HOT BAND ANALYSIS AND KINETICS MEASUREMENTS FOR ETHYNYL RADICAL, C_2H , IN THE 1.49 μm REGION

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Ethynyl, C₂H, is an important intermediate in combustion processes and has been widely observed in interstellar space. Spectroscopically, it is of particular interest because it possesses three low-lying electronic surfaces: a ground $^2\Sigma^+$ state, and a low-lying $^2\Pi$ excited electronic state, which splits due to the Renner-Teller effect. Vibronic coupling among these states leads to a complicated, mixed-character, energy level structure. We have previously reported work^b on three bands originating from the $\tilde{X}(0,0,0)^2\Sigma$ ground state to excited vibronic states: two $^2\Sigma-^2\Sigma$ transitions at 6696 and 7088 cm⁻¹ and a ${}^{2}\Pi - {}^{2}\Sigma$ transition at 7108 cm⁻¹. In this work, the radicals were formed in a hot, non-thermal, population distribution by u.v. pulsed laser photolysis of a precursor. Kinetic measurements of the time-evolution of the ground state populations following collisional relaxation and reactive loss were also made, using some of the stronger rotational lines observed. Time-dependent signals in mixtures containing a variable concentration of precursor in argon suggested that vibronically hot C₂H radicals were less reactive than the relaxed, thermalized, radical. Two additional hot bands originating in states $\tilde{X}(0,1^1,0)^2\Pi$ and $\tilde{X}(0,2^0,0)^2\Sigma$, have now been identified in the same spectral region. In a new series of experiments, we have measured the kinetics of formation and decay of representative levels involving all the assigned transitions, i.e. originating in $\tilde{X}(0, v_2, 0)$, with $v_2 = 0, 1, \text{ and } 2$, in various concentrations of mixtures of precursor, inert gas and hydrogen. The new spectra also show greatly improved signal-to-noise ratio in comparison to our previous work, due to the use of a transient FM detection scheme, and additional spectral assignments seem likely. Both kinetics and spectroscopic results will be described in the talk.

Acknowledgments: Work at Brookhaven National Laboratory was carried out under Contract No. DE-SC0012704 with the U.S. Department of Energy, Office of Science, and supported by its Division of Chemical Sciences, Geosciences and Biosciences within the Office of Basic Energy Sciences.

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