

ANOMALOUS BEHAVIOR OBSERVED UPON ANNEALING AND PHOTODETACHMENT OF ANIONIC COPPER CARBONYL CLUSTERS IN ARGON MATRICES^a

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Using matrix isolation FTIR, we have observed the formation of anionic copper carbonyl complexes $[\text{Cu}(\text{CO})_n]^-$ ($n=1-3$) following co-deposition of Cu^- and counter-cations (Ar^+ or Kr^+) into argon matrices doped with CO .^b When the deposition is carried out at 20 K, weak bands corresponding to the neutral copper carbonyl complexes $\text{Cu}(\text{CO})_n$ ($n=1-3$) are also observed, and these grow in steadily as the matrix is annealed up to 30 K. This is in contrast to what is observed at 10 K (c.f. ISMS 2014 abstract #P631), where no appreciable neutral bands are observed, and indicates that some neutralization occurs during the formation of the complexes in the 20 K matrix. In addition, sharp peaks not previously observed grow in around the anionic bands upon annealing to 30 K; this is somewhat odd, since annealing typically simplifies the spectra of matrix samples as kinetically trapped metastable species relax to more stable forms. In this case, higher-resolution (0.125 cm^{-1}) spectra reveal considerable new fine structure, with 5 and 20 peaks appearing in the regions of the mono- and tricarbonyl anions, respectively, each of which nominally has but a single IR-active CO-stretching mode. These new features are tentatively assigned (at least in part) to electric-field-induced splitting arising from long-range interactions with cationic species in the matrix. A second anomalous feature of these spectra is that, upon photodetachment, several new bands are observed in the region of the neutral copper carbonyl species. Upon annealing these bands then disappear, with concomitant growth of the expected neutral bands. This behavior raises the exciting possibility that these transient bands represent metastable "vertical detachment products", where the neutral species has been kinetically trapped by the matrix in the geometry of the anion. Evidence supporting this interpretation will be presented.

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^bRyan M. Ludwig and David T. Moore, *J. Chem. Phys.* 139, 244202 (2013).