THE PURE ROTATIONAL SPECTRUM OF CoCl ($X^3\Phi_i$): CHARACTERISTICS OF A HIGHLY PERTURBED MOLECULE

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The sub-millimeter wave spectrum of the CoCl radical has been observed in the frequency range 340 - 510 GHz using direct absorption techniques. This work is the first pure rotational study of this molecule in the laboratory. Rotational transitions from all three spin-orbit components (Ω = 4, 3, and 2) have been recorded, along with magnetic hyperfine splittings due to the ^{59}Co nucleus (I = 7/2). Transitions from the Co^{37}Cl isotopomer were also measured, as well as several excited vibrational modes. Interestingly, the Ω = 3 spin component was found to be shifted to lower frequency relative to the lowest spin state (Ω = 4), while the Ω = 2 lies to higher frequency. Thus, this molecule is undergoing large perturbations, likely caused by excited electronic states. The data were fit with a case (a) Hamiltonian, and spectroscopic constants have been determined, improving upon those derived from previous optical data. These include the first assignment of the spin-orbit constant A. The hyperfine parameters for CoCl, while similar to those found for other cobalt molecules, indicate a higher degree of covalency than in other such species. Comparison of periodic trends for transition metal chlorides and their fluoride analogues indicates that the two series are quite similar.