

REINVESTIGATING THE $\tilde{A} - \tilde{X}$ SPECTRUM OF ETHYNYL RADICAL: NEW INSIGHTS INTO THE SPECTROSCOPY OF ${}^2\Pi - {}^2\Sigma^+$ VIBRONIC BANDS

ERIN N. SHARP-WILLIAMS, MELANIE A. ROBERTS, DAVID J. NESBITT, *JILA, National Institute of Standards and Technology and University of Colorado, and Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309*; ROBERT F. CURL, *Department of Chemistry and Rice Quantum Institute, Rice University, Houston, Texas 77005*.

The ethynyl radical, C_2H , is an important reactive intermediate both in combustion processes, as it is readily formed in an acetylene (C_2H_2) flame, and in the chemistry of the interstellar medium, where it is suspected to be involved in the formation of longer carbon chain species (C_nH). We have recently interrogated several of the vibronic transitions to the low-lying excited \tilde{A} state from the vibrationless level of the ground electronic state via high resolution infrared spectroscopy. This was done using direct absorption laser spectroscopy in a slit-jet discharge supersonic expansion of C_2H_2 diluted in a Neon/Helium gas mixture. In comparing our spectra with those already published using magnetic rotation spectroscopy^{a,b}, we find discrepancies between rovibronic frequencies in the 0_0^0 band at 3600 cm^{-1} . The inconsistency is localized in the excited state, by comparison of 2-line combination differences with mm-wave measurements of the ground state by Thaddeus and coworkers^c. Calculating the ${}^2\Pi$ energy levels using both Hund's case (a) and (b) basis sets and revisiting the analysis in the aforementioned work, we have determined that the discrepancies arise from a parity mislabeling of the lambda-doubled excited states. The improved low J signal intensities and resolution of satellite transitions that are observable under sub-Doppler, jet-cooled conditions complement the previous data and permit refinement of the rotational, spin-rotational, and lambda-doubling constants.

^aW. B. Yan, C. B. Dane, D. Zeitz, J. L. Hall and R. F. Curl, *J. Mol. Spectrosc.* **123**, 486 (1987).

^bR. F. Curl, P. G. Carrick and A. J. Merer, *J. Chem. Phys.* **82**, 3479 (1985).

^cT. C. Killian, C. A. Gottlieb and P. Thaddeus, *J. Chem. Phys.* **127**, 114320 (2007).