2A3b Intramolecular Vibrational energy Redistribution(IVR) of CH stretching vibration of Benzene derivatives

○Minoru Yoshimizu, Ryoji Kusaka, Yoshiya Inokuchi, Takayuki Ebata
Hiroshima University

Introduction CH stretching vibrations are known to show Fermi resonance with the overtone of CH bending vibration. Fermi resonance is the first step of the Intramolecular Vibrational energy Redistribution(IVR). So, in this study we examine Fermi resonance and IVR of the CH stretching vibration of benzene and mono-substituted benzene, i.e. fluorobenzene(F-Bz), chlorobenzene(Cl-Bz) , phenol and toluene by time-resolved IR-UV pump-probe spectroscopy in molecular beam. We discuss IVR of these molecules in terms of a density of states and symmetry of the molecule.

Experiment The molecular beam was formed by skimming a supersonic jet of benzene or its delivatives diluted by carrier gas. We measured the IR spectra of the CH stretching vibration by IR-UV dip spectroscopy. IVR was measured by time-resolved IR-UV pump-probe spectroscopy. Fig.1 shows the excitation scheme of IR-UV pump-probe spectroscopy.

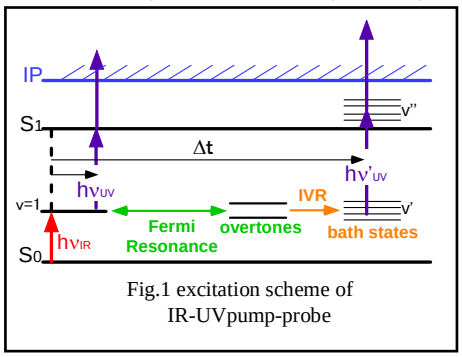

Fig.1 excitation scheme of IR-UVpump-probe

Result and Discussion Fig.2 shows the IR spectra of the CH stretching vibration of benzene and its delivatives. All the IR spectra show many bands due to Fermi resonance. Thus, the Fermi resonance of CH stretching vibration is common in these molecules. Fig.3 shows the electronic spectra of F-Bz with(red) and without(black) irradiation of the IR pulse tuned to the CH stretching vibration. The sharp band at 37875cm^{-1} assigned to the CH_1^1 resonant transition. Since the resonant transition is observed, IVR of CH stretching vibration does not occur for F-Bz. This situation is the same for Cl-Bz. Fig.4 shows the time evolution of toluene by a picoseconds IR-UV pump-probe spectroscopy. The IVR of the CH stretching vibration is obtained to be 14ps. Thus, there is a dramatic difference of the IVR rate between them. From previous studies, it is reported that IVR of CH stretching vibration of benzene does not occur[1], while IVR of CH stretching vibration of phenol occurs with a lifetime of 5ps[2]. From these results, it is concluded that Fermi resonance of CH stretching vibration is common to all benzene delivatives, however, IVR occurs only substituent has the structure.

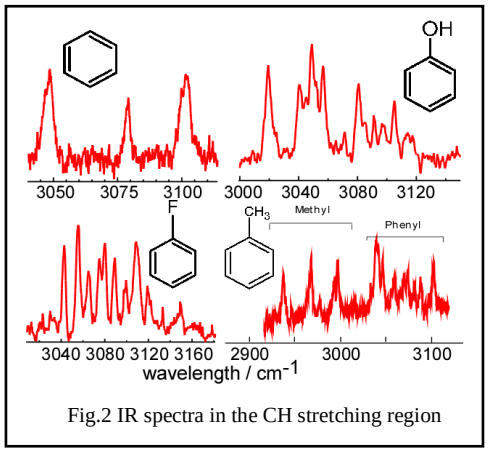

Fig.2 IR spectra in the CH stretching region

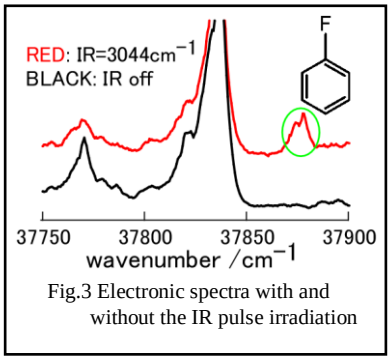

Fig.3 Electronic spectra with and without the IR pulse irradiation

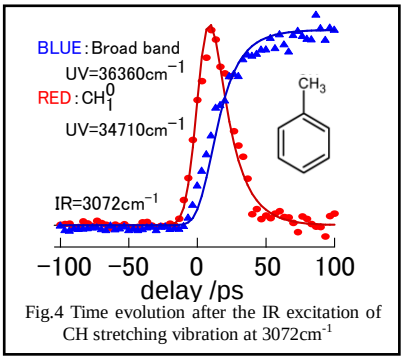

Fig.4 Time evolution after the IR excitation of CH stretching vibration at 3072cm^{-1}

Reference : [1] T. Ebata, M. Kayano, S. Sato, N. Mikami, J. Phys. Chem.A 105, 8623 (2001)
[2] Y. Yamada, T. Ebata, M. Kayano, N. Mikami, J. Phys. Chem. A120, 7400 (2004)