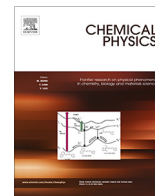




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Vibrational relaxation of small anions in a polymer film

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ABSTRACT

Steady-state and ultrafast vibrational spectroscopy can help to elucidate the interactions between small anions and their environment because the anions' infrared absorption frequencies and vibrational energy relaxation (VER) times depend strongly on those interactions. Their strong infrared absorptions also make many of these anions promising candidates for strong coupling to optical fields. Here, we report the vibrational energy relaxation of dicyanamide (DCA) in H₂O and D₂O and find that the so-called solvent isotope effect on VER is not as pronounced as for other anions. In addition, we report the infrared spectroscopy and VER lifetimes of DCA, N₃⁻, and NCS⁻ embedded in a polyelectrolyte polymer. We find that the polymer matrix accelerates VER in a similar fashion to H₂O, but the detailed mechanism of this acceleration remains unclear.

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1. Introduction

Vibrational spectroscopy and dynamics of ions in solution provide insight into ion solvation that mediates many important chemical processes in electrochemistry, environmental science and physiology. Understanding solution interactions with electronic spectroscopy is well established, relying on solvatochromism and solvation dynamics of dye molecules, which is the basis for polarity scales [1]. Similarly, solute-solvent interactions for small anions have been characterized through static and time-resolved infrared spectroscopy in which the bandwidth and frequency of infrared absorptions, as well as their population, dephasing, and reorientation lifetimes, reflect the strength and type of interactions with solvent molecules. As recognized in theoretical studies [2–4] and early experiments [5–7], these systems involve strong Coulombic interactions, as well as hydrogen bonding for protic or aqueous solvents, leading to relatively long-lived solvent structures and the involvement of librational bands that cannot be understood within the framework of weakly interacting models such as isolated binary collision theory [8–10]. The systems are interesting in part because their relaxation mechanisms depend, in detail, on the solution structure and tend to be governed by the extent of solute-solvent interactions that give rise to external vibrational relaxation (EVR). This is especially true for diatomics, CN⁻ in particular [5,11], where this is the only pathway

for energy dissipation, as opposed to larger systems that are often dominated by intramolecular vibrational redistribution (IVR).

Pseudohalide molecular anions, azide (N₃⁻), cyanide (CN⁻), cyanate (NCO⁻) and thiocyanate (NCS⁻), have strong absorptions in the mid-infrared near 5 μm and have been employed as probes of microscopically complex environments because of their sensitivity to their surroundings. Although much of this work has focused on examining local environments in proteins [12–17], other environments have received attention as well [18,19]. Together with another strongly absorbing anion used in ionic liquids, dicyanamide (N(CN)₂⁻, abbreviated DCA), these ions have also been used to gain an understanding of solvent effects at interfaces in confined systems like reverse micelles [20–22]. Over a range of molecular solvents, azide and DCA show a strong correlation between the center absorption frequency and the population relaxation rate (T₁) of the vibrational band. This rate-frequency correlation suggests that similar effects influence frequency shifts and relaxation mechanisms and provides a metric for behavior indicative of a typical molecular solvent [23]. While this correlation can break down for strongly interacting solvents like water or when there is an appreciable IVR and solvent assisted IVR contribution to the relaxation process [24], the correlation holds in ionic liquids, indicating that ionic liquids interact with solutes like typical aprotic organic solvents (e.g., DMSO). Thiocyanate, on the other hand, does not exhibit much of a shift, but it has a broader range of T₁ relaxation times (from about 3 ps in water to 80 ps in DMSO) [25,26], which also serves as an indicator of interaction strength.

The strength and narrowness of their infrared absorptions also make small anions excellent candidates for coupling to optical

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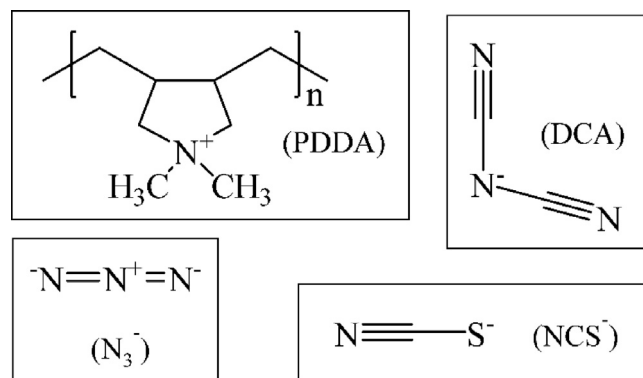
modes, a rapidly developing field of study [27–31]. When a strong absorber is confined in an optical cavity, the material absorption and an optical mode of the cavity can couple to one another if conditions pertaining to the absorption strength and mode lifetimes are met. This strong coupling leads to the formation of two new polariton modes, each with partial vibrational and optical character. The coupling strength depends, in large part, on the absorption strength of the absorber, the square root of the concentration of absorbers, and the similarity of the widths of the absorption and optical mode. Achieving strong coupling requires, in one simple approximation, that the concentration of absorbers, C , satisfies the condition $C \geq 2.7n_B\Gamma_H/\epsilon$, where n_B is the index of refraction of the “background,” typically a solvent, Γ_H is the homogeneous linewidth of the absorber, and ϵ is the molar absorptivity of the vibrational transition [31]. It is instructive to recognize that in the strong coupling regime, the Rabi splitting does not depend on the cavity length but only the concentration. In one of the pioneering studies of vibration-cavity coupling, Simpkins et al., demonstrated that a positively charged polyelectrolyte, PDPA (or PDADMAL) can be infused with thiocyanate ions in sufficient concentration to reach the strong coupling regime [31]. Infrared chromophores in polymer matrices are potentially attractive as self-contained, stand-alone optical devices that avoid some of the complications that would arise from using solutions or neat liquids.

Strong coupling can substantially modify the transient response and relaxation timescales of the molecular system involved and the small molecular anions outlined above could be useful probes of the effects of strong coupling [27]. Polymer films containing those anions are advantageous because they allow for the simple construction of first-order cavities, which can be helpful in determining the effect of cavity and material properties on the ultrafast dynamics of coupled systems. The vibrational relaxation dynamics of these anions in polymers have not been reported, but would provide an important baseline for future strong coupling experiments. In this work, we report the population decay rate of the DCA strong, asymmetric C–N stretching band near 2150 cm^{-1} in H_2O and D_2O solution. The vibrational spectra and dynamics for DCA had been studied for solvents ranging from methanol to DMSO as well as ionic liquids, but the results in H_2O and D_2O were not reported. We include the values here to develop a more complete rate-frequency plot for DCA as a basis to evaluate results in PDPA. We report transient spectra and population dynamics for NCS^- , N_3^- and DCA in PDPA, whose structures are depicted in Scheme 1, and show that PDPA enhances the rate of population decay in a similar fashion to H_2O , albeit with the magnitude of the enhancement quite different for each of the three anions, indicating that the decay is not solely governed by the electrostatic interactions that give rise to the peak shifts.

2. Experimental methods

2.1. Static and time-resolved infrared spectroscopy

To obtain steady-state infrared spectra, we used a Thermo Scientific Fourier-transform infrared spectrometer with the resolution set to 0.5 cm^{-1} . For clarity of viewing, we present every fourth data point in Fig. 1. The time-resolved infrared spectrometer has been, in large part, described previously [27,32]. Briefly, a regenerative amplifier (Legend, Coherent, Inc.) supplies a 1 kHz train of 800 nm pulses which are then downconverted to the near infrared by an optical parametric amplifier (TOPAS, Light Conversion). A subsequent AgGaS₂ crystal difference-frequency mixes the near infrared pulses to generate mid-infrared pulses centered near $5\text{ }\mu\text{m}$ with approximately 150 cm^{-1} bandwidth. We use the small ($\sim 4\%$) reflection of the mid-IR beam from a CaF₂ window as the probe



Scheme 1. The structures of the anions and polymer matrix studied in this article.

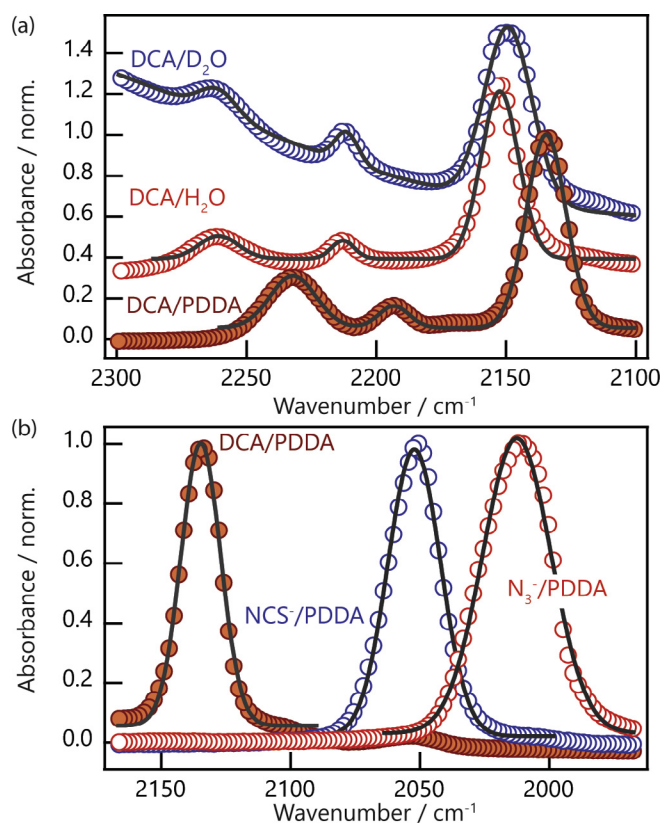


Fig. 1. a) Fourier-transform infrared (FTIR) spectra of DCA in D_2O (blue), H_2O (red), and PDPA (dark red, filled). Circles are experimental data, solid lines are fits to a sum of three Gaussian features. In D_2O , the O–D stretch begins to overlap the absorption spectrum; we use a fourth Gaussian to fit that large, broad feature. b) FTIR spectra of DCA in PDPA (dark red, filled), NCS^- in PDPA (blue), and N_3^- in PDPA (red). Circles are experimental data, solid lines are fits to single Gaussian features. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

pulse, which traverses a computer-controlled delay stage, and an optical chopper modulates the remainder of the beam to supply a 500 Hz excitation pulse train.

One significant departure from the previously reported instrument is the addition of a multichannel detector in the form of a 128×128 mercury-cadmium-telluride array (2DMCT, PhaseTech) [33]. The array detector and its paired spectrograph allow us to measure the spectrum of each laser shot. To obtain transient infrared spectra, we synchronize the array detector to the optical chopper and collect groups of 150 pairs of excitation-on and excitation-off measurements of the probe spectrum at a given time delay. The

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