THE MICROWAVE SPECTRUM OF THE $HCOOCD_2H$ SPECIES OF METHYL FORMATE[a]

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Methyl formate is a non-rigid molecule displaying internal rotation of its methyl group. The microwave spectra of its normal[b] and mono deuterated $HCOOCH_2D$[c] species have already been studied and values for the tunneling splitting due to the internal rotation were determined. The normal species displays a 405 MHz A/E splitting, the mono deuterated one, a smaller 84.76 MHz A'/A'' splitting. For the bideuterated species $HCOOCD_2H$, the value of this splitting is not known as its microwave spectrum has not been studied yet.
In this paper experimental and theoretical investigations of the microwave spectrum of $HCOOCD_2H$ are presented. More than 9000 transitions were measured with a submillimeter wave spectrometer. About 20 lines were recorded with a molecular beam spectrometer. Like for the mono deuterated species,[c] depending on the location of the only hydrogen atom of the methyl group, two configurations arise. The C_s-symmetry H-in plane configuration displays a rigid rotator spectrum and its data was analyzed using a Watson-type Hamiltonian. The C_1-symmetry H-out of plane configuration undergoes the large amplitude internal rotation. Its data was analyzed using the so called water dimer formalism[d] which allowed us to accurately reproduce the observed frequencies and to obtain the value of the tunneling splitting as well as the parameters involved in its rotational dependence. The hyperfine structure due to quadrupole coupling at the two deuterium atoms was also analyzed. Unexpectedly, for the H-out of plane configuration, the observed hyperfine patterns are neither those expected for two equivalent deuterium atoms nor those of a rigid molecule.

[a]This work is supported by the ANR-08-BLAN-0054 and ANR-08-BLAN-0225 contracts.
[b]Ilyushin, Kryvda, and Alekseev, *J. Mol. Spec.* **255** (2009) 32.
[c]Margulès, Coudert, Møllendal, Guillemin, Huet, and Janečkovà, *J. Mol. Spec.* **254** (2009) 55.
[d]Hougen, *J. Mol. Spec.* **114** (1985) 395; and Coudert and Hougen, *J. Mol. Spec.* **130** (1988) 86.