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## Collaborative molecular dynamics and SFG study on the interface of organic carbonate liquids

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**[Introduction]** Organic carbonates, such as propylene carbonate (PC) and dimethyl carbonate (DMC), are widely employed as electrolytes in modern lithium ion batteries due to their wide electrochemical window. The performance of the solvents is largely related to the interface to the electrodes. However, it is generally a challenging task to investigate the details of solvation structure at electrode-electrolyte interfaces.

Sum frequency generation (SFG) spectroscopy has been shown to be a powerful tool to investigate various interface structures. It also provided unique opportunities to understand the electrode-electrolyte interface structure in a molecular level. Recently, several experimental SFG studies of electrode/electrolyte interfaces have been reported.<sup>[1-2]</sup> However, it is well known that the observed SFG spectra are often not amenable to intuitive interpretation, and reliable theoretical support is strongly desirable to fully extract microscopic information from the SFG spectra.

In this work, we investigate the vapor liquid interface structure of PC, DMC and their mixture using both MD simulation and SFG spectra.<sup>[3]</sup> This work provides detailed understanding of the SFG spectra and interface structure of organic carbonates in a molecular level and will guide to the future work of solid-liquid interfaces in battery systems.

**[Model and Method]** First, we take PC as an example and build a flexible and polarizable model from *ab initio* calculations. Flexible model is described by natural internal coordinates, while polarizable model is described by the charge response kernel (CRK) theory. CRK calculation has already been implemented into the Gaussian09 program by us, which is readily applied to various systems. Force constants of the intra-molecule potential are derived by fitting to the molecular Hessian in quantum mechanical (QM) calculations. Partial charges and CRK are also calculated at the B3LYP/aug-cc-pVTZ level. After the validation of the PC model thus constructed, the whole procedure to generate model is then directly transferred to the DMC case.

**[Results and Discussion]** First, MD simulations for bulk PC liquid are carried out to validate the performance of the presented PC model. The calculated molecular properties, such as density and heat of vaporization, are in good agreement with experimental results.

IR and Raman spectra are also calculated and compared with experimental data. The calculated results show good agreement with experimental data, especially for C=O stretching part around 1800 cm<sup>-1</sup>. By implementing a Morse potential to describe the C=O stretching, we

successfully reproduced the red-shift of the C=O peak from that in the gas phase ( $\sim 1860\text{ cm}^{-1}$ ) to the condense phase ( $\sim 1800\text{ cm}^{-1}$ ). And also the relative intensity between C=O stretching and C-H stretching is reproduced in both the IR and Raman spectra.

After the validation, the PC model is readily implemented into interface calculation. The calculated SFG spectra of *ssp* and *sps* polarizations around C=O stretching region are shown in Figure 1. The non-resonant background is properly assumed for both *ssp* and *sps* polarizations. The molecular orientations of PC were investigated at varying depth coordinate  $\hat{z}$  from the Gibbs surface ( $\hat{z}=0$ ), and the calculated results are represented in Figure 2 by two angles. As shown in the inset,  $\theta_{\text{nor}}$  is the angle between surface normal and the normal vector to the molecular plane including the carbonyl group (red arrow), and  $\theta_{\text{CO}}$  is the tilt angle of C=O bond from the surface normal. Figure 2 shows that PC molecules tend to orient themselves with their carbonyl group parallel to the interface and methyl group toward the vapor phase. Detailed analysis of the SFG spectra of PC, DMC and their mixtures will be discussed in the presentation.

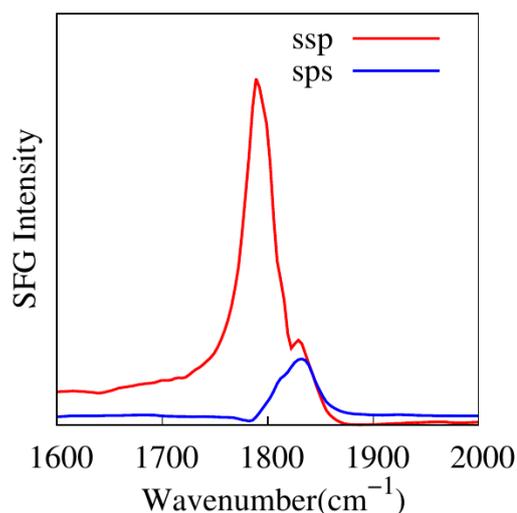


Fig. 1. Calculated *ssp* and *sps* polarized SFG spectra of PC liquid interface.

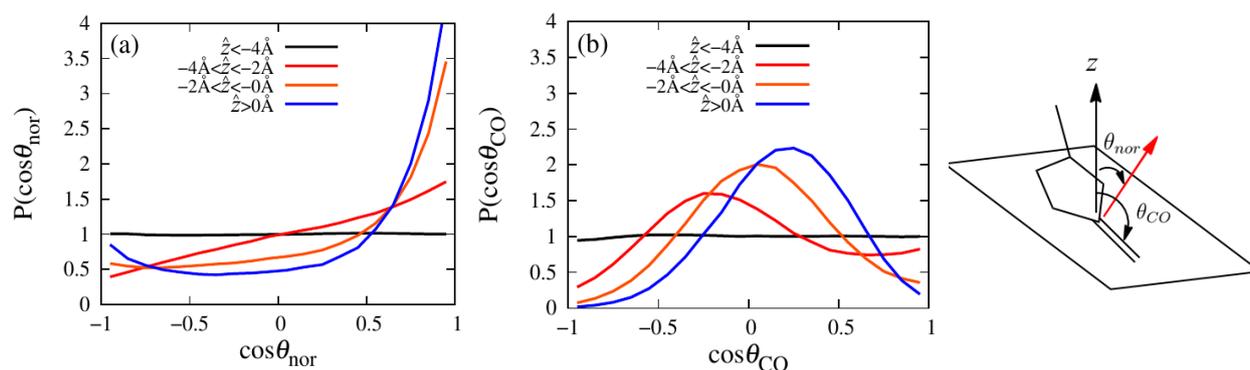


Fig. 2. Probability distribution of (a)  $\cos\theta_{\text{nor}}$  and (b)  $\cos\theta_{\text{CO}}$  of PC in various depths from interface. The definition of the two angles are illustrated in the inset.

## [References]

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