A NEW HYBRID PROGRAM FOR FITTING ROTATIONALLY RESOLVED SPECTRA OF METHYLAMINE-LIKE MOLECULES: APPLICATION TO 2-METHYLMALONALDEHYDE

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*.

A new hybrid-model fitting program for methylamine-like molecules has been developed, based on an effective Hamiltonian in which the ammonia-like inversion motion is treated using a tunneling formalism, while the internal-rotation motion is treated using an explicit kinetic energy operator and potential energy function. The Hamiltonian in the computer program is set up as a 2x2 partitioned matrix, where each diagonal block consists of a traditional torsion-rotation Hamiltonian (as in the earlier program BELGI), and the two off-diagonal blocks contain all tunneling terms. This hybrid formulation permits the use of the permutation-inversion group G_6 (isomorphic to C_{3v}) for terms in the two diagonal blocks, but requires G_{12} for terms in the off-diagonal blocks. Our first application of the new program is to 2-methylmalonaldehyde. Microwave data for this molecule were previously fit (essentially to experimental measurement error) using an all-tunneling Hamiltonian formalism to treat both large-amplitude-motions [a]. For 2-methylmalonaldehyde, the hybrid program achieves a fit of nearly the same quality as that obtained by the all-tunneling program, but fits with the hybrid program eliminate a large discrepancy between internal rotation barriers in the OH and OD isotopologues of 2-methylmalonaldehyde that arose in fits with the all-tunneling program. Other molecules for application of the hybrid program will be mentioned.

[a] V.V. Ilyushin, E.A. Alekseev, Yung-Ching Chou, Yen-Chu Hsu, J. T. Hougen, F.J. Lovas, L. Picraux, J. Mol. Spectrosc. 251 (2008) 56-63