A NEW FIT OF THE MICROWAVE SPECTRUM OF 2-METHYLMALONALDEHYDE

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We have used the G_{12} group-theoretical formalism[a] derived by Ohashi and Hougen for methylamine to refit the microwave spectrum of 2-methylmalonaldehyde[b] [HO-CH=C(CH_3)-CH=O]. This molecule exists in the gas phase as a six-membered hydrogen-bonded ring and has two large amplitude motions: an intramolecular hydrogen transfer and a methyl torsion. Information concerning the hydrogen transfer from one oxygen atom at the top of the ring to the other is transmitted to the methyl rotor attached to the bottom of the ring via the interchange of the C-C single bond and the C=C double bond adjacent to each other in the ring.

In 1981 Sanders recorded the microwave spectrum of 2-methylmalonaldehyde. His spectrum is the only rotationally resolved spectrum of 2-methylmalonaldehyde, and is also the only rotationally resolved data available in the literature for a system exhibiting the hydrogen-transfer–methyl-torsion–overall-rotation interaction. In Sanders' work, the four sublevels A(+), A(-), E(+), and E(-) of the ground vibrational level were not simultaneously fitted because no appropriate theory was available at that time. From the viewpoint of molecular symmetry, the interaction between hydrogen transfer and CH_3 torsion in 2-methylmalonaldehyde is similar to the interaction between CNH_2 inversion and CH_3 torsion in methylamine. Hence, the formalism for the inversion–torsion–overall-rotation interaction in methylamine should be able to describe the hydrogen-transfer–torsion–overall-rotation interaction in 2-methylmalonaldehyde. We thus used the G_{12} methylamine formalism to refit the four-sublevels, and obtained root-mean-square deviations of 0.16 and 0.10 MHz for 2-methylmalonaldehyde-d0 and -d1. This represents an improvement by a factor of 10 or more for some of the E levels.

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[a] N. Ohashi and J. T. Hougen, *J. Mol. Spectrosc.* **121**, 474 (1987).

[b] N. D. Sanders, *J. Mol. Spectrosc.* **86**, 27 (1981).