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**Global nonresonant vibrational-photoelectron coupling in molecular photoionization** ERWIN POLIAKOFF, Louisiana State University, ALOKE DAS, IISER Pune, DAVID HARDY, Louisiana State University, JOHN BOZEK, LCLS Stanford University, ALEX AGUILAR, Lawrence Berkeley Laboratory, ROBERT LUCCHESI, Texas A&M University — Using photoelectron spectroscopy and Schwinger variational scattering theory, we have investigated the coupling between vibrational motion and the exiting photoelectron over extended ranges of photoelectron kinetic energy. Photoelectron spectroscopy is performed with vibrational resolution over uncommonly large ranges of energy (*ca.* 200 eV). We find clear and significant changes in vibrational branching ratios as a function of photon energy, in direct contradiction to predictions of the Franck-Condon principle. While it is well known that resonances lead to coupling between electronic and vibrational degrees of freedom, nonresonant mechanisms that result in such coupling are not expected or well-documented. Photoelectron spectra are presented for several electronic states of  $\text{N}_2^+$ ,  $\text{CO}^+$ , and  $\text{NO}^+$ , and we find that valence isoelectronic channels behave very differently, which is also surprising. Theoretical results indicate that Cooper minima are the underlying cause of these effects, and we are currently working to understand the reasons for the sensitivity of the Cooper minima on bond length.

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