SPECTROSCOPY OF CHLORINE MONOFLUORIDE ISOLATED IN RARE GAS MATRICES

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We report for the first time spectroscopy of chlorine monofluoride (ClF) isolated in rare gas matrices. The strongest absorption is to the dissociative $^1\Pi_u$ state around 275 nm. Upon laser excitation at 308 nm into this state we observe in emission a vibrational progression from 580 to 930 nm which can be safely attributed to $A' \rightarrow X$ with $\omega_e = 780.7$ cm^{-1} and $\omega_e x_e = 6.5$ cm^{-1}. The population accumulates in the A' state with a phosphorescence lifetime of the order of one second. Excitation from A' to the ionic manifold results in two broad emission bands at 425 and 510 nm respectively.

ClF is an interesting molecule in the perspective of condensed phase photochemistry. Upon excitation at 308 nm it dissociates with a quantum yield similar to the F_2 molecule. But as a heteronuclear molecule the two fragment atoms behave extremely differently: From experiments on matrix isolated Cl_2 in Kr and Ar it is known that cage exit of Cl atoms is negligible. In contrast, the fluorine atom leaves the cage with up to unit probability with increasing excess energy. The fragmented fluorine atoms and the parent molecules are recorded spectroscopically and the dissociation and recombination kinetics are analysed. The blue fluorescence bands after two-photon excitation are established as a channel for femtosecond pump-probe spectroscopy and time-resolved measurements of the dissociation in a condensed-phase environment are discussed.