

Terahertz spectroscopy of polar solute molecules in non-polar solvents

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Abstract

Low frequency spectra of liquid solutions of non-polar solvents were measured in the frequency range of 15–80 cm⁻¹ at room temperature by terahertz time-domain spectroscopy to investigate the solute–solvent interaction. The extinction coefficient of the solutions with polar solutes decreases as a function of frequency, whereas that of a non-polar solute increases. It is concluded that the observed spectral change of the polar solute is caused by fast reorientational dynamics due to librational motion of solutes.

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1. Introduction

Solvent–solute interaction is a central issue to understand solvent effects on chemical reactions and various relaxation processes in liquid phases [1]. The intermolecular interaction often has its characteristic frequencies in the region lower than 100 cm⁻¹. To investigate such low frequency interactions, there are two major strategies. One is to examine solvent effect on higher frequency transitions closely such as electronic transitions by optical excitation or vibrational transitions of intramolecular modes by infrared (IR) excitation. More direct way is to investigate the low frequency spectrum of the solutions. However, the low frequency transition is quite weak compared to those in the higher frequency region, and, furthermore, the spectrum is often broad and lacks specific structures, which makes discussion on the spectra difficult and unclear. Recently, two major techniques based on femtosecond

short-pulse lasers have been proven to be powerful to investigate low frequency spectra of the condensed phases. One is optical heterodyne-detected Raman-induced Kerr-effect spectroscopy (OHD-RIKES), in which a pump pulse creates transient anisotropy in index of refraction, whose relaxation is probed by the second pulse [2,3]. The other technique is terahertz time-domain spectroscopy (THz-TDS). Recently, developments have taken place in the coherent generation and detection of light pulses in the far-IR or THz range [4]. The frequency region achievable by this technique is 0.1–10 THz depending on the emitter/detector technology. In this work we have investigated low frequency spectra of liquid solutions of non-polar solvents to investigate interactions between solute and non-polar solvents.

2. Experimental

The detail of the experimental set up of THz-TDS was already described elsewhere [5,6]. Briefly, femtosecond pulses from a Ti:sapphire oscillator were used for generation and detection of the THz radiation. A major part of

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the pulse is focused to a (1 0 0)-InAs wafer with a 45° incidence to generate the THz radiation. The wafer is placed in a magnetic field (1.6 T) to enhance the intensity of the radiation. The rest of the femtosecond pulse is used to detect an electric field of the pulsed THz radiation by the electro-optic sampling method with a (1 1 0) ZnTe crystal (1 mm in thickness). THz-TDS measures the electric field of the radiation through a sample, providing the phase- and amplitude-changes of the radiation. Therefore, the index of refraction n and the extinction coefficient κ (or absorption coefficient α , $\alpha(\tilde{\nu}) = 4\pi\tilde{\nu}\kappa(\tilde{\nu})/\ln 10$) of the sample are obtained. The signal-to-noise ratio of the power spectrum of the THz radiation at around 40 cm^{-1} , which is near the peak of the field, is more than 10^4 . The wavenumber region under which the experimental data are fit for quantitative analysis is 15–80 cm^{-1} . The radiation field outside from this region is too weak to make reliable discussion. The measurements were done at room temperature, 293 K. The sample solutions were contained in a cell with Teflon windows with an optical path length of 15 mm. Samples, nitrobenzene, benzonitrile, chlorobenzene, carbon tetrachloride (Wako Pure Chemicals), and hexamethylbenzene (Aldrich) were used without further purification. The concentrations of the solutions were from 50 mM to 500 mM.

3. Results

Fig. 1 shows the molar extinction coefficient (κ_M) of nitrobenzene in carbon tetrachloride (CCl_4) as a function of the wavenumber. The signal intensity monotonically decreases with the wavenumber. Other polar molecules such as chlorobenzene (Fig. 2) or benzonitrile (Fig. 3) show similar spectral features in CCl_4 . On the other hand, for a non-polar solute such as hexamethylbenzene (HMB) in CCl_4 , the extinction coefficient is small compared to those of polar solutes as shown in Fig. 4. Moreover, the non-polar solute solution shows increase of the signal intensity with the wavenumber, which is an opposite trend to the polar solute cases. We also measured THz spectra of the benzonitrile solutions with different concentrations as shown in Fig. 3.

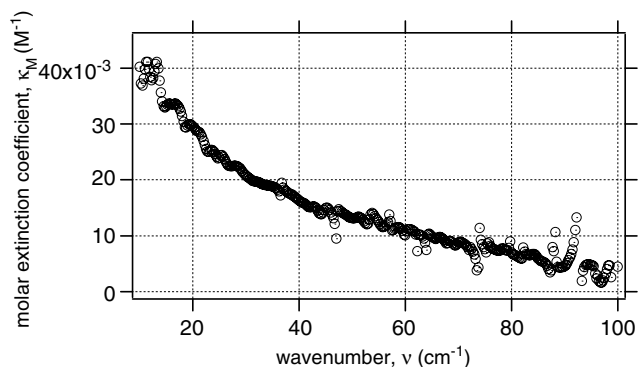


Fig. 1. Molar extinction coefficient of nitrobenzene in carbon tetrachloride as a function of the wavenumber. The concentration of the solution is 50 mM.

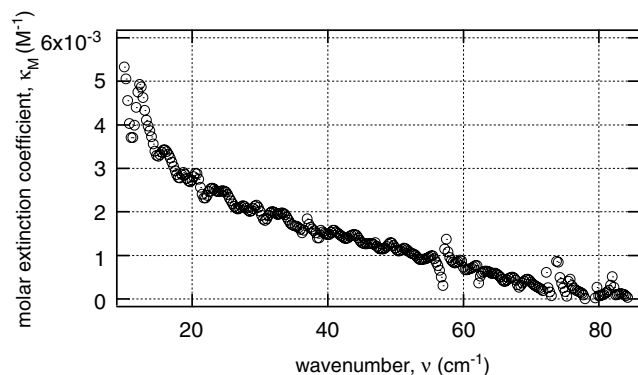


Fig. 2. Molar extinction coefficient of chlorobenzene in carbon tetrachloride as a function of the wavenumber. The concentration of the solution is 400 mM.

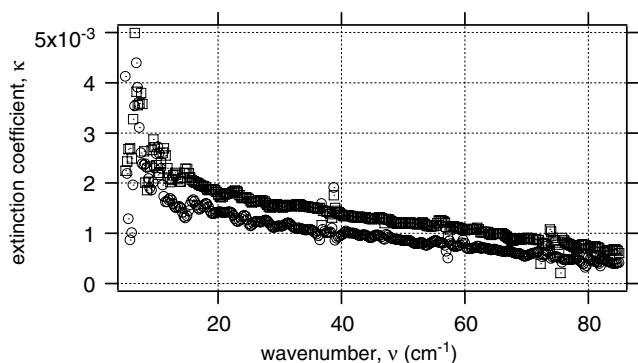


Fig. 3. Extinction coefficient of benzonitrile in carbon tetrachloride as a function of the wavenumber. The concentrations of the solution are 70 mM (rectangular) and 50 mM (circle).

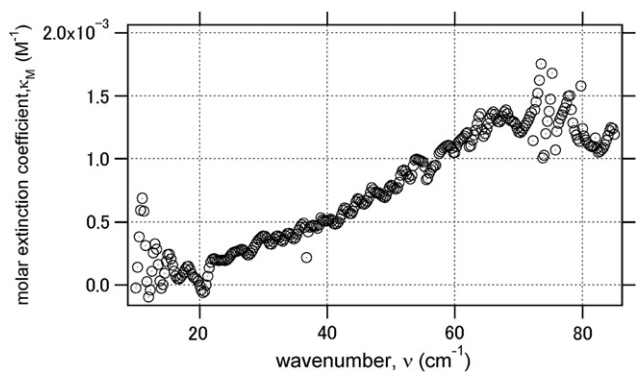


Fig. 4. Molar extinction coefficient of hexamethylbenzene in carbon tetrachloride as a function of the wavenumber. The concentration of the solution is 500 mM.

Although the variation of the concentration is not so large, the spectral intensity change follows the Beer's law, and we did not see significant difference in the spectrum when the concentration was changed. It seems that the signal intensity of the polar solute system is sensitive to the dipole moment of the solute. Nitrobenzene ($\mu = 4.2$ D, where μ denotes the dipole moment in the ground state) and benzonitrile ($\mu = 4.1$ D) have similar molar extinction coefficients.

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