HIGH RESOLUTION DIRECT FREQUENCY COMB SPECTROSCOPY OF VINYL BROMIDE (C$_2$H$_3$Br) AND NITROMETHANE (CH$_3$NO$_2$) IN THE CH STRETCH REGION

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We present high resolution rovibrational spectra of buffer gas cooled vinyl bromide (C$_2$H$_3$Br) and nitromethane (CH$_3$NO$_2$) in the 3 μm CH stretch region, acquired via cavity-enhanced direct frequency comb absorption spectroscopy. The ~ 10 K translational and rotational temperatures of the molecular gas, as well as the narrow linewidth of the frequency comb, yield well resolved rotational structure, isotope shifts, and nuclear hyperfine splittings. Given the wide bandwidth of the light source and the long path length of the enhancement cavity, we measure entire vibrational bands in a single shot with high signal-to-noise ratios. We discuss spectra of the entire fundamental CH stretch manifolds of both C$_2$H$_3$Br and CH$_3$NO$_2$, which provide contrasting examples of rovibrational structure of rigid and non-rigid systems. C$_2$H$_3$Br is a relatively normal asymmetric top, exhibiting local perturbations to its rotational structure. Conversely, CH$_3$NO$_2$ contains an essentially unhindered methyl rotor. Of particular interest are its quasi-degenerate asymmetric CH stretch modes. Here, one must consider multiple couplings between torsional, rotational, and vibrational angular momentum, leading to qualitatively new level patterns and structure.