

Vibrational SFG spectrum prediction from classical molecular dynamics simulations

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Interfaces attract a lot of scientific attention due to their ubiquitous occurrence in a wide range of natural and industrial environments, since the surface of any material is the principal pathway for its interaction with the surrounding environment. Interfaces induce inhomogeneous environment where numerous properties differ significantly from their homogeneous (bulk) values and intriguing phenomena take place. Experimental techniques such as X-ray scattering, neutron diffraction, adsorption measurements, surface titration, electrokinetic experiments, photoelectron emission spectroscopy, among others, provide invaluable information on phenomena occurring at liquid/vapor, liquid/liquid, or solid/liquid interfaces. During last decades, nonlinear optics experiments, namely Sum Frequency Generation (SFG), Second Harmonic Generation (SHG) and Second Harmonic Scattering (SHS), also referred to as hyper-Rayleigh scattering (HRS) as representatives of the second-order nonlinear optical techniques, became respected and powerful tools for exploring a variety of topics ranging from fundamental questions of molecular dynamics at liquid interfaces to more applied problems of material surfaces, polymer chemistry, environmental chemistry, electrochemistry, and life sciences. These techniques are highly suitable to study processes at surfaces and interfaces since the signal arises solely from the non-centrosymmetric regions at the interface. They provide direct information about the average orientation of the water molecules at the interface; monitor ion adsorption at the surface with micromolar sensitivity; infer interfacial electrostatic potentials, or even monitor the time-resolved evolution of interfacial processes. We present a simulation technique to predict vibrational SFG non-linear optics spectra from classical molecular dynamics simulations of solid-liquid and solid-air interfaces [1]. The method requires ab initio calculated parameterizations of change of dipole moment and polarization tensor of a water molecule upon its vibration. However, the trajectory to analyze is calculated by classical molecular dynamics simulations of non-polarizable flexible water models. This strongly reduces computation cost compared to ab initio calculations [2] and opens the possibility to study larger systems for long periods of time. The analysis allows detailed investigation of the origin of the SFG spectra, including contributions from water molecules differing in location at the interface. We successfully predict phase-resolved vibrational sum frequency generation (vSFG) spectra of air/water, fluorite (111)/water and α -alumina (0001)/water interfaces. The role of various water models on the predicted spectra, parameters affecting the calculation, as well as inclusion of so far often neglected cross-correlation terms in evaluation of the necessary time-correlation functions [3], will be discussed.

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FIGURES

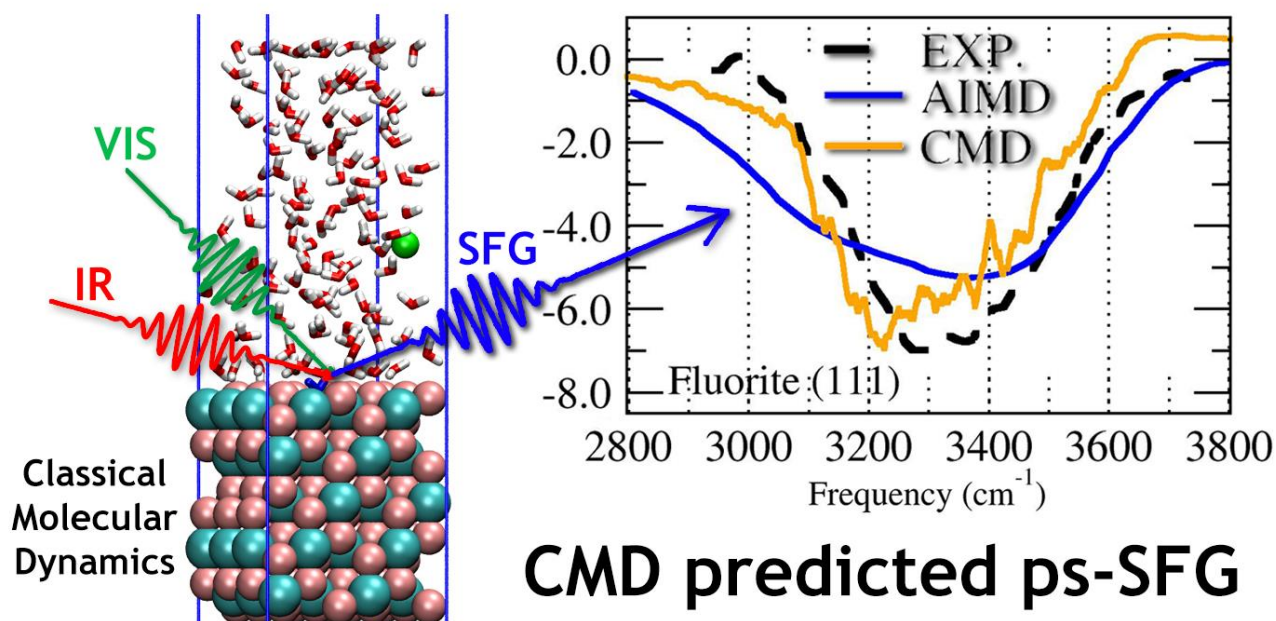


Figure 1: Schematics of the origin of SFG signal (left) and predicted imaginary part of second-order susceptibility $\chi^{(2)}$ for fluorite (111)/water interface from classical molecular dynamics (CMD), ab initio molecular dynamics (AIMD) and experiment.