HIGH RESOLUTION INFRARED SPECTRA OF THE ν_9 AND $2\nu_4$ BANDS IN METHANOL

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Jet-cooled high resolution infrared absorption spectra of the A_2 asymmetric C-H stretch in methanol, the ν_9 band, were recorded from 2945 to 2991 cm^{-1}. A large part of the bending overtone $2\nu_4$ appears in the same region and was also recorded. The analysis has resulted in 38 subband assignments for the ν_9 and $2\nu_4$ reaching K' up to 4 for ν_9 and up to 2 for $2\nu_4$. A plot of the upper state torsional energies versus K' shows the expected cosine patterns that result from the interaction of the torsion with K-rotation; however the torsional tunnelling splitting at K'= 0 is inverted for ν_9 with the E levels below the A levels. The A and E K'= 0 subband origins for ν_9 are 2966.6437(4) and 2952.040(3) cm^{-1}, respectively, and for $2\nu_4$ are 2958.3586(11) cm^{-1} and 2957.565(6) cm^{-1}. The ν_9 band origin (average of A and E) was found to be about 11 cm^{-1} below the estimate from low resolution spectra (2970.0 cm^{-1}). A number of perturbations in the $2\nu_4$ band have been identified.

The inverted torsional structure of the ν_9 band supports the local mode Hamiltonian that was developed to explain the inverted torsional structure of the ν_2 asymmetric C-H stretch and the regular torsional splitting of the ν_3 symmetric C-H stretch. The model takes into account the difference in the local C-H frequency between the *trans* and *gauche* positions. The local mode parameters are the local C-H frequency ω = 2934.0 cm^{-1}, the local-local coupling parameter λ = −42.2 cm^{-1}, and the stretch-torsion coupling parameter μ = 12.9 cm^{-1}. This model yielded the correct A/E ordering and fit the 6 K'= 0 subband origins with a standard deviation of 0.4 cm^{-1}. Qualitative agreement with the K'-dependence of the torsional energies was obtained.