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Journal of Molecular Structure 735–736 (2005) 135–143

Journal of
MOLECULAR
STRUCTURE

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Vibrational dephasing of the –N=C=N– anti-symmetric stretching mode of carbodiimide studied by infrared photon echo method

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Received 31 August 2004; revised 30 October 2004; accepted 30 October 2004
Available online 15 December 2004

Abstract

We have studied vibrational dephasing of the carbodiimide (–N=C=N–) anti-symmetric stretching mode of di-cyclohexylcarbodiimide (DCCD) in carbon tetrachloride and *N*,*N*-dimethylformamide by infrared photon echo technique. Both time-integrated and frequency-resolved photon echo measurements have been carried out. The time-integrated signal shows a nonexponential decay with a time scale of a few picoseconds. The signal shows its peak at around the origin of the delay time, suggesting that the vibrational frequency fluctuation is in the fast modulation limit. We found unusual frequency dependence in the rise of the frequency-resolved photon echo signals. Simulations of the photon echo signal based on the conventional formalism of nonlinear infrared spectroscopy cannot reproduce the dependence. The origin of the unusual behaviors is discussed.

Keywords: Infrared photon echo; Carbodiimide; Vibrational dephasing

1. Introduction

Vibrational dynamics in liquids such as population relaxation, reorientational relaxation, or dephasing provide microscopic information such as local structures and dynamical fluctuations [1–5]. Recently, nonlinear infrared (IR) vibrational spectroscopy has received considerable attention with advent of technical development of generation of short IR pulses with high intensities [5]. Information obtained by nonlinear IR spectroscopy contains dynamical fluctuations, such as fluctuations of a vibrational transition frequency and an anharmonicity of the vibrational modes. Interactions between the vibrational state and its surroundings in liquids change a transition frequency from the average value continuously. A key physical quantity characterizing the fluctuation is time correlation function (TCF) of the time-dependent transition frequency, which can be obtained from three-pulse IR photon echo method. The technique has been applied to triatomic ions [6–10], cyanoferrates [10,11], metal carbonyl compounds [12–18], amide and peptide [19–22], and hydrogen bonding compounds and liquids [23–28].

In this study, we have applied IR photon echo spectroscopy to a vibrational mode of polyatomic molecule, the carbodiimide (–N=C=N–) anti-symmetric stretching mode of di-cyclohexylcarbodiimide (DCCD). There are a couple of reasons to select this mode for the IR photon echo experiment. First, we investigated vibrational population relaxation of this mode by transient grating technique in the previous work [29]. The transient grating measurements revealed that the population relaxation of the $v=1$ state shows a nonexponential decay and was reproduced well by a biexponential function with time constants of 200–300 fs and 1.4–1.5 ps with almost equal amplitudes. A time scale of the reorientational relaxation was found to be longer than a few picoseconds. We interpreted the biexponential behavior by a model of rapid population distribution with

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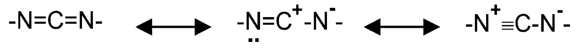
doi:10.1016/j.molstruc.2004.10.085



$$\text{-N=C=N-} \longleftrightarrow \text{-}\underset{\cdot\cdot}{\text{N}}\text{=C}^{+}\text{-N}^{-}\text{-} \longleftrightarrow \text{-N}^{+}\text{≡C-N}^{-}\text{-}$$

Scheme 1.

other modes and irreversible relaxation from these modes. When the time scales of vibrational population relaxation and/or reorientational relaxation are similar to that of the dephasing, they significantly contribute to the dephasing. Especially, vibrational population relaxation of organic polyatomic molecules in solution sometimes proceeds on a sub-picosecond time scale [22,24,30]. Furthermore, some vibrational modes exhibit nonexponential vibrational relaxation on a similar time scale to that of the vibrational dephasing. Therefore, it is interesting to study the vibrational dephasing of such a mode with ultrafast, nonexponential population relaxation.

Second, carbodiimides are important compounds as versatile reagents in organic and biochemical synthesis such as synthesis of nucleotides and peptides, heterocycle synthesis, oxidation with dimethyl sulfoxide, cycloaddition reactions, and so on [31–35]. The carbodiimide molecule has two centers of reactivity; the central carbon is electrophilic and the terminal nitrogens are electron-rich. Most of the reactions of carbodiimides involve nucleophilic attack to the carbon atom. It is also extensively known that interchange among three structures with different charge distributions and covalent bonds is considered to take place [36] (Scheme 1).

In the past, the equilibrium structure and physical properties of carbodiimides were studied theoretically and experimentally [37–39], however, dynamical aspects such as charge fluctuation described above were not investigated, though this is one of the key concepts to understand the reactivity of this molecule. The electronic resonance structure of the carbodiimide may induce frequency fluctuations of the –N=C=N– mode, therefore, this mode is a good target to be investigated by nonlinear IR spectroscopy.

2. Experimental

The experimental setup was described previously [9,40]. Briefly, IR pulses are generated by mixing near IR pulses from an optical parametric generator and amplifier pumped by the fundamental from a Ti:sapphire regenerative amplifier. The IR pulse has a gaussian-shaped spectrum with a full width at half maximum of about 120 cm^{-1} and an energy of about 4 μJ/pulse at a central frequency of 2120 cm^{-1}. After compressing the pulse by passing through a silicon window, a pulse width is estimated to be about 150 fs by autocorrelation measurement.

For the IR photon echo experiment, the IR pulse is split into three parts by two CaF$_2$ beam splitters. In the experiment, τ and T denote the delay time between the pulse 1 (denoted by its wavevector $\mathbf{k}_1$) and pulse 2 ($\mathbf{k}_2$), and between pulses 2 and 3 ($\mathbf{k}_3$), respectively (Fig. 1). The origin of the delay time is determined within an error of a few tens of femtoseconds by an autocorrelation method. The three pulses are aligned in a boxcar geometry and focused into a sample cell with an off-axis parabolic mirror. A signal generated into a phase matching direction of $-\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3$ is collimated with a parabolic mirror and separated spatially from the residual pump pulses. The signal detected by a liquid nitrogen cooled InSb detector was processed by a boxcar gated integrator and a lock-in amplifier. The $\mathbf{k}_1$ pulse was synchronously chopped at a half of the repetition rate of the regenerative amplifier. For the photon echo experiment, the delay time τ was scanned at a fixed delay time $T=0$ fs. In order to measure a spectral intensity of the photon echo signal, the signal was dispersed in a monochromator and was detected with a liquid nitrogen cooled InSb detector. Under the same experimental condition, nonresonant responses from CCl$_4$ and CaF$_2$ windows were not observed.

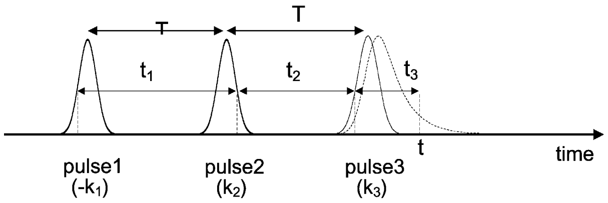


Fig. 1. Definition of the delay time between the pulses.

Samples (DCCD (Aldrich), CCl$_4$ and DMF (Wako Pure Chemicals)) were used without further purification. The sample solution is retained in a sample cell with a spacer (an optical path length of 200 μm) between CaF$_2$ windows (a thickness of 3 mm), and the concentration of the solution was adjusted so that the maximum optical density at the excitation wavelength was about 1.0. A typical concentration was 35 mM. An IR absorption spectrum of the DCCD solution was measured by a FT-IR spectrometer (PERKIN ELMER, Spectrum 1000). All measurements were performed at ambient temperature (22±1 °C).

3. Theory

The detailed theoretical formalism of nonlinear IR spectroscopy is summarized in literatures [3,5]. The third-order nonlinear polarization $P^{(3)}(t;\tau,T)$ is described by a sum of nonlinear response functions convoluted with the electric fields E of the three IR pulses

$$P^{(3)}(t;\tau,T) = \left(\frac{i}{\hbar}\right)^3 \int_0^\infty \mathrm{d}t_3 \int_0^\infty \mathrm{d}t_2 \int_0^\infty \mathrm{d}t_1 \times \sum_i R_i(t_1,t_2,t_3)E(t-t_3)E(t+T-t_3-t_2) E(t+T+\tau-t_3-t_2-t_1) \qquad (1)$$

For the nonlinear polarization with wavevector of $-\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3$, there are eight quantum pathways to be considered