Weak-field few-femtosecond VUV photodissociation dynamics of water isotopologues

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We present a joint experimental and theoretical study of the VUV-induced dynamics of H2O and its deuterated isotopologues in the first excited state (1A1B1) utilizing a VUV-pump VUV-probe scheme combined with ab initio classical trajectory calculations. 16-fs VUV pulses centered at 161 nm created by fifth-order harmonic generation are employed for single-shot pump-probe measurements. Combined with a precise determination of the VUV pulses’ temporal profile, they provide the necessary temporal resolution to elucidate sub-10-fs dissociation dynamics in the 1+1 photon ionization time window. Ionization with a single VUV photon complements established strong-field ionization schemes by disclosing the molecular dynamics under perturbative conditions. Kinetic isotope effects derived from the pump-probe experiment are found to be in agreement with our by ab initio classical trajectory calculations, taking into account photoionization cross sections for the ground and first excited state of the water cation.

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I. INTRODUCTION

The VUV-induced photodissociation reaction of water via the first excited state (1A1B1) has been the subject of an abundance of theoretical and experimental studies, as a prototype for a repulsive, barrierless, adiabatic dissociation reaction. The potential energy surface [1,2] of the first excited state has been calculated with high precision by Staemmler and Palma [1]. This is a widely utilized calculation and has been further improved by different groups [3–5]. Based on these calculations, previous theoretical studies focused on the interpretation of the 1A1B1 absorption spectrum [6–9], as well as on the rotational fine structure of the dissociation products [10]. These calculations are supported by a multitude of experiments, such as high-precision absorption spectroscopy [11], Rydberg-tagging experiments [12,13], photoemission spectroscopy [14], or studies of isotope effects on the dissociation dynamics [6,15–19].

With the availability of laser systems capable of generating femtosecond VUV pulses, experimental studies have been extended to the time domain. Farmanara et al. [20,21] were able to identify an upper bound of 20 fs for the photodissociation time constant in the 1A1B1 state, limited by their temporal resolution in a 155-nm single-color pump-probe experiment. Furthermore, Trushin et al. [22] performed a VUV-pump multiphoton IR-probe experiment and were able to identify different time windows for this pump-probe scheme, defining the time the molecular wave packet needs to exit the Franck-Condon region (1.8 fs) and leave the 1+5 photon ionization window (3.5 fs). In addition to these experimental studies Imre and Zhang [8], as well as Henriksen et al. [7], deduced the time a wave packet created by vertical excitation of the 1A1B1 state needs to leave the Franck-Condon region is 5 fs.

To gain further insight into the wave-packet dynamics, the present work utilizes 16-fs, 161-nm pulses [23] to study the photodissociation dynamics of H2O and its deuterated isotopologues in the first excited state. By combining the ultrashort 161-nm pulses with a single-shot VUV pump/probe approach [24], we are able to disclose sub-10-fs photodissociation dynamics, while greatly reducing acquisition time by collecting a complete pump-probe data set at the repetition rate of the laser system. In addition to the pump-probe measurement, we experimentally determine the instrument response function by means of an intensity autocorrelation of the VUV pulse, enabling deconvolution of the investigated ultrafast dynamics.

This VUV pump-probe approach complements previous studies relying on multiphoton ionization in the probe step, where a sufficiently high infrared field strength is needed. These strong fields may influence the molecular potentials [25] and affect the intrinsic molecular dynamics, as discussed in our previous study on the photodissociation of O2 [26]. In our weak-field approach these effects, as well as the influence of intermediate states, which might be accessed resonantly in the probe step, are excluded, allowing a simplified theoretical

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description of the experimental observables for the molecular dynamics. Furthermore, the weak-field case represents a valuable reference for assessing the relevance of strong-field effects at higher intensities, but lower photon energies.

The interpretation of the delay-dependent dynamics of the water isotopologues is supported by a mixed quantum-classical approach to calculate not only the molecular trajectories in the dissociative \(^1B_1\) state, but also investigate the influence of different final electronic states, accessible by photoionization with a single probe photon, on the observed delay-dependent ion yield. Vertical excitation energies and photoionization cross sections along the reaction coordinate have been calculated, resulting in the delay dependence of the vertical ionization energy from the \(^1B_1\) state to the electronic ground and first excited states of the ion for an evolving wave packet, which is pivotal in the interpretation of the pump-probe experiment.

II. METHODS

A. Experimental methods

35-fs pulses with an energy of up to 15 mJ per pulse delivered by a Ti:Sa laser system relying on chirped-pulse amplification with a central wavelength of 800 nm and a repetition rate of 25 Hz were loosely focused into a length-variable gas cell to generate high-order harmonic radiation. The generation conditions were optimized for fifth harmonic (161.0-nm, 7.7-eV) pulses with a duration of 16 fs and an energy up to 1.1 \(\mu\)J [27].

The single-shot pump-probe technique is described in detail in [24], so here only a short description is provided; a sketch of the optical setup is shown in Fig. 1. The wave front of the harmonic beam was split into two halves by a Si wedge cut at Brewster’s angle for 800 nm, suppressing the fundamental pulse and creating a pair of spatially separated VUV pulses. Each VUV pulse followed a separate symmetric beam path, where the fifth harmonic was spectrally purified by focusing multilayer mirrors (HR160 nm, \(f = 150\) mm, Layertec, 2\(^\circ\) angle of incidence). Both beams were then redirected by Al-coated plane mirrors, bringing the two focused beams in a counterpropagating geometry. A pulsed gas valve provided a gaseous target in the common focal region, where the target was excited and further ionized. The photoionization products were imaged with a time-of-flight ion microscope with a spatial resolution of <3 \(\mu\)m onto a position-sensitive detector, similar to the one described in [28]. Individual ion species were selectively imaged based on their time of flight by applying a high-voltage pulse to the detector, acting as a temporal gate. The temporal delay between the counterpropagating pulses was mapped onto a spatial coordinate in the ion image (see Fig. 2), thus enabling single-shot autocorrelation and pump-probe measurements. Reference measurements with a fringe-resolved interferometric autocorrelation technique [23] were performed using the exact experimental conditions to precisely calibrate the delay-time axis. These measurements resulted in a conversion factor of (1.3 ± 0.1) fs/pixel of the CCD camera used to image the detector.

Furthermore, the pump-probe signal as well as the spatial ion signal of each individual beam path can be observed with the detector in real time, which allows the experimentalist to precisely optimize the spatial overlap between both beam paths and measurement conditions.

Nonresonant two-photon ionization of Kr was used for single-shot intensity autocorrelation measurements in order to experimentally determine the instrument response function. \(\text{H}_2\text{O}\) and \(\text{D}_2\text{O}\) were supplied from the heated vapor of pure liquids, while \(\text{HDO}\) was supplied from the vapor of a mixture of both. By applying a backing pressure of less than 200 mbar

![FIG. 1. Sketch of the optical setup used to perform the single-shot pump-probe experiment.](image)
the formation of water dimers or clusters could be excluded, verified by ion time-of-flight spectrometry.

B. Computational methods

The ultrafast dynamics of a water molecule and its deuterated derivatives, HDO and D₂O, on their first electronically excited state was studied using a mixed quantum-classical approach in which the nuclear motions were treated classically by Newton’s equations of motion and the electrons were described quantum mechanically. Since the molecules are sufficiently cold in the experiment, the nuclear coordinates and momenta were sampled from the harmonic Wigner distribution [31] for the ground vibrational level of the $\tilde{X} \,^1A_1$ electronic ground state, in which the zero-point vibrational energy is given to each normal mode. It is also assumed that all water molecules are initially in the rotational ground state. In this way initial conditions for 20 classical trajectories on the $\tilde{A} \,^1B_1$ potential energy surface were obtained. The trajectories were then divided into two subsets of ten trajectories. Similar temporal evolutions of the two subsets confirmed sufficiently good statistics. For each trajectory 0.1-fs time steps were used for the numerical integration of Newton’s equations using the velocity Verlet algorithm [32].

On-the-fly $ab\,\text{initio}$ calculations of the electronic structure, including the gradients, were done with the complete active space self-consistent field method using six active electrons in four active orbitals, CASSCF(6,4) (complete active space self-consistent field), and the augmented double-$\zeta$ basis set, aug-cc-pVDZ [33,34], utilizing the MOLCAS program package [35]. In order to improve the numerical stability of the CASSCF calculations, the excited-state Hartree-Fock molecular orbitals of the positive ion were used as the initial molecular orbitals. The energies were reevaluated with single point calculations at the multireference single and doubles configuration-interaction level with eight correlated electrons and seven active orbitals, MR-CISD(8,7), and the aug-cc-pVDZ basis set. Both CASSCF and MR-CISD were employed because only CASSCF allows one to compute gradients analytically within MOLCAS, which is optimal for calculating chemical trajectories, whereas MR-CISD provides higher accuracy for ionization energies. Since the analytic gradients are calculated based on the CASSCF potential energy surface, the location of the atoms in space depends on the CASSCF force and therefore it is very crucial to have a correct shape of the CASSCF potential, especially at the FC region for the $\tilde{A} \,^1B_1$ state, where the photodissociation reaction of water takes place. The MR-CISD potential is used as a reference to check the validity of the CASSCF potential. The closer the CASSCF potential shape is to the MR-CISD shape, the more reliable the CASSCF potential is [see Fig. 3(a)]. The accuracy of the shape of the MR-CISD potential itself is checked based on the expected vertical ionization values at both the FC region and at the asymptotic region, where one OH bond is broken (Table I). As it can be seen from Table I, at the FC region, the value of MR-CISD vertical ionization energies from the first electronic excited state of neutral water to the ground and first excited electronic states of water cation obtained from the MR-CISD potential are in a very good agreement with the corresponding experimental values. At the asymptotic region,

![Figure 3](image.png)

**FIG. 3.** (a) Cuts through the potential energy surfaces for the ground and first excited electronic states of H₂O and H₂O⁺ calculated at the MR-CISD(8,7) and MR-CISD(7,7) level, respectively (solid lines), and for the $\tilde{A} \,^1B_1$ state of H₂O calculated with CASSCF(6,4) (dashed line). The dissociation coordinate is obtained by changing the length of one of the O-H bonds (ROH) and maintaining the other O-H bond length and the angle HOH at the equilibrium values of 0.958 Å and 104.47°, respectively. $R_{OH} = 0$ corresponds to the equilibrium bond length. (b) The dominant configurations for the $\tilde{A} \,^1B_1$ state of a neutral water molecule, and $\tilde{X} \,^2B_1$ and $\tilde{A} \,^2A_1$ states of the cation and their corresponding CI coefficients at the equilibrium geometry (W) are obtained from the MR-CISD calculation.

### Table I. Vertical ionization energies of H₂O at the experimental equilibrium position (top) and at the asymptotic region (bottom) calculated with (a) MR-CISD and (b) CASSCF with the OH bond length kept fixed at the equilibrium OH bond length of H₂O. Experimental ionization energies for H₂O, OH in their respective ground state, in which the zero-point vibrational energy is given to each normal mode. It is also assumed that all water molecules are initially in the rotational ground state.

<table>
<thead>
<tr>
<th>Electronic states</th>
<th>(a) Calc.</th>
<th>(b) Calc.</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tilde{A} ,^1B_1 \rightarrow \tilde{X} ,^2B_1$</td>
<td>5.000</td>
<td>5.168</td>
<td></td>
</tr>
<tr>
<td>$\tilde{A} ,^1B_1 \rightarrow \tilde{A} ,^2A_1$</td>
<td>7.302</td>
<td>7.192</td>
<td></td>
</tr>
<tr>
<td>$\tilde{A} ,^1B_1 \rightarrow \tilde{X} ,^2B_1 , (H + OH^+)$</td>
<td>12.247</td>
<td>13.017</td>
<td></td>
</tr>
<tr>
<td>$\tilde{A} ,^1B_1 \rightarrow \tilde{A} ,^2A_1 , (H^+ + OH)$</td>
<td>13.420</td>
<td>13.598</td>
<td></td>
</tr>
</tbody>
</table>
MR-CISD vertical ionization energy for H⁺ + OH, which is in principle the ionization energy of a hydrogen radical, is in excellent agreement with the experimental ionization energy [see Table I and Fig. 3(a)]. The ionization energy of H + OH⁺ depends on the OH bond length. The vertical ionization energy of OH radical, calculated with MR-CISD, deviates from the corresponding experimental value by 0.77 eV, which is not a negligible deviation [see Table I and Fig. 3(a)]. This deviation, however, is not due to the inaccuracy of the MR-CISD potential energy surfaces, but it is stemming from the difference between the length of the OH bond in our calculations with that in the experimental conditions. For the scan underlying Table I, the OH bond length was kept fixed at the equilibrium OH bond length of H₂O; therefore its length at asymptotic region differs from its optimal experimental value.

The time windows in which the neutral molecule can be ionized to the electronic ground and first excited states of the cation with a single photon of 7.7 eV energy are obtained by averaging over 20 trajectories. Outside these time windows, the geometry is so far distorted in comparison to the equilibrium geometry that the cation could no longer be created with a single photon of 7.7-eV energy.

Photoionization cross sections \( \sigma(\tilde{X}^2B_1) \) and \( \sigma(\tilde{A}^2A_1) \) were calculated for 7.7-eV photon energy as a function of the molecular geometry, applying the orthogonalized plane-wave approximation to the photoelectron wave function [36]. At each molecular geometry the MR-CISD(8,7) wave function for the \( \tilde{A}^2B_1 \) state and the MR-CISD(7,7) wave functions for the \( \tilde{X}^2B_1 \) and \( \tilde{A}^2A_1 \) states were used for these calculations.

### III. RESULTS AND DISCUSSION

The time constant for the VUV photodissociation of H₂O is expected to be on the order of the duration of the pump-and-probe pulses according to previous studies [22]. To analyze reaction dynamics on this short time scale, a detailed knowledge of the instrument response function, which is given by the second-order intensity autocorrelation (IAC), is necessary. To achieve this, the direct two-photon ionization of Kr has been measured directly before and after each pump-probe experiment.

The resulting averaged ion image for Kr⁺ is shown in Fig. 2(a) for a data set of 3000 images, exhibiting a pronounced intensity increase where both counterpropagating pulses overlap in space and time. In order to retrieve the intensity autocorrelation of the VUV pulse, the central position of individual ion hits in a single-shot image is extracted to increase the spatial resolution by eliminating the influence of the spot size of individual ion signals on the detector. Considering the delay time-space calibration, the delay-dependent ion yield is given by the profile of the spatial distribution of the ion image along the propagation axis. The resulting trace, Fig. 2(b), exhibits a peak-to-background ratio near the theoretically expected value of 3:1 for a second-order intensity autocorrelation, which is given by the Gaussian fit (blue). For the shown measurement a FWHM of the intensity autocorrelation of \((23.1 \pm 1.4) \text{ fs}\) is retrieved, which corresponds to the instrument response function. Although a different temporal profile of the VUV pulse, e.g., a sech² pulse, does result in a shorter retrieved pulse duration, the instrument response function is hardly changed and the possible impact on the pump-probe data sets is negligible.

To reliably distinguish the effect of systematic and statistical uncertainties on the measured pump-probe signal, not only the mean instrument response function is of interest. Utilizing the single-shot capabilities of the colliding-pulse geometry, the effect of shot-to-shot instabilities, such as beam pointing or the temporal stability of the pulses, as well as the long-term stability of the pulse properties become accessible. In Fig. 2(c) the single-shot intensity autocorrelation is shown for each laser pulse. To increase the signal-to-noise ratio a 10-shot average is used to retrieve the temporal jitter of the instrument response function. Figure 2(d) shows the mean FWHM of the instrument response function \((23.1 \pm 1.4) \text{ fs}\) as a blue line and its root-mean-square uncertainty as a gray box. Since the root-mean-square uncertainty of \(\pm 1.7 \text{ fs}\) is comparable to the uncertainty of the average measurement and no temporal drifts of the FWHM are visible, a high stability of the instrument response function over time is ensured.

In contrast to the nonresonant two-photon ionization of Kr, the delay-dependent ion yield for H₂O and its isotopologues is not only determined by the duration of the VUV pulses, but also by the internal dynamics of the molecule. Figure 3(a) shows a one-dimensional cut through the potential energy surfaces, which are relevant for this pump-probe experiment. The potential energy surfaces have been calculated at MR-CISD(8,7) and MR-CISD(7,7) level for H₂O and H₂O²⁺, respectively. The CASSCF calculation for the \( \tilde{A}^1B_1 \) state (light red) is shown in addition, emphasizing the excellent agreement between both calculation methods. In the excitation scheme employed in this pump-probe experiment, the first VUV photon (7.7 eV) excites the molecule from its electronic ground state (black) into the \( \tilde{A}^1B_1 \) state (red). Since this state is unbound in the direction of the asymmetric stretch vibration, the molecule starts to dissociate. Not only is the bond distance of the dissociating bond shown in Fig. 3(a) changing during this dissociation reaction, but also the HOH angle and the second O-H bond distance are changing and have been taken into account in the calculation. Due to the increasing energy difference between the excited \( \tilde{A}^1B_1 \) state and the electronic ground state of the H₂O⁺ ion (blue), as well as the first excited state (orange), the observation of the dissociation dynamics is confined to a limited time range. Thus, we precisely clock the time when the molecular structure is distorted such that a single VUV-probe photon cannot ionize the molecule anymore [37] [depicted as the gray ionization window in Fig. 3(a)].

The duration of the ionization window can be extracted from the trajectory calculations for each isotopologue. Hence, the vertical excitation energies for the transition from the molecular \( \tilde{A}^1B_1 \) state to the electronic ground state and to the first excited state of the ion are calculated for the evolving molecular coordinates after each time step. Figure 4 shows the time evolution of the vertical excitation energies for (a) H₂O, (b) HDO, and (c) D₂O, as well as the photon energy of the probe pulse as a reference. As soon as the excitation energy for each transition exceeds the probe photon energy, the ionization window for the respective excitation scheme closes. The shortest window for ionization to the ground cationic state corresponds to H₂O and is 6.4 fs, increasing to 8.2 fs for

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HDO, due to the higher mass of the fragment. D$_2$O exhibits
the longest time window of 9.4 fs.

The corresponding ionization window for a probe transition to
the first electronically excited state of H$_2$O$^+$ and its
deuterated derivatives is much shorter than the time window for
ionization to their ground electronic state. Depending on the
ratio between their respective photoionization cross sections,
both probe transitions may contribute to the experimentally
observed ionization window. The longest ionization window is
observed if the photoionization cross section $\sigma$ for the
$\tilde{X}^2B_1$ channel is much larger than $\sigma$(\tilde{A}^2A_1). On the
other hand, the apparent ionization window gets shorter as the ratio
$\sigma$(\tilde{A}^2A_1)/$\sigma$(\tilde{X}^2B_1) increases. It should be noted that, even at
distances where ionization is still possible, $\sigma$ is not necessarily
constant.

According to our calculations, $\sigma$(\tilde{A}^2A_1) is negligible in
comparison to $\sigma$(\tilde{X}^2B_1) at all molecular geometries where
ionization to both states is possible. This can even be
demonstrated at the independent-particle level, which implies that
a single photon can remove an electron from a configuration
only without influencing the rest of the configuration.

Figure 3(b) shows the dominant configurations for the \tilde{A}^1B_1
state of H$_2$O and the \tilde{X}^2B_1 and \tilde{A}^2A_1 states of H$_2$O$^+$
and their corresponding MR-CISD coefficients at the equilibrium
geometry. It can be seen from Fig. 3(b) that a transition from the
dominant configuration of \tilde{A}^1B_1 to the dominant configuration
of \tilde{X}^2B_1 is possible at the independent-particle level, because
only one electron is removed in the single-photon probe step.

In contrast, the transition to the dominant configuration of
\tilde{A}^2A_1 is forbidden, since an additional electron is excited
to another orbital, requiring a two-photon absorption. Other
configurations of \tilde{A}^1B_1 provide a negligible contribution to the
photoionization probability to the state \tilde{A}^2A_1. The configurations
shown in Fig. 3(b) are dominant for the corresponding
states at all geometries where photoionization is possible.
Thus, since $\sigma$(\tilde{A}^2A_1) is negligible in comparison to $\sigma$(\tilde{X}^2B_1), the
photoionization time windows are determined exclusively by the vertical excitation time from the \tilde{A}^1B_1 to the \tilde{X}^2B_1
potential energy surface in the employed single-photon probe
scheme. For a given pump photon energy the time evolution
shown in Fig. 3(a) is universal and the \tilde{A}^2A_1 state of the ion
will be relevant for a multiphoton probe scheme.

The experimentally obtained pump-probe signal for H$_2$O
and its deuterated derivatives is determined by the convolution
of the instrument response function and the internal dynamics
of the respective molecule. To deconvolve these dynamics
from the experimental data sets, where the instrument response
function is on the same time scale as the expected ionization
window, an appropriate fit function needs to be applied. As has
been shown in our trajectory simulations, the first trajectories
start leaving the ionization window after more than 5 fs and up
until this time the population in the ionization window stays
constant. This behavior can be modeled by a rectangular func-
tion, where the duration of the ionization window is given by its
half-width. The convolution of this function and the instrument
response function, fitted with a Gaussian, is given by

$$I(\Delta t) = \Delta t^3 \left[ \text{erf} \left( \frac{r_{1/2} - \Delta t}{\sqrt{2}\sigma_p} \right) + \text{erf} \left( \frac{r_{1/2} + \Delta t}{\sqrt{2}\sigma_p} \right) \right]. \quad (1)$$

Here $\Delta t$ is the delay between pump and probe pulse and $\sigma_p$ is the standard deviation of the instrument response function [$\sigma_p = \text{FWHM}/(2\sqrt{2\ln 2})$], while $r_{1/2}$, the half-width of the rectangular function, and the scaling factor $a$ are the free fit parameters.

For H$_2$O, with a corresponding FWHM of $(22.3 \pm 1.3)$
fs for the instrument response function, the fit yields $r_{1/2} =$
$(6.7 \pm 1.8)$ fs [Fig. 5(b)]. For HDO a slightly narrower
instrument FWHM of $(21.4 \pm 1.3)$ fs for the instrument
response function results in $r_{1/2} = (7.5 \pm 1.7)$ fs. The internal
dynamics in D$_2$O are proceeding slower, which leads to a
stronger deviation from the intensity autocorrelation with a
FWHM of $(20.3 \pm 1.2)$ fs. $r_{1/2}$ is $(10.4 \pm 1.5)$ fs in this
case, which is consistent with a primary kinetic isotope
effect of $\sqrt{2}$ from doubling the fragment mass. When an
exponential decay function is used to deconvolve the duration
of the ionization window, its duration is underestimated,
because the delayed decrease of population in the ionization
window is not considered. Slight differences of the instrument
response function in the individual pump-probe experiments
are attributed to the daily optimization of the laser system.
By obtaining consecutive measurements it was ensured that
the pulse duration was stable over the time the pump-probe
measurement was performed.
the excited-state dynamics of the molecule. Instrument response function, indicating a kinetic isotope effect on deuterization, an increased FWHM is observed in respect to the non-deuterated isotopologue in Fig. 3. Depending on the degree of deuterization, an increased FWHM is observed in respect to the non-deuterated isotopologue in Fig. 3.

Assuming an exponential decay rate for the observable, as it is valid for most reactions studied by femtochemistry on the few-hundred-femtosecond or picosecond time scale, leads in this case to an underestimation of the duration of the ionization window, while the deconvolved duration of a rectangular window coincides well with our mixed quantum-classical trajectory calculation.

IV. CONCLUSION

The photodissociation dynamics of H2O and its isotopologues in the A 1B1 state have been studied in a combined single-shot autocorrelation and pump-probe experiment relying on a VUV-pump–VUV-probe scheme at 7.7-eV photon energy. This constitutes a measurement with sufficient time resolution and a single-color approach which does not perturb the system under study, in contrast to multiphoton IR-probe schemes. Furthermore, our single-shot approach allows us to drastically reduce the acquisition time compared to delay-scanning techniques, reducing the influence of long-term instabilities. By determining the instrument response function under the same conditions as the pump-probe experiment for single shots, it is possible to ensure a high stability of the pulse duration of pump and probe pulses and temporal drifts can be excluded.

The experiments are accompanied by ab initio calculations, which allowed us to identify the relevant probe transition scheme. From two possible transitions, the excitation to the ionic ground state is the relevant probe transition. The expected duration of the 1+1 photon ionization window was predicted by calculating the time-dependent vertical excitation energies for an evolving wave packet in the A 1B1 state. The experimentally deduced time of 6.7 fs for H2O molecule takes to leave the single-photon ionization window while dissociating, as well the influence of hydrogen substitution (7.5 fs for HDO and 9.4 fs for D2O), are consistent with the trajectory calculations using the ground-state ionization window.

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