Infrared Spectroscopy of Aromatic Molecular Ions Cooled at 0.37 K

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One of the high-sensitivity methods for cold molecular ion spectroscopy is with superfluid helium nanodroplets. Due to the superfluidity at a low temperature of 0.37 K and the small number of atoms, helium droplets are an ideal matrix to explore unstable molecular species such as radicals and cations. In these regards, the rotational and vibrational spectra of molecular cations embedded in helium droplets are perturbed to a very minimal extent. However, while rotational spectra of neutral molecules have been observed widely, the observations of ionic species at 0.37 K have yet to progress.

An infrared spectroscopic method for cold molecular ions in helium droplets has recently been established.[1] The helium droplets doped with neutral precursors are ionized by an electron impact ionizer. Since the ionization potential of ^{4}He is very high, the dopants are ionized via charge transfer and cooled to 0.37 K. Due to the rapid cooling of cations by the surrounding low-temperature helium droplets, doped molecular ions can remain in their metastable states.[2]

We performed the infrared spectroscopy of one of the aromatic molecular ions, aniline cation (c-C_6H_5–NH_2^+), and the H-loss cation in helium droplets in the N–H stretching region. In the gas phase, some H-loss cations of the 5-membered ring were reported by infrared spectra at the fingerprint region.[3] Some neutral 5-membered rings with a –CNH substitute were observed in the interstellar space. On the other hand, our experimental results of the infrared spectra in helium droplets indicated the N–H vibrational band at 3406 cm^{-1}, which disagreed with the 5-membered ring structures. Theoretical calculation suggests several candidate species, including a 7-membered ring structure. These results imply that the excess energy opened a new reaction pathway to this cation and competed with the pathway to the 5-membered rings.[4]

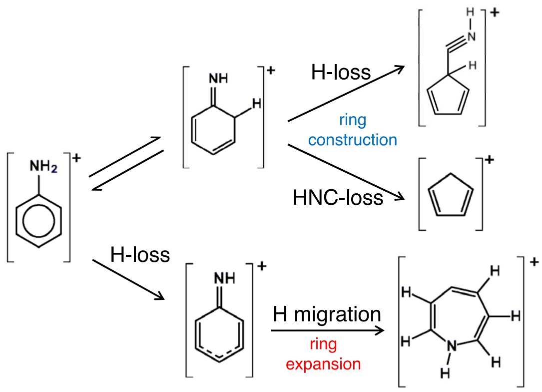

Figure 1. Some of the reaction pathways from aniline cations.

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