

SUMMARY OF Ph.D. DISSERTATION

School Science and Technology	Student Identification Number	SURNAME, First name TAKAHASHI Kaito
Title XH Stretching Vibrational Spectra: A Theoretical Perspective		
Abstract <p>The local mode(LM) model has shown great success in treating the stretching vibrational spectra of XH bonds, where X = C, O, and so on. In this model, we rationalize the observed spectra as transitions to states with the energy localized in one XH bond. Therefore, these spectra are sensitive to the bond strength and the molecular environment of the XH bond. Upon examining the vibrational spectra of several representative liquid hydrocarbons with various kinds of CH oscillators, Burberry and Albrecht suggested a “Universal Intensity Concept for the local mode model”(UIC): for a given CH stretching overtone transition, a single absorption cross section per CH oscillator, regardless of type, could account for the observed spectral intensity for the transitions to quantum states $v = 3, 4, 5,$ and 6. In the present dissertation, I report the calculated vibrational spectra for the OH bonds, the SH bonds, and the CH bonds. Furthermore, the curious UIC will also be investigated using these results.</p> <p>In the first two chapters, I give an overview of the LM model, namely, 1) comparison versus the normal mode(NM) model, and 2) validation on the use of the LM for the calculation of XH stretching spectra. The quantum vibrational Hamiltonian, with the potential energy surface calculated from the density functional theory(DFT) method, is solved using the grid variational method and the element free Galerkin method. Using the calculated vibrational wave functions and the dipole moment function(DMF) calculated by the DFT method, we obtain the theoretical absorption intensities. To gain understanding on the absorption intensities, I derive the effective direction of the transition moment using the sum rule of the intensities. This allows for the analysis on the absorption intensity, which depended on the DMF vector with three components, to simplify to a discussion on an effective one component DMF.</p> <p>In chapter three, the calculation results for the OH stretching vibration of water, acids, alcohols, and OH radical are presented. Using the water molecule, I discuss the failure of the NM picture to describe high energy vibrational states responsible for the overtone spectra. In addition, for molecules with rotational isomers, it is shown that the absorption intensities, as well as the transition energies are sensitive to the rotational conformation. Furthermore, with intent to gain understanding on the UIC, the absorption intensities are analyzed using the wave function expansion method and the semiclassical method. These analyses reveal that the apparent difference seen in the DMF of the molecules is only responsible for the fundamental intensity, and does not cause variance in the overtone transition moment. In chapters four, I analyze the calculated vibrational spectra for the SH bond of thioacids and thiols in relation to those of the OH bond of acids and alcohols. The comparison on the CH stretching spectra of the simple hydrocarbons with different hybridization on the carbon atom is reported in chapter five.</p> <p>I conclude with a summary of the knowledge obtained from the theoretical calculations.</p>		