Boundary Effects and Quadrupole Contribution in Calculation of Sum Frequency Generation Spectra

(*[1]Graduate School of Science, Tohoku University*) ○Tomonori Hirano[1]
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Understanding the structure and dynamics of liquid surfaces at molecular level is essential to various research fields, such as atmospheric chemistry, electrochemistry, biological chemistry, etc. Sum frequency generation (SFG) spectroscopy is widely used to investigate the orientation of molecules and the solvation environment at liquid interfaces because they are surface selective under the dipole approximation. However, the obtained spectra are often complicated because they contain a lot of information which stems from the inhomogeneity of the interface. Therefore, molecular dynamics (MD) simulation can be a powerful tool to analyze the obtained SFG spectra. In MD simulations, SFG spectra can be calculated as the Fourier-Laplace transform of the time correlation functions of the dipole moment and the polarizability of the interfacial system[1]. MD analyses of SFG spectra have been applied to various interface systems, such as pure water, aqueous solution, organic liquid interfaces, etc. However, we found that conventional calculations of the time correlation functions have fundamental issues which are related to the treatment of the boundary at the bulk to define the interfacial region[2]. In this study, the origins and the influences of the following two issues related to the boundary treatment at the bulk are thoroughly examined, and the proper treatment to resolve these issues are presented.

1. *Boundary treatment at the bulk to define interfacial dipole and polarizability*
   To obtain interfacial spectra, the dipole and the polarizability at the interfacial region should be defined. It is realized by imposing some spatial boundary at the bulk to restrict sampling region of dipole and polarizability. Under the dipole approximation, SFG signals arise from interfacial region where the inversion symmetry is broken, therefore the boundary treatment at the bulk may seem to be unimportant. However, we found that an improper treatment of the boundary brings large artifacts to the calculated spectrum (Figure 1). This issue originates from the asymmetric treatment of intermolecular correlations which breaks the inversion symmetry of the bulk region, and it is resolved by symmetric sampling of the intermolecular correlations.
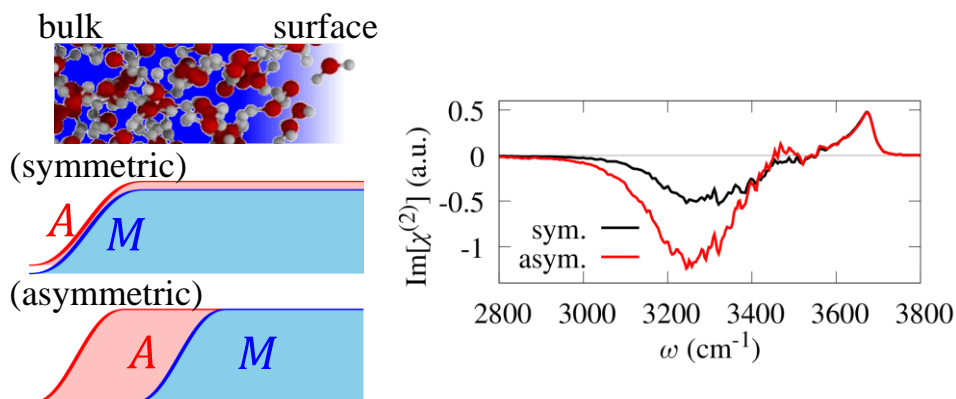
Figure 1. Left panel: conceptional representations of spatial restrictions to define the surface dipole (M) and polarizability (A). Right panel: calculated SFG spectra of air/water interfaces with the symmetric (black line) and asymmetric (red line) spatial restrictions.

2. *Bulk quadrupole contribution to the effective surface polarization*

The calculated SFG spectra under the dipole approximation depend on the choice of molecular origin which is used to judge whether a molecule is located in the interfacial area restricted by the boundary at the bulk. We demonstrated that an improper choice of the molecular origin produces largely distorted SFG spectra as shown in Figure 2. This issue is resolved by considering the quadrupole contribution to the SFG spectra, which arises from the bulk. We evaluated the quadrupole contribution by performing quantum chemical calculations, and calculated the SFG spectrum by MD simulations which effectively incorporates the quadrupole contribution.
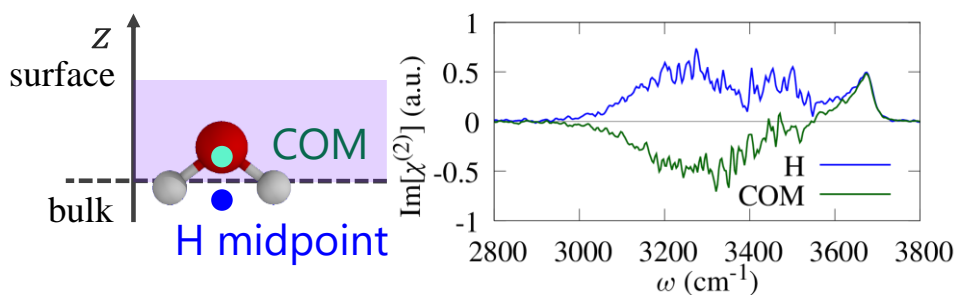

Figure 2. Left panel: the definitions of molecular center of a water molecule. The shaded area represents the surface region, and the dotted line indicates the boundary. Right panel: the calculated spectra of the air/water interfaces with the center of mass (green line) and the midpoint of hydrogen atoms (blue line) as the molecular origins.

1) "*Theory of Sum Frequency Generation Spectroscopy*", A. Morita, Springer, Singapore, 2018.
2) Boundary effects and quadrupole contribution in sum frequency generation spectroscopy. T. Hirano and A. Morita, *J. Chem. Phys.* **2022**, *156*, 154109.