Infrared spectroscopy of carbocations in helium droplets

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Molecular ions are important intermediates in the chemistry of condensed phase and upper atmosphere as well as in astrochemistry. Therefore, great strides were done in developing new techniques for spectroscopy of ions. Recently, several groups demonstrated spectroscopy of ions in He droplets based on photoionization and electrospray. Spectroscopy of ions with small number of attached He atoms produced upon electron impact ionization of doped He droplets was also reported.

Here we show that the electron impact ionization of the helium droplets doped with different hydrocarbon molecules such as acetylene, ethylene, propene, butene and others yields diverse $C_XH_Y^+$ (X=1-4, Y=1-8) cations embedded in the droplets of few thousand He atoms. The primary ions result from the ionization and fragmentation of the precursor molecules, whereas larger ions are also produced in ion molecule reactions. [1,2] Infrared spectra of specific ions are obtained using release of the cations from the droplets upon laser excitation, followed by mass spectrometric detection. The spectra of the embedded cations show well resolved vibrational bands with a few wavenumber widths an order of magnitude less than those previously obtained in solid matrices or molecular beams by tagging techniques. The obtained spectra are in good agreement with previous measurements in gas phase or by tagging when available. In addition, the spectra for many ions were observed for the first time. For some ions the spectra indicate the presence of different isomers, which abundance depends on the precursor molecules.

This work demonstrates a facile technique for the production and spectroscopic study of diverse carbocations, which could be expanded using the appropriate neutral precursors.

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[2] Erukala, S; Verma, D; Vilesov, A. F. Rotation of CH_3^+ cations in helium droplets. *J. Phys. Chem. Lett.* 12, 5105–5109 (2021).