

A NEW ANALYSIS OF A VERY OLD SPECTRUM: THE HIGHLY PERTURBED $A^2\Pi_i - X^2\Pi_i$ BAND SYSTEM OF THE CHLORINE CATION (Cl_2^+)

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Although the $A^2\Pi_i - X^2\Pi_i$ band system of the chlorine cation has been known since 1928 and has been studied by many investigators, no satisfactory vibrational assignment has been achieved due to substantial vibronic perturbations. In the present work, laser-induced fluorescence and single vibronic level (SVL) emission spectra of the jet-cooled chlorine cation (Cl_2^+) have been investigated in the region of 500-312 nm. The cation was produced in a pulsed electric discharge jet using a precursor mixture of 10% chlorine gas in high pressure argon. The spectrum has been extended further to the red than previously known and the 1-0 band has been identified. The 0-0 band was undetectable due to a very small Franck-Condon factor for this transition. Due to efficient cooling in the supersonic expansion, no hot bands and no transitions from the $X^2\Pi_{1/2}$ spin-orbit component were observed in our coldest spectra. Chlorine isotope shifts and the number of nodes in the SVL emission spectra were used as diagnostics in assigning the vibrational quantum numbers. SVL emission spectra of $^{35}\text{Cl}_2^+$ terminated on levels up to $v'' = 15$ and these data were used to determine $\omega_e'' = 645.0(1)$ and $\omega_e x_e'' = 2.927(7) \text{ cm}^{-1}$. High resolution spectra of the 1-0 and 2-0 bands of $^{35}\text{Cl}_2^+$ and $^{35}\text{Cl}^{37}\text{Cl}^+$ have been recorded and rotationally analyzed, yielding $r_e' = 2.2287(7)$ and $r_0'' = 1.8944(3) \text{ \AA}$.