Electronic Supplementary Information:
Anharmonicities and coherent vibrational dynamics of phosphate ions in bulk H$_2$O

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Table S1: IR frequencies of the H$_2$PO$_4^-$ x 5H$_2$O water cluster

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1 **H$_2$PO$_4^-$×xH$_2$O cluster geometries**

Fig. S1 shows the geometries of H$_2$PO$_4^-$×xH$_2$O clusters for (a) $x$=7 without symmetry restriction and (b) $x$=5 for $C_2$ symmetry.

![Fig. S1 Structures of H$_2$PO$_4^-$×xH$_2$O, x= 5, 7 water clusters: (a) $x$ = 7, $C_1$ symmetry; (b) $x$ = 5, $C_2$ symmetry.](image)

2 **Pump-probe data of ν$_{AS}$(P-(OH)$_2$)**

In order to extract the vibrational lifetime, we performed pump-probe experiments on ν$_{AS}$(P-(OH)$_2$) using pulses with a bandwidth of 160 cm$^{-1}$ (FWHM) centered at 960 cm$^{-1}$ (cf. Fig. S2). Transient spectra at early delay times consist of reduced absorption signal centered around 955 cm$^{-1}$ due to ground state bleach and stimulated emission after excitation of the ν=1 state, whereas the red-shifted enhanced absorption is caused by the excited state absorption. Vibrational lifetimes are extracted from the decay of the excited state absorption at 928 cm$^{-1}$ (Fig. S2b) that shows a characteristic time constant of 450 fs.

Note that transient spectra at a delay time of 2 ps show a residual absorbance change consisting of an enhanced absorption in the red and a reduced absorption in the blue part of the spectrum. Such signals remain constant on a picosecond timescale and are a hallmark of weakened phosphate-water hydrogen bonds due to the dissipation of excess energy into the water solvent. Such a response is similar to the one of the PO$_2^-$ stretching vibrations, however, ν$_{AS}$(P-(OH)$_2$) shifts to the opposite direction, i.e., to the red. This result is in agreement with the cluster analysis that suggests a blue-shift of ν$_{AS}$(P-(OH)$_2$) upon solvation whereas the PO$_2^-$ stretching vibration shift to the red.

3 **Simulation details of nonlinear response function**

3.1 **Simulation of 2D spectra**

Linear absorption and 2D IR signals are simulated in the sum-over-states approach with the response function evaluated by the cumulant expansion of Gaussian fluctuations. We employ the Doorway-Window...
factorization\textsuperscript{4,5} of the third order response function

\[
\hat{R}(t_3,t_2,t_1) = R^{(c)}(t_3,t_2,t_1) + \sum_{\mu,\nu} W_\mu(t_3) G_{\mu\nu}(t_2) D_\nu(t_1) + W_0(t_3) D_0(t_1)
\]  

(1)

where $R^{(c)}$ denotes the coherent contribution to the response function, $G_{\mu\nu}$ is the Green’s function describing exciton hopping and $W_\mu$ and $D_\nu$, as well as $W_0$ and $D_0$, represent Doorway- and Window-wavepackets, respectively. $R^{(c)}(t_3,t_2,t_1)$ is given by

\[
R^{(c)}(t_3,t_2,t_1) = R(t_3,t_2,t_1) - R(t_3,\infty,t_1).
\]  

(2)

Invoking the RWA, the coherent contributions for the rephasing photon echo signal ($k_I = -k_1 + k_2 + k_3$) are given as

\[
R^{(c)}_{k_1}(t_3,t_2,t_1) = R_I(t_3,t_2,t_1) + R_{II}(t_3,t_2,t_1) + R_{III}(t_3,t_2,t_1)
\]

(3)

\[
R_I(t_3,t_2,t_1) = -i \sum_{\mu,\nu} d_\mu d_\nu d_\nu \exp\left(-f^{(1)}_{\mu\nu}(0,t_2 + t_1,t_3 + t_2 + t_1,t_1)\right) \times \\
\exp(-i\epsilon_\mu(t_3 + t_2) + i\epsilon_\nu(t_2 + t_1))
\]

(4)

\[
R_{II}(t_3,t_2,t_1) = -i \sum_{\mu,\nu} d_\mu d_\nu d_\nu \exp\left(-f^{(1)}_{\mu\nu}(0,t_1,t_3 + t_2 + t_1,t_2 + t_1)\right) \times \\
\exp(-i\epsilon_\mu t_3 + i\epsilon_\nu t_1)
\]

(5)
\( R_{III}(t_3,t_2,t_1) = -i \{ \sum_{\mu \nu \sigma} d_{\mu \sigma} d_{\nu \sigma} d_{\nu} d_{\mu} \exp(-f^{(2)}_{\mu \nu \sigma}(t_1,t_2 + t_1,t_3 + t_2 + t_1,0)) \times \\
\exp(-ie_{\mu}(t_3 + t_2 + t_1) + i\epsilon_{\sigma}(t_3 + t_2 + t_1)) \}^* \)

where \( \mu, \nu \) and \( \sigma \) denote single and bi-exciton states, respectively, with state energies \( \epsilon_i \), dipole moments \( d_i \) and the auxiliary functions \( f^{(1)}_{\mu \nu} \) and \( f^{(2)}_{\mu \nu \sigma} \). The coherent contributions of the non-rephasing signal \( (k_{II} = +k_1 - k_2 + k_3) \) read

\[ R_{kII}^{(c)}(t_3,t_2,t_1) = R_{IV}(t_3,t_2,t_1) + R_{V}(t_3,t_2,t_1) + R_{VI}(t_3,t_2,t_1) \]  

\[ R_{IV}(t_3,t_2,t_1) = -i \sum_{\mu \nu} d_{\mu \nu} d_{\nu} d_{\nu} \exp(-f^{(1)}_{\mu \nu}(t_1,t_2 + t_1,t_3 + t_2 + t_1,0)) \times \\
\exp(-ie_{\mu}(t_3 + t_2 + t_1) + i\epsilon_{\nu}(t_2)) \]  

\[ R_{V}(t_3,t_2,t_1) = -i \sum_{\mu \nu} d_{\mu \nu} d_{\nu} d_{\nu} \exp(-f^{(1)}_{\mu \nu}(t_3 + t_2 + t_1,t_2 + t_1,t_1,0)) \times \\
\exp(-ie_{\mu}t_1 + i\epsilon_{\nu}t_3) \]  

\[ R_{VI}(t_3,t_2,t_1) = -i \{ \sum_{\mu \nu \sigma} d_{\mu \sigma} d_{\nu \sigma} d_{\nu} d_{\mu} \exp(-f^{(2)}_{\mu \nu \sigma}(t_1,t_3 + t_2 + t_1,t_2 + t_1,0)) \times \\
\exp(-ie_{\mu}(t_2 + t_1) + i\epsilon_{\sigma}(t_3 + t_2 + t_1)) \}^* \]

with \( f^{(1)}_{\mu \nu} \) and \( f^{(2)}_{\mu \nu \sigma} \) in eqs. 4-10 given by

\[ f^{(1)}_{\mu \nu} = g_{\mu \mu}(\tau_2 - \tau_1) - g_{\mu \nu}(\tau_3 - \tau_1) + g_{\mu \nu}(\tau_4 - \tau_1) \] 

\[ + g_{\mu \nu}(\tau_3 - \tau_2) - g_{\mu \nu}(\tau_4 - \tau_2) + g_{\mu \mu}(\tau_4 - \tau_3) \]  

and

\[ f^{(2)}_{\mu \nu \sigma} = g_{\mu \mu}(\tau_2 - \tau_1) - g_{\mu \sigma}(\tau_2 - \tau_1) + g_{\mu \sigma}(\tau_3 - \tau_1) - g_{\mu \nu}(\tau_3 - \tau_1) + g_{\mu \nu}(\tau_4 - \tau_1) \] 

\[ - g_{\mu \sigma}(\tau_3 - \tau_2) + g_{\mu \nu}(\tau_3 - \tau_2) - g_{\mu \nu}(\tau_4 - \tau_2) + g_{\sigma \sigma}(\tau_3 - \tau_2) - g_{\sigma \sigma}(\tau_3 - \tau_2) \] 

\[ + g_{\nu \nu}(\tau_4 - \tau_2) - g_{\nu \nu}(\tau_4 - \tau_2) + g_{\mu \mu}(\tau_4 - \tau_3). \]

Here \( g(\tau) \) denotes the lineshape functions of single \( (\mu, \nu) \) and bi-exciton \( (\sigma) \) states.

The cumulant expansion of Gaussian fluctuations formulation of the response function holds for purely diagonal frequency fluctuations with arbitrary timescales; Population relaxation can be incorporated perturbatively in the off-diagonal fluctuations by employing the Doorway-Window factorization with the Doorway-wavepacket \( D \) describing the preparation process and the Window-wavepacket \( W \) describing detection:

\[ \sum_{\mu \nu} W_{\mu}(t_3) G_{\mu \nu}(t_2) D(t_1) = -i \sum_{\mu \nu} d^2 \exp(i\epsilon_{\nu}t_1 - g_{\nu \nu}^*) G_{\mu \nu}(t_2) \times \\
\left[ \frac{d^2}{d\mu} \exp(-ie_{\mu}t_3 - g_{\mu \mu}^*) + 2i\lambda_{\mu \mu}t_3 \right] \\
- \sum_{\nu} d^2 \exp(-i(\epsilon_{\nu} - \epsilon_{\mu})t_3 - g_{\mu \nu}(t_3) - g_{\nu \nu}(t_3) + 2g_{\mu \nu}(t_3) + 2i(\lambda_{\mu \nu} - \lambda_{\nu \nu})t_3) \right] \]  

\[ (13) \]
where the exciton reorganization energy is given by
\[ \lambda_{\mu \nu} = -\lim_{\tau \to \infty} \text{Im} \left[ \frac{dg_{\mu \nu}(\tau)}{d\tau} \right]. \]  

(14)

Incoherent transport within the secular approximation is incorporated phenomenologically by the Green’s function of the generalized master equation for exciton-hopping \( G_{\mu \nu}(t_2) \) and accounts for the experimentally observed lifetime broadening \((1/k_{\mu 0} = 300 \text{ fs})\), while inter-mode transport \((k_{\mu \nu})\) is neglected. The coherent part \( R^{(c)}(t_3,t_2,t_1) \) of the response function is responsible for the observed quantum beats (cf. Fig. 5-6; Fig. S3-S5) in 2D and pump-probe signals.

The long time response
\[ R(t_3,\infty,t_1) = \sum_{\mu} W_{\mu}(t_3)D_{\mu}(t_1) + W_0(t_3)D_0(t_1) \]  

(15)

with
\[ \sum_{\mu} W_{\mu}(t_3)D_{\mu}(t_1) = -i \sum_{\mu} d_{\mu}^2 \exp(i\epsilon_{\mu}t_1 - g^{*}_{\mu \mu}(t_1))\{d^2 \exp(-i\epsilon_{\mu}t_3 - g_{\mu \mu}(t_3) + 2i\lambda_{\mu \mu}t_3) \]
\[ -\sum_{\nu} d_{\mu \nu}^2 \exp(-i(\epsilon_{\nu} - \epsilon_{\mu})t_3 - g_{\mu \nu}(t_3) - g_{\nu \nu}(t_3) + 2g_{\mu \nu}(t_3) + 2i(\lambda_{\mu \nu} - \lambda_{\mu \mu})t_3) \]  

(16)

and
\[ W_0(t_3)D_0(t_1) = -i \sum_{\mu \nu} d_{\mu}^2 d_{\mu \nu}^2 \exp(i\epsilon_{\mu}t_1 - g^{*}_{\nu \nu}(t_1)) \exp(-i\epsilon_{\mu}t_3 - g_{\mu \mu}(t_3)) \]  

(17)

has minor contributions for the evaluated delay times < 1 ps. The delay time \( T \) used in the main paper corresponds to \( t_2 \). 2D absorptive signals are obtained by a 2D Fourier transform of the time-domain response function \( \hat{R}(t_3,t_2,t_1) \) followed by summation of the real parts of the rephasing and non-rephasing signals\(^6,7\).

**Lineshape function \( g(t) \):**

The lineshape function of the over damped Brownian oscillator (OBO) model in the high temperature limit is given by\(^3\)
\[ g(t) = \frac{2\lambda k_B T}{\hbar \Lambda^2} \left[ \exp(-\Lambda t) + \Lambda t - 1 \right] \]
\[ -i\left( \lambda / \Lambda \right) \left[ \exp(-\Lambda t) + \Lambda t - 1 \right]. \]  

(18)

By assuming a real valued classical frequency-frequency correlation function (main text, eq.1) the OBO model can be simplified to the stochastic Kubo model\(^8\). For the parametrization of eq. 18 we fit the parameters (oscillator timescale \( \Lambda \), fluctuation bandwidth \( \delta \nu_{\text{hom}} \)) of a Kubo model with static offset \( \delta \nu_{\text{stat}} \) to the frequency-frequency fluctuation correlation function directly calculated from the fluctuations of instantaneous frequencies of the hybrid QM/MM trajectory (cf. Ref. 1, \( \Lambda = 50 \text{ fs} \)). By recognizing the relation \( \lambda = \delta \nu_{\text{hom}}^2/2k_B T \) the OBO model can be fully parametrized from the instantaneous frequency fluctuations of the classical trajectories. The derived (static) inhomogeneous contribution is used for the generation of random single-exciton Hamiltonians centered around the single exciton transition frequency \( \omega_0 \) with Gaussian width \( \delta \nu_{\text{i,stat}} \).
3.2 Lineshape analysis of diagonal peaks

In section 2.2.1 of the main paper, we analyze the frequency fluctuations of $v_{AS}(P\text{-}(OH)_2)$ by fitting the calculated third-order nonlinear response to the experimental spectra. For the calculation we use the six Feynman diagrams that describe the rephasing (eq. 19) and non-rephasing (eq. 20) contribution to the GSB, SE and ESA $^{3,7}$. The used response functions reads

$$R_{I,II,III}(\tau,T,t) = \left(e^{-i\omega_{01}(t-\tau)} - e^{-i((\omega_{01} - \Delta)t - \omega_{01}\tau)}\right) e^{-(\tau+t)/(2T_1)} e^{-(\tau+t)/T_2^*}$$

$$e^{-T/T_1} \cdot e^{-g(t) + g(T) - g(t) - g(t) - g(T) + g(T + t)}$$

and can be obtained from the formalism described in $^{2,3,5}$ and outlined above by neglecting transport contributions. Here, $\omega_{01}$ is the transition frequency corresponding to 940 cm$^{-1}$, $\Delta$ is the anharmonicity (12 cm$^{-1}$), $T_2^*$ is the pure dephasing time used as a fit parameter, $T_1$ is the vibrational lifetime (450 fs), and $g(t)$ is the line shape function of the Kubo model. Since the latter is only used to describe the minor inhomogeneous broadening, the single free parameter is the distribution of frequencies $\Delta \omega_{inh}$: $g(t) = \Delta \omega^2_{inh} t^2/2$.

4 Coherent wave packet dynamics

4.1 Pump probe: Beating of PO$_2^-$ modes

In the manuscript we followed the wave packet dynamics of $v_5(PO_2^-)$ and $v_{AS}(PO_2^-)$ through the relative amplitudes of 2D cross peaks. Pump-probe data as presented in ref. 1 with a better sampling of the delay times provides additional proof of the underlying dynamics. The oscillatory contribution to the signals at a frequency of 1170 cm$^{-1}$ are shown in Fig. S3a which presents residuals of a multiexponential fit to the experimental data (cf. inset). The power spectrum of the oscillatory feature has a peak at $\approx 90$ cm$^{-1}$, corresponding to the difference frequency of $v_5(PO_2^-)$ and $v_{AS}(PO_2^-)$.

4.2 Decomposition of 2D spectra into rephasing and non-rephasing components

Experimental absorptive 2D spectra are decomposed into the underlying rephasing and nonrephasing spectra in Fig. S4. All spectra were normalized to a 300 fs decay corresponding to the vibrational lifetime of $v_5(PO_2^-)$ and $v_{AS}(PO_2^-)$. The same scale was used for absorptive, rephasing and non-rephasing spectra to facilitate a direct comparison of the different signal contributions. The tilt of the cross peaks shown in the absorptive spectra (Fig. 5, main paper) can be rationalized by the time-dependent cross peak amplitude in the rephasing signal.

For $T = 0$ fs the tilt of SE and ESA cross peaks relative to the $v_1$ axis originates from the tilting of the rephasing cross peak with respect to the $v_1$ axis while the non-rephasing cross peak appears upright. For increased waiting time ($T = 100$ fs) the rephasing cross peak intensity is reduced leading to a reduced cross peak tilt in the absorptive 2D signal. The reversed tilt for $T=200$ fs arises from the interplay of signal evolution in rephasing and non-rephasing contributions: the rephasing cross peak intensity reaches its minimum while non-rephasing cross peak intensity appears practically constant. Accordingly the non-rephasing contribution with anti-diagonal tilt becomes the dominant contribution to the absorptive cross-
Fig. S 3 Extraction of the oscillatory part in $\nu_{AS}(\text{PO}_2^\text{−})$. (a) Oscillatory part of the pump-probe signal measured at 1170 cm$^{-1}$ which was extracted by subtracting a multi-exponential fit from the total pump-probe response (cf. inset, experiment: symbols, multiexponential fit: red line). (b) Normalized power spectrum of the Fourier transform of the oscillatory signal.
Fig. S4 Dissection of the oscillatory part in crosspeak (ν₁, ν₃)=(νₛ(PO₂⁻), νₐₛ(PO₂⁺)): (a) absorptive 2D signal, (b) rephasing 2D signal, (c) non-rephasing 2D signal for delay times T = 0, 100, 200, 300 fs, respectively. The signals have been normalized to a 300 fs decay imposed by the lifetime of νₛ(PO₂⁻) and νₐₛ(PO₂⁺) modes. The boxes in the first panel of each row enclose the cross peaks shown in Fig. 5 of the manuscript.

peak for T=200 fs. As the rephasing cross peak intensity increases again for T=300 fs the opposite tilts of rephasing and non-rephasing cross peaks cancel and the absorptive 2D signal appears upright.

4.3 Coherent oscillations in the reduced two-state model

Fig. S5 presents 2D spectra of the reduced model which takes into account energy levels of νₐₛ(PO₂⁻) and νₐₛ(PO₂⁺) stretching modes together with the dark Fermi-resonance mode and neglects contributions of bending modes (δₐₛ(P-(OH)₂), δₛ(P-(OH)₂)) and the νₐₛ(P-(OH)₂) stretching mode. The reduced model is designed to closely resemble the experimental excitation conditions which due to the limited spectral bandwidth of pulses coherently excite νₐₛ(PO₂⁻) and νₐₛ(PO₂⁺) stretching modes only. The inlay shows coherent beating of diagonal (dashed) and off-diagonal peaks (solid) at the position of the ESA and SE contribution together with their Fourier transform. The coherent beating at different positions (diagonal and off-diagonal peaks) arise from the non-rephasing and rephasing contributions to the absorptive signals.
Fig. S 5 2D spectra of the reduced model consisting of $v_{AS}(PO_2^-)$ and $v_{AS}(PO_3^-)$ stretching modes together with the dark Fermi-resonance mode for waiting time $T = 0, 100, 200, 300$ fs. The inlay shows coherent beating of diagonal (dashed) and off-diagonal peaks (solid) at the position of the ESA and SE contribution together with the normalized power spectrum of the Fourier transform of the oscillatory signal.

References

Table. S1 Calculated IR frequencies and intensities of H$_2$PO$_4^-$ (in cm$^{-1}$): top - mean instantaneous frequencies from hybrid QM/MM trajectory; bottom - H$_2$PO$_4^- \times 5$ H$_2$O on VSCF / DFT(PBE0) level of theory (C$_2$ symmetry); Basis: 6-311++G(d,p) diagonal anharmonicity: $\Delta_{20} = 2 * \nu_{\text{VSCF/VCI}}(v=0\rightarrow1) - \nu_{\text{VSCF/VCI}}(v=0\rightarrow2)$; $^a$ VSCF (VCI) level of theory.

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<th>VSCF</th>
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