Vibrational Spectroscopy of Ions Trapped in Helium Nanodroplets: Application to the Analysis of Biomolecules

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Synopsis The capture of trapped ions in helium nanodroplets allows for vibrational spectroscopy of cold ions ranging from tens of Da to several kDa in mass. Here we take advantage of this method to gain detailed insight into the structure of biomolecular ions, including peptides, proteins, and oligosaccharides.

Helium nanodroplets provide an ideal environment for vibrational spectroscopy due to their extremely low equilibrium temperature (~0.4 K) and minimal matrix-induced spectral perturbation. Whereas the capture of a neutral molecule in a nanodroplet is accomplished using a pickup chamber containing analyte vapor, ions can be captured in helium nanodroplets by instead directing a nanodroplet beam through an ion trap (Figure 1a). In addition to providing a direct method to embed ions in helium nanodroplets, such an approach has the added advantage that significantly larger molecules can be made available for uptake. Thus, large biomolecules up to tens of kDa in mass can be captured in helium nanodroplets and studied by vibrational spectroscopy.

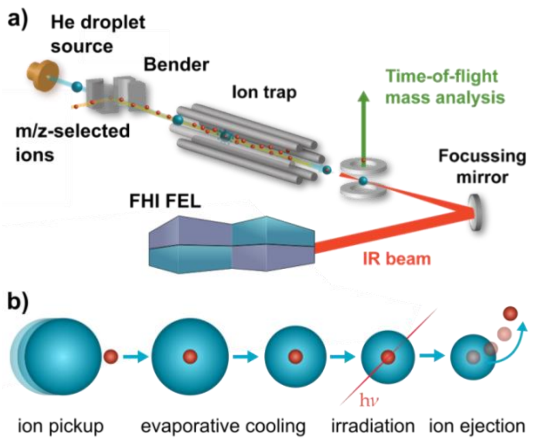

Figure 1. (a) schematic of instrument utilized for the vibrational spectroscopy of ions captured in helium nanodroplets [1]; (b) schematic of process leading to cooling of ions and subsequent ejection upon absorption of resonant infrared photons.

An overview of the instrumentation utilized for vibrational spectroscopy of biomolecular ions is shown in Figure 1a [1]. Ions are generated by electrospray ionization and m/z selected by a quadrupole mass filter before transfer to a hexapole ion trap. A fraction of these ions are then picked up by a pulsed beam of helium nanodroplets traversing the trap. The helium droplet with embedded ion possesses sufficient kinetic energy to escape the potential well of the hexapole trap and travel to the laser interaction region. Ions are ejected from the helium droplet by the absorption of resonant photons and detected by a TOF MS. The measurement of ion signal as a function of wavelength therefore provides an infrared spectrum of the embedded ions.

Figure 1b illustrates the process of ion uptake and ion ejection upon absorption of resonant infrared radiation. Following ion uptake, the doped nanodroplet undergoes evaporative cooling to return to a temperature of ~0.4 K, and subsequent absorption of resonant photons results in ion ejection. Although the exact ejection mechanism is not known, studies to date suggest a nonlinear process in which ions are ejected prior to complete droplet vaporization [2, 3].

This experimental approach can be utilized to capture both cationic and anionic molecules ranging in size from tens of Da to several kDa and subsequently probe their structure utilizing vibrational spectroscopy. This work will discuss the latest applications of the method to the structural analysis of biomolecular ions, including the structure of peptides and proteins in the gas phase as well as the detailed fingerprinting of complex oligosaccharide molecules.

References

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