THEORETICAL CALCULATION OF THE TORSIONAL SPECTRUM OF THE PARTIALLY DEUTERATED SPECIES OF METHANOL

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The first spectroscopic investigations of the partially deuterated species of methanol, CH_2DOH and CD_2HOH, have shown that these species display a dense torsional spectrum[a] difficult to assign. With a view toward understanding these spectra, a theoretical calculation of their rotation-torsion energy levels has been undertaken aided by *ab initio* calculations. This calculation accounts for the complicated torsion-rotation interaction displayed by these molecules and is based on the following features:

- The kinetic energy part of the Hamiltonian is calculated numerically taking into account all 12 internal degrees of freedom of the molecules. The angle of internal rotation is treated as an active coordinate.[b]
- The Schrödinger equation for the internal rotation is solved using Gaussian quadrature.[c]
- Internal degrees of freedom corresponding to the other small amplitude motions are treated using the harmonic approximation, for each value of the internal angle of rotation corresponding to the DVR grid.[d]
- The potential energy function of the molecule is obtained using *ab initio* calculations.

After making some reasonable assumptions for the dipole moment function, the last step of the calculation involves evaluating the intensity of the rotation-torsion transitions. In the paper we hope to be able to show plots of room-temperature absorption spectra.

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[a] Mukhopadhyay, Perry, Butler, Herbst, and De Lucia, 57th International Symposium on Molecular Spectroscopy, paper **RH06** (2002) and Mukhopadhyay, Perry, Lock, and Klee, 57th International Symposium on Molecular Spectroscopy, paper **RH07** (2002).

[b] Lauvergnat and Nauts, *J. Chem. Phys.* **116,** 8560 (2002).

[c] Light and Bačić, *J. Chem. Phys.* **87,** 408 (1987).

[d] Lauvergnat, Nauts, Justum and Chapuisat, *J. Chem. Phys.* **114,** 6592 (2001).