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Observation of a long-lived triplet excited state and strong electron correlation effects in the copper oxide anion (CuO^-) using cryogenic photoelectron imaging

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In this Note, we report photoelectron imaging of cryogenically cooled CuO^- anion ($^1\Sigma^+$) and the observation of a long-lived triplet electronically excited state ($^3\Pi$) of CuO^-. The photoelectron spectrum of vibrationally cold CuO^- is obtained at 355 nm along with photoelectron angular distributions, enabling the assignment of the long-lived excited state and revealing the multiconfigurational nature of the ground state of CuO ($^2\Pi$).

Metastable triplet excited states of diatomic molecules, such as alkali dimers, have received renewed interest as products of cold collisions in atom trapping and Bose–Einstein condensation experiments, where diatomic species are formed as products of three-body collisions between two atoms and a resonant photon.[1–3] The production of cold molecules is not trivial, with only a few methods such as photo-association and Feshbach resonance association of cold atoms being the main mechanisms.[2,4] However, such techniques are reliant on the laser-cooling of atoms, limiting their general effectiveness on molecular systems.

Anions are rarely considered suitable targets for ultracold chemistry studies, despite their relevance to astrophysics and chemistry.[5,6] There are two major issues concerning the production of cold anions for such studies. First, the production of anions is difficult and requires methods that introduce significant heat of formation that must be quenched effectively. Second, state-specific control is challenging: valence-bound excited states are not common for anions because the electron binding energies of anions are usually low.[7] On the other hand, anions produced through high energy methods, such as ion sputtering or laser vaporization, have a relatively high probability of producing some population of excited electronic states during the ion formation process. If such excited states have long lifetimes, state-specific reactions of cold anions may be achievable. Furthermore, anions in the interstellar medium are typically formed in electronically excited states, which may be long-lived, depending on the rates of radiative association and three-body collisions.[5,6]

Our group previously reported the photoelectron spectra of CuO^- at various photon energies.[8] During this early study, distinct weak spectral features were observed at energies much lower than the electron detachment threshold, suggesting the population of a metastable electronically exited state of the anion. The ground state of CuO^- is closed-shell ($^1\Sigma^+$), and the observed excited state was assigned as the lowest triplet state ($^3\Pi$), which was confirmed subsequently by theoretical calculations.[9,10] We have revisited this system as a testing case with our recently renovated photoelectron imaging apparatus newly equipped with a cryogenically cooled ion trap coupled to a laser vaporization cluster source.[11,12] We have found surprisingly that the triplet excited state of CuO^- survived the 45 ms trapping and cooling time via collisions with a 1 mTorr He/H_2 buffer gas.

The CuO^- anions were produced by laser-vaporization of a copper disk target with a He carrier gas seeded with 1% O_2. Following a skimmer, the collimated molecular beam traveled straight to a 3D Paul trap held at 4.1 K. Anions were trapped for 45 ms and cooled through collisions with an ~1 mTorr He/H_2 buffer gas (19:1 by volume), before being extracted into a time-of-flight mass spectrometer. The cold CuO^- anion was mass-selected and detached by a 355 nm laser beam in the interaction zone of a velocity-map imaging (VMI) spectrometer.[13] In order to capture low binding energy electrons (high kinetic energies), we used a high extraction voltage

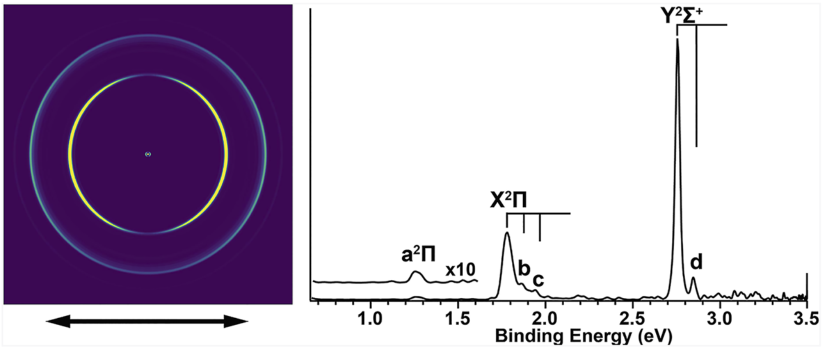

FIG. 1. Photoelectron image and spectrum of cold CuO⁻ at 355 nm (3.4958 eV). The double arrow indicates the laser polarization.

TABLE I. Assignment of the observed transitions for CuO and CuO⁻.

Peak	Assignment	Binding energy (eV)	β
a	$^3\Pi \rightarrow {}^2\Pi$	1.27(1)	0.88
X	$^1\Sigma^+ \rightarrow {}^2\Pi$, v = 0	1.78(1)	0.72
b	v = 1	1.86(2)	0.63
c	v = 2	1.92(2)	0.03
Y	$^1\Sigma^+ \rightarrow {}^2\Sigma^+$ v = 0	2.76(1)	1.83
d	v = 1	2.85(2)	1.81

of −800 V on the VMI lens at the expense of energy resolution. The obtained photoelectron image and spectrum of CuO⁻ is shown in Fig. 1. This spectrum is similar to our previous 355 nm data using a magnetic-bottle analyzer,[8] but its resolution is lower than that reported by Polak *et al.*,[14] who resolved the spin–orbit splitting in the detachment transition to the CuO ground state ($X^2\Pi$). The major difference in the current spectrum is the elimination of vibrational hot bands.

The results and assignments for the spectrum in Fig. 1 are summarized in Table I, along with the anisotropy parameters (β) of each transition.[15] The measured binding energies are similar to those we reported previously.[8] More accurate values were reported by Polak *et al.*[14] The spectroscopic constants of the X and Y ($^2\Sigma^+$) states of CuO were known accurately from optical and microwave spectroscopies.[16–18] The most surprising observation in the current spectrum was the presence of peak *a* ($^2\Pi$), which was due to the triplet excited state of the CuO⁻ anion (Table I).

In the ionic bonding limit, the valence molecular orbitals (MOs) of CuO⁻ are

$$^1\Sigma^+ : \ 3d^{10}2p\sigma^2 2p\pi^4 4s\sigma^0. \tag{1}$$

The peak *a* is derived from electron detachment from the triplet excited state, due to the promotion of an electron from the 2pπ HOMO to the 4sσ LUMO,

$$^3\Pi : \ 3d^{10}2p\sigma^2 2p\pi^3 4s\sigma^1 \tag{2}$$

to the $^2\Pi$ ground state of CuO. The *p*-wave distribution of peak *a* ($\beta = 0.88$, Table I) is consistent with the detachment of the 4sσ electron. This anion excited state was not observed by Polak *et al.*,[14] who only presented the spectra around transitions to the X and Y states. In our earlier study, we found that the detachment cross section from the $^3\Pi$ excited state exhibited strong photon energy dependence.[8] The relative intensity of peak *a* was about 2% of the X band at 355 nm, similar to what we observed currently in Fig. 1. However, at 532 nm, the relative height of peak *a* was more than 30% of that of the v = 0 peak of band X. The time scale of our previous experiment was about 40 μs. It is astonishing that we observed the same population of the triplet excited state of CuO⁻ in the current experiment, after the anions were trapped and cooled by collisions with the He/H_2 buffer gas for 45 ms in the 3D Paul trap. This observation suggests an extremely stable and long-lived triplet excited state for CuO⁻ (>45 ms).

The X ($^2\Pi$) and Y ($^2\Sigma^+$) bands represent electron detachment from the $2p\pi^4$ HOMO and the $2p\sigma^2$ HOMO-1, respectively. Both bands show clear *p*-wave distributions with positive β values (Fig. 1). The β value of the X band seems to strongly depend on the final vibrational state (Table I). Our β values are consistent with those reported by Polak *et al.*,[14] who reported 0.35 and 1.5 for the X and Y bands, respectively. While the positive β value for the Y band is expected for the electron detachment from the 2pσ MO, the positive β value for the X band is not consistent with electron detachment from the 2pπ MO, which should yield an $s + d$ wave angular distribution with a negative β value. Polak *et al.* explained the positive β value by suggesting that the 2pπ MO "cannot be entirely nonbonding,"[14] as revealed by the increased bond length in the ground state of CuO relative to that of the CuO⁻ anion. Indeed, an early *ab initio* calculation on CuO incorporating electron correlations using the configuration interaction (CI) and coupled pair functional (CPF) methods yielded spectroscopic properties in excellent agreement with experiment.[19] The CI and CPF methods found three dominant electron configurations for the ground state of CuO ($X^2\Pi$),[17,19]

$$Cu^+(3d^{10})O^-(2p^5): \quad 3d\sigma^2 3d\delta^4 3d\pi^4 2p\sigma^2 2p\pi^3, \tag{3}$$

$$Cu^+(3d^{10}4s)O(2p^4): \quad 3d\sigma^2 3d\delta^4 3d\pi^4 2p\sigma^2 2p\pi^3, \tag{4}$$

$$\mathrm{Cu}^+(3d^9 4s4p)\mathrm{O}(2p^4): \quad 3\mathrm{d}\sigma^1 3\mathrm{d}\delta^4 3\mathrm{d}\pi^4 2\mathrm{p}\sigma^2 2\mathrm{p}\pi^3 4\mathrm{s}\sigma^1, \quad (5)$$

where configuration (3) describes the ionic bonding between Cu and O, configuration (4) describes the covalent bonding between Cu and O, and configuration (5) describes the backbonding from O to Cu4*p*. While the ionic bonding configuration (3) would contribute to the expected $s + d$ wave angular distribution, the covalent configurations (4) and (5) are expected to contribute to *p*-wave angular distributions because of the involvement of the 4*s* orbital in the chemical bonding. Thus, the observed *p*-wave angular distribution for the detachment transition to the ground state of CuO ($X^2\Pi$) is a direct manifestation of the covalent bond nature of the Cu–O chemical bonding and the strong electron correlation effects in CuO^- and CuO.

This Note confirms a long-lived triplet excited state of CuO^- using cryogenic photoelectron imaging. The observation of the triplet excited state ($^3\Pi$) of CuO^- after 45 ms of trapping and collisional cooling in the 3D Paul trap suggests that it is highly stable with a lifetime being significantly longer than 45 ms. The measured photoelectron angular distributions further confirm the assignment of the triplet excited state, providing evidence of the covalent bonding and strong electron correlation effects in CuO and CuO^-. The intrinsic stability of the triplet excited state of CuO^- may have possible applications in state-controlled chemistry and implications in interstellar chemistry.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

G. Stephen Kocheril: Data curation (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal). **Han-Wen Gao**: Data curation (equal); Investigation (equal); Writing – review & editing (equal). **Lai-Sheng Wang**: Conceptualization (equal); Funding acquisition (equal); Investigation (equal); Project administration (equal); Supervision (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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