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Vibrational predissociation of the phenol–water dimer: a view from the water

Daniel Kwasniewski,  Mitchell Butler  † and Hanna Reisler  *

The vibrational predissociation (VP) dynamics of the phenol–water (PhOH–H₂O) dimer were studied by detecting H₂O fragments and using velocity map imaging (VMI) to infer the internal energy distributions of PhOH cofragments, pair-correlated with selected rotational levels of the H₂O fragments. Following infrared (IR) laser excitation of the hydrogen-bonded OH stretch fundamental of PhOH (Pathway 1) or the asymmetric OH stretch localized on H₂O (Pathway 2), dissociation to H₂O + PhOH was observed. H₂O fragments were monitored state-selectively by using 2+1 Resonance-Enhanced Multiphoton Ionization (REMPI) combined with time-of-flight mass spectrometry (TOF-MS). VMI of H₂O in selected rotational levels was used to derive center-of-mass (c.m.) translational energy (E_T) distributions. The pair-correlated internal energy distributions of the PhOH cofragments derived via Pathway 1 were well described by a statistical prior distribution. On the other hand, the corresponding distributions obtained via Pathway 2 show a propensity to populate higher-energy rovibrational levels of PhOH than expected from a statistical distribution and agree better with an energy-gap model. The REMPI spectra of the H₂O fragments from both pathways could be fit by Boltzmann plots truncated at the maximum allowed energy, with a higher temperature for Pathway 2 than that for Pathway 1. We conclude that the VP dynamics depends on the OH stretch level initially excited.

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1. Introduction

Recent advances in biological research have created an immense drive not only to broaden but also to deepen our understanding of the fundamental interactions that govern the behavior of biologically relevant systems. Hydrogen bonds (H-bonds) play a central role in numerous biochemical structures and processes, and thus elucidating their characteristic behavior should be helpful, for example, in protein and enzyme design efforts. However, detailed experimental characterizations of the dynamics of H-bonds are sparse. This is due in large part to difficulties in isolating and studying H-bonded systems that are sufficiently small and amenable to experimental interrogation.

Clusters of small molecules weakly bound to water provide excellent model systems for studying H-bonds at the most fundamental level. Phenol (PhOH) and its derivatives are ubiquitous in biochemical systems, such as the side chain of the amino acid tyrosine, and phenolic compounds play essential roles in electron transport, signaling pathways, and other biological processes. It is therefore not surprising that numerous studies have focused on the phenol–water (PhOH–H₂O) H-bonded dimer

in the gas-phase and elucidated its structure, spectroscopy, and energetics.^{1–19}

The geometry of PhOH–H₂O in the ground electronic state is shown in Fig. 1.⁹ Bond lengths and angles were determined using microwave spectroscopy.⁹ The angle β between the plane of H₂O and the H-bond coordinate is 108.7°. The PhOH and H₂O moieties are individually planar, but the planes are mutually nearly perpendicular.

Experimental studies of the PhOH–H₂O dimer have focused on infrared (IR) and ultraviolet (UV) spectroscopy; energy transfer following vibrational excitation; and determination of the H-bond dissociation energy (D_0). Courty *et al.*⁴ and Braun *et al.*² independently determined D_0 by similar methods. In both studies, thermochemical cycles based on the energies of

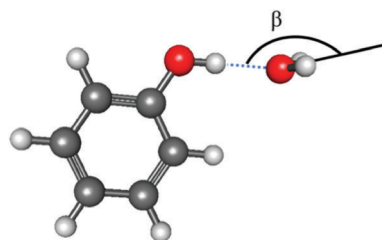


Fig. 1 Structure of the PhOH–H₂O dimer. The angle $\beta = 108.7^\circ$ represents the angle between the plane of H₂O and the H-bond coordinate.⁹

Department of Chemistry, University of Southern California, Los Angeles, California 90089-0482, USA. E-mail: reisler@usc.edu

† Present address: University of Illinois at Chicago College of Medicine, Chicago, Illinois, 60607.

several ground (S_0) and excited (S_1) electronic state transitions in bare PhOH and PhOH-H₂O were used. D_0 values of $1960 \pm 40 \text{ cm}^{-1}$ and $1916 \pm 30 \text{ cm}^{-1}$ were determined for S_0 by Courty *et al.*⁴ and Braun *et al.*,² respectively. Miyazaki *et al.*¹³ examined the vibrational dynamics of the PhOH-H₂O dimer and its deuterated analog by using time-resolved IR-UV picosecond pump-probe spectroscopy; they inferred the mechanisms and timescales of intramolecular vibrational energy redistribution (IVR) and predissociation of the dimer after excitation of the H-bonded phenol OH(D) stretch vibration.

The only velocity map imaging (VMI) study that examined PhOH-H₂O was reported by Mazzoni *et al.*¹¹ Using available data on the electronic spectroscopy of PhOH, measurements of the electronic spectrum of PhOH-H₂O, and photoelectron images of the ionized dimer, these investigators obtained a D_0 value for S_0 that was in good agreement with previous determinations.^{2,4} They also attempted to obtain the translational energy distribution of the PhOH fragment ions produced by two-photon two-color ionization of PhOH-H₂O, but due to energy and momentum conservation, the ions velocities were too low to allow a detailed study. Several studies from our group have employed VMI to investigate the vibrational predissociation (VP) dynamics of H-bonded dimers, as well as to derive the predissociation dynamics and accurate D_0 values.^{20–34}

To date, direct interrogation of the H₂O fragment in the VP of PhOH-H₂O has not been reported. This is largely due to predissociation in the upper electronic state used for state-selected 2+1 Resonance Enhanced Multiphoton Ionization (REMPI) detection of the H₂O fragment and spectral congestion of the rovibronic transitions.³⁵ In this paper, we report the first study of the energetics and VP dynamics of the PhOH-H₂O dimer obtained by examining the H₂O fragment. VMI was exploited to obtain complementary information on the PhOH cofragment. Our goal was to elucidate and characterize more completely the H-bond predissociation dynamics of PhOH-H₂O upon excitation of the two different OH stretch vibrations: the H-bonded OH stretch fundamental of PhOH and the asymmetric OH stretch localized on H₂O. The dynamical information derived from the experiments described herein provides fundamental insights into the H-bonding interactions in the PhOH-H₂O dimer.

2. Experimental details

VP of the PhOH-H₂O dimer generated in a pulsed supersonic molecular beam was studied following IR laser excitation of either the H-bonded OH stretch fundamental of PhOH or the asymmetric OH stretch of H₂O. Three experimental methods were utilized in the data collection: (1) time-of-flight mass spectrometry (TOF-MS) combined with 2+1 REMPI for spectroscopic investigations of H₂O fragments; (2) TOF-MS combined with 1+1 REMPI for spectroscopic investigations of the PhOH-H₂O dimer; and (3) VMI for deriving internal energy distributions of the PhOH cofragment (undetected fragment) and estimating D_0 for PhOH-H₂O $\rightarrow$ PhOH + H₂O.

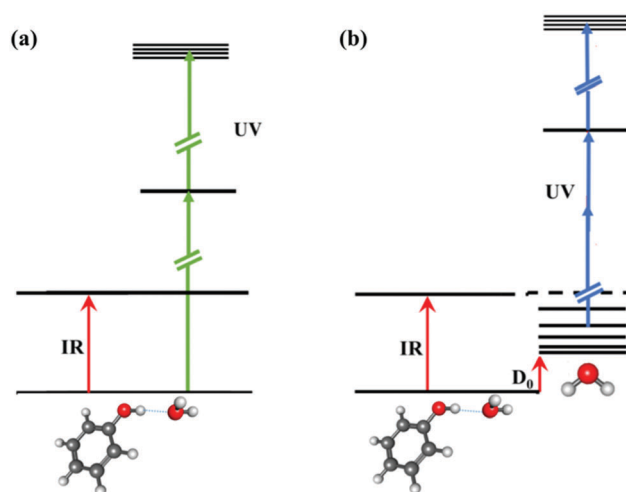


Fig. 2 Experimental scheme for the VP of PhOH-H₂O. IR radiation excites one of the OH-stretch fundamental vibrations of PhOH-H₂O. (a) The dimer is detected by 1+1 REMPI via its S_1 state. (b) H₂O fragments in the ground vibrational state are detected by 2+1 REMPI via the $\tilde{C}^1B_1(000)$ state.

Fig. 2 depicts the laser excitation and detection scheme. Upon excitation of the OH-stretch fundamental of the PhOH or H₂O moiety, energy couples to the H-bond dissociation coordinate and VP ensues. The excess energy is distributed among the center-of-mass (c.m.) translational energy, the rotational levels of H₂O, and the rovibrational levels of PhOH.

The experimental procedures are similar to those used in previous H-bonded cluster studies.^{20–26,32} PhOH-H₂O was generated in the pulsed molecular beam by bubbling He gas (Gilmore, 99.9999%) at 2 atm through 10 mL of liquid water and passing the mixture over 200 mg of solid phenol (Sigma-Aldrich, 99.5%) at room temperature (vapor pressure 0.4 Torr). PhOH was shielded from light to avoid sample degradation. The cluster sample was then expanded through a 0.5 mm orifice of a pulsed piezoelectric valve ($\sim 200 \mu\text{s}$ opening time) operating at 10 Hz. Expansion conditions (H₂O and PhOH concentration, and He backing pressure) were optimized to maximize the signal of the PhOH-H₂O dimer and minimize the concentration of higher order phenol-water clusters. The skimmed molecular beam was intersected at right angles by two counter-propagating laser beams in the interaction region.

IR radiation [1.5 mJ per pulse, $\sim 0.4 \text{ cm}^{-1}$ linewidth, focused by a 20 cm focal length (f.l.) lens] excited the H-bonded OH stretch of phenol or the asymmetric OH stretch localized on H₂O in PhOH-H₂O at 3522 cm^{-1} and 3744 cm^{-1} , respectively. IR radiation was generated by an optical parametric oscillator/amplifier (OPO/OPA) system (LaserVision), pumped by radiation from a seeded Nd:YAG laser (Continuum Precision II 8000). The IR frequency was calibrated using the photoacoustic spectrum of gaseous NH₃.³⁶

UV radiation for the detection of H₂O at $80\,353\text{--}80\,808 \text{ cm}^{-1}$ was generated by frequency-doubling (Inrad Autotracker III) the output of the dye laser (Continuum ND 6000, Coumarin 500) pumped by a Nd:YAG laser (Continuum Surelite); the spectra were frequency calibrated by the known 2+1 REMPI spectrum of H₂O.³⁵ Tightly focused UV radiation ($\sim 0.2 \text{ mJ}$ per pulse, lens

f.l. = 20 cm; 0.4 cm^{-1} linewidth) ionized state-selected H_2O fragments while scanning through the $\tilde{\text{C}}^1\text{B}_1(000) \leftarrow \tilde{\text{X}}^1\text{A}_1(000)$ transition using 2+1 REMPI. The H_2O REMPI spectra were simulated using the PGOPHER program³⁷ with rotational constants from Yang *et al.*³⁵ From the rotational temperature of background H_2O monomers in the molecular beam, we estimated the dimer temperature at $25 \pm 10\text{ K}$.

UV radiation for the detection of $\text{PhOH-H}_2\text{O}$ at $35\,998\text{ cm}^{-1}$ was generated by frequency doubling the output of the dye laser (Coumarin 540). The $\text{PhOH-H}_2\text{O}$ spectrum was frequency calibrated using published phenol-water cluster spectra at $35\,995\text{--}36\,400\text{ cm}^{-1}$.¹² Unfocused UV radiation (0.3 mJ per pulse, 0.4 cm^{-1} linewidth) ionized the $\text{PhOH-H}_2\text{O}$ dimer by 1+1 REMPI while scanning through the $\text{S}_1 \leftarrow \text{S}_0$ band of the dimer. Spectra were collected by alternating “IR ON” and “IR OFF” conditions at each frequency. In “IR ON,” the IR laser was fired 65 ns before the UV laser, and in “IR OFF” the IR laser was fired $2\text{ }\mu\text{s}$ after the UV laser. The UV laser conditions for each experiment were varied to optimize the signal-to-noise ratio. Laser timings were adjusted by using delay generators (Stanford, DG535) controlled through a GPIB interface (National Instruments).

The VMI arrangement has been described previously.^{20–26,32} Briefly, the apparatus consists of a four-electrode ion acceleration assembly, a 60 cm field-free drift tube, and a microchannel plate (MCP) detector coupled to a phosphor screen (Beam Imaging Solutions, Inc.) that is monitored by a charge coupled device (CCD) camera (LaVision, Imager). In VMI mode, two-dimensional projections were collected using an event counting method (DaVis) and reconstructed to three-dimensional images using the BASEX method.³⁸ Speed distributions were obtained by summing over the angular distribution of each radius and were converted to c.m. E_T distributions using momentum conservation, the appropriate Jacobian,³⁹ and calibration constants obtained from previous experiments.²³ The angular distributions were all isotropic.

3. Results and discussion

3.1 IR depletion spectrum

The H-bonded and asymmetric OH stretch fundamental transitions of the $\text{PhOH-H}_2\text{O}$ dimer have previously been assigned and

characterized in the gas phase.^{5,6,12,16,17,19,40} In this study, IR depletion spectra were obtained by scanning the frequency of the IR laser while monitoring the vibrationless ground state of $\text{PhOH-H}_2\text{O}$ by REMPI via the $\text{S}_1 \leftarrow \text{S}_0$ transition. The position and shape of the dimer peaks agree with the previously reported depletion spectra. Fig. 3 shows the depletion spectra of two different OH stretch transitions of $\text{PhOH-H}_2\text{O}$: the H-bonded OH stretch localized on phenol and the asymmetric OH stretch localized on H_2O . The observed vibrational band for the H-bonded OH stretch, centered at 3522 cm^{-1} , is well isolated from neighboring OH stretching bands of higher order clusters such as $\text{PhOH-(H}_2\text{O)}_2$ (3505 cm^{-1} and 3550 cm^{-1})¹⁹ and $(\text{H}_2\text{O)}_3$ (3536 cm^{-1}).²² The observed vibrational band of the corresponding OH stretch of the H_2O moiety, centered at 3744 cm^{-1} , is located between the closely lying free OH stretch vibrations of $\text{PhOH-(H}_2\text{O)}_2$ and $(\text{H}_2\text{O)}_2$ at 3725 cm^{-1} and 3729 cm^{-1} , respectively, and the ν_3 asymmetric stretch of the H_2O monomer at 3755 cm^{-1} .⁴¹ The OH asymmetric stretch localized on H_2O of the dimer will be referred to henceforth as the free OH stretch to note that the H atoms do not form hydrogen bonds. The symmetric stretch transition of H_2O in $\text{PhOH-H}_2\text{O}$ was also observed in the gas phase but was found to be very weak.^{6,12,17,19}

High backing pressure and high H_2O concentration can result in the formation of larger clusters; therefore, we optimized the expansion conditions to minimize the formation of larger clusters, as described in Section 2. The temperature of the molecular beam was adjusted to maximize the concentration of dimers. It is essential to ensure that the H_2O fragments are produced following one-photon absorption by $\text{PhOH-H}_2\text{O}$. To achieve this, great care was taken to minimize multiphoton absorption. This was achieved by reducing the IR laser fluence and slightly defocusing the radiation passing through the 20 cm IR lens. Decreasing the IR fluence lowers the signal-to-noise ratio, and the H_2O signal is further reduced due to the large number of accessible fragment monomer states as well as predissociation in the upper state in the H_2O REMPI scheme.³⁵

3.2 REMPI spectroscopy of H_2O fragments

In the REMPI and VMI measurements of H_2O fragments, the H-bonded and free OH stretch fundamentals were excited at

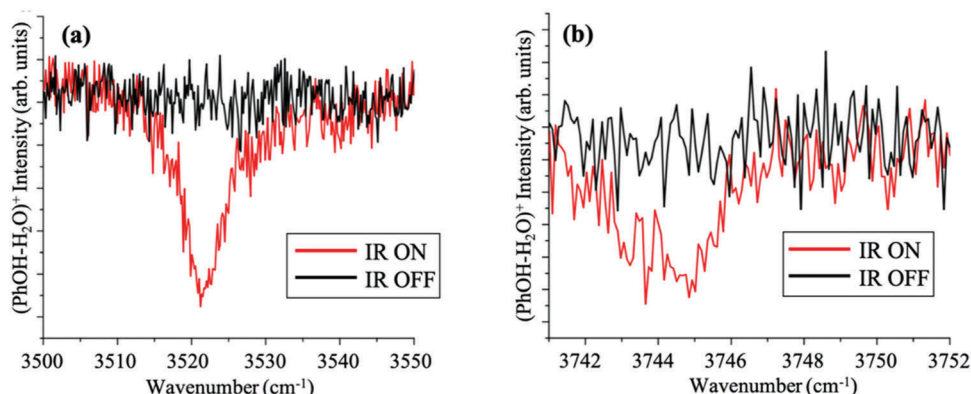


Fig. 3 IR depletion spectra of (a) the H-bonded OH stretch and (b) the asymmetric (free) OH stretch localized on H_2O of $\text{PhOH-H}_2\text{O}$. The dimer is probed using 1+1 REMPI via the $\text{S}_1 \leftarrow \text{S}_0$ transition at $35\,998\text{ cm}^{-1}$. The IR timing alternates between ON/OFF conditions at each frequency.

3522 cm⁻¹ (Pathway 1) and 3744 cm⁻¹ (Pathway 2). The excitation energy was (more than) sufficient to induce VP. Fig. 4 displays the “IR ON–IR OFF” 2+1 REMPI spectra of H₂O fragments following VP. Spectra were obtained by scanning the UV laser frequency in the region of the $\tilde{C} \ ^1B_1(000) \leftarrow \tilde{X} \ ^1A_1(000)$ H₂O transition. As stated previously, fast predissociation in the $\tilde{C}$ state and spectral congestion limit the state-selective detection of H₂O. Nevertheless, the 2+1 REMPI spectra were simulated fairly well by rotational temperatures (see Fig. 4). The H₂O fragment rotational distribution *via* Pathway 1 was fit best with a temperature of 165 ± 25 K, which corresponds to an average rotational energy of 115 ± 17 cm⁻¹. The excess energy in VP in this case is 1562 ± 60 cm⁻¹. In the experiments, rotational levels of the H₂O fragments up to $J_{K_a,K_c}'' = 7_{1,6}$ (704 cm⁻¹ energy) could be clearly observed. The REMPI spectrum obtained for Pathway 2 was fit with a rotational temperature of 310 ± 25 K, corresponding to an average rotational energy of 216 ± 17 cm⁻¹. The excess energy in this case is 1784 ± 60 cm⁻¹, and rotational levels up to $J_{K_a,K_c}'' = 8_{5,3}$ and $8_{3,6}$ were observed, which have energies of 1255 and 1006 cm⁻¹, respectively. The higher H₂O fragment temperature of Pathway 2 is consistent with these observations. This can also be seen in Fig. 4 by comparing the signal intensities of the $2_{2,1}$ and $3_{2,1}$ transitions. The $2_{2,1}/3_{2,1}$ peak ratio is larger in panel (a) than in (b), as expected from the increase in temperature.

There is not enough excess energy following excitation of the H-bonded OH stretch to populate one quantum of the ν_2 bending vibration of the H₂O fragment at 1595 cm⁻¹.⁴² However, the excess energy is just high enough to populate this level when exciting the free OH stretch. We searched for evidence of this excitation in the 2+1 REMPI spectrum obtained *via* the $\tilde{C} \ ^1B_1(000) \leftarrow \tilde{X} \ ^1A_1(010)$ H₂O transition, but the signal-to-noise ratio was far too low to obtain evidence for this pathway.

3.3 Velocity map imaging of the H₂O fragment

The isolated rotational transitions of H₂O (000) fragments used for imaging were: $J_{K_a,K_c}' \leftarrow J_{K_a,K_c}'' = 2_{0,2} \leftarrow 3_{2,1}$, $2_{0,2} \leftarrow 4_{2,3}$,

and $7_{1,7} \leftarrow 7_{1,6}$. The energies of the ground electronic state rotational levels of these transitions are 212, 300, and 704 cm⁻¹, respectively. The pair-correlated E_T distributions were derived from the images as described in Section 2 using conservation of energy:

$$h\nu_{\text{IR}} + E_{\text{int}}(\text{PhOH-H}_2\text{O}) = D_0 + E_T + E_{\text{rot}}(\text{H}_2\text{O}) + E_{\text{rot,vib}}(\text{PhOH}) \quad (1)$$

In eqn (1), $h\nu_{\text{IR}}$ denotes the excitation energy of one of the OH stretch vibrations; $E_{\text{int}}(\text{PhOH-H}_2\text{O})$ is the internal energy of the dimer, estimated at about 20 cm⁻¹ based on the temperature of H₂O monomers in the beam; $E_{\text{rot}}(\text{H}_2\text{O})$ is the energy of the monitored rotational level of H₂O; and $E_{\text{rot,vib}}(\text{PhOH})$ is the rovibrational energy of the PhOH cofragment.

The state-specific c.m. E_T distributions encode dynamical information about the VP process and the internal energy distributions of the PhOH cofragments pair-correlated with each monitored H₂O rotational level. Below we describe separately results obtained following excitation of the PhOH H-bonded OH stretch (Pathway 1) and the H₂O free OH stretch (Pathway 2).

3.3.1 Pathway 1. Fig. 5 displays the c.m. E_T distributions obtained following excitation of the H-bonded OH stretch of the PhOH moiety of PhOH–H₂O by monitoring several H₂O J_{K_a,K_c}'' levels. The arrows indicate the maximum allowed translational energies corresponding to $D_0 = 1960$ cm⁻¹, the value measured by Courty *et al.*⁴ The observed end points of all three images are in good agreement with this value, as well as with those reported by Neusser *et al.* (1916 ± 30 cm⁻¹)² and Mazzoni *et al.* (1975 ± 60 cm⁻¹).¹¹ The angular distributions of the images were isotropic, reflecting the fact that the lifetime of the dimer is of the order of tens of picoseconds.¹³

Based on the findings of Miyazaki *et al.* which showed complete IVR prior to dissociation,¹³ and considering the high density of rovibrational states in the PhOH cofragment, we did not expect distinct structures in the images. Indeed, the

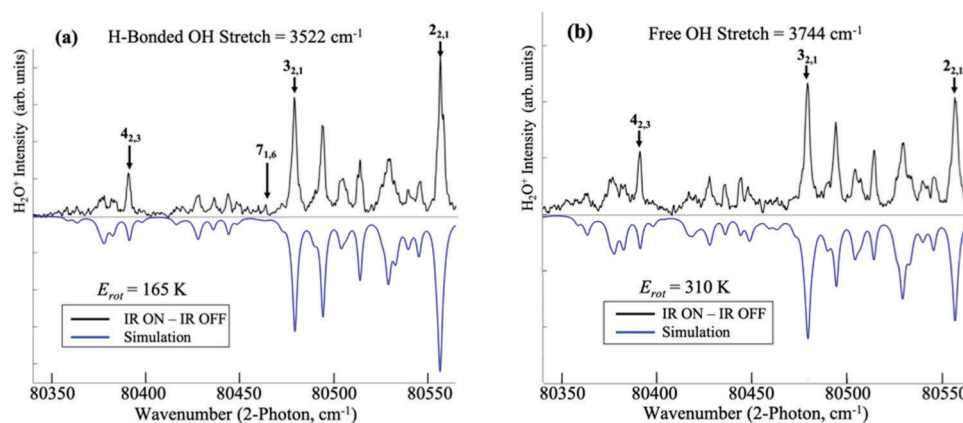


Fig. 4 2+1 REMPI spectra of H₂O fragments recorded *via* the $\tilde{C} \ ^1B_1(000) \leftarrow \tilde{X} \ ^1A_1(000)$ transition. The x-axis gives the wavenumbers required to reach the excited state of H₂O by 2-photon excitation. The “IR ON–IR OFF” spectrum (top panels, black) was obtained by exciting (a) the H-bonded OH stretch of the PhOH moiety at 3522 cm⁻¹, and (b) the free OH stretch of the H₂O moiety at 3744 cm⁻¹. The “IR OFF” spectrum, obtained by recording the background when the IR laser was fired 2 μs after the UV laser pulse, was subtracted from the “IR ON” spectrum in which the IR laser was fired 65 ns before the UV laser. The arrows mark the $J_{K_a,K_c}' \leftarrow J_{K_a,K_c}''$ transitions monitored in the VMI studies: (a) $2_{0,2} \leftarrow 3_{2,1}$, $2_{0,2} \leftarrow 4_{2,3}$, and $7_{1,7} \leftarrow 7_{1,6}$, and (b) $2_{0,2} \leftarrow 3_{2,1}$ and $2_{0,2} \leftarrow 4_{2,3}$. Assignments are based on simulated spectra (bottom panels, inverted scale, blue) created by the PGOPHER program.³⁷

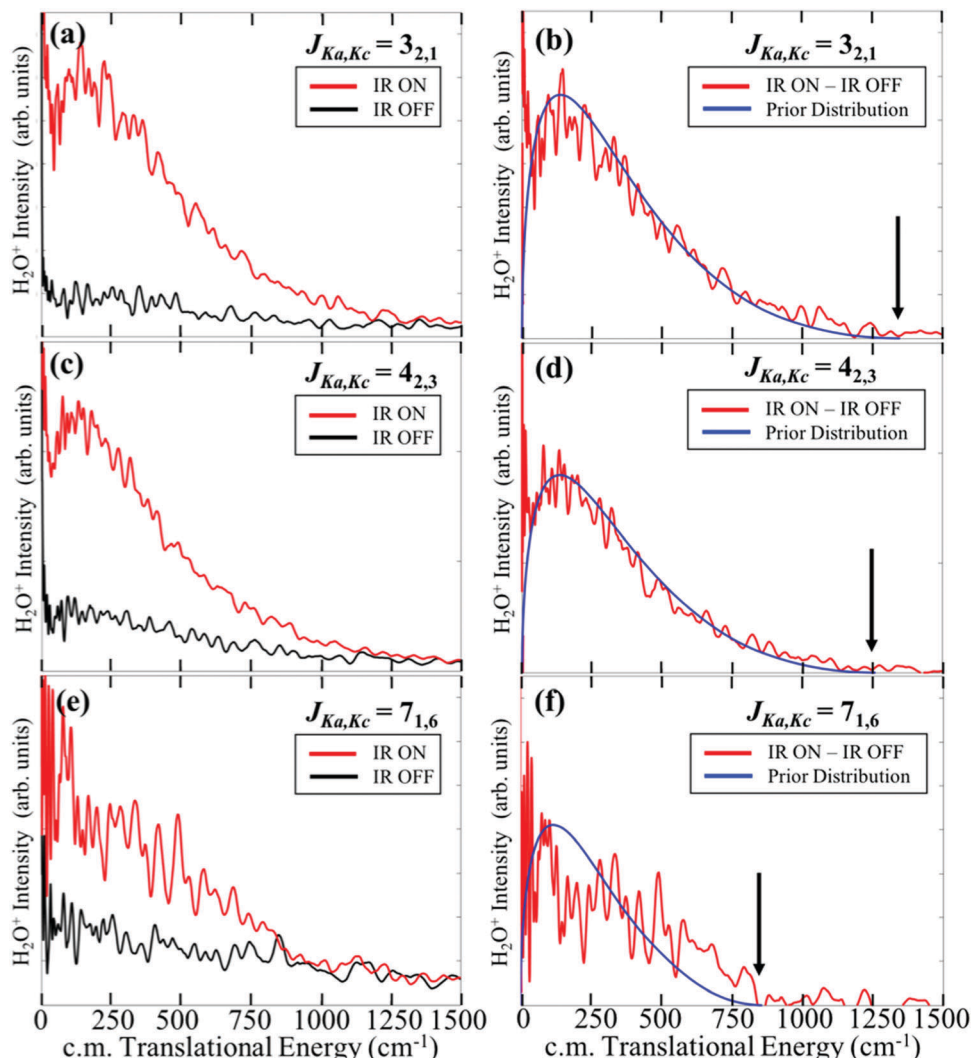


Fig. 5 Left column: “IR ON” (red) and “IR OFF” (black) c.m. translational energy distributions obtained by monitoring state-selected H_2O^+ fragments in $J_{Ka,Kc}$ levels: (a) $3_{2,1}$, (c) $4_{2,3}$, and (e) $7_{1,6}$ after excitation of the H-bonded OH stretch of PhOH (Pathway 1). Right column: “IR ON–IR OFF” (red) distributions for the same state-selected H_2O^+ fragments compared with prior distributions (smooth blue lines), (b), (d), (f), respectively. The arrows indicate the maximum allowed translational energies corresponding to $D_0 = 1960 \text{ cm}^{-1}$.⁴ This was the value used in the prior calculations as the maximum available energy.

E_T distributions obtained by monitoring H_2O fragments with different internal energies show no reproducible structures, and the three images sample the entire range of energetically accessible states. Therefore, the observed E_T distributions were compared to statistical predictions—specifically, the microcanonical prior distribution of product energies.⁴³ The prior distributions provide a good first-order picture of statistical behavior because they are based on an unbiased “democratic” model of state populations that imposes no constraints other than energy conservation. The model is based on volumes in phase space for each degree of freedom and involves no dynamics. It has been used successfully, for example, in assessing shapes of distributions in chemical reactions proceeding *via* a bound intermediates,⁴⁴ unimolecular reactions,⁴⁵ and pre-dissociation of dimers,⁴⁶ where detailed phase space calculations are unfeasible.

For the case of the PhOH– H_2O dimer, the relative probability of observing products with translational energy E_T at energy $E = E_{\text{avail}} - E_{\text{rot}}(\text{H}_2\text{O})$ is:⁴³

$$P^0(E_T; E) dE_T \propto \rho_T(E_T) \rho_{\text{rot,vib}}(E - E_T) dE_T, \quad (2)$$

where $\rho_T(E_T)$ is the translational density of states and $\rho_{\text{rot,vib}}(E - E_T)$ is the rovibrational density of states of the phenol fragment at energy $E - E_T$. This simple model gives the pair-correlated microcanonical statistical E_T distributions to which the measured distributions are compared. The calculated distributions for the three monitored rotational levels of H_2O are shown as the smooth blue lines in the right panels of Fig. 5 along with the background-subtracted experimental E_T distributions. Neglecting angular momentum conservation should not significantly alter the internal energy distributions of the PhOH cofragment because of its high density of internal states. The model also assumes complete

IVR among levels, disregarding their symmetry. On the other hand, as demonstrated before, the rotational angular momentum of the fragments cannot be too large because there is insufficient anisotropy in the potential energy surface of weakly bound dimers to support a large torque.^{28,30,31,47} We therefore limited the rotational angular momentum of the PhOH fragment to 115 cm^{-1} (165 K) based on the temperature of the H_2O fragment obtained experimentally from Pathway 1.

We computed the harmonic vibrational density of states of the PhOH cofragment using the Beyer–Swinehart algorithm with fundamental vibrational levels listed in Roth *et al.*⁴⁸ and Schumm *et al.*⁴⁹ The algorithm counts all possible harmonic vibrational levels up to the maximum accessible energy (1562 cm^{-1} , in our case), and therefore provides a lower limit for the density of vibrational states. Although PhOH is an asymmetric top, for the purpose of our computations, it was sufficient to approximate its geometry as an oblate symmetric top with $A = B$ and C rotational constants of 0.0597 and 0.1885 cm^{-1} , respectively.¹⁸ In our implementation, the rotational levels are first counted at discrete energy intervals and folded in before counting the density of vibrational states. The procedure is similar to the one described in ref. 43, which also provides sample computer programs.⁴³ This procedure gave the dependence of the rovibrational density of states of PhOH, $\rho_{\text{rot,vib}}$, on the available energy, as shown in Fig. 6. As expected, the density of rovibrational states is high, and can reach $1 \times 10^5\text{ cm}^{-1}$ when the fragment translational energy is low. Finally, we obtained the E_{T} distributions for the maximum available energies corresponding to each of the monitored $\text{H}_2\text{O } J_{K_a,K_c}''$ rotational levels. The pair-correlated calculated E_{T} distributions are in good agreement with the experimental results, and they support our assertion that the VP of PhOH– H_2O is statistical-like when the H-bonded OH stretch fundamental is excited.

3.3.2 Pathway 2. To the best of our knowledge this is the first report of the VP dynamics of a mixed dimer of water ($\text{HX–H}_2\text{O}$) induced by excitation of the free OH stretch vibration of the H_2O moiety. This study was made possible because in contrast to many other dimers of H_2O , the fundamental vibrational transition of the free OH stretch of PhOH– H_2O was separated from IR transitions of other clusters, as described above. The experiments, however, are more challenging for this pathway because the free OH stretch has a lower oscillator strength than the H-bonded OH transition, and at the same time, the excitation requires using low IR fluences to minimize multiphoton dissociation of larger clusters. As a result, the signals were much smaller than those obtained when exciting the H-bonded OH stretch. Nevertheless, two isolated rotational levels of the H_2O (000) fragment could be utilized for imaging. Fig. 7 shows the c.m. E_{T} distributions derived from velocity map images when monitoring the transitions: $2_{0,2} \leftarrow 3_{2,1}$ and $2_{0,2} \leftarrow 4_{2,3}$.

The c.m. E_{T} distributions for Pathway 2 appear qualitatively different from those observed for Pathway 1. Indeed, pair-correlated prior distributions fail to capture accurately the behavior of the lower- E_{T} region, which corresponds to higher cofragment internal energies; it appears that the populations of the higher rovibrational levels of the PhOH cofragment are

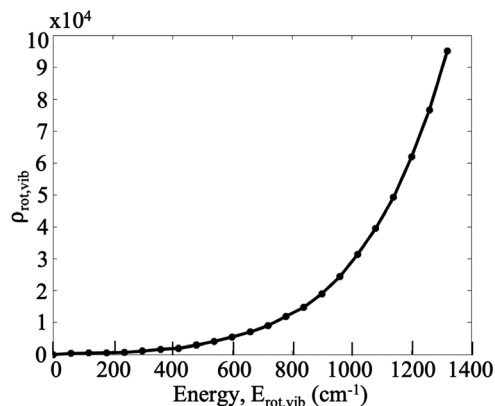


Fig. 6 Calculated rovibrational density of states of the PhOH cofragment as a function of energy. In our experiments the available energies are between 858 and 1350 cm^{-1} for Pathway 1.

underestimated by the prior statistical model. We also compared our results to a model proposed by Ewing,^{50–52} who used the energy gap law to predict trends in the VP rates of van der Waals dimers of small molecules. In addition to predicting higher VP rates when the energy gap is minimized, Ewing proposed that the “relaxation channel of a vibrationally excited molecule is efficient only when the total change in effective quantum numbers for the process is small.”⁵⁰ In other words, the energy transfer process favors channels with the smallest change in quantum numbers, resulting in a propensity to populate vibration over rotation over translational energy release. To exhibit this propensity, we used an exponentially decaying function to fit the observed E_{T} distributions. This function included a single fit parameter, C , which was the same for both rotational states shown in Fig. 7:

$$I = e^{-CE_{\text{T}}} \quad (3)$$

As seen in Fig. 7, the E_{T} distributions obtained by VMI are fit better with this function than with the statistical prior distribution.

3.3.3 VP mechanism. The internal energy distributions in fragments of H-bonded dimers following VP range from clearly nonstatistical to statistical-like. When the two subunits of the dimer have a low density of internal states, the internal state distributions often obey propensity rules suggested by Ewing as described briefly above.^{50–52} In these cases IVR is incomplete, and the internal state distributions conform to the momentum (or energy) gap law.^{28,30,31,34,53,54} Three dimers containing H_2O (or an isotope thereof) as a subunit, $\text{H}_2\text{O–HCl}$,^{20,23} $\text{H}_2\text{O–H}_2\text{O}$,^{21,24} and $\text{D}_2\text{O–D}_2\text{O}$,²¹ were examined experimentally in detail following excitation of the H-bonded OH stretch. In all three cases the rovibrational energy distribution of the H_2O fragment exhibited a clear propensity to populate rovibrational states with high internal energy. Thus, the distributions were found to be non-statistical obeying eqn (3), similar to those of other dimers with small subunits.^{34,54} Statistical-like distributions were observed when the H_2O was part of a larger cluster, such as $(\text{H}_2\text{O})_3$ ²² or $\text{HCl–}(\text{H}_2\text{O})_3$.^{25,26} In these larger clusters the density of states is large and the couplings between the subunits are more efficient; which in turn leads to complete IVR prior to VP.

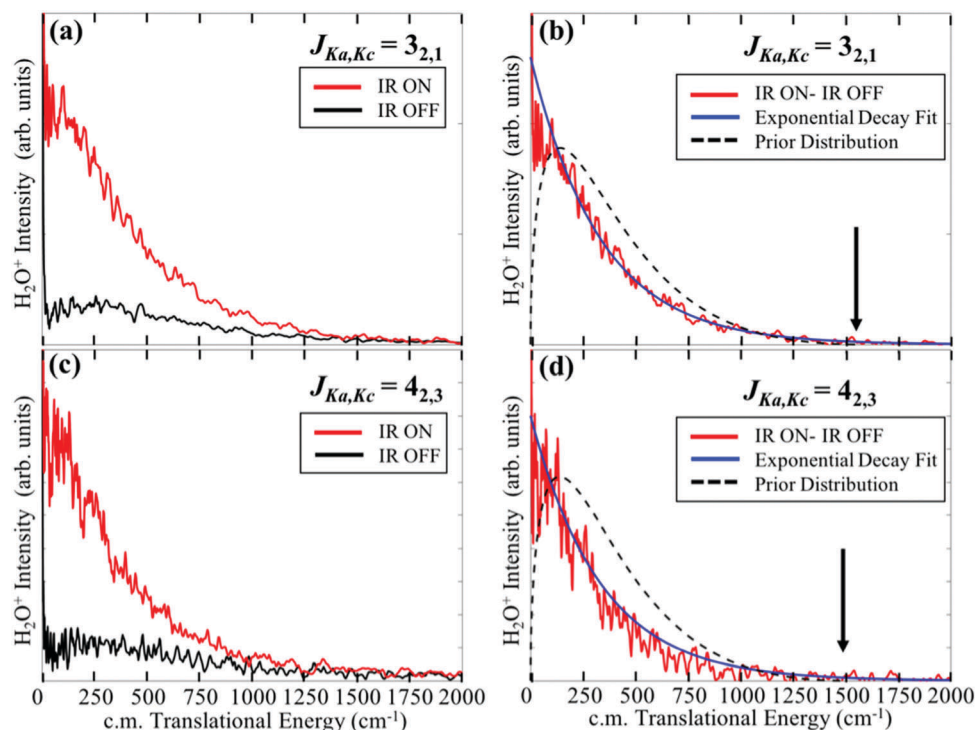


Fig. 7 Left column: "IR ON" (red) and "IR OFF" (black) c.m. translational energy distributions obtained by monitoring state-selected H_2O^+ fragments in J_{K_a,K_c} levels: (a) $3_{2,1}$ and (c) $4_{2,3}$, after excitation of the free OH stretch of the H_2O moiety. Right column: "IR ON–IR OFF" (red) signals for the same state-selected H_2O^+ fragments fitted with an exponential decaying function (smooth blue solid lines), (b) and (d), respectively. The black dashed lines represent the corresponding prior distributions. The arrows indicate the maximum allowed translational energies corresponding to $D_0 = 1960 \text{ cm}^{-1}$.⁴ This was the value used also in the prior calculations and in the decaying function fits.

The VP of $\text{PhOH-H}_2\text{O}$ is intermediate between the cases discussed above. Due to the large density of states in PhOH, the dimer may exhibit efficient IVR following excitation of the OH stretch. Miyazaki *et al.*¹³ determined energy transfer rates in bare PhOH and $\text{PhOH-H}_2\text{O}$ by using real time picosecond IR-UV measurements, and found that following excitation of the H-bonded OH stretch of PhOH in $\text{PhOH-H}_2\text{O}$, IVR in the dimer was faster than in bare PhOH.¹³ By analyzing the rise and fall curves of several internal levels of the phenol moiety populated by IVR in $\text{PhOH-H}_2\text{O}$ and $\text{PhOD-D}_2\text{O}$, they estimated that the IVR lifetime in these dimers is of the order of 10–30 ps, which is shorter by about a factor of 4–5 than the corresponding VP lifetime, estimated at 40 and 100 ps, respectively.¹³ They used a model based on anharmonic force fields^{13,15} to examine both IVR within the PhOH moiety and the slower energy transfer process involving the intermolecular modes. They also concluded that the experimental VP rates were in reasonable agreement with the ones calculated by RRKM theory.¹³

The results reported here following excitation of the H-bonded OH stretch of $\text{PhOH-H}_2\text{O}$ show statistical energy distributions in the PhOH fragments and therefore reinforce the previous conclusion that complete IVR precedes VP. Achieving complete IVR prior to dissociation is the first step to a statistical internal energy product distribution. Moreover, the test afforded by our results is more stringent because it is based on pair-correlated distributions in the PhOH fragment; this removes the effects of inherent averaging over some degrees of freedom. The H_2O

fragment rotational distribution, inferred from the REMPI spectrum, is well described by a temperature of 165 K and appears to be statistical as well.

We are not aware of any experiments that investigated the IVR in $\text{PhOH-H}_2\text{O}$ following excitation of the free OH stretch of H_2O . However, we can use for comparison results of IVR in the PhOH dimer following excitation of its H-bonded and free OH stretch vibrations reported by Ebata *et al.*⁵⁵ The authors of that study observed clear site specificity in the IVR lifetimes, which were 5 and 14 ps for the H-bonded and free OH, respectively. The latter value was similar to the IVR lifetime determined for the PhOH monomer. On the other hand, they found that the ensuing VP rate was faster for the free OH excitation than for the H-bonded case, apparently due to incomplete IVR prior to dissociation. Our results, which indicate nonstatistical internal energy distributions in the PhOH cofragments, also suggest incomplete IVR prior to dissociation.

Furthermore, the H_2O fragment rotational temperature following excitation of the free OH stretch is significantly higher than the corresponding one for the H-bonded OH stretch. Predissociation in the upper electronic state of H_2O used for the REMPI detection and spectral congestion prevent us from observing a clear propensity to populate high rotational levels of H_2O ; however, for free OH excitation we detected rotational levels higher than those observed with H-bonded stretch excitation. Also, the increase in rotational temperature—from 165 to 310 K—seems to be larger than what would be expected by the slight increase in

excitation energy for the free OH stretch excitation. Therefore, we suggest that following free OH stretch excitation, VP in PhOH–H₂O takes place before complete IVR in the PhOH moiety is achieved, and that the rovibrational energy distributions are hotter than expected by statistical considerations.

4. Conclusions

The VP dynamics of the phenol–water (PhOH–H₂O) dimer were studied by using velocity map imaging of H₂O fragments to infer the internal state distributions of PhOH cofragments, pair-correlated with selected rotational levels of the H₂O fragment. The parent cluster was excited at two different frequencies corresponding to the H-bonded OH stretch of PhOH (Pathway 1) and the asymmetric stretch (free) OH stretch of H₂O (Pathway 2) of the PhOH–H₂O dimer. We conclude that the predissociation dynamics depends on the OH stretch level initially excited. The results found in this study for Pathway 1, as well as previous results involving PhOH–H₂O,¹³ suggest that complete IVR occurs prior to VP. On the other hand, our results for Pathway 2, inferred from the c.m. E_T distributions of VMI and the H₂O 2+1 REMPI spectrum, suggest incomplete IVR prior to VP. Pathway 2 shows a propensity to populate rovibrational levels of PhOH higher in energy than those predicted by a statistical model and is in better agreement with an energy-gap model.

Conflicts of interest

There are no conflicts to declare.

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