Isolating site-specific non-covalent catalyst-substrate interactions using cryogenic ion vibrational spectroscopy

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We present the infrared photodissociation spectra of protonated peptides that are generated via electrospray ionization and collisionally cooled in a ~10 K quadrupole ion trap where the species are "tagged" with weakly bound D_2 molecules. The photodissociation spectra, acquired by monitoring the evaporation of the D_2 tag, are recorded over the range 600 – 4300 cm^{-1} using a table-top laser source and are shown to result from one-photon absorption events. This arrangement is demonstrated to recover sharp ($\Delta\nu$~6-10 cm^{-1}) transitions throughout the fingerprint region, despite the very high density of vibrational states in this energy range. This methodology is applied to the characterization of site-specific peptidic catalyst-substrate interactions. Isotopic labeling is used to track specific C=O and N–H oscillators in the catalyst-substrate complex. It is demonstrated that each isotopic substitution affects only one band in the spectrum, indicating that each of the C=O and N–H oscillators contributes a single distinct feature, effectively "reporting" its local chemical environment.

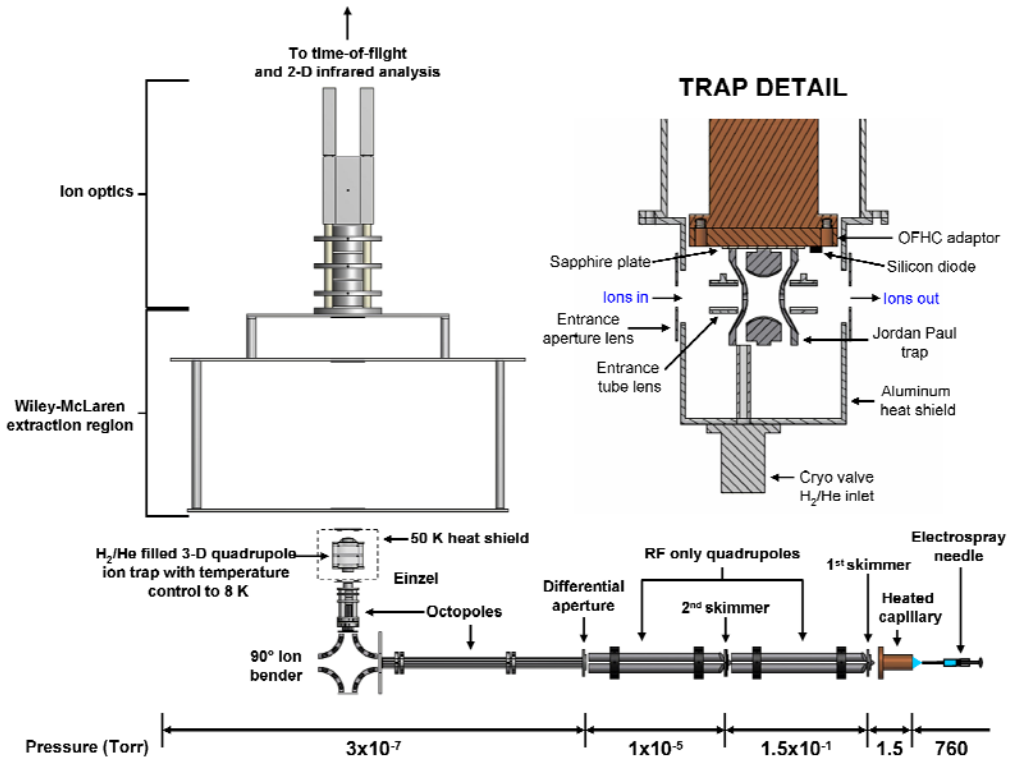

Figure 1. Schematic layout of the cryogenic ion source.

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