

Two isomers of CuO_2^- : The $\text{Cu}(\text{O}_2)$ complex and the copper dioxide

Hongbin Wu, Sunil R. Desai, and Lai-Sheng Wang^{a)}

Department of Physics, Washington State University, Richland, Washington 99352 and Environmental Molecular Sciences Laboratory, Pacific Northwest Laboratory, MS K2-14, P. O. Box 999, Richland, Washington 99352

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Photoelectron spectroscopy of CuO_2^- has been studied at three detachment wavelengths: 532 nm, 355 nm, and 266 nm. Vibrationally resolved spectra for two distinct isomers are observed: the $\text{Cu}(\text{O}_2)$ complex and the copper dioxide molecule. The $\text{Cu}(\text{O}_2)$ complex has an electron affinity (EA) of 1.503 (10) eV with a ground state vibrational frequency of 530 (50) cm^{-1} . Its first electronic excited state is 7400 (300) cm^{-1} above the ground state. The $\text{Cu}(\text{O}_2)^-$ anion is also observed to undergo photodissociation to $\text{Cu}^- + \text{O}_2$ at both 532 nm and 355 nm detachment wavelengths. The copper dioxide molecule is found to have a high EA of 3.46 (4) eV. Three low-lying excited states are observed within 1 eV above the ground state. The first two excited states of the copper dioxide molecule both possess a totally symmetric vibrational frequency of 640 (60) cm^{-1} . © 1995 American Institute of Physics.

The interaction between Cu atom and O_2 is an important process and has been studied both in low temperature matrix¹⁻⁶ and in the gas phase.⁷⁻⁹ Ground state Cu atom forms a molecular complex with O_2 , which takes on a bent CuOO (C_s) structure.¹⁰⁻¹² Upon photolysis of a Cu/O_2 matrix, a new form of CuO_2 is formed with distinct spectroscopic characteristics that are different from that of the $\text{Cu}(\text{O}_2)$ complex.¹⁻³ This new form has been proposed to be a linear copper dioxide molecule, OCuO .

The $\text{Cu}(\text{O}_2)$ complex has been well established both experimentally¹⁻⁶ and theoretically.¹⁰⁻¹² However, there are few studies on the copper dioxide molecule,^{9,13} and its structure is not firmly established. The electronic structure and low-lying excited states for both isomers are not well known. In this Communication, we report the first gas phase spectroscopic characterization of both these isomers by using anion photoelectron spectroscopy (PES), which provides key electronic structure information for the two molecules.

The CuO_2^- species is produced and studied using a laser vaporization cluster beam apparatus, equipped with a magnetic bottle time-of-flight (TOF) photoelectron analyzer.^{14,15} The details of the apparatus have been published elsewhere.¹⁶ Briefly, the CuO_2^- species is generated by laser-vaporizing a pure Cu target into a He carrier gas containing a small amount of O_2 (0.1 and 5% O_2/He , 10 atm backing pressure).¹⁷ As will be shown below, the CuO_2^- anions, formed in the laser plasma between copper atoms and O_2 , contain two forms of CuO_2^- . Their ratio can be slightly modified by seeding different amounts of O_2 in the He carrier gas. Typically, 10 mJ vaporization laser power (second harmonic output from a Q-switched Nd:YAG laser) is used. The laser beam is focused to a 1 mm diameter spot onto the Cu target. The clusters formed in the laser vaporization nozzle undergo a supersonic expansion to form a collimated beam by two skimmers down stream. The anions are extracted from the cluster beam perpendicularly into a TOF mass analyzer. A mass gate is used, and only allows CuO_2^- to enter the photodetachment chamber. Before, interaction with the detachment laser beam (532 nm, 355 nm, and 266 nm), the

CuO_2^- anions are decelerated by a momentum decelerator to eliminate Doppler broadening to the subsequent photoelectron analyses.¹⁶

In the current version of our magnetic-bottle TOF electron analyzer, a permanent magnet replaces the solenoid electromagnet which was described previously.^{15,16} The permanent magnet is found to yield superior spectral resolution and has been used before.¹⁸ The electron energy resolution in a TOF analyzer depends on the electron energies. The best resolution achieved is about 20 meV FWHM at 1 eV kinetic energy with full deceleration of the anion beam. Typically, the spectral resolution ranges from 20 to 40 meV, depending on the degree of anion deceleration. A weak anion signal often does not allow full deceleration, rendering an inferior electron energy resolution. At 266 nm detachment wavelength, PES spectra are taken at 20 Hz with the cluster beam on and off at alternating laser shot for background subtraction. Both the 532 and 355 nm spectra are taken at 10 Hz as there is no need for background subtraction at these wavelengths. The 266 nm spectrum is smoothed with a 5 meV window while the 355 and 532 nm spectra are smoothed with a 3 meV window. All PES spectra are calibrated with the known spectrum of Cu^- , and are subtracted from the photon energy to arrive at the presented binding energy spectra.

Figure 1(a) shows the spectrum of CuO_2^- obtained at 355 nm detachment wavelength (fluence: 30 mJ/cm^2). Surprisingly, the much familiar peaks due to Cu^- used in our routine calibration are observed in the spectrum as the strongest signals. When the detachment laser fluence is reduced to 7 mJ/cm^2 the ratio of the electron signals due to Cu^- and CuO_2^- is substantially decreased [Fig. 1(b)]. This suggests that the Cu^- anion comes from photodissociation of the parent CuO_2^- ion within the same detachment laser pulse (pulse width 8 ns FWHM). A vibrationally resolved band near 1.5 eV is observed due to CuO_2^- with a frequency of about 530 cm^{-1} . Transitions to excited states of CuO_2 are also observed starting at about 2.4 eV binding energy. The electron signals coming from the CuO_2^- anion are rather weak at the 355 nm

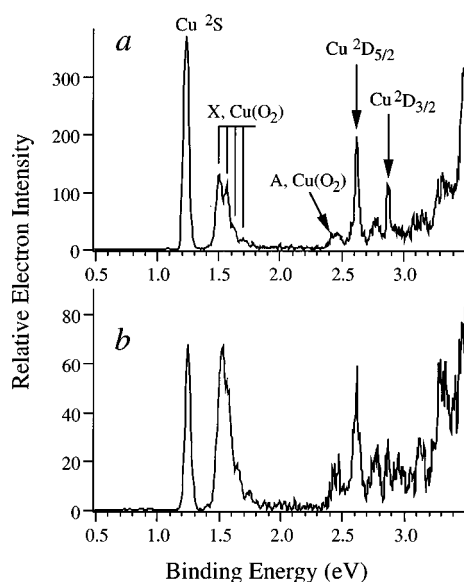


FIG. 1. Photoelectron spectra of CuO_2^- at 355 nm, showing signals from Cu^- due to photodissociation and that from a $\text{Cu}(\text{O}_2)^-$ complex (see text). (a) high laser fluence, 30 mJ/cm^2 ; (b) lower laser fluence, 7 mJ/cm^2 .

detachment wavelength even though the CuO_2^- mass signal is quite strong. However, a strong and rising signal is observed near 3.45 eV binding energy, suggesting strong transitions may be observed at higher photon energies.

Figure 2 displays a PES spectrum of CuO_2^- taken at 266 nm (fluence: 3 mJ/cm^2). Four intense and well-resolved bands (*X*, *A*, *B*, and *C*) are clearly observed. Vibrational structures are resolved for the *A* and *B* bands both with a similar frequency of about 640 cm^{-1} . Interestingly, the Cu^- peaks as seen in the 355 nm spectra (Fig. 1) are not present in the 266 nm spectrum while the 1.5 eV band is observed as a very weak feature. This indicates photodissociation does not take place at 266 nm for the CuO_2^- anion. This is true even at higher detachment laser fluence (up to 8 mJ/cm^2). The intensity of the 1.5 eV band increases slightly with the O_2 content in the He carrier gas when two different gas mixtures are used: 0.1% and 5% O_2/He . But its intensity never exceeds 5% compared to the *X* band. When the 0.1% O_2/He is used, this feature can become undetectable under certain

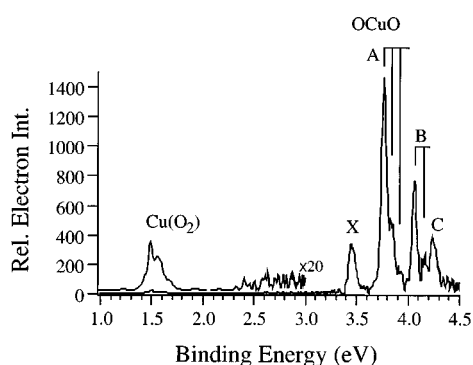


FIG. 2. Photoelectron spectrum of CuO_2^- at 266 nm , showing the strong signals from the copper dioxide isomer at high binding energies and the weak signals from the $\text{Cu}(\text{O}_2)^-$ complex at lower binding energies.

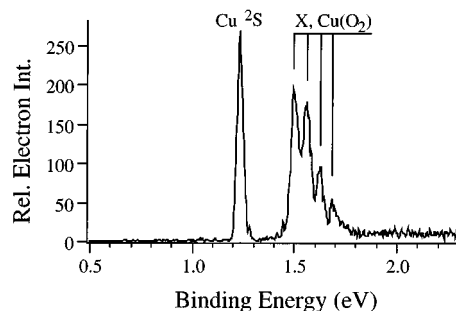


FIG. 3. Vibrationally resolved photoelectron spectrum of $\text{Cu}(\text{O}_2)^-$ complex at 532 nm and the Cu^- peak due to photodissociation.

cluster source condition. On the other hand, the ratio among the *X*, *A*, *B*, and *C* bands remains the same. All these suggest that we are dealing with two entirely different isomers. One isomer, constituting a very small portion of the CuO_2^- anion beam, is probed at 355 nm (Fig. 1). It has a low electron affinity of about 1.5 eV . The second isomer with dominating abundance yields the four main spectral features in the 266 nm spectrum (*X*, *A*, *B*, and *C* in Fig. 2). This isomer has a rather high EA of about 3.46 eV . Therefore, the 355 nm detachment wavelength (3.496 eV) is barely enough to detach this species, yielding the rising signal observed in Fig. 1 at the high binding energy end.

It is reasonable to assume that these two isomers correspond to the two isomers observed in the previous matrix studies.¹⁻⁶ The observed vibrational frequencies provide the key evidence. Figure 3 shows a spectrum taken at 532 nm detachment wavelength (fluence: 40 mJ/cm^2) to enhance the spectral resolution for the 1.5 eV band. The vibrational structure is resolved much better than at 355 nm , yielding a frequency of $530 (50) \text{ cm}^{-1}$. This frequency is in excellent agreement with the $\text{Cu}-(\text{O}_2)$ stretching frequency observed for the $\text{Cu}(\text{O}_2)$ complex,^{2,10,11} while the 640 cm^{-1} frequency observed in the *A* and *B* bands in Fig. 2 agrees with the symmetric stretching frequency assigned to the copper dioxide isomer in previous matrix studies.¹⁻³ Therefore, we conclude that the minor species in our CuO_2^- beam corresponds to the $\text{Cu}(\text{O}_2)$ complex, which has a low EA and is probed at the 532 and 355 nm detachment wavelengths. The dominating species generated in our CuO_2^- beam corresponds to the copper dioxide molecule, which has a very high EA and is probed at the 266 nm wavelength. Due to the weakly-bonded nature of the $\text{Cu}(\text{O}_2)^-$ complex, it is most likely that it is the dissociating species. A previous mass spectrometry study showed that the CuO^+ is the major dissociation product of the copper dioxide positive ion.⁹ We observed neither CuO^- , nor O^- . Hence, we conclude that the copper dioxide anion does not dissociate at any of the three wavelengths used. In the following, we will discuss each isomer separately.

As can be seen in Fig. 1, several excited state features can be identified for the $\text{Cu}(\text{O}_2)$ complex between 2.42 and 3.3 eV binding energies, overlapped with the two ^2D peaks of Cu. These excited state features are hardly observable at 266 nm , as shown in Fig. 2. Thus, the weak abundance of the $\text{Cu}(\text{O}_2)^-$ complex in the anion beam, plus the dissociation and the interference from the Cu^- signal at 355 nm detach-

TABLE I. Spectroscopic constants and energies of the Cu(O₂) complex.

	Term values (cm ⁻¹)	Vibrational frequency (cm ⁻¹)
X	0	530 (50)
A	7,400 (300)	
EA (eV)	1.503 (10)	

ment wavelength, prevents us from characterizing these excited states of the Cu(O₂) neutral complex. We can only conclude that the lowest excited state of Cu(O₂) occurs near 2.42 eV binding energy, as shown in Fig. 1, yielding a term value of about 7,400 cm⁻¹. The obtained spectroscopic information for the Cu(O₂) complex is summarized in Table I.

The ground state of Cu(O₂), ²A'', has a bent CuOO structure with an unpaired electron.¹⁰⁻¹² Its main bonding character can be described as Cu⁺O₂⁻ with covalent bonding character. The bonding energy is measured to be about 15 kcal/mol.⁸ The ground state of the anion is expected to be closed shell with a ¹A'' symmetry. The fact that we observe anion photodissociation at 532 and 355 nm suggests that the anion probably has resonance absorptions at these wavelengths. It appears that the dissociation efficiency is lower at 532 nm than at 355 nm, judged from the moderate Cu to Cu(O₂) peak ratio in Fig. 3 and the high fluence used compared to Fig. 1(a). The anion can dissociate into two final states: I. Cu⁻+O₂, and II. Cu+O₂⁻. Only process I is observed in our experiment. On the basis of the neutral Cu(O₂) bonding energy and our measured EA for Cu(O₂) and the known EAs of Cu(1.235 eV) and O₂ (0.451 eV), we estimate the bonding energies of Cu(O₂)⁻ anion with respect to I and II to be 0.93 and 1.71 eV, respectively. Note the accuracy here is limited by the bonding energy of the neutral Cu(O₂) which has a quite large error bar.^{8,11} The large bonding energy difference between processes I and II explains why only Cu⁻ is observed in the dissociation process.

Now we turn to the copper dioxide isomer spectrum as shown in Fig. 2. The X band represents the ground state of the neutral molecule, yielding an EA of 3.46 eV, which is considerably higher than the Cu(O₂) complex. The A, B, and C bands represent low-lying excited states of the copper dioxide molecule. Both the A and B bands exhibit vibrational structures with a similar frequency of about 640 cm⁻¹. As pointed out above, this is in good agreement with the frequency of the symmetrical stretching mode derived from matrix studies which gave a value of 610 cm⁻¹.¹⁻³ The obtained spectroscopic information for the copper dioxide molecule is gathered in Table II.

We will use a simple molecular orbital scheme to give a

TABLE II. Spectroscopic constants and energies of the copper dioxide molecule.

	Term values (cm ⁻¹)	Vibrational frequency (cm ⁻¹)
X	0	
A	2,500 (150)	640 (60)
B	4,960 (150)	640 (60)
C	6370 (250)	
EA (eV)	3.46 (4)	

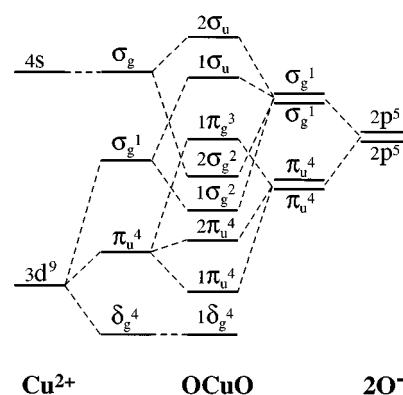


FIG. 4. A schematic molecular orbital diagram for the copper dioxide molecule.

qualitative interpretation of the PES spectrum and the electronic structure of the copper dioxide molecule, whose true ground state structure is not known. However, a linear OCuO structure is consistent with previous matrix studies and was assumed for the copper dioxide isomer previously.¹⁻³ There is only one previous *ab initio* calculation on the OCuO isomer.¹³ The authors adopted a linear structure and calculated its low-lying electronic states without optimizing the geometry. The predicted first excited state is 2 eV above the ground state, and this put it in doubt that this calculation is useful to interpret the PES spectrum at hand. Ozin *et al.* proposed a O⁻Cu²⁺O⁻ formulation to describe the bonding in the copper dioxide molecule.² This is a reasonable assumption by considering the related diatomic CuO, which has been more extensively studied.¹⁹ The CuO molecule can be approximately described as Cu⁺O⁻ with significant covalent bonding character. Bondybey and English discussed the bonding in OCuO by considering it as a 13 electron system with a linear ground state structure and disregarding the Cu 3d as a closed shell.³ The later assumption is problematic because it is expected that there should be more extensive covalent bonding contributions to the Cu–O bond between the Cu 3d and O 2p. We proceed to discuss the bonding in the copper dioxide molecule by considering a Cu²⁺ (*d*⁹) ion interacting with 2 O⁻ (*p*⁵) ions in a linear structure.

Figure 4 shows a schematic of the MOs formed from the 3d and 4s orbitals of the Cu atom with the 2p orbitals of the O atoms. The relative ordering and occupations of these MOs are not known. Figure 4 depicts one such possibility, which we think is reasonable based on the MOs from the CuO diatomics, and can give a reasonable account of the observed spectrum. The ground state of CuO is ²Π with an MO configuration of 1δ⁴1π⁴1σ²2σ²2π³, where 1δ⁴1π⁴1σ² are mainly from Cu⁺ 3d and 2σ²2π³ are mainly from O⁻ 2p, respectively. In the CuO⁻ anion, whose PES spectrum has been studied before,²⁰ the extra electron is added to the 2π orbital, yielding a closed shell ground state for the anion. The detachment of a 2π electron yields the ²Π ground state with a spin-orbit splitting of 277 cm⁻¹. The detachment of a 2σ electron yields a ²Σ state, which has a higher intensity than the ²Π peak. We have also obtained a PES spectrum of CuO⁻ at 355 nm.²¹ Our resolution is not high enough to

resolve the spin-orbit component in the ${}^2\Pi$ state, resulting in a broader peak.

According to Fig. 4, the copper dioxide ground state should be ${}^2\Pi_g$, with a configuration of $1\sigma_g^4 1\pi_u^4 2\pi_u^4 1\sigma_g^2 2\sigma_g^2 1\pi_g^3$. Therefore, the OCuO^- anion should have a closed shell ${}^1\Sigma_g^+$ ground state. The $1\pi_g$ and $2\sigma_g$ orbitals are similar to the 2π and 2σ orbitals in CuO . Removal of an electron from these two orbitals results in the X and A bands that also have similar intensity ratio compared to that of the CuO^- spectrum, resulting in a ${}^2\Pi_g$ and a ${}^2\Sigma_g^+$ state, respectively. The X band has a width of about 75 meV compared to the 50 meV peak width of the A band, consistent with the assignment of the ${}^2\Pi_g$ ground state which is expected to have a small spin-orbit splitting. The C band also has a broader width similar to the X band and is assigned to the detachment of a $2\pi_u$ electron, yielding a ${}^2\Pi_u$ state also with a small spin-orbit splitting. The B band is assigned to the detachment of a $1\sigma_g$ electron, resulting in a ${}^2\Sigma_g^+$ state. This is a plausible assignment for the OCuO^- PES spectrum. A more definitive assignment will require accurate *ab initio* calculations for the molecular structure and its low-lying electronic states. The OCuO copper dioxide molecule may be considered the simplest case involving an open d shell and should be a good test case for *ab initio* calculations intended to treat open d shells.

In conclusion, we have reported vibrationally resolved PES spectra of the two isomers of CuO_2 and provided important electronic structure information. The $\text{Cu}(\text{O}_2)^-$ anion complex is found to dissociate at 532 and 355 nm, consistent with its weakly-bonded nature, and its bonding energies are estimated based on the known neutral value. The $\text{Cu}(\text{O}_2)$ complex has a low electron affinity close to that of Cu atom and its first excited state is about $7,400\text{ cm}^{-1}$ above its ground state. The copper dioxide molecule is found to have a very high electron affinity and three low-lying excited states are observed. The spectrum is interpreted based an MO picture formed from a Cu^{2+} and 2O^- in a linear geometry. In light of the importance of the nature of chemical bonding in copper dioxide in other field of study, like in copper oxide based-high temperature superconductors, the lack of theoretic

studies on this molecule is surprising. The information provided in the current work will be useful for the confirmation of an accurate theoretical description of the chemical bonding in the copper dioxide molecule.

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^{a)}To whom correspondence should be forwarded.

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