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Two dimensional infrared spectroscopy and relaxation of aqueous cyanide

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Abstract

The 2D IR spectra of water in the region of the bending/librational mode near 5 μm and the cyanide ion whose vibrational mode is in the same frequency range show that the combination mode and the cyanide mode undergo spectral diffusion on ultrafast time scales. The signals are dominated by a water grating formed by energy deposition following infrared excitation. The grating is formed more rapidly from the combination mode than from the water background mode excitation indicating more effective breaking and making of hydrogen bonds.

Keywords: Cyanide; Water; Combinational mode; Bending/libration; Hydrogen bond; Ultrafast; Photon echo; 2D IR; Transient grating

1. Introduction

A microscopic description of the ultrafast motions in liquid water has been sought over a period of many years through applications of virtually all the pulsed laser methods that have been available. Most recently two dimensional infrared spectroscopy (2D IR) was shown to provide an interesting new perspective on this question [1–4]. Of course the unusual properties of liquid water determine its properties as a solvent for both neutral and charged species so the ultrafast structural changes of water around solutes present equally interesting, tractable and important problems for experiment and theory.

For sometime now this laboratory has been interested in designing experiments that characterize the various features of the ultrafast motions of small molecules or ions in aqueous solutions [5–8] and in this paper we extend these measurements to the 2D IR of the cyanide ion in water. Through studies of photon echoes of molecular ions such as N_{3-} in water [7] and relaxation studies of aqueous pseudohalogen ions [9,10] and CN^- [6], there now exists a solid base of data on the ultrafast dynamical parameters of simple ions. The vibrational frequency correlation functions obtained from the three pulse photon echoes of azide gave information regarding the motions of H_2O molecules that were bound to the ion with the correlation functions being dominated by a ca. 1 ps process.

The dynamical aspects of water structures around small ions have also received considerable theoretical attention. In particular, Skinner and co-workers have given a quantitative description of the population and spectral relaxation of the azide ion [11,12] from first principles calculations of the three pulse photon echo responses that were measured. The simulations by Hynes and co-workers on CN^- [13] have found energy relaxations in encouraging agreement with experiment and they have made predictions regarding the dephasing of the CN^- vibrational transition. One assumption of that theoretical study is that the vibrational frequency distribution of aqueous CN^- is motionally narrowed and this prediction is easily evaluated by photon echo experiments which measure whether there is spectral diffusion.

Another view of the effect of ions on water structure was obtained from recent work by Bakker and co-workers

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[14,15] which focused on direct observations of the water vibrational modes. Our longer term objective is to combine the concept of these different types of experiments by obtaining information both from the viewpoint of the ion vibrator and the water dynamics in the presence of ions using the methods of dual frequency 2D IR [16,17]. In this paper, we present the 2D IR results for the cyanide ion in H_2O. We have already characterized the population relaxation dynamics of the cyanide ion and some of its isotopomers in H_2O and D_2O and the time scales were found to be between 28 and 120 ps depending on the isotope composition of the solvent and/or the solute [6]. The heterodyned photon echo signal from the ion, with vibrational frequency ca. 2100 cm^{-1} is expected to provide the fluctuations of the ion vibration in response to the local solvent motions.

2. Experimental

2.1. The samples

One of the objectives of the present work was to accomplish the echo experiments in very thin samples (ca. 1 μm) that are at the same time transparent in the regions of the main water absorption bands. This is anticipating our forthcoming results on the dual frequency 2D IR. Therefore, the concentration of CN^- must be larger than would be required in say a 25 μm pathlength which is what was used in the previously reported relaxation experiments of cyanide in H_2O [6]. A concentration of 2.5 M was chosen because the Raman and IR spectra of CN^- in water are only very slightly different at this concentration compared with dilute solution. However, it is possible that there are some counterion and aggregation effects that contribute to the signal differently than in more dilute solutions and it will be interesting to further evaluate them. In our previous study of IR transients of CN^-, we proved that a 0.9 M solution was in the dilute solution limit as far as measurements of the population lifetime was concerned. However, although the Raman spectral shapes are hardly changed from dilute solutions to 2.5 M a shortening of the population lifetime for solutions at 2.5 M was noted [18]. However, the lifetimes measured were still considerably longer than the inverse bandwidths of the vibrational spectra and coherence times recorded in the present work. We estimated the population lifetime in our samples from the waiting time dependence of the integrated 2D IR spectrum (see below) and find a value of longer 6 ps which is consistent with the previous work. The FT-IR spectra of 2.5 M NaCN in pure water is shown in Fig. 1 at a sample thickness of ca. 1 μm. A sharp peak from the CN^- absorption sits on top of a water absorption band that corresponds to the combination mode of a libration and a bending vibration. By fitting the CN^- stretch mode with a Lorentzian line shape, we find a peak position of 2080.4 cm^{-1} and a full width at half maximum of 15.8 cm^{-1}. These results are very close to those reported previously for $^{12}C^{14}N^-$ in H_2O [6]. The present values are based on fitting the underlying combination band of water to a Gaussian line shape peaking at 2132 cm^{-1} with a full width at half maximum of 249 cm^{-1}. For the experiments on the cyanide dynamics, the center frequency of the IR pulse was chosen at 2080 cm^{-1}. For the water dynamics, the center frequency was 2132 cm^{-1} and for the transient grating experiment, we chose to compare two different center frequencies of 1885 cm^{-1} and 2132 cm^{-1}. These center frequencies are indicated in Fig. 1.

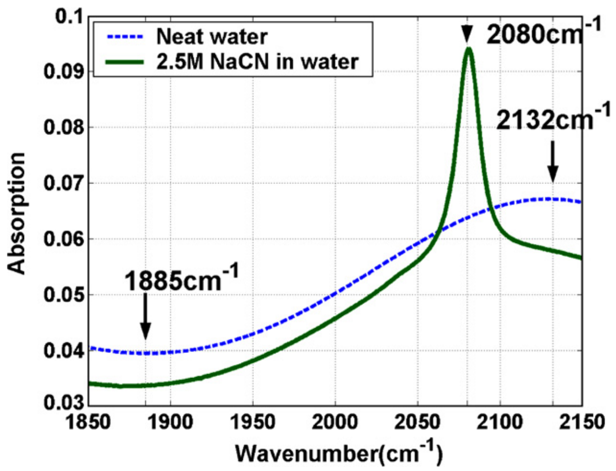

Fig. 1. Linear IR absorption spectra of 2.5 M aqueous NaCN (solid line) and of neat water (dashed line). The sample thickness is ca. 1 μm. Also indicated are the three center frequencies employed in the experiments discussed in the text.

2.2. The 2D IR method

Fourier-transform limited 75 fs pulses with center frequency ca. 2100 cm^{-1} were used in the 2D IR experiments. Three of these pulses each with energy 400 nJ and wavevectors k_1, k_2, and k_3 were incident on the sample. The phase-matched signal at wave vector $-k_1 + k_2 + k_3$ was detected by heterodyning it with a local oscillator pulse that always preceded the signal pulse by a fixed interval of ~1.5 ps. The interval between pulses 1 and 2 is denoted as τ, that between 2 and 3 as T, and that between 3 and the detected signal as t. The rephasing sequence (labeled as R) is one in which the beam k_1 arrives earlier than k_2 by an amount τ. The sequence when k_2 arrives earlier than k_1 by τ is named the nonrephasing sequence (labeled as NR). The signal and local oscillator pulses were combined at the focal plane of a monochromator having a 64-element MCT array detector (IR Associates, Inc.). Each detector element is 200 μm in width and 1 mm in height. The focal length of the monochromator is 270 mm and the groove density of the grating used in our experiments was 120 lines/mm. The raw data collected using this method was in the form of a two dimensional array of time τ, in 2 fs steps from −2.5 ps to 2.5 ps, and wavelength in ~6 nm steps. To obtain absorptive or correlation spectra, rephasing and nonrephasing 2D frequency spectra were added. The waiting time, T, was varied