High-Resolution Infrared Spectra of Polyacetylenes in a Supersonic Plasma Jet

D. Zhao, K. Doney, and H. Linnartz

Sackler Laboratory for Astrophysics, Leiden Observatory, Leiden University, PO Box 9513, 2300 RA Leiden, The Netherlands, Tel.:+31-71-5278475, Fax: +31-71-5275819,
E-mail: zhao@strw.leidenuniv.nl

Polyacetylenes ($HC_{2n}H$) form an important series of unsaturated hydrocarbons that are of great astrophysical interest.[1] Small polyacetylenes have been detected from infrared observations in dense atmosphere of Titan,[2] in protoplanetary nebulae of CRL 618 and CRL2688,[3] and in the exogalactic LMC.[4] We present here high-resolution mid-infrared spectra of diacetylene (HC_4H) and triacetylene (HC_6H) that are recorded in a supersonic hydrocarbon plasma jet, using an ultra-sensitive infrared detection technique. This method uses a fiber-laser-based optical parametric oscillator (OPO), in combination with continuous wave cavity ring-down spectroscopy (cw-CRDS) as a direct absorption detection tool. A hardware-based multi-trigger concept is developed to apply cw-CRDS to pulsed plasmas.[5]

Small polyacetylenes are generated in a pulsed planar plasma expansion by discharging a C_2H_2/He/Ar gas mixture. Experimental spectra are recorded at a sub-Doppler resolution of ~100 MHz in the 3305-3340 cm^{-1} region, which is characteristic of the C-H stretch vibrations of polyacetylenes. Jet-cooling in our experiment reduces the rotational temperature of both HC_4H and HC_6H to ~17 K. In total, more than 2000 lines are recorded. Sixteen bands, nine of which are newly observed, of HC_4H are assigned and analyzed, resulting in accurate spectroscopic parameters for seriaes of vibrational levels of HC4H over energy regions of 0 - 1800 and 3300 - 5100 cm^{-1}. Six rovibrational transition bands of HC_6H involving heavy perturbations are also analyzed.

The vibrational temperatures of HC_4H in the supersonic plasma jet are found to be ~ 125(10) K for the lowest-lying bending vibration (v_9), and ~570(50) K for other bending vibrations (v_6, v_7, and v_8), respectively. The high vibrational tempertures indicates the favorable formation of vibrationally excited polyacetylenes via chemical reactions of carbono-bearing species, and the non-equilibrium collision-induced vibrational relaxation of HC_4H in a plasma jet. These results imply that chemically formed HC_4H in the interstellar medium likely play a role of an important transient intermediate in the formation of carbon-chain radicals and large polyaromatic hydrocarbons.

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