ANOMALOUS HYPERFINE STRUCTURE OF NSF_3 IN THE DEGENERATE VIBRATIONAL STATE v_5=1: LIFTING OF THE PARITY DEGENERACY BY THE FLUORINE SPIN-ROTATION INTERACTION

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For the principal isotopomer $^{14}N^{32}S^{19}F_3$ of thiazyl trifluoride in the degenerate fundamental state (v_5=1), the hyperfine structure has been investigated in the Q-branch spectrum between 8 and 26.5 GHz using microwave Fourier transform waveguide spectrometers with a resolution limit of $\approx$ 30 kHz. In addition to l-type doubling spectra and l-type resonance transitions with ($\Delta k = \Delta l = \pm 2$), perturbation-allowed spectra were measured with $\Delta(k-l) = \pm 3, \pm 6$. The range in J was from 13 to 61; for the lower states, $kl = -3, -2, -1, 0, +1$. For all the transitions, the hyperfine patterns observed are predicted to be doublets when only the nitrogen quadrupole Hamiltonian H_Q^N is taken into account. Doublets were indeed measured for transitions with $\Gamma_{RV} = A_1 \leftrightarrow A_2$, where Γ_{RV} is the rovibrational symmetry. However, when $\Gamma_{RV} = E \leftrightarrow E$, triplets and quartets were observed in addition to doublets. These anomalous hyperfine patterns are shown to be due to the ($\Delta k = \pm 1$) and ($\Delta k = \pm 2$) matrix elements of the fluorine spin-rotation Hamiltonian H_N^F characterized by the fluorine spin-rotation constants $c(1) = (c_{xz} + c_{zx}^*)$ and $c(2) = (c_{xx} - c_{yy})$, respectively. These terms in H_N^F lift the parity degeneracy for $\Gamma_{RV} = E$. The rovibrational Hamiltonian H_{RV} was adopted from an earlier partner study.[1] A good fit to the hyperfine data was obtained with a standard deviation of 3.1 kHz. In the fitting process, 12 rovibrational parameters were varied, while the remaining constants in H_{RV} were left at the values of Ref. (1). In addition, 6 hyperfine parameters were determined: four in H_Q^N, and two in H_N^F. It was found that $|c(1)| = 7.48(24)$ kHz and $|c(2)| = 2.423(22)$ kHz. This determination of $|c(1)|$ is the first to be reported based on frequency measurements. The key to the observation of the parity doubling lies in the severe mixing into the eigenvectors of basis vectors with several different values of kl as a result of the clustering[1] of rovibrational levels at low K.

[1] S. Macholl, H. Harder, H. Mäder, L. Margulès, P. Dréan, J. Cosléou, J. Demaison, and P. Pracna, J. Phys. Chem. A 113, 668 (2009).