CH_2 ANTISYMMETRIC STRETCHING VIBRATIONS OF THE ALLYL RADICAL

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A glow discharge, slit supersonic expansion in conjunction with direct infrared laser absorption have been utilized to record high resolution vibration-rotation spectra of the C_3H_5 allyl radical. The slit supersonic expansion results in efficient rotational cooling ($T_{rot} \leq 20K$),thereby facilitating assignment. Specifically, approximately 50 transitions are assigned for both the in-phase (ν_1) and out-of-phase (ν_{13}) CH_2 antisymmetric vibrations. Least squares fits of the transition frequencies to an asymmetric top Hamiltonian provide both ground and excited state rotational constants. While the overall quality of the fits ($\sigma \approx 5 \times 10^{-4}$ cm^{-1}) are good, residuals do indicate perturbations in the vibrationally excited state. Due to the high instrumental resolution (slit supersonic Doppler width $\approx$ 70 MHz) spin-rotation broadening is observed in several low J transitions. Small step size (4 MHz) scans over selected transitions coupled with a detailed lineshape analysis indicate a spin-rotation constant ε_{aa} of -47(4) MHz.