A Theoretical Method for Infrared Absorption Spectroscopy based on the Multipolar Hamiltonian

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Recent development of vibrational spectroscopy extends to the field of nano optics by adopting near field, i.e., a highly localized electromagnetic field. In these spectroscopic techniques, molecules are interacting with the nonuniform electric field, requiring a theoretical method beyond the dipole approximation. Also, the spatial variation of the electric fields depends on the shape of the tip used and inclusion of the field gradients is not always enough. Here we propose a theoretical method to account the full spatial variation of electric fields by using the multipolar Hamiltonian as a starting equation.[1] The interaction between nonuniform electric fields and molecular vibrations is expressed as a vibrational normal-coordinate derivative of a spatial integral of the inner product of the total polarization of a molecule and an electric field so that the polarization is treated rigorously without invoking the conventional dipole approximation. The square of the derivative gives the infrared absorption intensity with an electric field with arbitrary shapes. The formulation is applied to small molecules. IR spectra with a model near field is clearly different from one obtained with uniform electric field (i.e.,. the dipole approximation). The peak intensities depend on the directions and intensity gradients of the applied E-field. With this method, scanning image using near-fields can be also studied.

[1] T. Iwasa, M. Takenaka, and T. Taketsugu, J. Chem. Phys. 144, 124116 (2016).