Fourier-transform microwave spectroscopy of the fluorovinyl radical

T. Oyama,[1] N. Sakai,[1] and Y. Endo[2]

[1] *RIKEN Pioneering research institute, Japan*
[2] *Department of Applied Chemistry, National Yang-Ming Chiao Tung University, Taiwan*

Reactions between acetylene and radicals play an important role in combustion chemistry and astrochemistry [1]. Halogenated vinyl radicals are considered intermediates in the addition reactions of acetylene with halogen atoms, and chlorovinyl radicals have been extensively studied both theoretically and experimentally [2,3]. In contrast, spectroscopic studies of fluorovinyl radicals have been limited to infrared spectroscopy in solid matrices [4,5]. In this study, we observed the pure rotational transitions of the fluorovinyl radical using a Fourier-transform microwave spectrometer. At the ae-RCCSD(T)-F12 level of calculation, the fluorovinyl radical was found to have three stable structures, α-H_2C=CF, β-*trans*-HFC=CH, and β-*cis*-HFC=CH, with the α-type being the most stable (Figure 1). The observed lines were analyzed using a doublet asymmetric rotor Hamiltonian, and the derived molecular constants agree well with values of *ab initio* calculations for β-type isomers. In this experiment, the most stable α-type was not detected. The fluorovinyl radical is considered to be formed via the addition of a fluorine atom, generated by discharge from fluoromethane, to the triple bond of acetylene, which produces the β-type isomers. Conversion from β- to α-type requires intramolecular hydrogen migration, which involves a high reaction barrier. Under the cryogenic conditions of the supersonic jet, this process is inhibited, explaining the absence of α-type isomer.

References

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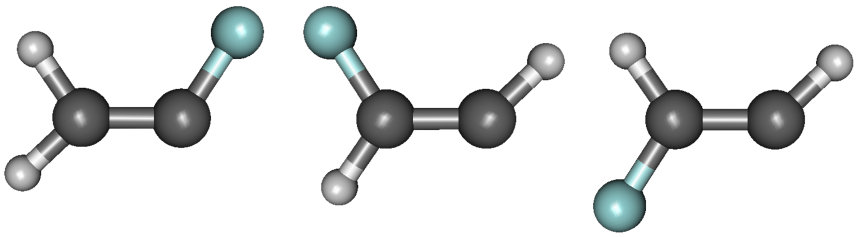

Figure 1. Three isomers of the fluorovinyl radical.