Ultrafast vibrational dynamics of aqueous acetate and terephthalate

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Abstract

We study the vibrational population relaxation and mutual interaction of the symmetric stretch (v_s) and antisymmetric stretch (v_{as}) stretch vibrations of the carboxylate anion groups of acetate and terephthalate ions in aqueous solution with femtosecond two-dimensional infrared spectroscopy. By selectively exciting and probing the v_s and v_{as} vibrations, we find that the interaction of the two vibrations involves both anharmonic coupling of the vibrations and energy exchange between the excited states of the vibrations. We find that the vibrational population relaxation and the energy exchange are both faster for terephthalate than for acetate.

I. INTRODUCTION

Ultrafast infrared spectroscopy enables the time-resolved study of the vibrational dynamics of molecules in complex and heterogeneous condensed phases. This technique has thus been widely employed to investigate the properties of different functional groups, and their interaction with their local molecular-scale environment¹⁻⁴. One of the most abundant functional groups in (bio)chemical species is the carboxylate group (-COO⁻). This functional group is often present in small biologically active molecules and in the side-chains of polymers, determining their geometry and charge, and thus playing a crucial role in various (bio)chemical processes 5-9. The carboxylate group also strongly interacts with metal cations, leading to the formation of metal carboxylates with characteristic coordination numbers. These metal-carboxylate complexes often show important catalytic and photocatalytic activity^{10,11}. The carboxylate (-COO⁻) group has two coupled vibrational modes: the symmetric C-O stretch vibration (v_s) and the antisymmetric C-O stretch vibration (v_{as}) , both absorbing in the 6 μ m region of the spectrum. These two vibrations are delocalized over the carboxylate group as a result of the sharing of negative charge by the two oxygen atoms thus making the oxygen atoms equivalent in their binding to the carbon atom. An interesting example of metal-carboxylate complexes are metal organic frameworks (MOFs). In many MOFs, the terephthalate (1,4 - benzenedicarboxylate) dianion and its derivatives play a crucial role as the linker between positively charged metal ions¹²⁻¹⁶. The terephthalate moiety also forms a crucial constituent of commercially produced polyesters such as polyetheleneterephthalate (PET)¹⁷. Another important carboxylate species is acetate (CH₃COO⁻). Acetate is widely used in organic synthesis reactions^{18,19}, and plays an important role in many biological processes²⁰. The vibrational dynamics of small carboxylates has been investigated with ultrafast infrared spectroscopy techniques, including pump-probe spectroscopy and two-dimensional infrared spectroscopy $(2D-IR)^{21-25}$. These studies focused on the solvation structure of the ions, their conformation, the interactions with other ions, and on the coupling of the carboxylate stretch vibrations to the C-H vibrations. It was also reported that the v_s and v_{as} modes of acetate are coupled^{23,24}. However, the precise nature of this coupling could not be studied in detail as these studies were either performed with pump-probe spectroscopy using the same broadband midinfrared laser pulse for excitation and detection of the separate vibrations²³, or involved a 2D-IR spectroscopic study of only the v_{as} mode²⁴. Here we report on of acetate and terephthalate ions in aqueous solution with femtosecond 2D-IRspectroscopy over a wide frequency range, covering both the absorption spectra of the v_s and v_{as} modes. In this study, we selectively excite and probe the different vibrational modes and measure the dynamics of the resulting nonlinear absorption signals with sub-picosecond time resolution. By measuring the dynamics of the transient absorption changes for different combinations of excited and detected vibrations, we identify the mechanisms by which the two modes interact with each other.

II. MATERIALS AND METHODS

We prepared aqueous solutions of 0.1 M sodium acetate (Sigma-Aldrich anhydrous for molecular biology, 99.9%) and 0.05 M disodium terephthalate (TCI, >99.0%) by mixing the appropriate amounts of salt with D₂O (Aldrich, 99.9 atom % D). We use D₂O instead of H₂O in order to avoid strong absorption of the bending mode of H₂O (δ_{H_2O}) in the absorption region of the v_{as} vibration of the carboxylates. The sample cell consisted of two circular 2 mm thick CaF₂ windows (Crystran) that are separated by a 25 μm thick PTFE spacer.

We recorded linear infrared absorption spectra with a commercial Bruker Vertex 80v Fourier-transform infrared spectrometer with a resolution of 2 cm⁻¹ in transmission geometry. An empty cell containing just the two CaF₂ windows was used for background measurements. To perform 2D-IR measurements, we generated ~250 cm⁻¹ FWHH pulses in the 6 μ m region. We probed the frequency regions near 1400 cm⁻¹ and near 1575 cm⁻¹ corresponding to the center frequencies of the v_s and v_{as} modes, respectively. A detailed description of the two-color time-domain 2D-IR setup can be found in previous studies²⁶. Briefly, we use a Coherent Legend Elite amplifier seeded by a Coherent Mantis oscillator. The amplified 800 nm pulses are used to pump two commercial Coherent TOPAS prime optical parametric amplifiers (OPA) both generating signal and idler pulses. Subsequently two home-built AgGaS₂ based difference-frequency generation (DFG) stages are used to generate mid-infrared excitation and detection pulses. The output of one of the OPA-DFG setup is used as the excitation pulse. This pulse has an energy of $\sim 20 \ \mu$ J and is sent into a Mach-Zehnder interferometer to obtain a pulse pair with a controlled mutual delay t. The output of the other OPA-DFG setup is used as the detection pulse. This pulse has an energy of $\sim 2 \mu J$ and is split into a probe and a reference pulse. The probe pulse is sent through a motorized delay stage to delay this pulse by a time T with respect to the central time of the excitation pulse pair. The excitation pulse pair and the probe pulse are focused in overlap in the sample, while the reference pulse is passing at a slightly different spot. When entering the sample, the polarization direction of the detection pulse is at an angle of 45° with respect to the polarization direction of the two excitation pulses. After the sample, the probe and the reference beams are recollimated and the probe beam is split into two beams each of which is sent through a wire-grid polarizer. One of the polarizers is set parallel to the polarization of the excitation pulses, while the other is set perpendicular to the polarization of the excitation pulses. The two mutually perpendicularly polarized probe pulses and the reference pulse are detected by a 3×32 liquid nitrogen cooled mercury-cadmium telluride (MCT) array. The excitation pulse pair excites a few percent of the studied species to the first excited vibrational state, the probe pulse is used to monitor the transient absorption changes $\Delta \alpha$ resulting from this excitation. The reference pulse is used to correct the signals for pulse-to-pulse energy fluctuations. The transient absorption is recorded as a function of the probe frequency $\omega_{detection}$, the time t between the two excitation pulses, and the waiting time T between the probe and the static arm of the interferometer output. By performing a Fourier transform with respect to t, we obtain the dependence of the transient absorption changes on the excitation frequency $\Delta \alpha(\omega_{detection}, \omega_{excitation}, T)$. By detecting probe pulses that are polarized parallel and perpendicular to the polarization of the pump, $\Delta \alpha_{\parallel}$ and $\Delta \alpha_{\perp}$ are obtained. These two transient absorption signals are used to construct the isotropic transient absorption: $\Delta \alpha_{iso} = (\Delta \alpha_{\parallel} + 2\Delta \alpha_{\perp})/3$ the dynamics of which represents the vibrational relaxation. The two transient absorption signals are also used to construct the anisotropy of the signals: $R = (\Delta \alpha_{\parallel} - \Delta \alpha_{\perp})/3\Delta \alpha_{iso}$.

III. RESULTS

In Fig. 1 we show IR absorption spectra of solutions of sodium acetate and disodium terephthalate in D₂O. Acetate shows absorption bands centered at 1415 cm⁻¹ and 1565 cm^{-1} , corresponding to the v_s and v_{as} vibrations of the carboxylate group. The IR absorption spectrum also shows a weak band at 1350 cm⁻¹ corresponding to the CH₃ deformation vibration of acetate²⁷. For terephthalate, we observe



FIG. 1. a. Chemical structures of acetate and terephthalate anions; b. Linear infrared absorption spectra of solutions of 0.1 M sodium acetate and 0.05 M disodium terephthalate in D_2O .

absorption bands centered at 1380 cm⁻¹ and 1575 cm⁻¹, corresponding to the v_s and v_{as} vibrations of the carboxylate group. In addition, the spectrum contains a band at 1508 cm⁻¹ band that corresponds to a skeletal deformation of the aromatic ring¹⁷. Potentially, for terephthalate the absorption bands of the v_s and v_{as} vibrations could have been split due to coupling of the two carboxylate groups of the terephthalate anion^{17,22}. However, in view of the symmetry of terephthalate the in-phase v_s and the out-of-phase v_{as} vibrations are expected to have a negligible transition dipole moment, since the vibration-induced modulations of the dipole moment of the two carboxylate groups cancel each other²². As a result, only the out-of-phase v_s and the in-phase v_{as} vibrations are clearly visible in the spectrum.

In Fig. 2 we show two-dimensional spectra of a sodium acetate(a,b) and a disodium terephthalate solutions (c,d). The blue regions correspond to a negative absorption change (bleaching or stimulated emission), while the red regions reflect positive absorption changes (induced absorption). When the v_s region is probed (Fig. 2a,c), two clear signals are observed: a so-called diagonal signal at the excitation frequency of v_s and a so-called cross-peak signal at the excitation frequency of v_{as} . Similarly, when the v_{as} region is probed (Fig. 2b,d), we observe a diagonal signal at the excitation frequency of v_{as} and a cross-peak signal at the excitation frequency of v_s . The bleaching and induced absorption 2D-IR signals are somewhat tilted, especially for the diagonal signals, indicating a correlation of the excitation and the detection frequencies. With increasing delay, this frequency-frequency correlation decays. The dynamics of the frequency-frequency correlation function of the v_{as} mode of the carboxylate anion group has been extensively studied before for aqueous trifluoroacetate²¹, aqueous oxalate²¹, and aqueous acetate²⁴. These dynamics provided information on the structural dynamics of the molecular environment of the carboxylate groups, in particular of the solvation shell and the dynamics of the water molecules forming the solvation shell.^{21,22,24}. In this report, we will not further elaborate on the dynamics of the frequency-frequency



FIG. 2. Isotropic two-dimensional infrared spectra of solutions of sodium acetate (a,b) and disodium terephthalate (c,d) at a waiting time T of 0.3 ps. The signals are presented as a function of the detection frequency (horizontal axis) and the excitation frequency (vertical axis), and are drawn as contour plots of equal signal amplitude in steps of 3%. The red and blue colors represent positive and negative absorption changes respectively. At the right-hand side, we show the linear absorption spectra to clarify the assignment.

correlation function of the vibrations of the carboxylate group. The cross-peak signals reflect changes in the absorption bands of vibrations that are not excited by the excitation pulse, resulting from the coupling to other vibrations that were excited by the excitation pulse. The cross-peak signals in the 2D-IR spectra of Fig.2 clearly show that for both ions the v_s and v_{as} vibrations are coupled. We also measured the anisotropy $R(\omega_{detection}, \omega_{excitation}, T)$ of the diagonal and cross-peak signals, as shown in Figure 1 of the Supplementary Materials. For the diagonal signals we observe a value of R of ~0.4, as expected for a system of randomly oriented dipolar oscillators. For the cross-peak signals we observe a value of R of ~0.2, which means that the transition dipole moment of the detected vibration is oriented at an angle of ~90° with respect

to the transition dipole moment of the excited vibration. This finding perfectly agrees with the expected mutual orientation of the v_{as} and v_s modes. Moreover, as we show on Figure 3 of the Supplementary Materials, anisotropy of diagonal peaks and cross-peaks show very little dynamics that are not possible to reliably determine due to short relaxation time. The lack of the dynamics can be explained by slow reorientation of the relatively massive ions of acetate and especially terephthalate.

To identify the precise nature of the interaction between the v_s and v_{as} vibrations of acetate, we investigate the dynamics of the diagonal and cross-peak signals as shown in Fig. 3. The curves shown are obtained by plotting the resulting 2D-IR signal at the detection frequency that corresponds to the center of the detected bleaching signal as a function of the waiting time



FIG. 3. Isotropic transient absorption signals measured for a 0.1 M solution of acetate in D₂O as a function of waiting time *T*, detected at the maximum frequency of the v_s/v_{as} absorption band obtained by integrating the 2D signals over an excitation frequency interval of 100 cm⁻¹ around the maximum frequency of the v_s/v_{as} absorption band. a. Exciting the v_{as} signal and detecting at the maximum frequency of the v_s signal and detecting at the maximum frequency of the v_{as} signal and detecting at the maximum frequency of the v_{as} signal and detecting at the maximum frequency of the v_s sig

T, and by integrating the 2D signals over an excitation frequency interval of 100 cm^{-1} around the maximum frequency of each absorption band. The diagonal signal of the v_{as} vibration shown in Fig.3 has bimodal dynamics (Fig.3a). The initial fast decay component has also been observed in previous studies of carboxylate anions and has been assigned to energy transfer from the excited v_{as} vibration to the v_s vibration, enabled by fluctuations of the local environment^{22,23}. Such an energy transfer between v_{as} and v_s is expected to lead to a delayed maximum of the cross-peak signals^{28,29}. However, in Figs.3b,d we do not see a delayed maximum of the cross-peak signal neither for the downhill cross-peak, signal (Fig. 3b), nor for the uphill cross-peak signal (Fig. 3b). Both crosspeak signals are observed to rise with the cross-correlation of the excitation and detection pulses. Hence, we conclude that energy transfer is not the only mechanism leading the crosspeak signals. Another coupling mechanism that gives rise to cross-peak signals is anharmonic coupling of the vibrations. When two vibrations are anharmonically coupled, the excitation of one of the vibrations leads to a change of the frequency and/or cross-section of the other vibration. If this coupling mechanism dominates, the cross-peak signal closely follows the dynamics of the excited vibrations, meaning that the rise of the signal will follow the cross-correlation of the excitation and detection pulses, and the decay of the signal will follow the relaxation dynamics of the excited vibration^{3,28}. The dynamics of the downhill cross-peak signal (exciting v_{as} , detecting v_s vibration) would thus closely follow the dynamics



FIG. 4. Schematic picture of the vibrational relaxation model used for fitting the dynamics of Figs. 3 and 5.

of the diagonal signal of the v_{as} vibration in case the interaction of the vibrations would be dominated by anharmonic coupling. However, the dynamics of the downhill cross-peak signal clearly differ from that of the diagonal signal of the v_{as} vibration as the cross-peak signal does not show the fast component that is observed for the diagonal signal. Based on these observations, we conclude that the cross-peak signal is the result of the combined effect of energy transfer and anharmonic coupling.

We fit the dynamics of the diagonal and cross-peak signals

TABLE I. Rate constants of the vibrational relaxation and energy exchange of the v_s and v_{as} vibrations of acetate and terephtalate obtained by fitting the experimental data of Figures 3 and 5 to the kinetic model shown in Fig. 4

	$k_a = k_s$, ps^{-1}	k_{as} , ps^{-1}	k_{sa} , ps^{-1}
acetate	0.45	1.5	0.75
terephthalate	0.8	2.7	1

of Fig. 3 with the relaxation model shown in Fig.4. In Fig. 4 the different vibrational states are defined in the basis of the uncoupled symmetric and asymmetric stretch vibrations. The state (0,0) represents the ground states of the two vibrations. This model is similar to the approach that has been used to fit the population relaxation dynamics of the pump-probe dynamics of the v_{as} mode of trifluoroacetate²¹, oxalate²², and acetate²⁴. The model includes energy transfer between v_s and v_{as} with k_{sa} and k_{as} , and vibrational relaxation of the separate v_s and v_{as} modes to the vibrational ground state with rate constants k_s and k_a , respectively. The exchange rates obey the Boltzmann ratio $k_{sa} = k_{as} \exp(-\hbar\Delta\omega/kT)$, where $\Delta\omega$ is the frequency difference between the centers of the absorption bands of v_s and v_{as} , which is ~150 cm⁻¹ for acetate. As the exchange rate constants are large compared to the vibrational relaxation rate constants ks and ka, we observe a weighted average of these latter two rate constants after the energy exchange has equilibrated, i.e. at delay times >1 ps, which makes it impossible to determine the separate rate constants. Therefore, we took the relaxation rate constants $k_s = k_a$ to be the same. In fitting the data, we include an anharmonic coupling contribution to the cross-peak signals with the same amplitude for the downhill and uphill cross-peak signal. These contributions follow the dynamics of the excited vibration (i.e.the dynamics of the diagonal signal of v_{as} for the downhill cross peak and the dynamics of the diagonal signal of v_s for the uphill cross peak). We did not include the data at T < 0.25 ps in the fitting, as in this waiting time interval the signals show significant contributions from cross-phase modulation of the excitation and detection pulses and resonant coherent interactions (sometimes denoted as coherent artifacts). The model of Fig. 4 provides an excellent fit of all the data. The parameters extracted from the fit are: $k_s = k_a \sim 0.45 \text{ ps}^{-1}$, $k_{as} \sim 2k_{sa} = 1.5$ ps^{-1} . We also find that the cross-peak signals are best fitted with significant contributions from both anharmonic coupling and energy transfer. The ratio between the maximum contribution resulting from energy transfer and the maximum of the contribution due to anharmonic coupling equals 0.39 and 0.19 for the downhill and uphill cross-peak signals, respectively. The difference between these ratios reflect the slower uphill energy transfer compared to the downhill energy transfer.

In Fig. 5 we show the dynamics of the diagonal and crosspeak signals observed in the 2D-IR spectra measured for a solution of 0.05 M disodium terephthalate in D₂O. The observed dynamics are qualitatively similar to the dynamics observed for the acetate solution. The diagonal v_{as} signal shows a bimodal decay, and the downhill cross-peak signal of Fig. 5b differs from the diagonal v_{as} signal and does not show a delayed maximum. We fitted the dynamics of the diagonal and cross-peak signals with the model of Fig.4. The parameters extracted from the fit are: $k_s = k_a \sim 0.8 \text{ ps}^{-1}$, $k_{as} \sim 2.7 k_{sa} = 2.7 \text{ ps}^{-1}$. The larger difference in ratio between the exchange rates of terephthalate compared to acetate originates from the larger energy difference between the maxima of the absorption bands: $\Delta \omega \sim 195 \text{ cm}^{-1}$. The ratio between the maximum contribution caused by energy transfer and the maximum of the contribution due to anharmonic coupling are 0.41 and 0.15 for the downhill and uphill cross-peak signals, respectively.

IV. DISCUSSION

The results show that the interaction between the v_s and v_{as} vibrations of the carboxylate anion groups of acetate and terephthalate involves both energy transfer and anharmonic coupling. These two interactions are associated with a different waiting-time dependence of the cross-peak signal, and thus potentially the spectral shape of the cross-peak signal could change as a function of the waiting time T. However, we did not observe such a dependence of the spectral shape of the cross-peak signal on T. This can be explained from the fact that the frequency shifts due to the diagonal anharmonicity and the anharmonic coupling of the vibrations are smaller than the spectral widths of the absorption bands. As a result, the spectral shape of the cross-peak signal is largely determined by the spectral width of the detected vibrational band, and the frequency shifts resulting from the diagonal anharmonicity and the anharmonic coupling only determine the amplitudes of the positive and negative signals. It would be interesting to tune the relative contributions of anharmonic coupling and energy transfer to the cross-peak signal. An obvious method to achieve this tuning would be to change the interaction with the solvent, as the energy transfer process strongly relies on the compensation of the energy mismatch by the solvent, whereas the anharmonic coupling is relatively independent of the interaction with the solvent. The interaction with the water solvent can potentially be varied by changing the temperature. However, the temperature dependence of the energy transfer processes in aqueous media is hard to predict and can be quite anomalous, i.e. slow down with increasing temperature. Another option would be to change the nature of the solvent. Varying the relative contribution of anharmonic coupling and energy transfer to the cross-peak signal will be subject of a future study.

The vibrational dynamics of acetate has been studied before, with pump-probe spectroscopy using the same broadband mid-infrared laser pulse for excitation and detection of the vibrations²³, and with 2D-IR spectroscopy of only the v_{as} mode²⁴. In the study of Ref.²³ it was found that both v_{as} and v_s show a bimodal decay, with the contribution of the fast component being larger when pumping and probing the v_{as} mode than when pumping and probing the v_s mode. For the origin of this fast component different mechanisms were proposed, including energy transfer between the v_{as} and v_s modes. However, it was not possible to make a definite assignment because in the study of Ref.²³ it was not possible to



FIG. 5. Isotropic transient absorption signals measured for a 0.1 M solution of terephthalate in D_2O as a function of waiting time *T*, detected at the maximum frequency of the v_s/v_{as} absorption band obtained by integrating the 2D signals over an excitation frequency interval of 100 cm⁻¹ around the maximum frequency of the v_s/v_{as} absorption band. a. Exciting the v_{as} signal and detecting at the maximum frequency of the v_{as} band (diagonal v_{as} signal); b. Exciting the v_{as} signal and detecting at the maximum frequency of the v_s band (downhill cross-peak signal); c. Exciting the v_s signal and detecting at the maximum frequency of the v_s signal and detecting at the maximum frequency of the v_{as} band (uphill cross-peak signal). The black dashed lines represent fits to the dynamics, which in the case of the cross-peak signals contain two contributions (blue and red dashed lines), according to the model described in the text.

selectively excite one vibration and to detect the other vibration. In the 2D-IR study of Ref.²⁴ the population dynamics of the excited v_{as} mode were fit to a relaxation model that also includes the relaxation of the v_s mode, and the energy exchange of the two modes. However, in this study the v_s mode was not excited and detected and only the v_{as} mode was measured.²⁴ From the fit of the population dynamics of the excited v_{as} mode, the exchange rate constant k_{as} was estimated to be 2.09 ps⁻¹, which is not very different from the value of $k_{as} \sim 1.5$ ps⁻¹ that we obtain in the present work by studying the diagonal and cross-peak signals of v_{as} and v_s .

The rate constants resulting from the fits of data for both ions are summarized in Table I. We find that the vibrational relaxation and the energy exchange rates are both higher for terephthalate than for acetate. This difference is likely caused by the fact that the larger chemical structure of terephthalate gives rise to a much denser manifold of intramolecular vibrational combination states at the energy of the excited v_s and v_{as} vibrations than is the case of acetate. In particular, in terephthalate the vibrations of the carboxylate groups will be coupled to combination modes of the aromatic ring that are not present in acetate. As a result, the vibrational relaxation will be faster for terephthalate, leading to larger values for k_a and k_s than in acetate, and the compensation of the energy mismatch between the excited v_s and v_{as} vibrations required for the energy transfer is more efficient in terephthalate, leading to larger values for k_{as} and k_{sa} .

It is interesting to compare the vibrational relaxation and

energy exchange dynamics of terephthalate with the dynamics of the oxalate anion that like terephthalate contains two carboxylate anion groups but differently from terephthalate does not contain an aromatic ring. In Ref.²² the dynamics of the v_{as} mode of oxalate were studied, and fitting these dynamics to an exchange model that also included the not directly observed v_s mode, yielded a k_a of 0.98 ps⁻¹, a k_s of 0.45 ps⁻¹, and an energy exchange rate constant k_{as} of 1.55 ps^{-1} . The vibrational population relaxation rates of oxalate are thus similar to those of terephthalate and accelerated by a factor of ~ 2 compared to acetate. Interestingly, the rate constants for energy exchange between v_s and v_{as} are similar for oxalate²² and for acetate, but significantly smaller than we observe for terephthalate. It thus appears that the larger intramolecular vibrational density of states of the oxalate ion compared to acetate is effective in accelerating the vibrational population relaxation of v_s and v_{as} , but not in accelerating the energy exchange between these modes. The similarity in energy exchange rate of oxalate and acetate suggests that this process relies on the interaction with the solvent, i.e. the energy mismatch between v_s and v_{as} is compensated by lowfrequency solvent modes, as this interaction is expected to be very similar for oxalate and acetate. This notion agrees with the interpretation of the origin of the decay of the frequencyfrequency correlation functions of the v_{as} modes of acetate and oxalate^{22,24}. The faster energy exchange of terephthalate compared to both oxalate and acetate suggests that the interactions between the carboxylate groups and the surrounding

water molecules are enhanced by the nearby presence of the aromatic ring of the terephthalate ion. Another possible explanation for the faster energy exchange of terephthalate is that a coupling to the low-frequency modes of the aromatic ring aids in compensating the energy mismatch between the excited states of the v_s and v_{as} modes.

V. CONCLUSIONS

We performed femtosecond two-dimensional infrared (2D-IR) spectroscopy of the symmetric (v_s) and antisymmetric (v_{as}) vibrations of the carboxylate anion groups of acetate and terephthalate in aqueous solution. In this study we selectively excite and detect both vibrations, thus obtaining diagonal signals (exciting and detecting the same vibration), a downhill cross-peak signal (exciting v_{as} and detecting v_s), and an uphill cross-peak signal (exciting v_s and detecting v_{as}). We find that the cross-peak signals are not delayed with respect to the diagonal signals and show dynamics that differ from the dynamics of the diagonal signals. This finding indicates that the cross-peak signals result from the combined effect of energy transfer between the first excited states of the v_s and v_{as} vibrations, and anharmonic coupling of these two vibrations. We model the diagonal and cross-peak signals with a model in which we include the vibrational population relaxation of the first excited states of the v_s and v_{as} vibrations to the ground state, and their energy change with rate constants that obey detailed balance. In this modeling we include an anharmonic coupling contribution to the cross-peak signals that follows the dynamics of the excited vibration (i.e. the dynamics of the diagonal signal of v_{as} for the downhill cross peak and the dynamics of the diagonal signal of v_s for the uphill cross peak). From the modeling we obtain for acetate rate constants $k_s =$ k_a of ~ 0.45 ps⁻¹, and an energy exchange rate constant $k_{as} \sim 2k_{sa}$ of 1.5 ps⁻¹, and for terephthalate rate constants $k_s = k_a$ of ~ 0.8 ps⁻¹, and an energy exchange rate constant k_{as} $\sim 2.7 k_{sa}$ of 2.7 ps⁻¹. We thus find that the terephthalate ion shows a faster vibrational relaxation than acetate which likely can be explained from the denser manifold of accepting vibrational combination states of the larger terephthalate ion, probably also involving the aromatic ring modes of terephthalate. The energy exchange is also faster for terephthalate than for acetate, which may be due to the effect of the aromatic ring of terephthalate on the water molecules that solvate the carboxylate anion groups, leading to a more effective compensation of the energy mismatch between the excited states of the v_s and v_{as} , or due to a direct coupling to low-frequency aromatic ring modes, thereby facilitating the compensation of the energy mismatch.

SUPPLEMENTARY MATERIALS

Anisotropy of diagonal and cross-peaks as a function of detection frequency and waiting time; raw pump-integrated 2D-IR delay traces for diagonal and cross-peaks detected with detection pulse polarized parallel and perpendicular to excitation pulse; pump-integrated isotropic transient absorption spectra as function of waiting time

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available within the article [and its supplementary material].

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