Photodissociation Spectroscopy

International Edition: DOI: 10.1002/anie.201811362
German Edition: DOI: 10.1002/ange.201811362Experimentally Calibrated Analysis of the Electronic Structure of CuO^+ : Implications for Reactivity

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Dedicated to Professor Helmut Schwarz on the occasion of his 75th birthday

Abstract: The CuO^+ core is a central motif of reactive intermediates in copper-catalysed oxidations occurring in nature. The high reactivity of CuO^+ stems from a weak bonding between the atoms, which cannot be described by a simple classical model. To obtain the correct picture, we have investigated the acetonitrile-ligated CuO^+ ion using neon-tagging photodissociation spectroscopy at 5 K. The spectra feature complex vibronic absorption progressions in NIR and visible regions. Employing Franck–Condon analyses, we derived low-lying triplet potential energy surfaces that were further correlated with multireference calculations. This provided insight into the ground and low-lying excited electronic states of the CuO^+ unit and elucidated how these states are perturbed by the change in ligation. Thus, we show that the bare CuO^+ ion has prevalently a copper(I)-biradical oxygen character. Increasing the number of ligands coordinated to copper changes the CuO^+ character towards the copper(II)-oxyl radical structure.

Chemical transformations of both renewable and non-renewable resources to products of greater value, such as methane to methanol,^[1] or biomass polymers to simple sugars,^[2,3] represent one of the current challenges in catalysis.^[4] Both of these transformations occur in nature with the help of copper-containing enzymes. Methanotrophic bacteria transform methane to methanol using the particulate methane monooxygenase,^[5,6] whereas various bacteria and fungi decompose cellulose using lytic polysaccharide monooxygenases.^[2,7] Both of these enzymes are thought to oxidise substrates through a reactive copper(II)-oxyl species (CuO^+).^[8–12]

Our understanding of enzymatic (CuO^+) intermediates mostly originates from studies of model complexes^[13–17] and

from theoretical calculations.^[12–19] The special properties of the bare $[\text{CuO}]^+$ itself became clear from systematic studies.^[20–23] Out of the 3d metal–oxo cations, CuO^+ has the second highest count of d-electrons that participate in antibonding interactions with oxygen electrons. As a result, CuO^+ has an extremely weak bond with a 0.5 π bond-order and thus is very reactive.^[24–26] Although much effort has been devoted to describe and understand the CuO^+ electronic structure,^[27] spectroscopic data are still missing. These data would be important for benchmarking theoretical description of this challenging system as well as for interpreting the spectroscopic data obtained for putative enzymatic (CuO^+) intermediates.

Herein, we present a detailed study of the electronic structure of acetonitrile-ligated CuO^+ ion, $[(\text{CH}_3\text{CN})\text{CuO}]^+$, which also provides insight into the bare CuO^+ ion and larger ligand-supported species. We generated the ions of interest by electrospray ionization (ESI) of copper chlorate solution in acetonitrile.^[17] We also attempted to investigate bare $[\text{CuO}]^+$, which can be generated upon collisional activation of $[(\text{CH}_3\text{CN})\text{CuO}]^+$ in the collision cell.^[17] However, direct generation of $[\text{CuO}]^+$ in the ESI source was hampered by its high reactivity. Therefore, we focused on $[(\text{CH}_3\text{CN})\text{CuO}]^+$ and studied this ion using photodissociation spectroscopy in the infrared and visible ranges.

The spectra of gaseous $[(\text{CH}_3\text{CN})\text{CuO}]^+$ feature electronic absorption bands in both near-infrared (NIR) and visible regions (Figures 1 and 2). Figure 1 shows the NIR spectrum of $[(\text{CH}_3\text{CN})\text{CuO}]^+$ ranging from circa 4300 to circa

Figure 1. Ne-tagging infrared photodissociation (IRPD) spectrum of $[(\text{CH}_3\text{CN})\text{Cu}^{16}\text{O}]^+$ (black) and $[(\text{CH}_3\text{CN})\text{Cu}^{18}\text{O}]^+$ (red) measured at 5 K. The intensity of the laser strongly increases above 5000 cm^{-1} (see Figure S1) resulting in enhancement of the signal intensity in this range. Inset: The Cu–O stretching vibration in the ground state (see Figure S2 for the IRPD spectrum in the whole IR range).

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5600 cm^{-1} . The spectrum is composed of two prominent absorption bands, which we attribute to vibronic transitions. These transitions result from the coupling with the Cu–O stretching vibration in the excited state as indicated by the separation of 693 and 665 cm^{-1} for ^{16}O and ^{18}O isotopologues, respectively. The Cu–O frequencies in the excited state found in the NIR region are similar to those in the ground state, which are located at 672 and 644 cm^{-1} for ^{16}O and ^{18}O isotopologues, respectively (inset in Figure 1). Furthermore, the first, lower-energy (0–0) band is more intense than the second one (Figure S1, see the laser power in the absorption range). The large intensity of the 0–0 transition and similar Cu–O frequencies suggest a small nuclear distortion upon excitation to the first excited state.

The small changes in the length and the vibrational frequency of Cu–O upon excitation imply that the potential energy surfaces (PESs) of the ground and the first excited states have very similar curvatures and energy minima along the Cu–O coordinate. The energy difference between the minima of these two states is circa 4300 cm^{-1} .

The experimental results are reproduced by the theory (Figure S4). The two lowest PESs (1^3A_{GS} and 1^3E) calculated at the MS-RASPT2 (multi-state restricted active space second-order perturbation theory^[28]) level exhibit similar curvature along the Cu–O coordinate and have an equilibrium Cu–O length of circa 1.7 Å. The calculated energy gap between the 1^3A_{GS} and 1^3E states is circa 5800 cm^{-1} (see the Supporting Information for computational details).

Figure 2 shows the visible spectrum of $[(\text{CH}_3\text{CN})\text{CuO}]^+$ displaying a complex spectral structure starting from circa 16560 cm^{-1} . We have recorded the spectrum with low- and high-resolution lasers (blue and black traces in Figure 2); convolution of the high-resolution spectrum with a Lorentzian function (gray trace in Figure 2) reproduces well the low-resolution spectrum. The observed progressions in the region of 16500–20000 cm^{-1} are sensitive to $^{16}\text{O}/^{18}\text{O}$ labelling of the oxo ligand (inset in Figure 2 and Figure S6 in the Supporting Information), which indicates that these vibronic progressions

are associated with the Cu–O stretching mode. Analysis suggests that the high-resolution spectrum is composed of five different progressions with 0–0 transitions below 18000 cm^{-1} and one progression that starts at about 19300 cm^{-1} . Guided by the high-resolution data, we further analysed the low-resolution spectrum (Figure 2) because this spectrum allows us to use the harmonic approximation. The experimental spectrum can be reproduced with six Franck–Condon (FC) progressions with parameters that are in reasonable agreement with the high-resolution data (Figure 3).

Each FC progression is characterised by five experimentally derived parameters (see Table 1 and Figure 3), which can be directly translated to six harmonic excited-state PESs (Figure 3; refer to the Supporting Information for details, the theory for FC analysis is also given in Ref. [29]). The first two

Table 1: The key parameters derived from the Franck–Condon (FC) deconvolutions of the vibronic absorption spectrum from Figure 3. The theory for the vibronic structure analysis is provided in the Supporting Information.

FC fit	E_{00} [cm^{-1}] ^[a]	E_{vert} [cm^{-1}] ^[b]	ν [cm^{-1}] ^[c]	S ^[d]	$I_{\text{FC}}/I_{\text{tot}}$ ^[e]
1	16567	18167/18967	800	3.0	0.14
2	17100	18650	690	2.6	0.11
3	17630	17630	690	0.95	0.15
4	17800	17800	685	0.1	0.03
5	17965	17965	685	0.9	0.13
6	19310	19310/19640	330	1.3	0.44

[a] E_{00} = position of the first peak in each FC progression (adiabatic transition). [b] E_{vert} = position of the most intense peak in each FC progression (vertical transition). [c] ν = spacing between two adjacent peaks in each progression (frequency of a vibrational Cu–O mode in an excited state). [d] S = Huang–Rhys factor shaping the FC vibronic structure and reflecting the excited-state geometric distortion relative to the ground-state equilibrium, ΔQ . S is defined as $\sqrt{n!}(\text{Intensity}_{0-n}/\text{Intensity}_{0-0})$ with n being the vibrational quantum number. [e] $I_{\text{FC}}/I_{\text{tot}}$ = ratio between the FC structure intensity and the spectrum intensity integrated over 16500–20000 cm^{-1} (the ratio relates to the oscillator strength).

Figure 2. Visible photofragmentation spectra of $[(\text{CH}_3\text{CN})\text{Cu}^{16}\text{O}]^+$ measured at 3 K by monitoring the loss of the oxygen atom (blue, low resolution; black, high resolution; gray, convolution of the high-resolution spectrum with Lorentzian with full width at half maximum of 100 cm^{-1}). Inset: Detail of the spectral shift caused by ^{18}O labelling (red), the whole spectrum is in Figure S6.

Figure 3. The Franck–Condon (FC) fitting of the visible photodissociation spectrum of $[(\text{CH}_3\text{CN})\text{CuO}]^+$ (resulting from convolution of high-resolution spectra, gray in Figure 2) using six different FC progressions (left). The parameters are listed in Table 1. The excited-state harmonic PESs derived from the FC fits (right). Asterisks indicate positions of the most intense vibronic peaks in each progression, which correspond to the vertical excitation energies. The harmonic PESs were derived from FC fits using Equation (S3).

FC progressions (FC fits 1 and 2) have comparably large Huang–Rhys factors (S). Thus, their derived excited-state PESs (dark blue and orange in Figure 3) have similar displacements along the Cu–O coordinate (ΔQ) with respect to the ground-state PES. The three other FC progressions (FC fits 3, 4, and 5 in Table 1; cyan, black, and magenta in Figure 3) are similar to the FC fit 2 in terms of the Cu–O vibrational spacing ($\nu \approx 690 \text{ cm}^{-1}$) but have significantly smaller S values. The small S values indicate small geometry distortions upon electronic excitation (i.e., small shifts of excited-state PES minima relative to the ground-state equilibrium). Interestingly, all five FC progressions are comparably intense with the exception of the FC fit 4 (see $I_{\text{FC}}/I_{\text{tot}}$ in Table 1), which has a very low $I_{\text{FC}}/I_{\text{tot}}$ value. The low intensity may indicate a spin-forbidden transition that obtains intensity only due to weak spin-orbit coupling (SOC) interactions. The sixth, and the highest-energy, FC progression (green in Figure 3) has an approximately two-fold smaller spacing ν in comparison with all other FC fits, indicating a rather shallow profile (less convex curvature) of the corresponding excited-state PES. Notably, the transition intensity to this excited state is considerably larger than the intensities of the other states (see $I_{\text{FC}}/I_{\text{tot}}$ values in Table 1).

Furthermore, we correlated experimentally derived PESs from Figure 3 with PESs obtained from quantum chemical calculations. Employing the MS-RASPT2 method, we calculated PESs of 2^3A and three 3^3E states (2^3E , 3^3E , and 4^3E ; notation reflects C_3 symmetry) along the Cu–O coordinate going from 1.55 to 1.95 Å, and in the energy range of 15 000–19 000 cm^{-1} (Figure 4). These four triplet PESs agree well with the parabolas derived from the experiments (see PESs from Figures 3 and 4) as reflected by distortions with respect to the ground state (ΔQ), vertical (E_{vert}), and adiabatic transition energies (E_{00}). However, some discrepancies are observed. First, the curvatures of experimental and calculated triplet PESs are in qualitative rather than in quantitative agreement. Second, the PES for FC fit 4 is absent within MS-

Figure 4. Potential energy surfaces (PESs) calculated along the Cu–O coordinate for the ten lowest triplet states (C_1 symmetry) at MS-RASPT2 level (left panel); 11th and 12th roots (corresponding to two spatial components of the 5^3E state in C_3 symmetry) have been calculated separately as discussed in Figure S5. Right panel shows the 15 000–19 000 cm^{-1} region highlighting four PESs, which correspond to the experimental PESs from Figure 3. The Cu–O equilibrium bond length of 1.7 Å in the ground state was estimated using the state-specific RASPT2 calculation. Energies of all triplet states, the lowest eleven singlet states and the lowest quintet state (relative to the triplet ground state) are listed in Table S1.

RASPT2 calculations performed over the first ten low-lying triplet states (within the C_1 symmetry). The omitted state may correspond to an excited singlet state that interacts weakly with (an)other triplet state(s), leading to its small SOC-induced intensity. Indeed, the MS-RASPT2 calculations suggest that several singlet states are present in the region (Table S1). Note that the SOC interactions certainly affect the PESs and lead to a rather complex high-resolution structure of the electronic transitions (Figure 2 and Figure S6). Nevertheless, despite the complexity of the excited-state PESs and their interactions, we found our model to be well-balanced for providing a valuable insight into the electronic properties of the ground and the excited states of the acetonitrile-perturbed $^3[\text{CuO}]^+$ system.

All lower-lying excited triplet states arise mostly from antibonding-to-antibonding, non-bonding-to-antibonding, or bonding-to-non-bonding excitations within the Cu–O valence shell (see Table S2 and Figure 5 for molecular orbitals).

	$4s_{\text{Cu}}$	non-bonding
	$2p_{\pi^*}$	anti-bonding
	$3d_{\sigma^*}$	
	$3d_{xy/x^2-y^2}$	non-bonding
	$3d_{\pi}$	bonding
	$2p_{\sigma}$	

Figure 5. Molecular orbitals of the $[(\text{CH}_3\text{CN})\text{CuO}]^+$ valence shell, which were included in the active space of RASPT2 calculations (details in the Supporting Information).

Conversely, the sixth FC-derived PES (green in Figure 3), assigned as the 5^3E state, has predominantly the configuration resulting from the excitation from the bonding $2p_{\sigma}$ to the antibonding $2p_{\pi^*}$ orbitals. The 5^3E state corresponds to 11th and 12th triplet states in C_1 symmetry (this PES was calculated separately from the others; please refer to the caption in Figure S5). The bonding-to-antibonding character of the excitation (Table S2) is associated with a drastic weakening of the Cu–O bond as demonstrated by the reduced frequency (330 cm^{-1}) and the shallow profile of its PES. The bonding-to-antibonding excitation also concurs with the large oscillator strength of the $5^3\text{E} \leftarrow ^3\text{A}_{\text{GS}}$ transition, which qualitatively agrees with the observed large intensity of this transition (see $I_{\text{FC}}/I_{\text{tot}}$ values in Table 1).

Having the theoretical method, which describes the spectroscopic and electronic properties of $[(\text{CH}_3\text{CN})\text{CuO}]^+$ in reasonable agreement with the experimental results, we can analyse the Cu–O bond in detail. The MS-RASPT2 calculations with MS over 10 states predict the ground triplet state of $[(\text{CH}_3\text{CN})\text{CuO}]^+$ to be composed mostly from two electronic configurations. In the dominant configuration (56% weight), a triplet oxygen atom is bound to a copper(I) centre, while in the second most significant contribution

Table 2: Triplet ground-state electronic structures of CuO^+ complexes (PQ = 9,10-phenanthrenequinone, phen = 1,10-phenanthroline).

System ^[b]	Weight	Dominant configurations ^[a]	Valence bond description
$[\text{CuO}]^+$	62 %	$(2p_o)^2(3d_\pi)^4(3d_{xy/x2-y2})^4(3d_{o^2})^2(2p_{\pi^*})^2(4s)^0$	$\text{Cu}^{1+}-\text{O}^\bullet$
	26 % ^[c]	$(2p_o)^2(3d_\pi)^3(3d_{xy/x2-y2})^4(3d_{o^2})^2(2p_{\pi^*})^3(4s)^0$	$\text{Cu}^{2+}-\text{O}^{\bullet-}$
$[(\text{CH}_3\text{CN})\text{CuO}]^+$	56 % ^[d]	$(2p_o)^2(3d_\pi)^4(3d_{xy/x2-y2})^4(3d_{o^2})^2(2p_{\pi^*})^2(4s)^0$	$\text{Cu}^{1+}-\text{O}^\bullet$
	36 % ^[c]	$(2p_o)^2(3d_\pi)^3(3d_{xy/x2-y2})^4(3d_{o^2})^2(2p_{\pi^*})^3(4s)^0$	$\text{Cu}^{2+}-\text{O}^{\bullet-}$
$[(\text{PQ})\text{CuO}]^+$	40 %	$(2p_o)^2(3d_\pi)^4(3d_{xy/x2-y2})^4(3d_{o^2})^2(2p_{\pi^*})^2(4s)^0$	$\text{Cu}^{1+}-\text{O}^\bullet$
	52 % ^[c]	$(2p_o)^2(3d_\pi)^3(3d_{xy/x2-y2})^4(3d_{o^2})^2(2p_{\pi^*})^3(4s)^0$	$\text{Cu}^{2+}-\text{O}^{\bullet-}$
$[(\text{phen})\text{CuO}]^+$	38 %	$(2p_o)^2(3d_\pi)^4(3d_{xy/x2-y2})^4(3d_{o^2})^2(2p_{\pi^*})^2(4s)^0$	$\text{Cu}^{1+}-\text{O}^\bullet$
	55 % ^[c]	$(2p_o)^2(3d_\pi)^3(3d_{xy/x2-y2})^4(3d_{o^2})^2(2p_{\pi^*})^3(4s)^0$	$\text{Cu}^{2+}-\text{O}^{\bullet-}$

[a] Analysis of the configuration-interaction (CI) vector of the MS-RASPT2 wavefunction; MS over 10 lowest triplet states included (C_1 symmetry); corresponding active space orbitals are depicted in Figure 5. [b] Calculated for the geometry optimised at the B3LYP-D3/6-311G** level. [c] The sum of weights associated with all configurations that contribute to the $\text{Cu}^{2+}-\text{O}^{\bullet-}$ character. [d] The leading configuration has the weight of circa 85 % if only state-specific RASPT2 (MS involving only the lowest triplet state) calculation is employed. From that, we attribute the large oxyl character of the CuO unit in the triplet ground state to a strong configuration interaction mixing with other low-lying excited triplet states having dominant $\text{Cu}^{2+}-\text{O}^{\bullet-}$ character.

(36 % weight), an oxyl radical anion is ferromagnetically coupled to a copper(II) centre (Table 2; the oxyl contribution to the ground state arises mostly from a large admixture of the excited state responsible for the FC progression with $\nu = 800 \text{ cm}^{-1}$, FC in dark blue in Figures 3 and 4). The large ground-state biradical character of the O ligand implies its reactivity.^[16,30]

Next, we analogously analysed the wavefunction of the bare $[\text{CuO}]^+$ to understand the effect of acetonitrile ligation on the electronic structure of the CuO^+ unit (Table 2). We observe that $[\text{CuO}]^+$ has enhanced biradical-oxygen character (by ca. 10 %), whereas the oxyl configuration is reduced accordingly. The partial decrease of the biradical character of the O ligand caused by the acetonitrile ligation is due to electron donation from the ligand to the copper centre. Furthermore, the additional ligation to $[(\text{CH}_3\text{CN})\text{CuO}]^+$ may eventually produce a dominant oxyl character on the O ligand, which would reduce its radical character in comparison with the O ligand in the bare $[\text{CuO}]^+$ ion. Indeed, our calculations performed on ligated CuO^+ systems with a two-fold coordination bearing 9,10-phenanthrenequinone (PQ) or 1,10-phenanthroline (phen) ligands predict a dominant $\text{Cu}^{2+}-\text{O}^{\bullet-}$ configuration with an increased weight of 52 % or 55 %, respectively (Table 2). This is also consistent with the experimentally determined $\nu_{\text{GS}}(\text{CuO})$ in complexes with PQ or phen ligands (718 and 706 cm^{-1} , respectively; Figure S3). These frequencies are 46 and 34 cm^{-1} higher than in the $[(\text{CH}_3\text{CN})\text{CuO}]^+$ complex, which we attribute to an electrostatic interaction between Cu^{2+} and $\text{O}^{\bullet-}$ that is enhanced with a higher ligation.

In summary, the gas-phase $[(\text{CH}_3\text{CN})\text{CuO}]^+$ cation features a series of vibronic transitions in the NIR and visible regions that uncover the excited-state potential energy surfaces along the Cu–O stretching mode. The spectroscopic data are used to benchmark ab initio calculations that are further employed for elucidation of the electronic structure of $[(\text{CH}_3\text{CN})\text{CuO}]^+$, and consequently also of the bare $[\text{CuO}]^+$.

These results show that the ground state of $[\text{CuO}]^+$ is predominantly characterised as biradical-oxygen coordinated to copper(I). The acetonitrile and higher ligations of the CuO^+ unit decrease the biradical oxygen character and shift the electronic structure towards the monoradical oxyl-copper(II) configuration, which correlates with a decreased hydrogen atom-abstraction ability.^[16] The shift from the $\text{Cu}^{1+}-\text{O}^\bullet$ to $\text{Cu}^{2+}-\text{O}^{\bullet-}$ character is also associated with an increased stretching frequency of the Cu–O bond. Hence, counterintuitively, the addition of ligands to the $[\text{CuO}]^+$ core strengthens the Cu–O bond.

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Conflict of interest

The authors declare no conflict of interest.

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- [1] G. A. Olah, *Angew. Chem. Int. Ed.* **2013**, 52, 104–107; *Angew. Chem.* **2013**, 125, 112–116.
- [2] W. T. Beeson, V. V. Vu, E. A. Span, C. M. Phillips, M. A. Marletta, *Annu. Rev. Biochem.* **2015**, 84, 923–946.
- [3] J. Y. Lee, K. D. Karlin, *Curr. Opin. Chem. Biol.* **2015**, 25, 184–193.
- [4] H. Schwarz, *Catal. Sci. Technol.* **2017**, 7, 4302–4314.
- [5] E. I. Solomon, D. E. Heppner, E. M. Johnston, J. W. Ginsbach, J. Cirera, M. Qayyum, M. T. Kieber-Emmons, C. H. Kjaergaard, R. G. Hadt, L. Tian, *Chem. Rev.* **2014**, 114, 3659–3853.
- [6] M. A. Culpepper, A. C. Rosenzweig, *Crit. Rev. Biochem. Mol. Biol.* **2012**, 47, 483–492.
- [7] K. S. Johansen, *Trends Plant Sci.* **2016**, 21, 926–936.
- [8] R. J. Quinlan, M. D. Sweeney, L. L. Leggio, H. Otten, J.-C. N. Poulsen, K. Salomon Johansen, K. B. R. M. Krogh, C. I. Jørgensen, M. Tovborg, A. Anthonsen, T. Tryfona, C. P. Walter, P. Dupree, F. Xu, G. J. Davies, P. H. Walton, *Proc. Natl. Acad. Sci. U.S.A.* **2011**, 108, 15079–15084.
- [9] L. Ciano, G. J. Davies, W. B. Tolman, P. H. Walton, *Nat. Catal.* **2018**, 1, 571–577.
- [10] L. Cao, O. Caldararu, A. C. Rosenzweig, U. Ryde, *Angew. Chem. Int. Ed.* **2018**, 57, 162–166; *Angew. Chem.* **2018**, 130, 168–172.
- [11] L. Bertini, R. Breglia, M. Lambrugh, P. Fantucci, L. De Gioia, M. Borsari, M. Sola, C. A. Bortolotti, M. Bruschi, *Inorg. Chem.* **2018**, 57, 86–97.

- [12] E. D. Hedegård, U. Ryde, *Chem. Sci.* **2018**, *9*, 3866–3880.
- [13] C. E. Elwell, N. L. Gagnon, B. D. Neisen, D. Dhar, A. D. Spaeth, G. M. Yee, W. B. Tolman, *Chem. Rev.* **2017**, *117*, 2059–2107.
- [14] N. Gagnon, W. B. Tolman, *Acc. Chem. Res.* **2015**, *48*, 2126–2131.
- [15] S. Kim, J. W. Ginsbach, J. Y. Lee, R. L. Peterson, J. J. Liu, M. A. Siegler, A. A. Sarjeant, E. I. Solomon, K. D. Karlin, *J. Am. Chem. Soc.* **2015**, *137*, 2867–2874.
- [16] D. Schröder, M. C. Holthausen, H. Schwarz, *J. Phys. Chem. B* **2004**, *108*, 14407–14416.
- [17] G. Yassaghi, E. Andris, J. Roithová, *ChemPhysChem* **2017**, *18*, 2217–2224.
- [18] K. Yoshizawa, N. Kihara, T. Kamachi, Y. Shiota, *Inorg. Chem.* **2006**, *45*, 3034–3041.
- [19] S. Kim, J. Ståhlberg, M. Sandgren, R. S. Paton, G. T. Beckham, *Proc. Natl. Acad. Sci. U.S.A.* **2014**, *111*, 149–154.
- [20] D. Schröder, H. Schwarz, *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 18114–18119.
- [21] H. Schwarz, *Angew. Chem. Int. Ed.* **2011**, *50*, 10096–10115; *Angew. Chem.* **2011**, *123*, 10276–10297.
- [22] N. Dietl, M. Schlangen, H. Schwarz, *Angew. Chem. Int. Ed.* **2012**, *51*, 5544–5555; *Angew. Chem.* **2012**, *124*, 5638–5650.
- [23] H. Schwarz, S. Shaik, J. Li, *J. Am. Chem. Soc.* **2017**, *139*, 17201–17212.
- [24] M. T. Rodgers, B. Walker, P. B. Armentrout, *Int. J. Mass Spectrom.* **1999**, *182–183*, 99–120.
- [25] N. Dietl, C. van der Linde, M. Schlangen, M. K. Beyer, H. Schwarz, *Angew. Chem. Int. Ed.* **2011**, *50*, 4966–4969; *Angew. Chem.* **2011**, *123*, 5068–5072.
- [26] N. J. Rijs, P. Gonzalez-Navarrete, M. Schlangen, H. Schwarz, *J. Am. Chem. Soc.* **2016**, *138*, 3125–3135.
- [27] E. Rezabal, J. Gauss, J. M. Matxain, R. Berger, M. Diefenbach, M. C. Holthausen, *J. Chem. Phys.* **2011**, *134*, 064304.
- [28] P. Å. Malmqvist, K. Pierloot, A. R. M. Shahi, C. J. Cramer, L. Gagliardi, *J. Chem. Phys.* **2008**, *128*, 204109.
- [29] M. Srnc, S. D. Wong, M. L. Matthews, C. Krebs, J. M. Bollinger, E. I. Solomon, *J. Am. Chem. Soc.* **2016**, *138*, 5110–5122.
- [30] Note that the reactivity of (CuO⁺) species are examples of a two-state reactivity principle: a) S. Shaik, D. Danovich, A. Fiedler, D. Schröder, H. Schwarz, *Helv. Chim. Acta* **1995**, *78*, 1393; b) D. Schröder, S. Shaik, H. Schwarz, *Acc. Chem. Res.* **2000**, *33*, 139–145.

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