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The rotation of NO_3^- as a probe of molecular ion – water interactions

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Abstract. The hydration dynamics of aqueous nitrate, NO_3^-(aq), is studied by 2D-IR spectroscopy, UV-IR- and UV-UV transient absorption spectroscopy. The experimental results are compared to Car-Parinello molecular dynamics (MD) simulations. The 2D-IR measurements and MD simulations of the non-degenerate asymmetric stretch vibrations of nitrate reveal an intermodal energy exchange occurring on a 0.2 ps time scale related to hydrogen bond fluctuations. The transient absorption measurements find that the nitrate ions rotate in 2 ps. The MD simulations indicate that the ion rotation is associated with the formation of new hydrogen bonds. The 2 ps rotation time thus indicates that the hydration shell of aqueous nitrate is rather labile.

1 Introduction

The present work concerns the hydration dynamics of aqueous nitrate, NO_3^-. Aqueous nitrate is well suited for studying ionic hydration shell dynamics, because its spectroscopic properties depend on the strength and geometry of the hydrogen bonds. Hence, contrary to previous experiments, which measure the dynamics of the ion-water hydrogen bonds by vibration spectroscopy of the water molecules, the present experiments directly probe the dynamics of the ions. Direct probing of nitrate's rotation and vibration selectively yields information of the hydrogen bonds connected to the molecular anion with little, if any, background signal from bulk water.

2 Experimental and theoretical results

The hydration dynamics is first probed by 2D-IR spectroscopy. The infrared measurements excite and probe the two asymmetric stretch vibrations of nitrate. The isolated nitrate ion is planar (D_{3h}) with the excess negative charge delocalized over the molecule. Accordingly, the two asymmetric stretch vibrations of the isolated molecule are degenerate. However, hydration breaks the symmetry and lifts the degeneracy resulting in a double peaked absorption band with maxima at 1340 cm^{-1} and 1400 cm^{-1}. The vibrational transition dipole moments both lie in the plane of the molecule, but point in different directions [1]. The 2D-IR spectra are recorded at several delays between the pump and

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the probe pulse with parallel and perpendicular pump and probe pulse polarizations. Figure 1 shows the 2D-IR spectra of NO_3^-(aq) for zero time delay between excitation and probing of the asymmetric stretch vibrations.

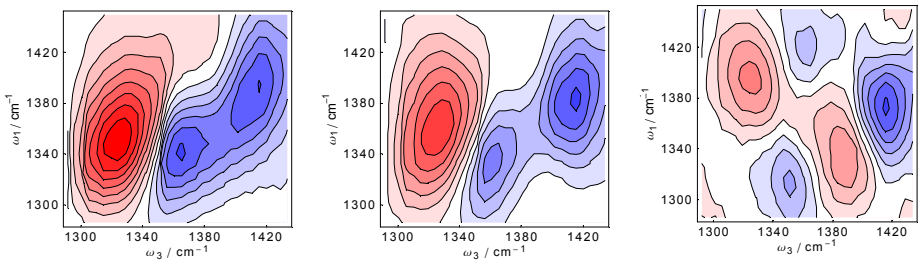

Fig. 1. 2D-IR spectra of NO_3^-(aq) recorded for parallel (left, $\Delta A_{||}$) and perpendicular (middle, $\Delta A_{\perp}$) pump and probe pulse polarizations at t=0 fs. Right: 2D-IR difference spectrum $3\Delta A_{\perp}$ - $\Delta A_{||}$, which suppresses the diagonal peaks. The vertical axis is the excitation frequency, while the horizontal axis is the probe frequency.

The diagonal of the 2D-IR spectra displays two bleach signals with excitation maxima at 1340 cm^{-1} and 1400 cm^{-1} reflecting the absorption band of the asymmetric stretch vibrations. The spectra also display a strong, red-shifted induced positive absorption predominantly caused by excited state absorption (ESA). Vibrational relaxation of the first excited state causes the diagonal as well as the off-diagonal signals to decrease with time. Plotting the peak signals with pump frequency of 1340 cm^{-1} and probe frequencies of 1320 cm^{-1} and 1360 cm^{-1} as a function of time, reveals the relaxation kinetics depicted in Fig 2a. Both graphs are well described by single exponential functions with a time constant of 0.4 ps.

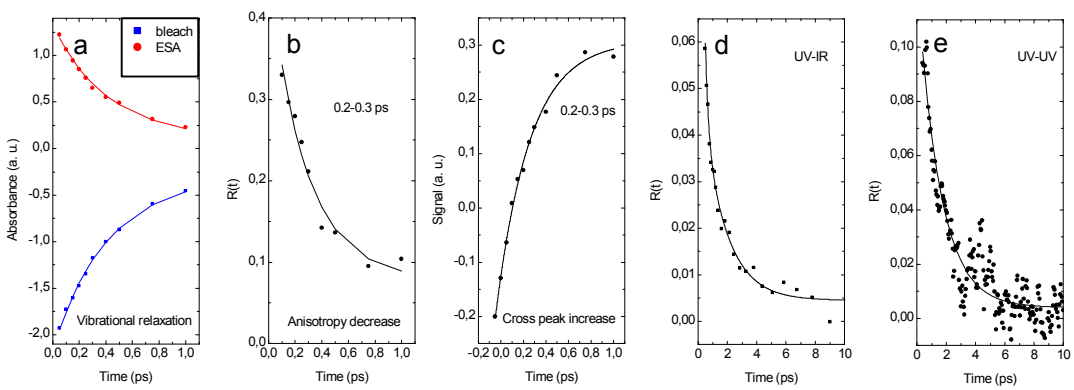

Fig. 2. a. The vibrational relaxation reflected by ground state and excited state absorption. b. Anisotropy kinetics extracted from the excited state absorption. c. Cross peak kinetics. d. The rotational anisotropy derived from UV pump-IR probe measurements. e. The rotational anisotropy derived from UV pump-UV probe measurements.

Visual inspection of the polarization dependence of the 2D-IR spectra clearly shows that they are anisotropic. The anisotropy is quantified by the rotational anisotropy parameter, R, defined as:

$$R(t) = \frac{\Delta A_{||} - \Delta A_{\perp}}{\Delta A_{||} + 2\Delta A_{\perp}} \tag{1}$$

Figure 2b shows $R(t)$ of the lower frequency diagonal bleach. It decreases from its maximum of R(t=0 fs) ≈ 0.4 to R(t=1000 fs) ≈ 0.1 on a 0.2-0.3 ps timescale. The residual anisotropy subsequently decays on a slower timescale that is not fully captured by the 2D-IR experiments. The initial anisotropy of R(t=0 fs) = 0.4 concurs with the value expected for non-degenerate transition dipole moment, illustrating the strong solvent-induced symmetry breaking. However, the 0.2–0.3 ps timescale is much faster than expected for a freely rotating nitrate ion, let alone a hydrated nitrate ion. The cause for the fast anisotropy becomes clear when subtracting the diagonal peaks from 2D-IR spectra presented in Figure 1. The resulting difference spectrum (Figure 1c) reveals two cross peaks between the two asymmetric stretch absorption bands, indicating a coupling between the two vibrations. Difference spectra obtained at longer delays show that the relative absorption of the cross peaks increases with time, as shown in Figure 2c. The data points in Figure 2c are well described by a single exponential function having a rise time of 0.2-0.3 ps. Within the experimental uncertainty the time constant for the relative cross peak growth is thus identical to the fast component of the anisotropy of the diagonal signal. This indicates that the fast component of the rotational anisotropy decay is caused by a redistribution of the excitation between the two asymmetric stretch vibrations of nitrate due to solvent fluctuations. Since the transition dipole moments of the two asymmetric stretch modes point in different directions this may look like the molecules are rotating. At the same time, fluctuations of the distortions of the D_{3h} structure can lead to efficient normal mode remixing. Indeed, our Car-Parinello simulations show reorientation of the transition dipole moments associated with the low and high frequency absorption bands on a sub-picosecond time scale. Furthermore, previous simulations have found a 200 fs timescale for hydrogen bond fluctuations [2].

Figure 2b shows that after one picosecond the diagonal peak anisotropy still has a finite value of 0.1. Scattering and the fast relaxation time of the excited asymmetric stretch hampers the 2D-IR detection of the anisotropy beyond 1 ps. Instead, the reorientation of the nitrate molecules is recorded using UV pump – IR probe transient absorption spectroscopy. The 200 nm pump pulse excites the $\pi\pi^*$ transition of nitrate [3]. The infrared probe pulse subsequently monitors the reorientation of the nitrate molecules remaining in the ground state by probing the asymmetric stretch vibration. The resulting rotational anisotropy is depicted in Figure 2d. The anisotropy is well approximated by a single exponential function with a time constant of 2 ps convoluted with the experimental response function. This time constant is confirmed by UV pump-UV probe measurements displayed in Figure 2e. Our Car-Parinello MD simulations indicate the formation of hydrogen bonds to new water molecules whenever the nitrate molecule rotates.

Both the timescale for hydrogen bond fluctuations and their lifetime is thus comparable for water molecules surrounding the nitrate ions and neat water [4]. As a result the hydration shell of the nitrate anion appears to be just as labile as water's hydrations shell.

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