Vibrational dynamics of a non-degenerate ultrafast rotor: The (C12,C13)-oxalate ion

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(Received 18 July 2013; accepted 4 October 2013; published online 30 October 2013)

Molecular ions undergoing ultrafast conformational changes on the same time scale of water motions are of significant importance in condensed phase dynamics. However, the characterization of systems with fast molecular motions has proven to be both experimentally and theoretically challenging. Here, we report the vibrational dynamics of the non-degenerate (C12,C13)-oxalate anion, an ultrafast rotor, in aqueous solution. The infrared absorption spectrum of the (C12,C13)-oxalate ion in solution reveals two vibrational transitions separated by approximately 40 cm^{-1} in the $1500\text{--}1600\text{ cm}^{-1}$ region. These two transitions are assigned to vibrational modes mainly localized in each of the carboxylate asymmetric stretch of the ion. Two-dimensional infrared spectra reveal the presence and growth of cross-peaks between these two transitions which are indicative of coupling and population transfer, respectively. A characteristic time of sub-picosecond cross-peaks growth is observed. Ultrafast pump-probe anisotropy studies reveal essentially the same characteristic time for the dipole reorientation. All the experimental data are well modeled in terms of a system undergoing ultrafast population transfer between localized states. Comparison of the experimental observations with simulations reveal a reasonable agreement, although a mechanism including only the fluctuations of the coupling caused by the changes in the dihedral angle of the rotor, is not sufficient to explain the observed ultrafast population transfer. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4826137>]

I. INTRODUCTION

The structure and dynamics of molecular ions in aqueous solutions and their relation with the solvation shell are of major importance in areas of chemistry and biology. However, the characterization of the solvation shell dynamical processes in the condensed phase remains a challenging subject in experimental and theoretical physical chemistry.¹ It is well known that in aqueous solutions ions are stabilized by water structures, where the water molecule dipoles point towards the ion. This structural arrangement of the solvation shell produces significant perturbations in the ion, as well as in the water molecules. One way in which the water affects the molecular ion is by fast rearrangements of the solvation shell which can significantly modify the geometrical structure of the ion, when compared to the structure in the gas phase.^{2,3} Due to the sensitivity to local environment and time resolution, ultrafast vibrational spectroscopy is now the method of choice for studying rapid dynamical processes of molecular ions in water.^{4–6}

Several different ions have been investigated using time resolved vibrational spectroscopy (e.g., cyanide,^{7,8} azide,^{9,10} thiocyanate,¹¹ guanidinium,^{12,13} trifluoroacetate,¹⁴ tricyanomethanide,⁶ etc.). However, only a few studies have focused directly on the effect of the water motions, when the

ion has a dynamical structure on the same time scale as the water rearrangement motions in the solvation shell.² The oxalate anion is such a dynamical ion, since it incorporates an ultrafast rotation around the C–C bond.²

The oxalate anion consists of two negatively charged carboxylate groups joined by their carbon atoms (Figure 1). In the gas phase, the lowest energy conformation of oxalate has a D_{2d} symmetry in which each of the planes containing the three atoms of the carboxylate group are perpendicular (Figure 1).¹⁵ This D_{2d} conformation has four vibrational modes involving the symmetric and antisymmetric stretch modes of the carboxylate groups.² Simple symmetry considerations for the D_{2d} symmetry group indicates that only three of these four vibrational modes are IR active in the $1300\text{--}1600\text{ cm}^{-1}$ region of the spectrum. While the lowest IR active vibrational mode consists of the antisymmetric combination of carboxylate symmetric stretches and is located at 1310 cm^{-1} , the other two asymmetric stretch vibrations of the carboxylate appear at $\sim 1575\text{ cm}^{-1}$ and are the components of the degenerate E mode.² Similar to the gas phase, the minimum energy conformation of oxalate in water has a D_{2d} symmetry. However, the solvated oxalate has a dynamical structure, in which the many different conformations with dihedral angles far from 90° can be observed.² In these configurations where the ion does not retain D_{2d} symmetry, the asymmetric stretch vibrational modes become more complex because the transition frequency and dipole magnitude depend on the dihedral angle between the two carboxylate groups. The

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FIG. 1. Oxalate geometry and the vibrational energy levels in the asymmetric stretch region. (a) and (b) energy diagram of two coupled vibrational transitions.

distribution of the conformations is given by two main factors: the Columbic interaction between the negatively charged carboxylate groups, and the ion-water interaction. In this particular case, the potential for the C–C rotation in water is sufficiently shallow, allowing fluctuations of the dihedral angle far from the 90° (i.e., displacements of $\theta = \pm 30^\circ$ are thermally allowed).² Moreover, the characteristic time for oxalate C–C rotation in the bottom of the potential is 0.8 ps.² This delicate equilibrium between structure and solvation presents new interesting questions regarding the structural and vibrational dynamics of the ion.

The (C12,C12)-oxalate ion has been previously investigated by time resolved vibrational spectroscopy.² Two-dimensional (2D) infrared vibrational echo spectra and ultrafast anisotropy measurements reveal that oxalate has vibrational excitonic states that are localized onto the carboxylate groups within 450 fs. Moreover, the localization of the vibrational excitation was found to be induced by the fluctuations in the carboxylate vibrational frequencies due to the solvation shell. Unfortunately, the presence of strongly coupled transitions did not provide any direct evidence on how changes in the dihedral angle affect the vibrational dynamics of the system.

In this study, the symmetry of the oxalate ion was purposely broken by labeling one of the carboxylate groups with carbon-13. This labeling tactic has been successfully employed to investigate isolated amide units in different peptides and proteins.^{16–18} Thus, the aim of this study was to explore the vibrational and conformational changes of the (C13,C12)-oxalate ion, from here on referred to as C13-oxalate. To this end, femtosecond IR transient absorption, ultrafast photon echo, and linear absorption IR spectroscopy were employed. In addition, to model the conformational, hydration, and vibrational dynamics of the oxalate ion, a theoretical model derived from DFT maps was developed.

II. EXPERIMENTAL AND THEORETICAL METHODS

A. Sample preparation

Sodium C13-oxalate employed in this study was prepared using a synthetic route with C13-benzyl acrylate as starting material (Figure 2).¹⁹ The sodium C13-oxalate was fully characterized by 500 MHz NMR and high resolution

FIG. 2. Synthetic scheme used to prepare C13-oxalate.

mass spectrometry. A water (D_2O) solution of circa 0.1 M of the sodium C13-oxalate was used for all the experiments. Samples were held between two CaF_2 plates separated by a $6\ \mu m$ spacer.

B. Linear IR spectroscopy

Linear FTIR spectra were obtained with a Thermo Nicolet 6700 FTIR spectrometer having $0.5\ cm^{-1}$ resolution. All the measurements were done at room temperature.

C. Pump-probe spectroscopy

The details of the ultrafast laser system used for the experiment have been previously described in Ref. 12. In brief, the frequency selective pump-probe experiment employs femtosecond laser pulses in the $6\ \mu m$ region, generated on an IR optical parametric amplifier (OPA), which is pumped with a Ti:sapphire based commercial regenerative amplifier (Spitfire, Spectra-Physics). The IR source delivers near transform limited 75 fs pulses centered at $1550\ cm^{-1}$ with $\sim 1.5\ \mu J$ energy. Note that the central frequency of the pump and probe pulses is selected such that it is half way between the two transitions of C13-oxalate, see below. The pump pulse is vertically polarized and has $\sim 500\ nJ$ energy at the sample. The probe pulse has a polarization of 45° with respect to the pump and an energy of $\sim 50\ nJ$. The probe beam is spectrally dispersed in a spectrometer (a 50 grooves/mm grating) and is detected on a liquid nitrogen cooled 32 elements MCT array detector. The different polarization components of the probe are selected with a polarizer placed after the sample.

D. 2D IR spectroscopy and transient grating

The 2D IR photon echo experiment has been described in detailed in previous publications.²⁰ Briefly, a Ti:Sapphire amplifier (Coherent Libra) coupled to a homemade OPA and a difference frequency generator is used to produce the Fourier transform limited infrared pulses. This IR source delivers 80 fs duration pulses centered at $1550\ cm^{-1}$ with 400 nJ energy. The IR pulses are split into three replicas (wavevectors: $\mathbf{k}_1$, $\mathbf{k}_2$, and $\mathbf{k}_3$) and focused at the sample using the box

configuration geometry. The polarization of each of the replicas is carefully set by a set of polarizers before the sample.²¹ The photon echo signal in the phase matching direction ($-\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$) is heterodyned with a fourth IR pulse (LO) and detected by liquid nitrogen cooled 64 element MCT array detector after dispersion in a monochromator (50 grooves/mm). In all the experiments LO preceded the signal field by ~ 1 ps. To obtain the corresponding two-dimensional spectra, two time sequence of pulses are used. The rephasing (non-rephasing) echo signal is measured when the pulses with the wavevector $\mathbf{k}_1(\mathbf{k}_2)$ arrived at the sample before those with wavevector $\mathbf{k}_2(\mathbf{k}_1)$. The coherence and waiting time intervals consist of a total time interval of 3 ps with a 2 fs step and of 2.55 ps in steps of 150 fs, respectively. To accurately phase the rephasing and non-rephasing parts of the data, the projection of the 2D IR spectrum was matched with the pump-probe data at the selected waiting time. Also to verify the correct phasing, the experimental 2D IR spectra were compared with simulated 2D IR spectra.

For heterodyne transient grating (HTG) experiments, the experimental setup is the same as in the 2D IR experiments, where the signal is collected in the $-\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$ phase matching direction. However, the HTG signal collection requires a time sequence of pulses in which the pulses with wavevectors $\mathbf{k}_1$, and $\mathbf{k}_2$ are maintained at $\tau = 0$, while the pulse with wavevector $\mathbf{k}_3$ is scanned every 10 fs for up to 3 ps.

E. Molecular dynamics

A detail description of the molecular dynamics simulations has been previously published.² In brief, the molecular dynamics (MD) simulations were performed using AMBER 9 program package.²² The oxalate ion and water are parameterized according to parameterized model number 3 (PM3) semi-empirical formalism and with the transferable intermolecular potential 3P (TIP3P) force field, respectively. The system consists of one oxalate ion embedded in a box of ~ 1400 water molecules. The production run at normal pressure and temperature is recorded for 1 ns and snapshots were extracted every 2 fs.

F. *Ab initio* calculations

Density functional theory (DFT) calculations were performed at the B3LYP/aug-cc-pVDZ level using the GAUSSIAN 09 software package.²³

III. RESULTS

The FTIR spectrum of ~ 0.1 M sodium C13-oxalate ion in D_2O presents two narrow absorption bands on top of the broad and weak combination band of the solvent in the 1500–1600 cm^{-1} region (Figure 3). The two absorption peaks correspond to the vibrational states involving the asymmetric stretches of the C12 and C13 carboxylate groups of the C13-oxalate ion. The C13-oxalate spectrum is not well modeled either by two Gaussian or Lorentzian line shape function,

FIG. 3. FTIR spectra of ~ 0.1 M solution of C13-oxalate ion in D_2O with solvent background subtracted. The open circles represent the experimental data points, whereas the line represents a model fit with Voigt profiles. The solid black line represents the fit and the dotted red and dashed green lines are its individual components.

but by two Voigt profiles. The fit of the IR spectrum yields a low frequency peak located at 1535 cm^{-1} with Gaussian and Lorentzian components of 16 cm^{-1} and 19 cm^{-1} , respectively, and a high frequency band at 1581 cm^{-1} with only a Lorentzian component of 45 cm^{-1} . Moreover, the ratio of the peak areas between the high and the low frequency peaks is ~ 2.6 . Note that the observed ratio of areas might not reflect the actual ratio of transition dipole magnitudes, see below.

The isotropic transient spectral response, $I_{iso} = I_{\parallel}(t) + 2I_{\perp}(t)$, of the aqueous C13-oxalate ion after the ultrafast IR excitation is displayed in Figure 4. Note that the response arising from the neat solvent was subtracted from these transient signals. The pump-probe spectrum at $T = 0.35$ ps

FIG. 4. Experimental pump-probe signals of the C13-oxalate ion. Top panel shows parallel polarization (XXXX) pump-probe spectra of 0.1 M oxalate ion in water at $T = 0.35$ ps. The middle and lower panels show the isotropic signal of the low frequency at photo-induced absorption band (1518 cm^{-1}) and the high frequency at bleach band (1590 cm^{-1}), respectively. Black open squares correspond to the experimental data and the red line to the fitting described in the text.

TABLE I. Parameters of the population and anisotropy dynamics fit for the different parts of the transient spectrum.

Transition/location	Population dynamics				Anisotropy		
	A_1	τ_1 (ps)	A_2	τ_2 (ps)	A_1	τ_1 (ps)	A_2
Low freq./ESA	0.54 ± 0.02	0.29 ± 0.03	0.46 ± 0.03	1.31 ± 0.06	0.32 ± 0.04	0.6 ± 0.2	0.08 ± 0.02
High freq./BSE	0.54 ± 0.02	0.33 ± 0.03	0.46 ± 0.03	1.32 ± 0.05	0.28 ± 0.03	0.5 ± 0.2	0.13 ± 0.02

(Top panel, Figure 4) reveals a pair of negative and positive bands each corresponding to the two different transitions of the C13-oxalate ion. The first two transient bands, from right to left, are a negative ($\sim 1590 \text{ cm}^{-1}$) and a positive ($\sim 1565 \text{ cm}^{-1}$) band, and are assigned to the $V = 0$ to $V = 1$ transition signals (bleach of the ground state and stimulated emission) and $V = 1$ to $V = 2$ transition signal (excited state absorption) of the high frequency transition of C13-oxalate ion, respectively (see Figure 1). Similarly, the other set of bands located at $\sim 1540 \text{ cm}^{-1}$ (positive) and at $\sim 1520 \text{ cm}^{-1}$ (negative) correspond to the low frequency vibrational transitions of the C13-oxalate ion. The anharmonicity of the transitions (i.e., frequency difference between $V = 0$ to $V = 1$ and $V = 1$ to $V = 2$ transitions) is approximately 18 cm^{-1} for both carboxylate asymmetric stretch transition of C13-oxalate ion. Due to the overlap between the transient bands of the two transitions, the dynamics is measured in regions where the overlap between bands is minimized [i.e., in the spectral region of the bleach/stimulated emission signals for the high frequency transition ($\sim 1590 \text{ cm}^{-1}$) and in the region of the new absorption for the low frequency transition ($\sim 1520 \text{ cm}^{-1}$)]. Discarding the first 0.1 ps of the transient signal due to the presence of other non-resonant signals, the dynamics of both transient signals is well modeled with two exponential decays (see Figure 4 middle and lower panels). The fit of the normalized transient signal yields two sets of parameters which are summarized in Table I. The vibrational population dynamics presented by C13-oxalate is in agreement with the well-known bi-exponential decay of the carboxylate group.¹⁴ In addition, the anisotropy dynamics of these two transient signals, computed from the parallel ($I_{\parallel}$) and perpendicular ($I_{\perp}$) components of the probe pulse as: $r(t) = (I_{\parallel}(t) - I_{\perp}(t)) / (I_{\parallel}(t) + 2I_{\perp}(t))$, reveal a fast decay for both transitions (Figure 5), which is well described with a single exponential decay function of the form: $r(t) = A_1 e^{-t/\tau} + A_2$. The parameters obtained for the fitting of the low and high frequency transition anisotropies are summarized in Table I.

The 2D IR spectra of C13-oxalate ion for different polarization components and waiting times, T , are presented in Figure 6. At $T = 0$, the 2D IR spectrum measured with $\langle XXXX \rangle$ pulse polarizations is composed of sets of diagonal peaks (negative and positive), corresponding to each of the two resolvable transitions of C13-oxalate observed in the carboxylate asymmetric stretch region. In each pair of diagonal peaks, the positive and negative signals arise from the different third order field interactions.²⁴ While the excited state absorption (ESA) pathways produce the positive peak (red peaks in Figure 6), the bleach and stimulated emission (BSE) pathways yield the negative peak (blue peaks in Figure 6). As the wait-

ing time increases, the 2D IR spectra reveal not only changes in the shape of the diagonal peaks, but also the appearance, growth, and shape-change of cross-peaks. Besides the obvious change in peaks amplitude due to the vibrational lifetime, the diagonal peaks acquire an upright shape as the waiting time is increased [i.e., more elongated along ω_{τ} , from their initially elongated shape along the diagonal ($\omega_{\tau} = \omega_l$)]. The cross-peaks show a spectral shape evolution similar to the diagonal peaks, but with much faster dynamics (see below). In addition, cross-peaks and the time evolving features are more clearly observed in the 2D IR, acquired with a sequence of pulses with $\langle XYY \rangle$ polarization.²⁵ While the changes in the diagonal peaks are indicative of a system undergoing spectral diffusion,²⁶ the appearance and growth of cross-peaks with waiting time is a clear manifestation of the process of ultrafast energy transfer between the two transitions of the C13-oxalate ion.²⁴

IV. DISCUSSION

A. Theoretical modeling

To interpret the vibrational spectra and the ultrafast internal motions of the sodium oxalate ion, a previously developed dynamical model for the unlabeled oxalate ion is used in here.² This model assumes that oxalate is a pair of rigid rotors, freely rotating in space where each planar carboxylate is one rotor and the only internal coordinate that can evolve in

FIG. 5. Experimental anisotropy dynamics of oxalate ion. Anisotropy of the low frequency at the new absorption band at 1518 cm^{-1} (top panel) and the high frequency at bleach/SE band at 1590 cm^{-1} (lower panel). Solid black lines correspond to the experimental data, and solid red and dashed blue are the fitted curves as described in the text.

FIG. 6. Absorptive 2D IR spectra of C13-oxalate ion in D₂O. 2D IR spectra for the XXXX (left column) and XXYY (right column) pulse polarizations at different waiting times: $T = 0, 0.45, 1.5$, and 2.15 ps. Black dashed line corresponds to the diagonal ($\omega_t = \omega_i$).

time is the dihedral angle relating the two carboxylate planes (see Figure 1).

The Hamiltonian used in here consists of two coupled asymmetric stretches of the carboxylates undergoing vibrational frequency fluctuations ($\delta\omega_i(t)$) due to the bath interactions where their transition frequencies $\omega_i^0(\theta(t))$ and coupling $\beta(\theta(t))$ depends on the dihedral angle $\theta(t)$. Although in our previous vibrational model of the oxalate ion² the transition frequencies were assumed to be constant, this approximation is not valid for C13-oxalate ion¹⁹

$$H(t) = \begin{bmatrix} \omega_i^0(\theta(t)) + \delta\omega_i(t) & \beta(\theta(t)) \\ \beta(\theta(t)) & \omega_j^0(\theta(t)) + \delta\omega_j(t) \end{bmatrix}. \quad (1)$$

The corresponding eigenstates and frequencies are obtained by diagonalizing the vibrational Hamiltonian [Eq. (1)]. The instantaneous eigenstates are linear combinations of the local site states,

$$\begin{aligned} |i'(t)\rangle &= c_1(t)|i\rangle + c_2(t)|j\rangle \\ |j'(t)\rangle &= c_1(t)|i\rangle - c_2(t)|j\rangle, \end{aligned} \quad (2)$$

where the time-dependence of the coefficients $c_1(t)$ and $c_2(t)$ appears because of the dihedral angle changes with time $\theta(t)$.

To calculate the instantaneous frequencies $\omega_i'(t) = \omega_i^0(\theta(t)) + \delta\omega_i(t)$, the uncoupled frequencies $\omega_i^0(\theta(t))$ of the asymmetric stretches and their coupling constant $\beta(\theta(t))$ are computed.¹⁹ Note that $\omega_i^0(\theta(t))$ are a combination of the unperturbed frequencies, observed when oxalate is in a 90° conformation ω_i^0 , and the changes in the vibrational frequency are due to changes in the electronic structure $\delta\omega_i^{bond}(\theta(t))$.¹⁹ Newly developed DFT maps are used to obtain the relationship among the dihedral angle $\theta(t)$, the coupling constant $\beta(\theta(t))$, and the uncoupled frequencies $\omega_i^0(\theta(t))$.¹⁹ The fluctuations of the site frequencies $\delta\omega_i(t)$ of the asymmetric stretches due to solvent dynamics are calculated from the DFT frequency maps and electric field parameters.²⁷ Similarly, the transition dipole magnitudes of the two oxalate transitions are derived from the map containing the dipole strengths and dihedral angles.¹⁹

B. Assignment of the vibrational states

The C13-oxalate ion presents two transitions in the asymmetric stretch region: one located at 1535 cm⁻¹ and the other at 1581 cm⁻¹. In comparison, pure (C12,C12)-oxalate and (C13,C13)-oxalate show single bands located at 1536 cm⁻¹ and 1579 cm⁻¹, respectively.^{5,15} These two transition frequencies for the isotopically pure ions are very close to the frequencies of the C13-oxalate ion. Since the most probable and stable conformation of the oxalate ion has a dihedral angle of 90° and correspond to uncoupled sites,² the maximum of the peak of the transition provides a good approximation to the transition frequency. Thus, it appears proper to assign the low frequency transition to the vibrational mode where the largest contribution is given by the transition frequency of the asymmetric stretch of the C13-carboxylate and vice versa, even though neither of these transition is a pure asymmetric stretch (see below). *Ab initio* theoretical calculations support this assignment. The computed vibrational frequency of the two asymmetric stretch transitions for C13-oxalate is 1500 cm⁻¹ and 1541 cm⁻¹. Moreover, the DFT calculations reveal that either vibrational mode involves mainly one carboxylate asymmetric stretch. Although a small but not negligible contribution from the carbon of the other carboxylate is observed, even in the 90° conformation of the oxalate ion, the motion of this carbon atom is an out of plane motion perpendicular to the asymmetric stretch vibration.¹⁹

C. Energy levels of the C13-oxalate ion

The vibrational energy level diagram of the $V = 0$, $V = 1$, and $V = 2$ vibrational states for the C13-oxalate ion are presented in Figure 1, where ω_i^0 is the frequency of the one-quantum state for the i th transition, Δ_i is the diagonal anharmonicity, and δ is the off-diagonal anharmonicity corresponding to the combinational band. The transition frequencies of $V = 0$ to $V = 1$ and $V = 1$ to $V = 2$ of C13-oxalate in the diagram of Figure 1 can be directly measured from the FTIR and 2D IR spectra. The transition frequency of the

combinational mode is determined from the pump-probe anisotropy at zero delay time.²⁸ As previously shown in Ref. 28, the pump probe anisotropy at $T = 0$ is given by

$$\begin{aligned} r(T = 0, \omega) &= \frac{I_{ZZ} - I_{ZX}}{I_{ZZ} + 2I_{ZX}} \\ &= \frac{0.9S_F(\omega_0 - \omega) - 0.1S_C(\omega_0 - \delta - \omega) - 0.4S_D(\omega_0 - \Delta - \omega)}{3S_F(\omega_0 - \omega) - S_C(\omega_0 - \delta - \omega) - S_D(\omega_0 - \Delta - \omega)}, \end{aligned} \quad (3)$$

where $S_F(\omega_0 - \omega)$, $S_D(\omega_0 - \Delta - \omega)$, and $S_C(\omega_0 - \delta - \omega)$ are the spectral shape factors for the fundamental transitions, excited state transitions, and the transitions from the fundamentals to the combination modes, respectively.²⁸ In the case where δ is zero and Δ is sufficiently large, $r(0, \omega_0) = r(0, \omega_0 - \Delta) = 0.4$. This is the case observed for the low and high frequency transitions of C13-oxalate ion where the anisotropy of low frequency ESA and high frequency BSE bands at $T = 0$ ps are $r(0, 1518 \text{ cm}^{-1}) = r(0, 1590 \text{ cm}^{-1}) \simeq 0.4$ within the experimental error (see Figure 5). Similar initial values of the anisotropy are also measured in the transient grating

signal (not shown). The observation of anisotropy values of 0.4 strongly suggest that anharmonicity of the combinational band is close to zero.

D. Dipole reorientation

In the C13-oxalate ion, the anisotropy of the transient absorption signal has ultrafast dynamics well modeled with a sub-picosecond decay time for both vibrational transitions (see Table I). In a previous study of the (C12,C12)-oxalate ion, a similar ultrafast dynamics in the anisotropy was observed and attributed to the population exchange between two excitonic states.² Although it is difficult to foresee that a sub-picosecond population transfer will be observed in transitions separated by $\sim 40 \text{ cm}^{-1}$, all the new experimental data suggest that the population transfer between states is most likely the process that produces the ultrafast decay of anisotropy in the C13-oxalate ion.

Population exchange between vibrational states results in changes in the dipole orientations. The model of the anisotropy for a system undergoing population exchange between vibrational states is given by²

$$r(T, \omega) = \frac{2}{5} e^{-6Dr} \frac{\sum_{i,j} \{ \langle P_2(\hat{\mu}_{0i}(0) \cdot \hat{\mu}_{0i}(T)) \rangle \langle \mu_{0i}^2(0) \mu_{0i}^2(T) \rangle_\theta P_{ii}(T) S(\omega_i^0) + \langle P_2(\hat{\mu}_{0i}(0) \hat{\mu}_{0j}(T)) \rangle \langle \mu_{0i}^2(0) \cdot \mu_{0j}^2(T) \rangle_\theta P_{ij}(T) S(\omega_j^0) \}}{\sum_{i,j} \{ \langle \mu_{0i}^2(0) \mu_{0i}^2(T) \rangle_\theta P_{ii}(T) S(\omega_i^0) + \langle \mu_{0i}^2(0) \mu_{0j}^2(T) \rangle_\theta P_{ij}(T) S(\omega_j^0) \}}, \quad (4)$$

where $P_{ii}(T)$ and $P_{ij}(T)$ are the probabilities that if the molecule is initially pumped to the state $|i\rangle$ will remain in state $|i\rangle$ or will be transferred to the state $|j\rangle$ after time T , respectively; $\mu_i(T)$ is the transition dipole magnitude, $\langle P_2(\hat{\mu}_{0i}(0) \hat{\mu}_{0i}(T)) \rangle$ is the dynamics of the dipole reorientation in the molecular frame,²⁹ and $S(\omega_i^0)$ is the spectral factor at the transition frequency ω_i^0 . The spectral factors $S(\omega_i^0)$ are derived from the sum of all the different Liouville path diagrams that contribute to the signal (see Ref. 30).

The terms $P_{ii}(T)$ and $P_{ij}(T)$ derived from the kinetic equation $i \xrightleftharpoons[k_{j \rightarrow i}]{k_{i \rightarrow j}} j$ are

$$P_{ii}(T) = \frac{k_{j \rightarrow i} + k_{i \rightarrow j} \exp[-(k_{i \rightarrow j} + k_{j \rightarrow i})/T]}{k_{i \rightarrow j} + k_{j \rightarrow i}} \quad (5)$$

and

$$P_{ij}(T) = 1 - P_{ii}(T), \quad (6) \quad \text{where}$$

where i and j indexes are interchangeable. Moreover, $k_{i \rightarrow j}$ and $k_{j \rightarrow i}$ are related by the Boltzman factor [i.e., $k_{j \rightarrow i} = k_{i \rightarrow j} \exp[-\Delta E_{ij}/RT]$ when $\Delta E_{ij} > 0$].

Because of the spectral separation between the transition frequencies of the two states, the different spectral components of the anisotropy appear at specific frequencies of the spectrum (i.e., one is located at ω_i^0 and the other at ω_j^0). Moreover, the auto-correlation function of the transition dipole direction for single carboxylate group was found to have a slow dynamics ($\tau \approx 4 \text{ ps}$)^{2,14} and the dynamics of the autocorrelation of the transition dipole magnitude was found to be ultrafast ($\tau \approx 0.05 \text{ ps}$).¹⁹ Thus, Eq. (4) can be further simplified to

$$r(T, \omega) = r_{i,j \rightarrow i}(T, \omega_i^0) + r_{j,i \rightarrow j}(T, \omega_j^0), \quad (7)$$

$$r_{i,j \rightarrow i}(T, \omega_i^0) = \frac{0.4 \{ \langle P_2(\hat{\mu}_{0i}(0) \cdot \hat{\mu}_{0i}(T)) \rangle P_{ii}(T) + \langle P_2(\hat{\mu}_{0j}(0) \cdot \hat{\mu}_{0i}(T)) \rangle \frac{|\mu_{0j}|^2}{|\mu_{0i}|^2} P_{ji}(T) \}}{\{ P_{ii}(T) + \frac{|\mu_{0j}|^2}{|\mu_{0i}|^2} P_{ji}(T) \}}. \quad (8)$$

This model predicts that the anisotropy depends on the dipole reorientation terms caused by the internal rotation of the C13-oxalate ion. Computations of the terms $\langle P_2(\hat{\mu}_{0i}(0) \cdot \hat{\mu}_{0i}(T)) \rangle$ and $\langle P_2(\hat{\mu}_{0i}(0) \cdot \hat{\mu}_{0j}(T)) \rangle$ using the values from the MD simulation and modeling reveal that these two terms have a very fast dynamics and reach a constant value of $\langle P_2(\hat{\mu}_{0i}(0) \cdot \hat{\mu}_{0i}(T)) \rangle \approx 0.9$ and $\langle P_2(\hat{\mu}_{0i}(0) \cdot \hat{\mu}_{0j}(T)) \rangle \approx -0.4$ at 200 fs. These values are only 20% different from the expected values for an averaged conformation of 90° , which are 1 and $-1/2$, respectively.¹⁹ The fast dynamics and the small effect on the anisotropy hinder any possible measurement of the rotational dynamics of the C13-oxalate ion. Thus, in this model the average of the dipole reorientation in the molecular frame is assumed to be constant. The computed anisotropy using the values of 0.9 and -0.4 for the dipole reorientation terms is $r(T=0) = 0.36$, which is the measured experimental value, within the error. At $T = \infty$, the value of anisotropy will depend on the ratio of the transition dipole magnitudes and spectral position,

$$r(\infty, \omega_i^0) = \frac{2}{5} \frac{\langle P_2(\hat{\mu}_{0i}(0) \cdot \hat{\mu}_{0i}(T)) \rangle + \langle P_2(\hat{\mu}_{0i}(0) \cdot \hat{\mu}_{0j}(T)) \rangle |\mu_{0j}|^2 / |\mu_{0i}|^2}{1 + |\mu_{0j}|^2 / |\mu_{0i}|^2}. \quad (9)$$

Moreover, if the ratio of transition dipole magnitudes $|\mu_{0j}|^2 / |\mu_{0i}|^2$ is 1 and $\langle P_2(\hat{\mu}_{0i}(0) \cdot \hat{\mu}_{0i}(T)) \rangle \approx 0.9$ and $\langle P_2(\hat{\mu}_{0i}(0) \cdot \hat{\mu}_{0j}(T)) \rangle \approx -0.4$, the anisotropy becomes 0.1 at $T = \infty$, giving the same result as an average of the transition dipole on a plane.^{29,31} In the case of $|\mu_{0i}|^2 / |\mu_{0j}|^2 = 0.85$ as observed from the peak maximum of the FTIR (Figure 3), the limiting value of the anisotropy is $r(\infty, \omega_i^0) = 0.08$ and 0.12 for the low and high frequency, respectively. These predicted values are also in agreement with the experimental measurements (Table I).

The fit of the experimental anisotropy of the C13-oxalate with this model and assuming that $\langle P_2(\hat{\mu}_{0i}(0) \cdot \hat{\mu}_{0i}(T)) \rangle = 1$ and $\langle P_2(\hat{\mu}_{0i}(0) \cdot \hat{\mu}_{0j}(T)) \rangle = -1/2$, yields a $k_{i \rightarrow j} = 0.9 \pm 0.1 \text{ ps}^{-1}$ and $|\mu_{0i}|^2 / |\mu_{0j}|^2 = 1.0 \pm 0.1$ (see Figure 5). Note that other fits where the averaged dipole orientation parameters are varied to $\langle P_2(\hat{\mu}_{0i}(0) \cdot \hat{\mu}_{0i}(T)) \rangle = 0.9$ and $\langle P_2(\hat{\mu}_{0i}(0) \cdot \hat{\mu}_{0j}(T)) \rangle = -0.4$ (see Ref. 19) produced the same transfer rate constant. The good agreement between the model and the experimental data provides further support to the population exchange as the mechanism of the anisotropy decay.

E. Population transfer

Another source that can provide information regarding the population transfer is the 2D IR spectra. Since the 2D IR spectrum is the sum of all the different processes involved in the dynamics of the bleaching, stimulated emission, and new absorption signals, the presence of a population exchange process during the waiting time affects how these signals contribute to the spectrum. In particular in a system undergoing population exchange, cross-peaks between the two transitions are expected to appear.^{24,32} The experimental 2D IR spectra (Figure 6) reveal the presence of cross-peaks which are

enhanced in the XXYY polarization.²⁴ However, because of the ultrafast time scales of the vibrational dynamics observed for the C13-oxalate ion, retrieval of the cross-peak dynamics from the 2D IR spectrum is very challenging. Thus a transient grating method was used to evaluate the dynamics of the cross-peak from the photon-echo experiments.

In any photon echo experiment, it is possible to isolate or enhance the signal of the cross-peaks from that of the diagonal peaks using specific pulse polarization sequences.^{24,25} For example, the 2D IR spectrum of cross-peaks can be obtained by using the polarization combination:^{24,32} $S(\omega_\tau, T, \omega_t) = \langle XXXX \rangle - 3 \langle XXYY \rangle$.

Similarly, the cross-peak dynamics can be isolated and evaluated from the HTG signals, $S^{HTG}(\tau = 0, T, \omega_t)$, produced by the same pulse polarization sequence $S^{HTG}(\tau = 0, T, \omega_t) = \langle XXXX \rangle - 3 \langle XXYY \rangle$. As in the 2D IR spectrum, the HTG signal arises from the sum of the different Liouville pathways, each containing the dynamics of the system.^{21,33} For impulsive excitation with femtosecond pulses, the HTG signal is

$$S^{HTG}(\omega, T) = \sum_n S_n^{HTG}(\omega, T) f(T), \quad (10)$$

where $f(T)$ are the dynamic factors produced by processes such as population transfer.³⁰ Here, these factors are assumed to only occur during the waiting time T . The $S_n^{HTG}(\omega, T)$ terms in Eq. (10) correspond to the individual Liouville pathway diagrams³⁰ such that,

$$S_n^{HTG}(\omega, T) \propto \langle k_A l_B m_C n_D \rangle \int_0^\infty R_n(T, t) e^{i\omega t} dt = \langle k_A l_B m_C n_D \rangle S_n^{klmn}(\omega, T), \quad (11)$$

where $\langle k_A l_B m_C n_D \rangle$ represents an ensemble-averaged orientational factor of the i, j, k, l Feynman path for a sequence of pulses with A, B, C, D polarization in the laboratory coordinates, $R_n(T, t)$ is the n th response function, and $S_n^{klmn}(\omega, T)$ is the n th spectral amplitude of the path i, j, k, l . Considering the experimental evidence that the rotational diffusion is slow compared to the other oxalate vibrational processes,^{2,14} and that the anharmonicity of the combinational mode is $\delta = 0$ (see Sec. IV C), and assuming that the lifetime of the two asymmetric stretches as well as their combinational mode are equal ($T_1^i \approx T_1^j \approx T_1^{i+j}$), the HTG signal for the $\langle XXXX \rangle - 3 \langle XXYY \rangle$ can be simplified to

$$S^{HTG}(\omega_t = \omega_i^0) = \left[\sum_n (\langle i_X i_X j_X j_X \rangle - 3 \langle i_X i_X j_Y j_Y \rangle) \right] |\mu_{0i}|^2 |\mu_{0j}|^2 \times 2(P_{ji} + 1 - P_{ii}) \left(\exp\left(-\frac{T}{T_1}\right) \right), \quad (12)$$

$$S^{HTG}(\omega_t = \omega_i^0 - \Delta_i) = \left[\sum_n (\langle i_X i_X j_X j_X \rangle - 3 \langle i_X i_X j_Y j_Y \rangle) \right] \times |\mu_i|^2 |\mu_j|^2 P_{ji} \left(\exp\left(-\frac{T}{T_1}\right) \right), \quad (13)$$

where i and j represent the two asymmetric vibrational states of the system and T_1 is the vibrational lifetime. Note that the i and j indexes are interchangeable. Substituting the population transfer probabilities [Eqs. (5) and (6)] into Eqs. (12) and (13) yields

$$S^{HTG}(\omega_t = \omega_{0i}) = 2A(1 - \exp[-(k_{i \rightarrow j} + k_{j \rightarrow i})/t]) \left(\exp\left(-\frac{T}{T_1}\right) \right), \quad (14)$$

$$S^{HTG}(\omega_t = \omega_{0i} - \Delta) = A \frac{k_{i \rightarrow j}}{k_{i \rightarrow j} + k_{j \rightarrow i}} (1 - \exp[-(k_{i \rightarrow j} + k_{j \rightarrow i})/t]) \times \left(\exp\left(-\frac{T}{T_1}\right) \right), \quad (15)$$

where A is $[\sum_n (\langle i_X i_X j_X j_X \rangle - 3 \langle i_X i_X j_Y j_Y \rangle)] |\mu_i|^2 |\mu_j|^2$.

Assuming that $\langle i_X i_X j_X j_X \rangle$ and $\langle i_X i_X j_Y j_Y \rangle$ are constant in time because of their fast relaxation,¹⁹ Eqs. (14) and (15) predict that the dynamics of the HTG signal will only depend on the population transfer rate ($k_{i \rightarrow j} + k_{j \rightarrow i}$) and the lifetime (T_1) that are manifested as a rise and a decay of the signal with waiting time, respectively. This is exactly what is observed in the experimental data (Figure 7). Thus, the first principle model of the S^{HTG} is used to obtain the characteristic time of the cross-peak growth from the HTG signal.

The fitting of the experimental HTG signal to Eqs. (14) and (15) yields a characteristic time of population transfer ($1/(k_{i \rightarrow j} + k_{j \rightarrow i})$) of 0.6 ± 0.3 ps and a population relaxation (T_1) of 0.6 ± 0.3 ps and 0.9 ± 0.3 ps for the low and high frequency transitions, respectively. The time constants for the population transfer and vibrational lifetimes derived from modeling of the cross-peak growth in the HTG signal (Figure 7) are in good agreement with $k_{i \rightarrow j}$ and $k_{j \rightarrow i}$ values

FIG. 7. Vibrational population transfer of C13-oxalate in water. Experimental HTG signal for the $\langle XXXX \rangle - 3 \langle XXYY \rangle$ in the cross-peak region at: 1510 cm^{-1} (top panel) and 1590 cm^{-1} (bottom panel). Open squares correspond to the experimental data and the red line to the fit with Eqs. (14) and (15).

obtained from the dipole reorientation model and the pump-probe experiment.

Overall, the matching between the time constants from the pump-probe anisotropy and HTG signals provides sufficient evidence to propose the population transfer between the vibrational states of oxalate as the main mechanism responsible for the sub-picosecond anisotropy decay and growth of the cross-peak.

F. Frequency–frequency correlations

The vibrational dynamics of the C13-oxalate ion was further investigated by evaluating the dynamics of the frequency–frequency correlation time. The waiting time evolution of the 2D IR spectra contains information of the characteristic times of the frequency–frequency auto-correlation (FFCF) and cross-correlation (FFXCF) functions. For those correlation components with amplitudes (Δ) and characteristic correlation times (τ_c) fulfilling that $\Delta \tau_c \gg 1$ for Kubo-like functions,³⁴ it has been shown that various 2D spectral parameters can be used to describe their time evolution.^{26,35} In particular, the correlation times of the FFCF can be measured from the slope of the nodal line (defined simply as “slope” from here on), which is the line separating the positive and negative diagonal peaks of the 2D IR spectrum.²⁶ The FFXCF can be measured from the slope of the cross-peaks. Although a detailed theoretical analysis of the response functions²⁴ is necessary to prove analytically the relationship between the cross-peak slope and the FFXCF, theoretical 2D IR simulations of the system reveal that the slope of the cross-peak evolves with a similar time scale as the characteristic time of the cross-correlation.¹⁹ Here, the waiting time evolution of the slope is quantified for each of the two transitions at the frequency corresponding to the maximum of the positive peak in a range of 10 cm^{-1} . To measure the time evolution of the cross-peak, the slope is evaluated in the lower right corner cross-peak ($\omega_t = 1510\text{--}1500 \text{ cm}^{-1}$, $\omega_i = 1550\text{--}1590 \text{ cm}^{-1}$) of the 2D IR spectra measured from pulses with XXYY polarization, where the signal of the cross-peaks is enhanced with respect to the diagonal peaks.

The slope retrieved from the diagonal and cross-peaks of the 2D IR spectrum for each transition and the corresponding results of the global fitting to the functional form $S(T) = a_1 \exp(-T/\tau_c) + a_2$ are presented in Figure 8. The fitting parameters describing the FFCF and the FFXCF are summarized in Table II. Interestingly, the FFCF shows a correlation time ($\tau_c = 1.1 \pm 0.2$ ps), which is slower than that observed for the single carboxylate ($\tau_c = 0.8 \pm 0.1$ ps).¹⁴ In addition, the existence of a slow component in the FFCF of either diagonal peak suggests the presence of an inhomogeneous process which has not been previously observed in the isolated carboxylate. Moreover, the difference in the amplitudes of the FFCF, a_1 , for both transitions reveals the presence of an extra homogeneous component in the FFCF of the high frequency transition³⁵ which cannot be attributed to the negligible difference between the lifetimes of the two vibrational transitions³⁵ of C13-oxalate (see Table I), but could arise from other

FIG. 8. Slope versus waiting time for diagonal and cross-peaks. (a), (b), and (c) panels correspond to the slope of the low frequency diagonal peak, high frequency diagonal peak, and the right lower corner cross-peak, respectively. The filled squares are the experimental data points and the solid red line is the fit to a single exponential function.

chemical species present in the solution such as ion pairs.⁵ In addition, the difference between the FFCF characteristic times of the C13-oxalate ion and of the isolated carboxylate reinforce the idea that the vibrational states of the ion not only sense the bath interactions, but also changes in the frequency due to vibrational coupling or equivalently changes in the conformation. Note that if the C13-oxalate ion maintains a 90° dihedral angle the coupling between the carboxylate groups is expected to be null and consequently the FFCF should be that of the isolated carboxylate ion. In other words, the experimental FFCF of each asymmetric stretch transition does not directly represent the frequency fluctuations of the local sites caused by the solvent fluctuations because the changes in the dihedral angle produce non-negligible interactions and frequency shifts of the two asymmetric stretches.³⁶ In the case of the FFXCF of C13-oxalate, the observed dynamics is very fast (i.e., $\tau_c = 0.9$ ps). Moreover, the amplitude of the FFXCF is negative, indicating that the frequency fluctuations of the

TABLE II. Parameters of the experimental frequency auto- and cross-correlation functions.

Parameters	Autocorrelation (FFCF)		Cross-correlation (FFXCF)
	High frequency	Low frequency	
a_1 (norm.)	0.42 ± 0.05	0.21 ± 0.05	-0.5 ± 0.2
τ_1 (ps)	1.1 ± 0.3	1.1 ± 0.3	0.9 ± 0.5
a_2 (norm.)	0.14 ± 0.05	0.06 ± 0.03	0.6 ± 0.1

FIG. 9. Theoretical FFCF and FFXCF of the oxalate ion of the asymmetric stretch vibrational modes. The top and bottom panels correspond to the frequency–frequency autocorrelation and cross-correlation functions, respectively. Panels (a) and (b) correspond to the auto- and cross-correlation, respectively. The red lines correspond to the fitting with a sum of exponential functions (see text).

two transitions are anticorrelated. The time evolution of the FFCF and the FFXCF is also evaluated theoretically from the instantaneous frequencies computed from the MD simulation (see Sec. IV A).

The theoretical FFCF and FFXCF are presented in Figure 9. The FFCF and the FFXCF reveal a dynamics well modeled with a sum of exponential functions. The fitting results are presented in Table III. The theoretical correlation time constants of 2.2 ps (FFCF) and 2.0 ps (FFXCF) present a satisfactory agreement with those measured experimentally from the slope of the diagonal ($\tau = 1.1$ ps for the FFCF) or the cross-peaks ($\tau = 0.9$ ps for the FFXCF) of the 2D IR spectra. The theoretical results also indicate that the frequencies are anti-correlated and that the anti-correlation evolves with a similar time scale as the FFCF. However, comparison between the theoretical FFCFs, considering only frequency fluctuations due to the solvent and the full Hamiltonian [Eq. (1)] for determining the vibrational transitions, shows the opposite trend than that observed experimentally (Tables II and III, and Ref. 14): the FFCF becomes faster for coupled transitions perturbed by the bath ($\tau = 0.1$ ps) than when only fluctuations due to solvent are considered ($\tau = 0.5$ ps). Although the theory seems to contradict the experimental findings, the ways in which the correlation times appear in the FFCF might explain this strange behavior. For two asymmetric stretch transitions, the FFCF correlation times are expected to be faster for the frequencies computed from the full Hamiltonian [Eq. (1)] than those computed only for the unperturbed local site where only the solvent fluctuations $\delta\omega_i(t)$ are considered. However, in the case of the vibrational frequencies derived from the full Hamiltonian, the fastest correlation time becomes so fast that it contributes homogeneously to the FFCF²⁴ and leaves the FFCF with a single correlation component, which is essentially much slower than that observed for the local sites. This trend is observed experimentally: the FFCF characteristic time is 1.1 ps for C13-oxalate

TABLE III. Parameters of the theoretically predicted frequency auto- and cross-correlation functions.

Parameters	Autocorrelation (FFCF)		Cross-correlation (FFXCF)	
	Full Hamiltonian	Solvent fluctuations	Full Hamiltonian	Solvent fluctuations
a_1 (cm ²)	89.6	105.4	−44.0	−66.6
τ_1 (ps)	0.1	0.5	0.1	0.5
a_2 (cm ²)	36.4	93.1	−35.1	69.5
τ_2 (ps)	2.2	8.5	2.0	10.8

and 0.8 ps for trifluoroacetate.¹⁴ Although there is not direct connection between the changes in the FFCF and the fluctuations of vibrational frequencies for coupled transitions undergoing ultrafast energy transfer and bath fluctuations, the modeling of the FFCF allow us to infer that in the C13-oxalate ion not only the frequency fluctuations due to the bath interactions $\delta\omega_i(t)$ are important, but also the frequency fluctuations $\delta\omega^{bond}(\theta(t))$ and the coupling $\beta(\theta(t))$ produced by the changes in the dihedral angle of the C13-oxalate ion.

The similarity between theory and experiment suggests that the correlation time is properly measured from the 2D IR spectra even in a system undergoing ultrafast vibrational dynamics, population transfer, and conformational changes. Moreover, the theoretical FFCF correlation time that is deducted from a set of vibrational states further supports the necessity of including all effects, solvation, and dihedral angle rotation, for computing the vibrational frequencies of the C13-oxalate ion in the asymmetric stretch region.

G. Mechanism of population transfer

To investigate the molecular processes involved in the population transfer, the time evolution of the density matrix is examined. In the density matrix, the diagonal terms $\rho_{nn}(t)$ contain the information regarding the population dynamics. The time dependence of the population $\rho_{nn}(t) = \langle c_n^*(t)c_n(t) \rangle$ is obtained by solving the time dependent Schrodinger equation [Eq. (16)] for the coefficients, c_i and c_j , and averaging the result over an ensemble of molecules (see Refs. 37 and 2),

$$\begin{aligned} i \frac{dc_i}{dt} &= \omega'_i(t)c_i + \beta(t)c_j \\ i \frac{dc_j}{dt} &= \omega'_j(t)c_j + \beta(t)c_i. \end{aligned} \quad (16)$$

The terms ω'_i and $\beta(t)$ necessary to solve Eq. (16) are calculated from the theory (see Sec. IV A).

The results of the terms $\rho_{nn}(t) = \langle c_n^*(t)c_n(t) \rangle$ are presented in Figure 10. When the system is initially prepared as a pure site state, the time evolution of the site population shows a rapid decay ($\tau = 0.15$ ps) to 90% of the initial value, follow by a much slower decay ($\tau = 6$ ps) to the statistical average of 0.5. While the first decay represents the damping of the coherence transport,³⁷ the slower decay is caused by the fluctuations of the coupling between sites.³⁶ Note that a similar time evolution is observed when the time dependent Hamiltonian is solved with an initial condition consisting of the eigenstate computed for the time averaged values of the Hamiltonian ($\langle\beta\rangle = 6.35$ cm^{−1}, $\langle\omega'_i\rangle = 1497$ cm^{−1}, and $\langle\omega'_j\rangle$

$= 1540$ cm^{−1}), see Figure 10. Thus the population dynamics indicate that the population transfer rate does not depend whether the system is coupled or not because the value of the coupling constant (β) is small compared to the energy separation between states ($\langle\omega'_j\rangle - \langle\omega'_i\rangle \sim 45$ cm^{−1}). The difference between the experimental and the theoretical transfer rate shows either that the system is not well parameterized by theory, or that the population transfer might involve other vibrational modes. While the former possibility is very unlikely given the good agreement between the experimental FTIR and the one predicted by the theory (see Sec. IV H), the latter is highly possible given that C13-oxalate has other vibrational states, two involving the symmetric stretch transitions and others with out of plane motions where the carbon atom has the same type of motion as in the carboxylate asymmetric stretches.¹⁹ Although other vibrational modes were not included in the Hamiltonian used to describe the system, the coupling of the carboxylate asymmetric stretches with other vibrational modes will certainly induced a faster decay of the initially quasi-localized population to the statistical average.

Another different mechanism that can explain the rapid population flip is through bond transfer. It has been shown experimentally that through bond transfer plays a special role in many small and large systems.³⁸ Moreover, some of these molecular systems showed a fast through bond population transfer, when the vibrational modes involved in the transfer are delocalized,³⁹ which is the case of the C13-oxalate ion. Essentially, the through-bond transfer mechanism consists on ballistic energy transfer through vibrational wavepackets involving nearly degenerate and highly delocalized vibrational states.⁴⁰ Although the through-bond mechanism is a valid possibility, a detailed theoretical study is necessary to assess whether this mechanism is responsible for the ultrafast vibrational population transfer observed on the C13-oxalate ion.

FIG. 10. Time dependence of the population probabilities, P_i . Open squares and black lines represent the time evolution of the site populations with the single site as an initial condition. Filled triangles and red lines show the time dependence of the site populations for the eigenstate coefficient derived from the time averaged Hamiltonian.

H. FTIR spectra

To corroborate that the MD simulations and the DFT maps provide a good theoretical description of the oxalate ion, the linear IR spectrum was calculated. In the semiclassical limit, the linear spectrum for a $V = 0$ to $V = 1$ vibrational transition, ω_i^0 , for an isolated oscillator is given by⁴¹

$$I(\omega) = \int_{-\infty}^{\infty} e^{-i\omega t} e^{-t/2T_1 - 2Dt} \times \left\langle \mu_{0i}(0) \mu_{0i}(t) \exp \left[i \int_0^t \omega_i^0(\tau) d\tau \right] \right\rangle dt, \quad (17)$$

where D is the overall rotational diffusion constant (assumed to be independent of changes in the dihedral angle), and μ_{0i} is the transition dipole magnitude.² Equation (17) assumes that the rotational reorientation is not correlated with the changes in the transition dipole magnitude and has the lifetime (T_1) incorporated as an empirical factor.

Since the oxalate ion has two possible vibrational transitions, $|0\rangle \rightarrow |i\rangle$ and $|0\rangle \rightarrow |j\rangle$, the infrared spectrum is the sum of the contributions of the two states. Thus Eq. (17) becomes

$$I(\omega) = \int_{-\infty}^{\infty} e^{-i\omega t} e^{-t/2T_1} e^{-2Dt} \times \sum_{i,j} \left\langle \mu_{0i}(0) \mu_{0i}(t) \exp \left[i \int_0^t \omega_i^0(\tau) d\tau \right] \right\rangle dt. \quad (18)$$

To calculate the theoretical IR spectrum, the transition frequencies and the magnitudes of the transition dipole moments are computed for each snapshot of the MD simulation (see Sec. IV A). The value of T_1 is 0.4 ps. The statistical average necessary to simulate the FTIR spectrum is achieved by averaging 500 adjacent pieces of the trajectory each containing a 20 ps time window.

The simulated FTIR spectrum is presented in Figure 11. Overall, the simulated FTIR spectrum matches the experimental spectrum. In particular, the ratio of peak extinction coefficients and the difference in the transition frequency between transitions have excellent agreement with the experiment. In contrast, the theory does not correctly reproduce either the central frequencies or the width of the experimental spectrum on the high frequency side. In the case of the transition frequencies, the calculated frequencies underestimate the experimental values by 41 cm^{-1} . The difference in the linewidth might arise from a wrong parameterization of the transition frequencies or by other chemical species present in the solution such as ion pairs.⁵ In addition, the ratio of the integrated areas of each transition gives a ratio of transition dipole magnitudes of $|\mu_{0i}|^2 / |\mu_{0j}|^2 = 0.8$, suggesting that the ratio of areas derived from the fitting of the FTIR spectrum might not reflect the true values of the transition dipole magnitudes.

Overall, the good agreement between the experiment and theory indicates that the theoretical modeling of the vibra-

FIG. 11. Theoretical and experimental FTIR spectra of C13-oxalate ion in D_2O . The open circles (bottom axis) represent the experimental data points, whereas the solid black, dashed red, and dotted blue lines (top axis) represent the total FTIR and the ω_-^0 and ω_+^0 components predicted by the theory, respectively.

tional transitions produce a good representation of the system. Moreover, the agreement also demonstrates that the main dynamical properties affecting the vibrational dynamics of the oxalate ion, such as the fluctuations of the local site frequencies and the coupling between states, are well parameterized from the theory.

V. CONCLUSION

The non-degenerate asymmetric stretch transitions of the C13-oxalate ion at 1500–1600 cm^{-1} in D_2O shows two well separated transitions assigned to the asymmetric stretches of the C12 and C13 carboxylate groups. Unexpectedly for a system having two transitions separated by $>40 \text{ cm}^{-1}$, the vibrational asymmetric stretches of carboxylate undergo an ultrafast population transfer ($\tau \approx 0.6 \text{ ps}$) upon excitation with ultrafast pulses. This ultrafast population transfer causes a very fast decay of the pump-probe anisotropy and hinders the observation of the conformational dynamics of the ion by this method which is very similar to what has been observed in the C12,C12-oxalate ion. In contrast with the unlabeled oxalate ion, the ultrafast population transfer for the C13-oxalate ion is also manifested as the appearance and growth of cross-peaks in the 2D IR absorptive spectrum and the transient grating signal as a function of waiting time. The match between the cross-peak dynamics and the anisotropy decay provides the evidence necessary to conclude that the population transfer is the process responsible for the dipole reorientation and the cross-peak growth. Unlike of the C12,C12-oxalate ion, the computation of the density matrix shows that the mechanism of energy transfer cannot be simply explained by a model in which only the vibrational asymmetric stretches of the C13-oxalate are included.

The waiting time dependence of 2D IR spectra of the C13-oxalate ion reveals a vibrational frequency–frequency correlation time unexpectedly slower than that observed for single carboxylate groups. This result strongly suggests that the asymmetric stretches of the two carboxylate groups are strongly coupled and that through bond effects due to the conformational dynamics of oxalate must play an important role in the vibrational dynamics of the C13-oxalate ions. Molecular dynamics simulations and *ab initio* computations confirm the changes in the correlation time and support the

molecular picture in which the oxalate ion undergoes solvent interaction as well as conformational changes in the dihedral angle.

ACKNOWLEDGMENTS

We would like to thank Dr. Tom Troxler for many helpful discussions and Professor Feng Gai for many helpful discussions and advice. This research was supported by grants to R.M.H. from NIH-GM12592, and NIH-9P41GM104605 for instrumentation.

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