

## INFRARED SPECTROSCOPIC STUDY ON FERMI RESONANCE OF THE EXCESS PROTON VIBRATION IN BINARY CLUSTERS

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Infrared photodissociation spectroscopy was applied to  $(\text{CH}_3)_3\text{N-H}^+-\text{X}$  ( $\text{X} = \text{Ar}, \text{N}_2, \text{CO}, \text{C}_2\text{H}_2, \text{H}_2\text{O}, \text{CH}_3\text{OH}, \text{C}_2\text{H}_5\text{OH}, \text{CH}_3\text{COCH}_3, \text{NH}_3, \text{CH}_3\text{NH}_2, (\text{CH}_3)_3\text{N}$ ) clusters, and the excess proton vibration ( $\text{N-H}^+$  stretching vibration) was observed. In a protonated binary cluster, the excess proton location and its magnitude of delocalization is determined by the difference of the proton affinities of the two components<sup>a</sup>. We observed that the  $\text{N-H}^+$  stretching frequency goes down as the proton affinity of X increases. When the  $\text{N-H}^+$  stretching frequency gets to the overtone region of the  $\text{N-H}^+$  bending mode, complicated Fermi resonance was always seen. This indicates that the Fermi resonance necessarily occurs in the excess proton vibration at this frequency region. At least two vibrations seem to couple with the  $\text{N-H}^+$  stretching mode, demonstrating the requirement of multi-dimensional mode analyses to understand this coupling. In addition, we confirmed that the Fermi resonance also occurs by changing the proton affinity of the amine moiety (from  $(\text{CH}_3)_3\text{N}$  to  $\text{CH}_3\text{NH}_2$  and  $(\text{CH}_3)_2\text{NH}$ ).

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<sup>a</sup>J. R. Roscioli, L. R. McCunn, M. A. Johnson, *Science* **316**, 249 (2007).