

AR-PREDISSOCIATION SPECTROSCOPY OF PROTONATED IMIDAZOLE CLUSTERS

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We present Ar-predissociation spectra of cationic systems involving imidazole (Im): $\text{Im}^+ \cdot \text{Ar}$, $\text{Im} \cdot \text{H}^+ \cdot \text{Ar}$, $\text{Im}_2 \cdot \text{H}^+ \cdot \text{Ar}$, and $\text{Im}_3 \cdot \text{H}^+ \cdot \text{Ar}$ in the range of $3000\text{-}3800\text{ cm}^{-1}$. 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 $\text{Im} \cdot \text{H}^+ \cdot \text{Ar}$ 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.

^aM. Y. Choi, R. E. Miller, *J. Phys. Chem. A* 110, 30 (2006).