Hyperfine Splittings in the First Excited Torsional State of Methanol

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Background. Extensive Lamb-dip measurements of hyperfine splitting patterns in methanol in the submillimeter and microwave spectral regions began more than five years ago in Nizhny Novgorod, Russia, and then gradually spread to Kharkov, Ukraine and Lille, France. Observed splittings lie in the range of 20 to 120 kHz, and many of the corresponding hyperfine components are clearly resolved under the available instrumental resolution of about 20 kHz. The nuclear spins in normal CH_3OH have the values $I_C = I_O = 0$ and $I_H = ½$, so that these hyperfine splittings must arise only from magnetic dipole effects, and not from electric quadrupole effects. We consider here three types of interaction involving the proton spins in methanol: spin-rotation, spin-torsion, and spin-spin, represented by the Hamiltonians H_{sr}, H_{st}, and H_{ss}. Each of these Hamiltonians contains its own set of about 30 different interaction constants. In this talk, we consider these interactions only in $v_t = 1$ levels of E symmetry species.

Two theoretical approaches. Two different types of theoretical treatment have been applied in the literature to the observed data. The first [1,2] involves using quantum chemistry packages to calculate ab initio values for the approximately 60 interaction constants in H_{sr} and H_{ss}. H_{st} cannot be well predicted, however, since only some of the contributions to the constants in H_{st} can be computed using presently available packages. Because of the limited number of hyperfine splittings experimentally available, the majority of these computed constants must be kept fixed, with only a judiciously chosen small set varied in any fit to experimental data. The second approach [3], which we use in the work reported here, involves relying on intuition and trial-and-error to construct an effective hyperfine Hamiltonian H_{eff}, containing the minimum number of interaction terms (and their adjustable coefficients) required to fit the data.

Description of H_{eff}. To simplify matters, the effective Hamiltonian discussed today is restricted to torsion-rotation states of E symmetry in methanol. At the time of preparing the abstract, H_{eff} contains nine terms. There are three spin-rotation interaction terms for the $I_1=½$ spin system of the hydroxyl proton, and three more for the $I_2=½$ spin system of the three methyl protons in torsion-rotation states of E species in the $G_6 = C_{3v}$ molecular symmetry group. These six terms are represented by operators of the form $(I_i)_x J_x$, $(I_i)_y J_y$, and $(I_i)_z J_z$, with $i = 1$ or 2, where $\mathbf{I}_i$ is a

proton spin operator and J is the rotational angular momentum operator. There is one term for interaction of each of the $I=\frac{1}{2}$ nuclear spin systems with the magnetic field generated by internal rotation in methanol. These two terms are represented by operators of the form $(I_i)_z P_\alpha$, with $i = 1$ or 2, where P_α is the angular momentum conjugate to the torsional angle. Finally, there is one very empirical term representing spin-spin interaction between spin systems 1 and 2, with the approximate form $(I_1 \cdot I_2)[J_z^2/J(J+1)]$.

Composition of the data set. There are four series of E species lines with $v_t = 1$ and successive J values that dominate the available data: (1) a $K = 6 \leftarrow 7$ Q branch, with J from 7 to 15, where quartet hyperfine splitting patterns are observed for all J transitions; (2) a $K = 3 \leftarrow 2$ Q branch, with J from 3 to 18, which starts off as quartets, changes to doublets at $J = 7$, and then changes to singlets at $J = 17$; (3) a $K = -2 \leftarrow -3$ P branch, with J'' from 8 to 12, where doublets are observed for all J values; (4) a $K = 8 \leftarrow 7$ Q branch, with J from 8 to 24, where the series starts off as triplets with a weak central component, and then changes to doublets at $J = 15$. There are 5 or 10 other E species lines with $v_t = 1$ that show clear hyperfine splittings. Measurement precision for the data set is thought to be between 0.5 and 1 kHz, but independent confirmation of this estimate by combination differences is not possible.

Status of fits. We have successfully fit various combinations of lines from the above data set to various combinations of interaction parameters. Standard deviations of the fits range from 0.4 kHz (for fits of partial data sets with < 50 lines) to 1.3 kHz (for fits of full data sets with > 130 lines). Details of our best fits will be presented during the talk.

Two interesting points. (1) The $v_t = 1$ E state is just below the top of the barrier in methanol, so we expected, and we believe we have found, that nearly-free internal-rotation effects lead to much larger spin-torsion coupling constants in $v_t = 1$ than can be seen in the $v_t = 0$ torsional ground state. (2) We speculate that the weak central features of the triplets in series (4) above are due to an unusual double-N crossover resonance. Some parts of the theory needed to quantitatively model such crossover resonances are outside the expertise of the present authors.

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[2] J. Chem. Phys. 145 (**2016**) 244301-1-15, B. Lankhaar, G.C. Groenenboom, Ad van der Avoird, "Hyperfine interactions and internal rotation in methanol".
[3] J. Chem. Phys. 145 (**2016**) 024307-1-20, S.P Belov, G.Yu. Golubiatnikov, A.V. Lapinov, V.V. Ilyushin, E.A. Alekseev, A.A. Mescheryakov, J.T. Hougen, Li-Hong Xu, "Torsionally mediated spin-rotation hyperfine splittings at moderate to high J values in methanol".