# ON THE CORRELATION BETWEEN PHOTOELECTRON ENERGY AND BENDING EXCITATION IN MOLECULAR PHOTOIONIZATION

J. SCOTT MILLER, ERWIN D. POLIAKOFF, *Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803*.

A frequent topic in vacuum ultraviolet spectroscopy is the correlation between electronic and nuclear degrees of freedom when a photoelectron is ejected. However, there have been no previous investigations that have probed the correlation between the bending vibration and the photoejection dynamics over a wide spectral range. We report on the first such study. In order to acquire data over a broad range, we use dispersed fluorescence spectroscopy. Specifically, we report on the influence of bending on the photoionization dynamics following ejection of an electron from the $3\sigma_u$ orbital of $CO_2$ and the $7\sigma$ orbital of $N_2O$. These studies are performed over a broad spectral range (18 eV $\leq h\nu_{exc} \leq$ 190 eV excitation energy for $CO_2$, 16 eV $\leq h\nu_{exc} \leq$ 160 eV for $N_2O$), and features persist over these extended ranges. We employ vibrationally resolved dispersed fluorescence following photoionization using tunable synchrotron radiation to determine the $v^+ = (0,1,0) / v^+ = (0,0,0)$ vibrational branching ratio for $CO_2^+$ $B\,^2\Sigma_u^+$ and $N_2O^+$ $A\,^2\Sigma^+$ ionic states. We find that the extent of bending excitation varies over a broad range, and in ways that are largely unanticipated. These branching ratios exhibit a strong thermal dependence, and we are able to separate out effects due to hot-band excitation from those that are due to vibronic coupling. The extent over which these changes occur underscore the necessity of broad range studies to elucidate slowly varying characteristics in molecular photoionization (such as contributions from a continuum electron). In the $N_2O$ study, the branching ratio displays changes of a factor of two in the branching ratio in the near threshold region due to the presence of shape resonant phenomena in this photoionization channel. For $CO_2$ $3\sigma_u$ photoionization, deviations in the vibrational branching ratio persist from near threshold to more than an order of magnitude above threshold. The data indicate that the continuum electron is involved in the vibronic coupling responsible for the observed energy dependence in $CO_2$ $3\sigma_u$ photoionization. To our knowledge, vibronic coupling involving a continuum photoelectron channel has not been reported previously, and implications for future studies are discussed.

*Acknowledgement:* This work supported by NSF Grant CHE-9616908.