

MEASUREMENTS OF LINE INTENSITIES OF SOME LINES OF AMMONIA SELF-PERTURBED IN THE ν_2 , $2\nu_2$ AND ν_4 BANDS

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Using Fourier Transform spectra (Bruker IFS 120 HR, resolution $\approx 0.004 \text{ cm}^{-1}$) of NH_3 in several branches of the ν_2 , $2\nu_2$ and ν_4 bands, absolute line intensities have been determined at room temperature ($T = 295 \text{ K}$) for more than 400 rovibrational lines located in the spectral range $1000\text{-}1800 \text{ cm}^{-1}$. A non-linear least-squares multispectrum fitting procedure, including line mixing effects, has been used to retrieve the line intensities from eleven experimental spectra recorded at different pressures of pure ammonia. The present results are compared with previous measurements^{1,2,3} in which the collisional absorption coefficient is a Voigt profile. The line intensities determined in the present work are smaller than those determined by these authors. For example, the difference in percent between our values and the values of C. Cottaz¹ is about 6%. For almost all lines and pressures considered in this work, it was shown that the first-order Rosenkranz absorption coefficient taking into account line-mixing effects is adequate to extract with sufficient accuracy the line intensities of NH_3 . An examination of these line intensities shows a pronounced J and K quantum numbers dependencies.

Our results have been analyzed to obtain effective transition moments, vibrational band strengths and correction parameters of symmetric and asymmetric partial bands of the fundamental ν_4 band, as well as those of asymmetric partial bands of ν_2 and $2\nu_2$ bands. Since these bands are affected by the rotation-vibration interactions, the zero-order theory where the Hermann-Wallis factors are not included is not able to describe the intensity anomalies in these bands. As shown by Aliev et al.⁴, it is necessary to include these interactions into theoretical line strengths expressions. These authors have developed a third-order theory of the line strengths of the vibrational transition from the ground vibrational state to the rovibrational levels of molecules with C_{3v} symmetry using the method of contact transformation applied to the electric dipole moment operator. A suitable expression for the line strength was derived to fit the experimental intensities.

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