

ENERGY-LEVEL-CLUSTER RELATED NUCLEAR-SPIN EFFECTS AND SUPER-HYPERFINE SPECTRAL PATTERNS: HOW MOLECULES DO SELF-NMR

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At several points in his defining works on molecular spectroscopy, Herzberg notes that “because nuclear moments . . . are so very slight . . . transitions between species . . . are very strictly forbidden. . .” Herzbergs most recent statement of such selection rules pertained to spherical top spin-species^a.

It has since been shown that spherical top species (as well as those of lower symmetry molecules) converge exponentially with momentum quanta J and K to degenerate level clusters wherein even “very slight” nuclear fields and moments cause pervasive resonance and total spin species mixing^b. Ultra-high resolution spectra of Borde, et .al^c and Pfister et .al^{de} shows how SF₆ and SiF₄ Fluorine nuclear spin levels rearrange from total-spin multiplets to NMR-like patterns as their superfine structure converges.

Similar super-hyperfine effects are anticipated for lower symmetry molecules exhibiting converging superfine level-clusters. Examples include PH₃ molecules^f and asymmetric tops. Following this we consider models that treat nuclear spins as coupled rotors undergoing generalized Hund-case transitions from spin-lab-momentum coupling to various spin-rotor correlations.

^aG. A. Herzberg, *Electronic Spectra of Polyatomic Molecules*, (Von Norstrand Rheinhold 1966) p. 246.

^bW G. Harter and C. W Patterson, *Phys. Rev. A* 19, 2277 (1979); W. G. Harter, *Phys. Rev. A* 24, 192 (1981).

^cCh. J. Borde, J. Borde, Ch. Breant, Ch. Chardonnet, A. Van Lerberghe, and Ch. Salomon, in *Laser Spectroscopy VII*, T. W Hensch and Y. R. Shen, eds. (Springer-Verlag, Berlin, 1985).

^dO. Pfister, F. Guernet, G. Charton, Ch. Chardonnet, F. Herlemont, and J. Legrand, *J. Opt. Soc. Am. B* 10, 1521 (1993).

^eO. Pfister, Ch. Chardonnet, and Ch. J. Bord, *Phys. Rev. Lett.* 76, 4516 (1996).

^fS. N. Yurchenko, W. Thiel, S. Patchkovskii, and P. Jensen, *Phys. Chem. Chem. Phys.* 7, 573 (2005).