I-M Molecular Vibrations and Intermolecular Interactions in Condensed Phases

In this project, intermolecular interactions and their effects on molecular vibrations in condensed phases are analyzed theoretically to clarify the relation between the structures and dynamics of the systems and the frequency- and time-domain spectroscopic features. Specifically, (1) the resonant transfer of vibrational excitations, vibrational dephasing, and their competition in liquids and biomolecules and (2) the relation between electronic structural features of molecules and intermolecular interactions are analyzed with great emphasis.

I-M-1 The Role of Atomic Quadrupoles in Intermolecular Electrostatic Interactions of Polar and Nonpolar Molecules

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For the purpose of getting insight into the reason for the anomalous vibrational frequency shifts observed in some usually used solvents for a mode that has a large dipole derivative, the role of atomic quadrupoles in intermolecular electrostatic interactions is studied for some halogen-containing molecules (CX_4, HX, and X_2 with X = F, Cl, and Br), CH_4, CO_2, and CS_2. From the fitting to the electrostatic potentials around the molecules, large atomic quadrupoles are obtained for the chlorine, bromine, and sulfur atoms, suggesting that the atomic quadrupolar effect is important for electrostatic interactions around covalently bonded atoms on the third and higher rows in the periodic table. Taking the case of the chlorine atoms as an example, the electron densities inside the atoms in CCl_4, HCl, and Cl_2 are examined. It is found that these electron densities are highly anisotropic. This anisotropy in electron densities is reasonably explained by the forms of the occupied molecular orbitals, and is considered to be the electronic structural origin of the large atomic quadrupoles.

I-M-2 Pressure Dependence of the Liquid Structure and the Raman Noncoincidence Effect of Liquid Methanol

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Pressure dependence of the liquid structure and the Raman noncoincidence effect of liquid methanol is examined with the combination of molecular dynamics (MD) simulations and the intermolecular resonant vibrational interactions determined by the transition dipole coupling (TDC) mechanism (MD/TDC method). It is shown that the observed decrease of the Raman noncoincidence ν_{NCE} of the CO stretching band with increasing density reported in the literature is quantitatively reproduced by the present calculation. As the density increases, the hydrogen bonds get slightly shorter, but molecules belonging to different hydrogen-bond chains get closer to each other to a greater extent. This anisotropic change in the liquid structure is the reason for the behavior of ν_{NCE}. It is also shown that the concentration dependence of ν_{NCE} in the methanol/CCl_4 binary mixtures reported in a previous study and the pressure dependence of ν_{NCE} in methanol may be described in a consistent way as a function of the number density of methanol in the liquid systems.

I-M-3 Extent of Delocalization of Vibrational Modes in Liquids as a Result of Competition between Diagonal Disorder and Off-Diagonal Coupling

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The changes in the extent of delocalization of vibrational modes in liquids arising from the competition between diagonal disorder and off-diagonal coupling in the vibrational exciton picture are examined theoretically. Calculations of vibrational modes and polarized Raman spectra are carried out on a model liquid system, in which spherical particles interact with each other by the Lennard-Jones and dipole-dipole interactions, and a one-dimensional oscillator (representing a vibrational degree of freedom) with a transition dipole and a Raman tensor is buried in each particle. The diagonal disorder is assumed to be in a Gaussian form, and the transition dipole coupling is introduced as the off-diagonal coupling in the vibrational Hamiltonian. The magnitude of the Raman noncoincidence effect (NCE), which is the phenomenon that the vibrational frequency positions of the isotropic and anisotropic components of a Raman band do not coincide and is often used as an experimental measure of the delocalization of vibrational modes, is calculated. In addition, two theoretical measures of the delocalization of vibrational modes are introduced, and their changes with the thermodynamic state of the liquid, the diagonal disorder, and the strength of the off-diagonal coupling are examined. It is shown that the extent of delocalization of vibrational modes is correlated with the “NCE detectability,” defined as the ratio of the magnitude of the NCE and the isotropic or anisotropic Raman band width. This result indicates that the extent of delocalization of vibrational modes in a vibrational band that shows the NCE may be estimated from the observed spectral profile of the band. The size of the space in which vibrational spectra can probe structural formation is also discussed.