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Perturbation theory treatment of pseudorotation in cyclic-N_3

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A relatively simple treatment using perturbation theory is proposed to describe spectrum of pseudorotational states in cyclic-N_3. The purpose is to develop an analytical expression that could be used to fit the experimentally determined spectrum of cyclic-N_3, with purpose of identifying this molecule in the laboratory and deriving parameters of its potential energy surface directly from the experimental data. The perturbation theory expression derived in this work is used to fit the spectrum calculated numerically in the previous work [D. Babikov and B. Kendrick, J. Chem. Phys. 133, 174310 (2010)]. It is found that the second order of perturbation theory works well, giving a very good fit of the spectrum, with the rms deviation of only 0.26 cm^{-1}. Analysis reveals that important characteristics of the potential energy surface, such as equilibrium geometry and pseudorotation barriers, are directly related to the features of spectrum, such as splittings, and can be readily derived from experimental data, when those become available.

are present in the expansion of Eq. (6), the splitting occurs only for $m = 3/2, 3, 9/2$, etc., states.

Analysis of the spectrum presented in Table I shows that the first order of perturbation theory is qualitatively consistent with the numerical results. The values of splittings are $_{3/2} = 100.46$ cm^{-1}, $_{3} = -22.55$, and $_{9/2} =$

individual states, while the first-order correction gives only the m-independent shift of the entire zeroth-order spectrum by a constant number. Note that the second-order correction affects the splittings of states with integer values of m only, i.e., affects only the splittings of the BO states.

D. Third-order correction

The third order of theory uses ideas of the first and second orders. For the purpose of brevity we skip the derivations and give the final result

$$E_m^{(3)} = - H_{mm}^{(0)} \sum_{m = m} \frac{|H_{mm}^{(0)}|^2}{\left(E_m^{(0)} - E_m^{(0)}\right)^2}$$

$$= - \sum_n \left(\frac{V_n}{2}\right)^3 \frac{l_m^2}{2n^4} \left(\delta_{m,n} 2s + \left[1 - \delta_{m,n/2} \frac{1}{2} s \right] \right.$$

$$\times \left\{ n, \right.$$