

PREDISSOCIATION DYNAMICS OF OH $A^2\Sigma^+$ ($v = 4$)

ERIKA L. DERRO, LOGAN P. DEMPSEY, ILANA B. POLLACK, MARSHA I. LESTER, *Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323.*

Predissociation of the excited $A^2\Sigma^+$ electronic state of the OH radical results from curve crossings with repulsive potentials, namely $4\Sigma^-$, $2\Sigma^-$, 4Π , producing O(3P_J) + H(2S) fragments. Previous experimental and theoretical studies of the $v = 4$ level of the OH $A^2\Sigma^+$ state indicate that predissociation occurs at least 10-fold faster than in lower vibrational levels, resulting in a fluorescence quantum yield that is essentially zero. In the present study, Fluorescence Depletion Infrared (FDIR) spectroscopy, a UV-IR double resonance technique, is employed to characterize the linewidths and corresponding lifetimes of highly predissociative rovibrational levels of the excited $A^2\Sigma^+$ electronic state of the OH radical. A least-squares fit to a Voigt line profile is used to extract the Lorentzian linewidths of the individual dips in the FDIR spectra. The homogeneous linewidth measurements, ranging from 0.23 to 0.31 cm^{-1} FWHM, demonstrate that the $N = 0 - 7$ rotational levels of the OH $A^2\Sigma^+$ ($v = 4$) state undergo rapid predissociation, with lifetimes ≤ 23 ps. The experimental linewidths are in near quantitative agreement with first principle theoretical predictions.