I-S 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-S-1 Vibrational Interactions in the Amide I Subspace of the Oligomers and Hydration Clusters of *N*-Methylacetamide

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The diagonal and off-diagonal vibrational interactions in the amide I subspace are examined for the oligomers and hydration clusters of *N*-methylacetamide (NMA). A method called the average partial vector method is developed for constructing the force constant matrix (F matrix) in the amide I subspace from that in the full Cartesian space. It is shown that the F matrix thus constructed can reproduce quantitatively the vibrational frequencies and vibrational patterns of the amide I modes calculated in the full Cartesian space. For the NMA oligomers consisting of three or more NMA molecules, the cooperative effect on the C=O bond length (and on the diagonal force constant of the amide I mode as well) is seen. Including the values for those oligomers, the shifts in the diagonal terms in the amide I subspace (δk_I) and in the C=O bond length ($\delta S_{C=O}$) of the NMA oligomers and NMA–water clusters from the values of an isolated NMA molecule are approximately proportional to each other. In addition, $\delta S_{C=O}$ is shown to be approximately proportional to the electric field (originating from the other molecules in the NMA oligomer or NMA–water cluster) evaluated at a specified point on the C=O bond, indicating that the origin of the cooperative effect is the enhancement of the electric field operating among the molecules. The effect of mechanical anharmonicity on δk_I is examined by introducing the internal-normal mixed coordinate system representation for the cubic force constants, and is shown to overestimate the variation of δk_I. The partial cancellation by the effect of electrical anharmonicity (dipole second derivative) is also important. For the off-diagonal terms, it is shown that the TDC model provides a good approximation. However, for the (small) coupling constants between distant peptide groups, the effect of the polarization of the intervening peptide group(s) (also called the third-body mediation and may be regarded as a dipole-induced dipole effect) is also recognized.

I-S-2 Atomic Quadrupolar Effect in the Methanol-CCl_4 and Water-CCl_4 Intermolecular Interactions

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The intermolecular interactions in the methanol-CCl_4 and water-CCl_4 systems are examined by carrying out *ab initio* molecular orbital calculations on the 1:1 molecular clusters. It is found that, for both systems, the molecular configuration with the C–Cl···O interaction is the most stable. The two-body electrostatic part, especially the effect of the atomic quadrupoles of the Cl atoms of CCl_4, dominates the interaction energy of this configuration. This result suggests that the atomic quadrupolar effect is significant in the structural formation and energetics in the methanol-CCl_4 and water-CCl_4 systems as well as in other related systems.

I-S-3 Atomic Quadrupolar Effect in Intermolecular Electrostatic Interactions of Chloroalkanes: The Cases of Chloroform and Dichloromethane

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The atomic quadrupolar effect in intermolecular electrostatic interactions is studied for chloroform and dichloromethane. From the fitting to the electrostatic potentials around these molecules obtained by *ab initio* molecular orbital (MO) calculations, atomic quadrupoles of the magnitude as large as $\Theta \cong 1.5\ ea_0^2$ are obtained for the chlorine atoms in these molecules. It is shown that a reasonably good fit to the electric field around the molecules can be obtained only by including those atomic quadrupoles, indicating that atomic quadrupoles are essential for correct representation of the intermolecular electrostatic interactions of these molecules. From the calculations of the radial distribution functions (rdfs) of liquid chloroform and dichloromethane by the Monte Carlo and molecular dynamics methods, it is shown that a significant atomic quadrupolar effect is seen in the rdfs of the C···C, C···H, and H···H pairs. The intermolecular distances in the optimized structures of the dimers of chloroform and dichloromethane calculated by the *ab initio* MO method support the new features in the rdfs of the liquids that are seen upon including the effect of atomic quadrupoles. It is suggested that an atomic quadrupole has a significant effect on the angular (rather than radial) component of the location of the atoms of neighboring molecules.