MOLECULAR BEAM STUDY OF THE $^6\Pi - X^6\Delta$ ELECTRONIC TRANSITION IN FeCl

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The $^6\Pi - X^6\Delta$ band system of $Fe^{35}Cl$ near 357 nm has been recorded at 0.3 and 0.08 cm^{-1} resolution by laser fluorescence excitation in a free-jet supersonic expansion of photolyzed $Fe(CO)_5$ diluted in seed gases containing CCl_4. The $^6\Pi_{\Omega'=\Omega''-1} - X^6\Delta_{\Omega''}$ subbands for Ω' = 7/2, 5/2, and 3/2 and $v' \leq 4$ of the Δv = 1, 0, -1, and -2 sequences were assigned, and excitation energies and rotational constants were derived for the relevant upper and lower vibronic levels. With the exception of the (0,0) band, for which one subband could be rotationally analyzed, it was not possible to assign any of the subbands with Ω' = 1/2, $-1/2$, or $-3/2$; these fine-structure components are expected to be strongly affected by homogeneous spin-orbit interactions with nearby sextet electronic states, leading to large parity splittings in the Ω' = 1/2 and $-1/2$ components. A subband with a large upper-state parity doubling was rotationally analyzed and assigned as the $^6\Pi_{1/2} - X^6\Delta_{3/2}$ (0,0) subband. The effect of the off-diagonal spin-orbit interactions is discussed in light of the present results and previous theoretical work.