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Dioxygen Activation by Photoexcited Copper Atoms

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Abstract: $^2P \leftarrow {}^2S$ photoexcited Cu atoms react with O_2 in mixed rare gas/O_2 matrices to form CuO_2, which is found from UV-visible absorption/fluorescence, infrared, and electron spin resonance to be spectroscopically and chemically distinct from mono(dioxygen)copper, $Cu(O_2)$, the latter being the product of the reaction of ground-state ^2S Cu atoms with dilute rare gas/O_2 matrices. CuO_2 reacts with excess oxygen under cryogenic conditions to form copper ozonide, $Cu(O_3)$, and ozone, O_3, whereas $Cu(O_2)$ yields bis(dioxygen)copper, $Cu(O_2)_2$. The bonding between the copper and oxygen atoms in CuO_2 can be described as the interaction between a Cu^{2+} and two equivalent O^- ions, having covalent contributions to the Cu-O bonding, in contrast to $Cu(O_2)$, which is formulated as an interaction between Cu^+ and O_2^- ions, a tight-ion pair, having nonequivalent oxygen atoms with the odd electron residing mainly on the dioxygen moiety, that is, mono-η^1-superoxocuprous(I). Attention is focused on mechanistic aspects of the copper atom-dioxygen photochemical reaction, especially the differences in the reactivity of the Cu atom in its ground ^2S and excited ^2P and ^2D electronic states. It is proposed that the generation of CuO_2 following the $^2P \leftarrow {}^2S$ photoexcitation of Cu atoms in the presence of nonnearest neighbor O_2 molecules involves $^2P \rightarrow {}^2D$ relaxation, diffusion of a long-lived Cu ^2D atom to an O_2 molecule, and insertion of a Cu ^2D atom into O_2 to yield CuO_2. This should be contrasted with ^2S Cu atoms reacting spontaneously with a neighboring O_2 molecule via electron transfer to form $Cu(O_2)$.

Introduction

The known chemical reactions of group 1B metal atoms in their *ground electronic states* with dioxygen under matrix isolation conditions are summarized in Scheme I, where stoichiometric and structural assignments and bonding conclusions have been generally drawn from a combination of metal and oxygen concentration experiments, $^{16}O/^{18}O$ isotopic labeling studies with UV-visible absorption, infrared, and ESR spectroscopic detection.[1-6]

In earlier studies from this laboratory the photoprocesses of copper and silver atoms in rare gas,[7,8] methane,[9] and mixed rare gas/hydrogen[10] matrices have been discussed. A common feature of these systems is that whereas optical and ESR studies indicate that the entrapped metal atom in its ground electronic state (ns^1, $^2S_{1/2}$) is relatively unperturbed, optical excitation to the first resonance excited state (np^1, $^2P_{3/2,1/2}$) results in strong guest-host interactions, which are manifested in perturbed fluorescence spectra, photoinduced diffusion and aggregation processes, or chemical reactivity.[7-10]

In this paper, the results of an investigation of the photochemistry of copper atoms in mixed rare gas/O_2 matrices are described. This system differs from those considered previously[9,10] in that, for the Cu/O_2 system, chemical reactivity is important for both the ground and excited electronic states of the metal atom, but of a quite different type.

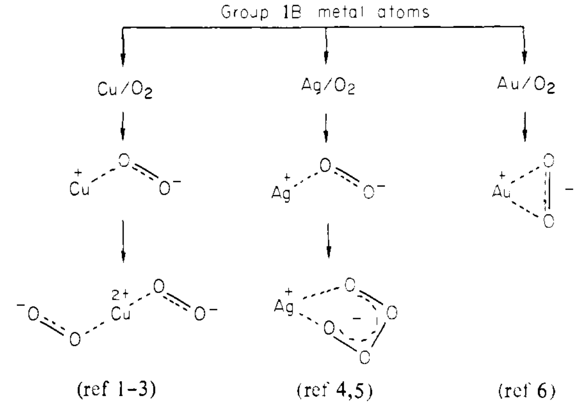
Experimental Section

The experimental arrangement for matrix preparation and UV-visible absorption/fluorescence, infrared, and ESR studies have been described previously.[8,11] Copper wire (99.99%, 0.010-in. diameter) was supplied by A.D. McKay, New York, and research-grade Ar, Kr, Xe, and $^{16}O_2$ gases were supplied by Matheson of Canada. Stohler Isotopes of Montreal supplied the $^{18}O_2$ (95% enriched). Absorption spectra were recorded on a Unicam SP 8000 spectrometer, fluorescence spectra (230-900nm) on a Perkin-Elmer MPF 44B fluorescence spectrometer (both the excitation and emission wavelengths being selected with scanning monochromators), infrared spectra (4000-250 cm^{-1}) on a Perkin-Elmer 180, and X-band ESR spectra (0-6000G) on a Varian E4. The photolysis source was a 1000 W Xe arc lamp and Shoeffel Model GM 100 monochromator.

UV-Visible Absorption, Fluorescence, and Infrared Studies

Copper atom matrix cocondensation reactions with molecular dioxygen have been studied by UV-visible absorption,[1] infrared,[1,2] and ESR[3] spectroscopy. The occurrence of a bis(dioxygen)copper complex, $Cu(O_2)_2$, is well established and forms most readily in oxygen-rich matrices (e.g., $O_2/Ar \simeq$ 1:1 - 1:10) and is characterized by an intense LMCT optical absorption around 295 nm, as illustrated in Figure 1A,B, and a ν_{OO} stretching mode around 1100 cm^{-1}. There is also evidence to indicate that in higher dispersion oxygen/rare gas matrices (e.g., $O_2/Ar \simeq$ 1:10-1:50) the mono(dioxygen)copper complex, $Cu(O_2)$, also forms and is characterized by an optical absorption around 224 nm, Figure 1B,D, and a ν_{OO} stretching mode around 1000 cm^{-1}. A dioxygen complex, in the context of the present study, is defined as one in which molecular dioxygen is bound as a unit, with a strong bond persisting between the oxygen atoms. Both nonlinear, end-on and symmetric, side-on structures have been suggested for metal atom-O_2 complexes.[1-6,38]

Scheme I



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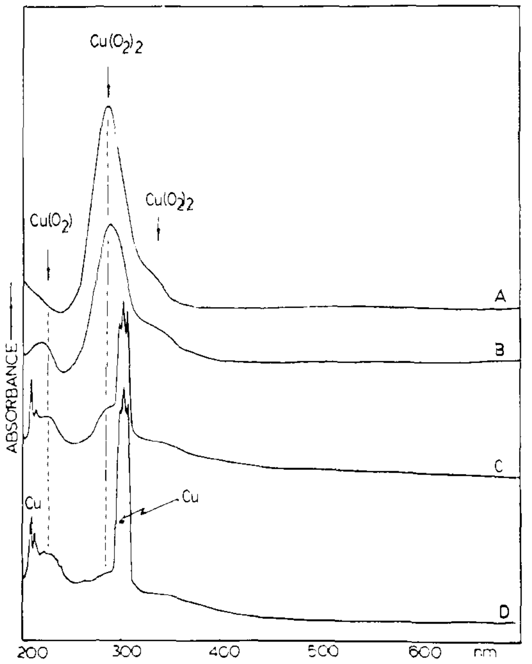

Figure 1. UV-visible absorption spectra showing the products of the $Cu/O_2/Ar$ matrix cocondensation reaction at 12 K: (A) $O_2/Ar \simeq 1:1$, (B) $O_2/Ar \simeq 1:10$, (C) $O_2/Ar \simeq 1:25$, and (D) $O_2/Ar \simeq 1:50$. The spectra depict the gradual transformation of a matrix containing mainly $Cu(O_2)_2$ (A) to one with $Cu(O_2)$, $Cu(O_2)_2$ (B), to one with Cu, $Cu(O_2)$, $Cu(O_2)_2$, (C), to finally one with mainly Cu, $Cu(O_2)$ (D) (see text). Cu/rare gas $\simeq 1:10^4$ in all experiments.

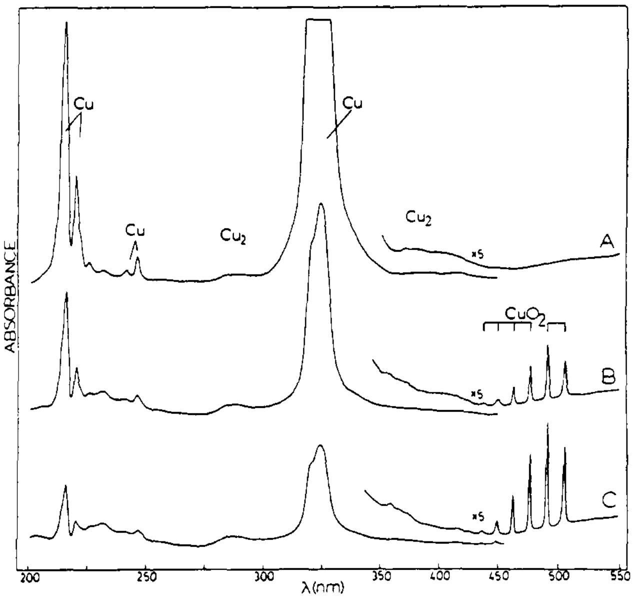

Figure 2. UV-visible absorption spectra showing decay of bands due to isolated copper atoms and growth of new bands near 500 nm as a result of 324-nm photolysis of a $Cu/O_2/Xe \simeq 1:10^2:10^4$ matrix at 12 K: (A) freshly deposited matrix; (B) 30 min, 324-nm photolysis; (C) 60 min, 324-nm photolysis.

The UV-visible absorption spectrum of copper atoms isolated in a $Cu/O_2/Xe \simeq 1:10^2:10^4$ matrix at 12 K is illustrated in Figure 2A. The spectrum is essentially identical with that obtained for a $Cu/Xe \simeq 1:10^4$ matrix, although the copper atom absorption bands are somewhat less intense owing to the formation of $Cu(O_2)$ and $Cu(O_2)_2$, which are at too low a concentration under high O_2 dispersion conditions to be readily observed by UV-visible spectroscopy (cf. $Cu/O_2/Ar \simeq 1:(2 \times 10^2):10^4$, Figure 1D).

As shown in Figure 2, $4p^1, {}^2P \leftarrow 4s^1, {}^2S$ photoexcitation of the entrapped copper atoms at 324 nm caused the Cu atom absorption bands to diminish in intensity, and resulted in the appearance and pronounced growth of a progression of sharp absorption bands near 500 nm. The photolysis treatment caused only a slight growth of the bands due to Cu_2.[7,12] The 324-nm photoinduced decay of the copper atom absorption bands was found to follow *first-order* kinetics in the photolysis time. A typical kinetic plot for a $Cu/O_2/Kr \simeq 1:(5 \times 10^2):10^4$ matrix is shown in Figure 3.

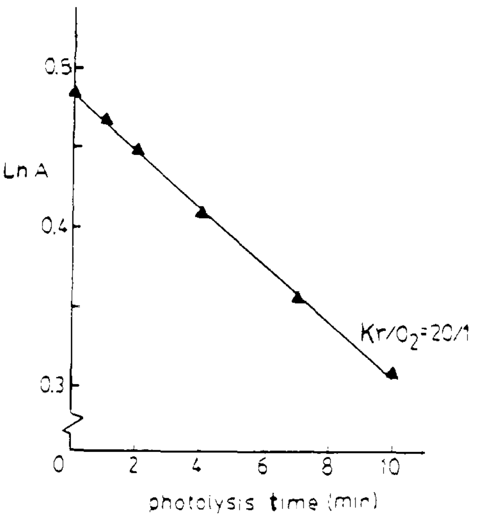

Figure 3. First-order kinetic plot showing a linear relationship between the natural logarithm of the absorbance due to isolated copper atoms and the cumulative photolysis time at 320 nm for a $Cu/O_2/Kr \simeq 1:(5 \times 10^2):10^4$ matrix.

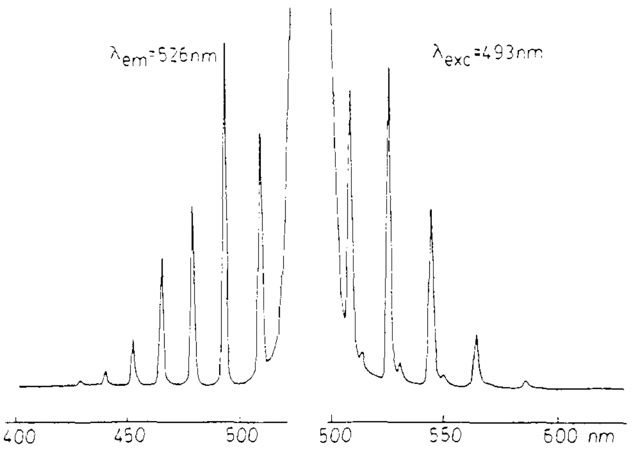

Figure 4. Fluorescence excitation (left side) and fluorescence emission (right side) spectra of a $Cu/O_2/Xe \simeq 1:10^2:10^4$ matrix following 30 min photolysis at 324 nm (note scale change on wavelength axis). The corresponding emission and excitation wavelengths are indicated, and their positions are given approximately by the steeply rising portions of the spectra. The ordinate represents fluorescence intensity in arbitrary units.

Photoexcitation of a $Cu/O_2/Xe$ matrix in the region of the new absorption bands near 500 nm resulted in the appearance of intense fluorescence, as illustrated in Figure 4. The left-hand side of Figure 4 shows the fluorescence/excitation spectrum obtained by scanning the excitation monochromator over the absorption bands with the emission monochromator held at 526.0 nm. This spectrum shows explicitly which absorption bands produced the 526.0-nm emission band. The intensity profile and peak positions of the absorption spectrum are reproduced in the fluorescence/excitation spectrum. On the right-hand side of Figure 4 is shown the fluorescence spectrum obtained by scanning the emission monochromator with the excitation monochromator held at 493.3 nm. The first member of the excitation (absorption) progression corresponds exactly with the first member of the emission progression at 508.1 nm. The wavelengths of the individual absorption and emission maxima are listed in Table I.

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Table I. Absorption and Fluorescence Spectra of CuO_2 in Solid Xe at 12 K

absorption			fluorescence[a]		
λ (nm)	v', v''	ΔG (cm^{-1})	λ (nm)	v', v''	ΔG (cm^{-1})
508.1 ± 0.1	0, 0		508.1 ± 0.1	0, 0	
		615 ± 5			670 ± 5
492.7	1, 0		526.0	0, 1	
		611			653
478.3	2, 0		544.7	0, 2	
		598			660
465.0	3, 0		565.0	0, 3	
		594			634
452.5	4, 0		586.0	0, 4	
		597			
440.6	5, 0				

[a] Excited at 493 nm. Very weak fluorescence peaks are observed at 513.3, 531.2, and 550.0 nm (see Figure 4).

Absorption and fluorescence spectra similar to those described above have been observed by others using several different methods of matrix preparation. Absorption bands essentially identical with those listed in Table I were observed by Shirk and Bass[13] following vacuum ultraviolet (VUV) photolysis of Xe/O_2 = 500:1 matrices containing isolated copper atoms. Similar absorption spectra were observed for vuv-photolyzed $Cu/O_2/Ar$ and $Cu/O_2/Kr$ matrices. It is known that vuv photolysis of O_2-doped rare gas matrices results in dissociation of O_2 to form isolated oxygen atoms.[14] Carstens et al.[15] found that an Ar matrix absorption spectrum the same as that reported by Shirk and Bass[13] resulted when the trapped species were produced by a copper hollow cathode sputtering source operated in the prescence of a Ar/O_2 = 100:1 gas mixture. The vuv photolysis technique was used by Shirk and Bass[13] and Rojhantalab et al.[16] in laser-induced fluorescence studies involving $Cu/O_2/Ar$ matrices. (It should be noted here, that d → p electronic transitions of Cu atoms are known to occur in the vuv region.[17]) The fluorescence spectra reported by these workers exhibited peak positions, splittings, and intensity profiles closely similar to those found for $Cu/O_2/Xe$ matrices in the present study. Tevault[18] found that krypton ion laser photolysis of $Cu/O_2/Ar$ matrices (probably exciting $Cu(O_2)$, see later) resulted in the formation of a species showing laser-induced fluorescence spectra essentially identical with those observed in the vuv photolysis experiments. Griffiths and Barrow[20] reported that absorption spectra the same as those found by Shirk and Bass[13] could be produced by near-UV photolysis ($\lambda > 300$ nm) of rare gas/O_2 = 200:1 matrices containing isolated copper atoms. The results of Griffiths and Barrow[19,20] are exactly analogous to those illustrated in Figure 3. It can be concluded that all of the above-mentioned methods of matrix preparation resulted in the formation of an entrapped species which was the same as that observed in the present study.

The absorption and fluorescence wavelengths observed in the above experiments are close to those of the F–X system of CuO in the gas phase,[21] and this prompted the initial assignment of the matrix spectra to CuO.[13] However, by means of experiments involving $^{16}O_2/^{18}O_2/^{16}O^{18}O$ isotopic substitution, Tevault[18] has very recently shown that the matrix fluorescence spectra which had been attributed to CuO are in fact due to a molecule containing *two equivalent oxygen atoms*. Although it has not been proven that only one copper atom is present, this is certainly most likely to be the case (see below), and thus it is reasonable to assign the absorption and fluorescence spectra illustrated in Figures 3 and 4 to the species denoted CuO_2. It should be noted that this species is distinct from the mono(dioxygen) copper complex denoted $Cu(O_2)$. It is clear that a distinction exists, because, whereas the $Cu(O_2)$ complex is formed simply by depositing copper atoms together with molecular oxygen in a rare gas matrix,[1-3] the CuO_2 species was detected only after photolysis of the deposited matrix (see Figure 3). Further consideration of this point is presented in the discussion below.

The coincidence of the first members of the absorption and emission progressions of Xe-entrapped CuO_2, as described above, is suggestive of a $(v', v'') = (0, 0)$ transition, and this is confirmed by the $^{16}O_2/^{18}O_2$ isotope substitution experiments of Shirk and Bass,[13] Griffiths,[19,20] and Tevault,[18] where it was observed that the first members showed very small or undetectable isotope shifts while the second and later members of both the absorption and emission progressions showed much larger isotope shifts. Thus the individual absorption and emission bands may be assigned according to the vibrational numbering given in Table I. The results of the present study indicate that the fluorescence of CuO_2 in solid Xe is almost completely relaxed. That is, fluorescence occurs primarily from the $v' = 0$ level of the excited electronic state, regardless of which vibrational level is initially populated in absorption. Clear evidence of unrelaxed emission was however, observed. Thus, excitation to the $v' = 3$ level resulted in the appearance of a relatively weak emission band attributable to the $(v', v'') = (1, 0)$ transition, together with stronger bands associated with transitions from $v' = 0$, these features corresponding to unrelaxed and relaxed emission, respectively.

According to the selection rules for vibronic transitions,[22] the vibrational structure corresponding to relaxed emission arises from excitation of a totally symmmetric mode of vibration. The closeness of the first vibrational spacing of the vibronic progression in emission illustrated in Figure 4 (670 cm^{-1}) to the value for monomeric CuO in the gas phase (631 cm^{-1}) is suggestive of a Cu–O stretching vibration for CuO_2, and thus the vibrational quantum number in Table I is most likely associated with the symmetric OCuO stretch of CuO_2.

It can be seen in Figure 4 that in addition to the intense vibronic progression corresponding to relaxed emission, there is a considerably weaker progression shifted approximately 200 cm^{-1} to longer wavelength. Higher resolution absorption and emission spectra[19,20] show further splittings not seen in Figure 4; the spectra of CuO_2 in solid Ar show similar structure.[13,16] The origin of these splittings is not clear, but it is likely that they are caused by multiple trapping site effects.[18]

The mechanism of CuO_2 formation in 324-nm photolyzed $Cu/O_2/Xe$ matrices was investigated in this study by means of infrared spectroscopy. Infrared scans of freshly deposited matrices showed bands attributable to the dioxygen complexes $Cu(O_2)$ and $Cu(O_2)_2$, the relative intensities of which were governed by the Xe/O_2 ratio. Previous workers[1,2] have assigned an Ar matrix band at 1109 cm^{-1} to an oxygen–oxygen stretching mode of $Cu(O_2)_2$ and have noted the presence of an intense, broad band centered near 850 cm^{-1}. The origin of the 850-cm^{-1} band is not known, although it has recently been suggested from Xα calculations that it could be due to an intraligand π^* electronic transition associated with coordinated dioxygen in $Cu(O_2)_2$.[3] The Xe matrix counterparts of the 1109- and 850-cm^{-1} Ar matrix bands were observed in the present study at 1106 and 837 cm^{-1}. For Xe/O_2 ratios in the range 100:1 to 20:1, a prominent band was observed at 530 cm^{-1}. This band shifted to 507 cm^{-1} when $^{18}O_2$ was used in place of $^{16}O_2$. In view of the indication from ESR studies[3] that the mono(dioxygen)copper complex, $Cu(O_2)$, may be isolated in rare gas matrices, and has a nonlinear end-on bonded structure (like

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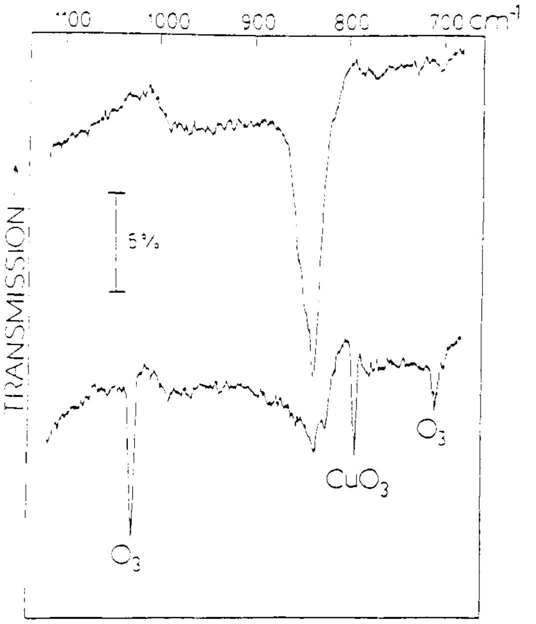

Figure 5. Infrared spectra of a $Cu/O_2/Xe \simeq 1{:}(5 \times 10^2){:}10^4$ matrix showing changes caused by 324-nm photolysis. The upper trace shows the spectrum obtained for the freshly deposited matrix and the lower trace shows the spectrum following 3 h of photolysis at 324 nm. Absorptions assigned to ozone and copper ozonide are indicated (see text).

that of $Ag(O_2)^5$), it is likely that the 530-cm^{-1} ($Xe/^{16}O_2$) and 507-cm^{-1} ($Xe/^{18}O_2$) bands are associated with the Cu–O stretching vibration of $Cu(O_2)$. Consistent with this assignment is the measured oxygen-18/oxygen-16 frequency ratio of 0.957, which compares with the value 0.954 calculated for the diatomic molecule CuO, and is thus indicative of a copper–oxygen stretching vibration. Furthermore, the 530-cm^{-1} ($Xe/^{16}O_2$) band was not observed for $Xe/O_2 = 1{:}1$ matrices, which is consistent with the indication from infrared and UV–visible absorption studies (e.g., Figure 1) that under these conditions $Cu(O_2)_2$ is formed at the expense of $Cu(O_2)$.

Photolysis of a $Cu/^{16}O_2/Xe \simeq 1{:}(5 \times 10^2){:}10^4$ matrix at 324 nm, corresponding to the maximum of the $4p^1,{}^2P \leftarrow 4s^1,{}^2S$ atomic resonance absorption band of the entrapped copper atoms, resulted in a diminution of the strong band at 837 cm^{-1} and growth of new absorption bands at 1027, 793, 706, 275, and 262 cm^{-1}. The 530-cm^{-1} band discussed above was not affected by the photolysis treatment. In a series of experiments involving different Xe/O_2 ratios, the 1027-, 793-, and 706-cm^{-1} bands tended to show constant relative intensities, as did the 275- and 262-cm^{-1} bands, but the relative intensities of these two groups of bands showed a significant variation, the bands at lower frequency being favored at higher Xe/O_2 ratios. The photoinduced changes in the 700–1100-cm^{-1} spectral region in the case of a $Cu/^{16}O_2/Xe \simeq 1{:}(5 \times 10^2){:}10^4$ matrix are illustrated in Figure 5. When the same experiment was performed using a $Xe/O_2 = 1{:}1$ ratio, the new absorption bands just described did not appear, although a diminution of the strong 837-cm^{-1} band was observed. Substitution of $^{18}O_2$ for $^{16}O_2$ in the case of a $Xe/O_2 = 20{:}1$ matrix caused the 1027- and 793-cm^{-1} bands to shift to 973 and 749 cm^{-1}, respectively. The 706-, 275-, and 262-cm^{-1} bands observed for $Xe/^{16}O_2$ also underwent isotope shifts, but the $Xe/^{18}O_2$ counterparts were not observed. The low-frequency bands apparently shifted beyond the lower working frequency limit of the spectrometer (250 cm^{-1}).

The higher frequencies noted above are similar to those observed by Brewer and Wang[23] for ozone isolated in solid Xe (1030 cm^{-1} for $^{16}O_3$ and 978 cm^{-1} for $^{18}O_3$) and by Tevault et al.[24] for copper ozonide, $Cu^+(O_3^-)$, isolated in solid Ar (802.3 cm^{-1} for $Cu(^{16}O_3)$, and 758.9 cm^{-1} for $Cu(^{18}O_3)$). Tevault et al.[24] prepared copper ozonide by depositing copper atoms together with ozone in an Ar matrix. The analogous alkali- and alkaline earth–ozone reactions have been studied in detail by Andrews and co-workers.[25-27] The Ar matrix frequencies observed by Tevault et al.[24] for $Cu(^{16}O_3)$ (802.3 cm^{-1}) and $Cu(^{18}O_3)$ (758.9 cm^{-1}) are approximately 10 cm^{-1} higher than those observed for photolyzed $Xe/^{16}O_2/Cu$ (793 cm^{-1}) and $Xe/^{18}O_2/Cu$ (749 cm^{-1}) matrices in the present work. A red shift from Ar to Xe matrices is not unexpected, and since the observed oxygen-16/oxygen-18 shifts are in excellent agreement, it seems certain that the same species was detected in both studies. Thus the 793-cm^{-1} band illustrated in Figure 5 may be assigned to the antisymmetric O–O stretching mode of the ozonide ion in $Cu(O_3)$. Brewer and Wang[23] have identified strong absorptions due to $^{16}O_3$ and $^{18}O_3$ trapped in Xe matrices at 1030 and 978 cm^{-1}, resepctively, together with much weaker bands at both higher and lower frequencies. The frequencies observed for the strong bands are in close agreement with those found for $Xe/^{16}O_2$ (1027 cm^{-1}) and $Xe/^{18}O_2$ (973 cm^{-1}) matrices in the present study. The weak band at 706 cm^{-1} illustrated in Figure 5 may correlate with the band observed by Brewer and Wang[23] at 695 cm^{-1}. It is possible that the 11-cm^{-1} frequency shift between these two bands arises from the occurrence of markedly different trapping site arrangements, which may come about because the ozone molecules are introduced into the matrices in different ways (direct deposition in the case of the experiments of Brewer and Wang[23] and chemical reaction within the solid in the present experiments; see below). The weak 706-cm^{-1} band underwent an oxygen-16/oxygen-18 shift but the oxygen-18 counterpart was not observed, possibly because of a shift into a region obscured by atmospheric CO_2 absorption (670 cm^{-1}). In any case, the closeness of the frequencies observed for the strong bands at 1027 cm^{-1} ($Xe/^{16}O_2$) and 973 cm^{-1} ($Xe/^{18}O_2$) to those reported by Brewer and Wang[23] for $^{16}O_3$(1030 cm^{-1}) and $^{18}O_3$(978 cm^{-1}), respectively, gives a strong indication that the species responsible for these absorptions is ozone.

It is pertinent to mention that 295-nm photolysis into the LMCT absorption[1] of $Cu(O_2)_2$ in $Xe/O_2 \simeq 1{:}1$ matrices at 12 K causes rapid bleaching of the $Cu(O_2)_2$ spectrum with concomitant growth of an absorption around 325 nm. A shoulder at 345 nm, also assigned to a LMCT band of $Cu(O_2)_2$,[1] remains essentially unaltered during the photolysis treatment. Bands in the visible region around 500 nm that could be attributed to CuO_2 (see above) are not observed under these conditions. Subsequent photolysis at 325 nm causes bleaching of the new absorption around 325 nm and partly reinstates the band at 295 nm belonging to $Cu(O_2)_2$. This behavior, together with the corresponding IR observations (ν_{OO} doublet at 1106/1090 cm^{-1}), can be interpreted in terms of a photointerconversion of two slightly different forms (sites) of $Cu(O_2)_2$, which could be semantics for a photoisomerization of end-on bonded nonlinear cis and trans forms of $Cu(O_2)_2$. Further work will be needed to establish this point.

Discussion

Continuous $4p^1$, $^2P \leftarrow 4s^1$, ^2S photoexcitation of copper atoms in $Cu/O_2/Xe \simeq 1{:}(5 \times 10^2){:}10^4$ matrices at 12 K results in rapid *first-order* decay of the copper atom absorption bands (Figure 3) and growth of new absorption bands attributable to CuO_2, consistent with the occurrence of the following reaction:

$$Cu + O_2 \xrightarrow[\text{Xe, 12 K}]{h\nu(324\text{nm})} CuO_2 \qquad (1)$$

CuO_2 exhibits intense UV–visible absorption and fluorescence spectra, the oxygen-16/oxygen-18 isotopic splitting patterns of which have been shown to be indicative of the presence of two equivalent oxygen atoms.[18] Thus the fluorescence spectra show distinct and well-resolved progressions in the symmetric OCuO stretching mode which may be assigned to the three isotopic variants $^{16}OCu^{16}O$, $^{16}OCu^{18}O$, and $^{18}OCu^{18}O$, with no evidence

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of splitting of the central $^{16}OCu^{18}O$ features due to inequivalent oxygen atoms. The present results strongly suggest that the carrier of the fluorescence may be formed according to reaction 1, involving a single copper atom, so that the presence of only one copper atom in the molecule is indicated.

The photochemically generated species CuO_2 is distinct from the mono(dioxygen)copper complex $Cu(O_2)$, which may be formed by depositing copper atoms with molecular oxygen in a rare gas matrix. Whereas the UV-visible absorption spectrum of CuO_2 consists of a progression of sharp peaks near 500 nm, as illustrated in Figure 2, the spectrum of $Cu(O_2)$ shows a single broad band near 224 nm (Figure 1). Furthermore, the fluorescence spectrum of CuO_2 is indicative of a symmetric OCuO stretching mode near 670 cm^{-1}, while the infrared spectrum of $Cu(O_2)$ shows a band attributable to a copper-oxygen stretch at 530 cm^{-1}. The ESR spectrum of $Cu(O_2)$ is quite clearly orthorhombic and suggestive of a nonlinear, end-on bonded structure,[3] with the spin density residing primarily on the dioxygen unit, consistent with substantial ionic character and a $Cu^+(O_2^-)$ tight ion-pair formulation. Thompson et al.[28] recorded ESR spectra of vuv photolyzed $Cu/O_2/Ar$ matrices and found that the carrier of the observed absorption spectrum exhibited no detectable ESR spectrum. Negative observations concerning the ESR spectrum of CuO_2 were also obtained in our studies. Although Thompson et al.[28] and others[13,15,16] assigned their absorption spectrum to the diatomic species CuO, it is now recognized that the correct assignment is CuO_2.[18] Thus CuO_2 and $Cu(O_2)$ exhibit distinct electronic, vibrational, and magnetic spectral characteristics, and are formed under different matrix conditions.

The evidence for two equivalent oxygen atoms in CuO_2 implies that the molecule is either a linear or a bent dioxide species, in which no direct chemical bonding exists between the oxygen atoms, or a symmetrical side-on bonded mono(dioxygen)complex. A number of complexes of the latter type involving alkali metal atoms have been prepared in rare gas matrices and characterized by UV-visible absorption,[29] infrared,[30] and ESR[31] spectroscopy. These compexes show spectroscopic properties which are uniform in a number of respects, reflecting the presence of the superoxide anion (O_2^-) bound to the metal cation in all cases. Whereas the UV-visible absorption and ESR spectra of the nonlinear, end-on bonded mono(dioxygen)copper complex $Cu(O_2)$ show striking similarities with those of the alkali systems, the spectra for the CuO_2 species are quite distinct and do not fit the same pattern. Although it is conceivable that isomeric forms of a mono(dioxygen)copper complex could be stabilized in a rare gas matrix, it is highly unlikely that such isomers would show radically different spectra. Furthermore, it is difficult to understand why one isomer should be formed exclusively during deposition of the matrix and the other exclusively during subsequent photolysis. The formulation of CuO_2 as a dioxygen complex may therefore be rejected, and it is necessary to consider a dioxide formulation. It was noted earlier that CuO_2 may be formed by vuv photolysis of $Cu/O_2/$ rare gas matrices.[13,16] It is easy to see how a copper dioxide species could be formed under these conditions, because the vuv photolysis treatment results in dissociation of molecular oxygen[14] and/or production of highly electronically excited Cu atoms.[17]

Crystalline copper oxides are known in which the copper atoms are found in the +1, +2, and +3 oxidation states, the +3 state occurring in solid $NaCuO_2$ and $KCuO_2$,[38] but there are no known compounds of copper in a +4 oxidation state, and thus the occurrence of a molecular copper dioxide species is unexpected. Although the +4 state of copper is formally indicated for CuO_2, as in the known dioxides of the lanthanide and actinide elements Pr, Tb, Th, U, and Pu,[33] this seems an extreme and unlikely circumstance in the case of copper, and a more readily acceptable description of the charge distribution is given by $O^-Cu^{2+}O^-$, i.e., a +2 oxidation state for copper and a −1 state for oxygen. A formal −1 oxidation state of oxygen is unusual, but it occurs in the radical OH, in the diatomic alkali metal oxide molecules,[21] as well as in photogenerated V-centers in a number of inorganic oxides.[34] Furthermore, there is evidence to indicate that the dominant configuration contributing to the ground state of the diatomic molecule CuO is that corresponding to Cu^+O^-.[19,20] Covalent contributions to the bonding in CuO_2 are expected, and one may envisage a situation in which the tendency of the oxygen atoms to attain a stable "octet" configuration results in a sharing of electrons between the two O^- ions and Cu^{2+}, the electrons being supplied by the 3d orbitals of copper. While the occurrence of a stable CuO_2 species may perhaps be rationalized in the manner outlined above, the details of the electronic structure and mode of bonding remain obscure and require further study. It is interesting to note that evidence for a similarly unusual dioxide species ZnO_2 in a nitrogen matrix has recently been reported by Prochaska and Andrews.[27]

A further unusual feature of the CuO_2 molecule is found in its vibrational properties. Tevault[18] has noted that CuO_2 is unique among molecules containing one metal atom and two oxygen atoms in that the symmetric stretching vibration occurs at higher frequency than the fundamental of the corresponding diatomic molecule CuO (670 cm^{-1} for CuO_2 and 631 cm^{-1} for CuO). Examples of molecules showing the reverse trend include several symmetric side-on bonded mono(dioxygen) complexes,[26,30] and the lanthanide and actinide dioxide species referred to in the previous paragraph.[33]

A puzzling aspect of the infrared results described earlier is that no bands were observed which could be associated with stretching vibrations of CuO_2. Assuming that CuO_2 has a nonlinear structure, one would expect to find a band due to a symmetric stretch at 670 cm^{-1} (possibly low intensity), corresponding to the first vibrational spacing of the relaxed emission spectrum (Table I), and an additional band due to an antisymmetric stretch at lower frequency. Although no such bands were detected, weak absorptions were observed at 275 and 262 cm^{-1}. As noted earlier, these bands exhibited variable intensities relative to the absorption attributed to $Cu(O_3)$ which suggests that they are not associated with copper ozonide. In view of the occurrence of an oxygen-16/oxygen-18 isotope shift for these bands, a reasonable assignment would be the bending vibration of CuO_2. It is possible that the presence of two bands is a reflection of a multiple trapping site effect, or one may be an anomalously low frequency stretching vibration. An examination of the region below 250 cm^{-1} for $Cu/^{18}O_2/Xe$ matrices would be useful in confirming this assignment.

Copper atom reactions with molecular oxygen are remarkable in that distinctly different reaction products are formed for the ground and excited states of the copper atoms. Whereas an end-on bonded, nonlinear mono(dioxygen)copper complex is produced in the case of the ground state ($4s^1$, ^2S) Cu atom, $4p^1$, $^2P \leftarrow 4s^1$, ^2S photoexcitation of atomic copper results in the formation of the novel dioxide species CuO_2. It is interesting to note that a common feature of the matrix photochemical reactions of copper atoms with CH_4[9] and O_2 is the occurrence of an insertion product in both cases. Similarly, an initial insertion step was invoked in the case of the matrix reaction of photoexcited copper atoms with molecular hydrogen.[10] A similarity may be noted between the Cu/O_2 photochemical reaction and the reactions of ground-state Ge and Sn atoms with molecular oxygen in nitrogen matrices,[35,36] which have been shown to proceed by a direct insertion mechanism

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to form the linear, covalent species GeO_2 and SnO_2, isoelectronic with CO_2.

It is apparent that in order for a photochemical reaction to proceed between Cu and O_2 in a rare gas matrix, the copper atom in its excited electronic state must be placed adjacent to the oxygen molecule in the matrix. *This trapping site arrangement is, however, not feasible for ground-state copper atoms because such an arrangement results in reaction to form the mono(dioxygen)copper complex.* The mechanism of the photochemical reaction is therefore not immediately clear, and it would appear to be necessary to invoke migration of electronically excited copper atoms to O_2. No such migration process need be invoked in the cases of the Cu/CH_4[9] and Cu/H_2[10] photochemical reactions, because ground-state copper atoms are unreactive in these systems, so that reactive pairs may be formed by direct optical excitation of copper atoms initially adjacent to CH_4 or H_2 molecules. A qualitative discussion of the relaxation mechanisms of $4p^1$, $^2P \leftarrow 4s^1$, ^2S photoexcited copper atoms in rare gas matrices has been given in an earlier paper from this laboratory. It was seen that $3d^{10}4p^1$, $^2P \rightarrow 3d^94s^2$, ^2D relaxation is important for these systems, and that there is evidence to indicate that metastable, long-lived (2 ms),[37] ^2D copper atoms may migrate within the matrix and react with ^2S copper atoms to form electronically excited Cu_2 molecules in their $D,^3\Pi_u$ state.[7,37] It seems likely that a similar mechanism is operative in the case of the photochemical reaction of copper atoms with dioxygen in rare gas matrices. Such an excited state (^2D) copper atom migration process would allow for direct encounters between long-lived $Cu(^2D)$ and ground-state O_2, and could thus lead to reaction to form CuO_2, rather than the dioxygen complex $Cu(O_2)$. According to the considerations of previous studies which focused attention on guest-host interactions of Cu atoms in ground and excited electronic states,[7] it is anticipated that $Cu(^2P)$ interacts strongly with its rare gas neighbors to form a van der Waals complex,[7,8] and this makes it unlikely that a similar migration process occurs for $Cu(^2P)$. This implies that the reactive state of copper with dioxygen is $3d^94s^2$, ^2D and not the directly excited $3d^{10}4p^1$, ^2P state. The possibility of a reaction between $Cu(^2P)$ and O_2 cannot, however, be definitely ruled out. It is conceivable that matrix cage relaxation following $^2P \leftarrow {}^2S$ photoexcitation of copper atoms trapped nearby, but not adjacent to oxygen molecules, could cause the oxygen molecules to come into contact with the excited copper atoms.

If it is assumed that the photochemical reaction $Cu + O_2 + h\nu$ (324 nm) $\rightarrow CuO_2$ involves $Cu(^2D)$, as seems most likely, then overall exothermicity for the reaction requires that the binding energy of CuO_2 relative to ground-state copper and oxygen atoms be greater than the difference between the bond dissociation energy of molecular oxygen and the $^2D-{}^2S$ excitation energy of copper. Thus the binding energy must be at least 80 kcal mol^{-1}, so that the Cu-O bond energy in CuO_2 must be greater than 40 kcal mol^{-1}. This compares with the value 64.3 kcal mol^{-1} for the bond dissociation energy of the diatomic molecule CuO.[21] Comparable Cu-O bond energies for CuO_2 and CuO are not unexpected in view of the closeness of the respective Cu-O stretching frequencies noted above.

The results of the infrared study described earlier indicate that $^2P \leftarrow {}^2S$ photoexcitation of copper atoms in $Cu/O_2/Xe \simeq 1{:}(5 \times 10^2){:}10^4$ matrices results in the formation of ozone and copper ozonide. An interpretation of these results consistent with the above discussion would be that CuO_2 molecules formed in the primary photochemical process react with excess molecular oxygen to form $Cu(O_3)$ and O_3:

$$CuO_2 + 2O_2 \rightarrow Cu(O_3) + O_3$$

Strong support for this mechanism is derived from the results of a series of photolysis experiments involving different Xe/O_2 ratios. It was found that the increase in absorbance of the visible bands of CuO_2 (Figure 2) normalized to the corresponding decrease in absorbance due to isolated copper atoms exhibited a strong dependence on the Xe/O_2 ratio, such that for greater proportions of oxygen in the matrix the normalized growth of the CuO_2 absorption bands is relatively smaller. Thus the CuO_2 absorption bands were much weaker for Xe/O_2 = 20:1 than for Xe/O_2 = 100:1, even though the photolysis treatment resulted in comparably large decreases in the absorbance due to Cu. These results are suggestive of a secondary reaction of the initial photoproduct CuO_2 with oxygen. As an alternative explanation for the appearance of O_3 and $Cu(O)_3$, one may consider a photodecomposition process of $Cu(O_2)_2$. The occurrence of such a process is suggested by the observation of photoinduced decay of the broad 837-cm^{-1} absorption band, as illustrated in Figure 5. It has been proposed that this band is associated with $Cu(O_2)_2$.[3] That this alternative mechanism is unlikely to be correct is suggested by the following results. Weak infrared absorption due to O_3 was observed even for relatively low concentrations of oxygen (Xe/O_2 = 100:1), under conditions where the concentration of $Cu(O_2)_2$ was anticipated to be very low, and the 837-cm^{-1} absorption band was observed to be correspondingly very weak or absent from the spectrum. On the other hand, neither the O_3 nor the $Cu(O_3)$ absorptions were observed following photolysis of a Xe/O_2 = 1:1 matrix (as described earlier) even though the 837-cm^{-1} band was initially very strong and underwent a decrease in intensity as a result of the photolysis treatment (in line with the photoisomerization proposal for $Cu(O_2)_2$ as alluded to earlier). Photodecomposition of $Cu(O_2)_2$ may therefore be ruled out as a mechanism for O_3 and $Cu(O_3)$ formation, and it is necessary to invoke a secondary reaction of CuO_2 with oxygen.

The nature of the reaction of CuO_2 with excess oxygen in solid Xe to form $Cu(O_3)$ and O_3 is obscure, and it is not clear whether the initial products are $Cu(O_3) + O$ or $CuO + O_3$. The corresponding subsequent reactions would be $O + O_2 \rightarrow O_3$ and $CuO + O_2 \rightarrow Cu(O_3)$, respectively. The addition of atomic oxygen to O_2 to form O_3 has been observed in Kr matrices, and is known to be exothermic by 25 kcal mol^{-1}.[36] Also of possible relevance in this connection, in view of the suggested $O^-Cu^{2+}O^-$ ionic formulation for CuO_2, are reports of efficient reactions involving molecular oxygen and O^- defect centers in solids, resulting in the formation of O_3^- species.[34]

Conclusion

It is noteworthy that the products of the reactions of photoexcited copper atoms with methane to yield CH_3CuH,[9] and molecular dioxygen to yield CuO_2, are unusual and highly reactive species, whose formation is uniquely photochemical in nature and arises from differences in the reactivity of the metal atom in its ground and excited electronic states. The reactivity pathways determined for copper atoms in the ground and low-lying excited electronic states with dioxygen in rare gas matrices, from this study and earlier work, are summarized in Scheme II. One can surmise that the production of the CuO_2 species in earlier studies using different generation techniques arose from the processes outlined in Scheme III.

Thus from the results of the present study, it is thought that the generation of CuO_2 following the $^2P \leftarrow {}^2S$ resonance photoexcitation of Cu atoms in the presence of *nonnearest neighbor* O_2 molecules entails $^2P \rightarrow {}^2D$ relaxation, diffusion of a long-lived ^2D Cu atom to an O_2 molecule, and insertion of ^2D Cu atoms to yield CuO_2. This should be contrasted with ^2S Cu atoms reacting with a *neighboring* O_2 molecule, via electron transfer, to form $Cu(O_2)$. Further reaction of CuO_2 with excess dioxygen forms $Cu(O_3)$ and O_3, whereas $Cu(O_2)$ reacting with dioxygen yields $Cu(O_2)_2$. The production of copper ozonide $Cu(O_3)$ and ozone O_3 from $CuO_2 + O_2$, is consistent with a bonding description in CuO_2 in terms of the interaction between a Cu^{2+} and two equivalent O^- ions (cf. O^- V-center reactions with O_2 to yield O_3^-) having covalent contributions to the Cu-O bonding. This should be contrasted with $Cu(O_2)$ which is best formulated as an interaction between Cu^+ and O_2^- ions, as a tight-ion pair, having nonequivalent oxygen atoms with the unpaired electron density

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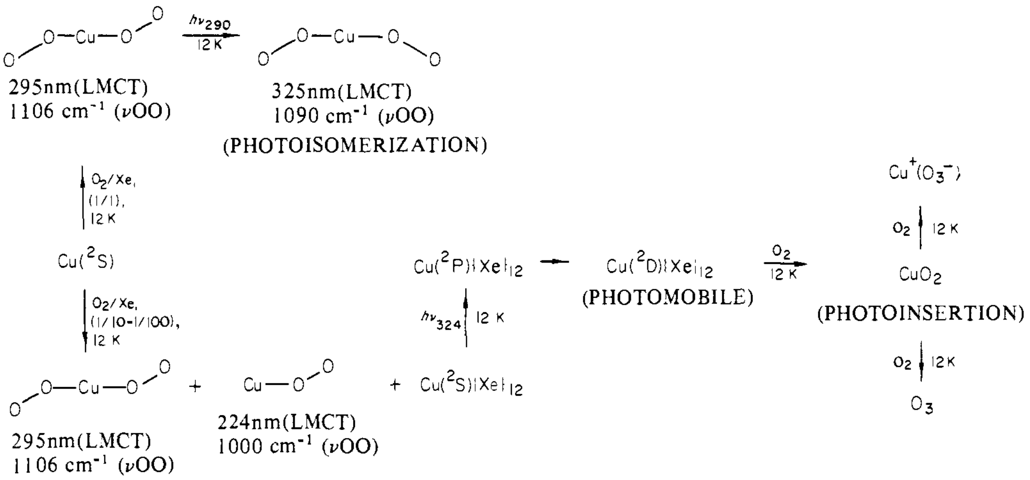
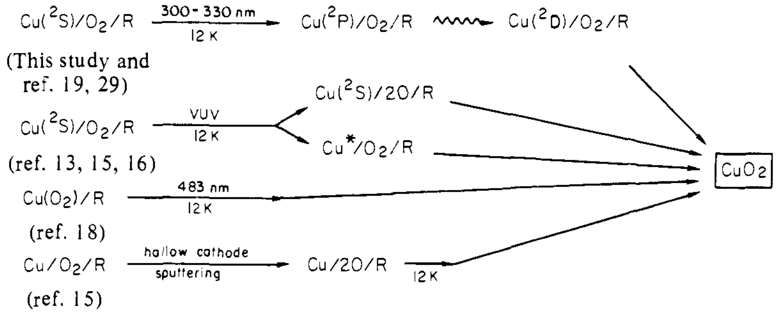
Scheme II. Ground and Excited Electronic State Reactivity Patterns of Copper Atoms towards Dioxygen[a]



[a] UV-visible absorption/fluorescence, infrared $^{16}O_2/^{18}O_2$ isotopic substitution, and ESR spectroscopy together with kinetic data support the steps indicated in the above scheme; see text and references.

Scheme III. Various Pathways for Generating the Species, CuO_2[a]



[a] (R = rare gas; vuv = vacuum UV photolysis).

located mainly on the dioxygen moiety and is best described as η^1-superoxocuprous(I).

On a final note, it is hoped that the opportunities for chemical and spectroscopic characterization of novel reactive species produced by means of "metal atom (cluster) photochemical techniques" of the type described in this paper, will serve as an impetus for further studies in this area.

Note Added in Proof. V. E. Bondybey and J. H. English (private communication) have recently studied the Cu/O_2/rare gas matrix system using laser-induced fluorescence spectroscopy. They conclude that the spectra observed following unfiltered Xe arc photolysis of their matrices are consistent with the formation of a linear, centrosymmetric OCuO triatomic but not a diatomic CuO. Their ground and excited state ν_{Cu-O} stretching frequencies are similar to those observed in our study of CuO_2. They view CuO_2 as a 13-electron "Walsh type" molecule which is expected to be linear in its ground electronic state with the odd electron residing in a π_g orbital. This could account for the non-observation of an ESR spectrum for CuO_2 in our study (g-tensor anisotropy line broadening effect of a $^2\Pi_g$ electronic ground state). Their matrices were very dilute (1/500–1/2000) compared to the most dilute (1/100) ones of our study. Furthermore, the power of their Xe arc lamp was only 50 W as opposed to 1000 W in our study. This may account for the low quantum yield of CuO_2 formation from Cu $^2P \leftarrow {}^2S$ excitation observed in their study compared to ours but a high quantum yield when excited in the Schumann–Runge region of O_2. The former mechanism (our study) requires migration of a Cu ^2D atom to a nearby O_2 molecule for reaction to proceed to CuO_2. This is expected to diminish in importance with O_2 dilution in the rare gas matrix. The latter mechanism (their study) implies either dissociation of O_2 close to a nearby Cu atom, UV photolysis of $Cu(O_2)$ in its absorption around 224 nm, or photoexcitation of a spin-forbidden Cu atom matrix line known to occur in the UV region of the spectrum, resulting in reaction of an electronically excited Cu atom with a nearby O_2 molecule (see Scheme III).

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Registry No. Cu, 7440-50-8; O_2, 7782-44-7; CuO_2, 86853-58-9; $Cu(O_2)$, 12019-06-6; $Cu(O_2)_2$, 73117-15-4; $Cu(O_3)$, 78523-96-3.

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Coupled Oscillator Interpretation of the Vibrational Circular Dichroism of Several Dicarbonyl-Containing Steroids

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Abstract: Vibrational circular dichroism spectra of several steroidal compounds containing two carbonyl groups on six-membered rings have been measured in the C=O stretching region. The results have been compared with the predictions of the degenerate coupled oscillator model. The sign and shape of the predicted spectra agree with the observed results in all but one case. The magnitudes agree to within a factor of 2, with two exceptions. Attempts made to correct the theory for misalignment of dipoles and nondegeneracy of the oscillators are discussed. In general, such corrections did not lead to an improved agreement. Other sources of error are discussed.

Introduction

In recent years, the measurement of circular dichroism of chiral molecules has been extended well into the infrared region.[1] The availability of vibrational circular dichroism (VCD) data for a wide variety of molecular vibrational transitions has rekindled promise of new experimental data of use for studies of molecular conformation or configuration.[2] Fulfillment of this potential is dependent on development and testing of a reliable theoretical model for correlation of structure and spectra. Many such models of varying complexity have been proposed.[3-7] In this paper we shall address the effectiveness of the simplest of these, the coupled oscillator model as formalized by Holzwarth and Chabay (HC).[3]

In their development, HC addressed the chirality and subsequent VCD of two identical, achiral dipolar oscillators μ_a and μ_b, that are mutually oriented in a chiral manner (noncoplanar). The lowest energy transitions of this system are to a pair of coupled excited states, ψ^+ and ψ^-, where $\psi^\pm = \phi_a{}^0\phi_b{}^1 \pm \phi_a{}^1\phi_b{}^0$ and ϕ^0,ϕ^1 represent the ground and first excited state of the single oscillator. The rotational strengths that result in first order for these transitions are equal in magnitude but opposite in sign. If these coupled states are not degenerate, a sigmoidal VCD line shape will result whose sign and magnitude are directly dependent upon geometrical parameters. Because of the chiral nature of their coupling, ψ^+ and ψ^- will not be exactly degenerate and, at minimum, will be perturbed by the electrostatic dipolar coupled interaction (or exciton effect). Subsequent workers have noted that both local chirality and nondegeneracy could be included in a coupled oscillator theory and have, somewhat incompletely, dubbed the simpler version of HC to be the degenerate coupled oscillator (DCO) model.[8]

Previously, we have applied the DCO model to the O—H and C=O stretching vibrations in dimethyl tartrate[9,10] and C=O vibrations in trans-substituted cyclopropanes[11] in an attempt to determine the relative geometry of those oscillators. In these cases, if the assumed geometries were correct, the oscillators were indeed degenerate, and the theoretical and experimental results were in satisfactory agreement. The DCO model also has been extended to polymeric systems[2,12] and has shown to agree with experimental VCD for the amide I (C=O stretch) vibration of those polypeptides having an α-helical secondary structure.[13,14]

In this paper, we present the VCD in the C=O stretching region of several steroidal compounds which contain two six-member-ring ketone carbonyls. These molecules were chosen to provide a variety of angles and interdipolar separations on a rigid framework[15] for two near-degenerate, strong dipolar oscillators. Evaluation of the ability of the DCO model to successfully predict the observed VCD of these transitions should help us determine the conditions in which the DCO model will be useful for structure–spectra correlations. Similar application of the coupled oscillator approach (there termed "exciton chirality") to the electronic CD of these systems has been quite successful.[16] VCD of an unsaturated steroidal ketone in this region has also been reported[17] and compared with predictions for a nondegenerate coupled oscillator.[8a]

Experimental Section

3,6-Dioxo-5α-cholestan (α36), 3,6-dioxo-5β-cholanic acid methyl ester (β36), 3,7-dioxo-5β-cholanic acid methyl ester (β37), 3,12-dioxo-5β-cholanic acid (β312), 7,12-dioxo-5β-cholanic acid (β712), 3α-hydroxy-7,12-dioxo-5β-cholanic acid (β712H), and 3-oxo-5β-cholanic acid were obtained from Steraloids, Inc., dissolved, filtered through activated charcoal, and recrystallized once from $CHCl_3$. They were then studied without further purification in $CHCl_3$ solution. Their structures are indicated schematically in Figure 1. VCD and absorption spectra were obtained on our previously detailed instrument.[1a] $CHCl_3$ solutions of acetone and, in some cases, methyl acetate were prepared to have the same absorbance in the C=O stretching region as found for the above samples. VCD of these achiral solutions were run after each steroid VCD experiment and were used as baselines. The instrument was constantly flushed with nitrogen gas to reduce interfering atmospheric H_2O absorption and thereby improve the VCD baseline. Four to eight scans of VCD with a resolution of 11 cm^{-1}, time constant 10 s, sample concentration of about 0.025 M, and path length of 0.035 cm were averaged for each sample and plotted with the appropriate baseline subtracted.

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