Abstract

In the scope of this work, high resolution rovibrational measurements have been performed on the linear carbon chains C_7 and C_8. The spectra have been recorded with the Cologne Carbon Cluster Experiment, which combines a high resolution tunable IR diode laser spectrometer with a UV laser ablation source. It was a main task of this work to modify the existing experimental setup aiming for a significant increase of the signal-to-noise ratio. The accomplished rearrangements enabled the investigation of weaker absorption signals like hot band transitions.

More than 70 rovibrational transitions occuring in the spectral region from 2066.8 to 2069.0 cm^{-1} have been observed and subsequently assigned to the ν_5 antisymmetric stretching fundamental of linear C_8. From a least squares fit, a band origin close to 2067.89 cm^{-1} and a rotational constant for the vibrational groundstate of approximately 0.0208 cm^{-1} have been derived. The analysis of the measured triplet splitting yields evidence for an uncoupling of the spin resulting in a transition between Hund's coupling case (a) and case (b) scheme.

For C_7, infrared measurements of the ν_4 fundamental antisymmetric stretching mode and associated hot bands have been recorded in the frequency range from 2135.0 to 2141.0 cm^{-1}. Spectra of the ν_4 fundamental, as well as the $\nu_4 + \nu_{11} - \nu_{11}$, $\nu_4 + \nu_8 - \nu_8$, and $\nu_4 + 2\nu_{11} - 2\nu_{11}$, $\ell = 2$ bands have been analysed and are compared to hitherto existing experimental results [1,2] and high-level *ab initio* calculations [3]. For the two energetically low-lying bending modes, ν_8 and ν_{11}, the obtained rotational constants differ only by 0.2 % from the ground state value, $B_0 = 0.0306259(29)$ cm^{-1}, in good agreement with recent calculations. From the hot band analysis, the ℓ-type doubling constants q and experimental values for the band origins of the ν_8 and ν_{11} fundamentals have been derived for the first time, namely $\nu_{11} = 54(11)$ cm^{-1} and $\nu_8 = 81(23)$ cm^{-1}. The results presented in this work give experimental evidence for the non-floppiness of C_7 and confirm the theoretical predictions of a rather regular chain molecule, similar to the cases of C_4, C_5, and C_9.

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[3] P. Botschwina. *Chem. Phys. Lett.* 354, 148–155, 2002