COMPETITION BETWEEN TWO LARGE-AMPLITUDE MOTION MODELS: NEW HYBRID HAMILTONIAN VERSUS OLD PURE-TUNNELING HAMILTONIAN

ISABELLE KLEINER, *Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), CNRS et Universités Paris Est et Paris Diderot, Créteil, France*; JON T. HOUGEN, *Sensor Science Division, National Institute of Standards and Technology, Gaithersburg, MD, USA.*

In this talk we report on our progress in trying to make the hybrid Hamiltonian competitive with the pure-tunneling Hamiltonian for treating large-amplitude motions in methylamine. A treatment using the pure-tunneling model has the advantages of: (i) requiring relatively little computer time, (ii) working with relatively uncorrelated fitting parameters, and (iii) yielding in the vast majority of cases fits to experimental measurement accuracy. These advantages are all illustrated in the work published this past year on a gigantic $v_t = 1$ data set for the torsional fundamental band in methyl amine[a]. A treatment using the hybrid model has the advantages of: (i) being able to carry out a global fit involving both $v_t = 0$ and $v_t = 1$ energy levels and (ii) working with fitting parameters that have a clearer physical interpretation. Unfortunately, a treatment using the hybrid model has the great disadvantage of requiring a highly correlated set of fitting parameters to achieve reasonable fitting accuracy, which complicates the search for a good set of molecular fitting parameters and a fit to experimental accuracy. At the time of writing this abstract, we have been able to carry out a fit with J up to 15 that includes all available infrared data in the $v_t = 1$-0 torsional fundamental band, all ground-state microwave data with K up to 10 and J up to 15, and about a hundred microwave lines within the $v_t = 1$ torsional state, achieving weighted root-mean-square (rms) deviations of about 1.4, 2.8, and 4.2 for these three categories of data. We will give an update of this situation at the meeting.

---

[a]I. Gulaczyk, M. Kreglewski, V.-M. Horneman, J. Mol. Spectrosc., in Press (2017).