SIX-DIMENSIONAL MODEL ANALYSIS AND INTERMOLECULAR VIBRATIONAL SPECTROSCOPY OF BENZENE-METHANE vdW COMPLEX

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The benzene-methane complex is a prototypical model for CH/π interaction. The binding energy[a] and UV spectra[b] of this system have been reported and *ab initio* calculations were performed[c]. However, full dimensional (6D) intermolecular potential energy surface (IPS) has not been evaluated because of difficulties caused by high dimensionality.

In order to reconstruct a full dimensional IPS in the benzene-methane system, stimulated emission pumping and wave-packet observation pertinent to the S_0 state were carried out. The latter was performed as a pump-probe experiment combining impulsive stimulated Raman excitation by femtosecond pulses with state-selective ionization by resonant two-photon ionization. A new 6D model potential analysis was also performed. Single-point energy calculations were performed at CCSD(T)/aug-cc-pVTZ level of theory for 525 different complex configurations, and calculated results were fitted by the new model potential. Observed intermolecular bands were assigned by comparing the theoretical prediction. Deviations of the prediction from the observation are well within 3 cm^{-1}, which verifies the utility of the present IPS for benzene-methane.

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[b] J. A. Menapace and E. R. Bernstein, *J. Phys. Chem.* **91**, 2533-2544 (1987).

[c] S. Tsuzuki, *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.*, **108**, 69-95 (2012).