

## Molecular dynamics analysis of organic solvent interface and nonlinear spectroscopy in relation to batteries

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### [Introduction]

Lithium ion (Li-ion) batteries are widely used as power storage device for many applications in the past decades due to their high energy density and long cycle life. Many experimental and theoretical studies have been investigated in order to improve the performance of the batteries. Among these studies, the electrode-electrolyte interface structure has attracted more attention in recent years. During the ion transport through the interface, solvation/desolvation process directly influences the performance of Li-ion batteries. However, the detailed mechanism of solvation/desolvation and electrode-electrolyte interface structure are still largely unknown due to a scarcity of surface sensitive technique.

Recently, 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.<sup>[1-2]</sup> Ye and coworkers<sup>[1]</sup> reported SFG study of adlayer of propylene carbonate (PC) solvent on the surface of LiCoO<sub>2</sub> to investigate the electrode-electrolyte interfaces structure in batteries. There results, as illustrated in Fig 1, suggested that two kinds of adsorption PC species with opposite orientations are observed according to the C=O stretching region of SFG spectroscopy.

In order to explain this special feature of SFG and give a detail understanding of interface structure, theoretical investigation is desperately needed. By combining both experimental and theoretical investigation, a complete feature of electrode-electrolyte interface structure will be obtained.

In this work, we take PC, which is one of the typical organic solvent in batteries, as example and calculate the structure and SFG in PC vapor-liquid interface using molecular dynamics simulation. The aim of this work is to propose a general model of PC molecule and validate it by calculating PC vapor-liquid interface structure and SFG. This work will give a

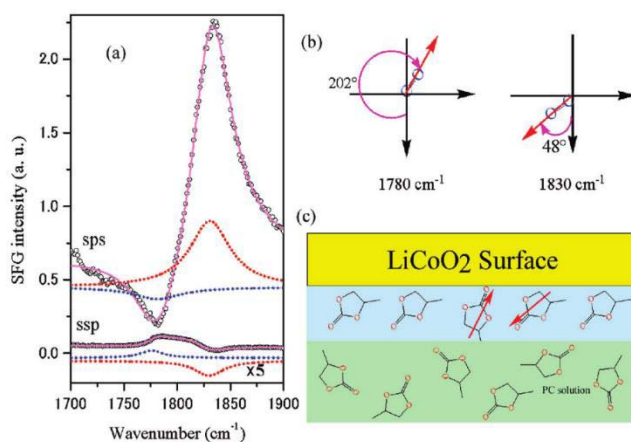


Fig 1. (a) sps- and ssp-SFG spectra (circles) of LiCoO<sub>2</sub> surface in contact with PC. (b) Two possible orientation structures for C=O group of PC observed at 1780 and 1830 cm<sup>-1</sup>. (c) Schematic illustration of PC absorption<sup>[1]</sup>

theoretical understanding of organic solvent interfaces and generate reliable model and method for future application in electrode-electrolyte interfaces.

### [Model and Method]

In order to investigate vibration spectra of PC, a flexible and polarizable model is required for the target molecules. Flexible model is described by nature internal coordinate, while polarizable model is described by charge response kernel (CRK) theory. CRK calculation has already been implemented into Gaussian09 program, which is readily to be applied to various systems. Force constants of intra-molecule potential are derived by fitting to the molecular hessian in quantum mechanics (QM) calculation. Partial charge and CRK are also calculated using QM at B3LYP/aug-cc-pVTZ level of theory. All parameters are nonempirically formulated and thus the accuracy of the model is directly guaranteed by that of the underlying electronic structure calculation.

### [Results and Discussion]

First, bulk simulations are carried out to validate the presented PC model. The calculate bulk properties, such as density, heat of vaporization, surface tension, are in good agreement with experimental results.

In order to examine the intra-molecular potential, we calculated IR spectra in the bulk phase and compared with experimental data, as illustrated in Fig 2. The calculated results show good agreement with experimental data, especially for C=O stretching part around  $1800\text{ cm}^{-1}$ . By implementing Morse potential to describe C=O stretching, we successfully reproduced the red-shift of C=O peak from gas phase ( $\sim 1880\text{ cm}^{-1}$ ) to condense phase ( $\sim 1800\text{ cm}^{-1}$ ).

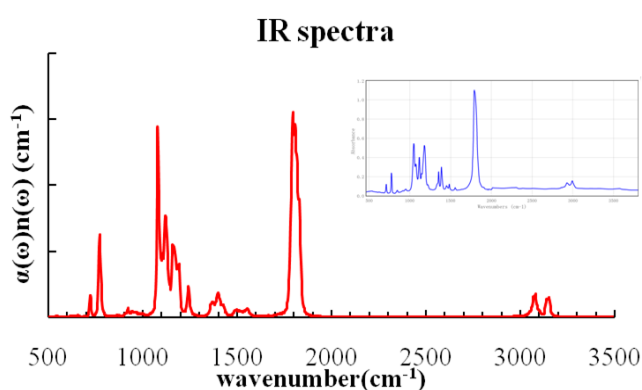


Fig 2. Calculated IR spectrum of PC liquid. Inset is experimental result<sup>[3]</sup>.

The model is readily implemented into the interface calculation. By analyzing the orientational structure at the interface, it has been found that the random distribution of C=O directions break on the vapor-liquid interface. Detailed analysis of the SFG spectra, including the phase information, will be discussed in relation to the orientational structure at the interface.

### [References]

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