THE 3μm VIBRATION-TORSION-ROTATION ENERGY MANIFOLD OF METHANOL

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The 3μm spectrum of methanol is an important gateway to the understanding of molecular dynamics and to the modeling of cometary spectra. The region is extremely complicated due to a dense vibrational structure and network of interactions among the *three* CH-stretch fundamentals, ν_2, ν_9, ν_3, *six* overtones and combinations of the three CH_3-bending modes, ν_4, ν_{10}, ν_5, and a variety of overtone combinations of the torsion ν_{12}, with the remaining lower-lying vibrations.

We have obtained FT spectra for the 3μm region under various conditions. The structure is dense with few easily recognized features above the ν_3 symmetric CH-stretch. However, in an extension of the color-center-laser slit-jet beam spectrum from 2945 to 2975 cm^{-1}, low K states could be identified, then allowing further assignment and confirmations of the medium K states from FTS. Altogether, about 25 vibration-torsion-K-rotational states have now been firmly assigned up to K = 4. Plots of K-reduced energies place these states into three distinguishable groups assigned as ν_9, 2ν_4, and ν_4+ν_{10}, although there are a number of extra subbands in the spectrum arising possibly from interactions with other states. Spectroscopic findings at the present time are: (i) the torsional A/E ordering is inverted for ν_9, normal for 2ν_4, and apparently normal for the presently observed K = 2 states of ν_4+ν_{10}; (ii) the K = 0 torsional A/E splittings are -5.48 and 8.28 cm^{-1} for ν_9 and 2ν_4, respectively, and an estimated much lower than ground state value for the ν_4+ν_{10} combination; (iii) the ν_9 and 2ν_4 states have virtually identical upper state term values around 3092 cm^{-1}, but show almost equal and opposite linear shifts with K with slopes of 2-3 cm^{-1}/K-value; (iv) the ν_4+ν_{10} combination is about 20 cm^{-1} lower in energy than ν_9 and 2ν_4, 10 cm^{-1} lower than the previous estimates for the band center.