ROTATIONAL ENERGIES IN VARIOUS TORSIONAL LEVELS OF CH_2DOH[a]

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Using an approach accounting for the hindered internal rotation of a monodeuterated methyl group,[b] an analysis of the torsional spectrum of the monodeuterated species of methanol CH_2DOH has been carried out recently and led to the assignment of 76 torsional subbands in its microwave, FIR, and IR spectra. Although this approach also allowed us to account for subband centers, the rotational structure of the torsional subbands is not well understood yet.

In this paper, we will deal with the rotational energies of CH_2DOH. Analyses of the rotational structure of the available subbands[b] have been performed using the polynomial-type expansion introduced in the case of the normal species of methanol.[c] For each subband, FIR or IR transitions and a-type microwave lines, within the lower torsional level, were fitted. The frequencies of the latters were taken from previous investigations[d] or from new measurements carried out from 50 to 950 GHz with the submillimeterwave solid state spectrometer in Lille. Subbands involving lower levels with $v_t = 0$ and $K \geq 3$ could be satisfactorily analyzed. For levels characterized by lower K-values, the expansion fails. In the case of the $K = 1, v_t = 1$ level, the frequencies of a-type microwave transitions involving the lower member of the K-type doublet cannot be well reproduced. For $K = 0$ levels with $v_t = 1$ and 2, a large number of terms is needed in the expansion.

We will try to understand why the rotational energies of these levels cannot be reproduced. The results of the analyses will be compared to those obtained with a global approach based on the rotation-torsion Hamiltonian of the molecule.[e]

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[b]El Hilali, Coudert, Konov, and Klee, *J. Chem. Phys.* **135** (2011) 194309.

[c]Ioli, Moruzzi, Riminucci, Strumia, Moraes, Winnewisser, and Winnewisser, *J. Mol. Spec.* **171** (1995) 130.

[d]Quade and Suenram, *J. Chem. Phys.* **73** (1980) 1127; and Su and Quade, *J. Mol. Spec.* **134** (1989) 290.

[e]Lauvergnat, Coudert, Klee, and Smirnov, *J. Mol. Spec.* **256** (2009) 204.