

A ROTATION-TORSION-VIBRATION 3-D INTERNAL COORDINATE TREATMENT FOR THE CH₃-BENDING FUNDAMENTALS OF METHANOL

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A theoretical model has been developed to account for certain features of CH₃-bending subbands of methanol observed between 1450 and 1570 cm⁻¹. The observed features in ν_4 include (i) an apparent inversion of the rotationless E-A torsional splitting with respect to the ground state, (ii) a pronounced upward slope in the K -reduced torsion-vibration energy pattern for the subband origins, and (iii) A₁-A₂ inversion of the $K = 2A$ and $3A$ J -rotational levels leading initially to ambiguity in identifying the vibrational mode as ν_4 (A₁) or ν_{10} (A₂). The model is an effective internal coordinate Hamiltonian constructed in G₆ molecular symmetry with the CH₃-bends coupled to each other and to torsion and including a - and γ -type Coriolis coupling terms. Experimental upper state energies for ν_4 , ν_{10} , and ν_5 have together been fitted successfully employing 12 adjustable parameters to give a standard deviation of ± 0.13 cm⁻¹. J -dependence is introduced via a rotational Hamiltonian including molecular asymmetry, plus b - and c -type Coriolis terms which account for the observed A₁-A₂ inversion of the rotational levels at low K . The computer program for our model was set up in a CH-stretch/CH₃-bend local mode polyad scheme, with polyad number $p=2(v_1+v_2+v_3)+(v_4+v_5+v_6)$, for ready extension to the 3 μ m CH-stretching region in future.