Photoelectron Spectroscopy of CuO⁻

Mark L. Polak, Mary K. Gilles, Joe Ho, and W. C. Lineberger*

Joint Institute for Laboratory Astrophysics, University of Colorado and National Institute of Standards and Technology and Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0440 (Received: February 13, 1991)

Laser photoelectron spectroscopy has been used to study the CuO⁻ anion and neutral CuO molecule. Analysis of the photoelectron spectrum yields an electron affinity of 1.777 (6) eV for CuO-. Equilibrium bond lengths and vibrational frequencies are obtained from a Franck-Condon analysis of the relative intensities of the observed transitions, yielding a CuO⁻ bond length of 1.670 (10) Å and a CuO⁻ vibrational frequency of 739 (25) cm⁻¹. The analysis also yields a bond length (1.704 (10) Å) and a vibrational frequency (682 (25) cm⁻¹) for the Y²Σ⁺ excited state of CuO⁻.

Introduction

Although neutral diatomic transition-metal monoxides have been the subject of extensive spectroscopic investigation,1,2 very little is known about the corresponding anions. To our knowledge there have been no reports of molecular parameters (i.e., bond lengths, vibrational frequencies, electron detachment energies, etc.) for these anions, with the exception3 of FeO⁻. In addition, ab initio studies of these metal monoxides have generally been confined to the neutral molecule or the corresponding cation.

Copper monoxide (CuO), and the corresponding anion, CuO⁻, are no exception to this pattern. The electronic spectra and structure of CuO, both experimentally and theoretically determined, have been reviewed by Steimle and Azuma,4 Appelblad et al.,5 and most recently by Merer.2 In brief, numerous spectroscopic investigations of CuO have mapped out most of the electronic energy levels (more than 15 of them) below 25 eV. The primary gas in the discharge is helium (0.4 Torr, flow rate = 5 SLPM) with trace amounts of argon to promote sputtering and trace oxygen to form oxides such as CuO-. The ions formed

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Figure 1. Photoelectron spectrum showing transitions from ground-state 
CuO\(\text{^0}\) to ground-state CuO(A'\(\Sigma\)\(^\text{II}\)). Each vibrational transition is split into 
two components by the CuO \(\text{^1}\) spin-orbit splitting. The experimental 
data are shown as points, the fit to the spectrum is shown as a solid curve, 
and the rotationless origins of each vibrational line are illustrated as solid 
vertical lines.

are allowed to equilibrate with the buffer gas in a \(1/4\) cm flow tube 
following the discharge. The negative ions formed in this source 
are extracted, focused, and accelerated to form an ion beam and are 
mass-selected in a Wien filter. A typical CuO\(\text{^-}\) current after 
kinetic energies to an accuracy of \(\pm 5\) meV.

Figure 2. Photoelectron spectrum showing transitions from ground-state 
CuO\(\text{^0}\) to the first excited state of CuO(Y\(\Sigma\)\(^\text{II}\)). It is illustrated in the 
same manner as for Figure 1.

Results and Analysis

Figures 1 and 2 display the photoelectron spectrum of CuO\(\text{^0}\) 
obtained with a photon energy of 3.531 eV and plotted in terms 
of electron binding energy \((h\nu - \text{eKE})\). The entire electron kinetic 
energy region of 0.10 eV up to the photon energy was searched; 
however, only the regions shown in Figures 1 and 2 displayed any 
photoelectron signal. The series of peaks in Figure 1 were assigned 
as vibrational transitions from the anion ground state to the \(\text{^2}\)\(\Sigma\) ground state of the neutral. The CuO spin-orbit splitting and 
vibrational frequency evident in the photoelectron spectrum are 
consistent with the values measured by Appelblad et al.\(^1\) for the 
\(\text{^2}\)\(\Sigma\) state, confirming this assignment. The vibrational progression 
in Figure 2 was assigned as a transition from the anion ground 
state to the Y\(\Sigma\)\(^\text{II}\) state of CuO based on the origin binding energy 
lying 7880 cm\(^{-1}\) above the ground-state binding energy, in good 
agreement with previous measurements.\(^2\)

Franck-Condon analyses of the vibrational progressions were 
employed to determine the magnitudes of the bond length changes 
involved in the photodetachment transitions; however, the direction 
of the bond length changes could not be determined from the 
analysis. In the analysis, the anion ground-state bond length was 
constrained to be smaller than that of the neutral ground state 
(\(\text{^3}\)\(\Sigma\)), because the larger vibrational frequency (739 cm\(^{-1}\) vs 640 

cm\(^{-1}\)) of the anion and the experimentally determined dissociation 
energy (from thermochemical cycle, see below) indicate that the 
anion is more strongly bound than the neutral. Similarly, one 
expects the bond length of the neutral Y\(\Sigma\)\(^\text{II}\) state to fall between 
that of the anion and neutral ground states because of its inter-
mediate vibrational frequency (680 cm\(^{-1}\); constraining the bond 
length to be larger than that of the anion ground state leads to 
the result that is consistent with these expectations.

A Franck-Condon analysis of the vibrational progression in 
Figure 1 was performed as follows. The diatomic potential 
functions were modeled as Morse oscillators; the neutral Morse 
parameters are fixed along with the neutral spin-orbital splitting 
(279 cm\(^{-1}\)) at the literature values,\(^1\) while the anion parameters 
\((r_\infty, \omega_\infty, \omega_x, y, \alpha, \beta, \gamma)\) are allowed to vary. Franck-Condon factors 
are determined by numerical integration of the Laguerre wave function 
solutions\(^2\) to the Morse potential. The rotational contours of each 
transition are modeled\(^2\) as a convolution of the instrumental function 
(a Gaussian with 10 meV fwhm) with a rigid-rotor rotational spectrum at 1200 K. The 
unusually high rotational temperature was necessary to account for the observed line width 
(\(15\) meV fwhm) and is likely due to rotational heating of the ions 
in the extraction process because exceptionally high extraction 
voltages (\(10-20\) V) were required for this particular experiment. Because we believe the ground state of CuO\(\text{^0}\) to be \(1\Sigma^+\) (see Discussion), the rotational spectrum was simulated as a perpen-

\(\begin{align*}
\text{de/d\Omega} &= (\sigma_0/4\pi)[1 + (\beta/2)(3 \cos^2 \theta - 1)] \\
\text{where \(\theta\) is the angle between the laser polarization vector and the} \\
\text{direction of electron ejection and \(\beta\) is the asymmetry parameter} 
\text{(-1 \leq \beta \leq 2). In order to measure \(\beta\) for each transition, the} 
\text{photoelectron spectrum was measured at \(\theta = 0^\circ\) and \(\theta = 90^\circ\).} 
\text{To determine \(\beta\) accurately for one peak, the angular dependence} 
\text{of the largest peak in the spectrum was carefully measured in 10^\circ} 
\text{intervals, and the observed intensities were least squares fit to eq} 
\text{1. This accurately determined \(\beta\) could then be used to scale the} 
\text{\(\theta = 0^\circ\) and \(\theta = 90^\circ\) spectra with respect to one another.} 
\end{align*}\)


TABLE I: Constants for the States of CuO and CuO\(^{+}\) Accessed in the Photoelectron Spectrum (Uncertainties Included Only for Those Constants Determined in This Work)

<table>
<thead>
<tr>
<th>Constant</th>
<th>CuO((X^1\Pi))</th>
<th>CuO((X^2\Pi^+))</th>
<th>CuO((Y^2\Sigma^+))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_0), cm(^{-1})</td>
<td>-14332 (48)</td>
<td>0</td>
<td>7880 (48)</td>
</tr>
<tr>
<td>(r_0), (\AA)</td>
<td>1.670 (10)(^a)</td>
<td>1.7244(^b)</td>
<td>1.780 (4)(^b)</td>
</tr>
<tr>
<td>(\omega_0), (\AA)</td>
<td>739 (25)</td>
<td>640.17(^c)</td>
<td>662 (25)</td>
</tr>
<tr>
<td>(\omega_0^x, \text{cm}^{-1})</td>
<td>d</td>
<td>4.45(^d)</td>
<td>d</td>
</tr>
</tbody>
</table>

\(^a\)Spin-orbit constant fixed at ref 11 value of 279 cm\(^{-1}\). \(^b\)Directions of bond length changes were assumed as explained in text. \(^c\)Fixed at ref 11 value. \(^d\)Could not be determined in fit.

dicular (\(\Pi-\Sigma\)) transition. The modeling of the rotational contour is necessary to properly account for the difference (5 meV) between the peak center and the true rotationless origin.

The following parameters were allowed to vary in a least-squares fit to the data: the anion Morse parameters, the \((0,0)\) position and peak height, and the vibrational temperature of the negative ion. The constants determined in the fit are listed in Table I, and the resulting simulated spectrum is illustrated in Figure 1. The error bars of the parameters given are determined from examining the change in \(x^2\) of the fit as the parameters are fixed at different values; these error bars approximately represent a 2\(\sigma\) level of uncertainty. Because only one vibrational hot band is observed \((T_{\text{vib}} = 500 \text{ K})\), the anharmonicity of the anion could not be determined; the large error limits on the harmonic vibrational frequency in Table I partially reflect this. The adiabatic electron affinity of CuO can be determined from

\[
EA(CuO) = hv(\text{laser}) - eKE(0,0) \tag{2}
\]

to be 1.777 (6) eV.

The Franck-Condon analysis for the spectrum in Figure 2 was carried out by fixing the anion Morse parameters and vibrational temperature at the values determined in the previous fit. The constants determined in this fit for the \(Y^2\Sigma^+\) state are listed in Table I; the simulated spectrum is shown in Figure 2. It should be noted that our choice for the direction of the bond length change in this fit is based solely on the change in vibrational frequency. While we feel that this is the best choice given the limited information available, independent confirmation would require the observation of the \(Y^2\Sigma^+\) state with rotational resolution.

The adiabatic dissociation energy of CuO\(^{+}\) (CuO\(^{-}\) \(\rightarrow\) Cu(S) + O\(^{(2P)}\)) can be determined from

\[
D_0(CuO^{+}) = D_0(CuO) - EA(CuO) - EA(CuO^{+}) \tag{3}
\]

The dissociation energy of CuO has been determined to be 2.79 (15) eV from mass spectrometric measurements of high-temperature equilibria, and the electron affinity of O\(^{-}\) (1.461 122 (3) eV) has been determined from photodetachment threshold measurements. Using the value for EA(CuO) obtained from this work, we obtain \(D_0(CuO) = 3.11 (15) \text{ eV} (72 (3) \text{ kcal/mol})\). The accuracy of this dissociation energy is clearly limited by the mass spectrometric determination of \(D_0(CuO)\). A quantity we measure very accurately is

\[
D_0(CuO^{-}) - D_0(CuO) = 0.316 (6) \text{ eV} (7.29 (14) \text{ kcal/mol})
\]

clearly demonstrating that CuO\(^{-}\) is more strongly bound than CuO.

Finally, the polarization measurements determined \(\beta\) for each electronic state; no vibrational dependence of \(\beta\) was measurable. For detachment to the \(\Pi\) ground state \(\beta\) was measured to be 0.35 (10), and for the \(2\Sigma^+\) excited state \(\beta = 1.5 (2)\).

**Discussion**

In the ensuing discussion, we attempt to explain the experimentally observed bond changes and photoelectron angular distributions in terms of simple molecular orbital concepts. It is firmly established that the X\(\Pi\) and Y\(2\Sigma^+\) states of CuO are well described by \(\sigma\tau^2\) \((\pi\text{ hole})\) and \(\sigma\tau^4\) \((\sigma\text{ hole})\) configurations. Assuming a simple one-electron process for photodetachment, this would suggest a \(\sigma\tau^2\) CuO\(^-\) ground state. We find that this configuration is the most likely ground state for CuO\(^-\).

The lowest lying dissociation asymptotes of CuO\(^{+}\) correspond to the ground-state atoms: Cu\((S, 3d^{10}4s^2) + O\(^{(2P, 2P)}\) and the 0.23 eV higher energy asymptote Cu\((S, 3d^{10}4s^2) + O\(^{(2P, 2P)}\). Because being higher in energy, the Cu\(^{+}\) + O\(^{+}\) asymptote is not favorable for bonding, because of the closed-shell configuration of Cu\(^{+}\). This leaves the Cu + O\(^{+}\) asymptote, which from can form \(3\Sigma^+\) and \(1\Pi\) states.

The molecular orbital configurations of these states are described in an ab initio study by Bauschlicher and Langhoff on the isoelectronic species ZnO, which has an isoelectronic asymptote to that of CuO\(^-\): Zn\(^{(2S)}\) + O\(^{(2P)}\). The \(\Pi\) states correspond to a \(p\) \(\pi\) hole on the oxygen, which couples to the copper 4\(s\) to yield either a singlet state with a covalent bond or a triplet state:

\[
\Sigma^+: 3d^{10}(4s + 2p)^22p^x \tag{4}
\]

Likewise, the \(\Pi\) states correspond to a \(p\) \(\pi\) hole on the oxygen with the configuration

\[
1\Pi: 3d^{10}2p^24s^12p^x \tag{5}
\]

For ZnO, the bonding of these states can be described in terms of a covalent picture for the \(3\Sigma^+\) state and in terms of an ionic picture \((Zn^{+}O^-)\) for the other three electronic states. The ab initio calculations of ZnO predict a \(1\Sigma^+\) ground state, however, the \(3\Pi\) state is of only slightly higher energy (209 cm\(^{-1}\)). Electrostatic interactions favor the ionic \(3\Pi\) state, while diminished Pauli repulsion favors the more covalent \(3\Sigma^+\) state, and these effects are of comparable magnitude. In the case of CuO\(^-\), one expects the electrostatic interaction to be greatly diminished—to first approximation the electrostatic term for the \(3\Pi\) state of CuO\(^+\) results only from an ion–neutral interaction. Therefore, for CuO\(^-\), the \(3\Sigma^+\) state is the most likely ground state and this state is even more heavily favored than in the case of ZnO.

Starting with the ground-state configuration of CuO\(^-\), \(3d^{10}(4s + 2p)^22p^x\), detachment of a \(p\) electron results in a \(\sigma\tau^4\(1\Sigma^+\) CuO configuration, and detachment of a \(\sigma\) electron results in a \(\sigma\tau^2\(1\Sigma^+\) state. The experimental results show that both orbitals are slightly bonding; detachment of the \(\pi\) electron results in a 0.05-Å increase in bond length, while detachment of the \(\sigma\) electron yields a 0.03-Å increase. The simple single-configuration picture we are using would indicate that the \(\pi\) orbital is nonbonding and the \(\sigma\) orbital is bonding; however, ab initio calculations on isoelectronic ZnO\(^3\) indicate that O\(^{-}\) 2\(p\) \(\pi\) donation to the metal-centered 4\(p\) \(\sigma\) orbitals plays a significant role (4\(p\) occupancy as high as 0.54) in the bonding of the \(3\Sigma^+\) state, suggesting the same could be true for CuO\(^-\). Furthermore, the large spin–orbit constant measured for the X\(\Pi\) state of CuO (279 cm\(^{-1}\)) indicates that the \(\pi\) electron cannot be completely localized on the oxygen.²

The observed photoelectron angular distributions are consistent with this picture. For photodetachment near threshold \((eKE < 2-4 \text{ V})\), detachment from an \(s\)-like orbital causes electron ejection parallel to the laser polarization to be favored (\(\beta\) positive), while detachment from higher angular momentum orbitals results in more isotropic or perpendicular ejection (\(\beta\) close to 0 or negative).²⁰ The observed \(\beta\) of 1.5 (parallel ejection is favored 10-fold over perpendicular) for detachment to the Y\(2\Sigma^+\) state is consistent with detachment from the \((4s + 2p)\) \(\sigma\) orbital, because of the large \(s\) contribution to the orbital. The relatively isotropic distribution \((\beta = 0.35)\) observed for detachment to the X\(\Pi\) state is not consistent with detachment from a completely oxygen-centered nonbonding \(O\) orbital, since photodetachment studies²⁰ of O\(^{-}\) have shown that detachment with 1.7 eV of an \(O\) \(2p\) electron is expected to yield \(\beta = -0.8\). This is in good agreement with the observed geometry change (+0.054 Å) and dissociation energy change (−0.36 eV) which both show that the detachment orbital cannot


be entirely nonbonding; in fact, the experimentally measured geometry changes would indicate that it is at least as bonding as the $\sigma$ orbital.

Finally, it must be noted that the preceding description is likely an oversimplification. Because of a closed-d-shell (3d$^0$) configuration, CuO and CuO$^-$ are more simply described than most transition-metal oxides; nevertheless, the details of the bonding in CuO have been the subject of some controversy. Our simplified picture is, however, sufficient to account for the essential features of the information available in the photoelectron spectrum, suggesting that it is a satisfactory first-order description.

Conclusion
Photoclectron spectroscopy has been used to measure transitions from the CuO$^-$ ground state to the two lowest lying electronic states of neutral CuO, the $X^2\Pi$ and $Y^2\Sigma^+$ states. The electron affinity of ground-state CuO was determined to be 1.777 (6) eV. Franck-Condon analyses of the vibrational progressions in both electronic transitions were used in conjunction with previously determined$^{14}$ spectroscopic parameters for the CuO ground state, to determine previously unknown vibrational frequencies and bond lengths for the CuO$^-$ ground state and the first excited state of CuO($Y^2\Sigma^+$). Our results can be explained in terms of detachment from a $1\Sigma^+$ CuO$^-$($\sigma^+$)$^*$ ground state to the CuO $X^2\Pi$ ($\pi$ hole) and $Y^2\Sigma^*$ ($\sigma$ hole) states.

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\[ \text{H NMR Procedure To Estimate the Extent of Metal Surface Covered by TiO}_x \text{ Overlayers in Reduced Rh/TiO}_2 \text{ Catalysts} \]

J. P. Belzunegui, J. M. Rojo,* and J. Sanz

\textit{Instituto Ciencia de Materiales, CSIC, C/Serrano 115 dpdo, 28006-Madrid, Spain}  
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Oxidation at different temperatures of an Rh/TiO$_2$ sample in the SMSI state has been studied by H NMR spectroscopy. In the range 273-473 K electronic perturbation of the metal is progressively eliminated. However, removing of TiO$_2$ species, which block physically the metal adsorption sites, requires oxidation at 673 K. At this temperature metal particles recover their maximum hydrogen adsorption capacity. From the difference between adsorbed hydrogen in the sample oxidized at 473 and 673 K, a measurement of the metal surface covered by TiO$_2$ species has been obtained. The influence of reduction pretreatments (temperature and time) on the degree of TiO$_2$ coverage has been also analyzed.

Reduction under flowing H$_2$ at 773 K of catalysts formed by group VIII noble metal supported on TiO$_2$ inhibits H$_2$ and CO adsorption on the metal. This phenomenon was first ascribed to a strong metal-support interaction (SMSI).$^{12}$ The two most accepted causes for the SMSI state are (i) coverage by titanium suboxide (TiO$_x$, 1 < x < 2) species of metal particles and (ii) formation of bondings between titanium cations and metal atoms.$^{13}$ Recently, it has been shown$^{16}$ in Rh/TiO$_2$ catalysts that the SMSI state is established in two consecutive stages: one when the catalyst is reduced in the range 373-673 K and the other for reduction temperatures above 673 K. In the first stage, the metal adsorption loss was related to incorporation of hydride-like species into the metal-support interface while, in the second one, formation of rhodium-titanium bondings and coverage by TiO$_2$ species of metal particles have been proposed to explain experimental data. A TiO$_2$ overlayer on metal particles has been observed$^7$ by HRTEM in Rh/TiO$_2$ catalysts reduced in H$_2$ at 773 K. However, information concerning hydrogen adsorption Suppression due to physical blocking of metal adsorption sites by that overlayer in real catalysts is still limited. In this work, we have investigated by H NMR spectroscopy elimination of SMSI state by oxidation of an Rh/TiO$_2$ sample at increasing temperatures. From analysis of NMR spectra corresponding to the sample oxidized at 473 K after different reduction treatments, a measurement of the metal surface covered by TiO$_2$ species has been obtained.

The catalyst Rh(2.5 wt %)/TiO$_2$ was prepared by the incipient wetness method described elsewhere.$^{17}$ Metal particle sizes are in the range 2-10 nm. Thermal treatments of the sample up to 773 K were performed in Pyrex tubular cells with high-vacuum stopcocks. The catalyst reduced in flowing H$_2$ at 773 K for 1 h is called hereafter H. Two types of experiments were done: (i)