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

JASON O. CLEVENGER, 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This talk summarizes experimental results from recent ion-dip spectroscopy studies of CaCl as well as previously unpublished optical-optical-double-resonance work with specific regard to predissociation processes of $^2\Sigma^+$ Rydberg states in the low-n* (n* 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 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 ($.6 < \Gamma < 1.2$ cm^{-1}) and computed Franck-Condon densities. With the assumption of a one-parameter form for the repulsive curve, $E(cm^{-1}) = \frac{C_{12}}{R^{12}} + D_e$, where C_{12} has the units $\mathrm{Å}^{12}\mathrm{cm}^{-1}$ and D_e = 33171 cm^{-1} for CaCl, the optimum value of C_{12} was found to be $2.354 \times 10^8 \mathrm{Å}^{12}\mathrm{cm}^{-1}$.