FIR SPECTROSCOPY OF BARE CH_5^+ USING LASER INDUCED REACTIONS

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Laser Induced Reaction (LIR) is a novel technique for the spectroscopy of molecular ions as well as the study of state-specific rate coefficients and lifetimes of excited states. It is based on trapping mass-selected ions in the cold environment of a reactant gas and probing the laser-induced excitation of the ion by the outcome of the corresponding endothermic ion-molecule reaction. The feasibility of this method has been demonstrated in the past for the electronic spectroscopy of N_2^+ in the charge transfer reaction with Ar, and the spectroscopy of the IR-active modes of the acetylene cation in the abstraction reaction of $C_2H_2^+$ with hydrogen[ab].
Recently, LIR has been applied to record the first far infrared spectra of bare CH_5^+ and some of its deuterated versions combining a low temperature 22–pole ion trap with the large tuning range of the free electron laser FELIX. To obtain the LIR spectrum, the product ions of the endothermic proton transfer reaction $CH_5^+ + CO_2 \longrightarrow CH_4 + OCOH^+$ have been counted as a function of the FELIX wavelength. In addition to the earlier observed C–H-stretching feature[c] at 3000 cm^{-1}, low-frequency extensions down to 2200 cm^{-1} become discernible, as well as a H–C–H bending feature at 1250 cm^{-1}. Comparison of the measured data to computed ones shows that CH_5^+ is fluxional at the temperature of the experiment, T=110K.

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