

2E13

## MD simulation and analysis of SFG spectrum of liquid/vapor interface of methanol

(東北大院理\*, 分子研\*\*) ○Sokolov Vladimir\*.,\*\*, 石山達也\*, 石田干城\*\*, 森田明弘\*

**[Introduction]** Sum Frequency Generation (SFG) spectroscopy is a powerful tool for investigating interface structure of many materials. In order to fully extract rich microscopic information from the SFG spectra, we have developed theory and computational methods of SFG spectroscopy using MD simulation. In our previous applications, we have mainly studied aqueous interfaces [1-4].

In the present work, we applied the computational methods to liquid methanol to investigate the C-H stretching vibration. While methanol is regarded as a small model containing one CH<sub>3</sub> group, the spectral structure of CH<sub>3</sub> moieties is complicated due to Fermi resonance with the C-H bending overtones. Detailed understanding of C-H stretching vibration is of crucial importance for further study on other alkyl molecules.

**[Modeling]** A flexible and polarizable model of the methanol molecule is developed for the present work, and part of the modeling procedure has been reported previously [5]. In brief, the intermolecular electrostatic interaction is described by the partial charges and Charge Response Kernel (CRK) [6]. Our model takes account of geometry dependence of these parameters, to accurately describe the dipole moment vector and polarizability tensor as a function of molecular vibrational configuration. In the description of intramolecular force field, the vibrational coupling of C-H stretching and bending is incorporated to treat the Fermi resonance.

**[MD Procedure]** Before calculation of the SFG spectrum, we checked our model by calculating the bulk properties of methanol. The MD simulation of bulk methanol was carried out with 216 molecules with the three-dimensional periodic boundary conditions. The density and temperature are set to be 0.787 g/cm<sup>3</sup> and 298.15K, respectively, using the NVT ensemble. Statistical sampling was taken using parallel computing of 16 independent trajectories.

**[Results and Discussion]** Calculated results are summarized in Table 1, Figures 1 and 2. These results show that our model reproduces the experimental bulk properties of methanol fairly accurately.

	Vaporization energy (Kcal/Mol)	Dipole moment (Debye)	Diffusion coefficient ( $\times 10^{-5}$ cm <sup>2</sup> /s)	Hydrogen bonds $N_{OH}$	Coordination number $N_{OO}$
MD	8.89 $\pm$ 0.41	2.72	2.42 $\pm$ 0.22	1.44	1.46
Exp.	8.99 $\pm$ 0.05	2.87	2.42	1.77 $\pm$ 0.07	1.6 $\pm$ 0.2

Table1. Calculated methanol properties in comparison with experiments.

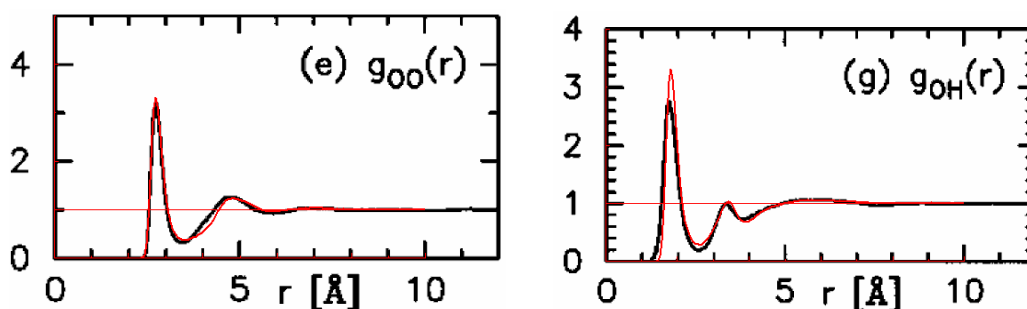


Fig.1. Experimental (black) [7] and MD simulated (red) radial distribution functions of OO (left panel) and OH (right panel), where H is the atom of hydroxyl moieties.

Figure 2 shows the calculated infrared spectrum of C-H and O-H stretching region, including the effects of Fermi resonance. The calculated SFG spectrum of liquid methanol will be reported and discussed on the conference.

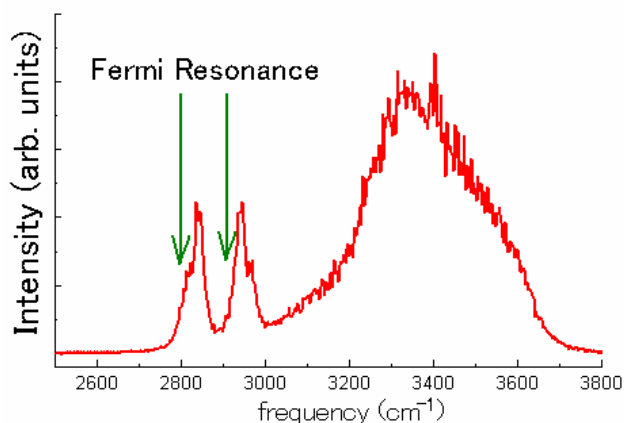


Fig.2 Calculated IR spectra of liquid methanol.

## [References]

- [1] T. Ishiyama, A. Morita, Chem. Phys. Lett., 431 (2006) 78.
- [2] T. Ishiyama, A. Morita, J. Phys. Chem. C, 111 (2007) 721.
- [3] T. Ishiyama, A. Morita, J. Phys. Chem. C, 111 (2007) 738.
- [4] T. Ishiyama, A. Morita, J. Phys. Chem. A, 111 (2007) 9277.
- [5] V. V. Sokolov, T. Ishiyama, T. Ishida, A. Morita, Annual Meeting of Japan Society for Molecular Science (2007), 2P063.
- [6] T. Ishida, A. Morita, J. Chem. Phys., 125 (2006) 074112.
- [7] T. Yamaguchi, K. Hidaka, A. K. Soper, Mol. Phys., 97 (1999) 603.