

MD 計算と SFG 分光による有機カーボネート表面構造の研究

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Organic carbonates, such as propylene carbonate (PC) and dimethyl carbonate (DMC), are widely employed as electrolytes in modern lithium ion batteries. 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.^[1-2] 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 and DMC using both MD simulation and SFG spectroscopy.^[3] We proposed a non-empirical flexible and polarizable model for organic carbonates. 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. The calculated SFG spectra of PC and DMC show good agreement with experimental data (Figure 1). The detailed analysis of $\text{Im}[\chi^{(2)}]$ suggests that both PC and DMC show bipolar peak in C=O stretching region. However, the sign of bipolar peak is opposite which is attributed to the different interface layer structure of PC and DMC (Figure 2). 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.

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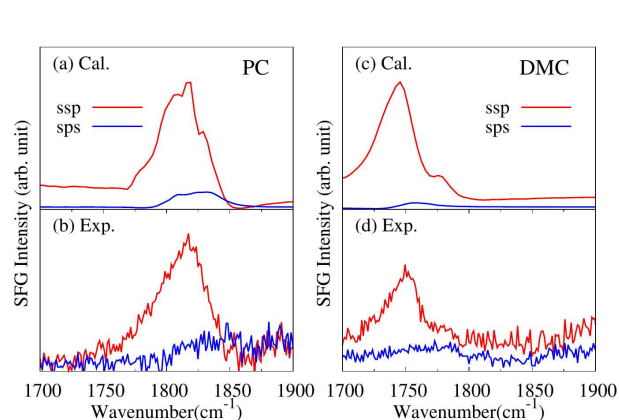


Figure 1. The calculated and experimental SFG intensity of PC and DMC interface.

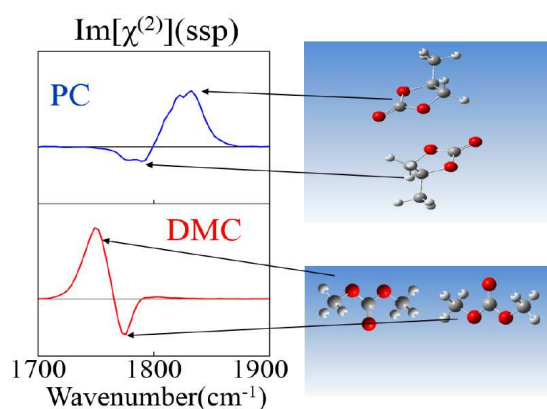


Figure 2. The opposite behavior of bipolar peak of $\text{Im}[\chi^{(2)}]$ between PC and DMC interface and the corresponding interface structure

References

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