Isotope dependent, temperature regulated, energy repartitioning in a low-barrier, short-strong hydrogen bonded cluster

Xiaohu Li

Department of Chemistry, Indiana University,
800 E. Kirkwood Ave, Bloomington, Indiana 47405, USA

Jos Oomens

FOM Institute for Plasma Physics 'Rijnhuizen',
Edisonbaan 14, 3439 MN Nieuwegein, The Netherlands

John R. Eyler

Department of Chemistry, University of Florida, Gainesville, Florida 32611, USA

David T. Moore*

Department of Chemistry, Lehigh University,
Bethlehem, Pennsylvania 18015, USA

Srinivasan S. Iyengar*

Department of Chemistry and Department of Physics, Indiana University,
800 E. Kirkwood Ave, Bloomington, Indiana 47405, USA

(Dated: April 23, 2010)

* Email: david.moore@lehigh.edu
* Email: iyengar@indiana.edu
Abstract

We investigate and analyze the vibrational properties, including hydrogen/deuterium isotope effects, in a fundamental organic hydrogen bonded system using multiple experimental (infrared multiple photon dissociation and argon-tagged action spectroscopy) and computational techniques. We note a qualitative difference between the two experimental results discussed here and employ ab initio molecular dynamics simulations to explain these results. A deeper understanding of the differences between the isotopically labeled systems arises from an analysis of the simulated cluster spectroscopy and leads to a system-bath coupling interpretation. Specifically, when a few active modes, involving the shared hydrogen/deuterium stretch, are identified and labeled as “system”, with all other molecular vibrational modes being identified as “bath” modes, we find critical differences in the coupling between the system modes for the shared proton and shared deuteron cases. These differences affect the energy repartitioning between these modes resulting in a complex spectral evolution as a function of temperature. Furthermore, intensity borrowing across modes that are widely distributed in the frequency domain play an important role on the simulated spectra.
I. INTRODUCTION

Hydrogen bonds and hydrogen transfer systems have a fundamental role in many biological\(^1\), materials\(^2,3\) and atmospheric\(^4-9\) processes. Experimentally, H/D isotope substitution is often used as a tool to probe these systems. In addition, there are many instances where temperature dependent primary and secondary isotope effects have been recorded on hydrogen bonded and hydrogen transfer systems to yield novel mechanistic insights\(^1,3\).

Here, we study a fundamental organic shared H/D system: a charged species that contains a short-strong hydrogen bond\(^10-17\) involving a proton or deuteron bound to two organic ethers, namely, \([R_2O-H-OR_2]^+\) and its deuterated analogue \([R_2O-D-OR_2]^+\), using multiple experimental and computational techniques. Similar low-barrier, short-strong hydrogen bonds have been widely explored with respect to significance in many enzyme catalytic reactions\(^10-17\). Furthermore, when the R-group is a hydrogen atom, the system studied represents the well-known Zundel cation\(^18-21\) which is a low-barrier hydrogen-bonded complex that plays an important role in proton transfer in condensed phase systems. The critical interactions involved in such systems are also seen in many host-guest systems\(^22\). Similar systems have also been utilized as models to understand secondary isotope effects in enzymes\(^23\).

We inspect the factors that determine the vibrational properties by considering isotope substitution as well as temperature effects. Our analysis is based on experimental infra-red multiple photon dissociation (IRMPD)\(^20,24-29\) and previously conducted argon-tagged single photon action spectroscopy studies\(^7\). These experimental results are supported through facilitating finite temperature ab initio molecular dynamics (AIMD) simulations\(^30-32\). The experimental techniques are both action spectroscopy methods and differ in the ion temperature and method of measurement. While the IRMPD uses non-coherent multiple photons with room-temperature ions, the argon-tagged measurement is a single photon process with cold ions.

We note, what appears to be, a qualitative difference between the experimental results for the deuterated species, \([\text{Me}_2\text{O-D-OMe}_2]^+\). While the argon-tagged spectrum\(^7\) is in reasonable agreement with the harmonic frequencies obtained from electronic structure calculations, the IRMPD spectral results are broad and appear to be very different. Finite temperature AIMD simulations constructed using a single (ground) electronic potential surface, provide good agreement with both experimental results and are utilized here to unravel
the energy distributions and mode couplings responsible for the differences between the two experimental results. In a nutshell, the vibrational properties of the deuterated system are dictated by coupling between modes that combine the shared deuteron stretch and ether backbone stretch. By comparison, the protonated species displays interactions between the shared proton stretch, the ether backbone symmetric stretch and other vibrational modes of the molecule. This difference, along with its temperature dependent modulation, explains a critical portion of the spectral differences between the protonated and deuterated systems and also the results from the two experiments. As far as we are aware, this is also the first time this level of concordance between these experimental techniques (IRMPD and Argon-tagged action spectroscopy) and theory has been reached for a set of spectra of a hydrogen-bound system, incorporating both a wide temperature range and isotopic effects.

The paper is organized as follows: In Section II the experimental and computational methods are described. Section III provides a discussion on the temperature dependence of the vibrational properties whereas in Sections IV and V we analyze the role of energy redistribution. Conclusions are given in Section VI.

II. EXPERIMENTAL AND COMPUTATIONAL METHODS

A. Infra-red multiple photon dissociation spectroscopy and Argon-tagged action spectroscopy

The Infra-red multiple photon dissociation spectroscopy was carried out using an Fourier transform ion cyclotron resonance (FTICR) mass-spectrometer interfaced with the infrared free-electron laser (FELIX) facility in the Netherlands; this apparatus has been discussed in detail elsewhere\textsuperscript{27}. Briefly, the deuteron-bound methyl ether dimers were created in situ inside the FTICR cell, and then irradiated with tunable IR light from FELIX. First, D\textsubscript{3}O\textsuperscript{+} ions were created from D\textsubscript{2}O vapor (\(\approx 10^{-7}\) torr) by electron impact ionization followed by ion-molecule reactions. Methyl ether vapor was then admitted from a pulsed valve (peak pressure \(\approx 10^{-6}\) torr), and the deuteron-bound dimer was formed in a stepwise fashion from ion molecule reactions, first D\textsuperscript{+}-transfer to form deuterated methyl ether monomer [Me\textsubscript{2}OD\textsuperscript{+}], followed by capture of a second methyl ether to form the dimer [Me\textsubscript{2}O-D-OMe\textsubscript{2}]\textsuperscript{+}. The dimers were then isolated in the trap and stored for one second to allow them to reach
radiative thermal equilibrium with the room temperature cell\textsuperscript{28}. Several (5-10) IR-pulses from the free-electron laser were then used to irradiate the ions while monitoring fragmentation signal in the m/z=48 mass channel, corresponding to [Me\textsubscript{2}OD\textsuperscript{+}]. IRMPD spectra, represented as the ratio of fragment ion signal to total ion signal, were recorded by repeating this sequence while scanning the laser wavelength. The reported intensities have been normalized to account for the power spectrum of the FELIX laser. It should be noted that no significant fragmentation into other mass channels was observed, and in particular, no signal was observed in the m/z=47 channel. This rules out contributions to the spectrum from structural isomers where the deuteron was exchanged with a methyl hydrogen to create a proton-bound, mono-deuterated species. Such parent ions would show competitive fragmentation into the m/z=48 or m/z=47 channels, so the absence of significant signal in the m/z=47 channel strongly suggests such isomers are not reflected in the spectrum.

In addition, as outlined in Ref. \textsuperscript{31}, these are non-coherent multiple-photon dissociation processes. For the IRMPD spectra presented here, and indeed in most other cases studied, the scaling of the measured intensities with laser power is linear\textsuperscript{33–35}, which is a strong indication that only single-photon processes are responsible for the observed spectra. Indeed, in Refs. \textsuperscript{28,33,35} it has been shown that the peak positions (frequencies) are in agreement with calculated spectra obtained from geometry optimization and harmonic frequency calculations, and with measured spectra obtained with other means\textsuperscript{28,33,35}. Furthermore, in Ref. \textsuperscript{31}, [Me\textsubscript{2}O-H-OMe\textsubscript{2}]\textsuperscript{+} has been studied using AIMD simulations at two different temperatures and the resultant spectra have been shown to qualitatively agree with IRMPD. Since the systems treated in this publication are quite similar to those studied in Refs. \textsuperscript{28,31}, one would expect a similar trend here as well.

The \textbf{argon-tagged spectra} shown here are from Ref. \textsuperscript{7}. For completeness we provide a brief overview of this experiment, with details in Ref. \textsuperscript{7,36}. Briefly, these spectra were recorded in the group of Mark Johnson using their cluster-ion spectroscopy apparatus\textsuperscript{7}. Electronic versions of these spectra were provided to us by the Johnson group (see acknowledgments). The argon-tagging method is a type of vibrational pre-dissociation spectroscopy, whereby argon atoms are attached to molecular or cluster ions in a cold molecular beam, and then resonantly detached by using an infrared laser to excite vibrations within the ion cluster. The vibrational spectra were obtained by scanning the laser frequency while monitoring the argon-loss fragmentation channel in a mass spectrometer. Since the binding energy of
TABLE I: Simulation parameters: temperature fluctuations in the AIMD, micro-canonical ensemble (NVE) simulations. All simulations shown are 15ps in length.

<table>
<thead>
<tr>
<th>Temp.(^a)</th>
<th>(\Delta E^{b})</th>
<th>Temp.(^a)</th>
<th>(\Delta E^{b})</th>
</tr>
</thead>
<tbody>
<tr>
<td>39K±6K</td>
<td>0.009</td>
<td>39K±6K</td>
<td>0.007</td>
</tr>
<tr>
<td>68K±10K</td>
<td>0.013</td>
<td>68K±11K</td>
<td>0.014</td>
</tr>
<tr>
<td>109K±15K</td>
<td>0.040</td>
<td>109K±16K</td>
<td>0.030</td>
</tr>
<tr>
<td>273K±39K</td>
<td>0.194</td>
<td>272K±39K</td>
<td>0.176</td>
</tr>
<tr>
<td>392K±54K</td>
<td>0.160</td>
<td>390K±56K</td>
<td>0.115</td>
</tr>
</tbody>
</table>

\(^a\)Average temperature and fluctuations for all the AIMD, NVE simulations (in Kelvin).
\(^b\)RMS deviation in the total energy during simulation (kcal/mol). The angular momentum of the system is conserved at \(J=0\) for all simulations, with fluctuations of the order \(10^{-8}\)ℏ.

An argon atom to the cluster is quite small, the dissociation thresholds for argon-tagged systems are much lower than for IRMPD, and a single infrared photon typically carries enough energy to dissociate the clusters.

### B. Computational methods

A large number of simulations have been conducted as part of our study employing the AIMD techniques, Born-Oppenheimer Molecular Dynamics (BOMD)\(^{37-39}\) and atom-centered density matrix propagation (ADMP)\(^{9,40-43}\), as implemented within a development version of the Gaussian series of electronic structure codes\(^{44}\). These simulations utilize the B3LYP hybrid density functional with double-zeta polarized-diffused 6-31+G** basis, as suggested from previous studies\(^{9,30,32,45-49}\) on similar systems. Geometry optimization and harmonic frequency calculations, at density functional as well as post-Hartree Fock (MP2) levels are performed to assist the decomposition and assignment of spectra obtained from AIMD simulations.

The AIMD simulations conducted here are similar in nature to those utilized in Refs. \(^{30-32}\). Briefly, all systems considered here are treated as gas-phase clusters to remain consistent with the experimental work. A time step of 0.5 fs was chosen for all BOMD dynamics studies while a fictitious mass-tensor scaling value of 0.1 \(amu \cdot bohr^2\) (\(\approx 180\) a.u.) and a time-step of 0.25 \(fs\) was used for ADMP. The AIMD simulations conducted here are micro-canonical (NVE), with acceptable fluctuations in the internal temperature (see Table I) and all nuclei are treated classically. Since time-correlation functions involving nuclear velocities
as well as molecular dipoles are utilized to obtain vibrational properties, a constant energy simulation with an associated conservative Hamiltonian corresponding to the real system is critical. The total energy was well conserved in our simulations as noted in Table I. The total angular momentum of the classical nuclear system was also well-conserved (with initial conditions corresponding to J=0) and residual angular forces, resulting from finite numerical precision, were projected out during the dynamics process. This also implies that any rotation-vibrational coupling effects are not included in the simulation. A body-fixed 3N-dimensional Cartesian coordinate system at the center-of-mass, which was conserved all through the dynamics, was used to represent nuclear positions and momenta. Many different sets of simulations were conducted, in the temperature range of 30K to 400K, five of which are discussed in the next section to help understand the experimental results (also see Table I). The choice of temperature determines the distribution of initial kinetic energy and the corresponding phase-space distribution function. The temperature for these simulations were chosen as follows: Since the Argon-tagged spectrum was recorded using low temperature ions, we have computed a few trajectories under 100K. This choice is consistent with the agreement seen between argon-tagged spectroscopy results and previous AIMD simulations\textsuperscript{30,45}. Similarly, we computed trajectories at 273±39K and 390±55K because the IRMPD experiments were performed using room temperature ions.

The dynamically averaged vibrational spectra were computed by using Fourier-transform of the nuclear velocity auto-correlation function (FT-VAC) and Fourier-transform of the dipole auto-correlation function (FT-DAC). The FT-VAC is defined as

\[
I_V(\omega) = \lim_{T \to \infty} \int_{t=0}^{t=T} dt \exp(-i\omega t) \langle V(0) \cdot V(t) \rangle
\]

\[
= \lim_{T \to \infty} \sum_{i=1}^{N_{Atoms}} \sum_{j=1}^{3} \int_{t=0}^{t=T} dt \exp(-i\omega t) \int_{t'=0}^{t'=T} dt' V_{i,j}(t') \ast V_{i,j}(t' + t)
\]

\[
= \lim_{T \to \infty} \sum_{i=1}^{N_{Atoms}} \sum_{j=1}^{3} \left| \int_{t=0}^{t=T} dt \exp(-i\omega t)V_{i,j}(t) \right|^2 , \tag{1}
\]

where the term \(\langle \cdots \rangle\), in the first equation, indicates ensemble average and is equal to the \(t'\)-integral in the second equation under the ergodicity condition. We have used the convolution theorem\textsuperscript{50} to reduce the second equation to the third equation. The FT-VAC provides the vibrational density of states.
The FT-DAC provides peak intensities proportional to the change in dipole moment of the system and the vibrational spectrum \(^{30-32,45,51-55}\). Inclusive of these intensities is computed as:

\[
\alpha_{\mu}^{QC}(\omega) \propto \frac{\omega}{1 - \exp(-\beta \hbar \omega)} \left\{ \omega [1 - \exp(-\beta \hbar \omega)] \lim_{T \to \infty} \int_{t=0}^{t=T} dt \exp(-i \omega t) \langle \mu(0) \cdot \mu(t) \rangle \right\}.
\]  

The terms inside the curly brackets (\{ \cdots \}) represents the power normalized absorption cross-section \(^{51,52}\). The pre-factor, \(\frac{\omega}{1 - \exp(-\beta \hbar \omega)}\), is a quantum-nuclear correction \(^{53-55}\) obtained based on the harmonic approximation. Over a series of publications \(^{30-32,36,45}\) it has been demonstrated that these correlation functions provide a good estimate to the vibrational spectrum obtained from experimental action spectroscopy. Utilizing the convolution theorem \(^{50}\) as above, Eq. (2) may be rewritten as

\[
\alpha_{\mu}^{QC}(\omega) \propto \omega^2 \lim_{T \to \infty} \sum_{i=1}^{3} \left| \int_{t=0}^{t=T} dt \exp(-i \omega t) \mu_i(t) \right|^2.
\]  

In this work, we have also computed the power normalized quantum nuclear corrected line-shape,

\[
I_{\mu}^{QC}(\omega) \propto \frac{\omega}{1 - \exp(-\beta \hbar \omega)} \left\{ \lim_{T \to \infty} \sum_{i=1}^{3} \left| \int_{t=0}^{t=T} dt \exp(-i \omega t) \mu_i(t) \right|^2 \right\}.
\]  

The spectral results from BOMD and ADMP are qualitatively similar and all data provided are from BOMD simulations. The value of \(T\) in Eqs. (1)-(4) is the length of simulation (15ps) stated in Table I, which is much larger than the usual vibrational scale in gas phase. The convergence of the simulated spectra has been confirmed by considering different simulation lengths.

**III. ANALYSIS OF VIBRATIONAL SPECTRAL BEHAVIOR**

We begin by examining the four experimental spectra (blue and red traces) in Figure 1. As noted in Section II, the ions in IRMPD are equilibrated to room temperature, whereas the system in the argon-tagged experiment is maintained at a much lower temperature. It is clear that the two low-temperature Ar-tagged spectra in Figures 1(a) and 1(b) are
The IRMPD (blue) and argon-tagged (red) action spectra for $[\text{Me}_2\text{O-H-OMe}_2]^+$ (Figure (a)) and $[\text{Me}_2\text{O-D-OMe}_2]^+$ (Figure (b)) are compared with computational results obtained here using harmonic approximation (black). Figure (a): the experimental spectra are reproduced from Ref. 28 (IRMPD) and Ref. 7 (Argon-tagged spectrum). Figure (b): the argon-tagged result is reproduced from Ref. 7, while the IRMPD spectrum is obtained here. The two figures on top display the respective protonated and deuterated systems, where the bound deuteron is purple.

Qualitatively quite different. The deuteron-bound dimer spectrum consists of a single strong peak near 700 cm$^{-1}$, while the proton-bound dimer spectrum shows much more structure, with a strong peak near 800 cm$^{-1}$, a strong doublet-like feature near 1050 cm$^{-1}$, and some broad weak bands at higher frequencies. On the other hand, the two high-temperature IRMPD spectra of the protonated and deuterated species are qualitatively quite similar. The only significant differences are the broadening towards the low wavenumber limit and the peak near 900 cm$^{-1}$ in the deuteron bound dimer spectrum, as well as the shift of the band near the high-frequency limit from 1600 cm$^{-1}$ (proton-bound) to 1500 cm$^{-1}$ (deuteron-bound).

One can also make similar comparisons between the high-temperature and low-
Figures (a) and (b) display the 39K and 390K AIMD spectra for [Me$_2$O-D-OMe$_2$]$^+$, obtained using Eq. (3) (red) and Eq. (4) (blue). The experimental argon-tagged and IRMPD results for are shown in black. Note that the argon-tagged results are reproduced well at 39K. The 390K AIMD spectra reproduce the IRMPD result.

FIG. 2: Figures (a) and (b) display the 39K and 390K AIMD spectra for [Me$_2$O-D-OMe$_2$]$^+$, obtained using Eq. (3) (red) and Eq. (4) (blue). The experimental argon-tagged and IRMPD results for are shown in black. Note that the argon-tagged results are reproduced well at 39K. The 390K AIMD spectra reproduce the IRMPD result.

temperature spectra for each species. In the proton-bound case, the high-temperature spectrum resembles a broader version of the low-temperature spectrum, with some shifts in relative band intensities. In contrast, for the deuteron-bound dimer, the high-temperature spectrum looks very different from the low-temperature spectrum, and in fact it is hard to see how both spectra could represent the same system. We have shown in Ref. 31 that the two proton bound experimental spectra in Figure 1(a) can be reproduced from AIMD simulations using a single (ground-state) potential energy surface, changing only the simulation temperature. In this publication we find it to be the case for the deuteron bound species as well. In addition, in the following sections, we inspect energy redistribution pathways that lead to the complex temperature dependence of the spectra and distinguish these pathways between the protonated and deuterated systems.

Two of the AIMD simulation spectra for the deuteron bound species are compared with the experimental spectra in Figure 2. The black traces reproduce the experimental spectra from Figure 1(b). The red and blue traces display the $\alpha_{\mu}^{QC}(\omega)$ intensities of Eq. (3) and $I_{\mu}^{QC}(\omega)$ intensities of Eq. (4), respectively, which are obtained from the AIMD simulations performed at 39K and 390K. As noted earlier, Eqs. (3) and (4) provide intensities proportional to the change in dipole of the system. Furthermore, since these are constructed
using finite temperature *ab initio* dynamics data, all potential energy surface parameters, including all anharmonicity contributions are accounted for in this study. It is clear in both cases that the 39K and 390K simulations produce good qualitative agreement with the low-(Argon-tagged) and high-temperature (IRMPD) experimental spectra, respectively. The spectra obtained from Eq. (4) are a little lower in intensity as compared to those obtained from Eq. (3). This is to be expected based on the $\omega$-dependent prefactors in these equations. While the pre-factor in Eq. (3) is quadratic in $\omega$, that in Eq. (4) is sub-linear. [Note that the proportionality constants in Eqs. (2) and (3) include, the temperature, speed of light and Planck’s constant. Since these are constants for a given simulation, they only contribute a uniform scaling to all spectra and are thus omitted from our discussion.] The 39K simulation reproduces the strong feature at 700 cm$^{-1}$ (Figure 2(a)), which is assigned to the anti-symmetric triatomic ODO stretch, based on the ab initio harmonic frequencies. The peak positions of several weaker features at higher wavenumber are also correctly reproduced in the 39K spectrum, although the calculated intensities are higher than in the argon-tagged experiment.

In Ref. 7, the weak features at $\approx 800$ and 1000 cm$^{-1}$ in the deuteron-bound dimer spectrum have been suggested as possibly arising from overlapping bands from the $^{13}$C-isotopologue of the proton-bound system. This analysis in Ref. 7 was based on calculations of harmonic frequencies of the shared proton and deuteron systems, with the mass-selected experimental conditions that allow the formation of the $^{13}$C-isotopologue of the proton-bound system with the $^{12}$C-isotopologue of the deuteron-bound system. The conclusions in Ref. 7 were also based on the absence of spectral features in the corresponding regions of the harmonic deuterated spectrum. In Figure 2(a), we show that the simulated AIMD spectrum at 39K (which includes anharmonic effects as a result of potential energy sampling during AIMD simulations) predicts a band near 1050 cm$^{-1}$, which correlates with a band from Ref. 7, as indicated by an arrow in the figure. Since this region of the experimental spectrum is congested and may contain several overlapping bands, it is likely that the $^{13}$C-isotopologue system as well as features found here for the $^{12}$C-isotopologue contribute. The assignment of this region in the current work is provided in Table III and discussed as part of Section IV B. It is noted that this region has contributions from harmonic normal modes corresponding to the shared deuteron stretch coupled with the ether backbone (C-O-C) stretch and methyl group wag.
FIG. 3: The progression of finite temperature AIMD spectra for [Me₂O-D-OMe₂]⁺ obtained using the $\alpha^{QC}_\mu(\omega)$ intensities of Eq. (3). As displayed in Figure 2, the 39K result (red) reproduces the argon-tagged spectrum well whereas the 390K result (red) reproduces the IRMPD spectrum. The AIMD spectra at intermediate temperatures (blue) “interpolate” between the two experimental results. [Fluctuations in simulation temperature and other computational details are presented in Table I.] Note that the primary peak at 39K shifts at 68K and then dominates at higher temperatures. All spectra are filtered in frequency domain using a Gaussian with full width half max $\approx 15.3\text{cm}^{-1}$. On account of rotational broadening (see text) spectrum filtered using full width half max about 50cm$^{-1}$ (green trace) is also provided.

Similarly, the 390K AIMD spectrum yields a qualitatively accurate reproduction of the positions, relative intensities and bandwidths of the major features in the room-temperature IRMPD spectrum. Even some of the weaker features, such as the small bands near 900 and 1175 cm$^{-1}$, and the apparent shoulder on the blue edge of the 1300 cm$^{-1}$ peak, are reproduced by the simulation. Since these results are obtained using a single electronic potential surface, it appears that the broad bands observed in IRMPD, through the use of incoherent multiple photons$^{31}$, do represent a high temperature form of the single photon spectrum.

It is interesting to consider the evolution of the spectrum as the temperature is increased from 39K to 390K. Such a progression is presented in Figure 3 for the shared deuteron case, where the $\alpha^{QC}_\mu(\omega)$ spectra at 68K, 109K and 272K have been added. (The $I^{QC}_\mu(\omega)$
results are also in similar agreement, but have relatively lower intensities in the higher frequency region consistent with those seen in Fig. 2. Here, the experimental spectra are shown in black, the simulated spectra at 39K and 390K, that are in close agreements with the experiments, are in red. Simulated spectra that interpose between the 39K and 390K temperatures are shown in blue. The dominant effect at low-temperature is a shift in intensity in the low frequency 600-860 cm$^{-1}$ region. As the temperature is increased from 39K, the predominant intensity contributions shift from the 665cm$^{-1}$ region towards higher frequencies as indicated by the broken arrow between 39K and 68K. This trend then continues in the 109K and 272K spectra, as other bands begin to fill in between 850 and 1050cm$^{-1}$. As we see below, this effect arises from coupling between the shared deuteron stretch and the ether backbone symmetric stretch. The other important effects pertain to the general broadening and growth in intensity of most peaks with increasing temperature. We analyze these differences in the next section through a spectral decomposition of the finite temperature features.

A similar progression of spectra with temperature for the shared proton case is presented in Figure 4. The results here differ from those in Ref. 31 in that additional temperature dependent AIMD spectra are provided. In Ref. 31, we discussed the relationships between the 68K AIMD spectra and the argon-tagged results and those between the 272K AIMD spectra and the IRMPD results. Here we have also included results at 39K, 109K and 390K to provide a description of the spectral evolution that is consistent with that provided for the deuterated case here. Clearly, the peak positions in Figure 4, obtained from the 39K simulation match the low-temperature experimental results. The peaks at $\sim$1000cm$^{-1}$ are reproduced here. Upon inspection of Figure 1, it is clear that this triplet is not recovered by the harmonic spectrum. This aspect is reminiscent of the Zundel cation$^{21}$ since the reason for the splitting at 1000cm$^{-1}$ for the argon-tagged spectrum is due to the coupled motion of the shared proton stretch and methyl wag$^{31}$. Furthermore, as the temperature is increased from 39K to 68K, the triplet takes the form of a doublet with a shoulder on the red-side of 1000cm$^{-1}$. This also maintains qualitative similarity with the low temperature experiment but as the temperature is increased even further, all spectral patterns including the feature at 1000cm$^{-1}$ become broad. But there are no spectral shifts like that seen for the deuterated case.

All AIMD spectra here have been filtered (or convoluted) in the frequency domain using a
FIG. 4: The progression of finite temperature AIMD spectra for $[\text{Me}_2\text{O-H-OMe}_2]^+$ obtained using the $\alpha^{QC}_\mu(\omega)$ intensities of Eq. (3). Notice the blue shift seen in the deuterated species is not present here. Fluctuations in simulation temperature and other computational details are presented in Table I. All spectra are filtered in the frequency domain using a Gaussian with full width half max $\approx 15.3\text{cm}^{-1}$. On account of rotational broadening (see text) spectrum filtered using full width half max about $50\text{cm}^{-1}$ (green trace) is also provided.

Gaussian with full width half max of approximately $15.3\text{cm}^{-1}$. A major contribution to the linewidth in the IRMPD spectra arises from rotational broadening, which is not accounted for in the $J=0$ simulations. Upon inspecting the narrowest feature in the IRMPD spectrum (the peak around $900\text{cm}^{-1}$ in Figure 2), we estimate this broadening to be approximately $50\text{cm}^{-1}$. To facilitate a consistent comparison between IRMPD and the theory, we have also convoluted the high temperature AIMD spectra with a frequency domain Gaussian filter with full width half max of approximately $50\text{cm}^{-1}$ which is represented using the green trace in Figs. 3 and 4. The convolution is found to smooth out some of the sharper features from the simulations, generally improving agreement with the IRMPD experiments. Note that this is only employed for the $390\text{K}$ spectrum.

Some of the computed $\alpha^{QC}_\mu(\omega)$ intensities for higher frequencies are not in agreement with the experiments. While the $I^{QC}_\mu(\omega)$ intensities are in closer agreement with the argon-tagged spectrum (Fig. 2(a)), it was also noted in Ref. 31 that a probable reason for this
discrepancy was due to the large density of harmonic mode states available to the system at
the high frequency range. More than a quarter of the $51 \quad [(3N-6)]$ harmonic modes appear
inside the $1450-1550 \text{cm}^{-1}$ window for the protonated species$^{31}$. The role of these modes on
the computed intensities is reconfirmed in Section IV B.

To summarize the results in Figure 3 and 4, we note that while the simulated spectra of
the proton bound dimethyl ether dimer is generally broadened as a result of temperature,
the deuterated species displays non-trivial changes with increasing temperature that include
both growth in intensity as well as apparent spectral shifts. These spectral properties are
analyzed in the following sections.

IV. ROLE OF ENERGY REPARTITIONING ON TEMPERATURE DEPEN-
DENCE

As discussed in Section III, the AIMD spectra agree reasonably well with all experimental
results over a range of temperatures. For the experiments, the change in spectrum can
be qualitatively understood from the temperature dependent population of the vibrational
eigenstates. At higher temperatures, excited vibrational states may be populated. Photon
absorption from these excited states may lead to hot combination bands in the spectrum.
To probe the reasons behind the change in the calculated dynamics spectra, we examine the
energy repartitioning phenomena in our dynamics simulations by analyzing contributions
from a basis of vibrational modes as a function of temperature. Specifically, two major
factors are discussed. In the Section IV B we analyze the blue-shift in intensity in the $600-
860 \text{cm}^{-1}$ region, for the shared deuteron, with increase in temperature. We also discuss the
effect of intensity borrowing on the computed spectrum. A theoretical analysis that allows
these descriptions is provided below in Section IV A. It is important to note that while
all the computational spectra are obtained using time-dependent AIMD trajectories, the
interpretation of the spectra for the remaining portion of this publication are constructed
in the frequency domain.
A. Decomposition of the finite temperature vibrational density of states

Energy redistribution in chemical systems has been well-studied\textsuperscript{56–68} in the past few decades. Influenced by the early work of Fermi, Pasta and Ulam\textsuperscript{56,63}, three of the present authors\textsuperscript{31,69} formulated a scheme to decompose and assign the finite temperature vibrational density of states utilizing harmonic normal mode vectors that are obtained by diagonalizing the nuclear Hessian matrix at minimum energy. Briefly, consider the simulation time averaged Fourier-transform of the mass-weighted nuclear velocity vectors, $\tilde{\mathbf{V}}(\omega)$, with elements,

$$V_{i,j}(\omega) = \int_{t=0}^{t=T} dt \exp (-i\omega t) \tilde{V}_{i,j}(t).$$

where $\tilde{V}_{i,j}(t) \equiv \frac{M^1}{T} V_{i,j}(t)$ and $V_{i,j}(t)$ are elements of the velocity vector defined in Eq. (1). Using Parseval’s theorem\textsuperscript{50}, the time-averaged kinetic energy associated with the element $(i, j)$ is given by

$$\bar{E}_{i,j} = \int_0^T dt |\tilde{V}_{i,j}(t)|^2 = \int_0^\infty d\omega |V_{i,j}(\omega)|^2.$$  

The quantities $\tilde{\mathbf{V}}(\omega)$ and $\tilde{\mathbf{V}}(t)$ are first written as a linear combination of mass weighted, orthonormal, complete, harmonic normal mode vectors, $\{\tilde{H}_i\}$ as

$$\tilde{\mathbf{V}}(\omega) = \sum_i C_i(\omega) * \tilde{H}_i$$

and

$$\tilde{\mathbf{V}}(t) = \sum_i \tilde{C}_i(t) * \tilde{H}_i$$

with expansion coefficients, $C_i(\omega) = \tilde{H}_i \cdot \tilde{\mathbf{V}}(\omega)$, $\tilde{C}_i(t) = \tilde{H}_i \cdot \tilde{\mathbf{V}}(t)$ and $\tilde{C}_i(t)$ is the inverse Fourier transform of $C_i(\omega)$. Since the AIMD dynamics trajectories conserve energy well, there is no center-of-mass translation during dynamics. Furthermore, due to conservation of angular momentum, free rotation is zero to within numerically precision (see Table I and associated discussion in Section II B).
Using Eq. (6), the kinetic energy of the system within a spectral range \([\omega_1, \omega_2]\) may be written as

\[
\frac{1}{\omega_2 - \omega_1} \int_{\omega_1}^{\omega_2} d\omega \left( \frac{1}{2} \vec{V}(\omega) \cdot \vec{V}(\omega) \right) = \frac{1}{\omega_2 - \omega_1} \int_{\omega_1}^{\omega_2} d\omega \left\{ \sum_i \frac{1}{2} \left| C_i(\omega) \right|^2 \right\},
\]

(9)

where the denominator \([\omega_2 - \omega_1]\) allows both sides of Eq. (9) to have units of energy. Thus Eq. (9) allows the introduction of a consistent energy partitioning scheme. Within this scheme, the net contribution of the \(i\)-th normal mode to the kinetic energy and the vibrational density of states in the frequency range, \([\omega_1, \omega_2]\), is then written as a net sum of all its contributions inside the frequency range as

\[
C_{i[\omega_1,\omega_2]} = \left[ \frac{1}{\omega_2 - \omega_1} \int_{\omega_1}^{\omega_2} d\omega \left| C_i(\omega) \right|^2 \right]^{1/2} = \left[ \frac{1}{\omega_2 - \omega_1} \int_{\omega_1}^{\omega_2} d\omega \left| H_i \cdot \vec{V}(\omega) \right|^2 \right]^{1/2}.
\]

(10)

Since mass-weighted coordinates and velocities are used, the amount of energy in mode \(i\) in the range \([\omega_1, \omega_2]\) is \(\frac{1}{2} \left\{ C_{i[\omega_1,\omega_2]} \right\}^2\). By contrast, the quantity \(\frac{1}{2} \left| C_i(\omega) \right|^2\) represents the amount of energy in mode \(i\) at frequency \(\omega\). These aspects are clear from Eqs (9) and (10), that is

\[
\frac{1}{2} \sum_i \left[ \frac{1}{\omega_2 - \omega_1} \int_{\omega_1}^{\omega_2} d\omega \left| C_i(\omega) \right|^2 \right] = \frac{1}{2} \sum_i \left\{ C_{i[\omega_1,\omega_2]} \right\}^2.
\]

(11)

The relative \(C_{i[\omega_1,\omega_2]}\) contributions arising from the various AIMD simulations:

\[
\frac{C_{i[\omega_1,\omega_2]}}{\sqrt{\sum_i \left\{ C_{i[\omega_1,\omega_2]} \right\}^2}} = \sqrt{\frac{1}{2} \left\{ C_{i[\omega_1,\omega_2]} \right\}^2} \equiv \sqrt{\frac{\text{Kinetic energy in } i\text{-th mode}}{\text{Total kinetic energy}}},
\]

(12)

are compared in the next section. Since the dynamics is studied at multiple temperatures, by maintaining a constant \(\left\{ \vec{H}_i \right\}\) for all simulations, the change in the \(C_{i[\omega_1,\omega_2]}\) coefficients with temperature will yield insight on the contribution from a given mode \(i\). By studying the temperature dependence of \(C_{i[\omega_1,\omega_2]}\) and the appropriate dipole weighted analogue:

\[
D_{i[\omega_1,\omega_2]} = I_i^{1/2} \ast C_{i[\omega_1,\omega_2]},
\]

(13)
TABLE II: Measure of completeness of \((3N-6)\) \(\bar{H}_i\) modes. The quantity \(\epsilon_1\) is unitless whereas \(\epsilon_2\) is in kcal/mol.

<table>
<thead>
<tr>
<th>Temp.(^a)</th>
<th>(\epsilon_1) (\text{(Eq. (14))})</th>
<th>(\epsilon_2) (\text{(Eq. (15))})</th>
<th>Temp.(^a)</th>
<th>(\epsilon_1) (\text{(Eq. (14))})</th>
<th>(\epsilon_2) (\text{(Eq. (15))})</th>
</tr>
</thead>
<tbody>
<tr>
<td>39K(\pm 6K)</td>
<td>0.00137</td>
<td>0.0029</td>
<td>39K(\pm 6K)</td>
<td>0.00157</td>
<td>0.0033</td>
</tr>
<tr>
<td>68K(\pm 10K)</td>
<td>0.00174</td>
<td>0.0063</td>
<td>68K(\pm 11K)</td>
<td>0.00140</td>
<td>0.0051</td>
</tr>
<tr>
<td>109K(\pm 15K)</td>
<td>0.00190</td>
<td>0.0112</td>
<td>109K(\pm 16K)</td>
<td>0.00176</td>
<td>0.0102</td>
</tr>
<tr>
<td>273K(\pm 39K)</td>
<td>0.00922</td>
<td>0.1348</td>
<td>272K(\pm 39K)</td>
<td>0.01034</td>
<td>0.1511</td>
</tr>
<tr>
<td>392K(\pm 54K)</td>
<td>0.01056</td>
<td>0.2209</td>
<td>390K(\pm 56K)</td>
<td>0.01423</td>
<td>0.2947</td>
</tr>
</tbody>
</table>

\(^a\)Average temperature and fluctuations for all the AIMD, NVE simulations (in Kelvin).

with IR intensities \(I_i\) for the \(i\)-th mode (computed within the harmonic approximation), important insight into the temperature dependent intra-molecular vibrational energy redistribution and partitioning is obtained in the next section. In practice, \(\omega_1\) and \(\omega_2\) are chosen to cover the relevant spectral feature. This is determined upon inspection of both the computed and experimental spectra.

1. **Issue of completeness and choice of basis**

It must further be noted that all analyses performed in Section IV B use the harmonic modes obtained at equilibrium geometry. However, in a dynamics simulation, anharmonicity is sampled and hence the moment of inertia tensor is not a constant and is asymmetrically sampled. As a result when only \((3N-6)\) internal modes are used for the decomposition in Eqs. (7) and (10), one expects a degree of incompleteness in the projection depicted by Eqs. (7) and (8). (There is, of course, no incompleteness when all \(3N\) modes are used.) To quantify the incompleteness in such an analysis we compute,

\[
\epsilon_1 = \frac{1}{T} \int dt \left\{ \frac{\vec{\tilde{V}}(t) \cdot \vec{\tilde{V}}(t) - \sum_{i}^{(3N-6)} |\vec{\tilde{C}}_i(t)|^2}{\vec{\tilde{V}}(t) \cdot \vec{\tilde{V}}(t)} \right\}, \tag{14}
\]

and

\[
\epsilon_2 = T \int dt \left\{ \vec{\tilde{V}}(t) \cdot \vec{\tilde{V}}(t) - \sum_{i}^{(3N-6)} |\vec{\tilde{C}}_i(t)|^2 \right\}, \tag{15}
\]
and present these in Table II. These quantities represent the relative and absolute loss in kinetic energy due to a decomposition that involves only \((3N - 6)\) internal \(\{\vec{H}_i\}\) mode vectors. The integrands in the equations above are always greater than or equal to zero. As can be seen from Table II, the errors are small, but the fact that these numbers are not zero, warrants a discussion. The higher temperature AIMD simulations deviate farther from the equilibrium geometry and hence the \(\vec{V}(\omega)\) vectors and the \(\vec{\tilde{V}}(t)\) vectors are not completely described by the \((3N-6)\) internal \(\{\vec{H}_i\}\) mode vectors obtained from a single minimum energy geometry. Indeed, the moment of inertia is not constant during the dynamics and fluctuates to a greater extent in the larger temperature simulations. However, the extent of incompleteness of the \((3N-6)\) internal modes constructed at the equilibrium geometry is numerically negligible for all simulations discussed here and hence this factor is not considered further.

B. Analysis of energy repartitioning in the AIMD spectra

We first analyze the differences between the H and D spectra in the 600-860cm\(^{-1}\) region. Towards this we decompose the finite temperature AIMD spectra in terms of the intrinsic harmonic normal modes, as outlined in Section IV A. In other words, we now utilize the harmonic mode vectors, \(\{\vec{H}_i\}\) from Eq. (7), as a basis to decompose the mass-weighted nuclear velocity vectors, \(\vec{V}(\omega)\), to obtain an interpretation of the differences in the 600-860cm\(^{-1}\) region.

The relative energy or relative-\(C_i^{[\omega_1,\omega_2]}\) contributions (Eq. (12)) of the major harmonic modes in this spectral range are depicted in Figures 5(a) and 5(b) as a function of simulation temperature. (Figure 6 defines the critical modes seen in Figure 5.) Figure 5(a) shows the temperature dependence of relative contribution defined in Eq. 12 for the major harmonic modes to the AIMD simulations in the 600-860cm\(^{-1}\) region for \([\text{Me}_2\text{O-D-OME}_2]^+\), while Figures 5(b) displays the same for \([\text{Me}_2\text{O-H-OME}_2]^+\). As stated earlier \(\frac{1}{2}\left|C_i^{[\omega_1,\omega_2]}\right|^2\) is the amount of energy in mode \(i\) in the frequency range \([\omega_1,\omega_2]\). (see Eq. 9) Thus, Figures 5(a) and 5(b) represent the temperature dependent relative energy content in all modes containing non-negligible contributions in the spectral range 600-860cm\(^{-1}\).

There are two dominant modes for both the proton and deuteron bound species. These are the symmetric and anti-symmetric combinations of the shared H/D stretch, the ether backbone symmetric stretch and the methyl wag. We represent these modes using notation
FIG. 5: Temperature dependent energetic contributions from harmonic modes to the finite temperature AIMD spectra in the 600-860\,cm$^{-1}$ region. The relative $C_i^{(\omega_1,\omega_2)}$ (see Eq. (12)) contributions from significant modes for the shared deuteron (Figure (a)) and proton (Figure (b)) bound dimers are displayed [$\omega_1 =$600\,cm$^{-1}$ and $\omega_2 =$860\,cm$^{-1}$]. The two dominant modes in these figures, $X_{\text{freq}}^{\text{S-S}}$ and $X_{\text{freq}}^{\parallel}$, are represented using solid red and black lines and are explained in Figure 6. In Figures (c) and (d) the cumulative contributions from all modes apart from $X_{\text{freq}}^{\text{S-S}}$ and $X_{\text{freq}}^{\parallel}$ are presented using the blue curve. These modes behave like “bath” mode that regulate energy flow\textsuperscript{70–72} between $X_{\text{freq}}^{\text{S-S}}$ and $X_{\text{freq}}^{\parallel}$. The relative $C_i^{(\omega_1,\omega_2)}$ contribution for the “bath” modes is defined as $\sqrt{\sum_i |C_i^{(\omega_1,\omega_2)}|^2}$, the summation here excludes the contribution from the $X_{\text{freq}}^{\text{S-S}}$ and $X_{\text{freq}}^{\parallel}$ (an includes only the dashed lines from Figures (a) and (b).
FIG. 6: (Enhanced online) Figure (a) displays $X_{freq}^{\text{OXO}_{A-S}-\text{COC}_{S-S}}$, where $X$ is H/D and “freq” represents the frequency in wavenumber, and the superscript represents the harmonic mode (eigenvector of the Hessian) corresponding to the coupled anti-symmetric stretch of the OXO tri-atom with the symmetric stretch COC triatomic stretch. Figure (b) displays $X_{freq}^{\text{X}_{\parallel}-\text{COC}_{S-S}}$ and corresponds to the parallel H/D motion with the symmetric stretch COC triatomic stretch. Note that these two modes have significant contributions in Figure 5. Notice the displacements have been mass weighted. In both cases the shared H/D are shown in purple.

$x_{freq}^{\text{OXO}_{A-S}-\text{COC}_{S-S}}$ and $x_{freq}^{\text{X}_{\parallel}-\text{COC}_{S-S}}$ respectively in Figure 5 and in further discussion below. The symbol “X” represents either hydrogen (H) or deuterium (D). The modes are shown using the solid black and red curves in Figures 5.

We first note the cross-over between the red and black curves in Figure 5(a). This indicates a relative repartitioning of energy between the corresponding modes. As temperature increases, the absolute energy content in both dominant modes increase, but, the relative contribution of $D_{665}^{\text{ODO}_{A-S}-\text{COC}_{S-S}}$ decreases compared to mode $D_{861}^{\text{D}_{\parallel}-\text{COC}_{S-S}}$ upto the point that the order of contributions is altered (Figure 5(a)). The cross-over between the red and black curves in Figure 5(a) indicates a relative reordering in contribution from these modes and is consistent with the blue-shift in intensity in the low frequency region with increase in temperature in Figure 3. This is a result of the fact that these modes are coupled by anharmonicity and is discussed further below.

We also note that a similar result is obtained upon inspection of the respective absolute $C_{i}^{[\omega_{1},\omega_{2}]}$ contributions (Eq. (10)) which are shown in the supplementary material section.

How does this scenario differ from that found for the protonated dimer? Figure 5(b) indicates that the nature of modes that contribute significantly to the signature in the 600-860 cm$^{-1}$ region for the shared proton system are essentially similar to that found in the shared deuteron system. That is in both cases, the motion in the 600-860cm$^{-1}$ region may
be characterized by the mixing of the $X^{\text{OXO}_{A-S}}_{\text{Freq}}$ and $X^{\text{X}_{i}}_{\text{Freq}}$ harmonic modes. One important distinction arises for the shared proton system through the fact that there is no reordering of contributions from the harmonic states like that seen for deuteron bound dimer in Figure 5(a). Compare the fact that the black and red curves cross in Figures 5(a), thus changing the ordering of contributions; this does not happen for the protonated system in Figures 5(b). An important reason for this is that there is minimal change in the relative $C_{i}^{[\omega_{1}, \omega_{2}]}$ contributions arising from $H^{\text{H}_{788}}_{\text{OHO}_{A-S}}$ in Figure 5(b). Thus the relative reduction in contribution from $H^{\text{OHO}_{A-S}}_{788}$ (indicated by the negative slope of the black curve in Figure 5(b)) is compensated by an increase in contributions from many “bath” modes, where the ”bath” modes are defined as all modes apart from $H^{\text{H}_{788}}_{\text{OHO}_{A-S}}$ and $H^{\text{H}_{940}}_{\text{COC}_{S-S}}$. This aspect is also clear from Figures 5(c) and 5(d) where the $C_{i}^{[\omega_{1}, \omega_{2}]}$ contributions from the ”bath” modes are presented using the blue curve. In Figure 5(c), there is energy redistribution between $D^{\text{ODO}_{A-S}}_{665} \text{– COCS-S}$, $D^{\text{D}_{\parallel} \text{– COCS-S}}_{861}$ and the bath modes. However, for the protonated species, the relative reduction in energy in $H^{\text{OHO}_{A-S}}_{788}$ is almost completely absorbed by the ”bath” modes. [Note that while contributions from the ”bath” (blue) and $D^{\text{D}_{\parallel} \text{– COCS-S}}_{861}$ (red) increase with temperature in Figure 5(c), only contributions from the ”bath” (blue) increase in Figure 5(d).]

In the higher frequency regions, the argon-tagged action spectrum as well as the harmonic spectral results in Figure 1 show very little intensity, while IRMPD provides much more structure. To further probe the reason for this spectral broadening in the high frequency regions, we provide the $C_{i}(\omega)$ contributions (Eq. (7)) from $D^{\text{ODO}_{A-S}}_{665} \text{– COCS-S}$ (Fig. 7(a)), $D^{\text{D}_{\parallel} \text{– COCS-S}}_{861}$ (Fig. 7(b)), $H^{\text{OHO}_{A-S}}_{788}$ (Fig. 8(a)) and $H^{\text{H}_{940}}_{\text{COC}_{S-S}}$ (Fig. 8(b)). We note that while the $C_{i}(\omega)$ contributions remain relatively localized in the frequency domain at lower temperatures, the contributions from the bright mode $D^{\text{ODO}_{A-S}}_{665} \text{– COCS-S}$ broaden and extends over the entire spectral range when temperature is increased. In fact, the $C_{i}(\omega)$ contribution from $D^{\text{ODO}_{A-S}}_{665} \text{– COCS-S}$ at 390K is almost identical to the IRMPD spectrum provided in Figure 1(b). Since $D^{\text{ODO}_{A-S}}_{665} \text{– COCS-S}$ is the only bright mode in the deuterated system, the higher frequency regions of the spectrum are generated by intensity borrowing. Thus there appears a close parallel between the temperature dependent spectral broadening phenomenon noted here, that is facilitated by the wider sampling of anhamonicity on the potential surface, and temperature dependent spectral diffusion in condensed phases where the energy deposited in a particular mode gets redistributed into the bath modes. For the
FIG. 7: The $C_i(\omega)$ contributions, computed using Eq. (7), from $D_{665}^{\text{ODOA-S-COC}_{S-S}}$ (Fig. (a)) and $D_{861}^{\text{DOAD-COC}_{S-S}}$ (Fig. (b)) to the deuterated spectrum. The summed contribution from the “bath” modes (corresponding to the blue traces from Fig. 5(c)) are shown in Fig. (c). For Figures (a) and (b), the corresponding harmonic frequencies are shown using a dotted vertical lines. The vertical axes in all figures have a uniform scale with a maximum value of 3.14 [kcal/mol]$^{1/2}$ for Figs. (a) and (b) and 11 [kcal/mol]$^{1/2}$ for Fig. (c). Note that the “spectral delocalization” of $D_{665}^{\text{ODOA-S-COC}_{S-S}}$ (Fig. (a)) is unique and not seen for the other modes (compare with Fig. (b) and with Figs. 8(a) and 8(b) which depict the behavior of the corresponding modes in the shared proton system).

Shared proton system, the number of bright modes are greater and hence there are contributions to the spectrum that arise from each of the bright modes with increase in temperature. It is also useful to note that while the contributions from the “bath” modes are qualitatively similar in Figures 7 and 8, there are large contributions that arise for both cases in the higher frequency range. This coincides with the region of the spectrum in Figures 3 and 4 where the $\alpha^Q_\mu(\omega)$ intensities obtained from AIMD are not in good agreement with experiment, more for the shared proton case than for the shared deuteron case. Since some of the “bath” modes have significant IR intensities\textsuperscript{31} for the shared proton case, the larger contribution from these modes in the higher frequency region, particularly at high temperatures, gives rise to a significant contribution in Fig. 4.
FIG. 8: The $C_i(\omega)$ contributions, computed using Eq. (7), from $H_{788}^{\text{H}_2\text{O}_{\text{AS}}-\text{COC}_{\text{S-S}}}$ (Fig. (a)) and $H_{940}^{\text{H}_2\text{COC}_{\text{S-S}}}$ (Fig. (b)) to the protonated spectrum. The summed contribution of the “bath” modes (corresponding to the blue traces from Fig. 5(d)) are shown in Fig. (c), and are observed to be qualitatively similar at all temperatures for H and D (compare with Fig. 7(c)). For Figures (a) and (b) the corresponding harmonic frequencies are shown using a dotted vertical lines. The vertical axis in all figures have a uniform scale with a maximum value of 3.14 $[\text{kcal/mol}]^{1/2}$ for Figures (a) and (b) and 11 $[\text{kcal/mol}]^{1/2}$ for Fig. (c).

In Figure 9 we analyze the relative energy contributions as defined in Eq. 12 from the harmonic modes as a function of temperature in the higher frequency regions. As is clear from this figure, there are two different kinds of modes that contribute in any given spectral range: (a) the “in-band” harmonic modes that belong to the spectral range being analyzed, i.e., these belong inside the range $[\omega_1, \omega_2]$ in Eq. (10) and (b) the “out-of-band” harmonic modes that are outside the spectral range or outside $[\omega_1, \omega_2]$ in Eq. (10). At lower temperatures the contribution from the in-band harmonic modes is always well separated from the out-of-band modes. As temperature increases, the in-band and out-of-band modes begin to mix giving rise to a greater spread in energy and associated broadening of the vibrational spectrum. When the out-of-band mode is a bright mode as is the case for
FIG. 9: The temperature dependent intensity contributions from harmonic modes to the AIMD spectra of [Me₂O-D-OMe₂]+ in the 860-1060 cm⁻¹ region (figure (a)), 1060-1240 cm⁻¹ region (figure (c)) and of [Me₂O-H-OMe₂]+ 860-1060 cm⁻¹ region (figure (b)), 1060-1240 cm⁻¹ region (figure (d)).

In all the displayed spectral regions, the “in-band” modes (that is the harmonic modes inside the chosen spectral region, that is inside the range [ω₁, ω₂]) always have higher contributions at lower temperatures. In fact, in most cases there is a clear separation in contributions arising from the in-band modes and out-of-band modes (modes outside the chosen spectral region, that is outside the range [ω₁, ω₂]) as seen in the shaded region of the plots. An increase in temperature facilitates energy transfer between these modes. To highlight the contributions, the “out-of-band” bright modes are shown in red, while the “in-band” bright modes are in green.

D_{665}^{ODOA-S-COCS-S}, this results in intensity borrowing into the dark modes in the high frequency regions as already noted from Fig. 7(a). Consequently, the “bright in-band” bonds are noted in green and the “bright out-of-band”, that lead to intensity borrowing, are shown in red in
TABLE III: Analysis of the vibrational harmonic frequency components that contribute in the 860—1060 cm$^{-1}$ region at 39K and 68K. The $C^{[\omega_1,\omega_2]}_i$ and $D^{[\omega_1,\omega_2]}_i$ decomposition coefficients are provided; $D^{[\omega_1,\omega_2]}_i$ inside parenthesis.

<table>
<thead>
<tr>
<th>Harmonic mode decompositions in the region 860—1060 cm$^{-1}$</th>
<th>39K</th>
<th>68K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.71 (0.63) D^{D_{1}-COCA-S}<em>{987}$ + $0.55 (0.06) D^{D</em>{1}-COCS-S}<em>{929}$ + $0.27 (0.10) D^{D</em>{1}-COCS-S}<em>{861}$ + $0.16 (0.18) D^{D</em>{1}-COCA-S-CH_{3}rock}_{1082}$</td>
<td>$D^{D_{1}-COCA-S}<em>{987}$ + $0.11 (0.04) D^{CH</em>{3}rock}<em>{929}$ + $0.11 (0.72) D^{ODO</em>{A-S}-COCS-S}_{665}$</td>
<td>$0.52 (0.05) D^{D_{1}-COCA-S}<em>{987}$ + $0.31 (0.10) D^{D</em>{1}-COCS-S}<em>{929}$ + $0.25 (0.23) D^{D</em>{1}-COCA-S-CH_{3}rock}<em>{1082}$ + $0.14 (0.81) D^{ODO</em>{A-S}-COCS-S}_{665}$</td>
</tr>
</tbody>
</table>

Fig. 9.

Using Fig. 9(a) we are also provide an assignment for the broad feature in the 860-1050cm$^{-1}$ region in the low temperature spectrum in Table III. [See discussion in Section III.] This region mostly has contributions from dark modes involving the motion of the shared deuteron along and orthogonal to the oxygen-oxygen axis coupled symmetric COC stretch and methyl wag. Spectral intensity is provided through contributions from the bright $D^{ODO_{A-S}-COCS-S}_{665}$ mode.

A few comments are in order with respect to the temperature dependent energy repartitioning among the harmonic mode vectors outlined above. As noted in Section IV A, the harmonic modes have been considered as a basis to describe the anharmonic motions encountered in AIMD. As the degree of anharmonicity increases, the elements of this bases couple, giving rise to the temperature-dependent trends shown in Figures 5, 7 and 8. Since the modes representing relative motion are reasonably complete (see Table II), these provide an numerically complete description of the dynamics data, which includes anharmonicity to all orders within the constraints of finite temperature dynamics. Furthermore, as temperature increases, two kinds of areas on the potential are sampled. (a) New local minima that were not populated at lower temperatures: This is important for many fluxional systems, such as those studied in Refs.9,30,32,45,46. But for the system considered here, this is not a factor since multiple optimization calculations beginning from different snapshots chosen from low and high temperature dynamics suggest that there is only one contributing minimum. (b) Greater sampling of anharmonicity at each local minimum: As temperature is increased the anharmonic regions sampled increase, and vibrational hot bands appear at higher temperatures. In both cases, the region of potential sampled at higher temperatures acts as a
perturbation to those sampled at lower temperatures and this further changes the coupling weights seen in Figures 5. This explains the appearance of additional bands in the spectrum as temperature is increased in this treatment.

V. ANALYSIS OF REDUCED DIMENSIONAL DISTRIBUTION FUNCTIONS

To further probe the energy redistribution and coupled motion of the two fundamental modes shown in Figure 6, we consider the projected motions along the two normal coordinates, \( X_{\text{Freq}} \) and \( X_{\text{Freq}} \), using the AIMD trajectory data. In Figure 10, we show the configurational distribution and Boltzmann averaged potential in the reduced two-dimensional phase space where the axes represent directions along the two chosen normal mode vectors for the case of the shared deuteron. To obtain these figures, the 3N-dimensional Cartesian coordinates at each dynamics step, was projected onto the two normal mode axes as

\[
H_{D_{665}}^{\text{ODOA-S-COC}_{S,S}} \cdot \vec{R}(t)
\]

and

\[
H_{D_{861}}^{\text{DOCO}_{S-S}} \cdot \vec{R}(t),
\]

where \( \vec{R}(t) \) represents the mass-weighted coordinates obtained from the AIMD trajectory. The quantities \( H_{D_{665}}^{\text{ODOA-S-COC}_{S,S}} \) and \( H_{D_{861}}^{\text{DOCO}_{S-S}} \) represent the mass-weighted harmonic mode vectors along \( D_{665}^{\text{ODOA-S-COC}_{S,S}} \) and \( D_{861}^{\text{DOCO}_{S-S}} \), respectively. The resultant data was used to obtain a reduced-dimensional distribution function that is averaged over all other coordinates (central column of Fig. 10). This central column indicates that, at low temperatures the motions along the two modes, are strongly correlated (verified by the tilted diagonal distribution in Figures 10(a)). It is further noted that as the temperature increases, the two modes get uncorrelated and the distribution becomes uniform (Figures 10(b) and 10(c)).

To confirm this qualitative trend we probe this effect by computing reduced dimensional quantum distribution functions. To obtain the quantum nuclear distribution, eigenstates are calculated and presented on the rightmost column in Figure 10. The eigenstates correspond
FIG. 10: Reduced dimensional potential (left column) and reduced dimensional configurational distribution function for classical (central column) and quantum (right column) treatment of the shared deuteron in the deuteron bound systems at temperatures 39K (Fig. (a)), 68K (b) and 272K (c). Potential energy is in kcal/mol. The horizontal axis represents the span along the normal, mass-weighted, coordinates $D_{665}^{\text{ODO}_{A-S}}-\text{COC}_{S,S}$, whereas the vertical axis represents motion along the $D_{861}^{\text{ODO}_{A-S}}-\text{COC}_{S,S}$. This behavior is qualitatively similar for both systems. While there exist quantitative differences between the quantum and classical treatments, both treatments predict the correlated (mixed) description of the two modes shown as a result of breakdown of spherical symmetry of the potential at lower temperatures.

to the two-dimensional Hamiltonian described in the coordinate representation as

$$H\left(\{x_{i}^{l}, x_{j}^{l}\}\right) = -\sum_{l=1}^{2} \frac{\hbar^2}{2} \tilde{K}\left(x_{i}^{l}, x_{j}^{l}\right) + V\left(x_{i}^{1}, x_{i}^{2}\right) \delta x_{1} x_{1} x_{2} x_{2},$$

where $\{x_{i}^{l}\}$ is the coordinate representation of the two mass-weighted modes in Fig. 10,
depicted using the index $I$ and the kinetic energy operator $\tilde{K}(x_i^I, x_j^I)$ is represented in each mass-weighted dimension using distributed approximating functionals (DAFs),\textsuperscript{74–77}

$$\tilde{K}(x_i, x_j) = \frac{1}{\sigma \sqrt{2\pi}} \left( -\frac{1}{\sqrt{2\sigma}} \right)^2 \exp \left( -\frac{(x_i - x_j)^2}{2\sigma^2} \right) \sum_{n=0}^{M/2} \left( -\frac{1}{4} \right)^n \frac{1}{n!} H_{2n+k} \left( \frac{x_i - x_j}{\sqrt{2\sigma}} \right).$$ \text{ (19)}

The $H_{2n+k}$ are Hermite polynomials. The potential energy,

$$V(x_i^1, x_j^2) \equiv \langle V(x_i^1, x_j^2; R_C) \rangle_{Q_C}$$ \text{ (20)}

represents the reduced dimensional potential energy surface computed from the ensemble averaged classical AIMD data (left column of Fig. 10) constructed the same way as the classical distribution functions shown in the central column of Fig. 10. The subscript $Q_C$ represents the fact that all other coordinates orthogonal to $X_{\text{freq}}^\text{OXA-S-COC-S}$ and $X_{\text{freq}}^\text{S-S freq}$ are averaged to obtained the reduced dimensional potential. The Hamiltonian in Eq. (18) is diagonalized using an efficient iterative Arnoldi iterative diagonalization scheme\textsuperscript{31,73,78–81} to obtain the lowest quantum eigenstates. The resultant eigenstates from Eq. (18) are used to make qualitative comparisons with the classical distribution.

The resultant quantum zero-point eigenstates are shown on the right column of Fig. 10. These modes are essentially the coupled anharmonicity corrected modes in this two-dimensional representation. The correlated behavior discussed above is generally consistent between the classical and quantum treatments. That is, in both cases the low temperature distribution shows that the two modes are correlated and this is displayed by the tilted diagonal distribution for the 39K and 68K results in Figure 10. In addition, the delocalization is roughly comparable in both cases. However, there are differences between the quantum and classical distributions as well such as the orthogonal spread in the top two panels of Fig. 10 and the difference in confinement in the bottom panels. While these differences do not change the qualitative result that shows how the two modes are correlated at lower temperatures, a detailed analysis of the differences between the quantum and classical distributions will be conducted in a future publication\textsuperscript{82}.  

29
VI. CONCLUDING REMARKS

In this publication we have investigated the temperature-dependent effects of H/D isotopic substitution on an organic dimer bound with a short, strong hydrogen bond, using multiple experimental and computational techniques. The critical interactions involved in the systems studied here are also seen in many host-guest systems\textsuperscript{22}, where hydrogen bond modulation allows complex molecular hosts to selectively bind a variety of molecular guests. Similar systems have been used as models to understand the role of secondary isotope substitution in modulating vibrational energy flow in enzyme active sites\textsuperscript{23}. When the R-group is a hydrogen atom, the system studied represents the well-known Zundel cation\textsuperscript{18–21} which plays an important role in proton transfer in condensed phase systems.

We find that when the proton in the intermolecular hydrogen bond is exchanged by a deuteron, qualitative changes are observed in the infrared spectra across a broad range of temperatures. The AIMD simulations reveal that for both isotopologues, the temperature-dependent changes in the spectra can be understood in terms of increased sampling of the anharmonic regions of the potential energy surface with increasing temperature. Harmonic decomposition analysis further reveals that the qualitatively different trends observed upon isotopic substitution can be understood in terms of the different mode-couplings in the H-bound and D-bound systems.

A key result of this work is that we have shown that a single potential energy surface is sufficient to computationally reproduce measured vibrational spectra recorded at different temperatures using different experimental schemes, including the effects of isotopic substitution, with temperature as the only independent parameter. This speaks to the robustness of the AIMD method for this sort of study, and shows that it can be a valuable tool for understanding complicated spectra that are not amenable to analysis using typical methods. Furthermore, the harmonic decomposition techniques applied here allowed us to examine the changes in the contributions of the various normal modes in different spectral regions as a function of temperature, and thereby to understand the observed differences between the spectra of the H-bound and D-bound systems. Specifically, the normal modes involving the stretching motion of the intermolecular H/D-bond, labeled $X_{\text{freq}}^{\text{OXO}_{A,S}-\text{COC}_{S,S}}$ and $X_{\text{freq}}^{\text{X}_{\parallel}-\text{COC}_{S,S}}$, show drastically different behavior. In the deuteron bound case, virtually all of the infrared intensity is carried by a single mode $D_{665}^{\text{ODO}_{A,S}-\text{COC}_{S,S}}$, which starts out as a spectrally local-
ized peak at low temperatures, but rapidly becomes delocalized with increasing temperature, until at 390K it extends across the entire measured spectral region from 600-1600 cm$^{-1}$. On the other hand, the $D_{861}^{\parallel} - COC_S$ mode stays fairly localized in the spectrum at all temperatures. Analysis of the integrated contributions of these modes to the spectral region between 600-860 cm$^{-1}$ indicates that there is temperature-dependent repartitioning of the energy in the $D_{665}^{ODO_A} - COC_S$ and $D_{861}^{D_D} - COC_S$ modes, with the contribution from the latter becoming dominant at high temperatures. This “cross-over” occurs at the same temperatures corresponding to a blue shift of the infrared band in the same spectral region, providing some evidence that the coupling between the 665cm$^{-1}$ and 861cm$^{-1}$ modes may be responsible for the blue shift; a hypothesis which will be further investigated in a future publication. Moreover, the fact that these two modes are coupled through anharmonicity is confirmed through reduced dimensional quantum nuclear calculations, where the distribution functions are in agreement with the classical AIMD calculations.

The situation is completely different in the proton-bound case, where both the $H_{788}^{OHO_A} - COC_S$ and $H_{940}^{H_D} - COC_S$ contribute to the spectral intensity at all temperatures. While these modes exhibit some spectral delocalization with increasing temperature, it is not nearly as pronounced as for the deuteron-bound case. This tends to suggest that the coupling between these modes is much less pronounced than in the D-bound system. One additional point is that both systems show qualitatively similar temperature-dependent trends for the weakly-contributing bath modes.

Finally, there appears a parallel between the temperature dependent spectral broadening process seen here and the idea of spectral diffusion in condensed phases where energy deposited in a particular mode gets dissipated into the bath modes. The upshot of this analysis is that the strongly anharmonic nature of the intermolecular potentials in these proton-bound systems leads to facile coupling of the shared H/D stretch to the harmonic modes of the monomer backbones. As we have seen, this can lead to qualitatively different behavior upon deuteration, which has general ramifications for H-D exchange process.

Acknowledgments

This research is supported by the National Science Foundation grant NSF CHE-0750326 (SSI) and the Arnold and Mabel Beckman Foundation (SSI). Author XL acknowledges sup-
port from the David Rothrock foundation. Author DTM acknowledges Professors Gerard Meijer and Gert von Helden for providing access to the FELIX (free-electron LASER) facility at FOM Institute for Plasma Physics 'Rijnhuizen', Nieuwegein, Netherlands. The IRMPD experiments discussed here were performed at the FELIX facility. The authors are indebted to Professor Mark Johnson for providing electronic versions of his published experimental data (the Argon-tagged trace in Figures 1-4) and for fruitful discussions during the course of the development of this manuscript. The simulations in this manuscript were conducted on the Indiana University supercomputer facilities Bigred and Quarry. Funding for these facilities is provided through National Science Foundation Grants ACI-0338618, OCI-0451237, OCI-0535258, and OCI-0504075 and is duly acknowledged.

52 D. A. McQuarrie, Statistical Mechanics (University Science Books, Sausalito, CA, 2000).
59 J. Jortner and R. Levine, Adv. Chem. Phys. 47 (Part 1), 1, OPTmonth = , OPTnote = ,

83 See Supplementary Material Document No. —— for absolute $C^{[01,02]}_i$ contributions (Eq. (10)).

For information on Supplementary Material, see http://www.aip.org/pubservs/epaps.html.
<table>
<thead>
<tr>
<th>Frequency (cm$^{-1}$)</th>
<th>39K</th>
<th>68K</th>
<th>109K</th>
<th>272K</th>
<th>390K</th>
</tr>
</thead>
<tbody>
<tr>
<td>IRMPD</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>