 Cryogenic multipole ion traps have become popular devices in the development of sensitive action-spectroscopic techniques. The low ion temperature leads to enhanced spectral resolution, and less congested spectra. In the early 2000s, a 22-pole ion trap was coupled to the Free-Electron Laser for Infrared eXperiments (FELIX), yielding infrared Laser Induced Reaction (LIR) spectra of the molecular ions $\text{C}_2\text{H}_2^+$ and $\text{CH}_5^+$. This pioneering work showed the great opportunities combining cold mass-selected molecular ions with widely tunable broadband IR radiation.

In the past year a cryogenic ($T>3.9\ \text{K}$) 22-pole ion trap designed and built in Cologne (FELion) has been successfully coupled to FELIX, which in its current configuration provides continuously tunable infrared radiation from 3 $\mu$m to 150 $\mu$m, hence allowing to probe characteristic vibrational spectra in the so-called "fingerprint region" with a sufficient spectral energy density also allowing for multiple photon processes (IR-MPD). Here we present the first infrared predissociation spectra of He-tagged protonated methanol and ethanol ($\text{MeOH}_2^+/\text{EtOH}_2^+$) stored at 4 K. These vibrational spectra were recorded with both a commercial OPO and FELIX, covering a total spectral range from 3700 cm$^{-1}$ to 550 cm$^{-1}$ at a spectral resolution of a few cm$^{-1}$. The H-O-H stretching and bending modes clearly distinguish the protonated alcohols from their neutral analogs. For $\text{EtOH}_2^+$, also IR-MPD spectra of the bare ion could be recorded. The symmetric and antisymmetric H-O-H stretching bands at around 3 $\mu$m show no significant shift within the given spectral resolution in comparison to those recorded with He predissociation, indicating a rather small perturbation caused by the attached He. The vibrational bands were assigned using quantum-chemical calculations on different levels of theory. The computed frequencies correspond favorably to the experimental spectra. Subsequent high resolution measurements could lead to a better structural characterization of these protonated alcohols.

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