

Photoelectron spectra of copper difluoride anion (CuF₂⁻)

During our first year of funding, we have worked in collaboration with Dr. Richard Mabbs and his group at Washington University in St. Louis to record photoelectron spectra of the copper difluoride anion (CuF₂⁻) at a variety of photon energies using the velocity map imaging technique. Figure 1 shows representative images, photoelectron spectra, and anisotropy parameters (β) describing the photoelectron angular distributions for each of the observed transitions.

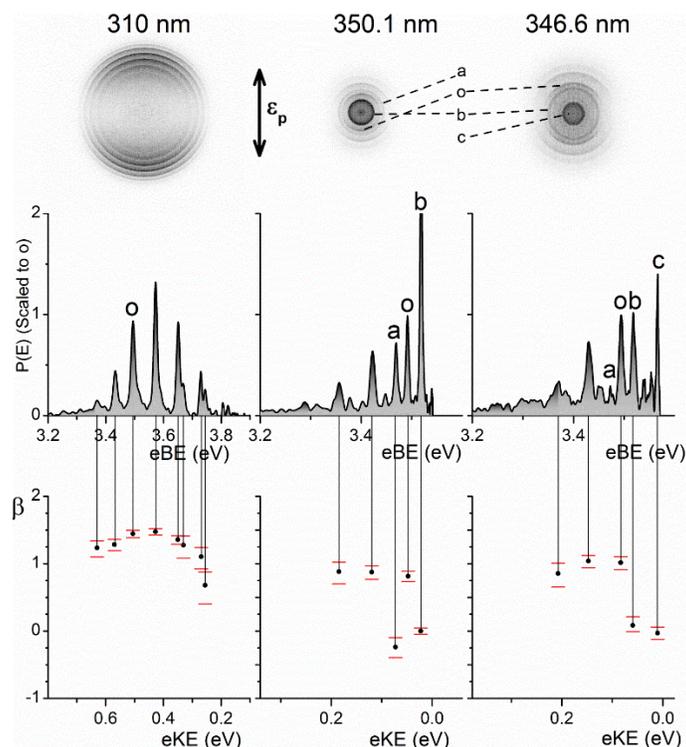


Figure 1. Photoelectron images (top row), spectra presented in the electron binding energy (eBE) domain (middle row), and anisotropy parameters of the indicated transitions presented in the electron kinetic energy (eKE) domain (bottom row). The results were obtained at wavelengths of 310 nm (photon energy of 3.999 eV), 350.1 nm (3.541 eV), and 346.6 nm (3.577 eV). The peak labeled o corresponds to the origin transition from the vibrational ground state of the anion to the vibrational ground state of the neutral.

Analysis of the band patterns in the photoelectron spectra enabled determination of the frequencies of the symmetric and bending normal modes for the ground electronic states of CuF₂⁻ and CuF₂. The frequency of the antisymmetric stretching normal mode of the anion was estimated based upon a previously measured value of the frequency of the normal mode of the neutral. Additionally, the adiabatic electron affinity of CuF₂ was determined to be 3.494 eV, slightly below the electron affinity of chlorine (3.613 eV), meaning that CuF₂ is not a superhalogen as had been recently suggested.

As can be seen in Figure 1, the intensity of the peaks labeled a, b, and c relative to the intensity of the peak labeled o is wavelength dependent. For example, the peak labeled b is absent from the photoelectron spectrum recorded at 310 nm (left column), is approximately twice as intense as o in the spectrum recorded at 350.1 nm (middle

column), and has roughly equal intensity to o in the spectrum recorded at 346.6 nm (right column). The angular distributions of the peaks labeled a, b, and c are all nearly isotropic with β values close to zero. In comparison, the other peaks in the spectra display parallel photoelectron angular distributions as indicated by their positive β values. The different angular distributions indicate that the transitions with $\beta \approx 0$ and $\beta \approx 1$ arise from different photodetachment processes. Specifically, the anisotropic peaks (positive values of β) result from direct detachment from the electronic ground state of the anion, which was assigned as a $^1\Sigma_g^+$. The isotropic peaks result from excitation to an excited anion state that has a greater energy than the neutral ground state, and thus is unstable with respect to electron loss. Therefore, these peaks result from a two-step process in which the first step is excitation to the excited state and the second step is autodetachment of the electron.

Impact

Washington University in St. Louis is approximately 120 miles from Millikin University in Decatur, IL. The funding provided by the ACS-PRF grant allowed the PI and undergraduate students working on the project to acquire temporary housing in St. Louis. Thus, this research would not be possible with ACS support. Additionally, this grant has allowed my group to purchase the computational software Gaussian 16 and WebMO Pro, as well as a multicore workstation to perform calculations on. This software will also be used by all students in the Introductory Chemistry Laboratory sequence starting in Fall Semester 2018. The grant has provided support for two students to conduct research during the summers of 2017 and 2018. As a result of this grant, the students were able to gain significant research experience, which has helped them develop their problem solving skills, as well as work with instrumentation that would not be readily available to most undergraduate students including a Wiley-McLaren time-of-flight mass spectrometer that is equipped with a photoelectron imager and multiple microchannel plate detectors, a pulsed Nd:YAG laser, a tunable dye laser, and a multichannel digital oscilloscope. The students gained familiarity with the simulation software SIMION and the computational software Gaussian. One of the students is in the process of applying to graduate school to pursue a PhD in chemistry upon graduation in the spring, a career trajectory that he had not envisioned before engaging in this project. He will be presenting on the research at the National ACS Meeting in Orlando, FL in spring 2019. The other student is currently planning to attend medical school when he graduates in spring 2020. Another student, not funded directly by the grant, will also be presenting at the National ACS Meeting in Orlando, FL. The research has thus far resulted in a publication in the *Journal of Chemical Physics*. I hope to use these results to provide the foundation for an NSF Research Opportunity Award application which would be used to provide the support necessary to continue our collaboration with the Mabbs group.