Electronic Supplementary Information

Large Amplitude Motion in Cold Monohydrated Dihydrogen Phosphate Anion H$_2$PO$_4^-$ (H$_2$O): Infrared Photodissociation Spectroscopy combined with Ab Initio Molecular Dynamics Simulations

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1. Experimental and Computational Details

A. Experimental methods

IRMPD experiments are carried out using an ion trap/tandem mass spectrometer.\textsuperscript{1,2} Briefly, gas-phase ions are continuously produced in a commercial Z-spray source from a 1 x 10\textsuperscript{-3} M aqueous solution of phosphate acid in a 1:1 water/acetonitrile solvent. A beam of negative ions passes through a 4 mm diameter skimmer and is then collimated in a radio frequency (RF) decapole ion guide. Parent ions are mass-selected in a quadrupole mass filter, deflected by 90° in an electrostatic quadrupole deflector and focused into a gas-filled RF ring electrode ion trap. To allow for continuous ion loading and ion thermalization, the trap is continuously filled with He gas at an ion trap temperature of 15 K, which is maintained by the cold head of a Sumitomo Heavy Industries closed cycle He cryostat. After filling the trap for 98 ms, all ions are extracted from the ion trap and focused both temporally and spatially into the center of the extraction region of an orthogonally mounted linear time-of-flight (TOF) mass spectrometer. Here, the ion packet is irradiated with the IR laser pulse prior to the application of high-voltage pulses on the TOF electrodes and the subsequent measurement of the TOF mass spectrum.

IR spectra in the 600–1800 cm\textsuperscript{-1} region are measured by the Free Electron Laser for Infrared eXperiments (FELIX) facility\textsuperscript{3} at the FOM Institute Rijnhuizen (The Netherlands) and those in the 2700–3900 cm\textsuperscript{-1} region using a Laservision OPO/OPA IR laser\textsuperscript{4} and a Herriott-type multipass cell\textsuperscript{5-8} in Berlin. FELIX is operated at 10 Hz with a bandwidth of ~0.2% RMS of the central wavelength and typical pulse energies of up to 30 mJ. The Laservision OPO/OPA IR laser produces 7 ns / 2 mJ pulses at 10 Hz with a spectral bandwidth of ~2 cm\textsuperscript{-1} and the laser wavelength is calibrated using a photoacoustic cell filled with methane. The photodissociation cross section $\sigma$ is determined from the relative abundances of the parent and photofragment ions, $I_0$ and $I(\nu)$, and the frequency dependent laser power $P(\nu)$ using $\sigma = -\ln[I(\nu)/I_0]/P(\nu)$\textsuperscript{9}.

B. Computational methods
Optimized structures and harmonic frequencies are obtained from standard density functional theory (DFT) calculations, using the Gaussian 03 package. The dynamic motion of the clusters are simulated by the Ab Initio Molecular Dynamics (AIMD) method, in which the atoms are treated as classical particles and the potential energy and forces on the atoms are calculated within the framework of DFT at each time step.

For 0 K structure, energy optimization is performed at the level of B3LYP/6-311++G(d, p) by Gaussian 03 package. Initial structures are generated by running molecular dynamic simulations over tens of thousands time steps at 200 K and taking random configurations along the trajectories. Harmonic frequencies are calculated by using a larger basis set, at the level of MP2=full/aug-cc-pVDZ. Scale factor is used to facilitate the comparison between the experimental and theoretical peak positions. In the high frequency region, the MP2 value for peak A is aligned to the experimental position, yielding a scale factor of 0.9646. In the low frequency region, the MP2 value for peak G is aligned, giving a scale factor of 0.9993. The resulting stick spectra are convoluted using a Gaussian line shape function with a fwhm width of 4 cm\(^{-1}\) to account for the laser bandwidth, as well as broadening due to rotational excitation.

CP2K package is employed for the AIMD simulations. The wave functions are expanded in a double zeta Gaussian basis set, while the electron density is expanded in Gaussians and auxiliary plane waves with an energy cutoff at 320 Rydberg for the electron density for the long 200 ps run. The atomic cores are modeled by the Goedecker-Teter-Hutter (GTH) type pseudopotentials. The exchange and correlation energy is calculated by PBE functional, with additional Grimme’s dispersion correction at D3 level, which produces harmonic frequencies in better agreement with experiment in our test calculations. A scaling factor of 1.0100 for is used for the low frequency region with respect to experimental peak G, and 0.9830 for the high frequency region with respect to experimental peak A.

A cluster ion is put at the center of a periodic cubic box, and the effects of the periodic charge density images are corrected by the decoupling technique developed by Martyna and Tuckerman. The box length is 16 Å for (HO)\(_2\)PO\(_2\)\(^-\)(H\(_2\)O). The convergence criterion for the SCF electronic procedure is set to be 10\(^{-7}\) a.u. at each time step. For molecular dynamics at a specific temperature, the temperature is controlled by a
Nose-Hoover thermostat,\textsuperscript{13,14} with a time step of 0.5 fs. An equilibration period of up to 10 ps (10ps trajectory) is performed first, with the temperature scaled to an interval of 20 K around the intended value. A data collection run is then followed in the NVE ensemble. Two sets of long AIMD simulations (140 K and 180 K) were performed, for a more extensive sampling of the phase space. At each temperature, two trajectories were simulated, one starting with 1-1 and the other with 1-2, each lasting 200 ps (200ps trajectory). Each trajectory was then cut into 10 ps interval for Fourier transform, and all 40 frequency profiles were then added up to produce the DTCF spectrum for a specific temperature.

Hydrated clusters are bound by hydrogen bonds, which are relatively weak and therefore fairly flexible at finite temperature. Dynamic simulations are essential for sampling the solvation structures and for examining the thermal stability of a particular structure. More importantly, the hydrogen bonds could have strong effects on the vibrations, which could be captured by the AIMD simulations. A vibrational spectrum can be directly simulated by the Fourier transformation of the dipole time-correlation function (DTCF),

\[ \alpha(\omega) = \frac{2\pi \beta \omega^2}{3 n(\omega) c V} \int_{-\infty}^{+\infty} dt \langle \vec{M}(t) \cdot \vec{M}(0) \rangle \exp(i \omega t) \]

where \( \beta = 1/kT \), \( n(\omega) \) is the refractive index, \( c \) is the speed of light in a vacuum, \( V \) is the volume, \( \vec{M} \) is the total dipole moment of the system calculated directly from first principles within the Berry phase scheme.\textsuperscript{15}

The vibrational density of state (VDOS) could also be easily obtained by the Fourier transform of the velocity time correlation function,

\[ VDOS(\omega) = \sum_{i=1}^{N} \int_{-\infty}^{+\infty} dt \langle \vec{v}_i(t) \cdot \vec{v}_i(0) \rangle \exp(i \omega t) \]

with the summation typically going over all atoms in a cluster. VDOS is not directly proportional to the signal intensity measured in a vibrational spectrum, which is determined by the dipole selection rule. But when the summation is restricted to one single atom, the total VDOS could then be decomposed into the contribution from this particular atom, which is helpful for the assignment of a vibrational spectrum.
References:


Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.


(15) Shapere, A.; Wilczek, F. Geometric Phases in Physics. World Scientific,
2. Supplementary Table and Figures

Table S1. Assignment for the IR spectra of H$_2$PO$_4^-$($\text{H}_2\text{O}$)$_{0,1}$ shown in Figures 1 and 2.

<table>
<thead>
<tr>
<th>Label</th>
<th>H$_2$PO$_4^-$</th>
<th>H$_2$PO$_4^-$($\text{H}<em>2\text{O}$)$</em>{0,1}$</th>
<th>Assignment</th>
</tr>
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<td>Exp. MP2 Harmonic</td>
<td>Exp. MP2 Harmonic (isomer)</td>
<td>1-1+1-2 (180K)</td>
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<tr>
<td>A</td>
<td>- -</td>
<td>3684 (1-1) 3684(1-2)</td>
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<tr>
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<td>- -</td>
<td>3546 (1-2) 3504</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>- -</td>
<td>3410-3520 (1-1) 3479 3453</td>
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</tr>
<tr>
<td>D</td>
<td>- -</td>
<td>3382 -</td>
<td>3380</td>
</tr>
<tr>
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<td>- -</td>
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</tr>
<tr>
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<td>2700-3100 (1-2) 2600-3100</td>
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</tr>
<tr>
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<td>L</td>
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<td>793 (1-1) 744(1-2) 720 740(1-2)</td>
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</table>
Fig. S1. Comparison of experimental spectrum of H$_2$PO$_4$·(H$_2$O) (bottom row) to simulated MP2 harmonic spectra of the isomers 1-1 and 1-2 (upper rows) in the high frequency region.
Fig. S2. Comparison of experimental spectrum of H$_2$PO$_4^-$($\text{H}_2\text{O}$) (bottom row) to simulated MP2 harmonic spectra of the isomers 1-1 and 1-2 (upper rows) in the low frequency region.
Fig. S3. Comparison of the experimental IRMPD spectrum of H$_2$PO$_4$ (H$_2$O) (bottom) to simulated DTCF spectra of isomers 1-1 and 1-2 at 140 K (200 ps trajectory) and 180 K (200 ps trajectory) (top).
**Fig. S4.** Time evolution of (a) H10…O3 and (b) H9…O2 distances for 1-1, and (c) H7…O8 and (d) H9…O3 distances for 1-2, both at 60 K (10 ps trajectory).
**Fig. S5.** Structural transformation observed for 1-1 in an AIMD simulation at 140 K (10 ps trajectory). Within 1 ps, the O8-H9…O2 hydrogen bond is broken, while at the same time, the PO4-H6…O8 bond is formed, and the O8-H10…O3 bond is strengthened, forming a 1D+1w structure which is maintained to the end of the 10 ps simulation.
Fig. S6. Simulated MP2 harmonic spectra of isomer 1-2 obtained from partial optimization of geometrical structures by constraining the O3---H9 hydrogen bond at different distances (see Fig. 3 for the specified atoms).
Fig. S7. Simulated DTCF spectra of isomers 1-1 and 1-2 at 140 K (200 ps trajectory) and 180 K (200 ps trajectory).
Fig. S8. Simulated MP2 harmonic spectra of first order transition stat (1-3) obtained from partial optimization of geometrical structures by constraining the O3---H9 hydrogen bond at different distances (see Fig. 3 for the specified atoms).