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Solvent-dependent intra- and intermolecular vibrational energy transfer of $W(CO)_6$ probed with sub-picosecond time-resolved infrared spectroscopy

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Abstract

Solvent-dependent intra- and intermolecular vibrational energy transfer from the triply degenerate CO stretch mode of $W(CO)_6$ is observed in nine alkanes (C_nH_{2n+2}, $n = 5$–13) with single-color sub-picosecond time-resolved infrared spectroscopy. In all the solvents, the vibrational relaxation process is well characterized by three time constants: τ_1 (<1 ps), τ_2 (3–13 ps) and τ_3 (124–160 ps). The solvent dependence of τ_2 and τ_3 cannot be explained by the macroscopic properties of the solvent. In particular, the longest time constant τ_3 shows the minimum value of 124 ps in decane among the nine alkanes. The rate of the vibrational energy relaxation is a sensitive measure of the microscopic environments.

1. Introduction

In solutions, solute molecules interact with the surrounding solvent molecules. In the processes of chemical reactions, intermolecular interaction between the reactant and solvent molecules has a crucial influence on their mechanism. Therefore, it is vital for understanding the chemical reactions to develop a sensitive method with which the intermolecular interaction in solutions can be probed.

When a molecule is vibrationally excited, it relaxes toward the ground state. The vibrational energy initially deposited to the excited state is distributed among other modes of vibrational, rotational, or translational degrees of freedom in the same molecule or is transferred to the surrounding solvent molecules [1]. The process of vibrational energy relaxation depends on the intermolecular interaction. For example, the observed rate of vibrational energy relaxation varies with the number of carbon atoms in the alkane solvent [2–4]. Observation of the process of this relaxation is an effective method to probe the intermolecular interactions.

Single-color pump–probe infrared (IR) spectroscopy is effective for investigating the vibrational energy relaxation in solutions. In this method, the pump light and the probe light have the same frequency. When the pump pulse excites the molecule vibrationally, the population of the ground state ($v = 0$) decreases while that of the excited state increases. This population change causes the bleaching of the ground state absorption band ($v = 1 \leftarrow 0$). The vibrational energy relaxation process ($v = 0 \leftarrow 1$) is observed as the recovery of the bleaching. This method has been applied to CH stretch modes of haloalkanes [5–7], CO stretch modes of metal carbonyl complexes [8–16], and other intramolecular vibrational modes [17–20].

By using the single-color pump–probe IR method with sub-picosecond mid-IR light pulses, we observe the vibrational dynamics of the triply degenerate CO

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stretch mode (T_{1u}) of $W(CO)_6$ in a series of alkane solutions. Because the vibration is strongly IR active, small changes caused by the vibrational excitation and the following recovery are easily detectable. The vibrational energy relaxation of $W(CO)_6$ has been studied with picosecond IR spectroscopy [8–11], femtosecond IR spectroscopy [12], or IR-pump Raman-probe spectroscopy [21]. Its vibrational energy relaxation rate was observed in carbon tetrachloride, chloroform, hexane, and benzene solutions [8]. Temperature dependence of the relaxation rate was also observed in carbon tetrachloride and chloroform [9], and in 2-methylpentane [10]. However, the mechanism of the vibrational energy relaxation has not yet been fully understood. We observe the vibrational dynamics while changing the solvent systematically, by changing the number of carbon atoms in the solvent molecule, and try to find the properties of the solvent that control the vibrational energy relaxation.

2. Experiment

We have developed a single-color sub-picosecond time-resolved IR pump–probe spectrometer to observe the vibrational dynamics. The apparatus is shown in Fig. 1a. The output of a Ti:sapphire regenerative amplifier (Spitfire; Spectra Physics) was introduced to an optical parametric amplifier (OPA-800CF; Spectra Physics). Acquired signal and idler pulses in the near-IR region were focused on an $AgGaS_2$ crystal, where a mid-IR laser pulse was generated by difference frequency mixing. The energy of the mid-IR laser pulse was 4 μJ. Its spectral width (FWHM) was 120 cm^{-1}. The 15% of the mid-IR light was separated by a ZnSe window and was used as the probe light. The 70% passing through the window was used as the pump light. The remaining 15% was lost by the backside reflection of the ZnSe window. After an optical delay line, the pump pulse was focused on the sample. The probe pulse was focused on the same point as well. The probe pulse passing through the sample was analyzed by a monochromator (MS-257; Oriel) and was detected by an MCT detector (KMPCP11-2.0-J1; Kolmar Technologies). In this experiment, the spectral resolution of the monochromator was set to 4 cm^{-1}. For anisotropy measurements, a MgF_2 half-wave plate and a ZnSe wire-grid polarizer were used for controlling the polarization of the pump and probe pulses. To correct the fluctuation of the output laser power, a portion

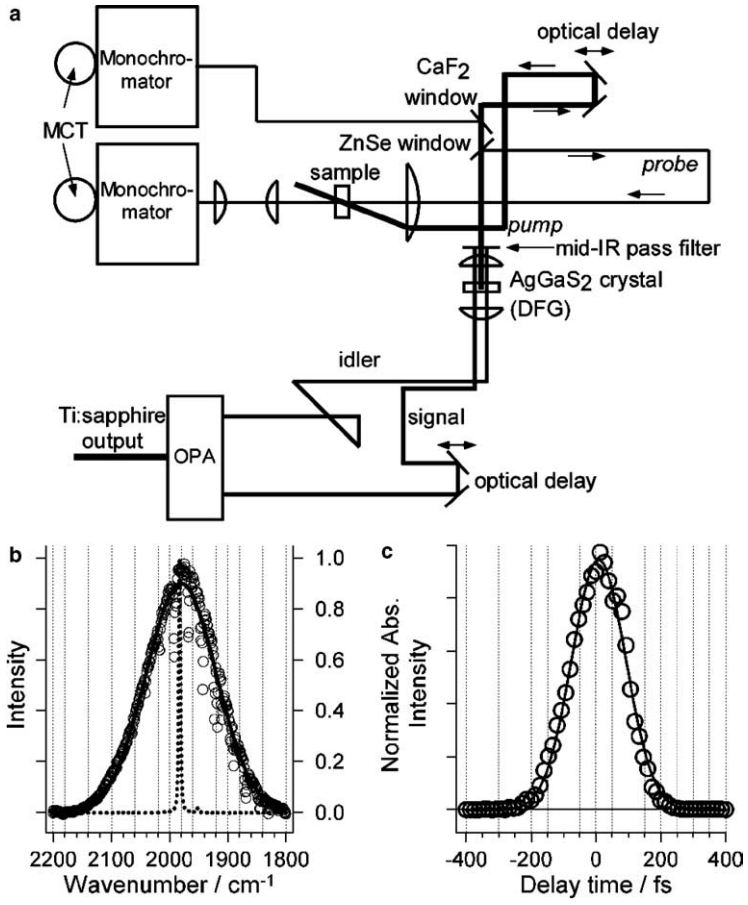

Fig. 1. (a) Block diagram of the time-resolved IR spectrometer. (b) Observed spectrum of the IR laser pulse (open circle), the best-fit Gaussian function (solid line) and the ground-state IR absorption of $W(CO)_6$ in heptane (dotted line). (c) Observed autocorrelation function of the IR laser pulse (open circle) and the best-fit Gaussian function (solid line).