RIXS Reveals Hidden Local Transitions of the Aqueous OH Radical

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Resonant inelastic x-ray scattering (RIXS) provides remarkable opportunities to interrogate ultrafast dynamics in liquids. Here we use RIXS to study the fundamentally and practically important hydroxyl radical in liquid water, OH(aq). Impulsive ionization of pure liquid water produced a short-lived population of OH(aq), which was probed using femtosecond x-rays from an x-ray free-electron laser. We find that RIXS reveals localized electronic transitions that are masked in the ultraviolet absorption spectrum by strong charge-transfer transitions—thus providing a means to investigate the evolving electronic structure and reactivity of the hydroxyl radical in aqueous and heterogeneous environments. First-principles calculations provide interpretation of the main spectral features.

The hydroxyl radical (OH) is of major importance for atmospheric, astrochemical, biological, industrial, and environmental research. In the gas phase, OH is the primary oxidizing agent that rids the atmosphere of volatile organic compounds and other pollutants [1]. It is a key tracer describing the evolution and thermodynamics of interstellar clouds [2]. Despite its reactive nature stemming from an open electronic shell, the gas-phase absorption spectrum of OH has been fully characterized in the microwave [3], infrared, optical/ultraviolet (UV) [4], and, more recently, the x-ray [5] spectral ranges. Beyond purely gas-phase processes, these OH fingerprints also characterize heterogeneous processes such as the generation of reactive oxygen species from photocatalysis [6].

Spectroscopic characterization of the hydroxyl radical in the condensed phase is more challenging, owing to its extreme reactivity and short lifetime. Of particular interest is the characterization of OH in aqueous environments, which impacts radiation biology [7] and chemistry [8]. Given its unpaired spin, electron spin resonance techniques are a natural choice to detect the presence of OH, either directly or through spin traps, but only microsecond timescales are accessible [6]. For faster timescales, desired for tracking reaction dynamics, one may consider UV spectroscopy. The UV spectrum of solvated OH obtained via pulsed radiolysis of water [9] is reproduced in Fig. 1. It is dominated by a strong feature at 230 nm (5.4 eV), whereas the dominant gas-phase absorption at 309 nm (4 eV), due to valence excitation from the ground (X) to the lowest excited electronic state (A), is barely visible. On the basis of electronic structure calculations [10–13], this dominant spectral feature of OH(aq) was attributed to charge-transfer (CT) transitions from the lone pair of nearby waters, filling the hole in the OH 1σ orbital (Fig. 1, bottom left).

Resonant inelastic x-ray scattering (RIXS) delivers atomic-site specific information about the local electronic structure and dynamics in condensed phase. The application of soft x-ray RIXS to liquids [14] has generated considerable attention; improvements in sensitivity [15] and energy resolution [16] continue to open new perspectives on fundamental liquid-phase interactions [17–19]. Recently, the combination of RIXS, liquid microjets, and x-ray free-electron lasers enabled time-resolved measurements of electronic structure of transient species in solutions [20, 21].

Here we report the RIXS spectrum for the short-lived OH radical in water (Fig. 1). In sharp contrast to the UV spectrum, the RIXS spectrum of OH(aq) features two peaks corresponding to transitions between the OH orbitals (Fig. 1, bottom right). The energy difference between the elastic and inelastic peaks corresponds to the X→A transition, which, in turn, roughly equals the energy gap between the 2σ and 1π orbitals. Thus, RIXS reveals intrinsic local electronic structure of solvated OH, which is obscured in the UV region by CT transitions.
FIG. 1. UV absorption and RIXS energy-loss spectra of OH(aq) (top) and molecular orbital diagrams (bottom). The electronic configuration of OH is 1s\(^2\)2s\(^2\)2p\(^3\). The lowest valence transition (2\(\sigma\) \(\rightarrow\) 1\(\pi\), marked as LT\(_{\text{val}}\) for local transition) has low oscillator strength due to its \(p_x \rightarrow p_x/p_y\) character; the UV spectrum is dominated by charge-transfer transition (CT\(_{\text{val}}\)) from nearby waters. In resonantly excited OH (1s\(^2\)1s\(^2\)2\(\sigma\)\(^2\)1\(\pi\)\(^4\)), both 1\(\pi\) \(\rightarrow\) 1s and 2\(\sigma\) \(\rightarrow\) 1s transitions are bright, giving rise to the elastic peak (zero energy loss) and a feature at \(\sim 4\) eV. The gap between the two RIXS peaks corresponds to the 2\(\sigma\) \(\rightarrow\) 1\(\pi\) energy.

In contrast to CT transitions, which are characteristic of the solvent and its local structure, local transitions (LT) are fingerprints of the solute and can, therefore, be used to track reactive hydroxyl radicals in various complex and heterogeneous environments. The CT transitions in the RIXS spectrum are suppressed because the compact shape of the core 1s\(_x\) orbital results in poor overlap with the lone pairs of neighboring waters. We confirm this by \textit{ab initio} RIXS calculations using a new electronic structure method [22, 23] based on the equation-of-motion coupled-cluster (EOM-CC) theory. These calculations also reproduce the relative RIXS line intensities, positions, and widths for the elastic and inelastic peaks of OH(aq) and OH\(^-\) (aq).

The OH(aq) spectra are also compared to the x-ray emission spectra (XES) of liquid water, where the role of hydrogen bonding and ultrafast dynamics has long been debated [15, 18, 24–28]. If core-ionized water dissociates prior to core-hole decay, a core-excited OH(aq) is formed in the 1s\(^2\)1s\(^2\)2\(\sigma\)\(^2\)1\(\pi\)\(^4\) intermediate RIXS state (Fig.1). The lower-energy component of the water XES doublet has been attributed to this ultrafast dissociation [15] and our measurement of the position of the OH(aq) RIXS resonance directly provides relevant information that previously was indirectly deduced [27].

We create the transient hydroxyl radical using strong-field ionization in pure liquid water [29]. The laser-induced ionization initially forms a water cation (\(\text{H}_2\text{O}^+\)), which undergoes ultrafast proton transfer with a neighboring water molecule on the sub-100-fs timescale [30] forming the hydroxyl radical and hydronium ion (\(\text{H}_3\text{O}^+\)). In the time window between proton transfer \((\sim 100\) fs) and geminate recombination, the ionized liquid water sample contains hydroxyl radicals. Because the 1s\(_O\) \(\rightarrow\) 1\(\pi\) transition in OH(aq) occurs cleanly in the “water window”, i.e., below the liquid water absorption edge, its kinetics can be readily probed via transient absorption [29] and, simultaneously, via RIXS. Importantly, the latter allows investigation of local valence transitions, which are chemically most relevant.

Briefly, optical-pump x-ray-probe RIXS was performed using the Soft X-ray Research (SXR) instrument [31] at the Linac Coherent Light Source (LCLS) at SLAC National Accelerator Laboratory. Monochromatized x-ray pulses were scanned from 518 to 542 eV \((\sim 10\)\(\mu\)J, \(\sim 40\)fs, 200 meV bandwidth). Three photon detection channels were simultaneously recorded: transmission, total fluorescence, and dispersed emission. A detailed description of the performance of the optical laser, water jet, and x-ray monochromator calibration, shot-by-shot normalization procedures can be found in [29]. Here we describe additionally the x-ray emission spectrometer and experimental geometries for RIXS measurements of OH(aq).

X-ray emission was collected perpendicular to the incoming x-ray beam and along the x-ray polarization axis using a variable-line-spacing grating-based spectrometer [32]. A CCD camera located at the exit plane of the spectrometer recorded images on a shot-by-shot basis.

The energy dispersion and absolute energy of the incoming monochromatized radiation were previously calibrated [29, 33]. The dispersion of the emission spectrometer was determined by fitting a first degree polynomial to the elastic line visible in Fig. 2(b).

To gain insight into the nature of main spectral features, we carried out electronic structure calculations using EOM-CC [34] with single and double excitations (EOM-CCSD), augmented by core-valence separation (CVS) [35] to enable access to core-level states [22, 36]. As a multistate method, EOM-CC treats different valence and core-level states on an equal footing and is particularly well suited for modeling molecular properties, including non-linear properties [34, 37–39]. To account for solvent effects, the spectral calculations of OH(aq)/OH\(^-\) (aq) were carried out within the QM/MM (quantum mechanics-molecular mechanics) scheme with water molecules described by classical force field and OH/OH\(^-\) described by EOM-CCSD by using snapshots from equilibrium \textit{ab initio} molecular dynamics simulations.

The electronic factors entering RIXS cross sections
are the RIXS transition moments given by the following Kramers-Heisenberg-Dirac (KHD) expression [40]:

$$M_{g}^{xy} = -\sum_{n} \left( \frac{\langle f | \mu^y | n \rangle \langle n | \mu^x | g \rangle}{\Omega_{ng} - \omega_{i,x} - i\epsilon_{n}} + \frac{\langle f | \mu^x | n \rangle \langle n | \mu^y | g \rangle}{\Omega_{ng} + \omega_{o,y} + i\epsilon_{n}} \right),$$

where $g$ and $f$ denote the initial and final electronic states (i.e., ground and valence excited state of OH), $\omega_{i}/\omega_{o}$ are the incoming/outgoing photon frequencies, and the sum runs over all electronic states; $\Omega_{ng} = E_{n} - E_{g}$ is the energy difference between states $n$ and $g$, and $i\epsilon_{n}$ is the imaginary inverse lifetime parameter for state $n$. In the present experiment, the dominant contribution to the RIXS cross section comes from the term corresponding to the $1s_{O}^{1} \ldots 1\pi^{4}$ state, which is resonant with excitation frequency of 526 eV, such that the spectra can be qualitatively understood within a three-states model. Within the EOM-CC framework, the KHD expression is evaluated using EOM-CC energies and wave functions. Rather than arbitrarily truncating the sum over states, we replace all $\epsilon_{n}$s with a phenomenological damping factor $\epsilon$ and use damped response theory to convert the KHD expression into a numerically tractable closed form [23, 38, 41]. Robust convergence of the auxiliary response equations is achieved by using CVS within the damped response domain [23]. The resulting method combines rigorous treatment of RIXS cross sections and high-level description of electron correlation. To describe vibrational structure in the RIXS spectrum, we computed Franck-Condon factors (FCFs) using three-states model (as was done in Ref. [17]) and harmonic approximation. To quantify relative strengths of local and CT transitions, we also carried out calculations on model water-OH structures. All calculations were performed using the Q-Chem electronic structure package [42]. Full details of computational protocols are given in the SI.

Theoretical estimates of key structural parameters of the isolated OH given in Table I agree well with experimental values [4, 5]. Theory overestimates the energy of the valence transition by 0.08 eV and underestimates the energy of the core-excited state by 0.7 eV; these differences are within the error bars of the method [22]. The variations in bond lengths and frequencies among different states are consistent with the molecular orbital picture of the electronic states. The structural differences between the states give rise to a vibrational progression in the x-ray absorption spectrum; the computed FCFs are in excellent agreement with the experimental ones (see SI).

Fig. 2 shows the RIXS maps before and after the ionization pulse. The RIXS map prior to ionization, Fig. 2(a), is in agreement with earlier measurements [15, 24, 26]. There is a threshold for emission at $\sim 534$ eV excitation energy and a pre-edge peak at $535$ eV. After ionization, Fig. 2(b), a new resonant feature appears at $526$ eV excitation energy that is identified as $1s_{O} \rightarrow 1\pi$ transition of OH(aq): its position is near that of gas-phase OH [5] and its kinetics are consistent with proton transfer [29]. The position of the quasi-elastic RIXS line of OH(aq) coincides with the lower-energy component of the water XES doublet (see dashed line in Fig. 3), provid-
TABLE I. Key structural parameters of isolated OH radical.

| State Character | $T_e$, eV | $r_e$, Å | $\omega_e$, eV | $\mu$, a.u. |
|----------------|----------|--------|-------|---------|
| X(2Π1)        | 1s$^2$1σ$^2$2σ$^2$π$^3$ | 0.000 | 0.972 | 0.468 | 0.701  |
|                |          | 0.000 | 0.970 | 0.463 |        |
| core $^2$Σ$^+$ | 1s$^2$1σ$^2$2σ$^2$π$^4$ | 525.1 | 0.916 | 0.543 | 0.814  |
|                |          | 525.8 | 0.915 | 0.533 |        |
| A(2Σ$^+$)     | 1s$^2$1σ$^2$2σ$^2$1π$^4$ | 4.128 | 1.014 | 0.398 | 0.801  |
|                |          | 4.052 | 1.012 | 0.394 |        |

*Theory, this work. Energies ($T_e$) and dipole moments ($\mu$): (cvs)-EOM-EE-CCSD, computed at the experimental geometries; $r_e$ and $\omega_e$: (cvs)-EOM-IP-CCSD. Basis set: uC-6-311(2+,+)G(2df,p). b Expt. Ref. 4. c Expt. Ref. 5.*

Table II summarises the main RIXS features of OH(aq) and OH$^-$ (aq), comparing experimental and theoretical values. The RIXS spectrum has a peak with 0.7 eV FWHM that assigned to quasi-elastic $GS \rightarrow 1s_G^{-1} \pi^+ \rightarrow GS$ scattering to the electronic ground state. We also observe a 1.5 eV wide structure beginning at 3.6 eV energy loss that corresponds to scattering to the first electronically excited state: $GS \rightarrow 1s_G^{-1} \pi^+ \rightarrow 2\sigma^{-1} \pi^+$. The calculations reproduce the gap ($\Delta E$) between the quasi-elastic and energy-loss peak well; however, the absolute position of the $1s_G \rightarrow 1\pi$ transition is 1 eV off. EOM-EE-CCSD excitation spectra for core-level transitions often exhibit systematic shifts of 0.5-1.5 eV, attributed to insufficient treatment of electron correlation [22], while the relative positions of the peaks are reproduced with higher accuracy. The intensity ratio of the two peaks stems from their $\pi$ and $\sigma$ character and is reproduced qualitatively by our calculations.

TABLE II. Positions and relative intensities of the RIXS peaks for OH(aq) and OH$^-$ (aq) as defined in the insets of Fig. 3.

| Species Source | $E$, eV | $\Delta E$, eV | Ratio |
|----------------|----------|--------------|-------|
| OH(aq) this work | 526.0 | -3.8 | 2.1 |
| OH(aq) this work | 525.0 | -4.0 | 2.04 |
| OH$^-$ Ref. 15 | 526.5 | -3.8 | 4.3 |
| OH$^-$ this work | 526.2 | -3.8 | 5.20 |

* Experiment. b Theory.*

Both quasi-elastic and energy-loss peaks are broadened due to the interaction with polar solvent and to vibrational structure. As shown in Table I, the dipole moment in electronically excited OH is 14% larger than in the ground state, suggesting larger inhomogeneous broadening for the energy-loss peak; this is confirmed by our QM/MM calculations where the effect of the solvent is treated explicitly. The analysis of structural differences between the ground X(2Π1), valence excited A(2Σ$^+$), and core-excited states suggests longer vibrational progression for the energy-loss peak, which is confirmed by the computed FCFs (see SI). This trend can be rationalized by the shapes of molecular orbitals: the bonding character of 2$\sigma$ orbital involved in the $GS \rightarrow 1s_G^{-1} \pi^+ \rightarrow 2\sigma^{-1} \pi^+$ transition renders it more sensitive to vibrational excitation.

The middle and bottom panels of Fig. 3 compare the RIXS of OH(aq) to that of OH$^-$ (aq) [15]. The two species show very similar emission spectra, as expected from the similarity of the intermediate RIXS state. There is a significant difference in the intensities of the quasi-elastic $\pi$ peak and the energy-loss ($\sigma$) feature. The observed $\pi/\sigma$ ratios for OH(aq) and OH$^-$ (aq) are 2.1:1 and 4.3:1, compared to the calculated 2.0:1 and 5.2:1. In OH$^-$ calculations, we assumed resonant excitation to the lowest XAS peak of solvated OH$^-$, which roughly corresponds to the transition to a diffuse $\sigma$-type orbital. The observed $\pi/\sigma$ RIXS ratio from OH$^-$ (aq) depends strongly on the

FIG. 3. Comparison of RIXS from OH and OH$^-$. Top: Experimental XES from water for excitation energies between 536-542 eV compared to XES of water excited at 550.1 eV [15]. Middle: RIXS from the 526-eV resonance of OH(aq) compared with theory (shifted +1.0 eV). Bottom: RIXS from OH$^-$ excited at 533.5 eV and compared with theory (shifted -0.2 eV). Ref. [15] data shifted -0.7 eV. Insets show molecular orbital diagrams for the RIXS transitions in OH and OH$^-$. 

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| OH(aq) this work | 525.0 | -4.0 | 2.04 |
| OH$^-$ Ref. 15 | 526.5 | -3.8 | 4.3 |
| OH$^-$ this work | 526.2 | -3.8 | 5.20 |

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Both quasi-elastic and energy-loss peaks are broadened due to the interaction with polar solvent and to vibrational structure. As shown in Table I, the dipole moment in electronically excited OH is 14% larger than in the ground state, suggesting larger inhomogeneous broadening for the energy-loss peak; this is confirmed by our QM/MM calculations where the effect of the solvent is treated explicitly. The analysis of structural differences between the ground X(2Π1), valence excited A(2Σ$^+$), and core-excited states suggests longer vibrational progression for the energy-loss peak, which is confirmed by the computed FCFs (see SI). This trend can be rationalized by the shapes of molecular orbitals: the bonding character of 2$\sigma$ orbital involved in the $GS \rightarrow 1s_G^{-1} \pi^+ \rightarrow 2\sigma^{-1} \pi^+$ transition renders it more sensitive to vibrational excitation.

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nature of the intermediate state and, therefore, would be very sensitive to the excitation frequency; thus, the discrepancy between the computed values and Ref. [15] could be due to different excitation regime.

To rationalize the apparent absence of the CT_{core} transitions in RIXS, we computed valence and core-level transitions for model OH-H_{2}O structures. For the hemi-bonded structure, thought to be responsible for the CT_{val} spectral feature in the UV-visible spectrum [11, 12], the oscillator strength for the local X→A valence transition is 5 times smaller than that of the CT_{val} transition. In contrast, the oscillator strength for the CT_{core} transition is ~50 times smaller than that of the LT_{core} due to the poor overlap of the lone pair of water with the compact 1_{sO} orbital of OH.

In summary, we have measured RIXS of the short-lived hydroxyl radical in pure liquid water. At the OH resonance of 526 eV, an energy-loss feature at 3.8 eV, corresponding to the localized X→A valence transition of OH(aq), was observed. The position of the OH resonance relative to bulk water XES provides information relevant to the long-standing debate on the structural versus dynamical interpretation of water XES. *Ab initio* calculations reproduce the positions, relative intensity, and broadening of the quasi-elastic and energy-loss peaks of OH(aq) and OH^-(aq) and provide insight into the relative intensities of the local and CT RIXS transitions. Time-resolved RIXS, enabled by the availability of intense, tunable ultrafast x-ray pulses from XFELs, highlights the localized transition in this transient species, which is otherwise hidden in direct UV absorption spectra. This ability to report on intrinsic electronic structure of OH rather than on the properties of the solvent and its structure (which is revealed by the CT transitions dominating the UV spectrum) represents the key advantage of RIXS, demonstrating that it may be used to track ultrafast reactions of the chemically aggressive hydroxyl radical in aqueous and potentially more complex environments.

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Supplemental Information

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1. EXPERIMENTAL DETAILS

Details about the liquid jet and calibration of the monochromator energy is described in the Supplemental Information of Ref. 1. In this document, we extend with the information about the x-ray emission spectrometer (XES).

The monochromator energy dispersion was calculated from motor encoder positions using the standard method at the SXR instrument. The absolute energy was calibrated by comparing the absorption in our 2-µm thick water jet with 800-nm thick water as measured by Ref. 2.

X-ray spectra were measured perpendicular to the incoming beam, using a varied line spacing-grating-based spectrometer\(^3\). The spectra were captured shot-by-shot using a CCD detector. Due to limitations in data transfer times the images were projected into one dimension before the readout. A dark background was subtracted from the detector data and values over a certain threshold were counted. The intensity of the pixel was discarded, and only the position was recorded. This method would fail to identify two photons hitting the same pixel, this is however unlikely with the low count rates in the experiment. Cosmic rays with substantially higher pixel values than photons were identified and discarded.

The RIXS maps (Fig. 2 in the main text) was created by binning x-ray spectra by incoming photon energy in 140 meV wide bins and then normalizing by the number of XFEL shots in each bin. The energy dispersion of the XES was determined to be 0.18 eV/pixel by fitting a first degree polynomial to the elastic line, visible in Fig 2 of the main text. The absolute energy of the XES was then set by shifting the emission scale such that the excitation energy at 526 eV matched with emission energy. The CCD detector had 2048 pixels, 204 pixels were used for creating the RIXS maps in Fig. 2. The narrowest peak observed during the experiment was 0.7 eV at FWHM.

XFEL shots with very low intensity, as measured shot by shot, were not considered in the data. Considering the RIXS maps (Fig. 2 in the main text), a total of 710053 XFEL shots were measured; after filtering there were 365846 shots considered (127931 before the valence ionizing pump and 237915 after the pump). A small region of time (0-0.2 ps) around the interaction region was removed. There were a total of 15054 counts on the XES in this measurement; 5228 before the valence ionizing pump and 9826 after the pump. For the OH RIXS spectrum (Fig 1. and Fig 3. in the main text), after removing low intensity shots and selecting a time (0.2 ps-1.4 ps after pump) and energy window (0.42 eV wide incident energy), there were 15194 shots with 448 counts on the XES.
2. THEORETICAL METHODS AND COMPUTATIONAL DETAILS

To gain insight into the nature of main spectral features, we carried out electronic structure calculations using equation-of-motion coupled-cluster singles and doubles (EOM-CCSD) theory\(^4\) augmented by core-valence separation (CVS)\(^5\) to enable access to core-level states. Specifically, fc-cvs-EOM-EE-CCSD and fc-cvs-EOM-IP-CCSD methods\(^6–8\) were used for computing XAS and XES, respectively. For the sake of brevity, below we skip the ‘fc’ prefix (denoting that the core electrons are frozen in the CCSD amplitudes) and refer to these methods as cvs-EOM-EE/IP-CCSD. Relevant valence states were computed using standard EOM-CCSD (with core electrons frozen).

RIXS spectra were computed using a recently developed approach\(^9\) for computing EOM-CC response properties in the X-Ray domain. The approach is based on recasting the two-photon sum-over-states expressions for RIXS transition moments into compact closed-form expressions using the damped response formalism\(^10–12\). The response equations are then solved invoking CVS, which decouples the response states from the autoionizing continuum. The combination of damped response theory with CVS results in a robust convergence of the response equations\(^9,13\). The essential features of the theory are summarized in the next section; full details can be found in Ref. 9.

2.1. RIXS theory

The RIXS cross section \(\sigma_{gf}^{\text{RIXS}}(\theta)\) is a function of the scattering angle \(\theta\)—defined as the angle between the polarization vector of the incoming photon and the propagation vector of the outgoing photon—and is given in terms of components of the RIXS transition strength tensor \((S_{gf})\) between the initial \((g)\) and final \((f)\) states:

\[
\sigma_{gf}^{\text{RIXS}}(\theta) = \frac{1}{15} \frac{\omega_o}{\omega_i} \sum_{xy} \left[ \left( 2 - \frac{1}{2} \sin^2 \theta \right) S_{gf}^{xy,xy} + \left( \frac{3}{4} \sin^2 \theta - \frac{1}{2} \right) \left( S_{gf}^{xy,yx} + S_{gf}^{xx,yy} \right) \right], \quad (1)
\]

where \(\omega_o\) and \(\omega_i\) are frequencies of the emitted and incident photons, and the indices \(x\) and \(y\) denote Cartesian components\(^9,11,13\). \(S_{gf}^{ab,cd}\) is given by

\[
S_{gf}^{ab,cd} = \frac{1}{2} \left( M_{gf}^{ab} M_{fg}^{cd} + (M_{gf}^{cd})^* (M_{fg}^{ab})^* \right), \quad (2)
\]
where * denotes complex conjugation$^{14,15}$. Here, $M_{fg}^{ab}$ are the RIXS moments given by the following sum-over-states Kramers-Heisenberg-Dirac (KHD) expression$^{16}$:

$$M_{fg}^{xy}(\omega_{i,x},-\omega_{o,y}) = -\sum_n \left( \frac{\langle \Psi_f | \mu^y | \Psi_n \rangle \langle \Psi_n | \mu^x | \Psi_g \rangle}{\Omega_{ng} - \omega_{i,x} - i\epsilon_n} + \frac{\langle \Psi_f | \mu^x | \Psi_n \rangle \langle \Psi_n | \mu^y | \Psi_g \rangle}{\Omega_{ng} + \omega_{o,y} + i\epsilon_n} \right). \quad (3)$$

In the KHD expression, $\Omega_{ng} = E_n - E_g$ is the energy difference between states $n$ and $g$ and $i\epsilon_n$ is the imaginary inverse lifetime parameter for state $n$. Within the EOM-CC damped response framework, the KHD expression is evaluated using EOM-CC energies and wave functions and all $\epsilon_n$s are replaced with a phenomenological damping factor $\epsilon$.

### 2.2. Computational details

In all EOM-CCSD calculations, we used the 6-311(2+,+)$G(2df,p)$ basis with uncontracted core (oxygen), which has been shown to adequately describe core-level states$^9$. The basis is given in Section 7. Below we denote this basis as uC-6-311(2+,+)$G(2df,p)$. All $(cvs)$-EOM-EE-CCSD calculations for the hydroxyl radical employ the UHF reference.

![FIG. S1: Snapshot from QM/MM molecular dynamics calculations. The QM part comprises OH (or OH−) and 5 water molecules and the MM part comprises 1018 water molecules. In the calculations of the spectra, only OH (or OH−) was included in the QM part and all 1023 waters were described by point charges.](image)

We carried out calculations of the spectra for isolated species as well as accounting for solvent effects by using polarizable continuum model (PCM) and explicit description of the solvent using QM/MM (quantum mechanics/molecular mechanics). In the XAS calculations for isolated OH and OH− we used $r_{OH} = 0.9697$ Å (experimental geometry of the hydroxyl radical$^{17}$). The same structure was used in the PCM calculations. The parameters for the PCM calculations were set up to describe water ($\epsilon=4.34$ and $\epsilon_\infty=1.829$).
To account for solvent-induced spectral shifts and inhomogeneous broadening, we carried out the calculations of the spectra of solvated species using the QM/MM scheme with the OH radical (or hydroxide) included in the QM part and with water molecules described by point charges taken from classical force field (charmm27, Ref. 18). The model system included OH or hydroxide solvated by 1023 water molecules (see Fig. S1). The spectra were computed using 100 snapshots taken from the equilibrium molecular dynamics (MD) simulations. The computed spectra were convoluted with Gaussians with FWHM=0.147 eV to account for the life-time broadening of the 1sO hole state19.

The starting structure for dynamics simulations was taken from the MD simulations of water (courtesy of Prof. John Herbert) and one water was replaced by OH. In the equilibrium dynamics simulations, OH (or OH−) and 5 water molecules were included in QM system (Fig. S1). The QM part was described with ωB97X-D/6-31+G* and the MM part was described by the charmm27 force field18. In the QM/MM setup, we used Janus interface and electrostatic embedding20,21. Time step for dynamics was 42 a.u. (0.0242 fs). Following brief equilibration run of the initial structure, MD was executed using the NVT ensemble with T=298 K. The trajectories were propagated for approximately 2 ps. 100 snapshots were collected after first 100 fs, when the temperature became stabilized. In the course of the simulations, the model droplet remained stable. The exact setup of the dynamics simulations is illustrated by the input given at the end of this document.

To quantify the differences between valence and core-level transitions of local and charge-transfer character, we carried out additional simulations on model OH-H2O structures constructed following Refs. 22 and 23; the respective Cartesian geometries are given in Section 8.

To analyze the character of electronic transitions, we used natural transition orbitals (NTOs), which allow one to describe electronic transitions between many-body states in terms of the minimal number of hole-electron excitations24–30. We used Gabedit31 to visualize the NTOs.

To evaluate the effect of vibrational broadening, we computed Franck-Condon factors (FCFs) for the relevant transitions within double-harmonic approximation using the ezSpectrum software32. Frequencies and structures for relevant electronic states of OH (ground state, valence and core excited states) were computed with (cvs)-EOM-IP-CCSD/uC-6-311(2+,+)G(2df,p). All calculations were carried out using the Q-Chem electronic structure package33,34.
3. RESULTS

3.1. Structural parameters of the OH radical

Table S1 compares the theoretical estimates of key structural parameters \((r_e, \omega_e, T_e, \mu)\) of OH with the experimental values\(^{19}\); a shorter version of this table is given as Table 1 in the main manuscript. The computed values are in good agreement with the experimental ones. The two different variants of EOM-CCSD—EOM-EE-CCSD and EOM-IP-CCSD—are in agreement with each other. We note that the EOM-EE-CCSD values are closer to the experimental ones, which we attribute to its more flexible ansatz.

| State          | Character                        | \(T_e\) (eV) | \(r_e\) (Å) | \(\omega_e\) (eV) | \(\mu\) (a.u.) |
|----------------|----------------------------------|--------------|-------------|-------------------|---------------|
| \(X(^2\Pi_1)\) | \((1s_O)^21\sigma^22\sigma^21\pi^3\) | 0.000        | 0.972/0.955 | 0.468/0.485       | 0.706/0.701   |
|                |                                  | 0.000        | 0.9697      | 0.463             |               |
| core \(^2\Sigma^+\) | \(1s_O^{-1}1\sigma^22\sigma^2\pi^4\) | 527.573/525.145 | 0.916/0.923 | 0.543/0.522       | 0.747/0.814   |
|                |                                  | 525.8        | 0.915       | 0.533             |               |
| \(A(^2\Sigma^+)\) | \((1s_O)^21\sigma^22\sigma^11\pi^4\) | 4.122/4.128  | 1.014/0.976 | 0.398/0.397       | 0.808/0.801   |
|                |                                  | 4.052        | 1.012       | 0.394             |               |

\(^a\) Theory, this work. \(T_e\) and \(\mu\): (cvs)-EOM-IP-CCSD/(cvs)-EOM-EE-CCSD, computed at the experimental geometries; \(r_e\): (cvs)-EOM-IP-CCSD/B3LYP; \(\omega_e\): (cvs)-EOM-IP-CCSD/B3LYP. Basis set: uC-6-311(2+,+)G(2df,p). \(^b\) Expt., from Ref. 17. \(^c\) Expt., from Ref. 19.

The differences in bond lengths and frequencies are consistent with the molecular orbital picture of the electronic states (see Fig. 1 of the main manuscript). We note that the valence excited state has a considerably larger dipole moment than the ground state (\(~14\%\) increase), suggesting a larger inhomogeneous broadening of the energy-loss peak in the RIXS spectrum\(^{35}\).
3.2. Calculations of XAS spectra

Tables S2 and S3 show the transitions giving rise to the XAS spectra of OH (vertical excitation energies for isolated species and with PCM solvent) and OH\(^-\) (vertical excitation energies with PCM solvent), respectively. Symmetry labels correspond to the C\(_{2v}\) subgroup used in the calculations (\(\pi\) orbitals belong to \(b_1\) and \(b_2\) irreps; \(\sigma\) and \(1s_O\) orbitals belong to \(a_1\)). Figure S2 shows the XAS spectra computed using the QM/MM snapshots. We considered six lowest transitions.

**TABLE S2:** XAS transitions in OH; cvs-EOM-EE-CCSD/uC-6-311(2+,+)/G(2df,p). Excitation energies in eV, oscillator strengths shown in parenthesis.

| Transition | OH       | OH/PCM   |
|------------|----------|----------|
| \(b_2\)    | 525.21 (0.048) | 525.17 (0.048) |
| \(a_1\)    | 536.02 (0.005) | 536.52 (0.004) |
| \(a_1\)    | 537.36 (0.016) | 537.83 (0.012) |
| \(b_1\)    | 539.56 (0.004) | 539.06 (0.005) |
| \(b_2\)    | 539.70 (0.001) | 539.41 (0.004) |
| \(b_1\)    | 540.90 (0.004) | 539.64 (0.001) |

The hole is in \(b_2\) \(\pi\)-orbital.

In the case of OH, the solvent effects appear to be small; for example, the inclusion of the solvent via PCM changes the energy of the lowest transition (\(1s_O \rightarrow 1\pi\)) by 0.04 eV (Table S2). The shifts for other transitions are also quite small. The explicit inclusion of the solvent via QM/MM is necessary for recovering the inhomogeneous broadening; it is also expected to yield more accurate estimates of solvent-induced shifts. In agreement with the PCM results, QM/MM calculations also show a small solvent effect for the lowest transition: the computed maximum for the lowest band is 525 eV and the peak is very narrow (~0.3 eV). The small effect can be explained by the compact nature of the valence \(\pi\) orbital and by relatively weak interactions of the neutral OH with water. The effect for higher bands is larger. We note that in these classical calculations, vibrational broadening is not fully recovered—the zero-point energy of OH is 2670 K, which is an order of magnitude more than the average thermal energy of OH in the MD calculation. The calculations of vibrational broadening are described in Section 3.4.

As clearly seen from Fig. S2 and Table S2, \(1s_O \rightarrow 1\pi\) has the largest intensity and dominates the spectrum. The large oscillator strength is consistent with the \(s \rightarrow p\) orbital character of the transition (see Fig. 1 of the main manuscript).
FIG. S2: Computed XAS spectrum of solvated OH (left) and OH$^-$ (right); QM/MM with cvs-EOM-EE-CCSD/uC-6-311(2+,+)G(2df,p).

In contrast to the neutral OH, solvent is crucially important for describing excited states in the hydroxide anion. Without solvent, there are no bound transitions—all excited states are shape resonances. The cvs-EOM-IP-CCSD IE corresponding to 1$s_O$ in OH$^-$ is 529.31 eV, considerably lower than 543.7 eV in the neutral OH. Solvent stabilizes the negative charge and makes the lowest transitions bound (the IE of 1$s_O$ increases to 534.5 eV in the PCM calculations). The difference between QM/MM and PCM is also larger than in the OH case; for example, the QM/MM maximum of the lowest peak is at $\sim$532 eV, to be compared with 531.3 eV in the PCM calculations. The lowest peak corresponds to the transition to a symmetric orbital (of $a_1$ symmetry) and appears to be well separated from the next band derived from the excitations to $\sigma$ and $\pi$ orbitals.

TABLE S3: XAS transitions in OH$^-$; cvs-EOM-EE-CCSD/uC-6-311(2+,+)G(2df,p). Excitation energies in eV, oscillator strengths shown in parenthesis.

| Transition | OH$^-$/PCM |
|------------|-------------|
| $a_1$      | 531.31 (0.006) |
| $a_1$      | 532.79 (0.008) |
| $b_1/b_2$  | 532.81 (0.009) |
| $a_1$      | 533.96 (0.005) |
| $a_1$      | 537.07 (0.011) |
3.3. Calculations of RIXS spectra

Figure S3 shows RIXS spectra of the OH(aq) radical computed with three different polarization (the experimental setup corresponds to $\theta = 0^\circ$). In these calculations, lowest three excited states of OH were included and damping factor $\epsilon=0.005$ hartree was used. We note that higher excited states of OH cannot be produced in the RIXS process with $1s_O \rightarrow 1\pi$ pumping transition, because they would require two-electron transitions.

The computed spectra show two peaks: the elastic band at 525 eV and the energy-loss peak at $\sim 521$ eV. Orbital analysis confirms that the energy-loss peak corresponds to the relaxation of the $2\sigma(p_z)$ electron. The energy gap between the two peaks is nearly identical to the XES transition computed using the same snapshots and cvs-EOM-IP-CCSD/uC-6-311(2+,+)G(2df,p). The relative intensity of the two peaks depends on polarization; at $\theta = 0^\circ$, the intensity of the elastic peak, which corresponds to the relaxation of doubly degenerate $\pi$ orbitals, is approximately twice higher than the intensity of the energy-loss peak. The widths of the peaks are 0.32 eV (elastic) and 0.35 eV (energy loss). Larger broadening of the energy-loss peak is consistent with the increased dipole moment of the final (valence excited) state (Table S1).

Computed RIXS emission spectra for OH$^-$(aq) are shown in Figure S4; Fig. S5 compares RIXS emission spectrum of OH$^-$(aq) with that of the OH(aq) radical. In these calculation, lowest 20 excited states of OH$^-$ were included. The spectra were computed with two pumping frequencies: 532.1250 eV and 534.1497 eV, corresponding to the maxima of the two lowest XAS bands (see Figure S2). The two dominant peaks in all spectra have the same origin as in the OH spectra; they correspond to the relaxation of $1\pi$ and $2\sigma(p_z)$ electrons; their positions are also close.

The absolute position of hydroxide’s $1\pi$ peak is blue-shifted by 1.2 eV relative to OH. There are two factors contributing to this value: differences in solvation-shell structure around the OH and OH$^-$ and the electronic differences (the presence of spectator electron in OH$^-$, see Fig. 3 of the main manuscript). By computing XES transitions of OH$^-$ using the two sets of snapshots (from equilibrium simulations of OH and OH$^-$), we observe that $\pi \rightarrow 1s_O$ transition computed for the hydroxide snapshots is red-shifted by 0.5 eV relative to the same transitions computed for the hydroxyl snapshots; thus, different solvation is responsible for $\sim 0.5$ eV. Thus, electronic effect is dominant and the computed large blue shift can be attributed to the presence of the extra electron in OH$^-$. Because of the compact nature of the core orbital, this additional
OH(aq): RIXS emission at 525.00 eV pump

FIG. S3: RIXS spectra of solvated OH computed with QM/MM with (cvs-)EOM-EE-CCSD/uC-6-311(2+,+)G(2df,p). The computed transitions are convoluted with Gaussians with FWHM=0.147 eV. Pumping frequency is 525.00 eV.

...electron is likely to destabilize the energies of the valence orbitals more that the energies of the core orbital, giving rise to a blue shift in $\pi \rightarrow 1s_O$ transition. The variations in the peak-to-peak energy gap and the widths of these peaks also reflect the effect of the spectator electron (see Fig. 3 of the main manuscript). The relative intensity of these two peaks varies depending on the pumping frequency due to different symmetries of the intermediate state. The spectrum reported by Fuchs et al.\textsuperscript{36} most likely corresponds to pumping the lowest transition (532 eV in our calculations). The relative intensity of the two dominant energy-loss peaks in this spectrum is roughly 4:1 (to be compared with 2:1 in the OH spectrum) and the energy gap between them is slightly less than 4 eV, in agreement with the experimental trend (in Fuchs’ spectrum\textsuperscript{36} of hydroxide, the position of the energy-loss peak is 3.9 eV and the relative intensity of the two peaks are $\sim$3:1).
FIG. S4: RIXS spectra of solvated OH$^-$ computed with QM/MM with (cvs-)EOM-EE-CCSD/uC-6-311(2+,+)G(2df,p). The computed transitions are convoluted with Gaussians with FWHM=0.147 eV. Pumping frequencies are: 532.1250 eV (top panel) and 534.1497 eV (bottom panel).
FIG. S5: RIXS spectra of solvated OH and OH\(^-\) computed with QM/MM with (cvs-)EOM-EE-
CCSD/uC-6-311(2+,+)G(2df,p). The computed transitions are convoluted with Gaussians with
FWHM=0.147 eV. \(\theta = 0^\circ\), pumping frequency is 525 eV for OH and 532.125 for OH\(^-\). The hy-
droxide spectrum is blue-shifted by 1.2 eV for maximum alignment; intensities are arbitrary.
3.4. Franck-Condon factors and vibrational broadening

Figure S6 shows schematically the potential energy curves of the three states relevant for XAS and RIXS transitions. We used ezSpectrum\textsuperscript{32} to compute the FCFs within the harmonic approximation for the initial state (\(X^2\Pi_1\)), the final state (\(A^2\Sigma^+\)), and the core-excited state ((1s\(O\))\(^{-1}\ldots(1\pi)^2\)) that is resonant with the incident photon frequency.

As one can see from Table S1, 1s\(O\) → 1\(\pi\) excitation results in shorter equilibrium distance and an increased vibrational frequency, as expected from the increased bond order due to filling of bonding \(\pi\) orbital and strong attractive potential of the core hole. This leads to a clear vibrational progression in the XAS spectrum\textsuperscript{19}; the computed FCFs (\(\nu_0 : \nu_1\) ratio = 100:16.3) agree with the experimental ones (\(\nu_0 : \nu_1\) ratio = 100:15.2)\textsuperscript{19}. These FCFs are also responsible for the vibrational broadening of the elastic peak in RIXS. The valence \(A^2\Sigma^+\) state has a longer bond length and softer frequency than the \(X^2\Pi_1\) and the core-excited states, also consistent with their orbital characters. These structural changes give rise to the FCFs shown in Figure S7. Computed FCFs are given in Table S8 in Section 9.
To compute vibrational structure in the RIXS spectra, we employ the three-states model (in which the sum over all states is reduced to just one term), similarly to the treatment in Ref. 35. We consider the following scenarios: (i) cold OH with only $\nu = 0$ populated in the ground state; (ii) hot OH with non-thermal populations of vibrational levels (equal populations of $\nu = 0, 1$ or $\nu = 0, 1, 2$); (iii) hot OH with thermal populations of $\nu = 0$ to $\nu = 2$. Within this three-states model and the Condon approximation, the RIXS scattering moments for a specific set of vibrational states ($p, q, r$) for the initial, intermediate, and final states are approximated as follows:

$$M_{gf}^{vib} \approx M_{gf}^{elec} \langle g\chi_p|c\chi_q\rangle\langle c\chi_q|f\chi_r \rangle,$$

where $M_{gf}^{elec}$s are given by Eq. (3) and computed with cvs-EOM-EE-CCSD. $n\chi_p$ represents the vibrational wave function of level $p$ for state $n$. $\langle n\chi_p|m\chi_q \rangle$ is the Franck-Condon factor between vibrational levels of states $n$ and $m$. The RIXS scattering strengths and cross sections for a specific set of vibrational states ($p, q, r$) for the initial, intermediate, and final states are approximated using Eq. (2) for the electronic part and Eq. (4) as follows:

$$S_{gf}^{vib} \approx S_{gf}^{elec} \langle \langle g\chi_p|c\chi_q\rangle\langle c\chi_q|f\chi_r \rangle \rangle^2;$$

$$\sigma_{vib}^{RIXS} (\theta) \approx \sigma_{elec}^{RIXS} (\theta) \langle \langle g\chi_p|c\chi_q\rangle\langle c\chi_q|f\chi_r \rangle \rangle^2.$$

The main difference with Ref. 35 is that here we use fixed averaged electronic cross section for each vibrational transition and do not account for small variations in the cross sections due to variations of the transition energies. The RIXS emission peak positions and intensities computed using Eq. (6) are given in Table S9 in Section 9.

Figure S7 shows the computed RIXS spectra. Both cold and hot OH spectra show vibrational broadening. Non-thermal population of $\nu = 1$ and $\nu = 2$ levels increases the relative intensity of side peaks, leading to an overall broadening of both elastic and inelastic bands. When smoothened with gaussians with FWHM extracted from the QM/MM simulations, one can see that energy-loss peak shows more broadening. The widths of the peaks from the bottom panel of Figure S7 are:

- For $\nu = 0$: elastic peak has width of 0.345 eV and inelastic peak has width of 0.691 eV. This spectrum is used in the main draft for comparisons between theory and experiment.
- For $\nu = 0, 1$: elastic peak has width of 0.380 eV and inelastic has 0.726 eV.
- For $\mu = 0, 1, 2$: elastic peak has width of 0.458 eV and inelastic has 0.722 eV.
FIG. S7: Computed RIXS cross sections using harmonic FCFs smoothed with (top) gaussians of FWHM=0.147 eV and (bottom) FWHM=0.33 eV for the elastic peak and FWHM=0.37 eV for the inelastic peak. Black curve shows the spectra computed assuming cold OH (only $\nu = 0$ populated in the ground state). Blue and red curve show the spectra for hot OH with equally populated $\nu = 0, 1$ and $\nu = 0, 1, 2$ levels, respectively.
3.5. Analysis of local and charge-transfer transitions in valence and core-level spectra

The dominant UV-visible peaks around 5.40 eV of the aqueous OH radical arise due to charge transfer between the solvent and the OH radical\textsuperscript{22,23} (see Fig. 1 of the main manuscript). On the basis of electronic structure calculations, Ref. 22 reported that hemibonding (or stacked) arrangements of the OH radical with a nearby water molecule results in charge-transfer transitions from the lone pair of nearby water molecule to the singly occupied $1\pi$ orbital of OH.

### TABLE S4: Hemibonded OH + H\textsubscript{2}O complex. Transition energies (eV), oscillator strengths ($f$), and NTOs for the transitions between the cvs-EOM-EE-CCSD core states and fc-EOM-EE-CCSD valence states with uC-6-311(2+,+)G(2df,p) basis. The corresponding values for transitions computed between cvs-EOM-IP-CCSD core states and EOM-IP-CCSD valence states are in parenthesis. $\sigma^2_K$ denotes the weight of the corresponding NTO pair in the transition. NTO isosurface is 0.05.

| Transition | Energy | Orb. trans. | $f$ | Hole NTO | $\sigma^2_K$ | Particle NTO |
|------------|--------|-------------|-----|----------|-------------|--------------|
| **Core excitation** | | | | | | |
| $X \rightarrow C$ | 524.58 (527.00) | $1s_O \rightarrow 1\pi$ | 0.049 (0.054) | | 0.91 (1.03) | |
| **Local transitions** | | | | | | |
| $X \rightarrow A$ | 4.63 (4.66) | $2\sigma \rightarrow 1\pi$ | 0.009 (0.011) | | 0.93 (0.97) | |
| $C \rightarrow A$ | 519.95 (522.34) | $2\sigma \rightarrow 1s_O$ | 0.037 (0.043) | | 0.89 (1.03) | |
| **Charge-transfer transitions** | | | | | | |
| $X \rightarrow CT$ | 6.63 (6.08) | $lp(H_2O) \rightarrow 1\pi$ | 0.051 (0.049) | | 0.84 (0.87) | |
| $C \rightarrow CT$ | 517.95 (520.92) | $lp(H_2O) \rightarrow 1s_O$ | 0.000 (0.001) | | 0.56 (0.85) | |
with large oscillator strength, whereas the hydrogen-bonded acceptor structures that also show these charge-transfer transitions have low oscillator strengths. In order to understand why these charge-transfer peaks have low RIXS cross sections, we considered two model OH$^+$ H$_2$O structures—one resembling a hemibonded complex and another an acceptor complex; the respective Cartesian coordinates are given in Section 8.

Table S4 shows the energies, oscillator strengths, and NTOs for one-photon transitions involving the $X$, $A$, $CT$, and the core-excited ($C$) states of the hemibonded structure calculated with (cvs-)EOM-EE-CCSD (and also (cvs-)EOM-IP-CCSD) and using the uC-6-311(2+,+)G(2df,p) basis set. Consistent with Ref. 22, the $X \rightarrow CT$ transition shows a larger oscillator strength compared to the $X \rightarrow A$ transition. The $\pi$-stacking hole and particle NTOs for the $X \rightarrow CT$ transition show a significant overlap, confirming its dominant signal in the UV spectrum. In contrast, the $X \rightarrow A$ transition has a $p_z \rightarrow px$ character, which although weakly allowed, has negligible transition dipole moment, giving rise to a weak signal in the UV-visible spectrum. The oscillator strength for the $CT \rightarrow C$ transition is negligible due to poor overlap between 1$s_O$ of OH and the lone pair of the water molecule, whereas the overlap between the core hole and the particle NTOs, both being local, for the $A \rightarrow C$ transition is significant.

In order to relate properties of these one-electron transitions ($X \rightarrow A$ and $X \rightarrow CT$) with RIXS cross sections, we invoke a simple three-state approximation of Eq. (3), similar to the poor-man RIXS calculations discussed in Ref. 9. Specifically, we truncate the sum over all states in Eq. (3) to just one term corresponding to the core-excited state ($C$) that is resonant with the excitation energy. The validity of this approximation, which is justified by the resonant nature of RIXS process, is supported by the RIXS cross sections presented in Table S5. The results show that RIXS cross sections are two orders of magnitude smaller for the $X \rightarrow CT$

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This approximation is valid for two reasons. First, the contribution from the off-resonant core states to the sum over states decays rapidly as $(\Omega - \omega_i)^{-1}$. If the products of the transition moments between the off-resonant core states with the initial and final states are large, off-resonant core states cannot be omitted in the few-states model. This, however, is not the case for our model structures. Second, the denominators in the sum-over-states terms for the low-lying valence intermediate states are order(s) of magnitude larger than that for the core states, giving negligible contribution. Although the sum-over-states terms involving only the initial and final states can show significant contributions for charge-transfer two-photon transitions, this is not the case for our model structures. Within the three-states model, the numerators in the RIXS scattering moment for the $X \rightarrow A$ transition are given as products of $X \rightarrow C$ and $C \rightarrow A$ one-photon moments, which are both non-negligible. On the other hand, the numerators in the RIXS three-states model for the $X \rightarrow CT$ transition are products of $X \rightarrow C$ and $C \rightarrow CT$ one-photon moments, the latter being negligible. This analysis with the three-states models is reflected in the computed cross sections.
transition than for the $X \rightarrow A$ transition.

TABLE S5: Energy loss (eV) and RIXS cross sections (a.u.) for hemibonded OH + H$_2$O complex computed with the (cvs-)EOM-EE-CCSD method and uC-6-311(2+,+)G(2df,p) basis. $\theta = 0^\circ$.

| Transition | Energy loss | RIXS cross section |
|------------|-------------|--------------------|
| Elastic    | 0.00        | 0.0386             |
| $\approx$ Elastic | 0.18 | 0.0763             |
| $X \rightarrow A$ | 4.63 | 0.0585             |
| $X \rightarrow CT$ | 6.63 | 0.0006             |

The computed RIXS cross sections for the hydrogen-bonded acceptor complex are given in Table S6. The trend in these RIXS cross sections, which is similar to that for the hemibonded complex, is consistent with the corresponding three-states models for the $X \rightarrow A$ and $X \rightarrow CT$ transitions and originates from the negligible oscillator strength of the $C \rightarrow CT$ transition relative to the $C \rightarrow A$ transition (see Table S7). In addition, in contrast to the hemibonded structure, the hydrogen-bonded acceptor complex also shows a negligible oscillator strength for the $X \rightarrow CT$ transition. Thus, the contribution of this transition to both the UV and RIXS spectra is negligible, consistent with Ref. 22.

TABLE S6: Energy loss (eV) and RIXS cross sections (a.u.) for hydrogen-bonded acceptor OH + H$_2$O complex computed with the (cvs-)EOM-EE-CCSD method and uC-6-311(2+,+)G(2df,p) basis. $\theta = 0^\circ$.

| Transition | Energy loss | RIXS cross section |
|------------|-------------|--------------------|
| Elastic    | 0.00        | 0.0377             |
| $\approx$ Elastic | 0.14 | 0.0741             |
| $X \rightarrow A$ | 4.15 | 0.0525             |
| $X \rightarrow CT$ | 5.33 | 0.0005             |
TABLE S7: Hydrogen-bonded acceptor OH + H₂O complex. Transition energies (eV), oscillator strengths (f), and NTOs for the transitions between cvs-EOM-EE-CCSD core states and fc-EOM-EE-CCSD valence states with uC-6-311(2+,+)G(2df,p) basis. The corresponding values for transitions computed between cvs-EOM-IP-CCSD core states and EOM-IP-CCSD valence states are in parenthesis. σ² represents the weight of the corresponding NTO pair to the electronic transition. NTO isosurface is 0.05.

| Transition | Energy          | Orb. trans. | f          | Hole NTO | σ²K | Particle NTO |
|------------|-----------------|-------------|------------|----------|-----|--------------|
|            |                 | Core excitation |           |          |     |              |
| X → C      | 525.22 (527.59) | 1s_O → 1π   | 0.048 (0.054) | 0.91 (1.04) |     |              |
|            |                 | Local transitions |        |          |     |              |
| X → A      | 4.15 (4.12)    | 2σ → 1π    | 0.002 (0.002) | 0.92 (0.96) |     |              |
| C → A      | 521.07 (523.47) | 2σ → 1s_O  | 0.034 (0.037) | 0.87 (1.01) |     |              |
|            |                 | Charge-transfer transitions |              |          |     |              |
| X → CT     | 5.33 (4.58)    | lp(H₂O) → 1π | 0.000 (0.000) | 0.82 (0.84) |     |              |
| C → CT     | 519.88 (523.00) | lp(H₂O) → 1s_O | 0.000 (0.003) | 0.61 (0.84) |     |              |
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5. INPUT FOR QM/MM AIMD SIMULATIONS

$rem

JOB_TYPE  aimd
BASIS  6-31+G*
METHOD  wB97XD
scf_convergence  8
scf_algorithm  gdm  does not converge with defaults
scf_max_cycles  200
thresh  14  use tight thresholds

!QM/MM keywords
qm_mm_interface  janus
user_connect  true
force_field  charmm27
model_system_mult  1
model_system_charge  -1

! aimd keywords
time_step  42  in au, 1 a.u. = 0.0242 fs
aimd_steps  2000  about 2 ps
aimd_init_veloc  thermal
aimd_temp  298

! Thermostat
aimd_thermostat  langevin
aimd_langevin_timescale  100

! From JMH input
sym_ignore  true
no_reorient  true
chelpg  true
chelpg_dx  10
chelpg_head  30
chelpg_H  50
chelpg_HA  50
mm_subtractive  true  Ewald requires mm_subtractive
ewald_on  true

$end

$forceman

ewald
alpha  .274  .0649
box_length  31.3192  31.3192  31.3192

$end

$qm_atoms
1:17

$end
6. INPUT FOR QM/MM RIXS CALCULATIONS

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METHOD = eom-ccsd
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cvs_ee_states = [0]
n_frozen_core = 1
cc_fullresponse = 0
cc_eom_rixs = 5
CC_REF_PROP = 1
CC_EOM_PROP = 1
cc_trans_prop = 1
cc_diis_size = 15 for better convergence of response equations
scf_algorithm = gdm does not converge with defaults
scf_guess = CORE
max_scf_cycles = 200
thresh = 14 tight thresholds for integrals

!QM/MM keywords
qm_mm_interface = janus
force_field = charmm27
user_connect = true
model_system_mult = 2
model_system_charge = 0
$end

$rixs
omega_1 4234411 500 1 0
damped_epsilon 0.005
$end

$qm_atoms
1 2
$end

$molecule
0 2
0 -2.0531082762 0.70286735 -0.1205079041 101 2 0 0 0 0
H -2.551746298 1.5791146684 -0.3299733637 88 0 0 0 0 0
0 -2.5462451975 -0.0172690537 2.6717170398 101 4 5 0 0 0
H -3.0521231806 -0.8313175012 2.8204185203 88 3 0 0 0 0
H -2.3438821345 0.065630876 1.7224541544 88 3 0 0 0 0
0 -4.0784774935 -1.0408141164 -0.9557557305 101 7 8 0 0 0
H -4.0119399393 -0.5415917412 -0.1213427646 88 6 0 0 0 0
H -3.5909641541 -1.8633962833 -0.7384154628 88 6 0 0 0 0
...
...
$end
7. UC-6-311(2+,+)G(2DF,P) BASIS

O 0
S 1 1.000000
  8.58850000E+03  1.89515000E-03
S 1 1.000000
  1.29723000E+03  1.43859000E-02
S 1 1.000000
  2.99296000E+02  7.07320000E-02
S 1 1.000000
  8.73771000E+01  2.40001000E-01
S 1 1.000000
  2.56789000E+01  5.94797000E-01
S 1 1.000000
  3.74004000E+00  2.80802000E-01
SP 3 1.000000
  4.21175000E+01  1.13889000E-01  3.65114000E-02
  9.62837000E+00  9.20811000E-01  2.37153000E-01
  2.85332000E+00 -3.27447000E-03  8.19702000E-01
SP 1 1.000000
  9.05661000E-01  1.00000000E+00  1.00000000E+00
SP 1 1.000000
  2.55611000E-01  1.00000000E+00  1.00000000E+00
SP 1 1.000000
  8.45000000E-02  1.00000000E+00  1.00000000E+00
SP 1 1.000000
  2.54518072E-02  1.00000000E+00  1.00000000E+00
D 1 1.000000
  2.58400000E+00  1.00000000E+00
D 1 1.000000
  6.46000000E-01  1.00000000E+00
F 1 1.000000
  1.40000000E+00  1.00000000E+00
****
H 0
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  3.38650000E+01  2.54938000E-02
  5.09479000E+00  1.90373000E-01
  1.15879000E+00  8.52161000E-01
S 1 1.000000
  3.25840000E-01  1.00000000E+00
S 1 1.000000
  1.02741000E-01  1.00000000E+00
S 1 1.000000
  3.60000000E-02  1.00000000E+00
P 1 1.000000
  7.50000000E-01  1.00000000E+00
****
8. CARTESIAN COORDINATES FOR MODEL OH-WATER STRUCTURES

Hemibonded structure

O  1.4689599962  -0.0675854865  0.0543544388
H  1.4892207572  0.5364418801 -0.3999323009
O  -1.3070289695  0.0556311190 -0.1037339247
H  -1.4210921138  0.4176221150  0.7621320309
H  -1.3635768572  -0.8584290545  0.0328361571

Nuclear Repulsion Energy = 31.83900810 hartrees

Hydrogen-bonded acceptor structure

O  1.5259508055  -0.1019172743  0.0560387357
H  1.8816264682  0.6459120289 -0.4385043272
O  -1.4611163710  0.0854104501  0.0769981233
H  -1.9178709826  -0.5428697210 -0.5149135605
H  -0.4824309615  0.0290122853  -0.1108769843

Nuclear Repulsion Energy = 29.49383243 hartrees


9. FRANCK-CONDON FACTORS

TABLE S8: Franck-Condon factors for relevant electronic transitions in OH radical.

| Label       | FCF  |
|-------------|------|
| $\langle \zeta \chi_0 | \zeta \chi_0 \rangle$ | 0.913 |
| $\langle \zeta \chi_0 | \zeta \chi_1 \rangle$ | -0.402 |
| $\langle \zeta \chi_0 | \zeta \chi_2 \rangle$ | 0.077 |
| $\langle \zeta \chi_0 | \zeta \chi_3 \rangle$ | 0.005 |
| $\langle \zeta \chi_0 | \zeta \chi_4 \rangle$ | -0.006 |
| $\langle \zeta \chi_1 | \zeta \chi_0 \rangle$ | 0.373 |
| $\langle \zeta \chi_1 | \zeta \chi_1 \rangle$ | 0.746 |
| $\langle \zeta \chi_1 | \zeta \chi_2 \rangle$ | -0.535 |
| $\langle \zeta \chi_1 | \zeta \chi_3 \rangle$ | 0.135 |
| $\langle \zeta \chi_1 | \zeta \chi_4 \rangle$ | 0.007 |
| $\langle \zeta \chi_2 | \zeta \chi_0 \rangle$ | 0.156 |
| $\langle \zeta \chi_2 | \zeta \chi_1 \rangle$ | 0.457 |
| $\langle \zeta \chi_2 | \zeta \chi_2 \rangle$ | 0.594 |
| $\langle \zeta \chi_2 | \zeta \chi_3 \rangle$ | 0.614 |
| $\langle \zeta \chi_2 | \zeta \chi_4 \rangle$ | 0.192 |
| $\langle \zeta \chi_3 | \zeta \chi_0 \rangle$ | 0.059 |
| $\langle \zeta \chi_3 | \zeta \chi_1 \rangle$ | 0.243 |
| $\langle \zeta \chi_3 | \zeta \chi_2 \rangle$ | 0.479 |
| $\langle \zeta \chi_3 | \zeta \chi_3 \rangle$ | 0.455 |
| $\langle \zeta \chi_3 | \zeta \chi_4 \rangle$ | 0.662 |
| $\langle \zeta \chi_4 | \zeta \chi_0 \rangle$ | 0.022 |
| $\langle \zeta \chi_4 | \zeta \chi_1 \rangle$ | 0.109 |
| $\langle \zeta \chi_4 | \zeta \chi_2 \rangle$ | 0.308 |
| $\langle \zeta \chi_4 | \zeta \chi_3 \rangle$ | 0.467 |
| $\langle \zeta \chi_4 | \zeta \chi_4 \rangle$ | 0.331 |
| $\langle \zeta \chi_0 | \zeta \chi_0 \rangle$ | 0.773 |
| $\langle \zeta \chi_0 | \zeta \chi_1 \rangle$ | -0.589 |
| $\langle \zeta \chi_0 | \zeta \chi_2 \rangle$ | 0.233 |
| $\langle \zeta \chi_0 | \zeta \chi_3 \rangle$ | -0.029 |
| $\langle \zeta \chi_0 | \zeta \chi_4 \rangle$ | -0.020 |
| $\langle \zeta \chi_1 | \zeta \chi_0 \rangle$ | 0.504 |
| $\langle \zeta \chi_1 | \zeta \chi_1 \rangle$ | 0.379 |
| $\langle \zeta \chi_1 | \zeta \chi_2 \rangle$ | -0.671 |
| $\langle \zeta \chi_1 | \zeta \chi_3 \rangle$ | 0.381 |
| $\langle \zeta \chi_1 | \zeta \chi_4 \rangle$ | -0.070 |
| $\langle \zeta \chi_2 | \zeta \chi_0 \rangle$ | 0.317 |
| $\langle \zeta \chi_2 | \zeta \chi_1 \rangle$ | 0.463 |
| $\langle \zeta \chi_2 | \zeta \chi_2 \rangle$ | 0.091 |
| $\langle \zeta \chi_2 | \zeta \chi_3 \rangle$ | -0.639 |
| $\langle \zeta \chi_2 | \zeta \chi_4 \rangle$ | 0.497 |
| $\langle \zeta \chi_3 | \zeta \chi_0 \rangle$ | 0.183 |
\[
\begin{array}{lcc}
\langle c\chi_3|f\chi_1 \rangle & 0.403 \\
\langle c\chi_3|f\chi_2 \rangle & 0.324 \\
\langle c\chi_3|f\chi_3 \rangle & -0.103 \\
\langle c\chi_3|f\chi_4 \rangle & -0.551 \\
\langle c\chi_4|f\chi_0 \rangle & 0.102 \\
\langle c\chi_4|f\chi_1 \rangle & 0.284 \\
\langle c\chi_4|f\chi_2 \rangle & 0.399 \\
\langle c\chi_4|f\chi_3 \rangle & 0.158 \\
\langle c\chi_4|f\chi_4 \rangle & -0.216
\end{array}
\]

TABLE S9: RIXS emission peak positions (eV) and intensities of elastic and energy-loss peaks computed using FCFs for the transitions between the ground state (g), core-excited state, and final valence excited state (f). We consider only \( \nu = 0, 1, 2 \) vibrational levels of the ground state. \( \sigma^{RIXS}_{\text{elec}} \) used for computing \( \sigma^{RIXS}_{\text{vib}} \) corresponds to the computed cross sections for snapshot \#2 (0.0367 a.u., 0.0720 a.u., and 0.0534 a.u. for the elastic \( 1\pi \rightarrow 1s_O \), near-degenerate elastic \( 1\pi \rightarrow 1s_O \), and \( 2\sigma \rightarrow 1s_O \) transitions, respectively).

| Transition | Position | \( \sigma^{RIXS}_{\text{vib}} \) | \( \sigma^{RIXS}_{\text{vib}} \) | \( \sigma^{RIXS}_{\text{vib}} \) |
|------------|----------|-----------------|-----------------|-----------------|
|            |          | Non-thermal     | T = 1,000 K     | T = 10,000 K    |
| g(v=0) \rightarrow c(v=0) \rightarrow f(v=0) | 521.1377 | 0.02655351 | 0.02655354 | 0.02655354 |
| g(v=0) \rightarrow c(v=0) \rightarrow f(v=1) | 520.7394 | 0.01542118 | 0.01542120 | 0.01542120 |
| g(v=0) \rightarrow c(v=0) \rightarrow f(v=2) | 520.3411 | 0.00241791 | 0.00241792 | 0.00241792 |
| g(v=0) \rightarrow c(v=0) \rightarrow f(v=3) | 519.9428 | 0.0003623 | 0.0003623 | 0.0003623 |
| g(v=0) \rightarrow c(v=0) \rightarrow f(v=4) | 519.5445 | 0.0001819 | 0.0001819 | 0.0001819 |
| g(v=0) \rightarrow c(v=1) \rightarrow f(v=0) | 521.6810 | 0.00188528 | 0.00188528 | 0.00188528 |
| g(v=0) \rightarrow c(v=1) \rightarrow f(v=1) | 521.2827 | 0.00106676 | 0.00106676 | 0.00106676 |
| g(v=0) \rightarrow c(v=1) \rightarrow f(v=2) | 520.8844 | 0.00333616 | 0.00333616 | 0.00333616 |
| g(v=0) \rightarrow c(v=1) \rightarrow f(v=3) | 520.4861 | 0.00107330 | 0.00107330 | 0.00107330 |
| g(v=0) \rightarrow c(v=1) \rightarrow f(v=4) | 520.0878 | 0.0003593 | 0.0003593 | 0.0003593 |
| g(v=0) \rightarrow c(v=2) \rightarrow f(v=0) | 522.2244 | 0.00013003 | 0.00013004 | 0.00013004 |
| g(v=0) \rightarrow c(v=2) \rightarrow f(v=1) | 521.8260 | 0.00027794 | 0.00027794 | 0.00027794 |
| g(v=0) \rightarrow c(v=2) \rightarrow f(v=2) | 521.4277 | 0.00010666 | 0.00010666 | 0.00010666 |
| g(v=0) \rightarrow c(v=2) \rightarrow f(v=3) | 521.0294 | 0.00052950 | 0.00052951 | 0.00052951 |
| g(v=0) \rightarrow c(v=2) \rightarrow f(v=4) | 520.6311 | 0.00032043 | 0.00032044 | 0.00032044 |
| g(v=0) \rightarrow c(v=3) \rightarrow f(v=0) | 522.7677 | 0.0000630 | 0.0000630 | 0.0000630 |
| g(v=0) \rightarrow c(v=3) \rightarrow f(v=1) | 522.3694 | 0.0003062 | 0.0003062 | 0.0003062 |
| g(v=0) \rightarrow c(v=3) \rightarrow f(v=2) | 521.9711 | 0.0001974 | 0.0001974 | 0.0001974 |
| g(v=0) \rightarrow c(v=3) \rightarrow f(v=3) | 521.5728 | 0.0000202 | 0.0000202 | 0.0000202 |
| g(v=0) \rightarrow c(v=3) \rightarrow f(v=4) | 521.1745 | 0.0005723 | 0.0005723 | 0.0005723 |
| g(v=0) \rightarrow c(v=4) \rightarrow f(v=0) | 523.3110 | 0.0000027 | 0.0000027 | 0.0000027 |
| g(v=0) \rightarrow c(v=4) \rightarrow f(v=1) | 522.9127 | 0.0000212 | 0.0000212 | 0.0000212 |
| g(v=0) \rightarrow c(v=4) \rightarrow f(v=2) | 522.5144 | 0.0000419 | 0.0000419 | 0.0000419 |
| g(v=0) \rightarrow c(v=4) \rightarrow f(v=3) | 522.1161 | 0.0000066 | 0.0000066 | 0.0000066 |
| g(v=0) \rightarrow c(v=4) \rightarrow f(v=4) | 521.7178 | 0.0000122 | 0.0000122 | 0.0000122 |
| g(v=1) \rightarrow c(v=0) \rightarrow f(v=0) | 521.1377 | 0.00514255 | 0.00002258 | 0.00298808 |

Note: The table includes the RIXS emission peak positions in eV and the corresponding intensities for elastic and energy-loss peaks computed using FCFs. The intensities are given for different temperatures (1,000 K and 10,000 K) and for non-thermal conditions. The calculations were performed for transitions between the ground state (g), core-excited state, and final valence excited state (f).
| g(v=1) → c(v=0) → f(v=1) | 520.7394 | 0.00298658 | 0.00001311 | 0.00173535 |
| g(v=1) → c(v=0) → f(v=2) | 520.3411 | 0.00046827 | 0.0000206 | 0.00027209 |
| g(v=1) → c(v=0) → f(v=3) | 519.9428 | 0.00000702 | 0.0000003 | 0.00000408 |
| g(v=1) → c(v=0) → f(v=4) | 519.5445 | 0.00000352 | 0.0000002 | 0.00000205 |
| g(v=1) → c(v=1) → f(v=0) | 521.6810 | 0.00755524 | 0.0003314 | 0.00438999 |
| g(v=1) → c(v=1) → f(v=1) | 521.2827 | 0.00427506 | 0.0001875 | 0.00248403 |
| g(v=1) → c(v=1) → f(v=2) | 520.8444 | 0.01336963 | 0.0005864 | 0.00776845 |
| g(v=1) → c(v=1) → f(v=3) | 520.4861 | 0.00430124 | 0.0001887 | 0.00249925 |
| g(v=1) → c(v=1) → f(v=4) | 520.0878 | 0.00014398 | 0.0000006 | 0.00008366 |
| g(v=1) → c(v=2) → f(v=0) | 522.2444 | 0.00111914 | 0.0000006 | 0.00006502 |
| g(v=1) → c(v=2) → f(v=1) | 521.8260 | 0.00239209 | 0.0001049 | 0.00138992 |
| g(v=1) → c(v=2) → f(v=2) | 521.4277 | 0.00009171 | 0.0000040 | 0.00005329 |
| g(v=1) → c(v=2) → f(v=3) | 521.0294 | 0.00455720 | 0.00001999 | 0.00264796 |
| g(v=1) → c(v=2) → f(v=4) | 520.6311 | 0.00275782 | 0.00001210 | 0.00160243 |
| g(v=1) → c(v=3) → f(v=0) | 522.7677 | 0.00010521 | 0.0000046 | 0.00006113 |
| g(v=1) → c(v=3) → f(v=1) | 522.3694 | 0.00051137 | 0.0000224 | 0.00029713 |
| g(v=1) → c(v=3) → f(v=2) | 521.9711 | 0.00032963 | 0.0000145 | 0.00019153 |
| g(v=1) → c(v=3) → f(v=3) | 521.5728 | 0.00003367 | 0.0000015 | 0.00001956 |
| g(v=1) → c(v=3) → f(v=4) | 521.1745 | 0.00095564 | 0.0000420 | 0.00055528 |
| g(v=1) → c(v=4) → f(v=0) | 523.3110 | 0.0000656 | 0.0000003 | 0.00003301 |
| g(v=1) → c(v=4) → f(v=1) | 522.9127 | 0.0005078 | 0.0000022 | 0.00002950 |
| g(v=1) → c(v=4) → f(v=2) | 522.5144 | 0.00001064 | 0.0000044 | 0.00005848 |
| g(v=1) → c(v=4) → f(v=3) | 522.1161 | 0.00001573 | 0.0000007 | 0.00000914 |
| g(v=1) → c(v=4) → f(v=4) | 521.7178 | 0.00002934 | 0.0000013 | 0.00001705 |
| g(v=2) → c(v=0) → f(v=0) | 521.1377 | 0.0018808 | 0.0000000 | 0.00006349 |
| g(v=2) → c(v=0) → f(v=1) | 520.7394 | 0.00010923 | 0.0000000 | 0.00003687 |
| g(v=2) → c(v=0) → f(v=2) | 520.3411 | 0.00001713 | 0.0000000 | 0.0000578 |
| g(v=2) → c(v=0) → f(v=3) | 519.9428 | 0.00000026 | 0.0000000 | 0.0000009 |
| g(v=2) → c(v=0) → f(v=4) | 519.5445 | 0.00000013 | 0.0000000 | 0.0000004 |
| g(v=2) → c(v=1) → f(v=0) | 521.6810 | 0.0038553 | 0.0000008 | 0.00131184 |
| g(v=2) → c(v=1) → f(v=1) | 521.2827 | 0.00219859 | 0.0000005 | 0.00074229 |
| g(v=2) → c(v=1) → f(v=2) | 520.8844 | 0.00687577 | 0.0000014 | 0.00232140 |
| g(v=2) → c(v=1) → f(v=3) | 520.4861 | 0.00221206 | 0.0000005 | 0.00074684 |
| g(v=2) → c(v=1) → f(v=4) | 520.0878 | 0.00007405 | 0.0000000 | 0.00002500 |
| g(v=2) → c(v=2) → f(v=0) | 522.2444 | 0.0018859 | 0.0000004 | 0.00063729 |
| g(v=2) → c(v=2) → f(v=1) | 521.8260 | 0.00403640 | 0.0000008 | 0.00136217 |
| g(v=2) → c(v=2) → f(v=2) | 521.4277 | 0.0005468 | 0.0000000 | 0.0000522 |
| g(v=2) → c(v=2) → f(v=3) | 521.0294 | 0.00768636 | 0.0000015 | 0.00259509 |
| g(v=2) → c(v=2) → f(v=4) | 520.6311 | 0.00046145 | 0.0000009 | 0.000157043 |
| g(v=2) → c(v=3) → f(v=0) | 522.3694 | 0.00199210 | 0.0000003 | 0.00067257 |
| g(v=2) → c(v=3) → f(v=1) | 521.9711 | 0.00128411 | 0.0000002 | 0.00043354 |
| g(v=2) → c(v=3) → f(v=2) | 521.5728 | 0.00013116 | 0.0000000 | 0.00004428 |
| g(v=2) → c(v=3) → f(v=3) | 521.1745 | 0.00372286 | 0.0000006 | 0.00125691 |
| g(v=2) → c(v=4) → f(v=0) | 523.3110 | 0.0005241 | 0.0000000 | 0.00001769 |
g(v=2) → c(v=4) → f(v=1) 522.9127 0.00040587 0.00000001 0.00013703

- Diagram starts here -
| g(v=0) → c(v=2) → dg(v=1) | 525.6188 | 0.00036492 | 0.00036493 | 0.00036493 |
| g(v=0) → c(v=2) → dg(v=2) | 525.1510 | 0.00061549 | 0.00061551 | 0.00061551 |
| g(v=0) → c(v=2) → dg(v=3) | 524.6831 | 0.00065928 | 0.00065929 | 0.00065929 |
| g(v=0) → c(v=2) → dg(v=4) | 524.2153 | 0.00064625 | 0.00064625 | 0.00064625 |
| g(v=0) → c(v=3) → dg(v=0) | 526.6300 | 0.00000090 | 0.00000090 | 0.00000090 |
| g(v=0) → c(v=3) → dg(v=1) | 526.1621 | 0.00001501 | 0.00001501 | 0.00001501 |
| g(v=0) → c(v=3) → dg(v=2) | 525.6943 | 0.00058487 | 0.00058487 | 0.00058487 |
| g(v=0) → c(v=3) → dg(v=3) | 525.2264 | 0.0005272 | 0.0005272 | 0.0005272 |
| g(v=0) → c(v=3) → dg(v=4) | 524.7586 | 0.0011137 | 0.0011137 | 0.0011137 |
| g(v=0) → c(v=4) → dg(v=0) | 527.1733 | 0.00000002 | 0.00000002 | 0.00000002 |
| g(v=0) → c(v=4) → dg(v=1) | 526.7055 | 0.0000042 | 0.0000042 | 0.0000042 |
| g(v=0) → c(v=4) → dg(v=2) | 526.2376 | 0.00000336 | 0.00000336 | 0.00000336 |
| g(v=0) → c(v=4) → dg(v=3) | 525.7698 | 0.00000775 | 0.00000775 | 0.00000775 |
| g(v=0) → c(v=4) → dg(v=4) | 525.3019 | 0.00000390 | 0.00000390 | 0.00000390 |
| g(v=1) → c(v=0) → dg(v=0) | 525.0000 | 0.00967129 | 0.00964246 | 0.00561951 |
| g(v=1) → c(v=0) → dg(v=1) | 524.5322 | 0.00187301 | 0.000892 | 0.0010832 |
| g(v=1) → c(v=0) → dg(v=2) | 524.0643 | 0.0006850 | 0.00000030 | 0.000000039 |
| g(v=1) → c(v=0) → dg(v=3) | 523.5965 | 0.00000029 | 0.0000000 | 0.00000017 |
| g(v=1) → c(v=0) → dg(v=4) | 523.1286 | 0.00000043 | 0.0000000 | 0.00000025 |
| g(v=1) → c(v=1) → dg(v=0) | 525.5433 | 0.00556548 | 0.00002441 | 0.00323384 |
| g(v=1) → c(v=1) → dg(v=1) | 525.0755 | 0.02230365 | 0.00009782 | 0.01295958 |
| g(v=1) → c(v=1) → dg(v=2) | 524.6076 | 0.01147039 | 0.0005031 | 0.00666490 |
| g(v=1) → c(v=1) → dg(v=3) | 524.1398 | 0.00072693 | 0.00000319 | 0.00042239 |
| g(v=1) → c(v=1) → dg(v=4) | 523.6719 | 0.0000221 | 0.00000001 | 0.00000128 |
| g(v=1) → c(v=2) → dg(v=0) | 526.0867 | 0.0036492 | 0.0000160 | 0.00021204 |
| g(v=1) → c(v=2) → dg(v=1) | 525.6188 | 0.00314075 | 0.00001378 | 0.000182493 |
| g(v=1) → c(v=2) → dg(v=2) | 525.1510 | 0.00529733 | 0.00023233 | 0.00307801 |
| g(v=1) → c(v=2) → dg(v=3) | 524.6831 | 0.00567144 | 0.0002489 | 0.00329696 |
| g(v=1) → c(v=2) → dg(v=4) | 524.2153 | 0.00055300 | 0.00000243 | 0.00032132 |
| g(v=1) → c(v=3) → dg(v=0) | 526.6300 | 0.0001501 | 0.0000007 | 0.00000872 |
| g(v=1) → c(v=3) → dg(v=1) | 526.1621 | 0.00025066 | 0.0000110 | 0.00014565 |
| g(v=1) → c(v=3) → dg(v=2) | 525.6943 | 0.00097648 | 0.0000429 | 0.00056739 |
| g(v=1) → c(v=3) → dg(v=3) | 525.2286 | 0.00088045 | 0.0000387 | 0.00051159 |
| g(v=1) → c(v=3) → dg(v=4) | 524.7586 | 0.00185981 | 0.0000816 | 0.00108066 |
| g(v=1) → c(v=4) → dg(v=0) | 527.1733 | 0.00000042 | 0.0000000 | 0.00000024 |
| g(v=1) → c(v=4) → dg(v=1) | 526.7055 | 0.0001008 | 0.0000004 | 0.00000586 |
| g(v=1) → c(v=4) → dg(v=2) | 526.2376 | 0.0008058 | 0.0000035 | 0.00004682 |
| g(v=1) → c(v=4) → dg(v=3) | 525.7698 | 0.0018603 | 0.000082 | 0.00010809 |
| g(v=2) → c(v=0) → dg(v=0) | 525.3019 | 0.00035371 | 0.0000000 | 0.00006433 |
| g(v=2) → c(v=0) → dg(v=1) | 524.5322 | 0.0006850 | 0.0000000 | 0.00002312 |
| g(v=2) → c(v=0) → dg(v=2) | 524.0643 | 0.0000251 | 0.0000000 | 0.0000085 |
| g(v=2) → c(v=0) → dg(v=3) | 523.5965 | 0.0000001 | 0.0000000 | 0.0000001 |
| g(v=2) → c(v=0) → dg(v=4) | 523.1286 | 0.0000002 | 0.0000000 | 0.0000001 |
| g(v=2) → c(v=1) → dg(v=0) | 525.5433 | 0.00286223 | 0.00000006 | 0.00096635 |
| Reaction                                      | Energy  | A         | B         | C         |
|----------------------------------------------|---------|-----------|-----------|-----------|
| \( g(v=2) \to c(v=1) \to dg(v=1) \)         | 525.0755| 0.01147039| 0.00000024| 0.00387264|
| \( g(v=2) \to c(v=1) \to dg(v=2) \)         | 524.6076| 0.00589903| 0.00000128| 0.00199163|
| \( g(v=2) \to c(v=1) \to dg(v=3) \)         | 524.1398| 0.00037385| 0.00000019| 0.00012622|
| \( g(v=2) \to c(v=1) \to dg(v=4) \)         | 523.6719| 0.00000114| 0.00000000| 0.00000383|
| \( g(v=2) \to c(v=2) \to dg(v=0) \)         | 526.0867| 0.0061549 | 0.00000012| 0.00207802|
| \( g(v=2) \to c(v=2) \to dg(v=1) \)         | 525.6188| 0.00529733| 0.00000011| 0.00178849|
| \( g(v=2) \to c(v=2) \to dg(v=2) \)         | 525.1510| 0.00893469| 0.00000018| 0.00316552|
| \( g(v=2) \to c(v=2) \to dg(v=3) \)         | 524.6831| 0.00957024| 0.00000019| 0.00321112|
| \( g(v=2) \to c(v=2) \to dg(v=4) \)         | 524.2153| 0.0093272 | 0.00000002| 0.00314911|
| \( g(v=2) \to c(v=3) \to dg(v=0) \)         | 526.6300| 0.00005847| 0.00000000| 0.00019744|
| \( g(v=2) \to c(v=3) \to dg(v=1) \)         | 526.1621| 0.0097648 | 0.00000002| 0.00329687|
| \( g(v=2) \to c(v=3) \to dg(v=2) \)         | 525.6943| 0.00380404| 0.00000007| 0.00128432|
| \( g(v=2) \to c(v=3) \to dg(v=3) \)         | 525.2264| 0.00342994| 0.00000006| 0.00115801|
| \( g(v=2) \to c(v=3) \to dg(v=4) \)         | 524.7586| 0.00724519| 0.00000013| 0.00244612|
| \( g(v=2) \to c(v=4) \to dg(v=0) \)         | 527.1733| 0.00000336| 0.00000000| 0.00000113|
| \( g(v=2) \to c(v=4) \to dg(v=1) \)         | 526.7055| 0.0008058 | 0.00000000| 0.00027214|
| \( g(v=2) \to c(v=4) \to dg(v=2) \)         | 526.2376| 0.00064409| 0.00000001| 0.00021746|
| \( g(v=2) \to c(v=4) \to dg(v=3) \)         | 525.7698| 0.00148699| 0.00000003| 0.00050204|
| \( g(v=2) \to c(v=4) \to dg(v=4) \)         | 525.3019| 0.00074734| 0.00000002| 0.00025232|