Reactions of Laser-Ablated Copper Atoms with Dioxygen. Infrared Spectra of the Copper Oxides CuO, OCuO, CuOCuO, and OCuOCuO and Superoxide CuOO in Solid Argon

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Laser-ablated copper atoms react directly with O_2 to make CuO (627.7 cm^{-1}), and linear OCuO (823.0 cm^{-1}) which are identified by copper and oxygen isotopic shifts, comparison to earlier work, and DFT frequency calculations. The highest frequency Cu−O vibration (995.3 cm^{-1}) exhibits a resolved copper isotopic triplet appropriate for the vibration of two equivalent copper atoms and oxygen isotopic components consistent with DFT-calculated frequencies for the nearly linear OCuOCuO molecule. Absorptions at 970.0 and 955.1 cm^{-1} are assigned to CuOCuO isomers. The simple addition product CuOO is characterized by O−O and Cu−O stretching frequencies at 1089.6 and 550.4 cm^{-1}, isotopic shifts, and DFT calculations. The CuOO molecule forms higher complexes $(O_2)_x$CuOO readily on annealing the matrix sample.

Introduction

Reactions of copper atoms with dioxygen have been extensively investigated over the past 20 years because of their important role in different processes ranging from corrosion of materials and catalytic oxidation to oxygen transport in biological systems. The nature of the initial weakly bound Cu+O_2 complex formed is not clear. Different matrix infrared absorptions have been assigned by several groups to cyclic Cu(O_2) (C_{2v}) and bent CuOO(C_s), but there is no clear agreement.[1−4] Electron spin resonance studies reveal magnetically inequivalent O atoms in the complex, which has been interpreted in favor of the C_s structure; however, magnetically inequivalent atoms do not preclude a C_{2v} structure.[5−7] ESR spectra show that this species is essentially $Cu^+(O_2^-)$ but cannot elucidate structure. The Cu+O_2 complex has been observed in the gas phase,[8−11] but its structure has not been determined. Although the favored gas phase structure is presumed to be the C_s bent CuOO complex,[11] the best theoretical calculations suggest that the C_{2v} equilibrium structure Cu(O_2) is more stable by about 1 kcal/mol.[12,13] Therefore, both Cu(O_2) and CuOO complex structures might be trapped in a solid argon matrix.

The higher OOCuOO bis(dioxygen) complex was proposed in concentrated matrix samples.[14] Further characterization of this molecule is of interest in comparison to other metal complexes involving two O_2 submolecules such as (O_2)Ni(O_2) and (O_2)FeO_2.[15,16]

The more strongly bound dioxide OCuO has been formed in solid matrices after photoexcitation of copper in the presence of dioxygen and characterized as a linear molecule by electronic spectroscopy.[3,4,17] This molecule has also been produced in the gas phase from laser-vaporized copper and observed by photodetachment spectroscopy from the molecular anion.[11] The linear OCuO dioxide molecule, however, has not been observed in the reported infrared spectra.

On the basis of recent studies of the reaction of laser-ablated Fe atoms with O_2, which observed infrared spectra of three isomers FeOO, Fe(O_2), and OFeO and characterized these species by DFT structure and frequency calculations,[16,18] a like investigation was done for the Cu+O_2 system with the goal of characterizing the several CuO_2 and CuO_4 species that can be formed.

Experimental Section

The technique for laser ablation and FTIR matrix spectroscopy was identical to that employed for the Fe+O_2 system.[16] Copper (Johnson Matthey, 99.9998%, and oxygen-free high-conductivity block) was used for laser targets. Oxygen isotopic samples (Yeda 97% and 55% ^{18}O) were used as received. Matrix dilutions included Ar/O_2 = 100:1, 200:1, 500:1, and 1000:1. Gas mixtures were codeposited for 1−2 h with 10−30 mJ pulses of 1064 nm radiation at the sample. Annealing cycles and photolysis by a medium-pressure mercury arc (Philips, 175 W) with the globe removed (240−580 nm) were also done. FTIR spectra were recorded with 0.5 cm^{-1} resolution and ±0.1 cm^{-1} accuracy on a Nicolet 750 with MCT detector.

Infrared Spectra

Infrared spectra of the Cu+O_2 system and the results of isotopic substitution are presented in Table 1 for $^{16}O_2$, $^{18}O_2$, $^{16}O_2$+$^{18}O_2$, and $^{16}O_2$, $^{16}O^{18}O$, $^{18}O_2$ samples. Typical spectra of this system are shown in Figure 1 for 100:1 samples; both copper targets gave the same spectra. Above 1000 cm^{-1} two strong bands were observed at 1124.3 and 1089.8 cm^{-1} with weak bands at 1110.2 and 1009.5 cm^{-1} in the codeposited sample in addition to ozone bands (Figure 1a). Broad-band photolysis decreased all of these bands but almost destroyed the 1110.2 cm^{-1} band (Figure 1b). However, annealing to 20 and 30 K (Figure 1c,d) slightly increased and sharpened the two stronger bands, markedly increased the 1110.2 cm^{-1} band, and decreased the 1009.5 cm^{-1} absorption. On annealing to 40 K, the sharp 1110.2 cm^{-1} band increases and dominates the spectrum followed by the 1124.3 cm^{-1}, band and the 1089.6 cm^{-1} band remains. Broad, weak 1688 cm^{-1} and sharp, weak 1544.7 cm^{-1} bands are not shown; the 1688 cm^{-1} band increased 4× on annealing, while the 1544.7 cm^{-1} absorption was destroyed.

Below 1000 cm^{-1} the spectra contained a sharp triplet at 995.3, 993.9, 992.6 cm^{-1} and sharp doublets at 955.1, 952.9

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TABLE 1: Absorptions (cm^{-1}) Observed for Laser-Ablated Cu + O_2 Reaction Products in Solid Argon

$^{16}O_2$	$^{18}O_2$	$^{16}O_2 + {}^{18}O_2$	$^{16}O_2 + {}^{16}O^{18}O + {}^{18}O_2$	$R(^{16}O/^{18}O)$	ann	assignment
1688	1612	1688, 1612	1688, 1669, 1630, 1612	1.0471	++	CuOCuO
1544.7	1457.3			1.0600	−	$(CuOO)^+$
1135	1072			1.0588		$CuOO(O_2)_x$
1124.3	1061.0	1124.3, 1061.0	1124.3, 1093.4, 1061.0	1.0597	+	$CuOO(O_2)$
1110.2	1047.4	1110.2, 1047.5	1110.2, 1079.0, 1047.8	1.0600	++	$CuOO(O_2)_2$
1092.0	1030.5	1092.0, 1030.5	1092.0, 1061.6, 1030.5	1.0597	++	CuOO site
1089.0	1028.7	1089.6, −	1089.6, 1060.0, 1028.7	1.0592	+ −	CuOO
1060.7	1001.0			1.0596		$Cu(O_2)$?
1009.5	953.2			1.0591	−	$(CuOO)^-$
995.3	949.8	995.3,	995.3, 954.1, 949.8	1.0479	++	$^{63}Cu_2O_3$
993.9	948.4	993.9, 948.4, 946.9	993.9, 952.3, 948.4	1.0480	++	$^{63}Cu^{65}CuO_3$
992.5	946.9		992.9, 950.8, 946.9	1.0483	++	$^{65}Cu_2O_3$
986.9	942.5	986.9, 942.5	986.9, 942.5	1.0465	++	$(Cu_2O_3)(O_2)$
970.0	926.2	970, 926	965, 930, 970, 926	1.0473	++	CuOCuO
955.1	911.4	955.1, 911.4	955.1, 952.5,	1.0479	−	Cu_2O_2
953.0	909.0	953.1, 909.0	915.7, 911.4		−	branched ring
933.2	?				++	?
845 sh	822 sh		830, 820	1.0280	++	$((O_2)Cu(O_2))$
836.6	814.1	836, 828, 814		1.0276	++	$((O_2)Cu(O_2))$
839.6	808.5	839.6, 825.6, 808.5	839.6, 825.6, 808.5	1.0385	−	$(O^{63}CuO)^-$
835.5	804.1	835.5, 821.3, 804.1	835.5, 821.3, 804.1	1.0390	−	$(O^{65}CuO)^-$
823.0[a]	792.5[a]	823.0, 809.2, 792.5	823.0, 809.2, 792.5	1.0385	+	$O^{63}CuO$
818.8	788.1	818.0, 805.0, 788.1	818.0, 805.0, 788.1	1.0390	+	$O^{65}CuO$
812.2	767.4			1.0584		CuO_3
802.7	758.4	796.6, 792.6, 788.0	796.6, 792.3, 787.7	1.0584	+	CuO_3
796.7	752.6	752.6	777.0, 769.0, 752.6	1.0584	+	CuO_3
792.2	748.5			1.0586		CuO_3
764.3	?			?	+	?
761.3	?					
657 br	626			1.0495	−	?
627.7	599.7	627.7, 599.7	627.7, 599.7	1.0467		^{63}CuO
625.8	597.7	625.8, 597.7	625.8, 597.7	1.0470		^{65}CuO
617.0	591.0	617.0, 591.0	617.0, 591.0	1.044		$CuO(O_2)$
597.5	565.0			1.0575	+	CuO_3, ν_2
555.0	531.3	555.0, 531.3	554.7, 531.5	1.0445	+	$^{63}CuOO$ site
553.1	529.3	553.1, 529.3		1.0452	+	$^{65}CuOO$ site
550.35	527.22	550.35, 527.22	550.25, 527.35	1.0439	+	$^{63}CuOO$
548.45	525.15	548.45, 525.15	548.35, 525.25	1.0444	+	$^{65}CuOO$

[a] Nitrogen matrix counterparts 826.7, 822.5 cm^{-1} and 796.0, 791.6 cm^{-1}.

cm^{-1}, 839.6, 835.5 cm^{-1}, 823.0, 818.8 cm^{-1}, 627.7, 625.8 cm^{-1}, and 550.4, 548.4 cm^{-1}. Photolysis markedly decreased the 955.1, 953.0 cm^{-1} doublet with little effect on other absorptions. Annealing increased the triplet at 995 cm^{-1} and the 986.9 and 970.0 cm^{-1} bands and produced strong new absorptions at 836.4, 796.7, and 792.2 cm^{-1}. The 823.0, 818.8 cm^{-1} doublet increased on first and then decreased on second annealing, while the 627.7, 625.8 cm^{-1} doublet decreased, the doublet at 550.4, 548.4 cm^{-1} sharpened and slightly increased, and another doublet increased at 555.0, 553.1 cm^{-1}. The 839.6, 835.5 cm^{-1} doublet decreased, while the broad underlying 836.6 cm^{-1} band increased. Note that the 550.4, 548.4 cm^{-1} doublet grew and sharpened in the same proportion as the 1089.8 cm^{-1} band.

The effect of dilution is illustrated in the O−O stretching region in Figure 2; the product bands sharpened and relative intensities changed from Figure 1a (100:1) to Figure 2a (200:1) to Figure 2b (500:1) to Figure 2c (1000:1). The sharp 1089.6 cm^{-1} band is clearly the dominant feature at highest dilution. Annealing of the 1000:1 sample produces the bands observed at higher concentrations with slightly different wavenumber positions 1135, 1123.4, 1109.5, and 1060.7 cm^{-1}, Figure 2d. Broad-band photolysis decreases all of these absorptions, but further annealing restores the 1092.0 cm^{-1} site splitting and decreases the 1089.6 cm^{-1} band, and the 1109.5 cm^{-1} absorption becomes dominant, Figure 2e,f.

A blank experiment was performed ablating copper into a condensing argon stream for 1 h. Three weak doublets were observed at 627.7, 625.8 cm^{-1}, 823.0, 818.8, and 951.1, 953.0 cm^{-1}, and broad bands were observed at 657 and 617 cm^{-1}; the 627.7 cm^{-1} band ($A = 0.004$) was 3× stronger than the 823.0 cm^{-1} band. Annealing decreased these features and produced a very weak 995.3, 994.0 cm^{-1} doublet and weak 1089.6, 802.7, and 550.4 cm^{-1} bands; no 1124 nor 1110 cm^{-1} absorption was observed.

The effect of isotopic substitution was explored in nine separate experiments using 100:1 to 1000:1 samples and is highlighted in important spectral regions: Figure 3 shows the 560−520 cm^{-1} region for four isotopic samples after 25 K annealing to sharpen the bands. The $^{16}O_2$+$^{18}O_2$ mixture gave the sum of pure isotopic components. Note the slight displacement (Table 1, average 0.1 cm^{-1}) of sharp bands in the $^{16}O_2$+$^{16}O^{18}O$+$^{18}O_2$ spectrum (hereafter called $^{16,18}O_2$) to the center from the pure $^{16}O_2$ and $^{18}O_2$ intermediate components. Figure 4 illustrates the 850−780 cm^{-1} region after deposition with (a) $^{16}O_2$+$^{16}O^{18}O$+$^{18}O_2$ and (b) $^{16}O_2$+$^{18}O_2$. Note the stronger triplet of doublets for the new 823.0 cm^{-1} band and the similar pattern for the weaker 839.6 cm^{-1} absorption in Figure 4a; however, in part b only weak intermediate $^{16}O^{18}O$ components were observed. Figure 5 gives the 1140−1020 cm^{-1} region after deposition and photolysis for $^{16,18}O_2$ reaction products at 1% total concentration. Note the strong triplet at 1124.3, 1093.4, 1061.0 cm^{-1}; the 1089.6, 1060.0, 1030.5 cm^{-1} triplet overlapped by other absorptions, and the weak 1110.2, 1079.0, 1047.8 cm^{-1} triplet. Annealing to 25 K slightly increases the former triplets and markedly (4×) increases the latter triplet (Figure 5b). The difference spectrum (Figure 5c) clearly shows major growth *only* for the 1110.2, 1079.0, 1047.8 cm^{-1} triplet. Note that the analogous difference spectrum for

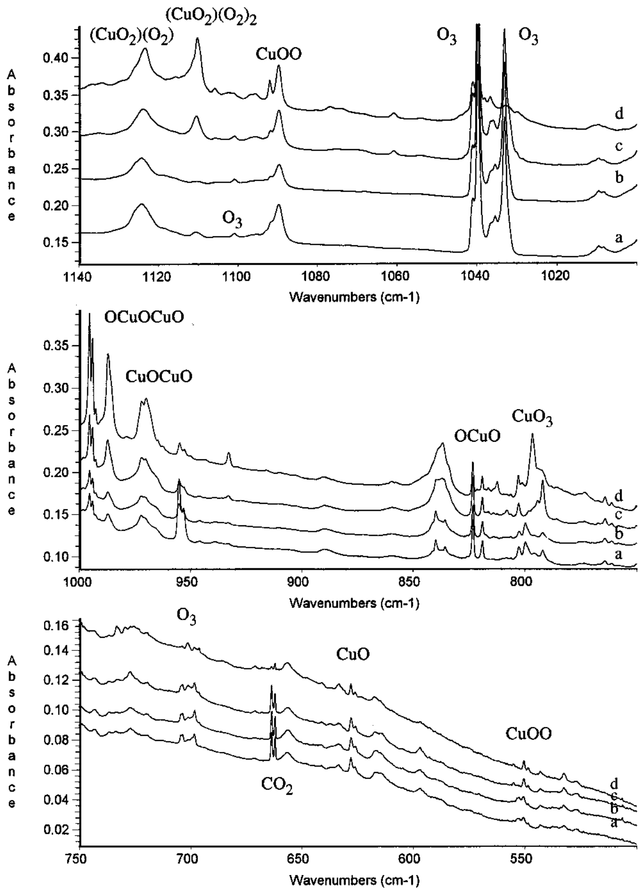

Figure 1. Infrared spectra in the 1140−500 cm^{-1} region for laser-ablated copper atoms codeposited with 1% O_2 in excess argon at 10 ± 1 K: (a) 2 h codeposit, (b) after broad-band photolysis for 30 min, (c) after 20 K annealing, and (d) after 30 K annealing.

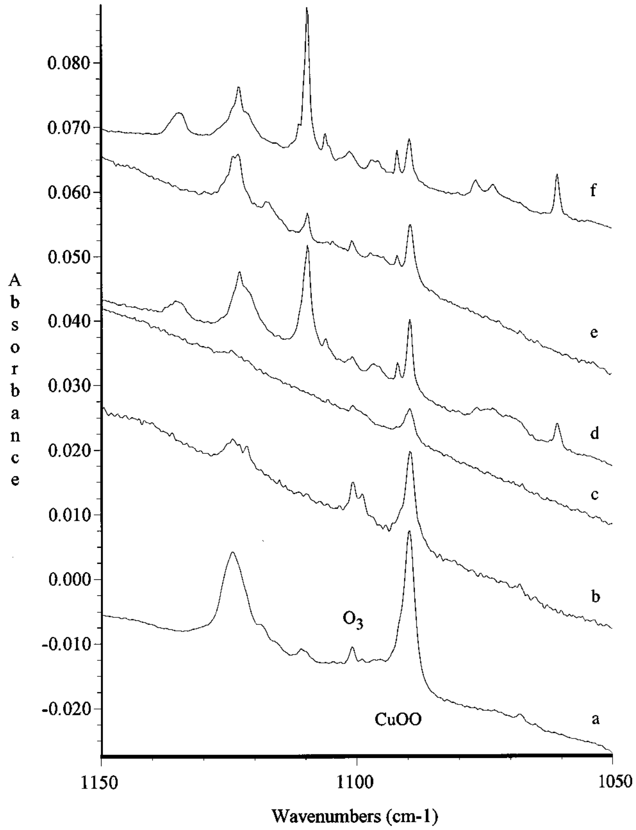

Figure 2. Infrared spectra in the 1150−1050 cm^{-1} region for laser-ablated copper atoms codeposited at 10 K with oxygen at different dilutions in argon: (a) Ar/O_2 = 200:1, (b) Ar/O_2 = 500:1, (c) Ar/O_2 = 1000:1, (d) after annealing to 30 K, (e) after broad-band photolysis, and (f) after annealing to 35 K.

$^{16}O_2$+$^{18}O_2$ shows major growth only for the pure isotopic 1110.2 and 1047.5 cm^{-1} bands (Figure 5d). Finally, the $^{16}O_2$+$^{16}O^{18}O$+$^{18}O_2$ experiment at 200:1 dilution produced the 1110.2, 1079.0, 1047.8 cm^{-1} triplet on 30 K annealing, and then photolysis destroyed it with little change in other absorptions in this region. At 500:1 dilution the sharp triplet appeared at 1109.2, 1078.8, 1047.4 cm^{-1} after annealing.

One experiment was performed with a 5% O_2 sample, and all product bands except 1544.7 cm^{-1} were stronger. Of more importance, band populations were altered: the 1110, 1124, 1135, and 836 cm^{-1} bands were stronger in the deposited sample and increased at the expense of the 1090 cm^{-1} band on annealing.

One experiment was done with N_2O reagent, and the relative band absorbances were different from the spectra shown in Figure 1 using O_2. The 627.7 and 970.0 cm^{-1} bands were increased 2×, the 995 cm^{-1} band was about the same, the 1089.8 cm^{-1} band was reduced 0.7×, the 823.0 cm^{-1} band was reduced 0.6×, the 1124.3 cm^{-1} band was reduced 0.5×, and the 955 cm^{-1} band was reduced 0.4×. The 1110.2 cm^{-1} band was not observed on deposition but appeared on annealing at half the 1124.3 cm^{-1} band absorbance, and the 836 cm^{-1} band was not observed in the initial sample but reached $A = 0.001$ on annealing. A weak new doublet was observed at 640.6, 638.4 cm^{-1}, and a new satellite feature was observed at 1095.0 cm^{-1}.

Finally, a series of experiments were done for 1% O_2 in nitrogen. A new 990.7 cm^{-1} band was destroyed on photolysis, and a sharp 2.2/1.0 doublet was produced at 826.7, 822.5 cm^{-1} with a weaker 821.3, 817.1 cm^{-1} doublet and weak NO and 1759.7, 1124, and 1092 cm^{-1} bands. Annealing decreased the lower doublet, slightly increased the upper doublet, and produced a new 810.3 cm^{-1} band. With $^{18}O_2$ the photosensitive band appeared at 936.3 cm^{-1}, and the photolysis product doublets were displaced to 796.0, 891.6 cm^{-1}, and 791.0, 786.6 cm^{-1}, the annealing product to 765.4 cm^{-1}, and the upper band to 1717.2 cm^{-1}.

Calculations

Density functional theory (DFT) was employed to support assignment of spectral bands, which will be discussed in the next section. All calculations were done using the Gaussian 92/DFT program[19] with the hybrid B3LYP functional.[20] Two basis sets were employed: the small O basis is the 6-31+G* set of Pople and co-workers,[21] and the small Cu basis is derived from the primitive set optimized by Wachters;[22] the s and p spaces are contracted using the number 3, while the d space is contracted (311). Two diffuse p functions (Wachters × 1.5) and the diffuse d function of Hay are also added.[23] This yields a small basis set of the form (14s11p6d)/[8s6p4d]. The big oxygen set is the 6-311+G(2df) set,[21] and the big copper set adds an f function ($\alpha = 2.3810$) to the small set.

Although there have been several high-level calculations including configuration interaction on the CuO ground state,[24−26] the calculated ω_e values are near the 586.4 cm^{-1} value obtained here with DFT, which is 6.6% below the observed value. Since our goal is to provide computational support for the identification of new copper oxide species at reasonable cost, the B3LYP functional and DFT were employed for higher oxide species.

Two previous high-level ab initio calculations on the $^2A''$ CuOO(C_s) species gave frequencies (CI, 1161, 535, 220 cm^{-1}; CASSCF, 1052, 391, 224 cm^{-1})[12,13] that are near the present

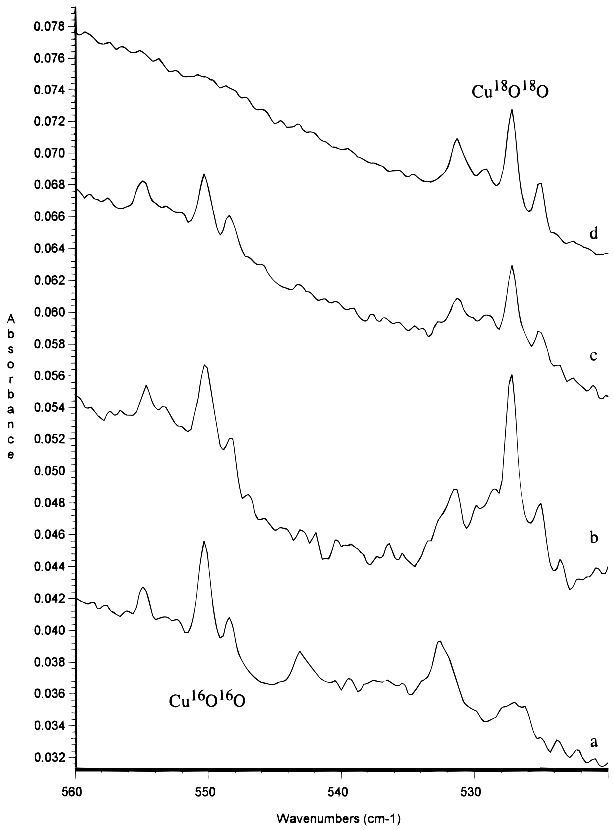

Figure 3. Infrared spectra in the 560−520 cm^{-1} region for laser-ablated copper atoms codeposited with isotopic oxygen samples (1%) in excess argon after annealing to 20 K to sharpen bands: (a) $^{16}O_2$, (b) $^{16}O_2$+$^{16}O^{18}O$+$^{18}O_2$, (c) $^{16}O_2$+$^{18}O_2$, and (d) $^{18}O_2$.

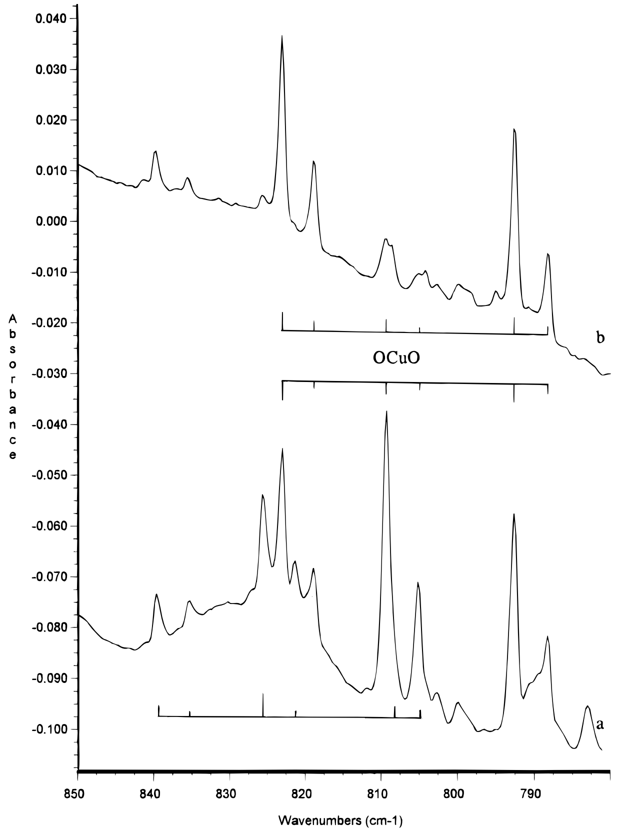

Figure 4. Infrared spectra in the 850−780 cm^{-1} region for laser-ablated copper atoms codeposited with mixed isotopic oxygen samples (1%) in excess argon at 10 K: (a) $^{16}O_2$+$^{16}O^{18}O$+$^{18}O_2$ and (b) $^{16}O_2$+$^{18}O_2$.

DFT values (1188, 438, 217 cm^{-1}). With the large basis DFT finds the $^2A_2$ $Cu(O_2)$(C_{2v}) species 14 kcal/mol above $^2A''$ CuOO, although two high-level calculations predict the C_{2v} form to be about 1 kcal/mol lower in energy.[12,13] One of these studies[12] predicts a comparable O−O frequency and a 100 cm^{-1} lower but more intense Cu−O_2 frequency for $Cu(O_2)$ as compared to CuOO. Another study describes CuOO as the ground state without considering $Cu(O_2)$.[27] Quartet states for both $Cu(O_2)$ and CuOO are essentially van der Waals complexes based on DFT calculations.

The OCuO molecule has been characterized by emission spectroscopy with a symmetric stretching fundamental at 658 cm^{-1} and a $^2\Pi_g$ ground state proposed.[11,17] A higher value of the antisymmetric stretching frequency is expected on going across the first transition metal row from OFeO.[15,16] Earlier CI calculations on OCuO considered only doublet states and identified the ground state as $^2\Pi_g$ with a CuO length of 1.765 Å but computed no vibrational frequencies.[28]

The present DFT big basis calculations find doublet OCuO to be 39 kcal/mol higher than CuOO, but the $^4\Pi_u$ state only 13 kcal/mol higher. Calculated frequencies are considerably higher for the doublet state (Table 2).

Calculations on CuO_3 structures and spin states are summarized in Table 3. Note that all of the $OCuO_2$ and OCuOO species have a strong O−O mode in the 1200−1400 cm^{-1}

TABLE 2: Calculated Frequencies (cm^{-1}) and Infrared Intensities (km/mol) for CuO and CuO_2 Molecules Using DFT/B3LYP

CuO, $^2\Pi$, 1.766 Å	586.4 (11)[a]
{CuO, $^2\Pi$, 1.760 Å	587.6 (11)}[a]
{$Cu(O_2)$ $^2A_2$	1036.3 (a_1, 1), 401.4 (a_1, 10), 170.7 (b_2, 6)}[a,b]
CuOO, $^2A''$, 1.912 Å, 1.290 Å, 116°	1188.5 (963), 437.8 (16), 217.1 (8)[c]
{$Cu^{16}O^{16}O$, $^2A''$, 1.908 Å, 1.281 Å, 117°	1181.8 (1030), 431.7 (18), 218.1 (9)}[b]
{$Cu^{18}O^{16}O$	1150.4, 411.7, 215.6}
{$Cu^{16}O^{18}O$	1146.6, 430.7, 208.5}
{$Cu^{18}O^{18}O$	1114.1, 410.7, 208.5}
$CuOO^+$, ^3A, 2.015 Å, 1.218 Å, 129°	1587.4 (7), 302.2 (2), 139.8 (1)
$CuOO^-$, ^1A, 1.868 Å, 1.361 Å, 118°	1009.5 (851), 456.2 (10), 218.2 (7)[d]
OCuO, $^2\Pi$, 1.659 Å	944.0 (29), 720.7 (0), 148 (22)
{OCuO, $^2\Pi$, 1.651 Å	953.1 (32), 727.0 (0), 142 (22)}[a,b]
{OCuO, $^4\Pi$, 1.750 Å	655.1 (24), 591.0 (0), 130 (21)}[e]
$(OCuO)^-$, $^1\Sigma$, 1.703 Å	842.1 (84), 676.5 (0), 160 (32)[f]
$(OCuO)^-$, $^3\Sigma_g$, 1.703 Å	841.5 (53), 672.6 (0), 188.7 (29)[d,f]
$(OCuO)^+$, $^1\Sigma$, 1.644 Å	963.0 (1), 716.9 (0), 111 (10)

[a] {Denotes large basis}; intensities (km/mol) given in parentheses. [b] $Cu(O_2)$ in C_{2v} structure not minimum with small basis; for large basis relative energy order is CuOO < $Cu(O_2)$ (+14 kcal/mol) < OCuO (+39 kcal/mol). [c] For small basis set CuOO is 14 kcal/mol more stable than OCuO. [d] For small basis set $OCuO^-$ is more stable than OCuO by 82 kcal/mol, in accord with the 80 kcal/mol electron affinity, ref 11. For small basis $CuOO^-$ is more stable than CuOO by 23 kcal/mol. [e] Quartet is 26 kcal/mol lower than doublet. [f] Triplet is 26 kcal/mol lower than singlet with both basis sets; frequencies ±4 cm^{-1} big basis.

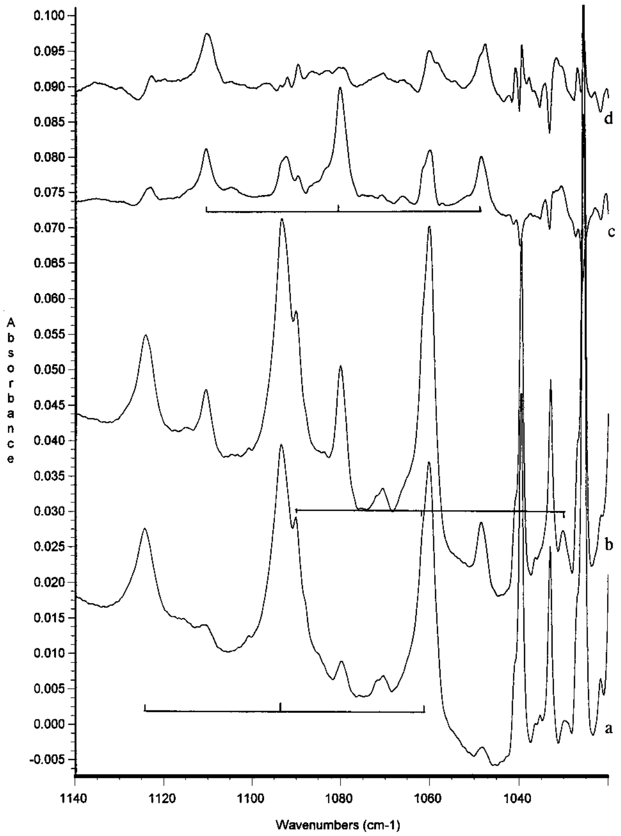

Figure 5. Infrared spectra in the 1140−1020 cm^{-1} region for laser-ablated copper atoms codeposited with mixed isotopic oxygen samples (1%) in excess argon: (a) $^{16}O_2$+$^{16}O^{18}O$+$^{18}O_2$ after 2 h codeposit and photolysis, (b) after 20 K annealing, (c) difference spectrum b minus a, and (d) analogous difference spectrum for $^{16}O_2$+$^{18}O_2$ mixture.

TABLE 3: Three Highest Calculated Frequencies (cm^{-1}) and Infrared Intensities (km/mol) for CuO$_3$ Molecules Using DFT/B3LYP and Small Basis Set

OCuO$_2$ (C_{2v}) doublet[a]	1263.5 (214), 815.5 (9), 436.0 (2)
CuO$_3$ (C_{2v}) doublet[b]	1055.2 (4), 879.2 (287), 723.8 (1)
OCuOO doublet[c]	1290.7 (260), 630.1 (12), 370.4 (8)
OCuOO quartet[d]	1351.3 (917), 634.5 (18), 400.1 (28)
OCuO$_2$ (C_{2v}) quartet[e]	1229.7 (313), 655.5 (15), 386.4 (4)

[a] Structure is 21.6 kcal/mol above global minimum energy structure. [b] 10.9 kcal/mol above ozonide structure: O−O = 1.354 Å, Cu−O = 2.044 Å, ∠O−O−O = 111°. [c] 7.4 kcal/mol above. [d] 5.6 kcal/mol above. [e] Global minimum.

region and that the ozonide has calculated frequencies near the alkali metal ozonide values.[30]

DFT calculations were done for three different O$_2$CuO$_2$ isomers in doublet and quartet spin states. With the B3LYP functional, the planar quartet (O$_2$)Cu(O$_2$) (D_{2h}) is the global minimum, quartet OOCuOO(C_{2v}) is 10 kcal/mol higher, and quartet (O$_2$)Cu(O$_2$)(D_{2d}) is 24 kcal/mol higher. All doublets are higher than quartet states (Table 4). With the B3LYP functional (O$_2$)CuOO(C_1) structures converged to the D_{2h} form; however, with the BP functional a stable doublet minimum was found that was 10 kcal/mol higher than the planar doublet form.

Several dicopper species were considered with B3LYP and the small basis set. Dicopper monoxide was found to be a bent (^{1}A) molecule (94°, 1.788 Å bond length) with frequencies 597.2 cm^{-1} (a$_1$, 37 km/mol), 578.8 cm^{-1} (b$_2$, 71), and 103.4 cm^{-1} (a$_1$, 3). Three structures for Cu$_2$O$_2$ have energies within 1.3 kcal/mol: the singlet rhombus, the pseudolinear triplet CuOCuO, and the branched ring triplet (Table 5). Such branched ring structures have been found to be stable in other systems (e.g. Se$_2$O$_2$).[29] The most stable OCuOCuO structure was also a pseudolinear triplet (Table 6); both pseudolinear triplet OCuOCuO and CuOCuO molecules are calculated to have strong Cu−O stretching modes in the 900 cm^{-1} region.

Discussion

Assignment of spectral bands together with results of DFT calculations will be presented.

CuO. The 627.7, 625.8 cm^{-1} doublet was observed after deposition and slightly decreased on annealing. The relative intensity is appropriate for ^{63}Cu/^{65}Cu in natural abundance for a molecule containing a single copper atom. Scrambled oxygen isotopic substitution produced a doublet of doublets denoting the vibration of a single oxygen atom and defined the 16/18 ratios 1.0467 and 1.0470, which are slightly lower than harmonic diatomic ratios for ^{63}CuO and ^{65}CuO of 1.0476 and 1.0479. The 63/65 ratios for the ^{16}O and ^{18}O counterparts are 1.0030 and 1.0033, which are in good agreement with the harmonic values 1.0031 and 1.0034. These bands are assigned to the ^{63}CuO and ^{65}CuO molecules, in agreement with previous matrix work and the gas phase fundamental at 631.4 cm^{-1}, respectively.[2,30]

Note that gas phase reaction between Cu atoms and O$_2$ molecules to produce CuO is endothermic by 54 kcal/mol[31] and that CuO is formed here by the reaction of energetic Cu atoms produced by laser ablation,[32] reaction 1. The DFT energy (big basis) value for ΔE is 64 kcal/mol.

$$\mathrm{Cu} + \mathrm{O_2} \rightarrow \mathrm{CuO} + \mathrm{O} \tag{1}$$

OCuO. The 823.0, 818.8 cm^{-1} doublet was observed in the spectra after deposition, and the intensity increased with oxygen

TABLE 4: Calculated Frequencies (cm^{-1}) and Infrared Intensities (km/mol) for CuO$_4$ Molecules Using DFT/B3LYP and Small Basis Sets

(O$_2$)Cu(O$_2$) quartet (D_{2h})[a]	1228.7 a$_g$, (0), 1152.7 b$_{2u}$ (540), 512.1 b$_{2u}$ (5), 371.1 b$_{3u}$ (0.1)
(O$_2$)Cu(O$_2$) doublet (D_{2h})[b]	1213.6 (0), 1146.2 (452), 525.3 (15), 384.7 (0.03)
$^{16}O^{16}OCu^{16}O^{16}O$ quartet[c,d] (C_{2v})	1390.3 (a$_1$, 2), 1207.3 (b$_2$, 3435), 455.0 (a$_1$, 0.1), 352.7 (b$_2$, 2)
$^{16}O^{18}OCu^{16}O^{16}O$	1372.5 (45), 1189.1 (3291), 447.2 (0.2), 342.5 (2)
$^{18}O^{16}OCu^{16}O^{16}O$	1372.6 (46), 1187.8 (3299), 454.4 (0.1), 352.0 (2)
$^{18}O^{18}OCu^{16}O^{16}O$	1358.0 (169), 1165.3 (3076), 446.8 (0.1), 341.7 (2)
$^{16}O^{18}OCu^{18}O^{16}O$	1351.2 (1), 1174.5 (3734), 437.9 (0.3), 333.7 (2)
$^{16}O^{18}OCu^{16}O^{18}O$	1351.1 (2), 117.3 (3243), 446.6 (0.1), 341.9 (2)
$^{18}O^{16}OCu^{16}O^{18}O$	1351.1 (2), 1172.1 (3253), 454.0 (0), 351.2 (2)
$^{16}O^{18}OCu^{18}O^{18}O$	1333.0 (2), 1154.2 (3095), 437.4 (0.2), 333.1 (2)
$^{18}O^{16}OCu^{18}O^{18}O$	1332.8 (48), 1153.2 (3107), 446.1 (0.1), 341.1 (2)
$^{18}O^{18}OCu^{18}O^{18}O$	1310.6 (2), 1138.2 (3052), 436.9 (0.1), 332.4 (2)
(O$_2$)Cu(O$_2$) quartet[e,f] (D_{2d})	1231.4 (a$_1$, 0), 957.0 (b$_2$, 3557), 365.5 (b$_2$, 131), 323.8 (e,0)
(^{18}O$_2$)Cu(^{18}O$_2$)	1160.9 (0), 903.0 (3151), 354.9 (126), 306.1 (0)
(O$_2$)CuOO doublet (C_1)[g]	1266.4 (280), 1145.2 (375), 570.8 (29), 359.3 (14)

[a] Global minimum. [b] Doublet is 1 kcal/mol higher than quartet. [c] Cis (C_{2v}) is 10 kcal/mol higher than global minimum. [d] Doublet OOCuOO (C_{2v}) is 10 kcal/mol higher than quartet and has similar frequencies. [e] Distorted tetrahedron (D_{2h}) is 24 kcal/mol higher than global minimum. [f] Doublet (O$_2$)Cu(O$_2$) (D_{2d}) is 9 kcal/mol higher and has similar frequencies. [g] Doublet (O$_2$)CuOO is 14 kcal/mol higher.

TABLE 5: Highest Calculated Frequencies (cm^{-1}) and Infrared Intensities (km/mol) for Cu_2O_2 Molecules Using DFT/B3LYP and Small Basis Set

CuOCuO nearly linear triplet[a]	920.6 (162), 731.2 (30), 291.9 (4)
Cu_2O_2 rhombus singlet[b]	668.5 (0), 607.9 (48), 458.2 (0), 399.2 (40)
CuOCuO branched ring triplet[c]	763.6 (73), 632.3 (18), 516.0 (18)

[a] Structure is 1.3 kcal/mol above global minimum, Cu−O = 1.775 Å. O−Cu = 1.723 Å, Cu−O = 1.698 Å. [b] Structure is 0.6 kcal/mol above minimum, Cu−O = 1.818 Å, angle Cu−O−Cu = 81°. [c] Global minimum, branched ring terminal O−Cu = 1.718 Å, central Cu−O = 1.750 Å, bridged Cu−O = 1.795 Å, Cu−Cu = 2.910, angle O−Cu−O = 179°.

TABLE 6: Four Highest Calculated Frequencies (cm^{-1}) and Infrared Intensities (km/mol) for Cu_2O_3 Molecules Using DFT/B3LYP and Small Basis Set

OCuOCuO "W" triplet[a]	1055.6 (2), 794.0 (581), 674.0 (.4), 371.8 (220)			
OCuOCuO linear singlet[a]	1016.7 (.3), 828.4 (0), 764.8 (56), 355.7 (18)			
$^{16}O^{63}Cu^{16}O^{63}Cu^{16}O$ nearly linear triplet[b]	939.5 (321), 705.1 (39), 636.0 (3), 277.0 (3)			
$^{16}O^{63}Cu^{16}O^{65}Cu^{16}O$	938.4	704.6	634.2	
$^{16}O^{65}Cu^{16}O^{65}Cu^{16}O$	937.1	702.5	634.2	
$^{18}O^{63}Cu^{18}O^{63}Cu^{18}O$	895.0	675.0	606.0	

[a] Structures are 51 kcal/mol above global minimum. [b] Global minimum; terminal O−Cu = 1.728, 1.706 Å and central Cu−O = 1.742 Å.

concentration and laser power. Their relative intensity was always 2.2/1.0, which is required for $^{63}Cu/^{65}Cu$ isotopes in natural abundance for a molecule with one copper atom. The isotopic ratio 1.00513 is very close to the harmonic value of 1.005 20 for the ν_3 fundamental of a linear OCuO molecule. Oxygen isotopic substitution produced a triplet structure for each band with the 16/18 ratios 1.0385 and 1.0390 for each copper isotope, which are again very close to harmonic ratios for the linear molecule (1.0391 and 1.0395) and show that this molecule contains two equivalent O atoms. Note that the 1:2:1 intensity distribution was observed only in experiments with scrambled oxygen, but in experiments with $^{16}O_2/^{18}O_2$ mixtures, weaker intermediate components were also detected. These bands are assigned to the ν_3 fundamental of the linear $O^{63}CuO$ and $O^{65}CuO$ molecules.

The main mechanism of formation is direct insertion of energetic, laser-ablated atomic Cu into the O_2 molecule, followed by relaxing in the condensing matrix; however, the

$$\text{energetic Cu} + O_2 \rightarrow [\text{OCuO}]^* \xrightarrow{\text{relax}} \text{OCuO} \qquad (2)$$

slight growth of these bands on annealing to 25 K indicates that the reaction between CuO and O can also take place with diffusing O atoms. Note that ozone absorptions also increase on annealing.

$$\text{CuO} + \text{O} \rightarrow \text{OCuO} \qquad (3)$$

The observation of a weak intermediate component in experiments with $^{16}O_2/^{18}O_2$ confirms that reaction 3 plays a minor role in OCuO formation.

Although B3LYP calculations predict the $^4\Pi_u$ state to be 26 kcal/mol lower than the $^2\Pi_g$ state for OCuO, the calculated ν_3 and ν_1 frequencies are 1.16 and 1.10 times the observed values for the doublet state and 0.80 and 0.90 times the observed values for the quartet state, respectively. The frequency calculations are more compatible with the doublet ground state identification.

Note that the average frequency for OCuO, $(823 + 658) \times 0.5 = 740$ cm^{-1}, is substantially higher than the frequency for CuO (628 cm^{-1}), suggesting a substantially stronger bond in the dioxide, as do the present calculated bond lengths (1.651 Å for OCuO *vs* 1.760 Å for CuO using the big basis). This was not the case for OFeO and FeO, which have almost identical average frequencies (OFeO, $(946 + 797) \times 0.5 = 872$ cm^{-1}, and FeO, 872 cm^{-1}) and calculated bond lengths.[16] The weak bond in CuO reflects stability of the +1 oxidation state for copper, which preserves the d^{10} shell. In the case of OCuO, the presence of another oxygen necessitates involvement of d orbitals in the bonding.

It is interesting to ask why the previous infrared spectra[3,4] failed to reveal the ν_3 fundamental of OCuO following photolysis that produced the fluorescence spectra. First, the xenon work[4] employed 5% oxygen and the appropriate region was dominated by the very strong $Cu(O_2)_2$ band; however, on photolysis, a very weak 825, 821 cm^{-1} doublet shoulder appeared as the 837 cm^{-1} band diminished. Second, OCuO is less stable than CuOO and relatively little OCuO will be easier to detect by electronic than by IR spectroscopy.

The sharp 823.0, 818.0 cm^{-1} copper isotopic doublet in solid argon did not increase on broad-band medium-pressure arc photolysis, in contrast to the more powerful Xe lamp production of OCuO for characterization by electronic spectroscopy,[4] presumably because of insufficient intensity. However, in solid N_2, the analogous 826.7, 822.5 cm^{-1} doublet did markedly increase on broad-band photolysis, showing that the OCuO produced here is in fact the same OCuO species identified previously by electronic spectroscopy.[3,4,17] Note the small difference between N_2 and Ar matrix fundamentals for the linear OCuO molecule with no dipole moment.

It is difficult to determine if the excess energy required for reaction 2 is kinetic or electronic. Ozin et al. suggest that it may in fact be metastable ^2D $(3d^94s^2)$ Cu atoms that insert to form OCuO.[4] The present experiments show that the insertion reaction to give OCuO occurs in argon but not in nitrogen condensing layers; a similar observation for laser-ablated Be, Mg, and Ca atoms led to the proposal that the reactive atoms were in metastable ^3P states.[33] It appears that N_2 is more effective in quenching metastable metal atom states. However, on photolysis, the Cu ^2P state is reached, which relaxes to the ^2D state and inserts into O_2 to form the dioxide, as suggested by Ozin et al.[4] Metastable ^2D Cu atoms formed in the laser ablation process thus have sufficient lifetime[34] to reach the condensing layer and insert into O_2. A similar reactivity has been attributed to laser-ablated metastable iron atoms.[16]

CuOO. The 1089.6 cm^{-1} band was observed on deposition; this band decreased slightly on photolysis and increased slightly, sharpened, and changed site splittings on annealing (Figure 1). Of considerable significance, the 1089.6 cm^{-1} band is the dominant feature at *lowest* O_2 concentration (Figure 2). Analogous behavior was found for the 550.4, 548.4 cm^{-1} doublet. Oxygen isotopic mixtures show that the upper band involves one O_2 submolecule, but the intermediate component is overlapped by another band, so possible further splitting could not be ascertained. The 16/18 ratio (1.0592) is also appropriate for an O−O stretching mode. The associated 550.4, 548.4 cm^{-1} doublet (relative intensity 1089.6/550.4 is 3/1 in 200:1, 500:1, and 1000:1 experiments) defines slightly different isotopic ratios than the above CuO diatomic molecule (63/65 ratio 1.0034 and 16/18 ratio 1.0440), revealing slightly more Cu and less O participation, which is appropriate for Cu vibrating against a slightly heavier mass than one O atom. The mixed $^{16}O_2/^{18}O_2$ spectrum is the sum of its parts and one O_2 subunit is involved, but small differences are found when $^{16}O^{18}O$ is included. The copper isotopic bands broaden (0.8 to 1.0 cm^{-1}) and shift 0.1 cm^{-1} to the center; this means that the $Cu^{16}O^{18}O$ absorption is 0.2 cm^{-1} lower than $Cu^{16}O^{16}O$, and the $Cu^{18}O^{16}O$ absorption is 0.2 cm^{-1} higher than $Cu^{18}O^{18}O$. The quartet nature of this band indicates that the two O atoms are inequivalent, and thus the CuOO molecule is identified.

This assignment to the Cu−O stretching mode of CuOO is in agreement with Tevault,[3] the highest level frequency calculations,[12] and the recent 530(50) cm^{-1} gas phase observation.[11] The 1089.6 cm^{-1} O−O stretch assigned here, however, differs from Tevault's assignment of 1124 cm^{-1}, which we believe is due to a higher O_2 complex of the same molecule, and Ozin's broad band at 1000 cm^{-1} in solid xenon.[35]

$(CuOO)(O_2)_x$ Complexes. The bands at 1110, 1124, and 1135 cm^{-1} grow on annealing and are favored by higher O_2 concentrations. These bands increase on annealing in different proportions. The 1124 cm^{-1} band increases slightly, the 1110 cm^{-1} band increases markedly, and the 1135 cm^{-1} band increases relative to the 1089.6 cm^{-1} band. These bands must be considered for CuO_4 species. In fact the 1110 cm^{-1} band has been assigned to the OOCuOO molecule.[14] However, the present mixed oxygen isotopic data provide no evidence of the coupling expected between equivalent O_2 submolecules, so we must conclude that the 1110 cm^{-1} band is due to a higher complex and not a CuO_4 molecule with equivalent O_2 subunits. The present DFT calculations show that higher multiplets should be observed for all of the CuO_4 isomers considered (Table 4), yet higher multiplets were not observed in the spectra. At most there is 0.5 cm^{-1} variation in the 1110.2 cm^{-1} band with $^{16}O_2+^{16}O^{18}O+^{18}O_2$, and this is probably due to site variations within these experiments. The observation of only "triplet" statistical oxygen isotopic absorptions shows that the 1124 and 1110 cm^{-1} bands involve the O−O stretching mode of one uncoupled O_2 submolecule, but the resolution may not be sufficient to determine equivalence of the atomic positions.

Two observations lead to the suggestion of $(CuOO)(O_2)_x$ complexes. First, the sharp 1092.0 cm^{-1} satellite increases on annealing relative to the 1089.6 cm^{-1} band, particularly at higher O_2 concentrations. The 1092.0 cm^{-1} satellite is probably due to an $(O_2)(CuOO)$ complex. In the N_2O experiments this satellite appeared at 1095.0 cm^{-1} and increased on annealing relative to the 1089.6 cm^{-1} band; the 1095.0 cm^{-1} band is probably due to the (NN)(CuOO) complex. Accordingly, we believe the best assignment for the 1124 cm^{-1} band is a $(CuOO)(O_2)$ complex and that for the 1110 cm^{-1} band is a $(CuOO)(O_2)_2$ complex where it is not possible to determine if the CuO_2 molecule is CuOO or $Cu(O_2)$. The weaker 1135 cm^{-1} band is probably due to a higher complex.

$$\text{cold Cu} + O_2 \rightarrow \text{CuOO} \qquad (4)$$

$Cu(O_2)$. The cyclic isomer is calculated to be more stable at high levels of theory,[12,13] but not with DFT; however, we do not have a definitive assignment for this isomer. The best possibility is the weak photosensitive band that grows in on annealing at 1060.7 cm^{-1}. In the Fe and Ni cases, the cyclic $Fe(O_2)$ and $Ni(O_2)$ isomers increased markedly on annealing.[15,16,18] The $^{18}O_2$ counterpart was clearly observed at 1001.0 cm^{-1} (ratio 1.0596), but a possible intermediate component was obscured by $Cu^{18}O^{18}O$ at 1030.5 cm^{-1}. This species might be formed on deposition but photodissociated by radiation from the laser plume on the copper target.

$(OCuO)^-$. The sharp doublet at 839.6, 835.5 cm^{-1} shows essentially the same isotopic ratios as the stronger sharp doublet at 823.0, 818.8 cm^{-1} and the same mixed oxygen isotopic triplet (Figure 3). Thus, the former doublet is also due to a linear OCuO species. The 839.6, 835.5 cm^{-1} doublet *is destroyed on annealing* cycles whereas the 823.0, 818.8 cm^{-1} doublet is slightly increased and then decreased; this shows that the weaker doublet is due to a more reactive species and is probably not an O_2 complex of OCuO, although this possibility cannot be completely ruled out. DFT calculations predict the ν_3 fundamental of the linear $(OCuO)^-$ anion (Table 2) at 842 cm^{-1}, which is higher than the OCuO radical, and a $^3\Sigma_g$ ground state, in contrast to the suggested $^1\Sigma_g$ ground state.[11] The 839.6, 835.5 cm^{-1} doublet is tentatively assigned to the ν_3 fundamental of linear $(OCuO)^-$. Recent photodetachment studies[11] have determined OCuO to have a high electron affinity (3.46 eV), so $(OCuO)^-$ is a stable anion that may be expected to form by capture of electrons produced in the ablation process. In this regard O_4^- was detected at 953.7 cm^{-1} in these experiments.[16,36] Diatomic CuO^- was also sought, but no products in the 700−790 cm^{-1} region[37] gave the correct isotopic shifts.

$(CuOO)^+$ and $(CuOO)^-$. The sharp, weak 1544.7 cm^{-1} band ($A = 0.001$) also disappears on annealing and exhibits a 1457.3 cm^{-1} $^{18}O_2$ counterpart, but intermediate components could not be observed owing to isotopic dilution of product absorbance. The 16/18 ratio (1.0601) is indicative of a pure O−O vibration with little anharmonicity. DFT calculations (Table 2) predict the O−O stretching fundamental of $CuOO^+$ at 1587 cm^{-1}, and the weak 1544.7 cm^{-1} band is appropriate for a tentative assignment to the $CuOO^+$ cation.

The weak 1009.5 cm^{-1} band decreases on annealing and has a 953.2 cm^{-1} $^{18}O_2$ counterpart, but intermediate components were masked by ozone absorptions. The 16/18 ratio (1.0591) also points to an O−O stretching vibration. DFT calculations predict this fundamental for $(CuOO)^-$ at 1009.5 cm^{-1}, which is fortuitous but nevertheless supportive of this identification.

$(O_2)Cu(O_2)$. The strong broad feature that grows strongly and peaks at 836.6 cm^{-1} on annealing (Figure 1) has been observed by earlier workers in argon[1,14] and xenon matrices,[4] and assignment to $Cu(O_2)_2$ has been considered but not demonstrated. In some experiments an 845 cm^{-1} shoulder is observed on 40 K annealing, and at high O_2 concentrations, this feature becomes a broad band at 850 cm^{-1} in solid argon[14] and at 837 cm^{-1} in solid xenon.[4] This absorber must be characterized by the 16/18 isotopic ratio, which has an *unusually low* 836.6/814.1 = 1.0276 value. Although the band is broad, annealing $^{16}O_2/^{18}O_2$ samples to 30 K reveals a broad 836, 828, 814 cm^{-1} triplet, and $^{16,18}O_2$ experiments give a broad 830, 820 cm^{-1} doublet. These features are unresolved versions of the spectra of MO_4 molecules.[15,33,38]

For a simple binary Cu_xO_y atomic system, the lowest 16/18 ratio for a normal vibration is that for the antisymmetric stretching mode of O−Cu−O, which is observed here as 1.0385. In order to decrease this ratio, the mass of O must be increased, for example to O_2, and the 16/18 ratio 1.0288 is predicted for an antisymmetric O_2−Cu−O_2 stretching mode. Agreement between this simple vibrational model and the unusually low observed 16/18 ratio, 1.0280, is good enough to substantiate the identification of a $(O_2)Cu(O_2)^-$ species as suggested from the mixed oxygen isotopic spectra.

One apparent problem with this seemingly obvious assignment is the lack of agreement with the present DFT calculations. The most stable $(O_2)Cu(O_2)$ molecule is predicted to have very strong 1152.7 cm^{-1} and weaker 512.1 cm^{-1} bands of b_{2u} symmetry with 16/18 ratios 1.0605 and 1.0292, respectively. The latter 16/18 ratio confirms the above mechanical model for an antisymmetric O_2-Cu-O_2 stretching mode, but the 836 cm^{-1} band is way above the predicted 512 cm^{-1} value and has no associated antisymmetric O−O stretching mode. We believe the best explanation for the 836 cm^{-1} band is a molecule $(O_2)Cu^{\delta+}(O_2)^{\delta-} \leftrightarrow (O_2)^{\delta-}Cu^{\delta+}(O_2)$, where charge exchange during the vibration gives rise to an extremely strong antisymmetric O_2-Cu-O_2 stretching mode.

Nickel and copper are clearly different with respect to the nature of the $(O_2)Ni(O_2)$ and $(O_2)Cu(O_2)$ molecules. The latter molecule is readily formed by the addition of O_2 to $Ni(O_2)$ and gives rise to a strong higher mixed oxygen isotopic multiplet for the coupled O−O stretching of two equivalent O_2 subunits; however, no such copper species is observed.

CuO_3. The 812.4, 802.7, and 792.2 cm^{-1} bands are near those assigned to CuO_3 by Tevault et al.,[2] and the present observations are in agreement. The strong 796.7 cm^{-1} band behaves likewise and is due to a slightly perturbed form of the same species. Note that the copper ozonide fundamentals calculated by DFT are in good agreement with the observed alkali ozonide values,[39] and the very strong copper ozonide band is predicted about 9% too high. Even though several $OCuO_2$ species are calculated to be more stable than CuO_3, these species are not observed here.

CuOCuO and OCuOCuO. The 995, 987, 970, and 955 cm^{-1} bands are very high for Cu−O stretching modes, but these bands are clearly due to such modes based on the observed 16/18 ratios. Furthermore the 995.3, 993.9, 992.5 cm^{-1} triplet (29:22:4) is in reasonable agreement with that expected for the vibration of two equivalent copper atoms with natural abundance ^{63}Cu and ^{65}Cu. The 63/65 ratio (1.00282) is slightly below the harmonic diatomic value, and the 16/18 ratio (1.0479) is slightly above. Following the OCuO dioxide band at 823 cm^{-1}, these absorptions are believed to be due to OCuOCuO and CuOCuO species, a suggestion supported by high Cu−O stretching modes predicted from DFT frequency calculations.

The broad 1688 cm^{-1} band tracks with the broad 970 cm^{-1} band on annealing, and the quartet scrambled isotopic multiplets for each band are in accord with the CuOCuO identification. Neglecting anharmonicity, the $1688 - 970 = 718$ cm^{-1} and $1612 - 926 = 686$ cm^{-1} bands are appropriate for the lower Cu−O stretching mode 16 and 18 counterparts for this molecule, in agreement with DFT calculations. Hence, the 970 cm^{-1} band is probably due to the nearly linear triplet CuOCuO molecule, in accord with the strong DFT-predicted mode at 920.6 cm^{-1} (Table 5). In fact the scrambled isotopic quartet is in accord with DFT-calculated spectra.

The 955.1 cm^{-1} band is the most photosensitive deposition product. The band shows a broad copper isotopic doublet and a mixed oxygen isotopic quartet for two inequivalent O atoms and a 16/18 ratio just in excess and a 63/65 ratio just below the harmonic diatomic value. This band is tentatively assigned to the triplet branched ring, which is subject to ring opening on photolysis. Such a branched ring is a stable isomer in the Se_2O_2 system.[29] We have no evidence for the singlet cyclic $(CuO)_2$ molecule, which is calculated to have a distinctly different spectrum and is suggested to be the isomer observed in the recent $Cu_2O_2^-$ photodetachment spectrum.[40] The 955 and 970 cm^{-1} bands identified here are clearly due to terminal Cu−O vibrations.

Perhaps the most interesting of these bands is the highest Cu−O stretching mode observed here, namely, the resolved Cu isotopic triplet at 995.3, 993.9, and 992.5 cm^{-1}. The highest frequency intense Cu−O stretching mode was calculated for nearly linear triplet OCuOCuO at 939.5 cm^{-1} (Table 6). Note there is very good agreement between the calculated 63/65 ratio (1.002 56) and the 16/18 ratio (1.0497) and the observed values. Furthermore, the calculations predict very little coupling between the terminal Cu−O modes such that the mixed oxygen isotopic sextet for all ^{63}Cu (939.5, 939.0, 937.9, 897.4, 896.7, 895.0 cm^{-1}) is difficult to resolve due to band overlap. However, the latter three all ^{63}Cu components are resolved at 954.0, 952.3, and 949.8 cm^{-1} in the scrambled oxygen isotopic experiment. Hence, the resolved copper isotopic splittings and agreement with DFT isotopic frequency calculations substantiate the identification of the nearly linear OCuOCuO molecule. The 986.9 cm^{-1} band has a similar contour and is likely due to an aggregate of OCuOCuO probably with O_2.

Conclusions

The copper−oxygen system is important but very complicated. With the excess energy present in laser-ablated copper atoms both monoxide (CuO) and dioxide (OCuO) as well as higher oxides (CuOCuO and OCuOCuO) can be formed. Note that frequencies increase in this oxide series, as higher copper oxidation states must involve d orbitals in the bonding.

The primary complex formed with cold copper atoms is CuOO, as documented by isotopic shifts in Cu−O and O−O stretching modes in dilute oxygen experiments. A number of higher secondary complexes $(O_2)_xCuOO$ are formed at higher O_2 concentrations, but none of these give evidence for coupling between O_2 subunits required for an O_2CuO_2 molecule with equivalent O_2 subunits.

The formation of two different CuO_2 species (the CuOO complex and the linear OCuO dioxide), where the CuOO complex is the lower energy isomer at all levels of theory employed here, arises because of kinetic stability. The linear dioxide formed from energetic Cu atoms has an energy barrier to rearrangement to the lower energy copper dioxygen complex. No calculations performed to date are sufficiently accurate to definitively determine the structure of the lower energy complex as end (CuOO) or side $(Cu(O_2))$ bonded. The present experiments, however, give a substantial yield of the CuOO complex and possible evidence for a low yield of a $Cu(O_2)$ complex both formed by cold copper atoms and of lower energy than the linear dioxide formed by excited copper atoms.

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