225.Title: Rovibrational spectra of ammonia. I. Unprecedented accuracy of a potential energy surface used with nonadiabatic corrections

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Abstract: In this work, we build upon our previous work on the theoretical spectroscopy of ammonia, NH3. Compared to our 2008 study, we include more physics in our rovibrational calculations and more experimental data in the refinement procedure, and these enable us to produce a potential energy surface (PES) of unprecedented accuracy. We call this the HSL-2 PES. The additional physics we include is a second-order correction for the breakdown of the Born-Oppenheimer approximation, and we find it to be critical for improved results. By including experimental data for higher rotational levels in the refinement procedure, we were able to greatly reduce our systematic errors for the rotational dependence of our predictions. These additions together lead to a significantly improved total angular momentum (J) dependence in our computed rovibrational energies. The root-mean-square error between our predictions using the HSL-2 PES and the reliable energy levels from the HITRAN database for J = 0-6 and J = 7/8 for (NH3)-N-14 is only 0.015 cm(-1) and 0.020/0.023 cm(-1), respectively. The root-mean-square errors for the characteristic inversion splittings are approximately 1/3 smaller than those for energy levels. The root-mean-square error for the 6002 J = 0-8 transition energies is 0.020 cm(-1). Overall, for J = 0-8, the spectroscopic data computed with HSL-2 is roughly an order of magnitude more accurate relative to our previous best ammonia PES (denoted HSL-1). These impressive numbers are eclipsed only by the root-mean-square error between our predictions for purely rotational transition energies of (NH3)-N-15 and the highly accurate Cologne database (CDMS): 0.00034 cm(-1) (10 MHz), in other words, 2 orders of magnitude smaller. In addition, we identify a deficiency in the (NH3)-N-15 energy levels determined from a model of the experimental data.