HYPERFINE SPIN-ROTATION INTERACTION IN THE $(H_2O)_2$ DIMER

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Hyperfine coupling in non-rigid molecular systems with several equivalent nuclei is very interesting because of the averaging due to the large amplitude motion(s). For instance, in the cases of the non-rigid $(D_2O)_2$ and $(C_2D_2)_2$ dimers, the molecule behaves as if quadrupole coupling was identical for all four deuterium atoms.[a] This result, only valid for nondegenerate tunneling levels, disagrees indeed with what one would obtain considering the equilibrium geometry of the molecule. In that case three different quadrupole coupling constants would be expected.

The present paper is concerned with a study of the hyperfine coupling in the non-rigid $(H_2O)_2$ dimer. In this species hyperfine coupling is mainly due to magnetic spin-rotation interaction. As expected, just like in the above deuterated species, large amplitude motions lead to a highly symmetrical hyperfine Hamiltonian. For nondegenerate tunneling levels, it is of the form $\mathbf{J} \cdot (\mathbf{I}_1 + \mathbf{I}_2 + \mathbf{I}_3 + \mathbf{I}_4)$, where $\mathbf{J}$ is the rotational angular momentum and $\mathbf{I}_i$ is the nuclear angular momentum of the hydrogen atom i. In the case of doubly degenerate tunneling levels, a less symmetrical expression arises.

Using these results, an analysis of the hyperfine patterns recorded for 15 tunneling-rotation transitions of the water dimer will be reported. These hyperfine patterns were obtained with the Hannover supersonic jet FT-MW spectrometer providing a resolution better than 2 kHz, sufficient to resolve most hyperfine patterns. Since the data set involves nondegenerate and doubly degenerate levels, we hope to be able to observe the difference in the hyperfine patterns. We will also attempt to evidence direct tunneling effects on the spin-rotation hyperfine Hamiltonian.

[a] Bhattacharjee, Muenter, and Coudert, *J. Chem. Phys.* **97,** 8850 (1992) *and* Stahl and Coudert, *J. Molec. Spectrosc.* **157,** 161 (1993).