4E09

MD simulation of liquid methanol/vapour interface. Calculation and analysis of SFG spectrum

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[Introduction]

This project aims at providing detailed analysis on interface structure and SFG spectroscopy with alkyl chain molecules. For this purpose, we have developed flexible and polarizable model of methanol and reported in the previous conference [1]. The model reproduced a number of properties for liquid methanol, including IR and Raman spectra. In this paper, we present MD calculations of liquid methanol/vapour interface and the SFG spectra. Main topics of our study include the assignment of the SFG spectra and investigation of the Fermi resonance effects.

[Modeling]

In our model of methanol, intermolecular electrostatic interactions are represented using partial charges Q_a at site a and the charge response kernel K_{ab} beween sites a and b, which depend on the structure of molecule as follows,

$$Q_a = Q_a^0 + \sum_j \frac{\partial Q_a}{\partial S_j} S_j + \sum_b K_{ab} V_b \,, \tag{1}$$

$$K_{ab} = K_{ab}{}^0 + \sum_j \frac{\partial K_{ab}}{\partial S_j} S_j \,, \tag{2}$$

where $Q_a{}^0$ and $K_{ab}{}^0$ are the partial charge and charge response kernel in equilibrium position, and S_j denotes the internal coordinate. The parameters in Eqs. (1) and (2) are determined based on the calculations by B3LYP/aug-cc-pVTZ.

The intramolecular potential includes the cubic coupling among C-H stretching and bending modes to account for the Fermi resonance. The form of the coupling is given as

$$\begin{aligned} U_{FR} = {} & f_1(2S_4S_9S_{10} + S_{10}^2S_2 - S_4^2S_2) + f_2(S_4^2S_3 + S_{10}^2S_3) \\ & + f_3S_5^2S_3 + f_4(S_2S_4S_5 + S_5S_9S_{10}) \end{aligned} \,, \tag{3}$$

where S_3, S_2, S_9 are symmetric and asymmetric C-H stretching coordinates, and S_5, S_4, S_{10} are symmetric and asymmetric bending coordinates. The coupling coefficients f_i was determined by B3LYP calculations with the quantum correction

factor. The details of the modeling will be reported elsewhere [2].

[Results and Discussion]

Calculated density profile and orientation distribution of methanol molecules at the liquid-vapor interface are shown in Fig. 1. We can see that the axis of methyl group is oriented with an average tilt angle of 66^{o} out of the liquid at the top layer. No strong orientation is observed in the second layer of the interface.

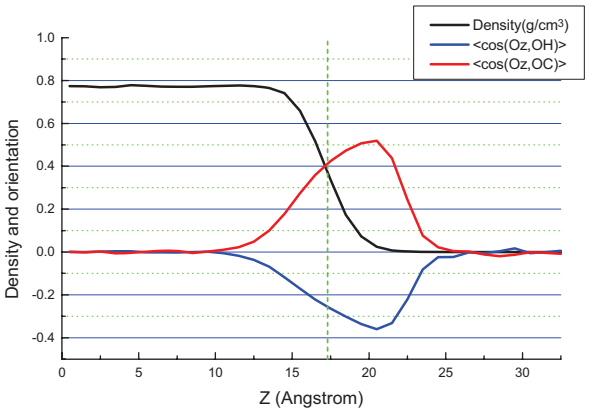

Fig.1 Density and orientation of methanol

Calculated SFG(ssp) spectrum of methanol is shown in the upper panel of Fig.2, which is in good agreement with experiment. From Fig.2 we can see that Fermi resonance makes significant influence on the shape of SFG spectrum. In comparison, the low panel shows the calculated spectrum without the Fermi resonance terms. In the lower panel, the spectral features at 2900-3000 cm^{-1} region are totally absent. Details of the analysis will be shown in the presentation.

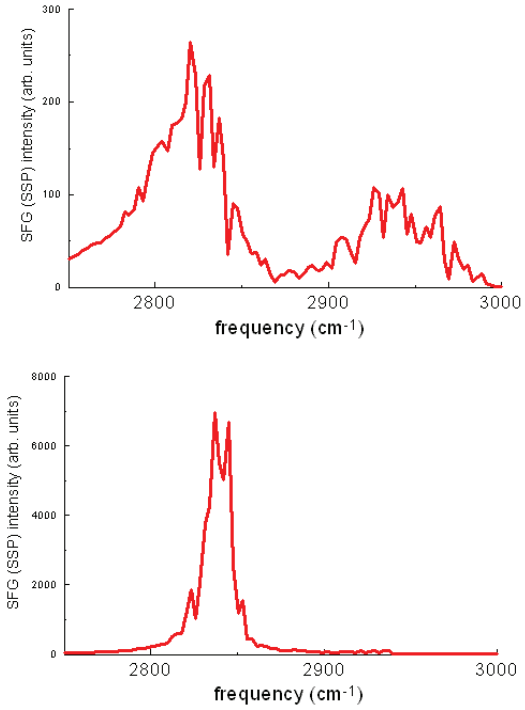

Fig.2 SFG (SSP) spectrum intensity calculated with (up) and without (down) Fermi resonance

[1] V. V. Sokolov, T. Ishiyama, T. Ishida, A. Morita, Annual Meeting of Japan Society for Molecular Science (2008), 2E13.

[2] V. V. Sokolov, T. Ishiyama, A. Morita, in preparation.