

FIRST OBSERVATION OF THE SPIN ROTATIONAL STRUCTURE OF THE HYDROXYMETHYL RADICAL (H₂COH) IN THE CH₂ ASYMMETRIC MODE

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Rotationally-resolved direct infrared absorption spectra of hydroxymethyl radical (H₂COH) in the CH₂ asymmetric mode (ν_2) were observed for the first time using the Boulder difference frequency generation infrared spectrometer. Hydroxymethyl radical was formed with chemical selectivity via the reaction of Cl radical with CH₃OH in a discharge slit-jet supersonic expansion. As a result of sub-Doppler linewidth and low rotational temperature, the *b*-type rotational structure and spin-rotation splitting were fully resolved. In particular, tunneling splitting was observed due to the large-amplitude COH torsional mode. Because of the feasible permutation of hydrogens in the methylenic group, nuclear spin intensity alternation was given as: 3:1 for K_a =even, odd in the 0⁺ level, and 1:3 for K_a =even, odd in the 0⁻ level of the ground vibrational state. The assignments were confirmed rigorously by four-line ground state combination differences, which agreed within the experimental frequency uncertainty (10 MHz). The identified transitions were fit with a Watson A-reduction Hamiltonian including the spin rotational interaction, leading to unambiguous determination of asymmetric top spectroscopic constants, as well as spin rotational constants (ϵ_{aa} , ϵ_{bb} , ϵ_{cc}) for the first time.