VARIATIONS IN TORSION-VIBRATION ENERGY STRUCTURE OF CH_3OH FROM FUNDAMENTAL, OVERTONE AND COMBINATION BANDS OF THE CH_3-ROCKING AND CO-STRETCHING MODES

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Torsion-vibration energy structures deduced from the ν_7 (A' CH_3 in-plane rock), ν_8 (A' CO stretch), ν_{11} (A'' CH_3 out-of-plane rock), $2\nu_7$, $2\nu_8$, $\nu_7 + \nu_8$ and $\nu_8 + \nu_{11}$ fundamental, overtone and combination bands of CH_3OH are compared and contrasted to that of the ground vibrational state. The $2\nu_7$ in-plane CH_3-rocking overtone and the $\nu_8 + \nu_{11}$ CO-stretch/out-of-plane-rock combination bands have only recently been identified in the high-resolution Fourier transform spectrum, and point to systematic trends in the excited-state torsional behaviour for methanol. Torsion-vibration substate origins for the 8 states have been fitted to a 5-parameter Fourier model to characterize the energy patterns. Excitation of the ν_8 mode has little influence on the torsional structure, but the $A - E$ torsional energy splittings are sharply reduced with excitation of ν_7 and inverted with excitation of ν_{11}. These changes are examined from the perspective of Hougen's torsion-vibration interaction model for states of degenerate E vibrational parentage.[a] The $K = 0$ substate energy pattern for the v_7 and v_{11} states supports the model but with some differences in detail. The values of the K-scaling parameter ρ determining the periodicity of the torsional energies appear to vary almost linearly with the number of quanta of vibrational excitation. The changes are suggestive of substantial zero-point effects on the axial moments of inertia, with implications for the structural determination of the CH_3 methyl top.

[a] J.T. Hougen, *J. Mol. Spectrosc.* **207**, 60-65 (2001).