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$_2$H, is an important reactive intermediate both in combustion processes, as it is readily formed in an acetylene (C$_2$H$_2$) 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$_n$H). 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$_2$H$_2$ 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$_0^+$ 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.