

Breakdown of overdamped limit and narrowing limit in low frequency Raman spectra of liquids

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Depolarized low-frequency Raman spectra of water and aqueous electrolytes are analysed by a superposition of one relaxation mode and two vibration modes. We adopt a relaxation function which takes into account the inertia effect and the non-white effect (memory effect) of the heat bath. We firstly deduce the structure making or breaking effect in electrolytes from the fitting parameter of Raman spectra. We apply this method to the other simple liquid such as CCl_4 .

Key word: low-frequency Raman, liquid, random telegraph process, water

1 INTRODUCTION

Low-frequency (LF) Raman spectroscopy provides us the information of intermolecular motions in liquids. Collective motion of molecules in liquid causes fluctuating polarizability which includes the information of molecular dynamics.

Solvation, especially hydration, is an interesting subject for chemistry, biochemistry and polymer science. For example, many biopolymers need hydrated water to maintain their structures. To understand the solvation phenomena, it is important to clarify the dynamical structure of solvent.

Numerous authors have reported studies on the low-frequency Raman scattering [1–5] and the depolarized Rayleigh scattering [6–9] of liquid water. Walrafen and coworkers assigned two Raman bands in the low-frequency region, around 180 cm^{-1} and 50 cm^{-1} , to stretching and bending modes of water pentamers, respectively [10–12]. Recently, Raman-induced Kerr effect spectroscopy (RIKES) was used to investigate the dynamic property of water [13–15].

In this article, we report an effective method of phenomenological analysis for LF-Raman spectra of liquid and the results which is a potentially important clue to understanding the nature of liquid dynamics.

2 EXPERIMENT

Depolarized Raman spectra were obtained by using a double grating spectrometer (Ramanor U1000, Jobin-Yvon). The exciting light source was an argon ion laser operating at 488 nm with

power of 400 mW. The right angle scattering geometry was adopted with (VH) configuration. The depolarized Raman spectrum was recorded in the frequency range from -50 cm^{-1} to 250 cm^{-1} . The spectral resolution was 0.2 cm^{-1} .

A high-resolution spectrometer (DMDP2000, SOPRA) is also used to measure below 1 cm^{-1} . The spectrometer was operating in the Double Monochromator/Single Pass (DMSP) configuration. The exciting light source was a diode-pumped solid-state frequency-doubled Nd:YAG laser (DPSS532, COHERENT) operating at 532 nm with power of 400 mW. Maximum spectral resolution is 0.038 cm^{-1} with the slit width $30\text{ }\mu\text{m}$.

3 PHENOMENOLOGICAL ANALYSIS

The dynamical susceptibility $\chi''(\nu)$ is given by

$$\chi''(\nu) = K(\nu_i - \nu)^{-3} [n(\nu) + 1]^{-1} I(\nu), \quad (1)$$

where $I(\nu)$ is the Raman spectral intensity measured by photon counting method, $n(\nu) = [\exp(hc\nu/kT) - 1]^{-1}$ is Bose-Einstein factor, $\nu (= f/c)$ and $\nu_i (= f_i/c)$ is the Raman frequency shift and the incident laser light frequency, respectively. The frequencies ν and ν_i are represented by cm^{-1} , f and f_i are represented by Hz, and c is light velocity. The K is the instrumental constant.

Fig.1 shows the LF Raman spectral intensity of water at room temperature.

Dynamical susceptibility calculated from Fig. 1 by Eqn.(1) is shown in Fig.2. Details of three peaks around 180 cm^{-1} , 50 cm^{-1} and 10 cm^{-1} are revealed in χ'' spectra.

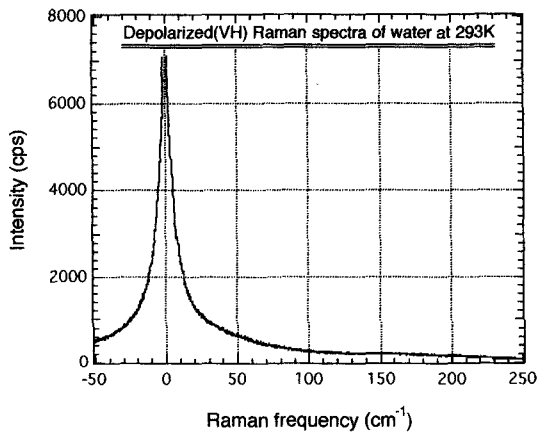


Figure 1: Intensity of low-frequency Raman spectra

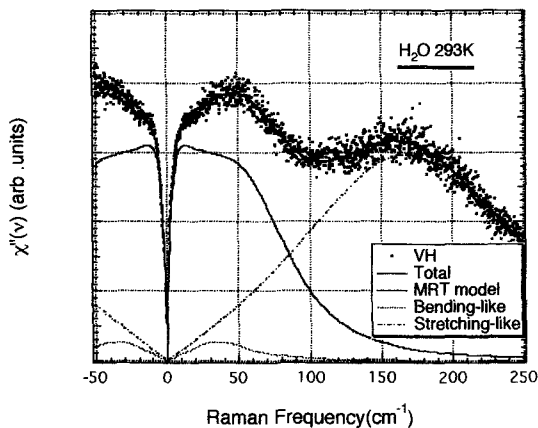


Figure 2: Dynamical susceptibility

To analyze the reduced Raman spectra, we use the superposition of one relaxation mode and two damped harmonic oscillator (DHO) modes. Equivalence between the reduced spectrum of light scattering and the far-infrared absorption spectrum has already been shown [16]. Therefore any function which describes dielectric relaxation is applicable to the reduced Raman spectra.

A Debye type relaxation function [17] and a Cole-Cole type relaxation function which is equivalent to the symmetrically broadened Debye function [18–21] have been used to fit the central component in the reduced low-frequency Raman spectra. The Debye function is based on the overdamped limit and the narrowing limit approximation for the Langevin equation of rotating dipoles. These approximations become unphysical in the high frequency region because the ab-

sorption energy of the relaxation mode becomes infinite. Therefore we use the imaginary part of the dielectric relaxation function which takes into account the inertia and memory effects [22] to analyze the low-frequency depolarized Raman spectra. This model is based on the multiple random telegraph(MRT) process.

The complex dielectric spectrum has the form

$$\chi^*(\omega) = 1 - i\omega v[s] \quad (2)$$

where $s = i\omega$.

In an asymmetric case, $v[s]$ is given by the continued fraction,

$$v[s] = \frac{1}{s + \frac{N\tilde{\Delta}_0^2}{s + \tilde{\gamma} + \frac{2(N-1)\tilde{\Delta}_0^2}{s + 2\tilde{\gamma} + \frac{3(N-2)\tilde{\Delta}_0^2}{s + 3\tilde{\gamma} + \dots}}}} \quad (3)$$

where $\tilde{\Delta}_0^2 = \Delta_0^2(1 - \sigma^2)$ and $\tilde{\gamma} = \gamma - 2i\sigma$. The MRT model is composed of N independent random telegraph processes each of which takes the value $\pm\Delta_0$. The γ is the inverse of the characteristic time of the random telegraph processes. A non-zero value of σ means that each probability of the random telegraph processes is asymmetric. This model naturally includes two specific cases: Gaussian-Markovian limit ($N \rightarrow \infty$) and narrowing limit ($\alpha_0 \ll 1$). The narrowing limit corresponds to the Debye type relaxation. We use Δ_0 , $\alpha_0 (= \Delta_0/\gamma)$, σ , N and relaxation strength as fitting parameters.

4 RESULTS AND DISCUSSIONS

4.1 WATER ISOTOPES [23, 24]

Depolarized low-frequency Raman spectra of H_2O , D_2O , H_2^{18}O , and D_2^{18}O are measured from 266 K to 350 K. Reduced spectra were fitted by the superposition of one MRT model and two DHO. An isotope effect between hydrogen and deuterium appeared in the relaxation time of the MRT model. The 180 cm^{-1} mode originated from the oscillatory motion of the oxygen atom in the hydrogen bonded water and frequency of this mode only depended on the mass of oxygen.

The intensity of the bending-like mode is disappeared in the best fitted results above 300K. The MRT model and one DHO can reproduce the reduced spectra. This result is consistent with the far-infrared absorption measurement: the 49 cm^{-1} band in the far infrared spectra is also disappeared at 303 K [25]. If the Debye type relaxation function is applied to the water spectra, the bending like mode is appeared above 300 K.

4.2 AQUEOUS ELECTROLYTE SOLUTIONS [26, 27]

The advantage of the MRT model is that the information of heat bath is included as α_0 (Kubo number). We found the change of α_0 correspond to the structure making and breaking effect of salts. α_0 becomes large with increasing the concentration of the structure making ions. This result is consistent with the proton relaxation rates measured by NMR [28] and self-diffusion constant [29]. The α_0 means the correlation rate of the heat bath originating from thermal fluctuation of water molecules. Large α_0 means the existence of the strong correlation in the fluctuating motion of water molecules.

Temperature dependence of the aqueous electrolyte solutions (LiCl, NaCl and KCl) are measured and analyzed. The relaxation times of aqueous solutions of 0.08 molar ratio is longer than that of water, and become shorter than 0.72 ps above 310~320 K. The intensity of the bending-like mode in aqueous solutions of 0.08 molar ratio exists up to 320K. We consider that the relaxation time means the average lifetime of the vibration unit for intermolecular vibrations. At high temperature, the vibration unit breaks during the time for several oscillations of the bending-like vibration. The strongly disrupted bending-like mode could not be distinguished from the relaxation mode which is taken into account the inertia and the memory effects. Thus the individual damped harmonic oscillation mode around 50 cm^{-1} disappeared in our fitting results. While in LiCl solution of 0.2 molar ratio, the relaxation time is much longer than that in water, and the bending-like mode exists in the whole temperature range.

4.3 SIMPLE ORGANIC SOLVENTS [30]

LF Raman spectra of liquid CCl_4 , CHCl_3 and acetone are also reproduced by single MRT model. Both Debye type relaxation and DHO cannot reproduce the spectra.

4.4 OTHER HYDROGEN-BONDED LIQUID [31]

The reduced Raman spectrum of ethylene glycol from 0.01 cm^{-1} to 300 cm^{-1} is reproduced with the use of a fitting function which contains two relaxation modes and three damped harmonic oscillator modes. The slow relaxation mode is characterized by the Gaussian-Markovian process under the narrowing limit. While for the fast relaxation mode the spectral profile cannot be reproduced by the function which is approximated by both narrowing limit and overdamped limit.

5 SUMMARY

Information about both relatively slow dynamics characterized by relaxation time and fast fluctuation corresponding to the heat bath are obtained from the reduced LF Raman spectra by using MRT model.

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