HIGH-RESOLUTION INFRARED SPECTRUM OF THE $3\nu_9 - \nu_9$ HOT BAND OF HNO₃: STUDY OF CORIOLIS COUPLED $3\nu_9$ AND THE NEARBY DARK STATE

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The high-resolution infrared spectrum of HNO₃ in the region of 805-853 cm⁻¹ has been measured and assigned for the $3\nu_9 - \nu_9$ hot band. The significant splittings in the upper state $3\nu_9$ arising from the torsional motion of H around ON were observed and identified. It was found that $3\nu_9$, which is around 1289 cm⁻¹, was involved in a strong Coriolis resonance with a dark state near 1301 cm⁻¹, apart from the slightly higher vibrational state ν_4 . To account for the corresponding Coriolis perturbations as well as the torsional splittings observed in the $3\nu_9 - \nu_9$ band, a comprehensive line-position fit was performed by simultaneously adjusting three sets of constants for $3\nu_{9,1}$, $3\nu_{9,2}$ and the dark state. Accurate rovibrational constants were obtained giving a fit of 947 unperturbed and 146 perturbed lines to the rms accuracy of 0.00062 cm⁻¹ and 0.00175 cm⁻¹, respectively. The interacting dark state, found at 1300.7331(19) cm⁻¹, can be assigned to $2\nu_6$ which proves to be responsible for the previously unjustified ^a $\Delta K_c = 6$ resonance observed in the strong ν_3 band.

^aA. Perrin, O. Lado-Bordowsky, and A. Valentin, Mol. Phys. 67, 249-270, 1989