INFRARED PREDISSOCIATION SPECTROSCOPY OF THE HYDROCARBON CATIONS C₃H⁺, C₂H⁺, and C₃H⁺₂

SANDRA BRÜNKEN, I. Physikalisches Institut, Universität zu Köln, Köln, Germany; FILIPPO LIP-PARINI, JÜRGEN GAUSS, Institut für Physikalische Chemie, Universität Mainz, Mainz, Germany; ALEXANDER STOFFELS, BRITTA REDLICH, LEX VAN DER MEER, GIEL BERDEN, JOS OOMENS, Institute for Molecules and Materials (IMM), Radboud University Nijmegen, Nijmegen, Netherlands; STEPHAN SCHLEMMER, I. Physikalisches Institut, Universität zu Köln, Köln, Germany.

Reactive hydrocarbon cations play an important role in the astrochemistry of the interstellar medium, but spectroscopic data, needed for their identification in astronomical observations, is sparse. Here we report the first gas-phase vibrational spectra of the linear C_3H^+ ($^{1}\Sigma$), the radical cation C_2H^+ ($^{3}\Pi$), and the linear-/cyclic- $C_3H_2^+$ ($^{2}\Pi$ / $^{2}A_1$, resp.). Broadband spectra were recorded by Ne- and He-messenger infrared-predissociation (IR-PD) action spectroscopy in a cryogenic (4 – 11 K) ion trap instrument (FELion) in the 250 – 3500 cm⁻¹ range using a free electron laser and a MIR-OPO at the FELIX (Free-Electron Laser for Infrared eXperiments) laboratory. The band positions (determined with a precision of $1 - 2 \text{ cm}^{-1}$) covering the C-H and C-C stretching as well as several bending modes are compared to high-level (CCSD(T) with large basis sets) quantum-chemical calculations with an emphasis on anharmonic effects and on the influence of the rare-gas messenger atom. The experimental and theoretical data provide a solid basis for subsequent IR high-resolution studies, with the ultimate goal to predict and measure accurate rotational spectra for a radio-astronomical search of these molecular ions in space.