

COHERENCE-CONVERTED POPULATION TRANSFER FTMW-IR DOUBLE RESONANCE SPECTROSCOPY OF CH₃OD IN THE C-H STRETCH REGION

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Coherence-converted population transfer microwave-infrared double resonance spectroscopy is employed to record the rotationally state-selected infrared spectra of jet-cooled CH₃OD in the C-H stretch region (2750–3020 cm⁻¹). The observed infrared spectra result from the E-species microwave transitions ($1_0 \leftarrow 1_{-1}$ at 18.957 GHz, $2_0 \leftarrow 2_{-1}$ at 18.991 GHz, and $3_0 \leftarrow 3_{-1}$ at 19.005 GHz). The present spectra of CH₃OD contain 17 interacting vibrational bands ($J' = 0$). In addition to the three C-H stretch fundamentals (ν_3 : 2841.7 cm⁻¹, ν_9 : 2954.4 cm⁻¹ and ν_2 : 2998.9 cm⁻¹), 14 additional band origins are found in the region of the binary combinations of the CH bends (2890–2950 cm⁻¹). Although the A-species was inaccessible in the present work, the pattern of E-species reduced energies suggests that the torsional tunneling splittings of ν_3 and ν_9 are normal, whereas ν_2 is inverted. The number and distribution of the observed vibrational bands support a stepwise coupling scheme in which the CH stretch bright state couples first to the binary C-H bend combinations, and then to all of the higher order vibrational combinations. A time-dependent interpretation in the asymmetric region indicates a fast (170 fs) initial decay of the bright state.