PICOSECOND TIME-RESOLVED IR-UV PUMP-PROBE SPECTROSCOPIC STUDY ON VIBRATIONAL ENERGY RELAXATION OF BENZENE DIMER AND TRIMER IN THE CH STRETCHING REGION

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Vibrational energy relaxation (VER) in the CH stretching region of benzene dimer (Bz_2) and trimer (Bz_3) has been studied by IR-UV pump-probe spectroscopy in supersonic beams. Firstly, we investigated isotope-substituted *hd* heterodimer, where *h*=C_6H_6 and *d*=C_6D_6, because the Stem and Top sites in the *hd* dimer can be site-selectively excited, different from *hh* homodimer. The two *h*(stem)*d*(top) and *h*(top)*d*(stem) isomers show remarkable difference in the lifetimes of intracluster vibrational energy redistribution (IVR). In the transient UV spectra, we observed a broad electronic transition due to the bath modes. The time evolutions of the bath modes can be described by a three step VER model involving IVR and vibrational predissociation (VP). This model was also confirmed by the observed rise profile of the Bz fragment. Secondly, we investigated *hh* homodimer. The *hh* homodimer shows the stepwise VER process with time constants similar to those of the *hd* dimer, suggesting a very weak excitation-exchange coupling of the vibrations between the two sites of the *hh* dimer. Finally, we found that Bz_3 also exhibits the stepwise VER process, though each step is faster than Bz_2.