

SUB-DOPPLER INFRARED SPECTROSCOPY OF JET COOLED CH₂Br RADICAL: CH₂ STRETCH VIBRATIONS

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The recent use of bromomethyl radical as a novel precursor for producing the simplest Criegee intermediates (CH₂OO) motivates our high-resolution investigation of CH₂Br. Cold CH₂Br (rotational temperature of 20 K) is generated by seeding CH₂Br₂ into a Ne/He pulsed supersonic slit-jet discharge expansion. Sub-Doppler infrared absorption in the CH₂ symmetric stretch band is fully resolved at high single-to-noise ratio, yielding band origins measured at $3052.9781 \pm 0.0004 \text{ cm}^{-1}$ for CH₂⁷⁹Br and $3052.9775 \pm 0.0004 \text{ cm}^{-1}$ for CH₂⁸¹Br, respectively. The rotationally resolved structure is fitted to a non-rigid rotor Hamiltonian with spin-rotation coupling, furnishing rotational constants and the spin-orbit coupling tensor for the vibrationally excited state. The results are consistent with a vibrationally averaged planar π radical with unpaired electron spin density in a partially filled p $_{\pi}$ -orbital on the central carbon atom. These measurements complete the set of high-resolution investigations of the symmetric-stretch mode for mono-halogen substituted methyl radicals (CH₃X, X = F, Cl, Br, I). We use this opportunity to examine trends in molecular properties with variation of the substituent halogen atom, for example, regarding vibrationally averaged geometries and symmetric stretch band origins. A combination band is also analyzed, likely originating from the lowest-energy, out-of-plane vibrational bending mode. Evidence of hyperfine structure is observed as well. Interestingly, despite high signal to noise on the symmetric CH stretch vibrational mode, we find no evidence for the asymmetric CH stretch spectrum at our current sensitivities, which we interpret as resulting from strong enhancement of the symmetric stretch band by vibrationally mediated "charge-sloshing" dynamics in the C-Br bond.