SUPEROXIDE PHOTOELECTRON ANGULAR DISTRIBUTIONS: VIBRATIONAL DEPENDENCE AS A CONSQUENCE OF BORN-OPPENHEIMER BEHAVIOR

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For atomic anions the photoelectron angular distribution (PAD) is a signature of the bound excess electron wavefunction. However, even for relatively simple molecular anions the relationship between the detachment orbital and the PAD is more complicated. We demonstrate this with a series of near threshold photoelectron images for superoxide detachment, recorded over small photon energy increments. The highest occupied, π_g orbital has a strong resemblance to an atomic d-orbital. Detachment from the superoxide anion via the O_2(X $^3\Sigma_g^-$, v$'$)←O_2^-(X $^2\Pi_g$, v$'' = 0$) transitions reveals that the electron kinetic energy dependence of the PAD resembles that of atomic anions. However, there is also a clear dependence on the vibrational energy deposited in the neutral O_2. Comparison with theoretical calculations reveals that this dependence is not due to non-adiabatic effects. Instead it arises in the change of the electronic transition moment across the X−X band, a direct consequence of the parametric dependence of the π_g orbital function on the internuclear separation.