DIRECT POTENTIAL FIT FOR THE $X^1\Sigma$ STATE OF F_2: PERTURBATION OF THE HIGHEST OBSERVED V=22 VIBRATIONAL LEVEL

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The high-resolution vacuum-uv spectrographic data[1] for the C - X emission and C,(D,E),H,h,I - X(v = 0) absorption transitions of F_2, in combination with pure rotation[2] and vibration-rotation[3] Raman data, have been employed in a least-squares analysis. Attention was given to the extensive blending in the absorption data and to account for plate-to-plate shifts in the emission data. The C - X data, with an estimated uncertainty of 0.05 cm^{-1}, sample X state vibrational levels v = 1 - 22,for which the potential energy function was fitted using the extended-MLR model[4]. 3549 line positions in the weighted fit provided estimates of 1303 term values of excited electronic states and 17 parameters for the ground state. The highest observed v = 22 level of the ground state, which lies only 114 cm^{-1}below the $F(^2P_{3/2})$ + $F(^2P_{3/2})$ dissociation limit, is found to be perturbed; all rotational levels (J = 0 - 19) lie at energies 5 - 13 cm^{-1}below their expected positions. A deperturbation model was employed within the direct potential fit; in this novel approach, the eigenvalue of each J-level in v = 22 was determined from a 2 x 2 matrix, with the diagonal level of the perturbing state represented by E_p + B_pJ(J+1), and the off-diagonal element by a + b(J + 1/2). However, the b-parameter was indeterminate; a successful fit of the entire data set with inclusion of the deperturbation model for v = 22 provided the estimates E_p = -70.5(3.7) cm^{-1}, B_p = 0.226(6) cm^{-1}, a = 16.2(8) $\mathrm{cm}^{-1}$and R_e = 1.412555(4)Å. There is much interest in an identification of the perturbing state. The results indicate a J-independent spin-orbit interaction with a weakly-bound perturbing state (R_e = 2.8Å), lying 40 - 50 cm^{-1}above v = 22. The absence of a J-dependent b(J + 1/2) Coriolis interaction implies a perturber with $0_g{}^+$ symmetry. A plausible candidate is the a'($0_g{}^+$) state which dissociates to the same atomic limit and which is repulsive at short-R.

1. E.A. Colbourn, M. Dagenais, A.E. Douglas, J.W. Raymonda, Can. J. Phys. 54 (13) (1976) 1343-1359. 2. H.G.M. Edwards, E.A.M. Good, D.A. Long, J. Chem. Soc. Faraday Trans. 272 (1976) 984-987. 3. R.Z. Martinez, D. Bermejo, J. Santos, P. Cancio, J. Mol. Spectrosc. 168 (1994) 343-349. 4. R.J. Le Roy, N.S. Dattani, J.A. Coxon, A.J. Ross, P. Crozet, C. Linton, J. Chem. Phys. 131 (2009) 204309.