However, molecular movies based on laser-induced orbital imaging have not yet been reported.

In the present work, we expand the method put forth in Ref.⁵¹ to study ultrafast molecular dynamics by combining delay-dependent CEI with orbital imaging through laser-induced tunnel ionization (Fig. 1). This enables visualization of both bound and dissociating nuclear wave packets by CEI, while simultaneously probing the transient electronic structure of the molecular cation in different channels by measuring the PMD in the molecular frame. Experiments are carried out for both H_2 and N_2O . Through numerical solutions of the electronic time-dependent Schrödinger equation for H_2^+ in the frozen nuclei model, we systematically study the dependence of the PMD on the internuclear distance. This translates into a pronounced difference between the PMDs arising from ionization of the bound and the dissociated species, such that they represent an indicator of the rearrangement of the electronic structure during nuclear motion. An intuitive imaging model, which captures the essential details, supplements the rigorous TDSE calculations. Our time-resolved coincidence data for the dissociation of N_2O^+ shows that the measured molecular-frame photoelectron momentum distribution is sensitive to the localization of the hole on one of the fragments.

Results and discussion

Nuclear dynamics in H_2^+

Experimental and theoretical (non-Born-Oppenheimer TDSE) results for the nuclear dynamics in H_2^+ , probed by time-resolved CEI, are presented in Fig. 2 (a) and (b). To interpret the features observed in the CEI results, the pump-induced time-dependent nuclear density is plotted with respect to the repulsive Coulomb potential of the two protons (V_{nn}) in Fig. 2(c). The delay-dependent KER distributions reveal two processes taking place after ionization and excitation by the pump pulse: bound vibrational motion, observed at high kinetic energies ($\text{KER} \gtrsim 4$ eV), and dissociation, observed at low energies. Note that as the non-Born-Oppenheimer model directly describes the field-induced electron dynamics it does not rely on any electronic states. However, for analysis, the electron dynamics can be projected onto adiabatic (Born-Oppenheimer) eigenstates. These projections show that the dynamics can be well described to occur on the two lowest electronic states of H_2^+ . Thus the bound vibrational motion is ascribed to the bound $1s\sigma_g$ ground state while dissociation is attributed to the dissociative $2p\sigma_u$ state.

The KER range covered by the high-energy part in the experimental data, $4 \text{ eV} \leq \text{KER} \leq 10 \text{ eV}$ corresponds to bond lengths in the range of approximately $7.0 \text{ a.u.} \geq R \geq 2.8 \text{ a.u.}$, well above the equilibrium internuclear distance of $R = 2 \text{ a.u.}$, which would correspond to $V_{nn} = 13.6 \text{ eV}$. Such large potential energies are clearly present in (Fig. 2(c)) but are not probed at the experimental intensity due to the very large ionization potential of H_2^+ at short R . The non-Born-Oppenheimer 1D-TDSE results (Fig. 2(b)), show a slightly narrower energy

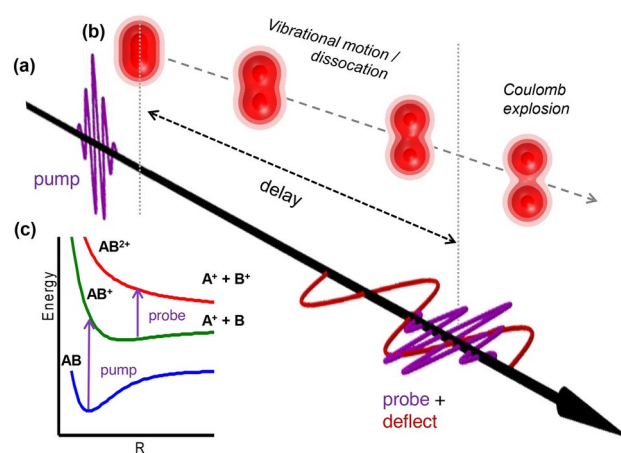


Fig. 1. The experimental scheme. (a) A few-cycle pump pulse ionizes the H_2 molecule. The induced nuclear and electronic motions in the resulting H_2^+ ion (shown as a sketch in (b)) are then monitored using the delay-adjustable probe pulse which is perpendicularly polarized to the pump pulse. Along with the probe pulse, a stable mid-infrared pulse is superimposed as a deflection field, which helps in distinguishing the photoelectron spectra generated by the pump pulse and the probe pulse by deflecting electrons generated by the probe pulse. The general ionization pathways in the diatomic molecule are depicted in (c).

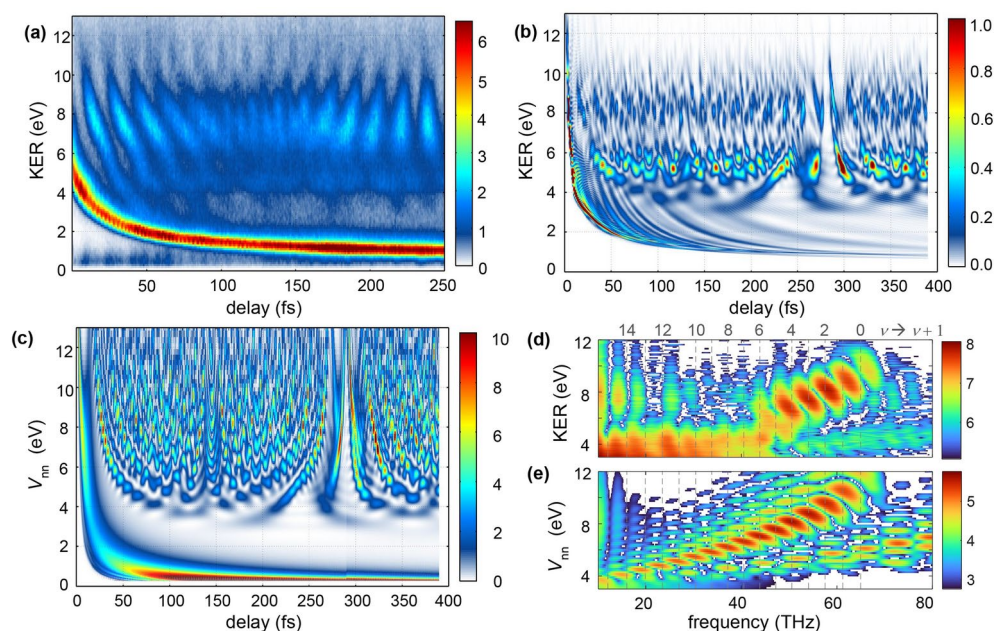


Fig. 2. Coulomb Explosion Imaging of the nuclear dynamics: **(a)** Measured KER distribution of protons detected in coincidence, **(b)** Results obtained with the non-Born Oppenheimer model and considering the interaction with the probe pulse. **(c)** Calculated evolution of the potential-energy density following interaction with the pump pulse. **(d)** Spectral power density calculated from the data shown in panel **(a)** by Fourier transform along the delay axis. The vertical dashed lines indicate beatings of adjacent vibrational states in the σ_g ground state. **(e)** Same as **(d)** but for the theoretical data.

distribution, probably due to a slightly lower intensity used for the calculations. The delay-dependent KER distributions show pronounced oscillations, which allow us to track the vibrational motion, taking place in the bound electronic ground state $1s\sigma_g$ of H_2^+ . As shown in Fig. 2(d) and (e), and previously demonstrated for D_2^+ in Ref.²¹, this type of data allows to accurately determine the composition of the vibrational wave packet contributing to the signal at different KER values. By performing a Fourier transform along the delay axis, we find, for example, that at a KER of 9 eV, the wave packet mainly consists of contributions from $0 \leq \nu \leq 3$, while $4 \leq \nu \leq 7$ contribute at the KER of 6 eV. The composition of the vibrational wave packets agrees for the experimental and the numerical results, despite the visual differences between the measured and calculated delay-dependent KER distributions. The faster oscillations, beyond the $\nu = 0 \rightarrow \nu = 1$ superposition, can be ascribed to superpositions $\nu \rightarrow \nu + 2$ (not drawn). They are more prominent in the theoretical data than in the experiment, likely due to the time resolution of the experiment. Besides, the lack of averaging over the molecular alignment in the 1D theoretical models may exaggerate the presence of the fast oscillations. Moreover, the strong enhanced-ionization signal around 5 eV in Fig. 2(b) is overestimated in the 1D model due to the reduced dimensionality, which does not allow incorporating the cross-polarized pump-probe pulses used in the experiment. As can be seen in the data, the nuclear wave packet disperses after a few oscillations and becomes delocalized. In the present case of H_2^+ , after approximately 250 fs, clear oscillations are once again observed as the vibrational wave packet rephases. This behavior is clearly observed in the delay-dependent potential energy distribution of Fig. 2(c) and also in the non-Born-Oppenheimer 1D-TDSE calculations of Fig. 2(b). The numerical calculations are extended to 400 fs, showing clear revival (rephasing) dynamics at 290 fs.

The low-energy part (KER < 4 eV) is dominated by a narrow distribution, whose central KER value decays with increasing delay. This signal corresponds to the dissociation of the molecular cation, which takes place when the molecular ion is excited to the first excited state, $2p\sigma_u$. The dissociation channel converges to an energy value of ≈ 1 eV, which is consistent with the kinetic energy gain from the dissociation on the $2p\sigma_u$ state of H_2^+ following single-photon excitation from the $1s\sigma_g$ ground state at $R = 6$ a.u.. Note that, in the numerical results, the signal at very low KER, corresponding to large internuclear distances, is lost due to the finite grid size. This leads to the discrepancy with the experimental data at low KER.

The nuclear dynamics, which are probed by the CEI results presented above, are accompanied by variations in the electronic structure. During the bound wave packet motion, the electron density in the molecular ion stretches along the bond. As long as significant density remains between the two nuclei, the chemical bond is intact. In the dissociated state, the electron density resides on one of the nuclei forming the hydrogen atom. Our goal to access this transition through photoelectron momentum imaging has not been reached by experimental means. Thus, we report on our theoretical studies of the R-dependent photoelectron momentum distributions below.

Calculated photoelectron momentum distributions for H_2^+

The variations of the electronic structure associated with the nuclear dynamics can be probed by direct imaging of the outgoing electron wave packets. In this section, we study the imaging of the electronic density using the 3D electronic TDSE model. Calculations are performed for various internuclear distances and for the hydrogen atom. To evaluate the orbital imprint in the PMD, the three-dimensional momentum space density $|\Phi(p_x, p_y, p_z)|^2$ is integrated over the polarization direction (z -axis) yielding the transversal momentum density,

$$\mathcal{M}(p_x, p_y) = \int_{p_z} |\Phi(p_x, p_y, p_z)|^2 dp_z, \quad (1)$$

where $\Phi \in [\mathcal{F}\{\Phi_0\}$ (ground state), ψ_p^{TDSE} (TDSE calculated PMD), Φ^{PFT} (PFT calculated PMD)]. For more details, see the Simulations section. In Fig. 3, the calculated momentum distributions of the bound electron orbital or electronic ground state (upper row) and the PMDs calculated by TDSE (middle row) and PFT models (bottom row) for various internuclear distances are shown. The direct comparison between the momentum distributions for the bound electron and the photoelectron reveals an obvious resemblance between them, albeit the logarithmic color scale used for the PMD due to a weak signal at large momenta. For example, the PMD for the hydrogen atom maintains the circular shape of the orbital. This circular symmetry is lost in the case of the molecular ion, which is narrower along the molecular bond due to the electron density being spread out over the two nuclei. As the bond stretches, a fringe structure emerges, which is also maintained in the PMDs obtained

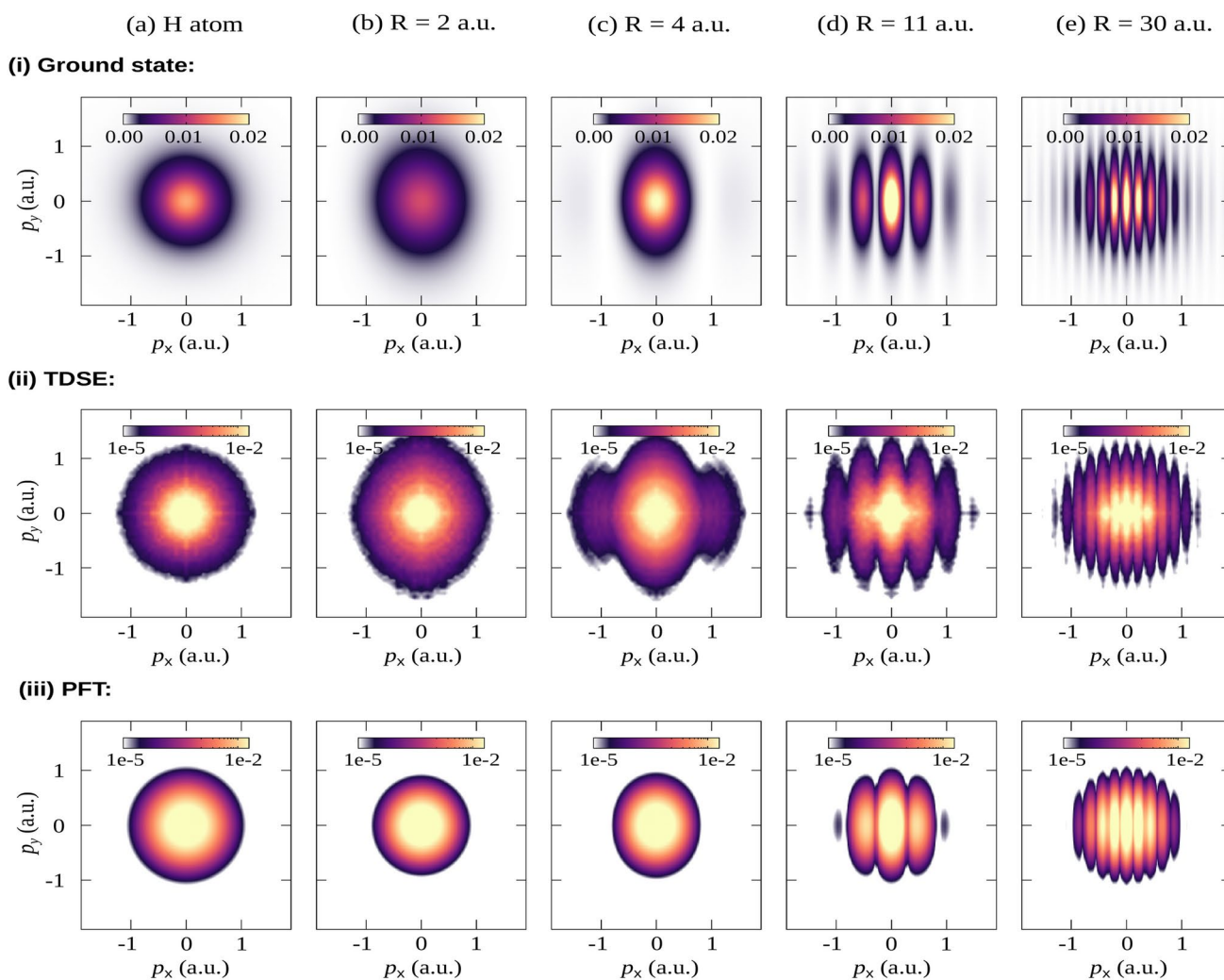


Fig. 3. Numerical results for the transversal photoelectron momentum densities $[\mathcal{M}(p_x, p_y; R)]$, where the (a) hydrogen atom (atomic case) is compared against increasing internuclear distance (b–e) in the H_2^+ molecule. The molecular bond is aligned along the x -axis. The (i) ground state (initial and bound) electron densities are shown in the upper row, while the photoelectron momentum spectra after the pulse calculated via the (ii) TDSE model and the (iii) PFT model are given in the middle and lower rows, respectively. The color map for the upper row is given in the linear scale, while for the PMDs, the logarithmic scale is used due to relatively low yields.

by both TDSE and PFT models. The number of fringes increases with the internuclear distance. The fringe pattern arises due to the interference between electron wave packets emitted from each nucleus, which creates a diffraction pattern similar to Young's double slit experiment⁵². The diffraction fringes can in fact be used to estimate the internuclear distance using the equation

$$R = \frac{2\pi}{\Delta p_x}, \quad (2)$$

where Δp_x is the separation between the two adjacent fringes. These types of double-slit interference in molecular photoionization have been observed in various experiments using intense-laser⁵³, XUV⁵⁴ and x-ray sources⁵⁵. At large R , the circular shape of the momentum distribution is restored with a fringe pattern superimposed. This indicates that the electron is in a superposition state of being localized on either of the hydrogen nuclei.

For a more quantitative analysis of the momentum distributions, the transversal densities are integrated over the p_y -axis, as shown in Fig. 4. This helps us to focus on the features along the molecular bond. In the case of an atom, the momentum distributions diminish monotonously at higher momenta. The decay is superimposed onto the fringe pattern for the molecular case. In comparison to the TDSE results, the PFT results show fewer fringes as the signal diminishes more steeply towards higher momenta. For this reason, the number of fringes appearing in the PFT results (up to a given signal level) is smaller than that for the TDSE results. This discrepancy indicates that the tunnel filter function used in the PFT model overestimates this decay. For the perspective of imaging the electronic density experimentally, this suggests that one may expect more signal at high momentum than predicted by the PFT model. Nevertheless, also for the TDSE results, the photoelectron yield decays much quicker towards higher momenta than the ground state density.

Normalized differences for H_2^+

As seen above, the PMDs of the bound and dissociation channels have distinct features along the molecular axis. However, they are dominated by the strong decay of the ionization yield, i.e. the effect of the tunnel filter. To suppress the effect of the tunnel filter and reveal the molecular-orbital imprint, normalized difference between two PMDs have been employed in previous works^{30,49,51}. The normalized difference between the transverse momentum distributions ($\mathcal{M}$) of a bound and a dissociated channel is defined as

$$\Gamma(p_x, p_y) = \frac{\mathcal{M}_{\text{atom}} - \mathcal{M}_{\text{mol}}}{\mathcal{M}_{\text{atom}} + \mathcal{M}_{\text{mol}}}, \quad (3)$$

where the dissociating (or atomic) PMDs ($\mathcal{M}_{\text{atom}}$) are compared against the bound (or molecular) PMD ($\mathcal{M}_{\text{mol}}$). Figure 5 displays the calculated normalized differences. Here, the internuclear distance of $R = 4$ a.u. is considered as the bound channel rather than the equilibrium distance $R = 2$ a.u.. This choice is due to the aforementioned low photoelectron yield obtained for the tightly bound molecule. In order to depict the case of the dissociating molecule, we take an average of the momentum densities over the internuclear distance of $R = 20$ a.u. to $R = 40$ a.u.. The similarity between the normalized difference of the initial momentum densities for the single hydrogen atom, shown in Fig. 5(a), and the dissociated molecule, shown in Fig. 5(b), confirms the loss of molecular character in the dissociated molecule.

In Fig. 5(c) and (d), the normalized differences for the PMDs calculated with PFT and TDSE models are shown, respectively. Compared with the results of Figs. 3 and 4, the normalized differences for the photoelectron resemble the normalized differences for the initial distributions much more closely. This is confirmed by the quantitative comparison in Fig. 5(e). Thus, normalized differences are in principle suitable to image variations in the electron density. However, as they require the usage of a reference distribution (here: the distribution for the molecular ion at $R = 4$ a.u.) the normalized differences display changes in the electron density rather than

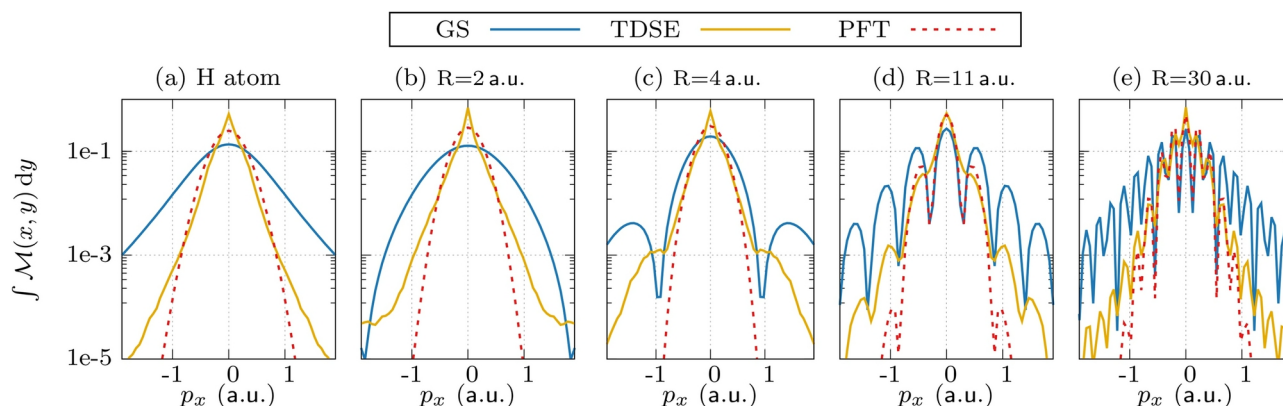


Fig. 4. The momentum distribution along the molecular bond. The momentum distributions of the ground state (GS) wavefunction (solid blue line), and the PMDs obtained using the TDSE (solid yellow line) and the PFT (dashed red line) are calculated by integrating the normalized $\mathcal{M}(p_x, p_y)$ over the p_y -axis.

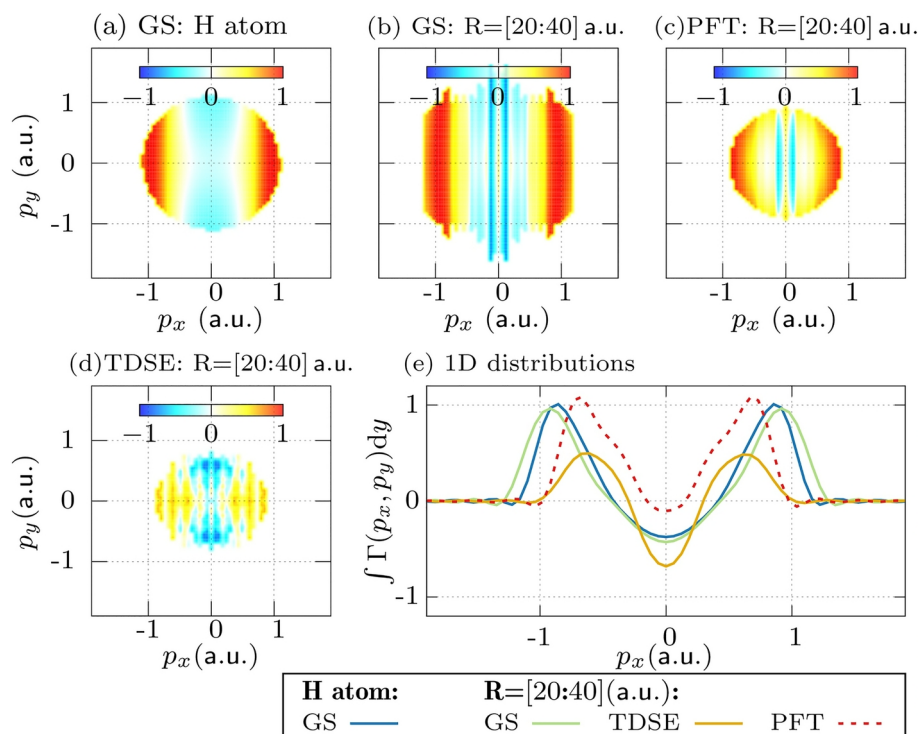


Fig. 5. The normalized difference (Γ) for atomic (a) and atom-equivalent (b–d) electron momentum distributions with respect to those of the bound molecule. Here, the corresponding distribution at $R = 4$ a.u. serves as the reference ($\mathcal{M}_{\text{mol}}$). For the atom-equivalent distributions, the results of the calculations performed for $20 \text{ a.u.} < R < 40 \text{ a.u.}$ were integrated. Results are presented for (a), (b) the ground state (GS) wavefunction, (c) for the PFT model, and (d) the TDSE. Panel (e) shows a quantitative comparison of the one-dimensional projections of the results presented in panels (a–d). The fringes have been removed for clarity by Fourier filtering.

absolute densities. The contributions of the two channels (signal and references) can be distinguished in the normalized difference, with the positive values (red) representing dominant contributions from the dissociated atomic orbital, and negative values (blue) representing dominant contributions from the bound molecular orbital. In the present case, the positive values for $|p_x| > 0.5 \text{ a.u.}$, can be attributed to the spherical shape of the atomic orbital, and the reduced widths of the momentum-space orbital of the molecular ion along its bond. Thus, the different widths observed in the normalized differences of the bound and dissociated channels can be understood as a result of the narrower confinement of the electron when bound to a single atom rather than the molecular ion.

Time-resolved coincidence measurements in N_2O

Compared to diatomic molecules, polyatomics offer significantly more complex dynamics, most notably different dissociation channels. One of the simplest molecules with two different bonds is N_2O . Its photodissociation dynamics have been studied rather extensively using soft x-ray⁵⁶, EUV^{57,58} and intense infrared light⁵⁹. When singly ionized by a few-cycle laser pulse, as used in the present experiment, dissociation along either the N–N bond or the N–O bond can result in the formation of any of the four possible ionic fragments (N^+ , O^+ , N_2^+ , NO^+)⁶⁰. For dissociation along the N–N bond, NO^+ fragments with a kinetic energy around 0.3 eV dominate over N^+ , while N_2^+ fragments dominate over O^+ for dissociation along the N–O bond^{60,61}. With this variety of dissociation channels, the molecule offers an interesting test ground for our pump-probe-deflect method.

The experiment was carried out using the same configuration and laser parameters as for H_2 . The pump pulse produces N_2O^+ , which may dissociate along either of the two bonds - or stay bound. The probe pulse ionizes the molecular cation, which coulomb explodes into either $\text{N}^+ + \text{NO}^+$ (“denitrogenation”) or $\text{O}^+ + \text{N}_2^+$ (“deoxygenation”). As above, the probe pulse is accompanied with the mid-IR deflection pulse which helps to identify the photoelectron emitted in the probe step. We focus on events where two ionic fragments are detected in coincidence with one photoelectron. While this data provides information about the dissociation dynamics in the cation, it is not directly possible to determine the site on which the hole localizes during dissociation. However, as we will demonstrate below, the photoelectron data provides strong evidence.

Figure 6 presents experimental results obtained for N_2O , where two ions and one electron have been detected in coincidence following double ionization by a time-delayed pulse pair. In close analogy to the H_2 results, the nuclear data, consists of two regions: one characterized by decreasing KER with increasing delay, corresponding to the dissociation of the molecular cation, and another one with larger and constant mean KER,

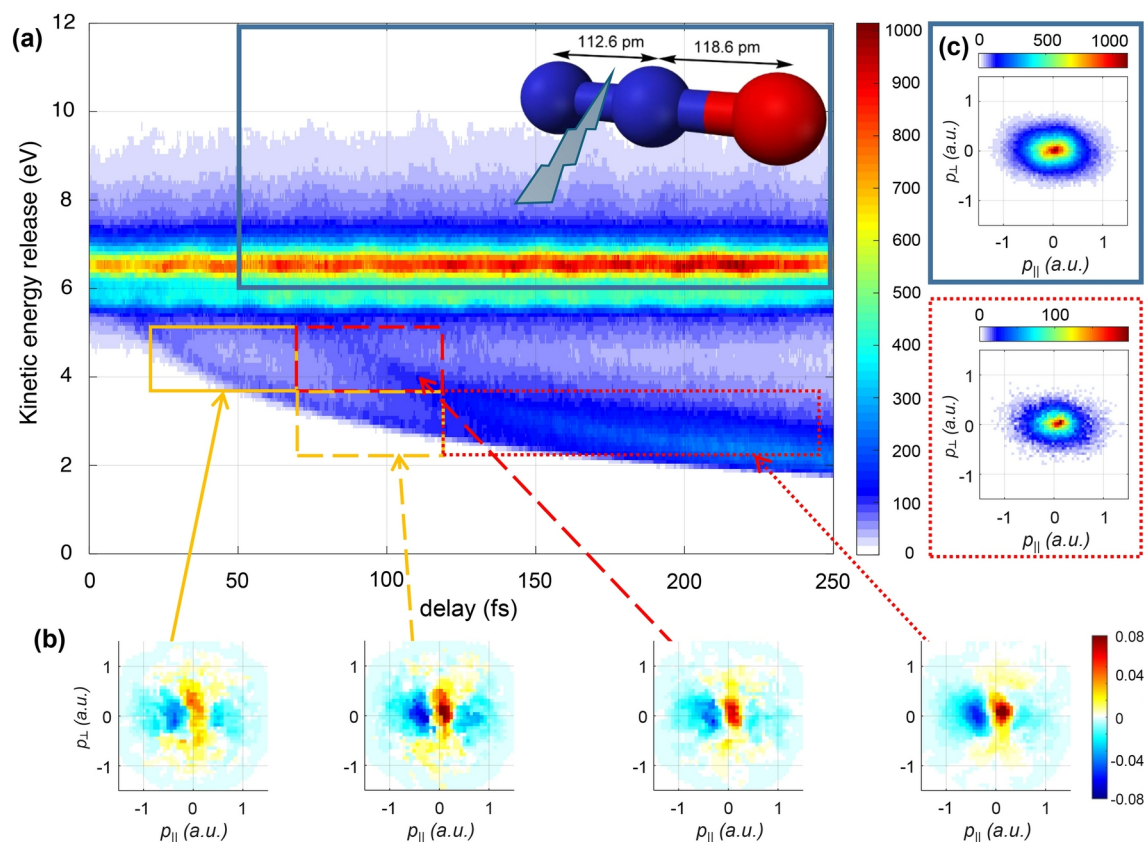


Fig. 6. Experimental results for denitrogenation of N_2O . **(a)** The delay-dependent nuclear kinetic energy release for the $\text{N}^+ + \text{NO}^+$ channel. **(b)** Normalized differences of molecular-frame PMDs measured in coincidence with ions falling into the indicated regions of panel **(a)**. The signal corresponding to ions in the blue box serves as the reference in all cases. The molecular frame is oriented as indicated by the ball-and-stick model, i.e. the N^+ ion is emitted to the left, while NO^+ is emitted to the right. **(c)** Lab-frame, raw PMDs corresponding to the dotted red box, and the solid blue box, respectively. Only electrons detected in coincidence with NO^+ (and N^+) ions emitted with positive (and negative) momentum i.e. to the right (left, respectively) are selected for the plot. The data was integrated over a cone with 30° opening, parallel to the pump polarization. The small shift of the centroid of the PMDs should be compared to the corresponding normalized difference plot in **(c)**.

corresponding to vibrational motion in the bound molecular cation. The latter one differs qualitatively from the one for H_2^+ , where strong signatures of vibrational motion were observed at large KER. Here, only slight delay-dependent oscillations are observed around 6 eV. This is a consequence of the flat potential energy curve of the $1^3\Sigma^-$ ground state N_2O^{2+} in the Franck-Condon region^{62,63}. Hence, the variations in the internuclear distance caused by vibrational motion result only in small oscillations of the KER. The dissociating contribution behaves similarly to H_2^+ . However, a short delay of approximately 20 fs before the onset of the dissociation curve can be seen. This is attributed again to the flat cationic potentials at short internuclear distances, which makes CEI insensitive at short internuclear distances. Interestingly, a second branch appears after approximately 80 fs, indicating delayed dissociation. The fact that this delay is significantly longer than the vibrational period suggests that the delay stems from a different electronic states in N_2O^+ . This is plausible as N_2O^+ possesses several close-lying dissociative channels, which produce NO^+ with differing energies⁶⁴ but the identification of the relevant state is not within the scope of this work.

The photoelectron data, represented by the molecular-frame, normalized-difference PMDs presented in Fig. 6(b) provide additional insights into the dissociation dynamics: along the molecular axis, a clear asymmetry with a maximum at positive momenta is observed. The asymmetry is present in both branches and its magnitude increases with increasing delay and decreasing kinetic energy release. In order to better understand the asymmetry along the molecular axis, it is insightful to turn to the raw laboratory-frame PMDs (without normalized difference) presented in panel Fig. 6(d). These are selected for NO^+ ions emitted with positive parallel momentum only. For the dissociative channel (red dotted box), a shift of the maximum in the photoelectron momentum distribution to the right, i.e. in the direction of the NO^+ emission, can be observed. When selecting NO^+ ions emitted to the left, the shift is inverted, validating the molecular-frame results of panel (c). Importantly, for the non-dissociative channel, the photoelectron momentum distribution is symmetric, with the maximum at $p_{\parallel} = 0$.

Our observations indicate, that the asymmetry or momentum shift in the molecular-frame PMDs arises from the dissociation process. It cannot arise from the laser field, as its component along the molecular axis would average out in the molecular-frame. A first candidate to explain the momentum shift is the velocity of the neutral fragment from which the electron is emitted. However, the fragment kinetic energy of approximately 1 eV (see Fig. 6(a)) corresponds to a velocity of less than 10^{-3} a.u., much less than the observed photoelectron momentum shift of 10^{-1} a.u.. This suggests that the momentum shift is acquired either during or after tunnel ionization through the effect of coulomb attraction by the nearby ionic fragment: either by Coulomb attraction of the liberated electron, or by displacing the site of tunneling.

The proposed mechanism causing the asymmetry in the molecular-frame PMDs relies on the localization of the previously created hole on one of the ions - in the present case, NO^+ . In the case of cleavage of the N-O bond, N_2^+ is the largest contribution⁶⁰. Thus, the probe laser predominantly ionizes O atoms in the presence of an N_2^+ ion. As a result, the photoelectron momentum distribution should be shifted towards the N_2^+ ion, i.e. to the left in the molecular frame. Figure 7 shows that this is indeed what we observe, confirming the prediction. Finally, the localization of the hole onto the ion also provides an explanation why the asymmetry increases with increasing delay and decreasing KER: as the molecule dissociates and the internuclear distance increases (leading to lower KER after the probe step), the hole localizes gradually onto the ion. Thus, the asymmetry increases until the localization of the hole is completed. At longer delay times, the asymmetry should decay again due to the eventually vanishing effect of the ionic field as the internuclear distance increases. Future work, which extends to longer time delays may address this prediction.

Conclusion(s) and outlook

In conclusion, using H_2 and N_2O , we have investigated a scheme to simultaneously track nuclear dynamics and the associated changes of the electronic structure. The scheme is based on time-resolved Coulomb explosion imaging in combination with photoelectron momentum imaging using intense few-cycle laser pulses. Our approach employs a mid-IR deflection field to separate photoelectron of the neutral precursor molecule from the photoelectron that reports on the molecular dynamics. We demonstrate experimentally that our scheme allows for sufficient time resolution to capture the fast nuclear dynamics of H_2^+ . The imaging of electronic structure is investigated using computational models, where the electronic 3D TDSE is solved in the fixed-nuclei approximation. The results show a pronounced dependence on the internuclear distance and can thus be used for visualizing the electronic structure changes during the dissociation process. We benchmark the approach of using normalized differences of PMDs to image molecular orbital features. Our work shows that despite some deviations with respect to the true electron density, the normalized differences captures the characteristics and symmetry of the bound wave functions. With time-resolved studies in mind, a particular strength of normalized differences is to sensitively detect changes in the electron density. While it has not yet been possible to image the electronic structure of the dissociating molecule experimentally, our results for N_2O demonstrate that our method is suitable to probe electron localization dynamics during the dissociation of molecular cations. The presented scheme offers a practical route to obtain complete molecular movies of both nuclear and electronic dynamics. A refined implementation of the experimental setup is currently in progress.

Methods

Experimental setup

The experimental setup is largely identical with the one used previously^{51,65}. Briefly, it consists of a femtosecond Ti:Sa laser (30 fs, 10 kHz, 1.6 mJ) and a Cold target recoil ion momentum spectrometer (COLTRIMS). The laser output is split into two parts. The first part (≈ 0.2 mJ) is postcompressed using an argon-filled hollow core fiber, chirped mirrors and glass wedges for dispersion fine tuning. Using a Mach-Zehnder interferometer equipped with a broadband half-wave plate and suitable beam splitters, cross-polarized few-cycle (pulse duration $\tau \approx 5$ fs full width at half-maximum of the intensity envelope) pump and probe pulses with adjustable time delay are obtained. The dispersion caused by the half-wave plate is compensated in the other interferometer arm using a 1 mm thick fused silica plate. The second part (≈ 1.4 mJ) of the Ti:Sa output is used to pump an optical parametric amplifier. The resulting CEP-stable mid-IR deflection pulse ($\tau = 40$ fs, $\lambda = 2300$ nm,

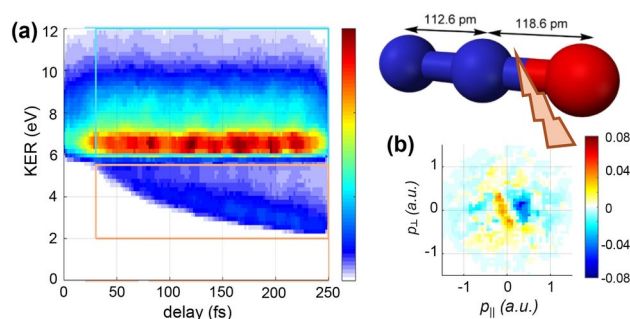


Fig. 7. (a) The delay-dependent nuclear kinetic energy release for the $\text{O}^+ + \text{N}_2^+$ channel. (b) Normalized differences of molecular-frame PMDs in the indicated regions of panel (a). The molecular frame is oriented as indicated by the ball-and-stick model, i.e. the N_2^+ ion is emitted to the left, while O^+ is emitted to the right.

p-polarization) is recombined with the cross-polarized pump and probe pulses on a Si plate at 70° angle of incidence. All laser pulses are focused ($f = 75$ mm) co-linearly into the center of the COLTRIMS where they intersect a molecular gas jet. The peak intensities of the pump and probe pulses are estimated as 3×10^{14} W/cm². The intensity of the deflection pulse is $\approx 2 \times 10^{13}$ W/cm², and causes no notable ionization on its own. The three-dimensional momentum distributions of ionic and electronic fragments generated in the laser focus are measured using time and position-sensitive detectors. The ion and electron count rates were approximately 5 and 8 kHz, respectively. This allows for the measurement of clean ion-ion coincidences. However, the electron data is subject to a significant contribution of false coincidences. Further, in the initial implementation of the experiment, which we report here, residual ellipticity in the probe pulse overshadows the orbital imprint in the PMDs, such that the presentation of the experimental results concentrate on the presentation of the data obtained from the ion detector only.

Fig. 1(a) shows the experimental scheme for the interaction with H₂. The usage of cross-polarized pump and probe pulses in the two-pulse double ionization scenario helps maximize the number of excited molecules aligned perpendicular to the probe laser polarization. The two generated protons are detected in coincidence with one of the two electrons. Owing to the mid-IR deflection field, those events where the detected electron is produced by the probe pulse, and not by the pump pulse, can be selected with high confidence. The comparison of electron momentum distributions produced by the pump only with those produced by the streaked probe pulse shows that electrons with $p_z < -0.6$ a.u. are produced almost exclusively by the probe pulse, see also⁵¹.

Three-dimensional momentum distributions of photoelectrons selected for the above condition, and detected in coincidence with ions of different kinetic energies are shown in Fig. 8. The molecular axis is along the x-axis, and the laser polarization is along the z-axis. The fact that the momentum distribution is wider along the x axis than along the y axis is due to a slightly elliptical laser polarization in the experiment.

Simulations

1D nuclear and 1D electron TDSE

The interaction of molecular hydrogen with the two laser pulses are described within a non-Born Oppenheimer time-dependent Schrödinger equation (TDSE) model. Here, the nuclear and electronic motion are co-linear and along the laser polarization (pump and probe pulses). All the following simulations employ atomic units ($\hbar = m_e = e = 4\pi\epsilon_0 = 1$), unless stated otherwise. The time-dependent Hamiltonian for our model is given as,

$$H(t) = T_n + T_e + V_{nn} + V_{ne} + xE(t), \quad (4)$$

$$T_n = \frac{p_R^2}{2\mu}, \quad T_e = \frac{p_x^2}{2}, \quad (5)$$

$$V_{nn} = \frac{1}{R}, \quad V_{ne} = -\frac{1}{\sqrt{(x \pm \frac{R}{2})^2 + \alpha(R)}} \quad (6)$$

where R and p_R are the internuclear distance and the corresponding momentum, x and p_x are the electron's distance from the system's center of mass and its corresponding momentum, μ is the reduced nuclear mass (918 m_e), $E(t)$ is the time-dependent electric field, and $\alpha(R)$ is the soft-core parameter, respectively. A detailed description of the model can be found in the work of Bandrauk et al.⁶⁶.

The dynamics are described in two steps. In the first step, the interaction of the H₂⁺ ion with the pump pulse and the subsequent dynamics is simulated assuming the instantaneous single ionization of H₂ near the pulse maximum, i.e. a vertical transition from H₂ electronic ground state to the H₂⁺ electronic ground state is performed. Thus, the initial state is defined with the Gaussian distribution along the nuclear coordinates centered around $R \approx 1.4$ a.u. (H₂ equilibrium distance) on the electronic ground state of H₂⁺ ion. The electronic ground state of the H₂⁺ ion is calculated using the imaginary time propagation. In the second step, the interaction with

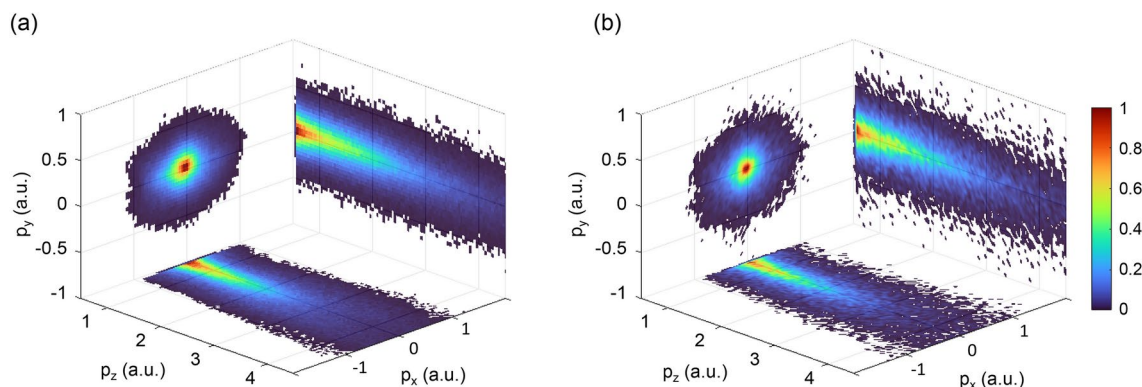


Fig. 8. Measured photoelectron momentum distributions for the H₂ experiment, selected for ion pairs in (a) the bound channel with KER > 5 eV, and (b) the dissociating channel with 2.5 eV > KER > 0.5 eV.

the probe pulse at delay τ is calculated, where the wave function obtained in the first step after propagation time τ is used as the initial state. Note that in these simulations, both the pump and probe pulses are polarized along the molecular axis, contrary to the experiment, and the IR deflection pulse is ignored entirely due to the low intensity. The same field parameters are used for the pump and probe pulses, which are of the form,

$$E(t) = E_0 \sin^2(\pi[t - \tau]/T) \cos(\omega[t - \tau] + \varphi), \quad (7)$$

with the field strength $E_0 = 5.14 \times 10^{10}$ V/m, angular frequency $\omega = 2.511$ PHz (or wavelength $\lambda = 750$ nm), phase $\varphi = 0$ and pulse width $T_{\text{FWHM}} = T/2 = 5$ fs. These calculations use an equispaced R -grid and x -grid spanning between $[0 : 112.5]$ a.u. and $[-204.8 : 204.8]$ a.u., respectively, with 2048 grid points each. The time evolution of the TDSE is carried out using the split-operator method. An absorber (also called mask function) is used to collect the escaped (ionized or dissociated) part of the wave function to avoid reflections off the grid boundaries. The utilized absorber function is described in the ref.⁶⁷ and reads

$$\zeta_{\text{ab}}(r; r_a) = \frac{1}{1 + e^{c(r-r_a)}}; \quad c > 0, \quad (8)$$

where c is the curvature parameter and r_a is the position of the absorber with r being a general grid. Here, for the x -grid: $c = 0.3$ and $r_a = |150|$ a.u., and for the R -grid: $c = 1$ and $r_a = 96$ a.u. are used.

The simplest way to follow the pump pulse-induced nuclear dynamics is to assume an instantaneous ionization by the probe pulse, instead of explicitly considering the probe pulse interaction. The kinetic energy release can then be estimated by from the nuclear density on the R -grid, $|\Psi(R, t)|^2 = \int |\Psi(x, R, t)|^2 dx$, using the nuclear repulsive potential V_{nn} (see fig 2(c)). However, in order to accurately describe the experimental method, the interaction with the probe pulse followed by the Coulomb explosion is also explicitly simulated. The resulting delay-dependent kinetic energy release (KER) spectra are obtained as follows. The ionized part of the wavefunction is collected using the aforementioned mask function situated near the x -grid boundary. This part is then further allowed to evolve in time on the nuclear grid under the nuclear repulsive potential (V_{nn}) and the vector field until the mask function on the nuclear grid is reached. The application of mask functions in TDSE for obtaining the photo-induced momentum distribution is described for atoms in ref.⁶⁸ and for molecules in ref.⁶⁶. At each time step the dissociated wavepacket, i.e. the wavepacket reached to the mask function, is Fourier transformed and added coherently to the already dissociated wavefunction $\chi_p(p_R, t)$. Thus, the momentum distribution and corresponding KER spectra of the dissociated nuclear wavepacket at the end of the time propagation are obtained by $|\chi_p(p_R, t_{\text{end}})|^2$.

3D electronic TDSE with frozen nuclei

The photoelectron spectra generated by ionization of the H_2^+ ion by the probe pulse are calculated by solving the three-dimensional electronic time-dependent Schrödinger equation (TDSE) with frozen nuclei. The molecular bond is set along the x -axis, while the laser polarization is perpendicular to the molecular bond along the z -axis and the field propagates along the y -axis. The TDSE for this model under dipole approximation reads

$$i \frac{\partial}{\partial t} \Psi(x, y, z, t; R) = (T_e + V_{ne}^{3D} + zE(t)) \Psi(x, y, z, t; R), \quad (9)$$

$$V_{ne}^{3D} = -\frac{1}{\sqrt{(x \pm \frac{R}{2})^2 + y^2 + z^2}}, \quad (10)$$

where E is the electric field.

Note that the soft-core parameters in the Coulomb attraction potential (V_{ne}) are not needed as we consider the complete 3D space and the singularities are taken care of by the finite grid spacing. Thus, these calculations are grid-sensitive. The grid dependency is minimized by ensuring the accuracy of hydrogen atom ground state energies ($I_p = 0.5$ a.u.) produced by the numerical imaginary time propagation calculations on the grid. It is also further validated by reproducing the ionization potential values of H_2^+ at different internuclear distances reported in the literature⁶⁹. The final spatial grid is defined wider and finer along the laser polarization axis (z -axis) spanning between $[-102.4 : 102.4]$ a.u. with 1024 grid points, while the x and y grids remain coarse with each spanning between $[-51.2 : 51.2]$ a.u. with 256 grid points.

Again, the split operator method is employed for the time evolution of the system, and the ground state Φ_0 obtained by imaginary time propagation is used as the initial state. The escaping wave packets in the ionization direction are smoothly absorbed using an absorber function (eq. 8) near the grid boundaries. In this model, $c = 0.6$ and $z_a = \pm 82$ a.u. are used. The absorber function also acts as a detector to collect the ionized wave packets along the polarization direction (outgoing flux). It is only applied along the laser polarization due to the negligible amount of the wave function reaching the boundaries in the x and y directions. The Fourier-transformed outgoing flux is coherently added at each time step and the photoelectron wavefunction at time t is given by,

$$\psi_p^{\text{TDSE}}(p_x, p_y, p_z, t; R) = \sum_{t'=t_0}^t \mathcal{F} \{ [1 - \zeta_{\text{ab}}(z; z_a)] \Psi(x, y, z, t'; R) \}, \quad (11)$$

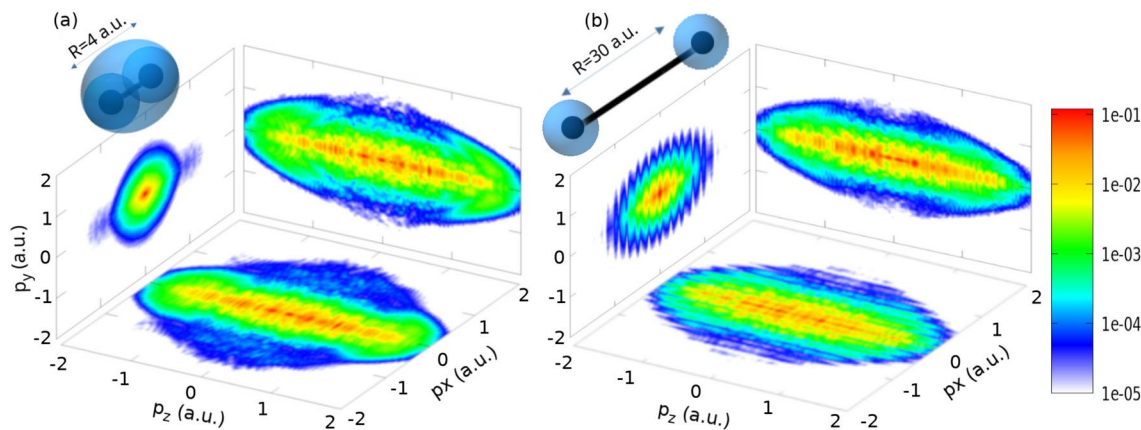


Fig. 9. Orthogonal projections of the three-dimensional photoelectron momentum spectra along with the cartoon depictions of respective spatial electron densities for internuclear distances of (a) $R = 4$ a.u. and (b) $R = 30$ a.u..

which is further propagated in the vector field without the Coulomb potential. Since the post-ionization propagation is conducted entirely in momentum space, reflections off the grid boundaries are avoided. Thus, the photoelectron momentum spectra can easily be calculated from the final photoelectron wavefunction densities $|\psi_p^{\text{TDE}}|^2$. These 3D momentum densities are shown in Fig. 9. Along the laser polarization (p_z) axis, the distribution spreads over a large momentum range, including high energy values ($p_z > 1.5$ a.u.). However, in this work, our interest lies in the plane perpendicular to the polarization, i.e. the $p_x p_y$ plane. The PMD in this plane retains information on the molecular orbital structure³⁰. The fringe pattern observed in the transverse plane originates from the interference between the nuclei separated spatially along the x -axis.

Partial Fourier Transform model

The Partial Fourier Transform (PFT) model^{46,47} is an intuitive approach to calculate the molecular orbital imprint in PMDs produced by laser-induced tunnel ionization. The central idea is that the transversal density in momentum space at the tunnel exit z_e can be obtained by multiplying the bound wave function at the tunnel entrance z_0 with a tunnel filter function. The latter can be derived using the WKB method and making the assumptions of small transversal momenta. It reads⁴⁷:

$$f(p_x, p_y) = \exp(-0.5(p_x^2 + p_y^2)\tau), \quad (12)$$

where $\tau = \sqrt{I_P/(2U_P)}/\omega$, with the ionization potential I_P , the ponderomotive potential U_P , and the laser frequency ω .

In our implementation, we use the ground state wave functions $\Phi_0(x, y, z)$ obtained by imaginary time propagation as the starting point. A Fourier transform is performed in the plane perpendicular to the laser polarization, and the result is multiplied with the tunnel filter function:

$$|\Psi(z_e, p_x, p_y)|^2 = |\Phi_0(z_0, p_x, p_y)|^2 \cdot f(p_x, p_y), \quad (13)$$

The longitudinal momentum at the tunnel exit z_e is assumed to equal zero. To obtain a three-dimensional momentum distribution, the acceleration in the laser field is described as a convolution with a Gaussian function,

$$|\Phi^{\text{PFT}}(p_x, p_y, p_z)|^2 = \frac{1}{2\pi w_z} |\Phi(p_x, p_y, 0)|^2 * \exp\left(-\frac{p_z^2}{w_z^2}\right), \quad (14)$$

where $w_z = 1$ a.u..

Data availability

The data are available from the corresponding author upon reasonable request.

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Declarations

Competing interests

The authors declare no competing interests.

Additional information

Correspondence and requests for materials should be addressed to M.K.

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