



The copper carbonyl complexes revisited: Why are the infrared spectra and structures of copper mono and dicarbonyl so different?



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ABSTRACT

New infrared absorption data have been obtained using isolation in solid argon and neon on copper carbonyl molecules, CuCO and Cu(CO)₂, two very reactive molecules. For CuCO, all three fundamentals are now observed and it presents an unusually large matrix effect, in line with former results indicating a weak metal carbon interaction and a large total dipole moment. With help of isotopic effects, new data indicates unambiguously that Cu(CO)₂ is linear and presents a notably stronger metal–carbon interaction than CuCO. Quantum chemical calculation have been carried out at the CCSD(T) level for determining energies and structural properties, as well as spectroscopic observables. The results enable an assessment of the high stability of the Cu(CO)₂ molecule (first bond dissociation energy of 66 kJ/mol) which suggest that observation at room temperature is possible and give a first evidence of Renner effect on a pentatomic molecule.

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1. Introduction

One chief application of rare gas matrix isolation (MI) is the trapping of reactive or unstable species, as large amounts (μmol range) of radicals or transient species can be stabilized in solid solution within a thin solid rare gas slab, enough to permit the use of a combination of various spectroscopic techniques [1]. Among the pioneers in the field [2] who developed co deposition of metal atoms with small molecules to model various reactions, Jacox was among the first to use alkali atoms to generate molecular anions by charge transfer mechanisms [3,4]. Among many contributions, she was one of the first to implement a variety of spectroscopic techniques, including far infrared spectroscopy, taking advantage of the fact that these reactive species are trapped and made long-lived. In more recent years, with the generalization of *ab initio* and DFT quantum chemical (QC) calculations and the improvement of its predictive power for spectroscopic properties, Jacox warned against the danger of relying solely on apparent matches between QC-predicted vibrational frequencies for making definite species identifications or transitions assignments and advocated combining and cross-checking these with extensive

isotopic effects [5]. These principles have been an inspiration to many and in particular to us here.

Neutral copper carbonyl complexes have been the object of many studies and came across to be intriguing objects, laboratory models for a number of concepts. For the copper mono-carbonyl after several conflicting studies, a consensus has emerged that it is a weakly bound, quite floppy species with a non-conventional, bent structure [6–9]. The situation for the di-carbonyl species is quite different: experimental data are much scarcer and all theoretical studies converge in predicting a much more strongly bound species with a linear structure. It has been observed in three separate infrared absorption MI studies, following the brief initial report of Ogden [10], the more complete work on binary copper carbonyl complexes by Huber and coworkers [11] who detected a very intense CO stretching fundamental vibration and, more recently, in the work by Andrews and coworkers [12] on the isolation of neutral and ionic copper carbonyls and the frequencies for this mode re-measured in solid argon and neon. On the basis of isotopic effects and of the inactivity of the second, symmetrical CO stretching, it was concluded that this species should be centrosymmetrical, presumably linear. Remarkably, it was not observed in two separate ESR MI studies by Kasai and Jones [13] and Chenier and coworkers [14], in samples where the other binary carbonyls (CuCO and Cu(CO)₃) were observed. This negative result was interpreted as a proof that this molecule is, indeed, linear and having a ²Π ground state, in which case it is expected to be ESR-silent. In

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1995, Barone, using various DFT-based calculations, predicted the electronic structures, energies, geometries and some spectroscopic vibrational properties of the CuCO, Cu(CO)₂ and Cu(CO)₃ series [15], predicting remarkably well the bent structure of CuCO and that Cu(CO)₂ should revert to linearity with a ²Π ground state. Even more recently, Cerón and Mendizabal examined in detail for the first time using high level *ab initio* methods, ranging from MP2 to CCSD(T), the reasons for the change in bonding strength when going from CuCO to Cu(CO)₂ [16]. In particular, they showed that the low stability of the copper–monocarbonyl [17] could be perfectly explained by calculating the induction and dispersion contributions, at the highest level of theory. In a parallel publication, Wu et al. reached quite similar conclusions [18] and compared the performances of several DFT methods. None of these theoretical studies confronted their predictions, however, to the available experimental data on the low frequency metal–ligand stretching and bending modes [19], most sensitive to the nature of the bonding and the chosen QC method.

In the course of studies devoted to the observation of the low frequency stretching and bending modes of transition metal carbonyls, new data pertaining to Cu(CO)₂ and Cu(CO)₃ were observed in our laboratory. If the data concerning the Cu(CO)₃ complex match reasonably well the former DFT predictions [15] and are readily understandable in terms of a vibrational spectrum of a trigonal, D_{3h} symmetry species, the data concerning Cu(CO)₂ present specific features which cannot be readily understood in terms of a purely vibrational spectrum of a linear species. In fact, with a ²Π ground state, Cu(CO)₂ constitutes a rare example of five-atomic molecule with a Renner–Teller effect. The goal of this contribution is thus threefold: make use of the unique possibilities of MI to investigate the IR spectroscopy of a linear five-atomic molecule with a Renner–Teller effect, give spectroscopic indicators of the bonding strength in Cu(CO)₂ and describe the specific features of the bonding with topologic arguments at the required level of theory.

2. Experimental details

Samples containing copper carbonyl complexes were formed by co-condensing Cu vapor and dilute CO–Ar or Ne mixtures (0.5–16% CO/Ar or 200–2000 ppm O₂/Ne), onto one of six flat, highly polished, Rh-plated copper mirrors maintained between 3 and 15 K using a pulse-tube, closed-cycle cryogenerator (Cryomech PT405, Syracuse, USA), the experimental procedures are described in Ref. [20].

Copper wire (99.998% purity, Alpha Aesar) was wrapped around a tungsten filament, and heated at 800–900 °C to generate the Cu metal vapor. The metal deposition rate was carefully monitored with the aid of a quartz microbalance and was varied from 1 to 10 nanomol/min. High purity Neon or Argon (Air Liquide, France; 99995%), carbon monoxide (Air Liquide, France; 99998%), ¹³CO (CEA, Saclay, France; 99% ¹³CO including 9% ¹³C¹⁸O), ¹²C¹⁸O (MSD; 98% ¹⁸O) were used to prepare the gas mixtures. Survey absorption spectra were recorded between 10000 and 50 cm⁻¹ on the same samples using a Bruker 120 FT spectrometer with 0.1 cm⁻¹ resolution and different beam splitter/sources/detector/window combinations covering the far infrared to near infrared range, as detailed in Ref. [20]. For selected spectral ranges, high resolution scans were acquired with 0.02 cm⁻¹ resolution. Diffusion experiments were performed by annealing the samples to 9–10 K (neon) or 25–30 K (argon) in the dark, the sample facing an 80 K radiation shield.

3. Computational details

Geometrical optimizations, vibrational frequency and Natural Bonding Orbital (NBO) calculations have been performed using

the Gaussian 09 quantum chemical package [21]. Optimized molecular structures and harmonic vibrational frequency of CO, CuCO, and Cu(CO)₂ compounds were determined by means of the coupled-cluster single and doubles and with perturbative triples [CCSD(T)] method with the 6-311+G(2d) Pople's basis set, as implemented in Gaussian 09 package. Additional optimization and harmonic vibrational frequency computations were carried out with the popular B3LYP functional.

The NBO figures have been obtained using the Multiwfn Version 3.3.5 software [22]. The nature of chemical bonding has been investigated in the framework of the AIM (“Atoms In Molecule” of Bader [23]) topological approach with help of the AIMAll code [24].

We recall that the “wfx” files, necessary to the AIM calculations, were obtained with a CCSD/6-311+G(2d) single-point calculation at the CCSD(T)/6-311+G(2d) optimized geometry and using the “Density = Current”.

4. Experimental results

Fig. 1 presents the infrared spectra observed for CuCO isolated in solid argon and neon. As noted earlier, the ν_2 and ν_3 metal–ligand bending and stretching fundamentals of this species are at low frequency [19]. Also, notably, while the ν_1 mode experiences a small blue shift from 2010 to 2034 cm⁻¹ (1.2%) from argon to neon, the low frequency modes experience a very large redshift (322.7–294.9 cm⁻¹, thus –9.7%, and 207.5–176.7 cm⁻¹, thus –17%). These latter values indicate an anomalously large matrix effect. For most rigid molecules, the compilation of matrix results by Jacox indicates an average gas-to matrix shift of –2% for argon and less than 0.4% for neon [1]. A large matrix effect for argon is expected when a highly polar molecule is embedded in this polarizable medium, especially for weakly bonded species [25]. In solid neon, much less polarizable, more reliable data are obtained and the frequencies observed here can serve as better reference point for QC calculations.

Remarkably, the known Cu(CO)₂ absorptions present only a slight argon to neon blue shift (0.8–0.1%, +0.4% on average), characteristic for a rigid, more covalently bound molecule, thus confirming that the bonding evolves markedly by adding a second carbonyl group (see theoretical section below).

As noted by earlier workers, the Cu(CO)₂ and Cu(CO)₃ species are favored in samples with relatively high CO content (typically 2–4% in argon) and can be easily discriminated in the CO stretching vibration region, between 2100 and 1850 cm⁻¹, from CuCO absorption with stepwise CO concentration increase (Figure 1 of Ref. [19]), with Cu(CO)₂ growing after CuCO, and Cu(CO)₃ appearing

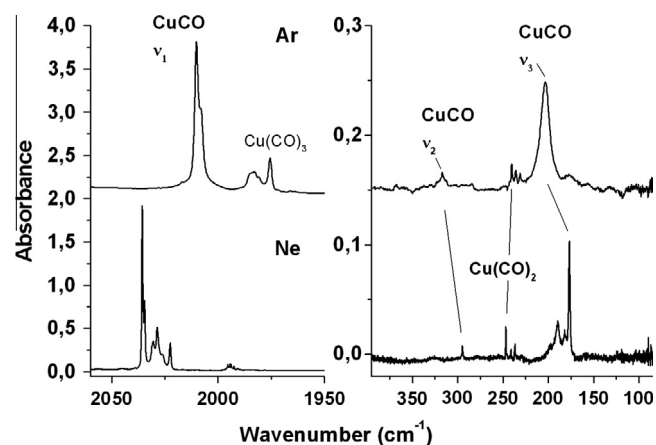


Fig. 1. Comparison of vibrational spectra for CuCO isolated in solid argon (top) and neon (bottom).

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