

Ultrafast intermolecular vibrational excitation transfer from solute to solvent: Observation of intermediate states



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ABSTRACT

Ultrafast two-dimensional infrared (2DIR) and IR pump–probe (PP) spectroscopy was used to study the intermolecular vibrational energy transfer process from the excited state of asymmetric stretching vibration of HN_3 to the overtone band of C–O stretching vibration of solvent methanol. A series of time-resolved 2DIR spectra indicate an intermolecular vibrational excitation transfer between the two modes, since the corresponding cross peaks appear at longer waiting times (>20 ps). However, detailed analyses of temperature-dependent FTIR, dispersed IR PP, and 2DIR spectra showed that the vibrational relaxation of the azido stretch mode and its energy transfer to solvent methanol C–O stretch overtone mode involve not only heat dissipation directly to the solvent bath modes but also production of transient intermediate states. The present experimental work demonstrates that ultrafast nonlinear IR spectroscopy is quite useful to shed light into the complicated vibrational relaxation dynamics of H-bonded solute–solvent systems.

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1. Introduction

Understanding intermolecular vibrational energy relaxation pathways and mechanism is an important step toward elucidating chemical reaction dynamics in condensed phases. An uptake of energy from solvent is required to initiate a barrier crossing process along the reaction coordinate. Subsequent dissipation of the excess energy after barrier crossing into surrounding solvent degrees of freedom is one of the crucial processes determining timescales of chemical reactions [1,2]. Such coupled fluctuation and dissipation process involves intermolecular energy transfers via multiple and often parallel pathways [3,4]. Nonetheless, obtaining a vibrational energy flow map for a given chemical or physical transformation process is highly challenging and needs a variety of experimental tools and theoretical efforts. In this regard, femtosecond IR pumping method has been found to be extremely useful to resonantly excite vibrational modes with sufficiently excessive energy [5]. Monitoring the fate of instantaneously pumped energy on certain vibrational eigenstate can be performed by using yet another femtosecond IR probe pulse, where its differential absorbance is measured in time. This gives information on the population transfer

from the initially excited parent mode to energy-accepting daughter modes that can be either intramolecular or intermolecular vibrations. Thus, such mode-to-mode vibrational energy transfer processes, once they can be monitored in real time, would provide important clues for understanding chemical reaction dynamics in solutions.

As a matter of fact, a variety of time-resolved spectroscopic methods have been used to investigate the intermolecular and intramolecular vibrational excitation transfer processes in solutions. Quite a few attempts were successful to directly monitor complicated population changes of acceptor modes. For instance, IR pump–probe (PP) experiments were carried out to detect the intermolecular relaxation-induced populations of lower-lying vibrational eigenstates by measuring distinctive transient absorption signals associated with transitions from low-lying vibrational states to their upper-lying combination states [6]. IR-pump anti-Stokes Raman scattering probe (IR-Raman) method developed by Dlott and coworkers in principle enables one to follow the time-dependent population changes of Raman-active modes, as demonstrated for a few molecular systems in solutions [7,8]. Recently, narrow-band IR pump broad-band IR probe-type 2DIR measurement method has been used to study intermolecular mode-to-mode excitation transfer. However, it should be noted that this method has an intrinsic time-resolution limit, since the frequency selection with a narrow-band (temporally broad) pump pulse was inevitable [9–12].

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In the present work, the vibrational population relaxation process of HN_3 in methanol is studied by using FTIR, 2DIR, and IR PP measurement methods. First, the temperature-dependent FTIR spectra show that the transition dipole moments of asymmetric azido stretch mode of HN_3 and methanol C–O stretch overtone decrease with increasing temperature. In addition to the temperature-induced line-broadening and weak frequency shift, vibrational transition dipole moment can also change due to its dependence on local solvent configuration and electrostatic environment, e.g., hydrogen-bonding interaction. This heat-induced transition dipole decrease could be responsible for experimentally observed waiting time (T_w)-dependent cross peaks in the 2DIR spectra, which is in fact strong evidence for an incoherent vibrational excitation transfer between the two vibrational modes. Although the main features of the time-resolved 2DIR spectra can be described in terms of local (in a microscopic sense around the pumped HN_3 molecule) heating effect related to the vibrational energy relaxation from HN_3 excited state to surrounding methanol C–O overtone modes, we found that there are transient intermediate states. In particular, it was the frequency-resolved IR PP signal that allowed us to quantitatively identify and characterize possible intermediate states that are transient in the course of vibrational relaxation of the initially excited asymmetric stretch mode of HN_3 to solvent bath modes. In summary, we were able to extract information on time-evolving vibrational spectra of the asymmetric stretching vibration of HN_3 , intermediate states of energy-accepting solvent and solute modes, and locally heated states, which occur in a few tens of picosecond timescales.

2. Experimental methods

2.1. Sample preparation

NaN_3 , methanol (CH_3OH), and anhydrous sulfuric acid (H_2SO_4) were purchased from Sigma–Aldrich. To prepare the sample solutions, NaN_3 salt was directly dissolved in methanol and then anhydrous sulfuric acid was added to the solution to produce HN_3 chemical species in the methanol solution. Upon addition of anhydrous sulfuric acid, $\text{Na}_2\text{SO}_4(\text{s})$ salt was precipitated because of its low solubility. $\text{Na}_2\text{SO}_4(\text{s})$ salt was removed from the solution by centrifugation. For the present experiments, 0.23 M HN_3 in methanol was used and housed in a home-made IR cell with two CaF_2 windows (3 mm thick) and the path length was adjusted by using a 12 μm thick Teflon spacer.

2.2. FTIR spectroscopy

The FTIR spectra were measured with a Varian 640-IR spectrometer with a 1 cm^{-1} resolution. For the temperature-dependent FTIR experiments, the cell was connected to a temperature controller (PIKE Technologies, USA) and the temperature was varied from 25 to 55 $^\circ\text{C}$ with an interval of 5 $^\circ\text{C}$. At a given temperature, the sample cell was allowed to reach its thermal equilibrium for at least 10 min. After the temperature-dependent FTIR experiments were performed, the sample cell was quickly cooled down to room temperature by using a fan, and then the FTIR spectrum was compared with the one before heating. Two FTIR spectra were found to be identical, which indicates that no notable degradation of the sample solution occurs during the temperature-dependent FTIR experiments.

2.3. IR pump–probe and 2DIR spectroscopy

Experimental details on polarization-controlled IR PP and 2DIR spectroscopy were previously presented elsewhere [13–16]. In brief, ~ 60 fs mid-IR pulse centered at $\sim 2100\text{ cm}^{-1}$ was used for

both 2DIR and IR PP experiments. In 2DIR spectroscopy, three mid-IR pulses were focused onto the sample and their relative time-delays were precisely controlled. The 2DIR signal emitted in a new phase-matched direction was heterodyne-detected by using a local oscillator. 2DIR signals were collected by scanning the delay time between the first two pulses with a fixed waiting time (T_w) and were also frequency-resolved through the monochromator onto the HgCdTe (MCT) array detector with 64 pixels, which provided us time-resolved spectral interferograms as a function of τ at the emission frequencies (ω_t). Numerical Fourier transformation of the temporal interferograms along the τ -axis was performed to obtain the 2DIR spectrum that is finally dependent on the excitation (ω_τ) and emission (ω_t) frequencies. 2DIR spectra, $S(\omega_\tau, \omega_t; T_w)$, were obtained by varying T_w times. To obtain purely absorptive (real) part of 2DIR spectra, rephasing and non-rephasing signals were collected by changing the pulse sequences and were added as well as 2DIR spectra should be properly phased, which was described in great detail elsewhere. [17,13] The absorptive (real part) 2DIR spectra are presented in this paper, unless indicated otherwise. For polarization-controlled IR PP experiments, the pump beam was vertically polarized with respect to the optical table plane and the polarization direction of the probe beam was set to be 45 degrees with respect to that of the pump beam [18]. The probe beam was collimated after the sample and went through the analyzer polarizer that was mounted on a motorized rotational stage. The IR PP signals, $S(\omega_{\text{pr}}, t)$, were frequency-resolved. The parallel and perpendicular IR PP signals ($S_{\parallel}(\omega_{\text{pr}}, t)$ and $S_{\perp}(\omega_{\text{pr}}, t)$) were obtained alternatively by properly rotating the analyzer polarizer. Here, the room temperature for the 2DIR and IR PP experiments was adjusted to be 22 $^\circ\text{C}$.

3. Results and discussion

3.1. FTIR spectroscopy

Fig. 1 displays the FTIR spectrum of HN_3 in methanol at room temperature (22 $^\circ\text{C}$). The high frequency peak at 2132 cm^{-1} corresponds to the fundamental transition of the asymmetric stretching mode of HN_3 ($\nu_{\text{HN}_3} = 2132\text{ cm}^{-1}$) and the broad low-frequency peak at 2044 cm^{-1} is the overtone band ($2\nu_{\text{CO}} = 2044\text{ cm}^{-1}$) of the C–O stretching vibration ($\nu_{\text{CO}} = 1033\text{ cm}^{-1}$) of methanol [7].

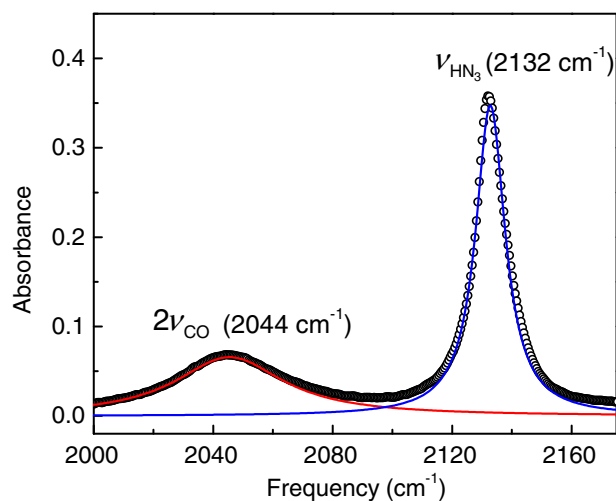


Fig. 1. FTIR spectrum of the azido stretch band of HN_3 in methanol. The high frequency peak at 2132 cm^{-1} corresponds to the asymmetric stretching vibration of HN_3 (ν_{HN_3}) and the low frequency peak centered at 2044 cm^{-1} is the overtone band of C–O stretch mode of solvent methanol ($2\nu_{\text{CO}}$) molecules. The solid lines are Lorentzian fits to the two bands.

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