

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  $h(\text{stem})d(\text{top})$  and  $h(\text{top})d(\text{stem})$  isomers show remarkable difference in the lifetimes of intracuster 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  $Bz_2$ .