AR-PREDISSOCIATION SPECTROSCOPY OF PROTONATED IMIDAZOLE CLUSTERS

GEORGE H. GARDENIER, MARK A. JOHNSON, *Sterling Chemistry Laboratory, Yale University, P.O Box 208107, New Haven, CT, 06520*.

We present Ar-predissociation spectra of cationic systems involving imidazole (Im): $Im^+ \cdot Ar$, $Im \cdot H^+ \cdot Ar$, $Im_2 \cdot H^+ \cdot Ar$, and $Im_3 \cdot H^+ \cdot Ar$ in the range of 3000-3800 cm^{-1}. We track the evolution of the C-H and N-H stretching vibrational frequencies as a function of the number of imidazole groups present in the cluster. The C-H stretching frequencies red-shift while the intensities of these transitions appear to equalize with the addition of imidazole molecules to the motif. Also, as the length of the proton-bound imidazole chain increases, we notice a blue shift in the frequency of the free (non-Ar-solvated) N-H stretch toward that of the analogous vibrational mode in neutral imidazole (3518 cm^{-1})[a]. The disappearance of Ar-bound N-H stretch when a second imidazole is added to the $Im \cdot H^+ \cdot Ar$ cluster strongly suggests a large-scale red shift of this feature as this proton becomes shared between two imidazole groups, illustrating the construction of an intermolecular proton-transfer scaffold. These data represent a microscopic model system for the ongoing effort to develop imidazole-based anhydrous PEM (Proton-Exchange Membrane) fuel cells.

[a] M. Y. Choi, R. E. Miller, J. Phys. Chem. A 110, 30 (2006).