REMEASUREMENT OF THE MICROWAVE SPECTRUM OF 2-METHYLMALONALDEHYDE AND ANALYSIS OF THE HYDROGEN-TRANSFER AND INTERNAL-ROTATION MOTIONS

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In the gas phase 2-methylmalonaldehyde [$\mathrm{HO-CH=C(CH_3)-CH=O}$] is a 6-membered hydrogen-bonded ring with two large-amplitude motions (LAMs): an intramolecular hydrogen transfer and a methyl torsion. The former is interesting because transfer of the H atom from the OH to the C=O triggers an exchange of single and double bonds in the ring and a 60° rotation of the attached $\mathrm{CH_3}$. Sanders presented the first microwave measurements and analysis of this molecule. Much later two of us reanalyzed Sanders' data using a tunneling-rotational Hamiltonian based on a G_{12}^m extended-group formalism. Present measurements on the OH and OD species were carried out from 8 to 26 GHz by FTMW spectroscopy and from 49 to 149 GHz by conventional absorption spectroscopy; they increase previous measurement accuracy by factors of 10 (FTMW) and 5 (mm wave). We use the same Hamiltonian as before to carry out global fits of over 2500 transitions for each species, obtaining an rms deviation of 15 kHz for both. This significant improvement in fitting accuracy allows us to confirm: (i) the validity of discarding a few lines from Sanders' tables in our previous fit, (ii) the stability of the molecular constants when more data are added, (iii) the surprising increase in internal rotation splitting from the OH to the OD species, and (iv) the ability of the two-dimensional tunneling model for H transfer and internal rotation to reach 10 kHz accuracy. Present effort is focussed on determining barrier heights for the two LAMs, which requires assumptions concerning the precise path for each LAM. These attempts, and the different barrier heights obtained from different assumptions will be reported.