Accurate modeling of CH vibrations for the analysis of alkyl molecules

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[Introduction] Sum Frequency Generation (SFG) is a powerful technique for probing vibrational spectra of a variety of interfaces, such as liquids and polymers. While experimental SFG spectra are known to be sensitive to the interface structure at a molecular level, precise interpretation of those spectra is still challenging in many cases. Therefore, we have developed theories and computational methods of the SFG spectroscopy using MD simulation, and applied them to aqueous interfaces with considerable success [1-4].

The present work aims at applying our computational methods to the interfaces including alkyl chains. Alkyl chains have ubiquitous importance in organic films and polymer interfaces, and their C-H stretching vibration has been extensively studied by SFG and IR spectra. Their spectral structure in C-H stretching vibration is often complicated by those of CH_3 and CH_2 moieties and Fermi resonance with the CH bending overtone. As the first step, we construct an appropriate model of methanol for describing interfacial vibrational spectra.

[Modeling] The present model of methanol is flexible and polarizable, and all the ingredient parameters are determined by B3LYP density functional theory with AUG-cc-pVTZ basis set.

In the description of intramolecular force field, a substantial part of the modeling is the treatment of the Fermi resonance. The intramolecular potential energy of methanol molecule has the following form;

$$
\begin{aligned}
U ={}& \frac{1}{2}k_1(r_1^2 + r_2^2 + r_3^2) + k_2(r_1 r_2 + r_2 r_3 + r_3 r_1) + \frac{1}{2}k_3(\alpha_1^2 + \alpha_2^2 + \alpha_3^2) \\
&+ k_4(\alpha_1\alpha_2 + \alpha_2\alpha_3 + \alpha_3\alpha_1) + \frac{1}{2}k_5(\beta_1^2 + \beta_2^2 + \beta_3^2) + \frac{1}{2}k_6 r_{CO}^2 + \frac{1}{2}k_7 r_{OH}^2 \\
&+ \frac{1}{2}k_8\theta_{HOC}^2 + k_9\cos(\tau_1 + \tau_2 + \tau_3) \\
&+ f_1(2S_4 S_9 S_{10} + S_{10}^2 S_2 - S_4^2 S_2) + f_2(S_4^2 S_3 + S_{10}^2 S_3) + f_3 S_5^2 S_3 + f_4(S_2 S_4 S_5 + S_5 S_9 S_{10})
\end{aligned} \tag{1}
$$

where S_i denote the natural internal coordinates as shown below, *i.e.*

$$S_1 = r_{OH} \quad , \quad S_2 = (2r_1 - r_2 - r_3)/\sqrt{6} \quad ,$$

$$S_3 = (r_1 + r_2 + r_3)/\sqrt{3} \quad ,$$

$$S_4 = (2\alpha_1 - \alpha_2 - \alpha_3)/\sqrt{6} \quad ,$$

$$S_5 = (\beta_1 + \beta_2 + \beta_3)/\sqrt{6} - (\alpha_1 + \alpha_2 + \alpha_3)/\sqrt{6}$$

$$, \qquad S_6 = \theta_{HOC} \quad ,$$

$$S_7 = (2\beta_1 - \beta_2 - \beta_3)/\sqrt{6} \quad , \quad S_8 = r_{CO} \quad ,$$

$$S_9 = (r_2 - r_3)/\sqrt{2} \quad , \quad S_{10} = (\alpha_2 - \alpha_3)/\sqrt{2} \quad ,$$

$$S_{11} = (\beta_2 - \beta_3)/\sqrt{2} \quad ,$$

$$S_{12} = (\tau_1 + \tau_2 + \tau_3)/\sqrt{3} \; .$$

C–H=1.094
C–O=1.421
O–H=0.963
<HCH=108.5
<COH=108.0
<OCH=110.4258
τ_i – dyhedral angles

Figure 1: internal coordinates and reference geometry of methanol

Note that the last four terms in eq. (1) are responsible for Fermi resonance, and the equivalence of three hydrogens in the methyl group is taken into account.

For modeling of electrostatic interaction and polarization, we used the Charge Response Kernel (CRK) method. The calculation of partial charges and CRK of methanol were performed using the GAMESS-UK program with our extension [5]. The present model takes account of geometry dependence of the partial charges and CRK, so that it is able to describe the dipole moment vector and polarizability tensor accurately as a function of molecular vibrational configuration. In the poster, we will present the details of molecular modeling and preliminary results of MD simulation using this model to evaluate its performance.

[References]
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