

# 学位論文の要約

題目 Full molecular dynamics simulations of molecular liquids for single-beam spectrally controlled two-dimensional Raman spectroscopy  
(分子動力学シミュレーションを用いた凝縮系のシングルビーム2次元ラマン分光法)

氏名 JO Ju-Yeon

## 序論

Two-dimensional (2D) Raman spectroscopy has been used to study vibrational motions in liquids both theoretically and experimentally, because it can capture the information regarding the inhomogeneity and anharmonicity of the system, which cannot be obtained from linear spectroscopy. The observables of 2D Raman spectroscopy are fifth-order response functions defined in terms of the correlation functions of molecular polarizabilities. It was found that this response is very difficult to measure experimentally due to the unforeseen cascading effect of light emissions. Even though there were many attempts to overcome this issue, cascaded signals were not easily eliminated. In recent years, two methods have been proposed to overcome this difficulty, 2D THz Raman spectroscopy and single beam 2D Raman spectroscopy. Using these methods, they could capture vibrational mode-mode coupling. However, compared to the 2D Raman spectroscopy that was mostly discussed in the time-domain, these two methods are implemented in the frequency-domain and can be very difficult to interpret. To address this problem, in this thesis we establish a formalism to connect the fifth-order response functions with single-beam 2D Raman spectroscopy. We demonstrate the methods using response functions generated by molecular dynamics simulations.

## 2D Raman and 2D THz spectroscopy

We explain the significant points for properly simulating 2D vibrational spectroscopic studies of intermolecular modes using the full molecular dynamics approach, in particular regarding the system size, the treatment of the thermostat, and the inclusion of the Ewald summation for the induced polarizability. Moreover, using the simulation results for water employing various polarization functions, we elucidate the roles of the permanent and induced optical properties in

determining the 2D profiles of the signal.

#### Coherent 2D Raman scattering

Frequency-domain two-dimensional Raman techniques, which are equivalent to coherent two-dimensional Raman scattering (COTRAS) techniques, are a tool which can capture the low-frequency vibrational dynamics of liquids and biomolecules. However, since this technique was only recently developed, the COTRAS data has not been as well tested against simulations and experiments, compared with the other two-dimensional vibrational spectroscopy methods. Here, we present the computation of the COTRAS spectra for liquid water and carbon tetrachloride by using an equilibrium-nonequilibrium hybrid molecular dynamics simulation algorithm. We elucidated the mechanisms governing the 2D signal profiles, which involve the anharmonic mode-mode coupling and the nonlinearities of the polarizability for the intermolecular and intra-molecular vibrational modes. Our data illustrates that the predicted signal profiles and intensities provide useful information for examining the consistency between the experiments and simulations.

#### Single-beam 2D Raman spectroscopy

Single-beam spectrally controlled two-dimensional Raman spectroscopy is a unique 2D vibrational measurement technique that uses signal generated from trains of short pulses produced using a pulse shaping technique from a single broadband pulse. This approach overcame the difficulty of the cascading effects and created a new possibility for measuring the intra- and inter-molecular modes of molecular liquids by means of fifth-order 2D Raman spectroscopy. Recently, a new pulse design for this measurement has been developed by Hurwitz, et al, in order to clearly separate the contribution of the fifth-order polarization and the third-order one. This allows for quantitatively investigating the mode-mode coupling mechanisms that are often overlapped. Here, we elucidate the methodology for simulating 2D Raman signals for single-beam coherently controlled measurements on the basis of the second-order response function approach. From water results, we find that the intra-molecular OH-stretching and inter-molecular HB-translation coupling should be observed as off-diagonal cross peaks in the 2D spectra.