

**Identification of ordered and disordered Langmuir films through computational sum frequency generation spectroscopy**

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**[Abstract]**

The structures and orientations of Langmuir films, formed by 1-dodecanol on water surface, were investigated by using molecular dynamics (MD) simulation and computational analysis of sum frequency generation (SFG) spectroscopy. A general model of long-chain alcohols was proposed on the basis of charge response kernel theory. The present model is constructed with parameters for constituent functional groups, and can be readily extended to analogous alkyl molecules. Using this model, molecular orientation, disorder and SFG spectra of Langmuir films were analyzed. The results allow us to clarify microscopic relationship between SFG spectra and molecular structure of Langmuir films.

**[Introduction]**

Amphiphilic molecules with long-chain alkyl moieties, such as phospholipids, long-chain alcohols and carboxylic acids, can form ordered monolayer structures on hydrophilic surface. Such ordered structure is seen in Langmuir films, self-assemble monolayer, Langmuir-Blodgett (LB) films, etc. The ordered structures are readily (often spontaneously) constructed, and widely utilized for various devices or functionalized interfaces. Detailed structural characterization of these film is important to understand the properties, though available techniques to characterize such wet and soft interfaces are rather limited.

The sum frequency generation (SFG) spectroscopy has been used to investigate Langmuir monolayers due to its highly surface sensitivity.<sup>[1]</sup> The SFG spectra are known to be sensitive to molecular orientation and conformational disorder of alkyl groups in the Langmuir monolayer. Reliable theoretical support to analyze the observed SFG spectra is essential to fully extract the microscopic information of Langmuir films.

The quantitative analysis of C-H stretching band of Langmuir monolayers is quite challenging to theoretical calculation. It requires an accurate model to describe symmetric stretching, asymmetric stretching and Fermi resonance included in the C-H band. At the same time, the contribution from different conformer should also be considered. We have developed suitable molecular model of C-H groups in the case of small alcohols so far.<sup>[2,3]</sup> Based on these development, the present work aims at proposing a general and transferable model for alkyl molecules, and extend our methods to investigate the ordered and disordered structures of Langmuir monolayers. This work will realize the computational analysis of C-H stretching vibrational spectra of large organic molecules through MD simulation, and lead to further computational studies of polymer and protein systems.

**[Model and Method]**

In this work, we chose 1-dodecanol [ $\text{CH}_3(\text{CH}_2)_{11}\text{OH}$ ] as target molecule. In reliable MD simulations of SFG spectra, molecular modeling is of key importance. The polarized model is based on charge response kernel (CRK), which can be obtained from *ab initio* calculations. However, it is time consuming to perform quantum mechanical (QM) calculations on large molecules, especially when different conformers are involved in systems. In this case, we proposed a systematic method to obtain the polarizable parameters from *ab initio* calculations of small molecules in training set (ethanol, propanol and butanol). The proposed strategy takes account of possible conformers, and allow us to theoretically investigate the C-H stretching SFG spectra of large organic molecules. It can also be readily transferred to other large molecules with acceptable computational cost.

## [Results and Discussion]

Table. 1. Calculated molecular properties of alcohols.

	Density(g/mL)		$\Delta H_v$ (kcal/mol)		Surface tension (mN/m)	
	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.
ethanol	0.774(0.003)	0.785	10.18(0.23)	10.12	23.7(4.0)	22
propanol	0.799(0.002)	0.799	11.40(0.19)	11.35	22.7(4.2)	23.3
butanol	0.797(0.002)	0.806	12.79(0.21)	12.52	21.9(4.1)	24.9
octanol	0.802(0.003)	0.822	15.53(0.26)	16.98	27.6(5.5)	27.1

First, MD simulations for bulk and interface of ethanol, propanol, butanol and octanol liquid were carried out to validate the performance of the presented model. The calculated molecular properties, such as density, heat of vaporization and surface tension are in good agreement with experimental results (Table 1). The SFG spectra of target molecules were also calculated and compared with experimental data<sup>[4]</sup> (Figure 1).

After the validation of the model, it is used to perform MD simulation of 1-dodecanol on water surface. Several surface areas were chosen to represent the different phase of Langmuir films on water. The orientation of tail chain, disordered ratio, and SFG spectra are simultaneously analyzed. The results will be shown in presentation.

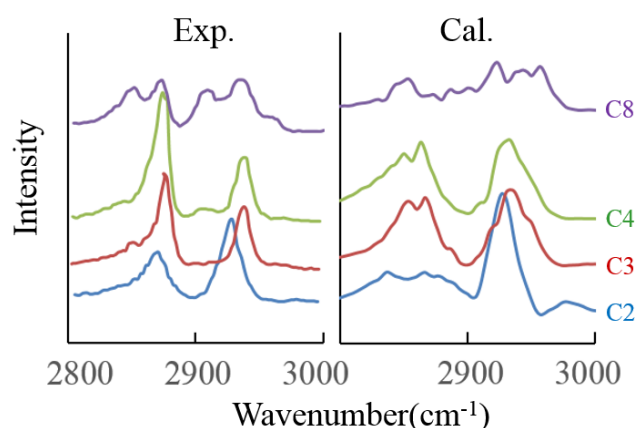


Figure. 1. Calculated and experimental<sup>[4]</sup> *ssp*-SFG spectra of alcohols.

## [References]

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