Step-by-step state-selective tracking of fragmentation dynamics of water dications by momentum imaging

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The double photoionization of a molecule by one photon ejects two electrons and typically creates an unstable dication. Observing the subsequent fragmentation products in coincidence can reveal a surprisingly detailed picture of the dynamics. Determining the time evolution and quantum mechanical states involved leads to deeper understanding of molecular dynamics. Here in a combined experimental and theoretical study, we unambiguously separate the sequential breakup via D+ + OD+ intermediates, from other processes leading to the same D+ + D+ + O final products of double ionization of water by a single photon. Moreover, we experimentally identify, separate, and follow step by step, two pathways involving the b 1Σ+ and a 1 Δ electronic states of the intermediate OD+ ion. Our classical trajectory calculations on the relevant potential energy surfaces reproduce well the measured data and, combined with the experiment, enable the determination of the internal energy and angular momentum distribution of the OD+ intermediate.

The measurement of reaction dynamics occurring on the femtosecond time scale has long been the target of various kinds of time-resolved spectroscopies and, more recently, has been accomplished with ultrafast X-ray measurements. Those measurements have exploited pump-probe strategies1, transient absorption2, and time-resolved X-ray scattering3,4, among other methods. Combining time-resolved X-ray measurements with momentum imaging coincidence detection5–7 that gives direct access to state-selective ionization and detailed insight into dissociation dynamics in the molecular frame remains a challenge.

Recent interest in such time-resolved spectroscopies extends to the IR, UV and VUV regimes8–12. Although it would seem intuitive that time resolution is necessary to see the steps in the unimolecular reactions that have frequently been the subjects of momentum imaging coincidence experiments, it was demonstrated that such experiments, without time-resolved X-ray or laser pulses, can in fact be used to distinguish the steps in a sequential reaction13–21. Recently, the native-frames analysis method was introduced21,22, and the authors...
showed that photo-induced momentum imaging observations can resolve the sequence of events in the dissociation of a molecule involving vibrational and rotational dynamics following multiple ionization. 

Here, the goal is to take a step further by combining such measurements with detailed ab initio theoretical calculations of the multiple Born–Oppenheimer potential surfaces governing such a reaction and the nuclear dynamics on those surfaces. With this methodology, the spectral signatures of the steps of a reaction, including non-adiabatic transitions that occur in those steps, can be identified experimentally. The expected result is a clear picture, not only of the steps, but of the electronic states of the transients involved in them.

In the present work, we accomplish the goal stated above. Specifically, we track sequential fragmentation step-by-step, by combining a kinematically complete measurement of all reaction products following single-photon absorption, computing the classical trajectories on the relevant potential-energy surfaces, and employing the native-frames analysis to separate the measured data into the steps of the process. Moreover, we are able to observe the internal-energy distribution of the intermediate molecule, which has sufficient energy to predissociate—demonstrating the power of the presented methodology.

**Results**

**Sequential fragmentation of water**

To explore the molecular dynamics causing sequential fragmentation we study, as a test case, the heavy water molecule that fragments into D⁺ + D⁺ + O (3P) following the absorption of a single photon. We focus on sequential fragmentation via an OD⁺ intermediate, which follows the steps listed below

\[
\text{D}_2\text{O}_2^+ \rightarrow \text{D}_1^+ + \text{OD}_\text{II}^+ \quad \text{(Step 1)}
\]

\[
\text{OD}_\text{II}^+ \rightarrow \text{D}_2^+ + \text{O}(3\Sigma) \quad \text{(Step 2)}
\]

Note that the D⁺ fragments are labeled I and II according to their ejection order in the sequential process, i.e., labeled by their fragmentation step according to Eq. (1) and Eq. (2), respectively (a notation used throughout). Despite the fact that these D atoms are indistinguishable, we show below that the sequential breakup step, i.e., the ejection order, can be associated with each detected D⁺ fragment.

It was suggested by Streeter et al. [7], who identified many measured concerted fragmentation paths in H₂O⁻¹, that one of the reaction pathways leading to the H⁺ + H⁺ + O(P) final state involves sequential breakup via an OH⁻ intermediate. Specifically, they speculated that a feature in the data, having broad angular spread between the protons’ ejection directions, may be due to transitions involving the 2 ¹A₁ state of the water dication, which undergoes two-body breakup to H⁺ + OH⁻(b' Σ⁺). This b' Σ⁺ state of OH⁻ is known to predissociate into H⁺ + O(P) via a crossing with the Λ' Π state [9]. We validate the sequential-breakup path described above and identify an unexpected additional sequential fragmentation pathway of D₂O²⁺. Moreover, we reveal details on each step of these stepwise reaction pathways leading to the H⁺ + H⁺ + O (3P)

**First fragmentation step**

The first step in sequential breakup requires one O–D₁ bond to break, while the OD⁺ II fragment remains bound. In Fig. 1a, we show a cut of the relevant potential energy surfaces (PES) of D₂O²⁺ leading to D₁⁺ + OD⁺ II breakup along the dissociation of one Dᵢ at the equilibrium bond angle of neutral water, which is the relevant angle in the Franck-Condon approximation. These states of D₂O²⁺ correlate with the b' Σ⁺ and a' Δ states of OD⁺, which are predissociative via a crossing with the Λ' Π state of OD⁺.

Figure 1b displays cuts in a few PES of D₂O²⁺ for the same bond angle, but when one Dᵢ is at 1000 a.u. and therefore its interaction with the remaining OD⁺ II is negligible. These cuts are effective radial potentials for fixed J of the OD⁺ II states correlating with the D₁⁺ + O(P) and D₁⁺ + O(D) dissociation limits, which are involved in the predissociation of the intermediate OD⁺ II molecule.

**Second fragmentation step**

The essence of the second step of the sequential fragmentation revealed in our experiment is the dissociation of the OD⁺ II ion produced in the first step in its b' Σ⁺ and a' Δ states by a spin-orbit induced transition to the Λ' Π state. Only if the OD⁺ II ion is produced in rovibrationally excited states above the effective radial barrier to the dissociation limit of the Λ' Π state, shown in Fig. 1b, can it be predissociated by this transition, and these dynamics leave clear signatures in the moments of the final products.

Using the PES information detailed above, we model the reaction dynamics by the propagation of ensembles of classical trajectories on the relevant potential surface for a few picoseconds, at which time the OD⁺ II population is evaluated. We assume that all OD⁺ II ions with internal energy above the D₁⁺ + O(P)

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*Image 339x209 to 509x335*

**Fig. 1 | Potential energy surfaces of water dication, V(R₀–Dᵢ–R₀–Dᵢ), at the equilibrium angle.** Cuts through the potential energy surfaces, relevant for sequential fragmentation of D₂O²⁺ via OD⁺ II intermediate, showing a the asymmetric stretch of D₂O²⁺ for a fixed bond angle (104.45°) and internuclear distance (R₀–Dᵢ–R₀–Dᵢ = 1.812 a.u.) of the other O–D bond for the three states of D₂O²⁺ that produce the diatomic intermediate which further dissociates (see text), and b the OD⁺ II potentials when the interaction with the other Dᵢ is negligible (R₀–Dᵢ–R₀–Dᵢ = 1000 a.u.), where solid lines are for J = 0, while the effective radial potentials for J = 30 are shown as dashed lines. The states in (a) plotted as solid blue and solid red curves produce the diatomic ion with enough internal energy to predissociate via the Λ' Π state. The energy scale is relative to the D₁⁺ + D₁⁺ + O (3P) dissociation limit. Note that on this energy scale the asymmetric stretch limits for the 1 Σ⁺ and 2 Σ⁺ states are -3.021 and -1.619 eV, respectively. Source data are provided as a Source Data file.
Fig. 2 | Native frames analysis of D+ + D+ + O breakup. a All the measured D+ + D+ + O events (shown using a √counts scale) as a function of the kinetic energy released upon ODII dissociation, KERODII, and the angle between the conjugate momenta, θODII,DI. Sequential fragmentation events via D+ + ODII are identified (see text) by the uniform angular distribution within the magenta-dashed rectangle (i.e., KERODII < 2.3 eV and 0° < θODII,DI < 80°). b Schematic diagram of the conjugate momenta and the angle between them (see Eqs. (5) and (6) in the “Methods” section). Sequential breakup via ODII analyzed in the ODII,DI frames, i.e., the correct and wrong fragmentation-step order of the D+ fragments, respectively (see text). As detailed in the “Methods” section, analysis of the events in the wrong reference frame, as is the case shown in panel (d) and indicated by the different axis labels (KERODI, and θODI,DI), yields a distribution significantly different than the one expected for sequential fragmentation21,22, specifically, a non-uniform angular distribution, a KERODI, that depends on the angle θODI,DI, and a much higher than expected KERODII. This sequential fragmentation distribution, analyzed in the wrong D+ ejection order, is marked by a red arrow in panel (a), while concerted breakup is indicated by a black arrow. c Energy-correlation map of the ionized electrons associated with sequential fragmentation via D+ + ODII (shown as counts). Source data are provided as a Source Data file.

Identifying sequential fragmentation of water

Rotation of the intermediate diatomic ion in the fragmentation plane provides a clear signature of sequential fragmentation18,21,22. In the native frames analysis this rotation manifests itself as a nearly uniform N(θODII,DI) angular distribution if the predissociation lifetime is long enough so the rotation of ODII wipes out any initial angular preference. As detailed in the “Methods” section, in Fig. 2a we show the distinct uniform angular distribution of sequential fragmentation via D+ + ODII (marked by the dashed-magenta rectangular boundary), which occurs at the expected kinetic energy release (KER) of ODII dissociation21,22, indicated by the appearance window in Fig. 1b.

Three observations are appropriate at this point: First, in Fig. 2c we show the complete angular distribution of this sequential-fragmentation channel of D2O2+, which was reconstructed taking advantage of the fact that N(θODII,DI) is nearly uniform21,22.

Second, one can associate each detected D+ with the relevant fragmentation step using the native frames analysis, as described in the “Methods” section. After correctly assigning which D+ comes from the ODII intermediate, we combine the data for all plots presented below, i.e., we use all sequential events via ODII.

Finally, we note that the high degree of rotational excitation in the intermediate ODII b Σ+ and a′Δ states found in the classical trajectory simulation, which leads to the signature of sequential breakup, has its advantage of the fact that N(θODII,DI) is nearly uniform21,22.

To explore the sequential-breakup mechanism experimentally, we initiate fragmentation by the absorption of a 61 eV photon, thereby producing a doubly-ionized water molecule at a well-defined energy (24.1 eV) above the lowest dissociation limit, D+ + D+ + O(Π). We measure all four charged fragments in coincidence and determine their momenta using cold target recoil ion momentum spectroscopy (COLTRIMS) technique18. Specifically, we focus on events producing two electrons, two deuterons, and a neutral oxygen whose final momentum is evaluated using momentum conservation.

We analyze the three-body fragmentation assuming an ODII intermediate using the native frames method18,22. In our present case, shown schematically in Fig. 2b, the conjugate momenta (of the Jacobi coordinates) associated with the first and second breakup steps are pODII,pDI, respectively, while θODII,DI is the angle between them—all defined in the “Methods” section.

dissociation limit and zero rotational energy, i.e., between the two horizontal dashed lines in Fig. 1b labeled appearance window, predissociate to D2+ + O fragments within a few picoseconds due to spin-orbit coupling with the A′1Σ+ state21,22. Nonzero rotational angular momentum adds a centrifugal barrier to this picture for all three states of ODII in Fig. 1b, modifying the appearance window, and leaving a clear signature of rotational excitation in the kinetic energy of the atomic fragments produced by this mechanism, as we discuss below.

Fragmentation experiment and analysis

To investigate the sequential-breakup mechanism experimentally, we initiate fragmentation by the absorption of a 61 eV photon, thereby producing a doubly-ionized water molecule at a well-defined energy (24.1 eV) above the lowest dissociation limit, D+ + D+ + O(Π). We measure all four charged fragments in coincidence and determine their momenta using cold target recoil ion momentum spectroscopy (COLTRIMS) technique18. Specifically, we focus on events producing two electrons, two deuterons, and a neutral oxygen whose final momentum is evaluated using momentum conservation. We analyze the three-body fragmentation assuming an ODII intermediate using the native frames method18,22. In our present case, shown schematically in Fig. 2b, the conjugate momenta (of the Jacobi coordinates) associated with the first and second breakup steps are pODII,pDI, respectively, while θODII,DI is the angle between them—all defined in the “Methods” section.
are created by the loss of two lone-pair electrons. From simple molecular orbital considerations, losing one or two electrons out of the in-plane 3a1 lone-pair orbital should lead to an opening of the bond. Streeter et al.23 found that this force is strong enough to cause the two D+ fragments, ejected initially near the 104° equilibrium bond angle in a concerted three-body fragmentation on these surfaces, to invert this angle to greater than 180° while they are still close to the oxygen atom. Similarly, trajectories leading to the two-body breakup into D+ + ODII impart a strong torque on the ODII fragment, resulting in high rotational excitation. Gervais et al.26 also found high rotational excitation in diatomic ion fragments from HOD having insufficient internal energy to predissociate, with the highest being from these two dication states. For the trajectories that produce the ODII fragment with enough internal energy to predissociate via the A1Π state, in our classical trajectory calculations these dynamics lead to angular momentum distributions peaking near J = 30 as shown in Fig. 3, i.e., even higher levels of rotational excitation than in ref. 26. We note that the angular distribution of the a1Δ state extends down to J = 0, while the b1Σ+ state of ODII cannot be produced rotationally cold. Moreover, this rotational distribution leaves its signature in the kinetic energies of the atomic fragments after dissociation as we discuss further below.

Dissociation limit of sequential fragmentation of water
First, we confirm that the selected sequential fragmentation events lead to the expected D+ + D+ + O(3P) dissociation limit. To that end, in Fig. 4 we present all the measured D+ + D+ + O + 2e− events (red-solid line), resulting from the absorption of a single 61 eV photon, as a function of the total energy release, i.e., \( E_{\text{release}} = KER + E_{r_1} + E_{r_2} \), where \( E_{r_1} \) or \( E_{r_2} \) is the kinetic energy of an electron in the continuum. Essentially, the measured \( E_{\text{release}} \) provides information about the dissociation limit, thus allowing one to determine the internal energy of the oxygen fragment. We evaluated the expected value of \( E_{\text{release}} \) for each dissociation limit from the known photon energy, the complete dissociation energy of water, and the initial state (i.e., ground state) of the heavy water molecule—those locations are marked by vertical lines and labeled by the oxygen final state in Fig. 4—though with a small shift down, ~0.4 eV, due to experimental uncertainties (see ‘Experimental method’ in the ‘Methods’ section for details). It is evident from the figure that the likelihood of fragmentation to the lowest two dissociation limits, i.e., O(1P) and O(1D), is approximately equal, and each of them is more likely than a breakup to the O(1S) limit. In the same figure we also plot (blue line) the sequential events via ODII, selected by KERODII < 2.3 eV (see ‘Native frames analysis’ in the ‘Methods’ section). Figure 4 clearly shows that the sequential fragmentation via ODII leads solely to the D+ + D+ + O(3P) dissociation limit. We also note that the electrons associated with this sequential breakup exhibit an energy sharing that is typical for direct double ionization involving no autoionization, as shown in Fig. 2e.

Sequential fragmentation pathways
As mentioned briefly in the introduction, Streeter et al.23 suggested that the ODII (b1Σ+) is the intermediate state that predissociates, due to spin-orbit coupling with the A1Π state (shown in Fig. 1b), into DII + O(3P) a few picoseconds after the D2O2+ breaks into D+ + ODII (b1Σ+). Inspection of Fig. 1a indicates that the b1Σ+ state
sequential fragmentation events selected by KERODII

D+

state, however we expect it to be similar to that of the b1

two sequential fragmentation paths (see text), speci-

Feature centered about the expected KERODII,DI

that both are coupled to the A3

population by a vertical transition from the D2O ground state (i.e.,
the feature centered about 2.1 eV). This clearly

distribution of this feature peaks near zero and tails off

about 5.5 eV. This is unexpected,

of trajectories on each dication surface, with no regard to the cross

for producing that dication state in double photoionization. As a

result, those calculations can accurately reflect the branching ratios

between two- and three-body breakup channels on each electronic
state, but provide no information about the photoionization cross
sections. In contrast, the experiment does determine the ratio between
the two, thus providing a test of the relative magnitudes of the cross
sections to be determined by future double photoionization
calculations.

Step-by-step comparison of measured and simulated KER
In Fig. 6 we compare the measured and calculated KER distributions
for both steps of each sequential fragmentation path. Because the
experiment measures the relative cross sections, we scale the theory
with an overall factor determined by a least squares fit to preserve the
measured information on the relative likelihood of the two sequential
fragmentation paths. Note that the calculated KER distribution
associated with the 21A1 \rightarrow bΣ\(^+\) path is scaled by a factor that is 1.17 times
larger than the scaling factor used to normalize the 11B1 \rightarrow aΔ path, as
indicated in Fig. 6. This difference is mainly due to the relative mag-
nitudes of the cross sections for double photoionization by a single
61 eV photon landing on the 21A1 and 11B1 states of D2O\(^+\).

At a glance, the calculated and measured KER distributions
associated with the D2O\(^+\) \rightarrow D\(^+\) + OD\(^+\) breaking, shown in Fig. 6a, match
each other nicely. However, a careful inspection shows that the calcu-
lated distributions are shifted up by about 0.15 eV. We suspect that
this difference stems from approximating the initial wave function of
D2O, which is projected to the D2O\(^+\) states, by a product of normal
mode harmonic oscillators instead of a more accurate representation
including the effects of the anharmonicity in the ground state PES.
Similar discrepancies have been observed in H2 and were corrected by
using a Morse potential to represent the initial state\(^9\).

The calculated and measured KER distribution associated with the
second fragmentation step, namely OD\(^+\) \rightarrow D\(^+\) + O\(^+\) shown in Fig. 6b,
much very well for both sequential fragmentation paths. The differ-
ences between the KER distributions associated with these two frag-
mentation paths, noticeable in Fig. 5, become more apparent. The
sequential fragmentation via the b Σ\(^+\) state yields a broad, relatively
flat, KER distribution peaked around 0.9 eV, while the fragmentation
via the a Δ state peaks at much lower KER, ~0.15 eV, and falls off
rapidly with increasing KER. The fact that the classical trajectory ana-
lysis faithfully reproduces the details of these distributions is a strong
verification of its validity and the accuracy of the potential surfaces on
which it is based.

Internal energy of the intermediate OD\(^+\) fragment
It is important to note that the KER in the predissociation of the OD\(^+\) images the internal energy of this diatomic ion above the O(\(^+\))
dissociation limit, i.e., the internal energy stored in highly excited rovibrational states. This assertion is correct if the assumption, used in our modeling, that all rovibrational states dissociate when their energy exceeds the effective potential barrier leading to the D^+ + O(P) dissociation limit, is valid. The comparison of experiment and theory in Fig. 6b validates this assumption. The remaining population, in the dissociation limit, is valid. The comparison of experiment and theory in trajectory simulations provides the angular momentum distribution, each state of OD^+_II due to spin-orbit coupling of the populated b ^Σ^+ and a ^Δ state with the A ^1Π state.

The results of our classical trajectory propagation on the D_2O^+ potential surfaces are overall in excellent agreement with the experimental data associated with both sequential dissociation pathways and the steps each one undergoes, which are detailed in Eqs. (3) and (4). We draw particular attention to our ability to calculate the internal energy of the intermediate OD^-II molecule and probe it experimentally above the D^+_II + O(P) dissociation limit. Likewise, the angular momentum distribution of the intermediate OD^-II molecule has been computed and the predicted impact on the low KER distribution has been measured. Though our methodology has been demonstrated for sequential fragmentation of water following double ionization by a single photon, it is not limited to this specific case, neither is it the only available methodology as covariance imaging analysis may also provide accurate results. In our methodology, the combination of kinematically complete momentum imaging measurements, classical trajectory simulations on the relevant PES, and the native frames method should be applicable to a wide range of polyatomic molecules as long as the energy deposited in the system is known and there is a clear signature enabling identification of sequential fragmentation from other processes, like the rotation of the intermediate molecular fragment in this case. This methodology enhances our capabilities for exploring molecular reaction dynamics on the PES around asymmetric stretch that is commonly the path for forming an intermediate molecular fragment en route to sequential fragmentation. The observation of sequential steps in a molecular dissociation reaction via their unambiguous signature in the momenta of the fragments has added the dimension of time evolution to an essentially time-independent measurement.

**Methods**

The methodology that enables us to compare theory and experiment step by step and state selectively is based on three main components, described briefly below. Further details are provided in the references.

**Angular momentum of the intermediate OD^-II molecule**

In addition to the internal energy of the OD^-II ion, our classical trajectory simulations provide the angular momentum distribution, P(j), of each state of OD^-II shown in Fig. 3. Similar to the KER distributions, here too the P(j) distributions of the a ^Δ and b ^Σ^+ states are different. The former peaks at a lower j (~26) and has a long tail extending all the way to j = 0, whereas the latter peaks around j = 30 and is much narrower.

There are two observable consequences of these predicted j distributions. First, the high rotational angular momentum implies that the orientation of the long-lived OD^-II fragment will not be correlated with the direction of emission of the first D^+_II fragment. This is in agreement with the nearly uniform \( \theta_{OD_{II}} \) angular distribution seen in the experiment displayed in Fig. 2. Second, the high rotational angular momentum of the OD^-II fragment results in a barrier with respect to the dissociation limit (i.e., centrifugal barrier) indicated in Fig. 3c, d. The internal energy of the OD^-II fragment is reflected in the distribution of KER_{OD_{II}} to which all angular momenta contribute. The threshold behavior in Fig. 6b in which the KER distribution vanishes as KER_{OD_{II}} goes to zero has its origin in the fact that only a small fraction of the OD^-II ions is produced with zero rotational angular momentum, and only this contribution can yield zero KER. This threshold behavior of the KER_{OD_{II}} distribution predicted by the trajectory calculations is seen to be in close agreement with the experimental data.

**Discussion**

We studied the sequential fragmentation of water following double ionization by a single photon in unprecedented detail. The events associated with this process were separated experimentally from other fragmentation processes leading to the same final three-body channel, namely \( D^+ + D^+ + O(P) \), using the native frames method and taking advantage of the rotation of the metastable OD^-II intermediate in the fragmentation plane. We identified two sequential-fragmentation pathways involving different electronic states and followed them step by step. Specifically, the routes are:

\[
D_2O^+ (2^1A^1) \rightarrow D^+_I + OD^-II (b ^1Sigma^+) 
\]

followed by OD^-II (b ^1Sigma^+) \( \rightarrow \) D^+_II + O(P),

and

\[
D_2O^+ (1^1B^1) \rightarrow D^+_I + OD^-II (a ^1Delta) 
\]

followed by OD^-II (a ^1Delta) \( \rightarrow \) D^+_II + O(P).

In both pathways, the second fragmentation step involves predissociation of the OD^-II due to spin-orbit coupling of the populated b ^Sigma^+ and a ^Delta states with the A ^1Pi state.
The PESs of the water dication are computed using the MOLPRO quantum chemistry suite in internally contracted multireference configuration interaction (icMRCI) methods at the configuration interaction singles and doubles level relative to the reference space including Davidson correction to the energy, by Gervais et al. and Streeter et al. The full dimensional surfaces are then fitted using a linear least squares fit to a functional form developed by Gervais et al. Those studies established the branching ratios between two-body (D+ + OD) and three-body (D+ + D+ + O) breakup on each potential surface of the nine states of the water dication that can be accessed at the photon energy used in our experiment. Three states of D2O+, the 1A', 2A', and 1B', states, shown in Fig. 1a, produce the b Σ' state (which correlates with the 2 A' state) and the two components of the degenerate a Σ' state of OD2+, both shown in Fig. 1b. However, only two of those, the 2 A' and 1 B', states, produce the diatomic ion with enough internal energy to dissociate appreciably by this mechanism and be seen in one-photon double photoionization, as is suggested by Fig. 5 of ref. 26.

We model the reaction dynamics by propagating ensembles of classical trajectories on the relevant potential surface for a few picoseconds and then evaluate the OD+ classical trajectories on the relevant potential surface for a few picoseconds. The Wigner phase space density for the initial vibrational state is propagating for three-body breakup in this system by excellent agreement with the experimental data. Such an appearance window was recently found to play an important role in another polyatomic molecule, i.e., in the valence fragmentation of O2. As stated above, the second fragmentation step involves predissociation of the D+ + OD+ intermediate molecule is long enough to completely deplete the populated OD+ states above the D+ + O(P) dissociation limit, and therefore the appearance window in this system is the contribution from double ionization of H2O and H2 molecules, both common residual gases in ultra-high vacuum systems, also producing H + H + 2e−. These residual gases are much warmer than the COLTRIMS jet and are present throughout the lightbeam propagation direction, therefore contaminating the momentum imaging, especially when one cannot use momentum conservation to eliminate them, as is the case for the breakup channel of interest. The D2O target choice should not affect the fragmentation pathways since each water isotopologue is expected to undergo similar dynamics.

Native frames analysis

In the native frames method, which we employ to analyze the three-body breakup, the key ingredient is the use of the conjugate momenta of the Jacobi coordinates, where these coordinates describe the relative positions of the three fragments. In the case of D2O, shown schematically in Fig. 2b, the conjugate momentum corresponding to the first fragmentation step is given by

\[
p_{\text{OD}_2\text{D}_2} = m_{\text{OD}} \frac{p_{\text{D}}}{M} - m_{\text{D}} \frac{p_{\text{D}}}{M} + p_{\text{O}}.
\]
where $P_{D}$ and $P_{O}$ are the measured momenta of the $D^+$ and $O$ fragments, respectively, $m_{D}$ is the mass of $D^+$, $m_{OD}$ is the mass of $OD_h$, and $M$ is the mass of the $D_2O^2_+$. Similarly, the conjugate momentum associated with the second step is

$$P_{OD} = \mu_{OD} \left( \frac{P_{D}}{m_{D}} - \frac{P_{O}}{m_{O}} \right),$$  \hspace{1cm} (6)$$

where $\mu_{OD}$ is the reduced mass of $OD_h$. Finally, the angle between the two conjugate momenta, $\theta_{OD,D_2}$, is computed from the dot product of these vectors. Equations (5) and (6) are the conjugate momenta of the Jacobi coordinates for the $D_2^+\cdot OD_h$ arrangement, and they can be used to compute the KER in each fragmentation step. For example, the KER in the second step (used in Fig. 2) is given by $KER_{OD} = P_{OD}^2 / 2\mu_{OD}$. The second ingredient needed to separate sequential fragmentation from other competing processes is a clear signature distinguishing it from the others. As mentioned above, rotation of the intermediate $OD^+$ in the fragmentation plane, persisting long enough to wipe out any initial angular preference, leads to a distinct nearly uniform $N(\theta_{OD,D_2})$ angular distribution. The KER in the second fragmentation step, $KER_{OD}$, combined with the molecular structure of this intermediate molecule, provides an additional constraint for identifying sequential breakup. Therefore, to identify and separate the sequential fragmentation via an $OD_2^+$ intermediate, we plot in Fig. 2a all the measured $D^+\cdot D^+\cdot O$ events as a function of $KER_{OD}$ and $\theta_{OD,D_2}$, where we arbitrarily designate one of the two $D^+$ fragments (denoted $D_1^+$) ejected first—a correct coin-flip assignment for half of the sequential events. Then, we identify the (properly assigned) sequential breakup as the uniform angular stripe marked by the dashed-magenta rectangular boundary in the figure. Note that the KER distribution of this stripe matches the predicted $0\to2.25$ eV range\cite{11. Endo, T. et al. Capturing roaming molecular fragments in real time. Science 370, 1072 (2020).}, indicated by the appearance window in Fig. 1b.

Then, we use the identified sequential events within the dashed-magenta boundary in Fig. 2a to create equivalent events by randomly rotating them to smaller angles until the whole range has a uniform yield within the uncertainty of the data. It is important to note that any other information from each event, like $KER_{OD}$, is preserved by this reconstruction algorithm\cite{11. Endo, T. et al. Capturing roaming molecular fragments in real time. Science 370, 1072 (2020).}. The resulting complete reconstructed angular distribution of the $D_2O^2_+\to D_1^+\cdot OD_2^+$ followed by $OD_2^+\to D_2^+\cdot O$ sequential fragmentation is shown in Fig. 2c.

Finally, in Fig. 2d we present the $N(\theta_{OD,D_2})$ distribution—a similar distribution to that shown in panel (c) but with the $D^+$ fragments associated incorrectly with their breakup-step order. Specifically, we are plotting sequential breakup occurring via the $OD_2^+$ intermediate in the frame assuming an $OD_1^+$ intermediate. To generate such a distribution with certainty, we use the events identified as sequential fragmentation via $D_1^+\cdot OD_2^+$ and shown in Fig. 2c, but analyze them as if the $D_1^+$ was ejected first, i.e., using the reference frames that are not associated with the relevant center-of-mass of each breakup step. In other words, their momenta are calculated in the other Jacobi coordinate arrangement, namely $P_{OD_1,D_2}$ and $P_{OD_2,D_1}$. One can clearly see that the two distributions, shown separately in panels (c) and (d) are significantly different from each other, and both are also visible in the all-events data shown in panel (a). Hence, one can associate each detected $D^+$ with the relevant fragmentation step.

### Data availability

The data that support the findings of this study are available in this article and its Supplementary Information. The raw data are available from the corresponding authors upon request. Source data are provided with this paper.

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Competing interests

The authors declare no competing interests.

Additional information

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