

IP046 Direct Observation of Aromatic C-H···X Hydrogen Bonds by Fluorescence-Detected Infrared Spectroscopy

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Among the variety of hydrogen-bonded systems, a study of weak C-H···X hydrogen bond, where X can be σ or π proton acceptor, is of considerable interest in both experimental and theoretical. Recently, Desiraju and coworkers showed the participation of an aromatic C-H···X hydrogen bonds in crystal engineering, biological systems and molecular recognition.¹ Using crystallographic data, they also indicated that the donor capability of aromatic C-H protons plays a quite significant role in the structural stabilization of protein-ligand complexes and benzene containing crystal structures. With such a varied participation in a variety of chemical and biological processes, the study of aromatic C-H···X hydrogen bonds has been assumed great significance. However, there is no direct experimental evidence available for gas phase aromatic C-H···X hydrogen bond in the literature. In our present work, we provide the first direct vibrational spectroscopic evidence for the gas phase aromatic C-H···X hydrogen bonds by taking the 1,2,4,5-tetrafluorobenzene (TFB)-X (where, X = water, methanol, dimethyl ether, acetonitrile, and ammonia) clusters as one of the examples (Figure 1).² The intermolecular structure of the isolated TFB-X clusters in a supersonic jet were characterized using fluorescence-detected infrared (FDIR) spectroscopy. The experimental studies were supported by ab initio computations performed at the MP2/6-31+G* level. The formation of the aromatic C-H···X hydrogen bond in the clusters was directly evidenced by a low-frequency shift and intensity enhancement of the hydrogen-bonded aromatic C-H stretch in the TFB moiety. This is the first direct observation of the aromatic C-H···X hydrogen bond formation in the isolated gas phase clusters. Also, this work clearly indicates that the aromatic C-H stretching vibration is the 'fingerprint' for the structural analysis of TFB-X clusters rather than the other stretching vibrations. Furthermore, the shift values of the hydrogen-bonded aromatic C-H stretching vibration in the cluster are qualitatively correlated with the proton affinity value of X. It implies that the aromatic C-H···X hydrogen bonded is strengthened with an increase of the proton affinity of X.

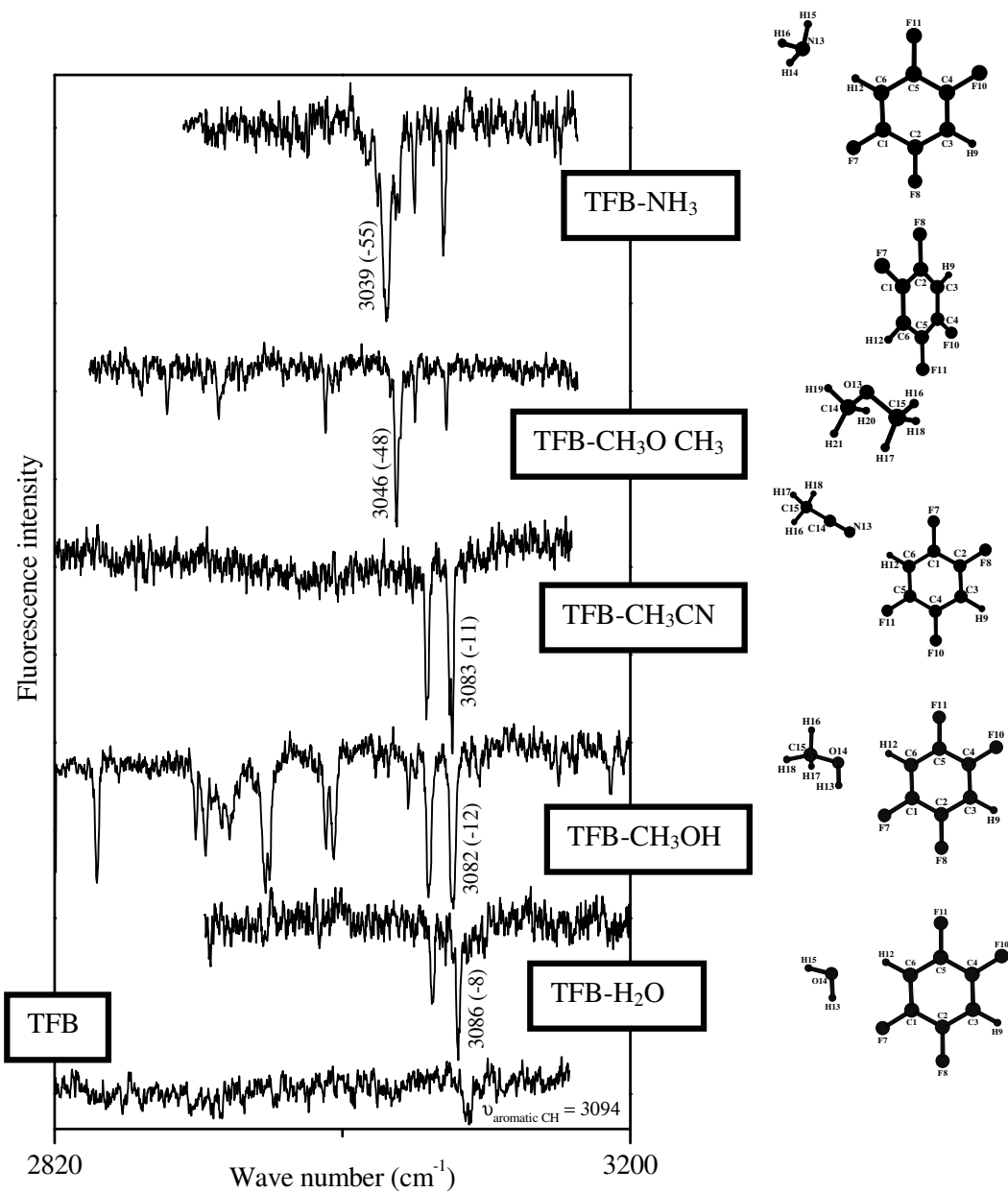


Figure 1. FDIR spectroscopy of TFB-X clusters in the C-H stretching vibrational region. Alongside the figure, the corresponding structures performed at the MP2/6-31+G* level are given.

1. G. R. Desiraju, T. Steiner, *The weak hydrogen Bond*, Oxford University Press, New York, 1999.
2. V. Venkatesan, A. Fujii, T. Ebata, N. Mikami, *Chem. Phys. Lett.* (in press).