

THE PREDISSOCIATION MECHANISM FOR $^2\Sigma^+$ RYDBERG STATES OF CALCIUM MONOCHLORIDE

JASON O. CLEVINGER, NICOLE A. HARRIS, and ROBERT W. FIELD, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139*; JIAN LI, *Department of Chemistry, Tsinghua University, Beijing, China 100084*.

This talk summarizes experimental results from recent ion-dip spectroscopy studies of CaCl as well as previously unpublished optical-optical-double-resonance work with specific regard to predissociation processes of $^2\Sigma^+$ Rydberg states in the low- n^* ($n^* < 7$, IP-E $\sim 2500\text{ cm}^{-1}$) region. A single repulsive state (assigned as $^2\Sigma^+$) was found to be responsible for all observed predissociations of $^2\Sigma^+$ Rydberg states. The n^* -dependent internuclear distances of the intersections between Rydberg and repulsive $^2\Sigma^+$ states were determined through the use of trial-and-error Franck-Condon calculations. Values of the n^* -scaled electronic matrix elements governing the Rydberg \leftrightarrow repulsive state interaction were obtained from the measured linewidths ($0.6 < \Gamma < 1.2\text{ cm}^{-1}$) and computed Franck-Condon densities. With the assumption of a one-parameter form for the repulsive curve, $E(\text{cm}^{-1}) = \frac{C_{12}}{R^{12}} + D_e$, where C_{12} has the units $\text{\AA}^{12}\text{cm}^{-1}$ and $D_e = 33171\text{ cm}^{-1}$ for CaCl, the optimum value of C_{12} was found to be $2.354 \times 10^8 \text{\AA}^{12}\text{cm}^{-1}$.