UNRAVELING THE COMPLICATED SPECTROSCOPY OF THE $A^1B_1 - X^1A_1$ SYSTEM OF CCl_2

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We report studies aimed at unraveling the complicated structure of the CCl_2 $A^1B_1 - X^1A_1$ system. We have remeasured the fluorescence excitation spectrum from 17 500 to 24 000 cm^{-1}, and report the term energies and A rotational constants of many new bands for both major isotopomers ($C^{35}Cl_2$, $C^{35}Cl^{37}Cl$). We fit the observed term energies to a polyad effective Hamiltonian model, and demonstrate that a single resonance term accounts for much of the observed mixing, which begins some 1300 cm^{-1} above the vibrationless level of the A^1B_1 state. The derived vibrational parameters are in excellent agreement with $ab\ initio$ predictions, and the mixing coefficients deduced from the polyad model fit are used to generate simulated single vibronic level (SVL) emission spectra for comparison with experiment. The approach to linearity and thus the Renner-Teller (RT) intersection is probed through the energy dependence of the A rotational constant and fluorescence lifetime measurements, which reveal an intriguing state selectivity in the RT interaction, and bracket the barrier height above the vibrationless level of the X^1A_1 state between 23 000 and 23 500 cm^{-1}, in excellent agreement with the predictions of $ab\ initio$ theory.