TORSIONAL MIXING AND FRACTIONATION IN THE FTIR SPECTRUM OF CH_3OH FROM 1050-1450 CM^{-1}

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At low resolution, the infrared spectrum of CH_3OH from 1050-1450 cm^{-1} appears as an enigmatic region of weak absorption with broad, unstructured peaks in strong contrast to the sharp CO-stretching fundamental lying immediately below. Under full rotational FTIR resolution, however, the spectrum comes alive and shows a wealth of detail with distinct subbands everywhere. The accurate ground-state combination differences currently available have made it possible to identify the lower levels for the majority of the stronger subbands, and then to predict and search for weaker related subbands arising from different ground-state torsional levels. Numerous connected parallel subbands have thereby been detected having the torsional separation of order 200 cm^{-1} and either common upper or lower levels. Parallel transitions with ΔK=0 but $\Delta\nu_t \neq 0$ are normally forbidden, hence the presence of such subbands signals mixing among the OH-bending, CH_3-rocking and CO-stretching modes and torsional fractionation of the original states.

Our progress in mapping the spectrum will be reported, and some interesting assignment problems discussed. While the ground-state data clearly identify the lower levels of the subbands, the vibrational and even torsional identity of the upper state is not always certain. Thus, despite the attention paid to the IR spectrum of CH_3OH over the past several decades, there is still work to be done to nail down definitive assignments and unperturbed harmonic wavenumbers for the weak vibrational fundamentals in the 1050-1450 cm^{-1} region. The present investigation has extended our knowledge of the torsion-vibration energy manifold of CH_3OH, however, and the observation of extensive torsional fractionation and wide spreading of the subband origins accounts in large measure for the broad contour of the IR absorption and the lack of recognizable low-resolution detail.