AN AB INITIO APPROACH TO ANALYZE FERMI RESONANCE IN AMMONIA CLUSTERS

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Anharmonic vibrational coupling among N-H stretching fundamental (ν_1 and ν_3) and N-H bending overtone ($2\nu_4$) vibrations in $(NH_3)_n$ (n = 1 to 5) are analyzed based a full dimensional Hamiltonian including third and quartic terms. In particular, we examine Fermi resonance between the symmetric N-H stretching (ν_1) and N-H bending overtone ($2\nu_4$) vibrations. As the cluster size increases, enhancement of the hydrogen bond strength makes ν_1 red-shifted while $2\nu_4$ blue-shifted. These shifts result in the crossing of the frequencies of ν_1 and $2\nu_4$ levels, and their energy order reverses between n = 3 to n = 4. Because the nature of Fermi resonance, although the zero-order ν_1 and $2\nu_4$ levels are shifted, the resultant mixed levels do not show remarkable changes in frequency. Instead, the major component of each mixed level largely changes and this causes significant redistribution of the intensity. Our results offer a solution to resolve puzzles on the intensity distribution and assignments of the Fermi mixing bands in the previously reported infrared spectra of $(NH_3)_n$.