A NEW PROGRAM FOR NON-EQUIVALENT TWO-TOP INTERNAL ROTORS WITH A C_s FRAME

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We have written a new program to calculate and fit torsion-rotation transitions in molecules containing two inequivalent methyl tops (C_{3v}) and having the rest of the atoms lying in a plane of symmetry. We based our work on the theoretical model and Hamiltonian described by Ohashi et al for the N-methylacetamide molecule[a]. In the absence of top-top interactions, each asymmetric top energy levels splits into AA, AE, EA and EE components where the individual letters A and E indicate the symmetry species of the wave function with respect to internal rotation of one of the methyl tops. The pair of letters taken together indicates the species in the G_{18} permutation-inversion group appropriate for the molecule, so AA, AE, EA, and EE correspond to A_1 (or A_2), E_2, E_1 and $E_3 \oplus E_4$, respectively. In the previous study, the torsion-rotation Hamiltonian was diagonalized directly in a one-step process using torsion-rotation functions $|J, K > |m_1 > |m_2 >$ where m_1 and m_2 represent the free-rotor basis functions for top 1 and top 2. The one-step diagonalization made however the least-squares fitting of moderate *J* values very slow, even for rather small values of m_1 and m_2. Our goal is to write a code which will be faster and which allows us to reach higher *J* values. We follow a two-step procedure to diagonalize the Hamiltonian and implemented a banded-matrix diagonalization routine in order to speed up the code. We tested the code with the published N-methylacetamide Fourier-transform microwave data. The principles of the method, as well as the limitations will be discussed[b] .

[a] N. Ohashi, J. T. Hougen, R. D. Suenram, F.J. Lovas, Y. Kawashima, M. Fujitake and J. Pyka, J. Mol. Spectrosc., 227, 28-42 (2004)

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