THE AMMONIA DIMER REVISITED

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The conclusion from microwave spectra by Nelson, Fraser, and Klemperer [a] that the ammonia dimer has a nearly cyclic structure led to much debate about the issue of whether $(NH_3)_2$ is hydrogen bonded. This structure was surprising because most *ab initio* calculations led to a classical, nearly linear, hydrogen-bonded structure. An obvious explanation of the discrepancy between the outcome of these calculations and the microwave data which led Nelson *et al.* to their "surprising structure" might be the effect of vibrational averaging: the electronic structure calculations focus on finding the minimum of the intermolecular potential, the experiment gives a vibrationally averaged structure. Isotope substitution studies seemed to indicate, however, that the complex is nearly rigid. Additional data became available from high-resolution molecular beam far-infrared spectroscopy in the Saykally group [b]. These spectra, displaying large tunneling splittings, indicate that the complex is very floppy. The seemingly contradictory experimental data were explained when it became possible [c] to calculate the vibration-rotation-tunneling (VRT) states of the complex on a six-dimensional intermolecular potential surface. The potential used was a simple model potential, with parameters fitted to the far-infrared data. Now, for the first time, a six-dimensional potential was computed by high level *ab initio* methods and this potential will be used in calculations of the VRT states of $(NH_3)_2$ and $(ND_3)_2$. So, we will finally be able to answer the question whether the conclusions from the model calculations are indeed a valid explanation of the experimental data.

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[a] D. Nelson, G. T. Fraser, and W. Klemperer *J. Chem. Phys.* **83** 6201 (1985)

[b] J. G. Loeser, C. A. Schmuttenmaer, R. C. Cohen, M. J. Elrod, D. W. Steyert, R. J. Saykally, R. E. Bumgarner, and G. A. Blake *J. Chem. Phys.* **97** 4727 (1992)

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