Vibrational Spectrum of Matrix-Isolated Propargyl Radical $HCCCH_2$: Detection of ν_8 and Overtone Bands

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The recombination reaction of propargyl radicals ($HCCCH_2$) is likely to play an important role for the formation of benzene in Titan's lower atmosphere [refs.1-3]. Generating and understanding the propargyl radical is the first key step in the study of its recombination reaction. In this study, infrared (IR) absorption spectra of matrix-isolated $HCCCH_2$ have been measured and propargyl radicals have been generated in a supersonic pyrolysis nozzle, using a method similar to that described in a previous study [ref.4]. Besides the nine vibrational modes observed in the previous study, this investigation detected the CH_2CCH $\tilde{X}$ $^2B_1$ out-of-plane bending mode (ν_8) at 378 (±2) cm^{-1} in a cryogenic argon matrix. This is the first experimental observation of ν_8 for the propargyl radical. In addition, several overtone and combination modes have also been assigned. *Ab initio* coupled-cluster anharmonic force field calculations (CCSD(T)/ANO) were used to help guide some of the assignments. The measured frequency for ν_8 is about 20 cm^{-1} lower than the CCSD(T) value. These results improve the understanding of propargyl radical spectroscopy and also lay a foundation for our subsequent study of its recombination reaction.

The products of propargyl recombination in the supersonic pyrolysis nozzle have been observed. The thermal decomposition of 1,5-hexadiyne ($HCCCH_2CH_2CCH$) in the supersonic pyrolysis nozzle at different temperatures has also been investigated. The results and their possible implications will be discussed.

References:

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