MAR06-2005-001433

Abstract for an Invited Paper
for the MAR06 Meeting of
the American Physical Society

Recent Progress in Molecular Dynamics Simulation of Vibrational Sum Frequency Generation Spectroscopy

AKIHIRO MORITA, Institute for Molecular Science

While the visible-IR Sum Frequency Generation (SFG) spectroscopy is a powerful probe of interfaces using a second-order optical process, understanding of the experiments involves many factors to be addressed, including surface density and thickness, molecular orientation, local environment, and higher-order bulk terms. Assignment of the spectra is also complicated by overlap or interference of vibrational components. Therefore, practical methods of analysis with the help of reliable theoretical calculations will greatly benefit the SFG experiments. We have developed computational methods of vibrational SFG spectroscopy in combination of ab initio molecular modeling and molecular dynamics simulation. These methods allow direct calculation of SFG spectra from a molecular model without resorting to empirical spectral fitting. An essential ingredient of the theoretical methods is calculation of frequency-dependent nonlinear susceptibility that may be dominated by vibrational effects. We have proposed two ways of modeling of the nonlinear susceptibility, based on the energy representation and the time-dependent representation. This talk summarizes the progress of these theoretical methods and application to aqueous interfaces.