THE SOLUTION TO THE ELECTRONIC SPECTRUM OF THE CHLORINE CATION (Cl_2^+)

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The highly perturbed $A^2\Pi_i$ - $X^2\Pi_i$ electronic band system of the chlorine cation (Cl_2^+) had previously been extensively studied, but no satisfactory vibrational analysis had been achieved. Although rotationally quite regular, the bands show substantial vibrational perturbations, irregular chlorine isotope splittings, and numerous weak extra features. We have succeeded in obtaining LIF spectra of jet-cooled Cl_2^+ that extend the known spectrum some 3000 cm^{-1} to the red of all previous measurements. The very weak 0 - 0 band has been positively identified and the v′= 0 - 3 levels are found to be unperturbed. Higher levels exhibit significant perturbations, which we have shown by high level ab initio studies of the relevant potential energy curves to be due to a homogeneous spin-orbit interaction between the $A^2\Pi_{3/2}$ and $B^2\Delta_{3/2}$ states. Non-adiabatic effects have been introduced using the coupled equations, which have been solved to yield the energies of the vibronic levels. The computed vibronic states are in good quantitative agreement with the experimental data, allowing assignments to be made for both the strong main bands as well as the weaker transitions to the interloper levels. After more than 80 years of study, the electronic spectrum of the chlorine cation can now be understood in considerable detail.