ANOMALOUS CENTRIFUGAL DISTORTION IN NH₂

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The NH₂ radical spectrum, first observed by Herzberg and Ramsay, is dominated by a strong Renner-Teller effect giving rise to two electronic states: the bent \(X^2B_1\) ground state and the quasi-linear \(A^2A_1\) excited state. The NH₂ radical has been the subject of numerous high-resolution investigations and its electronic and ro-vibrational transitions have been measured. Using synchrotron radiation, new rotational transitions have been recently recorded and a value of the rotational quantum number \(N\) as large as 26 could be reached. In the \(X^2B_1\) ground state, the NH₂ radical behaves like a triatomic molecule displaying spin-rotation splittings. Due to the lightness of the molecule, a strong coupling between the overall rotation and the bending mode arises whose effects increase with \(N\) and lead to the anomalous centrifugal distortion evidenced in the new measurements.

In this talk the Bending-Rotation approach developed to account for the anomalous centrifugal distortion of the water molecule is modified to include spin-rotation coupling and applied to the fitting of high-resolution data pertaining to the ground electronic state of NH₂. A preliminary line position analysis of the available data allowed us to account for 1681 transitions with a unitless standard deviation of 1.2. New transitions could also be assigned in the spectrum recorded by Martin-Drumel et al. In the talk, the results obtained with the new theoretical approach will be compared to those retrieved with a Watson-type Hamiltonian and the effects of the vibronic coupling between the ground \(X^2B_1\) and the excited \(A^2A_1\) electronic state will be discussed.

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\(^{a}\)Herzberg and Ramsay, J. Chem. Phys. 20 (1952) 347  
\(^{b}\)Dressler and Ramsay, Phil. Trans. R. Soc. A 25 (1959) 553  
\(^{d}\)Martin-Drumel, Pirali, and Vervloet, J. Phys. Chem. A 118 (2014) 1331  
\(^{e}\)Coudert, J. Molec. Spectrosc. 165 (1994) 406