THEORETICAL EVIDENCE FOR THE FORMATION OF ROTATIONAL ENERGY LEVEL CLUSTERS IN THE VIBRATIONAL GROUND STATE OF PH_3

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We investigate theoretically the rotational dynamics of pyramidal XY_3 molecules in highly excited rotational states. Towards this end we compute, by a variational method,[a] the rotational energy levels in the vibrational ground state of PH_3 for $J \leq 80$ from a potential energy surface determined previously.[b] At $J \geq 50$ the calculated energy levels show a distinct cluster pattern. By monitoring the cluster formation we follow the various stages of the rotational dynamics. We analyze the wavefunctions for the cluster states and compute expectation values which show that the $\mathbf{C}_{3v}$ geometrical symmetry of PH_3 is broken at high rotational excitation. The conclusions drawn from the quantum-mechanical calculations are confirmed by semi-classical theory, i.e., by an analysis of the stationary points on the rotational energy surface.

[a] S. N. Yurchenko, M. Carvajal, P. Jensen, H. Lin, J. Zheng, and W. Thiel, *Mol. Phys.* **103**, 359-378 (2005) and references therein.
[b] S. N. Yurchenko, M. Carvajal, P. Jensen, F. Herregodts, and T. R. Huet, *Chem. Phys.* **290**, 59-67 (2003).