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

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Predissociation of the excited $A\,^2\Sigma^+$ electronic state of the OH radical results from curve crossings with repulsive potentials, namely $^4\Sigma^-$, $^2\Sigma^-$, $^4\Pi$, producing O(^{3}P$_J$) + H(^{2}S) 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 $\leq$ 23 ps. The experimental linewidths are in near quantitative agreement with first principle theoretical predictions.