NON-RIGIDITY EFFECTS IN THE HYPERFINE STRUCTURE OF THE CD_4–H_2O COMPLEX

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In CD_4–H_2O the hyperfine structure arises mainly from quadrupole coupling of the four deuterium atoms. This complex is a very non-rigid one in which each subunit undergoes internal rotation.[a] In the case of the CD_4 subunit this internal rotation is nearly free while it is more hindered in the case of the H_2O subunit. Although the hyperfine structure of the normal species of the complex, CH_4–H_2O, has already been studied,[b] hyperfine effects arising from the CH_4 subunit were fairly weak and could not be easily studied using the microwave data. In the CD_4–H_2O complex, these effects are much stronger and they could be easily observed in the spectra recorded using a pulsed-nozzle Fourier-transform microwave spectrometer. In order to analyse these observed patterns, a theoretical calculation of the hyperfine structure of this complex has been undertaken and takes into account the various large amplitude motions it displays.
The theoretical approach involves setting up a complete quadrupole coupling Hamiltonian for the four deuterium atoms, which is allowed to depend on the large amplitude coordinates necessary to fully describe the various configurations of the molecule. Simple symmetry considerations shows that this Hamiltonian can be written as the sum of products of Casimir operators by rovibrational operators. The latter ones involve a completely symmetrical term and a less symmetrical one corresponding to the F_2^+ symmetry species of G_{48}. The symmetrical term contributes to the quadrupole coupling for all rovibrational levels, while the contribution of the F_2^+-type terms depend on the symmetry species of the rovibrational level being considered. The effects of these two terms will be discussed in the paper and by comparing observed and calculated spectra we hope to determine the values of the corresponding effective coupling constants.

[a] Dore, Cohen, Schmuttnmaer, Busarow, Elrod, Loeser, and Saykally, *J. Chem. Phys.* **100,** 863 (1994).
[b] Suenram, Fraser, Lovas, and Kawashima, *J. Chem. Phys.* **101,** 7230 (1994).