Molecular Structures and Vibrations of neutral and anionic CuO$_x$ (x=1 – 3,6) clusters

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We report equilibrium geometric structures of CuO$_2$, CuO$_3$, CuO$_6$, and CuO$_6^-$ clusters obtained by an all-electron linear combination of atomic orbitals scheme within the density functional theory with generalized gradient approximation to describe the exchange-correlation effects. The vibrational stability of all clusters is examined on the basis of the vibrational frequencies. A structure with C$_1$ symmetry is found to be the lowest energy structure for CuO$_2$ while a Y shaped structure with C$_2v$ symmetry is the most stable structure for CuO$_3$. For the larger CuO$_6$ and CuO$_6^-$ clusters, several competitive structures exist with structures containing ozonide units being higher in energy than those with O$_2$ units. The infra-red and Raman spectra are calculated for the stable optimal geometries.

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I. INTRODUCTION

The copper-oxygen complexes have received significant attention because of their role in various processes such as catalytic oxidation, applications in the bio-inorganic chemistry, and corrosion to name a few. Numerous studies, both theoretical as well as experimental, have been reported to elucidate the chemical bonding between copper and oxygen in such complexes. Most of these studies were confined to small sizes of CuO$_x$ systems such as CuO and CuO$_2$ molecules. These earlier studies have been recently extended to larger systems by Wang and coworkers$^{1,2,3,4,5}$ who reported photoelectron spectra (PES) studies of CuO$_x$ (x = 1 – 6) species. They found that the Cu/O complexes containing either an odd or even number of oxygen atoms had similarities among themselves with respect to their PES. They also found several new copper-oxide molecules including CuO$_6$ and proposed some structures for these molecules on the basis of their PES study. Massobrio and coworkers$^{5,6,7}$ subsequently performed a systematic search for the lowest energy structure for CuO$_6$. In their density functional calculations with ultrasoft pseudopotentials they found the lowest energy structure of CuO$_6$ to possess ozonide Cu(O$_3$)$_2$ units contrary to the prediction in Ref$^2$ of an oxide structure Cu(O$_2$)$_3$ on the basis of photo-electron spectra. They also found that the structures containing the Cu(O$_2$)$_3$ units to be roughly within 0.2 eV. Cu is known to form OCUO or Cu(O$_3$) upon reaction with O$_2$ only under UV radiation at low temperature$^5$. The Cu atom at room temperature can form only Cu(O$_2$)$_2$ complexes with O$_2$ because the O atom transfer reaction is endothermic.

The present work is aimed at providing a detailed picture of the stationary points on the potential energy surface of the CuO$_2$, CuO$_3$, CuO$_6$ and anionic CuO$_6$ clusters. For this purpose, we perform a systematic search for possible candidate structures for the ground state geometries of these clusters, followed by calculation of the vibrational spectra to identify the nature of stationary points. As the energy differences between the isomers are small, we employ an all-electron treatment thereby eliminating any question due to the ultrasoft pseudopotential approximation. The present work complements the previous investigation on these systems by Pouillon and coworkers$^{8,9,10}$. Additionally, we have also calculated vertical detachment energies of the CuO$_6$ isomers and also the infrared absorption and Raman scattering spectra of the lowest energy CuO$_6$ isomers. These may be useful for comparison with experimental measurements.

In the following section the computational procedures employed in this work are briefly described followed by the results and discussion in the subsequent section.

II. DETAILS OF COMPUTATIONAL PROCEDURE

The calculations have been performed within the Kohn-Sham formulation of the density functional theory with the generalized gradient approximation (GGA) to describe the exchange-correlation effects. We have used the PBE functional by Perdew and coworkers$^{11}$. Structural optimizations of all the clusters were performed by starting from a number of possible candidate structures, including those already reported in the literature$^{2,3}$. The optimization was performed using the conjugate-gradient as well as the LBFGS method. For the case of the anionic CuO$_6$ systems, the optimized neutral geometries are used as the starting geometries. All calculations have been performed using the Naval
Research Laboratory Molecular Orbital Library (NRL-MOL) package [9]. This suite of programs employs a Gaussian basis set where the exponents of the Gaussian basis are optimized for each atom [10]. The integrations are carried out using a grid based method with a variational mesh. Further, the magnetic moment is optimized during the self-consistency cycle from electron counting considerations. The geometries were optimized until the forces were less than 0.001 a.u. The nature of stationary points (optimized geometries) on the potential energy surface was examined by computing the vibrational frequencies. These were calculated by displacing the atoms from their equilibrium positions by ±0.07 a.u. along each Cartesian direction and constructing the dynamical matrix from the forces of the distorted molecules [11]. The vibrational frequencies were subsequently obtained by diagonalizing the dynamical matrix. This also allows one to compute the zero-point energies. We also calculate the IR and Raman spectra of the optimized 

\[ \text{CuO}_x \] molecule which are obtained from the derivatives of the dipole moments and polarizability tensors [27].

### III. RESULTS AND DISCUSSION

Our test calculations performed for \( \text{O}_2 \) and \( \text{O}_3 \) molecules yield the bond lengths of \( \text{O}_2 \) and \( \text{O}_3 \) as 1.22 and 1.28 Å which are in excellent agreement with the experimental values of 1.21 and 1.28 Å. The bond angle for \( \text{O}_3 \) is also well predicted, 118° (calc.) vs. 117° (expt. [28]). The calculated vibrational frequencies for \( \text{O}_2 \) and \( \text{O}_3 \), 1547 cm\(^{-1}\) and 708, 1061, 1185 cm\(^{-1}\) agree well with the experimental values [28, 29] of 1580 cm\(^{-1}\) and 705, 1042, 1110 cm\(^{-1}\) respectively. However, the calculated dissociation energies of \( \text{O}_2 \) and \( \text{O}_3 \) are 6.80 eV and 9.06 eV while the experimental values are 5.1 and 6.2 eV. Although the dissociation energies are grossly overestimated, there is good agreement for structural parameters between the calculated values and experiment. In the following we discuss the \( \text{CuO}_x \) complexes for \( x=1,2,3, \) and 6.

#### A. CuO

The calculated values of bond length, dissociation energy and the vibrational frequency of the CuO molecule are given in Table I. Earlier theoretical values calculated at different levels of theory along with the experimental values are also included for comparison. Our calculated value of bond length 1.72 Å is in excellent agreement with experimental value of 1.73 Å [28]. The PBE functional seems to provide significant improvement over the LSDA and also seem to perform better than the B3LYP in the bond length prediction. Our calculated value of the vibrational frequency (680 cm\(^{-1}\)) is again in good agreement with experiment (631 cm\(^{-1}\)). The dissociation energy is however overestimated in all the theoretical calculations including the present one.

#### B. CuO\(_2\)

The optimized structures of various isomers of the \( \text{CuO}_2 \) molecule are shown in Fig. 1.

The bent \( \text{CuOO} \) structure (A in Fig. 1) with Cs symmetry is the lowest energy structure amongst the \( \text{Cu(O}_2 \) complexes. It is lower than the linear \( \text{OCuO} \) molecule by 0.76 eV. The third structure with \( \text{C}_3 \) symmetry (C in Fig. 1) in which the Cu atom occupies a side on position with respect to the \( \text{O}_2 \) is higher in energy by 0.55 eV. The fourth isomer with \( \text{C}_2 \) symmetry (isomer D in Fig. 1) is not reported in earlier studies.

![Fig. 1: The various isomers of the CuO\(_2\) cluster. The isomer A is the lowest energy structure. Isomers A, B, and D are vibrationally stable.](image)

<table>
<thead>
<tr>
<th>( R_e ) (Å)</th>
<th>( D_e ) (eV)</th>
<th>( \omega ) (cm(^{-1}))</th>
<th>EA (eV)</th>
<th>Method</th>
</tr>
</thead>
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<tr>
<td>1.73</td>
<td>2.75</td>
<td>631</td>
<td>1.78</td>
<td>EXPT.(^a)</td>
</tr>
<tr>
<td>1.78</td>
<td>640</td>
<td>631</td>
<td></td>
<td>EXPT.(^b)</td>
</tr>
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<td>LSDA (^g)</td>
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</table>

\( ^a \)Experimental results, Ref. 22  
\( ^b \)Experimental results, Ref. 19  
\( ^c \)Experimental results, Ref. 20  
\( ^d \)Present Calculations (Zero-point energy is included in \( D_e \)).  
\( ^e \)Complete active space self-consistent field method, Ref. 25  
\( ^f \)Plane wave self-consistent field method, Ref. 5  
\( ^g \)Ref. 11  
\( \)Ref. 10  

TABLE I: The calculated values of bond length (\( R_e \) in Å), dissociation energy (\( D_e \) in eV), and the frequency (\( \omega \) in cm\(^{-1}\)) of CuO are compared with the experimental values as well as earlier theoretical values.
TABLE II: Calculated bond lengths ($R_e$ in Å), atomization energies ($D_e$ in eV), and vibrational frequencies ($\omega$ in cm$^{-1}$) of CuO$_2$. The experimental values as well as earlier theoretical values are included for comparison.

<table>
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<tr>
<th>Structure</th>
<th>Method</th>
<th>$R_e$ Cu-O</th>
<th>O-O</th>
<th>$\angle$OCuO</th>
<th>$\mu_B$</th>
<th>$D_e$</th>
<th>$\omega_1$</th>
<th>$\omega_2$</th>
<th>$\omega_3$</th>
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<td>Bent (A)</td>
<td>DFT/PBE$^a$</td>
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<td>1.29</td>
<td>1</td>
<td>1</td>
<td>2.57</td>
<td>240</td>
<td>452</td>
<td>1200</td>
</tr>
<tr>
<td>DFT/B3LYP$^b$</td>
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<td>1.3</td>
<td></td>
<td></td>
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<td>217</td>
<td>438</td>
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<tr>
<td>DFT/B3LYP$^f$</td>
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<td>1.3</td>
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<td>Linear (B)</td>
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<td>819,823</td>
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<tr>
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<td>2.27</td>
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<td>663</td>
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<td>Cl$^e$</td>
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<tr>
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<td>142</td>
<td>727</td>
<td>953</td>
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<tr>
<td>Side-on (C)</td>
<td>DFT/PBE$^h$</td>
<td>1.97</td>
<td>1.39</td>
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<td>1</td>
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<td>CAS$^g$</td>
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<td>Wide-angled (D)</td>
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<td>1.73</td>
<td>3.39</td>
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<td>3</td>
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<td>175</td>
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$^a$Experimental results from Ref. 12 and 16
$^b$Ref. Present Calculations, Zero-point energy is included in $D_e$.
$^c$Ref. 15
$^d$Ref. 21
$^e$Ref. 22
$^f$Ref. 14
$^g$Ref. 23
$^i$Ref. 30

works and is found to be lower than the structure C by 0.02 eV. In this wide-angled isomer the distance between the two oxygen atoms is much larger than that in the third structure. The OCuO angle in C is 41° while that in the isomer D is 157°. Our vibrational frequency calculations have shown that the side on C isomer has one imaginary frequency. Such imaginary frequency for this isomer has also been observed in the earlier density functional based work of Barone and Adamo [14]. Earlier quantum chemical calculation by Bauschlicher [23] found isomer C to be more stable than the bent structure A. They however note that the two structures are energetically very close with their order being dependent on the numerical details. More recent quantum chemical calculation (CCSD) using the effective core potential (ECP) reports the side-on structure C to be the lowest. The differences are possibly due to the use of ECP. The bent CuOO structure (A) found as the lowest energy structure in the present work is in agreement with the earlier DFT calculations [5]. However, the order of isomers as the structures A, C, and B in increasing energy observed in earlier DFT works is now altered in the present work due to the new isomer (D) found in this work. This isomer is the next low-lying isomer to the lowest energy structure. The calculated values of the Cu-O and O-O bond lengths, $\angle$OCuO, spin magnetic moment, atomization energy and vibrational frequencies are compared with the existing theoretical and experimental results in Table II. The earlier theoretical calculations have predicted the dissociation energy of CuO$_2$ with respect to Cu and O$_2$ to lie between 0.42 -0.56 eV [14, 21, 23]. The lowest-energy structure has a doublet state in agreement with the experimental observation [12, 16]. Our results show that in the linear structure B, the Cu-O distance is 1.67 Å which is in good agreement with the prediction based on the experimental absorption spectra [18] and is also consistent with the findings of another experimental result [6]. Another density functional based calculation [15] using the Perdew-Wang91 GGA [26], however predicts the quartet state to be lower in energy by 0.1 eV. Since the two GGA functionals, PBE in the present and PW91 in Ref. [15], are essentially similar, the prediction in Ref. [15] could be due to other numerical details like choice of basis set in Ref. 15. They however conclude the ground state to be a doublet on the basis of vibrational frequencies. Density functional calculation by Cherithin et al. [16] using the hybrid B3LYP GGA also predicts the quartet to be lower than the doublet, but again assign the
doublet to be the ground state on the basis of frequency calculations. Our predicted values of frequencies are in good agreement with the experimental values and earlier B3LYP calculation[16]. Unlike previous theoretical calculations, the present calculation correctly points doublet to be the ground state on the consideration of both the dissociation energy as well as the frequencies.

The frequency labeled $\omega_1$ in Table II corresponds to a bending mode in the bent structure or a flapping mode for the linear and the wide-angled structures. The $\omega_2$ refers to a stretching of Cu-O bonds resulting in a breathing mode of vibration for the symmetric structures. The third frequency corresponds to the O-O stretch mode in the bent structure while in the linear and wide-angled structures it corresponds to the vibration of the Cu atom. The O-O stretching mode of the bent structure at 1200 cm$^{-1}$ shows a large peak in the infrared absorption spectrum while the mode at 240 cm$^{-1}$ is strongly Raman active.

C. CuO$_3$

The equilibrium structures of CuO$_3$ are presented in Fig. 2. The first structure (A in Fig. 2) has a Y shape with Cu atom occupying the center of the fork position. The isomer B has a distorted rhombus structure while C and D structures are chain-like. One of the chain structures has a linear O-Cu-O unit while the other one has a wide-angled O-Cu-O unit. The spin magnetic moments, dissociation energies and the vibrational frequencies of the four isomers are given in Table III. Our results indicate that the Y shaped cluster containing a side-on CuO$_2$ unit is the lowest energy structure. The spin state of this structure is quartet. This result is in agreement with earlier published DFT calculations[3, 13]. The distorted rhombus structure has the Cu atom bonded with an O$_3$ unit which we refer to as copper ozonide structure. This isomer is higher in energy by 0.54 eV. The chain-like structures have energies lying between the Y shaped structure and the ozonide structure.

The calculated vibrational frequencies of all the four isomers are real indicating that all the four structures are local minima on the potential energy surface (Cf. Table III). In case of the lowest energy structure (Structure A), the lowest two modes correspond to bending motions, the first one in plane and the second one perpendicular to the plane of the molecule. The third mode pertains to the rotational motion of the O$_2$ unit about an axis perpendicular to the O-O bond. The next two modes correspond to Cu-O bond stretch modes. The largest frequency (1158 cm$^{-1}$) mode refers to the O-O stretch mode. Similar to the smaller clusters, this mode of vibration is strongly IR active while Cu-O stretch modes show significant Raman scattering.

In the ozonide isomer (B), the lowest three frequencies respectively involve the asymmetric stretch of the Cu-O bonds, vibration of the central O perpendicular to the plane of the molecule and a symmetric stretch of the Cu-O bond leading to a breathing mode. The frequencies from 687 to 987 cm$^{-1}$ pertain to the flapping, asymmetric O-O stretch and a symmetric O-O stretch modes of the ozone unit. However, the frequencies are lower than a free ozone unit indicating weaker O-O bonds in the O$_3$ unit due to the presence of the Cu atom. The mode at 807 cm$^{-1}$ shows strong infrared absorption while those around 200 cm$^{-1}$ are highly Raman active. Cherithin et al. [16] have observed peaks around 800 cm$^{-1}$ (812, 802 and 792 cm$^{-1}$) in their IR measurement which they have attributed to the Cu-ozonide structure. The present results are supportive of this assignment.

In the two chain-like structures the vibrational frequencies are comparable and the modes are same. The lowest two modes correspond to the vibration of the Cu atom in and out of the plane of the molecule. The next two frequencies refer to the asymmetric Cu-O stretch modes while the largest frequency corresponds to the O-O stretch mode which is also strongly IR active. The vibrational frequency of the O-O unit in the linear modes tends towards that of the free O$_2$ frequency (1547 cm$^{-1}$). The Cu-O stretch modes display Raman activity. The dissociation energies of the chain-like molecules C and D into CuO and O$_2$ are 1.14 and 0.76 eV.
TABLE III: The spin magnetic moments (in bohr magneton), atomization energies (eV) and vibrational frequencies of the various isomers of CuO₃.

<table>
<thead>
<tr>
<th>Isomer Method</th>
<th>μB</th>
<th>Dₑ</th>
<th>ωₑ cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXPT. a</td>
<td></td>
<td>660(90)</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>3</td>
<td>2.92 136, 143, 273, 378, 703, 1158</td>
<td></td>
</tr>
<tr>
<td>DFT/PBEc</td>
<td>3</td>
<td>2.90 366,683,1160</td>
<td></td>
</tr>
<tr>
<td>DFT/PW91d</td>
<td>3</td>
<td>386, 656, 1230</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>1</td>
<td>2.79 195,229,321,698,807,987</td>
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<tr>
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<td>DFT/B3LYPb</td>
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<tr>
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<td>792, 802, 812</td>
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</tr>
<tr>
<td>C</td>
<td>3</td>
<td>2.87 69, 95, 206, 458, 676, 1267</td>
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<td>98, 163, 277, 468, 800, 1358</td>
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</table>

aExperimental results, Ref. 2
bRef. 13
cRef. Present Calculations, Zero-point energy is included in Dₑ.
dRef. 15

d. CuO₆

In the CuO₃ clusters, we have seen that the ozonide cluster is higher in energy than the Y shaped structure which contains an O₂ unit. On the other hand, the CuO₂ triangular structure is higher in energy than a linear Cu-O-O structure. It would be interesting to see how the cluster structure changes in the presence of more oxygens.

The knowledge of structures for the smaller sizes is useful in building up the starting geometries for the optimization of CuO₆. We have started with several possible structures as input for optimization. The optimized geometries are presented in Fig. 3. The first two structures, labeled as A and B in the Fig. contain the three O₂ units and also a CuO₂ triangle. The difference in the structures lie in the orientations of the open-ended O₂ units. The isomers C and D contain closed Cu-O₃ rings. The isomer C is planar and the isomer D is 3-dimensional. The structure E has both O₃ and O₂ units of which the O₃ forms a closed ring with the Cu atom. For the next isomer (F) also, both O₃ and O₂ units are present and the Cu atom forms end-on bonds with these units. The last structure G has three O₂ units all of which form end-on bonds with the Cu atom. This structure was arrived at by starting the geometry optimization with the structure predicted by Wang et al. based on their photoelectron spectra. Our calculations have shown the structure labeled as A has the lowest energy among all the structures shown here. The structures B and G are comparable in energy and both are higher relative to structure A by 0.12 and 0.22 eV respectively. The isomers C and D with ozonide subunits are higher than A by 0.95 and 0.94 eV respectively. The ozonide planar structure C was reported to be the lowest energy structure by Pouillon and Massobrio. This difference in the present and their calculations for the lowest energy structure is probably due to their choice of ultra-soft pseudopotential for representation of core electrons and brings out the importance of treating all electrons at equal footing in the CuO₃ system. The structures E and F are higher in energy by 1.62 and 1.79 eV, respectively. The atomization energies of these isomers are presented in Table IV. The atomization energy includes the zero-point energy of the systems.

The vibrational frequencies of the isomers are presented in Table IV. Both the structures A and B are found to be vibrationally stable. In these two lowest energy structures A and B, the modes of vibrations are pretty similar. The low frequency modes are associated with the bending and flapping of the open-ended O₂ units. On the other hand the high frequency modes are associated with the stretching of the O-O bonds reflecting the strength of these bonds. The Cu-O bond stretch modes have frequencies lying between 250 to 525 cm⁻¹. The lower frequencies mainly correspond to the bond bending motions of the O₂ units. In the structure A the high frequency modes corresponding to the O-O bond stretching show significant IR absorption while the modes below 400 cm⁻¹ show Raman activity. On the other hand, the structure B is IR inactive and has modes below 200 cm⁻¹ that are Raman active.

The structure C comprising an ozonide unit is also vibrationally stable. This structure is both Raman and IR active. The Raman scattering is seen in the low frequency range of 300-350 cm⁻¹, where the modes correspond to bending of the molecule and also symmetric and asymmetric stretching of the four Cu-O bonds. The IR active

FIG. 3: The various isomers of the CuO₆ cluster. The isomer A is the lowest-energy isomer.
modes are the high frequency modes in the range of 800 - 920 cm\(^{-1}\). These are again O-O stretch modes which are asymmetric. The largest mode is also a symmetric O-O stretch mode leading to a breathing mode. However, unlike the other structure where the largest mode is strongly IR active, this mode is IR inactive. This is due to the fact that this mode is symmetric and does not lead to a change in dipole moment of the molecule.

The structure D with two orthogonal planar O\(_3\) units, is a saddle point with an imaginary vibrational frequency. The eigenvector of the mode shows it related to a bending motion which try to break the orthogonality of the two ozone units. This orthogonality was not enforced during the optimization. Both the structures E and F containing both O\(_2\) and O\(_3\) units are found to be vibrationally stable. However, they are very high on the energy scale. This is again consistent with the energy ordering seen in the CuO\(_3\) isomers in which both the ring-like and linear structures are higher in energy than the Y shaped one. The vibrational analysis of the structure G showed it to be a saddle point on the potential energy surface. The G isomer containing three open-ended O\(_2\) units shows IR activity in the range of 1200-1250 cm\(^{-1}\). These again are O-O stretching modes. However the largest frequency mode which corresponds to symmetric stretching of all the O-O bonds is found to be IR inactive. This can be attributed to the fact that this mode retains the overall symmetry of the molecule and does not lead to a change of the dipole moment.

We have also considered various possible anionic structures of the CuO\(_6\) molecule. The optimized structures of the anion are very similar to their neutral counterparts and are therefore not shown. These structures are obtained by starting the optimization with the geometries of neutral clusters. As in the neutral case, the structure A is found to be the lowest-energy structure. The relative energies, vibrational frequencies, vertical detachment energies of these structures are given in Table V. An analysis of the vibrational frequencies show that the structures A, B, C and D pertain to local minima on the potential energy surface. The structure E is the only structure to become somewhat modified from its neutral geometry in that the oxygen dimer tilts away from the Cu and Cu-O\(_2\) bond length increases to 2.3 Å. Also the CuO\(_3\) closed ring structure becomes opened at one end. This structure is vibrationally stable but energetically high. On the other hand, the high energy structure G has two imaginary frequencies associated with it. The optimization of the anionic counterpart of structure F was abandoned due to failure to obtain a convergent solution. The structure D in neutral form is vibrationally unstable but the anionic form is vibrationally stable. The adiabatic electron affinity of the lowest energy structure is found to be 2.75 eV in which the zero point motion of the molecule is also taken into consideration. The calculated values of the VDE (Cf. Table V) are in the range 2.8 – 3.5 eV. The experimental value of the electron binding energy in CuO\(_6\) as measured from photoelectron spectra is 3.2 eV. The structures with ozonide units as well as with O\(_2\) units, both have the VDE around this value and based on the consideration of the VDE alone, it is difficult to infer about the correct anion geometry. However, the VDE combined with total energy values indicate the oxide structure to be the candidate for the ground state geometry for the neutral CuO\(_6\).

The analysis of nature of bonding based on the charge density differences shows the expected behavior, that the O-O bonding is covalent while Cu-O bonds are more ionic in nature. The plot of isosurface of charge density are shown in Fig. 4 for the case CuO\(_6\). The lowest energy CuO\(_6\) is stable by 2.72 eV against dissociation into Cu atom and three O\(_2\) molecules. This translates to about 0.68 eV per Cu-O bond which is a relatively weak bond. A simple analysis of integrating charge density around each atom inside an atomic sphere of arbitrary radius shows the Cu atom to be in the +1 charge state and the O atoms in the -2 charge state. There is very little spin density on the Cu atom and most of the spin density is seen on the O\(_2\) units. This is consistent with the paramagnetic nature of O\(_2\) molecule. The spin density is largest on the O atoms farthest from the Cu atom.

**IV. SUMMARY**

In conclusion, we have performed a detail examination of various possible structures of the CuO\(_x\) molecule.
The vibrational stability of the isomers was examined by carrying out an analysis of the vibrational modes. A bent structure with $C_s$ symmetry is found to be the most stable structure for $\text{CuO}_2$. On the other hand, a $\text{Y}$ shaped structure with $C_{2v}$ symmetry is the lowest energy structure for $\text{CuO}_3$. Our study shows the potential energy surface is rather flat for $\text{CuO}_6$. Within our fairly exhaustive search we find two energetically nearly degenerate isomers as possible candidate structures for the ground state. Both of these structures contain $\text{CuO}_2$ subunits. This observation is consistent with the argument by Wang and coworkers based on the PES but it rules out their proposal of the structural form. Further, contrary to the earlier pseudopotential based study, the structures with ozonide subunits are found to be high energy isomers. The anionic clusters show trends similar to those of their neutral counterparts. The $\text{CuO}_6$ cluster in its most stable form is found to be strongly IR active. The IR active modes correspond to the O-O bond stretching and generally have high frequencies.

### V. ACKNOWLEDGMENT

TB acknowledges helpful discussion with S. L. Richardson. TB and MRP acknowledges financial assistance from ONR (Grant No. N000140211046) and by the DoD High Performance Computing CHSSI Program. RRZ acknowledges support from the GMU.

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**TABLE IV:** The atomization energies, spin states and the vibrational frequencies of the CuO$_6$ isomers. The dissociation energies include zero-point energy.

<table>
<thead>
<tr>
<th>Isomer</th>
<th>$D_e$ (eV)</th>
<th>$\mu_B$</th>
<th>$\omega_e$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3.29</td>
<td>3</td>
<td>30, 95, 107, 128, 148, 174, 264, 294, 299, 405, 476, 496, 1147, 1250, 1324</td>
</tr>
<tr>
<td>B</td>
<td>3.27</td>
<td>1</td>
<td>36, 69, 93, 101, 124, 141, 192, 236, 359, 381, 439, 525, 1168, 1233, 1298</td>
</tr>
<tr>
<td>C</td>
<td>3.15</td>
<td>1</td>
<td>70, 94, 116, 311, 312, 347, 365, 437, 456, 706, 722, 810, 826, 1015</td>
</tr>
<tr>
<td>D</td>
<td>3.16</td>
<td>1</td>
<td>64, 49, 88, 167, 246, 295, 342, 364, 389, 667, 751, 789, 909, 1010</td>
</tr>
<tr>
<td>E</td>
<td>3.06</td>
<td>3</td>
<td>53, 84, 103, 157, 170, 232, 303, 387, 494, 636, 695, 790, 993, 1340</td>
</tr>
<tr>
<td>F</td>
<td>3.03</td>
<td>1</td>
<td>29, 74, 87, 104, 128, 155, 183, 299, 364, 421, 570, 703, 752, 1179, 1400</td>
</tr>
<tr>
<td>G</td>
<td>3.26</td>
<td>5</td>
<td>251, 44, 45, 78, 94, 104, 175, 184, 221, 373, 387, 398, 1240, 1251, 1323</td>
</tr>
</tbody>
</table>

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**TABLE V:** The magnetic moment M (in Bohr magneton), relative energies $\Delta E$, vertical detachment energy (VDE) and the vibrational frequencies of the CuO$_6$ anionic isomers.

<table>
<thead>
<tr>
<th>Isomer</th>
<th>M ($\mu_B$)</th>
<th>$\Delta E$ (eV)</th>
<th>VDE (eV)</th>
<th>$\omega_e$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2</td>
<td>0.00</td>
<td>3.12</td>
<td>51, 71, 124, 130, 158, 185, 248, 265, 398, 413, 491, 499, 1138, 1209</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>0.06</td>
<td>3.35</td>
<td>27, 103, 131, 179, 185, 226, 249, 257, 417, 447, 489, 546, 907, 1133, 1201</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>0.53</td>
<td>3.25</td>
<td>58, 101, 127, 261, 286, 315, 324, 413, 458, 647, 669, 729, 749, 831, 930</td>
</tr>
<tr>
<td>D</td>
<td>2</td>
<td>0.49</td>
<td>3.33</td>
<td>29, 79, 90, 233, 234, 238, 291, 291, 397, 665, 794, 794, 932, 946</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>0.89</td>
<td>3.49</td>
<td>20, 37, 62, 80, 105, 114, 172, 220, 232, 410, 507, 681, 707, 1143, 1299</td>
</tr>
<tr>
<td>G</td>
<td>4</td>
<td>0.36</td>
<td>2.80</td>
<td>631, 311, 51, 65, 105, 130, 166, 196, 204, 379, 390, 405, 1093, 1105</td>
</tr>
</tbody>
</table>

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$x = 1 - 3.6$. The vibrationally stability of the isomers was examined by carrying out an analysis of the vibrational modes. A bent structure with $C_s$ symmetry is found to be the most stable structure for $\text{CuO}_2$. On the other hand, a $\text{Y}$ shaped structure with $C_{2v}$ symmetry is the lowest energy structure for $\text{CuO}_3$. Our study shows the potential energy surface is rather flat for $\text{CuO}_6$. Within our fairly exhaustive search we find two energetically nearly degenerate isomers as possible candidate structures for the ground state. Both of these structures contain $\text{CuO}_2$ subunits. This observation is consistent with the argument by Wang and coworkers based on the PES but it rules out their proposal of the structural form. Further, contrary to the earlier pseudopotential based study, the structures with ozonide subunits are found to be high energy isomers. The anionic clusters show trends similar to those of their neutral counterparts. The $\text{CuO}_6$ cluster in its most stable form is found to be strongly IR active. The IR active modes correspond to the O-O bond stretching and generally have high frequencies.