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

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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.

[a] W. B. Yan, C. B. Dane, D. Zeitz, J. L. Hall and R. F. Curl, *J. Mol. Spectrosc.* **123**, 486 (1987).
[b] R. F. Curl, P. G. Carrick and A. J. Merer, *J. Chem. Phys.* **82**, 3479 (1985).
[c] T. C. Killian, C. A. Gottlieb and P. Thaddeus, *J. Chem. Phys.* **127**, 114320 (2007).