

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

ANDREW KORTYNA, PRESTON G. SCRAPE, *JILA, National Institute of Standards and Technology and Univ. of Colorado, Boulder, CO, USA*; DANIEL LESKO, *Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO, USA*; DAVID NESBITT, *JILA, National Institute of Standards and Technology and Univ. of Colorado, Boulder, CO, USA*.

Bromomethyl radical (CH₂Br) has recently been used as a novel precursor for producing the simplest Criegee intermediates (CH₂OO). With the goal of spectroscopically investigating a Criegee intermediate, we have pursued high resolution characterization of the CH₂Br radical in our slit jet discharge spectrometer. The bromomethyl radical is generated by seeding CH₂Br₂ into a Ne/He/H₂ mixture in a pulsed slit discharge. The radical is produced through either electron dissociative attachment to form bromine anions or hydrogen abstraction of bromine, with subsequent cooling in a supersonic expansion to about 15 K. Infrared absorption in the CH₂ symmetric stretch vibrational band is fully resolved at high single-to-noise ratios for both the ⁷⁹Br and ⁸¹Br isotopologues. The sub-Doppler rotational structure is fitted to a rigid-rotor Hamiltonian with spin-rotation coupling, generating principal 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 C atom. Relative band intensities in the symmetric and antisymmetric CH₂ stretch manifolds provide further elucidation of the "charge-sloshing" mechanism noted in CH₂F, CH₂Cl, and CH₂I radical species due to vibrationally mediated shifts in electron density along the carbon-halogen bond axis.