

Ultrafast Nuclear Dynamics in Double-Core-Ionized Water Molecules

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Double-core-hole (DCH) states in isolated water and heavy water molecules, resulting from the sequential absorption of two x-ray photons, have been investigated. A comparison of the subsequent Auger emission spectra from the two isotopes provides direct evidence of ultrafast nuclear motion during the 1.5 fs lifetime of these DCH states. Our numerical results align well with the experimental data, providing for various DCH states an in-depth study of the dynamics responsible of the observed isotope effect.

I. INTRODUCTION

Double-core-hole (DCH) states refer to electronic states with two vacancies in the core level. Spectroscopy of DCH states stands out as a highly promising tool, showing a remarkably enhanced sensitivity to the chemical environment when compared to single-core-hole (SCH) spectroscopy [1–10]. Moreover, specifically for double vacancies in the K-shell, the significantly lower lifetime of these states, compared to SCH states [9, 11, 12], positions this emerging spectroscopy as a powerful femtosecond probe, enabling the tracking of nuclear dynamics occurring during the first (sub)femtoseconds of the interaction with the light.

Core-hole and double-core-hole states have received considerable attention due to the fact that these hollow electronic configurations have a temporarily reduced x-ray absorption cross section, leading to an effect termed x-ray-induced transparency or frustrated absorption [13, 14]. This becomes relevant for prospective

single-molecule diffractive imaging, where radiation damage can potentially be suppressed through sufficiently short x-ray pulses [5, 15].

Double vacancies in the core level have been first observed in nuclear reactions [16, 17], as well as collisions involving multicharged ions [18] and electrons [19]. Substantial progress has been made through the utilization of synchrotron source enabling the production of double-core-hole (DCH) states through one-photon absorption [6, 7, 9, 10, 12, 20–32]. In this case, DCH states appear as satellites of the one-photon core ionization [33] and are referred to as hypersatellites [17]. Furthermore, the use of highly intense light sources such as x-ray free-electron laser (XFEL) facilities, enable the creation of DCH states through sequential two-photon absorption [3, 4, 13, 14, 34–46]. For that purpose, the absorption of the second photon has to occur before the decay of the SCH state. Previous researches have explored a large variety of such states. Specifically for vacancies in the K-shell, states have been investigated, where either both core-level electrons have been ejected to the continuum (K^{-2} state) or one electron has been ejected to the continuum while the other one is excited to a vacant orbital V ($K^{-2}V$ states), or both core-level electrons have been excited to vacant orbitals ($K^{-2}VV'$ states). For low- Z elements, K-shell holes decay predom-

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inantly non-radiatively via Auger decay. In this process, an electron from a valence level fills one of the core holes, while another electron is emitted to the continuum. For DCH states in the K-shell, this Auger electron has significantly higher kinetic energy compared to the Auger electron created from SCH states. This difference in kinetic energy allows for the separation of the signal originating from DCH states from the signal of the SCH states. The emitted Auger electron is thereby a clear probe of DCH states.

In order to characterize the dynamics of DCH states, which is potentially relevant for X-ray diffractive imaging, and to exploit the chemical sensitivity of their spectroscopic signals, it is crucial to understand the electronic spectra of DCH states. Earlier studies demonstrated the presence of strongly dissociative potential energy surfaces (PES) in DCH states of HCl and CH₃I molecules [47, 48]. For water, a theoretical study by Inhester et al. [49] showed that the produced Auger spectrum is considerably influenced by the involved steep PES. This prediction was corroborated by a recent study [12], conducted by some of the authors, which revealed an indication of ultrafast proton motion within the very short lifetime (about 1.5 fs [49]) of the DCH states in water molecules, leaving significant fingerprints in the Auger emission spectrum. Furthermore, within the same study, theoretical predictions indicated significant variations in the dynamic response depending on the specific populated DCH states, namely K⁻² or K⁻²V. Notably, some K⁻²V states turned out to be more dissociative than the bare K⁻² state.

This theoretical finding could not be directly confirmed through experimental observation because the photon intensity provided by the synchrotron radiation source only allowed the simultaneous population of multiple DCH states via one-photon shake-up and shake-off processes. Consequently, only an overall Auger spectrum containing contributions from several DCH (K⁻², K⁻²V) states could be measured.

In this paper, we present a more direct measurement of the Auger emission from DCH states using an XFEL light source, combined with a comprehensive theoretical investigation of the ultrafast motion following the generation of *specific* DCH states in water molecules. In particular, by employing x-ray light of sufficient intensity, we study DCH states produced via sequential absorption of two photons. By tuning the employed photon energy, we explore the spectrum variations of the emitted Auger electron when addressing regimes leading predominantly to K⁻² states via sequential core-shell photoionization or to K⁻²V states via subsequent core-shell photoionization and core-shell photoexcitation. This enables distinct investigations of the subsequent dynamics associated with each of these states. Moreover, by comparing Auger spectra obtained from isolated water (H₂O) and heavy water (D₂O) molecules, we provide now an unequivocal evidence of ultrafast dynamics occurring during the 1.5 fs lifetime of the DCH state.

The outline of this article is as follows: Section II describes the experimental setup, Sec. III describes the calculation methodology. The resulting measured and calculated Auger spectra are discussed in Sec. IV and, in Sec. V, we draw final conclusions.

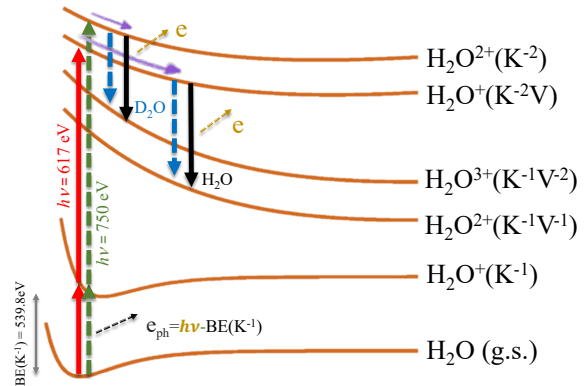


FIG. 1. Schematic illustration of the potential energy surfaces of K⁻² and K⁻²V along the dissociation coordinate. Using two photons of 750 eV energy, the K⁻² state is produced through sequential ionization: H₂O (g.s.) → H₂O⁺ (K⁻¹) → H₂O²⁺ (K⁻²). Nuclear motion occurs along the dissociative K⁻² potential energy surface. Over the 1.5 fs lifetime, the protons explore a greater distance along the dissociation coordinate than the deuterons, leading to noticeable differences in the Auger electron energy, which are for water (black arrow) larger than for heavy water (blue (light gray) arrow). With photons of 617 eV energy, the K⁻²V state is populated via the following excitation scheme: H₂O (g.s.) → H₂O⁺ (K⁻¹) → H₂O²⁺ (K⁻²V). In this case, a similar nuclear motion to that of the K⁻² state arises.

II. EXPERIMENT

The experiment was conducted using the atomic-like quantum systems (AQS) end-station at the Small Quantum System (SQS) instrument located at the SASE3 undulator of the European XFEL [50–52]. The XFEL beam, with a pulse energy of approximately 4 mJ, delivered 30 pulses per train at a repetition rate of 1.1 MHz within the train, while the trains operated at a repetition rate of 10 Hz. The XFEL beam pulses, with a duration of about 25 fs and a bandwidth of roughly 6 to 7 eV for photon energies in the range from 600 to 750 eV, were focused to approximately $1.5 \times 1.5 \mu\text{m}^2$. Electrons were detected with a time-of-flight (TOF) spectrometer installed, facing the AQS chamber ionization region, where the x-ray focus was optimized. The spectrometer was oriented at the magic angle (54.7°) with respect to the horizontal linear polarization of the photon beam. A retardation potential of 490 V was applied to improve the energy resolution of the spectrometer for the measured Auger electrons. The energy resolution was about 900 meV for kinetic energy around 550 eV. The electrons were detected using commercially available microchannel plate

(MCP) detectors. More details about the TOF spectrometer can be found elsewhere [53]. Water molecules H_2O and D_2O were introduced using a bubbler system connected to the ultrahigh-vacuum interaction chamber resulting in a pressure of about 4.6×10^{-8} mbar in the experimental chamber under gas load. The TOF spectrometer was energy-calibrated using the H_2O outer-valence photoelectron lines. The photon energy was calibrated with the K^{-2} states of water [12]. Additionally, the TOF transmission curves were derived by normalizing the yield of the H_2O photoelectron lines.

III. THEORETICAL CALCULATIONS

In order to calculate the DCH Auger spectra of water, we employed the XMOLECULE electronic-structure toolkit (version 3869) [54, 55]. Specifically, we computed double-core-ionized states (K^{-2} and various K^{-2}V configurations) using the restricted Hartree Fock method. Convergence to the desired states was achieved based on the maximum-overlap method [56, 57]. All calculations were performed using the aug-cc-pVTZ basis set [58, 59]. With the orbitals optimized for the initial, double-core-ionized state, we compute the final electronic states using configuration interaction. All direct final Auger configurations (one core hole and two valence holes) as well as configurations with additional excitation into previously unoccupied (virtual) orbitals (one core hole, three valence holes, and one virtual electron) were taken into account for the configurational expansion of the final states.

The Auger amplitudes were calculated using the one-center approximation [60] that treats the Auger process as a largely intra-atomic transition and approximates the molecular continuum wave functions with the corresponding atomic continuum wave functions. In XMOLECULE, atomic continuum matrix elements from atomic calculations using XATOM [61] are used.

The effects of nuclear dynamics in the spectrum were incorporated following Refs. 12 and 49. A set of 100 molecular dynamics (MD) trajectories were propagated on the respective double core ionized state with a time step of 0.1 fs for a total time of 20 fs. These trajectories started from initial conditions sampled from the neutral ground-state Wigner distribution. For each time step of the MD trajectories, instantaneous Auger spectra $T(E, t)$ were calculated, where for each transition a Lorentzian line shape was employed. The total Auger spectrum was then compiled using [12]

$$T(E) = \int dt T(E, t) e^{-\Gamma t}, \quad (1)$$

where Γ is the calculated reciprocal lifetime of the double-core-hole configuration. For the final spectrum, we also take into account a further convolution with a Gaussian function with a full width at half maximum of 900 meV to account for the finite resolution in the experiment. For a better comparison with the experiment, the calculated

Auger spectra were further shifted by 5 eV to lower energies. This shift compensates for an imbalance between the initial and final electronic states that occur due to the orbital optimization for the initial electronic state and the inclusion of several valence-to-virtual excitations for the final electronic states. In addition, it compensates for relativistic effects in the oxygen core level, that are not considered in the calculation. See appendix Sec. B for further discussion on the shift.

IV. RESULTS AND DISCUSSION

Figure 1 sketches the PESs that are populated in the experiment via subsequent core-ionization and core-excitation steps. Whereas there is little dynamics involved in the first core-ionization step [49], the second core-ionization or core-excitation step induces ultrafast dissociation of the molecule. The emission of an Auger electron brings the molecule energetically down either to the dicationic or the tricationic states. Because these states involve a larger charge in the molecule, the PESs along the dissociation coordinate become in general steeper. Because of this differential gradient of the PESs along the dissociation coordinate, the emission energy of the Auger electron shifts to higher energies, the further the dissociative dynamics in the DCH state proceeds. We note that the scheme presented in Fig. 1 is able to map out dynamics on a timescale much faster than the pulse duration, which is for the current experiment about 25 fs. This is enabled by focusing on features specifically related to DCH states that have a very short lifetime, and the fact that no essential dynamics occurs on the preceding SCH state [49].

The experimental Auger spectra, measured at a photon energy of 750 eV for both water and heavy water, are shown in Fig. 2 along with the calculated spectra for comparison. At this photon energy, the x-ray pulse can core-ionize the water molecule in sequential steps, producing mostly the bare K^{-2} state. The difference between water and heavy water can be seen mainly at 560 eV, on the high-energy side of the dominant Auger peak. One can see that the tail to higher energies is much more pronounced for water than for heavy water. This trend is in good agreement with the calculated Auger spectra.

Overall, the calculation reproduces all the characteristic features of the experimental Auger spectrum. However, in the experimental spectra additional contribution appear in the range 530–540 eV. We attribute this discrepancy to $\text{K}^{-2}\text{V}^{-1}$ configurations as discussed in the appendix Sec. A.

In Fig. 3, we show the Auger spectra measured at a photon energy of 617 eV. At these photon energies, DCH states are created by a sequence of core-ionization and resonant core-excitation steps, producing singly charged K^{-2}V configurations, as discussed in Fig. 1. The Auger features between 515 and 575 eV appear qualitatively similar to those measured at photon energy of 750 eV

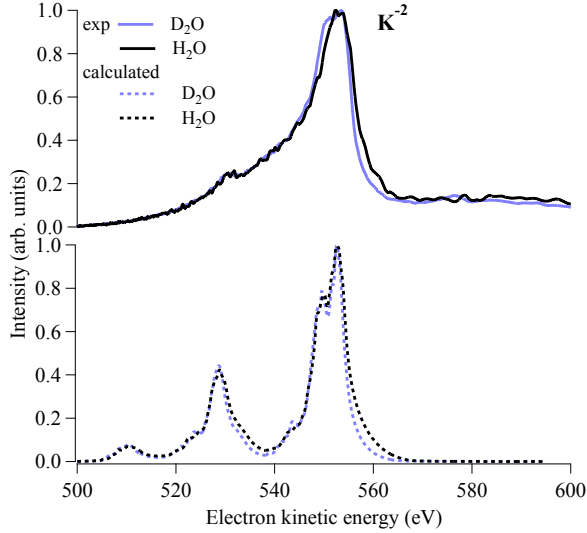


FIG. 2. Comparison of experimental Auger spectra measured with a photon energy of 750 eV (solid lines) with calculated Auger spectra for the K^{-2} state (dashed lines). Black lines show spectra for water, blue (light gray) lines show spectra for heavy water. The spectra are normalized to have similar peak heights.

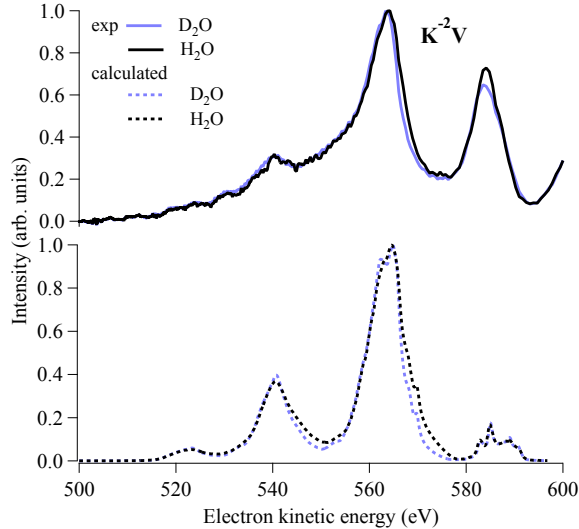


FIG. 3. Comparison of experimental spectra measured with a photon energy of 617 eV (solid lines) with calculated Auger spectra for a mixture of $K^{-2}V$ states (dashed lines). Black lines show spectra for water, blue (light gray) lines show spectra for heavy water. The spectra are normalized to have similar peak heights. The experimental spectra show valence photoelectron lines overlapping with the participator Auger contribution located around 585 eV.

[Fig. 2] but are shifted to higher kinetic energies. The feature observed at 585 eV can be partially attributed to participator Auger transitions involving the additional electron present in the V orbital. Because of the resonance condition, direct valence photoionization appears at the same photoelectron energy as the participator

Auger energies. In Fig. 3, the participator transitions thus overlap with the photoelectron signal from valence ionization of H_2O^+ (K^{-1}), as shown in Ref. [45]. Because the employed photon bandwidth is rather broad, it fully covers the participator-Auger contribution above 585 eV. Notably, the valence-photoelectron signal is not considered in the theoretical calculations, which explains the difference between the calculated and the observed intensity for this spectral feature.

The experimental spectrum shows a significant difference between water and heavy water in the main Auger peak at 565 eV following the same trend as previously observed in Fig. 2.

The broad photon bandwidth leads to the formation of a mixture of several $K^{-2}V$ states. For the comparison with calculation results, the corresponding calculated Auger spectra are compiled from a mixture that is determined using the configuration interaction calculations outlined in Ref. [45]. These calculations lead us to the following compositions of $K^{-2}V$ states: $0.24(K^{-2}4a_1) + 0.52(K^{-2}2b_2) + 0.16(K^{-2}2b_1) + 0.08(K^{-2}5a_1)$. Using this mixture, the computed Auger spectra shows a similar agreement with the experimental spectra as in Fig. 2. Specifically, the trend showing a more pronounced tail for water than for heavy water is reproduced. Similar as for Fig. 2, the lower-energy parts of the Auger spectra are considerably sharper in the calculated spectra as compared with the measured spectra. We attribute these discrepancies to additional valence-ionization and valence-excitation processes due to shake-processes and direct valence-ionization (see appendix Sec. A).

The clear isotope effect and the good agreement to the calculated spectra in Figs. 2 and Fig. 3 unequivocally establishes the pronounced effects induced by the rapid proton dynamics on the Auger spectra, confirming previous findings [12].

Figure 4 displays the calculated Auger spectra for the K^{-2} state and the individual $K^{-2}V$ states. The upper panel [Fig. 4(a)] shows an isosurface plot of the respective virtual orbitals of the K^{-2} dication that are populated in the respective $K^{-2}V$ states. The spectra highlight the individual contributions of the resonances towards shaping the high-energy tail of the main peak. As one can see, participator contribution above 580 eV appear for the $K^{-2}4a_1$ and the $K^{-2}2b_2$ configuration. For the higher excited $K^{-2}2b_1$ and $K^{-2}5a_1$ they are practically absent, because of the diffuse character of the orbitals leading to very small Auger amplitudes for the involved transitions. The Auger spectra of these two higher-excited DCH states is very similar to the one of the K^{-2} configuration but shifted by about 7 eV to higher energies, indicating that the impact of having an additional electron in the $5a_1$ or the $2b_1$ orbital essentially amounts to screening of the ion charge.

The computational results allow us to inspect the dynamics in the K^{-2} state and various $K^{-2}V$ states that are responsible for the isotope effect in more details.

Figure 5 shows calculated spectra from the ensemble

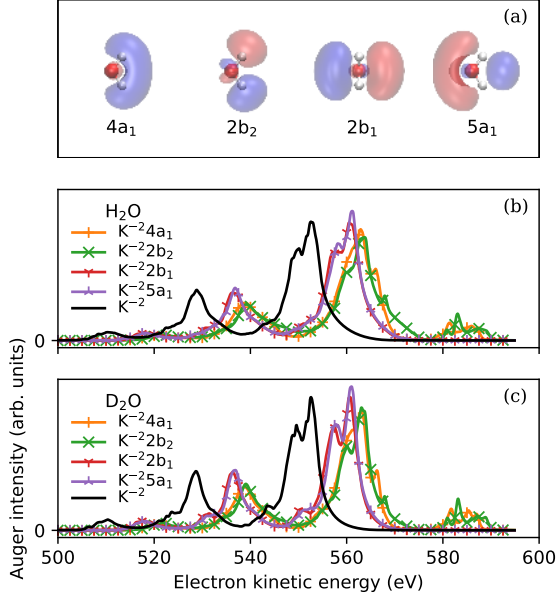


FIG. 4. (a) Isosurface plots for the virtual orbitals of the K^{-2} dication. (b) and (c) Calculated Auger spectra for individual K^{-2} and $K^{-2}V$ DCH states of H_2O (b) and D_2O (c).

of trajectories after selected times of dynamics for the ensemble of $K^{-2}V$ states considered in Fig. 3. Spectra for H_2O as well as for D_2O are shown. These instantaneous spectra nicely illustrate how the resulting spectra display effects of core-hole-state dynamics emerging in the marked tail at the high-energy side of the dominant Auger peak.

As time progresses, [Figs. 5(b-d)], the Auger spectrum gradually shifts to higher energies. This shift is stronger for H_2O and can be qualitatively understood from the fact that the emission of protons or deuterons transports charge away from the oxygen atom. At later times, valence electrons thus experience lower Coulomb attraction, which in turn gives rise to faster Auger electrons. Remarkably, this shift does not occur for the participator contributions above 580 eV. An observation that can be understood from the specific shape of the participator orbitals as discussed later.

Even though the dynamics can be overall characterized by a rapid symmetric explosion of the molecule, the individual satellite states can have a pronounced characteristic core-hole-state dynamics [12].

Figure 6 shows how the asymmetry, the average OH (OD) bond distance, and the bond angle α evolve as a function of time. To highlight these differences, the figures show the evolution of trajectories for up to 5 fs, even though one must keep in mind that the considered double-core-hole configurations have a lifetime of only about 1.5 fs, and it is thus, according to the exponential decay law, unlikely that such an electronic configu-

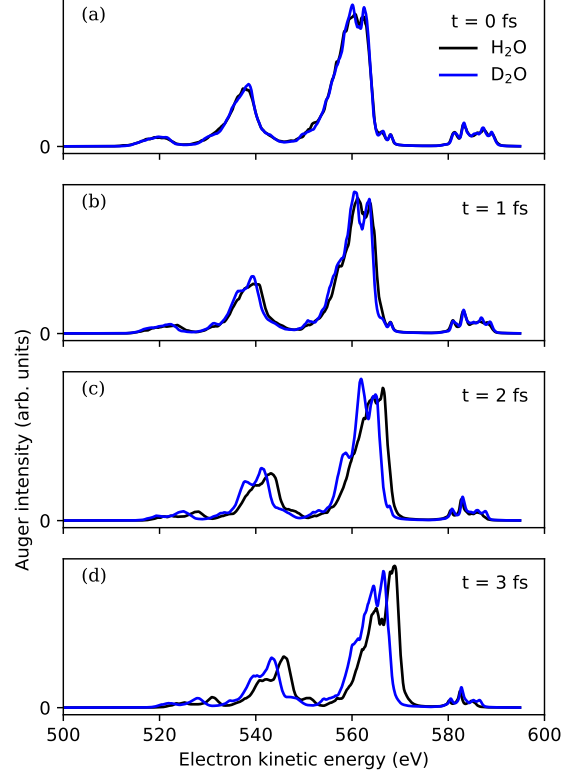


FIG. 5. Calculated instantaneous Auger spectra for selected times after core ionization for an ensemble of $K^{-2}V$ states for H_2O (black) and D_2O (blue (light gray)).

ration is present for such a long time. As one can see, the K^{-2} configuration involves a largely symmetric dissociation into a doubly core-excited oxygen and two protons. The $K^{-2}4a_1$ configuration shows a considerably strong asymmetric fragmentation [Fig. 6(c)]. In particular, the simulations reveal that this configuration involves asymptotically a fragmentation into a $K^{-2}V$ hydroxyl cation (OH^+) and a proton. Such a strong anti-symmetric character has also been reported before for the single-core-excited $K^{-1}4a_1$ state [62]. Moreover, the K^{-2} and $K^{-2}5a_1$ configurations show a trend for HOH angle opening dynamics, whereas the opposite (angle closing) can be seen for the $K^{-2}4a_1$ configuration [Fig. 6(a)]. The configuration $K^{-2}2b_2$ stands out by exhibiting a particularly rapid symmetric fragmentation [Fig. 6(b)]. Overall, one can see that the configurations $K^{-2}4a_1$ and $K^{-2}2b_2$ induce a somewhat more rapid fragmentation than the bare K^{-2} configuration, whereas higher excited states like $K^{-2}2b_1$ and $K^{-2}5a_1$ show a fragmentation dynamics similar to the K^{-2} configuration. The variations between the $K^{-2}V$ states can be understood from the influence of the electron in the previously unoccupied orbital [see

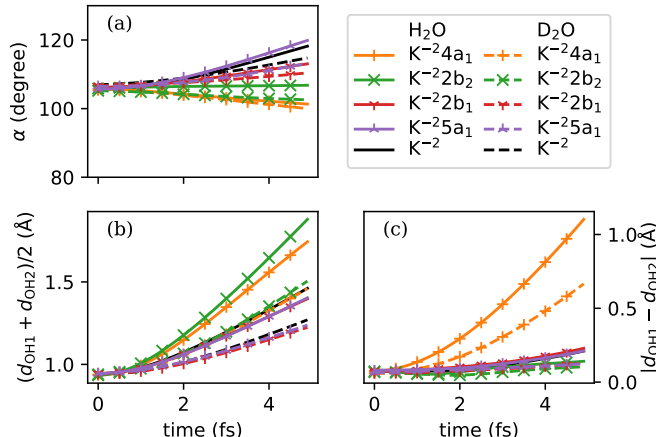


FIG. 6. Evolution of the internal coordinates (averaged over all trajectories) for individual double-core-hole states. (a) HOH (DOD) bond angle, (b) Average oxygen-hydrogen (oxygen-deuterium) distance, (c) Absolute difference between oxygen-hydrogen (oxygen-deuterium) distances.

Fig. 4(a)]. The antibonding character of the $4a_1$ and the $2b_2$ orbital along the OH bonds pushes the protons more rapidly away. In addition, the $4a_1$ orbital has some bonding character between the hydrogen atoms and thus induces lowering of the HOH angle.

The antibonding character of the orbitals $4a_1$ and $2b_2$ also explains the distinct behavior of the participator lines along the dynamics observed in Fig. 5. Whereas spectator Auger contributions become faster in energy as the dissociation proceeds because the involved valence orbitals become less bound as the Coulomb attraction to the protons reduces with increased OH bond length, the participator contributions are, in addition, impacted by the respective orbital's antibonding character along the OH bond, making them *stronger* bound as the dissociation proceeds. As a result, participator contributions do not shift that strongly in the instantaneous Auger spectra shown in Fig. 5.

V. CONCLUSIONS

We have experimentally and theoretically investigated double-core-hole states in isolated water and heavy water molecules generated through the sequential absorption of two x-ray photons. Theoretical calculations of the Auger process and the involved core-hole-state dynamics successfully reproduce the experimental data, enabling an in-depth examination of the dynamics in K^{-2} and $K^{-2}V$ states responsible for the observed isotope effect. Our measurements confirm earlier synchrotron measurements, where DCH states were created via one-photon absorption [12]. We note that analogous observations have very recently also been made for the one-photon DCH-Auger spectrum of liquid water [63] demonstrat-

ing a considerable impact of the liquid environment on the DCH-Auger electron energy. The comparison of the Auger spectra obtained from the two isotopic systems in the gas-phase provides an unequivocal confirmation of the ultrafast proton motion during the lifetime of the DCH states. By selectively populating different K^{-2} and $K^{-2}V$ states, Auger spectra of both species could be disentangled and distinct dynamic behaviors were observed. Further studies could consider investigating the ultrafast dynamics induced in DCH by employing coincidence detection of ion fragments and electrons, as it is feasible at the SQS instrument at European XFEL.

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I.I. and L.I. contributed equally to this work. M.S., M.N.P., T.M., O.T. I.I. conceptualized the work. I.I., T.M., F.T., A.V., A.D.F., D.E.R., D.P., D.K., E.K., F.P., G.D., G.S., J.D.B., K.L., L.Y., M.I., M.N.P., M.M., N.V., O.T., R.B., R.G., R.D., S.D., T.M.B., T.M., Y.O., R.P., M.S. conducted the experiments. I.I. and M.S. performed formal analysis. A.F., R.T., and S.C. provided relative DCH satellites intensities. L.I. performed the calculations of the Auger spectra. I.I. and L.I. drafted the manuscript. All authors contributed to the manuscript.

The experimental data were collected during user beamtime 2620. The metadata are available at <https://doi.org/10.22003/XFEL.EU-DATA-002620-00>.

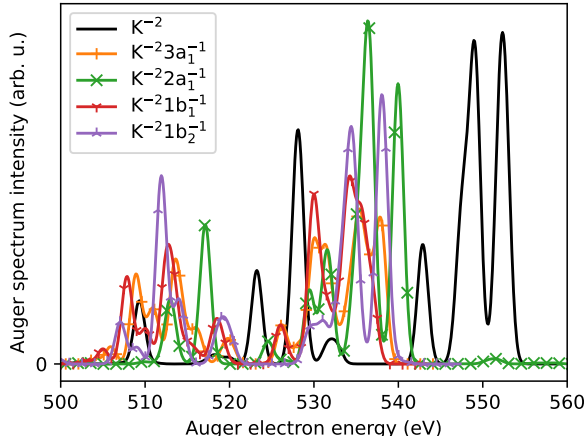


FIG. 7. Calculated DCH Auger spectra for additionally valence ionized configurations (equilibrium geometry only). The solid line shows results for the K^{-2} configuration, the dotted lines show results for various $K^{-2}V^{-1}$ configurations.

Appendix A: Contributions due to $K^{-2}V^{-1}$ configurations

In Fig. 7 we show additional results for $K^{-2}V^{-1}$ configurations, i.e., double core-hole configurations with an additional valence hole. In contrast to the results presented in the main text, for these calculations, only the equilibrium molecular geometry has been considered and the resulting transitions have been convoluted with a Gaussian function with a full width at half maximum. For each ionized configuration, the initial double-core- and valence-ionized state has been optimized in a multiple configuration self-consistent field calculation. The calculation procedure is otherwise the same as described in Sec. III. The results show that the Auger spectra of these additionally valence-ionized configurations have strong contributions in the region 530–540 eV. We thus think that the mismatch between the experimentally measured Auger spectra and the calculations in Figs. 2 and 3 can be largely attributed to these configurations. The presence of $K^{-2}V^{-1}$ configurations is plausible due to shake-off processes accompanying the core-ionization as well as due to direct valence ionization via 3-photon absorption.

Appendix B: Convergence of the calculations with respect to configurational space

In the calculation of the Auger spectra, we truncated the configurational expansion to make the calculations

feasible. This truncation leads to an unbalanced description of the initial and final electronic states. As a consequence, the Auger spectra had to be shifted by 5 eV in order to compare them with experimental measured spectra. In Fig. 8 we show results where we computed the Auger spectra employing an extended configuration

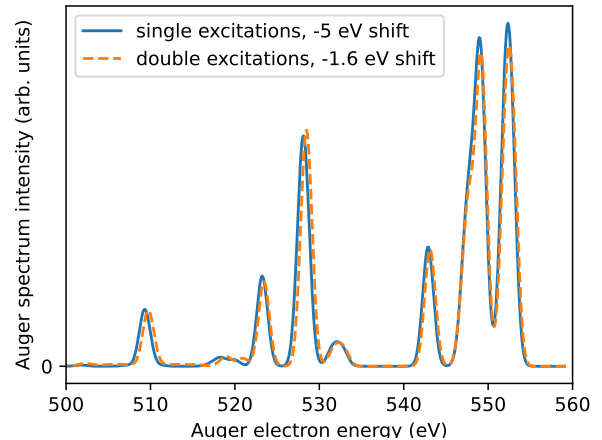


FIG. 8. Calculated DCH Auger spectra (equilibrium geometry only). The solid line shows results obtained with the configurational truncation described in Sec. III. The dashed line shows results employing an extended configurational space (see text).

space. Specifically, initial and final electronic states are described using also configurations with excitation of two electrons into the virtual orbital space (two core holes, 0–2 valence holes, 0–2 electrons in virtual orbitals for the initial states; one core hole, 2–4 valence holes, 0–2 electrons in virtual orbitals for the final states). Apart from the lower overall shift of 1.5 eV, the resulting spectra are almost identical, confirming that the shift is largely an artifact caused by the configurational truncation. We note that the remaining overall shift must partially be attributed to relativistic effects in the K-shell [64] that are not considered in the calculation.

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