

論文内容の要旨

論文題目 Liquid dynamics probed by vibrational bandshape analysis of carbon dioxide
(二酸化炭素の振動バンド形解析による液体ダイナミクス)

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Information on solvent-solute interaction is necessary in order to fully understand chemical processes in solution. This is because the environment around the solute molecule varies time to time with the motion of the solvent molecules and the fluctuation induced by the solvent motion either accelerates or decelerates chemical processes. The present study aims at understanding these dynamic environments around molecules by analyzing bandshapes of probe molecule solvated in various solvents. Carbon dioxide has been chosen to be the probe molecule for two reasons. One of the reasons is that the molecule has simple structure having well separated three vibrational bands. The other is that the molecule does not have permanent dipole moment, and thus soluble in both polar and non-polar solvents. The infrared bandshape of its antisymmetric stretch mode is precisely analyzed. This mode had been chosen because it has large absorption coefficient while absorption of the solvents are generally small in this region.

Infrared bandshape includes vibrational bandshape and rotational bandshape. Vibrational bandshape is determined by vibrational dephasing due to frequency modulation of the probe molecule. Rotational bandshape is determined by reorientational motion of the probe. Total bandshape is therefore obtained by Fourier transforming total correlation function; the product of vibrational correlation function and rotational correlation function. Therefore environment around solute molecule can be studied as follows. First, correlation functions are created for a model system. Second, corresponding spectrum for the correlation functions are calculated and compared to the observed spectrum. Finally rationality of the model system is evaluated and, if necessary, feedback is given to the model system and the bandshape is calculated again. For infrared measurement, sample chamber has been evacuated to 0.5-2 Torr (measured by a thermistor attached to the spectrograph) in order to reduce the concentration of carbon dioxide inside the spectrograph. Sealed cell has been constructed to prevent sample solution from evaporation. S/N ratio of the infrared spectrum has improved, and infrared spectra of carbon dioxide in various solvents have been successfully obtained. The solvents include polar solvents (water, alcohols, acetonitrile, acetone, and dimethyl sulfoxide), and non-polar solvents (alkanes and cycloalkanes).

Temperature controlled infrared spectra of carbon dioxide in hexane, dodecane and

ethanol has also been measured. A new temperature-tunable sealed cell has been constructed since sample is more likely to evaporate during temperature-controlled measurements compared to usual infrared measurements. There are few improved features to overcome this problem. Temperature can be controlled by circulating constant-temperature water from a chiller. Temperature has been controlled from 5 to 70 °C. A new side lid for the sample chamber has been constructed to introduce constant-temperature water, sample and thermocouple inside the evacuated sample chamber.

Polarized Raman scattering spectra in acetonitrile have been measured in order to estimate contribution of rotational broadening to the bandshape. Spectra have been measured on a Raman spectroscopic system build by Okajima et al.

Sub-picosecond time-resolved infrared spectroscopy has also been carried out in order to estimate rotational correlation. Measurements have been done on laboratory-build Time-resolved infrared spectroscopic system. Signal is hardly seen with natural-abundant $^{12}\text{CO}_2$ sample, since atmospheric carbon dioxide absorbs most of the infrared light. Isotope-selected $^{13}\text{CO}_2$ is used for probe. The solvent is ethanol.

The observed bandshape of the antisymmetric stretch band of carbon dioxide is slightly asymmetric due to a small band located at lower frequency region. This small band is proved to be a hot band by temperature-controlled measurements. It is neglected in the analysis. The observed bandshape is not reproduced by a single Lorentzian, indicating that the vibrational dephasing of the mode is not represented by a single exponential decay. In fact, the bandshape is well reproduced by the sum of two Lorentzians with identical center frequency. In all these solvents, the observed bandshapes are fitted only with two Lorentzians. The narrower components have the widths of 2.5–5.5 cm^{-1} and the broader components have the widths of 7.9–20 cm^{-1} . In temperature controlled measurements, the two components have been found to show different behaviors on increasing temperature.

In general, correlation of stochastic processes decay as an exponential function in the long time range. Therefore double-Lorentzian bandshape may due to two dephasing processes. Exchange model which argues multiple dephasing processes is used to analyze the bandshape. Obtained exchange rates (~ 100 ps) are large compared to dephasing time (\sim ps and ~ 100 fs), indicating that there is no exchange between the two states during the dephasing process. In other words, the two states are independent, so that the two components can be treated as two Lorentzians. The obtained two center frequencies are very similar for all the solvents studied. It is highly unlikely that the two states having different dephasing times (ps and 100 fs) always have very similar

center frequencies. This discussion has another weakness that infrared bandshape is directly analyzed without separating contributions of vibrational and rotational dephasing which assumes single exponential decay for both correlation functions. Raman and TRIR measurements are carried out to separate rotational distribution to the bandshape.

By polarized Raman spectroscopy, isotropic and anisotropic bandwidth is estimated to be 1.29 and 7.9 cm^{-1} , respectively (Lorentzian fit). Therefore the rotational bandwidth is estimated to be $7.9 - 1.29 = 5.9 \text{ cm}^{-1}$. This bandwidth exceeds the width of narrower Lorentzian component, 3.2 cm^{-1} in acetonitrile. Therefore the observed infrared bandshape is suggested to be almost pure rotational.

Anisotropy r has been calculated from the parallel signal and perpendicular signal. Anisotropy shows exponential decay with a time constant of 0.95 ps, which means, in frequency domain, rotational band is a Lorentzian with 5.6 cm^{-1} , which corresponds to the result of Raman measurement.

Computational method has been carried out in order to directly calculate time-dependent frequency and to obtain bandshape. A combination method of classical molecular dynamics (MD) simulation and quantum chemical calculation is used. First classical MD simulation is done. Next field parameters are calculated at each snapshot along the trajectory, which characterize the environment around the probe molecule. At the same time, instantaneous frequency is parameterized by the field parameter by quantum chemical calculation. Time-dependent frequency can be then obtained by substituting field parameters at each time step. Using this method, ab initio computations of time-dependent frequency can be done at low computational cost, without repeated ab initio computation as in quantum chemical simulations.

Instantaneous frequency is parameterized in terms of electric field and Van der Waals field. As for electric field, frequency fluctuation by coulomb interaction is expanded in terms of electric field on carbon atom up to second order. The first term vanishes due to the symmetry of the carbon dioxide molecule; frequency should be the same with an applied electric field of E or $-E$. Therefore only the second term is evaluated. Coefficients have been obtained with Gaussian 09 program. As for the LJ field, frequency fluctuation caused by Van der Waals interaction is expanded in terms of generalized LJ force up to second order using semi-classical perturbation theory. The first term again vanishes because there is no bond anharmonicity in carbon dioxide molecule. Therefore only the second term is evaluated. Vibrational correlation function is calculated by summing these two correlations. However, the correlation does not decay in the time range of picosecond, and the corresponding power spectrum has no bandwidth. This is due to the

amplitude of the fluctuation is too small to give dephasing to the correlation.

Rotational correlation function is calculated directly from the trajectory of the simulation. Molecule-fixed unit vector is set along the molecular axis of carbon dioxide. Correlation function is calculated as an autocorrelation of the unit vector. It seem to be a exponential decay within a few picoseconds. Corresponding power spectrum indicates that the rotational broadening is about 3 cm^{-1} .

Apodization is necessary for Fourier transformation of correlation function into frequency domain. Hamming apodization which gives the same instrument function as FT-IR measurement is used, so that the calculated spectra can be compared to observed infrared spectrum without any convolution or deconvolution.

Total calculated bandshape agrees well with the observed bandshape. The result indicates that the observed bandshape is almost pure rotational, which agrees with the experimental results of Raman (§4.5) and TR-IR (§4.6) measurements. Similar results have been shown for dodecane solution as well.

Rotational motion is often described using diffusion equations, which give exponential decay in correlation function. However, this method assumes “small angular steps”, which may not applicable to small molecules. Gordon has shown more generalized rotational diffusion models called m-diffusion model and J-diffusion model, which can treat both small angular steps and large angular steps over $1/2\pi$. Basically the models are rotors with angular frequency changing stochastically. The orientation of the rotors is not changed by the change in angular frequency.

FORTTRAN 90 programs have been written to simulate rotational correlation function, instead of solving recursive equations as Gordon has done. A rotor rotates freely with a constant angular frequency. The direction of the moment of inertia is stochastically changed with a certain probability. Correlation functions are calculated for 50 different angular frequencies, and they are summed up according to Maxwell-Boltzmann distribution.

As a result, free rotor ($\tau = \infty$) shows negative correlation, which means molecule rotates over $1/2 \pi$. With increasing probability of diffusion, negative peak disappears, whereas rapid decrease in first few 100 fs remains as dumped oscillation. This feature resembles the correlation function obtained in MD simulation.

To conclude, double-Lorentzian bandshape seem to correspond to the dumped oscillatory rotation. This is due to carbon dioxide being small, which rotates in large angle steps during diffusion. Also, the rotational dephasing process is able to be observed in vibrational spectra because the molecule is symmetric (non-polar) so that vibrational bandwidth is negligible.