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Equilibrium structure of CuO and CuS using the interionic force model

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The molecular structure of monomeric CuO and CuS has been determined by recent quantum chemical calculations and electron diffraction experiments. In the present work, the molecular dynamics of the interionic force model has been applied to obtain the equilibrium structure of these molecules. The equilibrium bond lengths and bond angles obtained have compared with the experimental data and reported values. It has been noted that the theoretical methods applied so far are mostly based on density functional theory and the reported results were much away from the experimental values. The results obtained in this work, are the overall agreement with experimental values. The partial pair distribution functions have been calculated with the HNC approximation using the interatomic pair potentials determined by the presented model.

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1. Introduction

It is well known that the transition metals play an important role in many areas of physics and chemistry. Many theoretical and experimental works have been done on oxides, sulfides and clusters containing transition metals [1-4]. Among various theoretical and experimental works, Das and co-workers recently reported results for spectroscopic constants and molecular properties of CuO and CuS using ab initio and density functional methods [5].They have been taken into account via Moller-Plesset perturbation theory (MP) and coupled cluster techniques and second-order Moller–Plesset perturbation theory (MP2) and coupled cluster CCSD(T) theory [6–12] which include single and double excitations and an estimate of connected triple excitations by a perturbation treatment and Becke's three parameter hybrid method with the Lee-Yang-Parr (B3LYP) correlation functional [13].

To date, most potential for oxides and halides have been investigated based on the assumption of the fully ionic model [14]. This assumption has been discussed with ionic polarisability treated by the shell model of Dick and Overhauser [15], and with central-force, pair wise short-range potentials described usually by a simple analytical function, most commonly the Born-Mayer potential. Further evidence for the non-transferability of shell parameters in oxides was found by Mahan [16] who has calculated ionic polarisabilities for a series of rocksalt oxides. Wilson and Madden have proposed a generic ionic potential model for alkaline earth oxides and anomalous structure of ZnO [17]. Recently polarizable ion model (PIM) studied with some researchers [18,19]. The phonons and other properties of crystalline MgO are predicted an "extended" ionic interaction model in which the polarization interactions resulting from the dipoles and quadrupoles induced on the oxide ions by both Coulombic and short-range interactions with other ions are explicitly represented [20].

On the other hand metal oxides are frequently used in several important technological applications, such as catalysis and microelectronics. These systems have been also studied with PIM [21]. In recent years, copper oxide systems have also attracted much interest because of their superconduction properties [22, 23]. However there are no studies with both CuO and CuS using ionic force model. The purpose of the present study was to determine the equilibrium and static structure of CuO and CuS with the interionic Force Model which for the static and dynamic structure and energetics of neutral and charged molecular clusters [24,25]. To our knowledge, this model has not been applied to the case of these systems. This important is issue to obtain a reliable description of interactions for molten cupper oxide and cupper sulphur would allow the investigation of the liquid structural properties.

In the present paper, we evaluate an ionic force model for the potential energy function of CuO and CuS. The results are tested by evaluating the molecular structural parameters for these systems which the spectral data are available in literature [26-29]. We show that the evaluated model for CuO and CuS are in a reasonably good agreement with observation. The calculated structural trends for these systems are compared with each other and discussed with the choice of parameters for the systems of present interest and the approximate theory used.

2. Theory

2.1 Interionic Force Model

Following the earlier study of the aluminium and gallium bromides [25], we use the interionic force model for cupper oxide and cupper sulfur clusters incorporates the Born model of cohesion and the shell model for vibrational motions and crystal defects.

The potential energy $U(\{r_{ij}\},\{p_i\})$ of a cluster is taken to be a function of the interionic bond vectors r_{ij} and of the dipole moments p_i carried by the bromides. We handle this function by a computer programme which performs two basic task: *(i)* from a given starting configuration the structure of a cluster is first optimized by searching for zero-force configurations corresponding to extreme in the total energy, and *(ii)* deformations of each

zero-force structure are then studied for an assessment of its mechanical stability and for the evaluation of its vibrational frequencies.

The adopted form for $U(\{r_{ij}\},\{p_i\})$ is

$$U=\sum_{i<j}\left[\frac{z_i z_j e^2}{r_{ij}}+\Phi_{ij}(r_{ij})-\frac{C_i C_j}{r_{ij}^6}\right]+U_{pol}^{cl}(\{r_{ij}\},\{p_i\})+U_{shell}(\{r_{ij}\},\{p_i\}) \quad (1)$$

The sum over ion pairs on the RHS of (1) includes *(i)* the Coulomb interaction of ionic point charges with effective valances z_i subject to exact charge compensation ($\sum_i z_i = 0$), *(ii)* the overlap repulsive interaction described by a central pair potential $\Phi_{ij}(r_{ij})$, and *(iii)* the van der Waals interaction with an interaction strength C_i being attributed to each ion. These rigid-ion terms are supplemented by the classical polarization energy U_{pol}^{cl} of the induced dipoles on the bromides and by the shell deformation energy U_{shell}. In these equations, α and α_s are its electrical and short-range polarizabilities, and $i(h)$ denotes a metal ion which is first neighbour of the h halogen (for more details see Ref. [25]). In the above equation the overlap potentials are written in the form proposed by Busing [30],

$$\Phi_{ij}(r)=f(\rho_i+\rho_j)\exp\left[\frac{R_i+R_j-r}{\rho_i+\rho_j}\right] \quad (2)$$

where R_i and ρ_i are characteristic radii and hardness parameters of the individual ions and f is chosen to have the standard value $f=0.05\,e^2/A^2$. Proportionality between R_i and ρ_i can be used for metal ions. Based on the interionic force model we define the rigid ion potential which is similar the TAPT potential [31] as

$$V_{ij}(r_{ij})=\frac{Z_i Z_j e^2}{r_{ij}}+\phi_{ij}(r_{ij})+\frac{C_i C_j e^2}{r_{ij}^6} \quad (3)$$

In our choice we have made use the potential parameters determined from the molecular structure calculations. Finally, the classical polarization energy is

$$U_{pol}^{cl}(\{\mathbf{r}_{ij}\},\{\mathbf{p}_i\})=\sum_{i\neq j}\left[-z_i e\frac{\mathbf{p}_j\cdot\mathbf{r}_{ij}}{r_{ij}^3}+\frac{1}{2}\frac{\mathbf{p}_i\cdot\mathbf{p}_j}{r_{ij}^3}-\frac{3}{2}\frac{(\mathbf{p}_i\cdot\mathbf{r}_{ij})(\mathbf{p}_j\cdot\mathbf{r}_{ij})}{r_{ij}^5}+\frac{1}{2\alpha_h}\sum_j p_j^2\right] \quad (4)$$

and the shell deformation energy is written as

$$U_{shell}(\{\mathbf{r}_{ij}\},\{\mathbf{p}_i\})=\frac{\alpha_s}{\alpha_h}\sum_{i_j,j}\mathbf{p}_j\cdot\hat{\mathbf{r}}_{ij}\left|\frac{d\Phi_{ij}(r_{ij})}{d\,r_{ij}}\right| \quad (5)$$

where α_h is the electrical polarizability of the halogen and α_s is a short-range polarizability. The sum is in restricted to run over i_j = metal ions which are first neighbours of the *j*-th halogen. Minimization of (1) with respect to the dipoles yields the dipole p_h on a halogen as

$$\mathbf{p}_h=\alpha_h\mathbf{E}_h(\{\mathbf{r}_{ij}\},\{\mathbf{p}_i\})+\alpha_s\sum_{i_j}\hat{\mathbf{r}}_{ih}\left|\frac{d\Phi_{ih}(r_{ih})}{d\,r_{ih}}\right| \quad (6)$$

where E_h is the self-consistent electric field on the halogen .

In our structural calculations, one of the integral equation theories which has shown to be very reliable theory of liquids VMHNC has been carried out [32]. However in the present work we use the HNC solution for our structural calculations. Like the most liquid state theories the VMHNC solves the Ornstein–Zernike (OZ) equation, which for a homogeneous, isotropic, binary system reads (i, j =1, 2)

$$h_{ij}(r)=c_{ij}(r)+\sum_{l=1}^{2}\rho_l h_{il}(r)*c_{lj}(r) \quad (7)$$

which defines the partial direct correlation functions, $c_{ij}(r)$, in terms of the total correlation functions $h_{ij}(r)=g_{ij}(r)-1$, where $g_{ij}(r)$ denote the partial pair distribution functions and ρ_l denote the partial ionic number densities. Now, Eq.(6) is supplemented by the exact closure relation

$$c_{ij}(r)=h_{ij}(r)-\ln\left[g_{ij}(r)e^{\beta v_{ij}(r)+B_{ij}(r)}\right] \quad (8)$$

where $V_{ij}(r)$ are the interatomic pair potentials and the $B_{ij}(r)$ assumed to be zero for the HNC solutions. Formally the generalization of liquid state from monatomic to binary fluids, we have now a set of three coupled integral equations relating the partial pair distribution functions $g_{ij}(r)$ to the pair potentials $V_{ij}(r)$. The partial pair distribution functions are related to Ashcroft-Langreth (AL) partial structure factors $S_{ij}(q)$. For the binary liquid alloys we have carried out the VMHNC integral equation theory in which was extended by Gonzalez *et al.* [32], so as to minimize the configurational Helmholtz free energy functional $f^{VMHNC}(\beta,\rho,x_l)$ by the variational condition taking into account $B_{ij}(r)=0$. For useful details about the VMHNC calculations of the partial structure factors, the reader is referred to Ref. [32]. The total structure factors for CuO and CuS are determined as a lineer combination of partial structure factors given by,

$$S(q)=\sum_{i,j}b_i b_j S_{ij}(q)/<b>^2 \quad (9)$$

$$<b>^2=\left(\sum_i b_i\right)^2 \quad (10)$$

Where b_i and b_j are the neutron scattering amplitudes which are taken from [33].

3. Results and discussion

The presentation of the results is divided into two parts. The first one concerns with molecular structure for which the experimental data are available. The second one deals with interionic pair interaction in CuO and CuS. The equilibrium of CuO and CuS molecules are described as follows: (a) This is for the optimization of the molecule by

minimization of its energy towards states of static (stable and unstable) equilibrium. (b) This is for the evaluation of its vibrational frequencies and of its dynamic evaluation constant energy.

3.1. Molecular Structure

Firstly, we now present the results for the molecular structure of CuO and CuS obtained from the interionic force model. The model parameters used in our calculations reported in Table 1. The parameters which enter the short – range overlap interactions involving O ion can be taken from earlier studies of oxides [34].

In our calculations, we choose the effective valance value to give the agreeable results. The effective valance equal Z_X under this condition. Also the R_M parameters taken from the Ref.[35]. The proportionality holds between R_M and ρ_M for the metal ions ($RM / \rho_M = 18.6$). The R_X parameters of CuO is taken from Ref.[34]. We use an approximation for S, we though that fluorine close to oxygen in periodic table so from this point of view Cl close to S. However the parameter ρ_x determined the same way. The C_X parameters which are given in Table 1 for CuO is taken Ref.[36]. There are also other C_X parameters in literature [37, 38].

Table 1. Interionic force parameters in CuO and CuS (M : Cu and X : O, S).

	Z_M	Z_X	R_M(Å)	ρ_M(Å)	R_X(Å)	ρ_X(Å)	C_X (eÅ$^{5/2}$)	α_X (Å^3)	α_S (Å^3)
CuO	0.6710	-0.6710	1.0	0.0509	1.020 [a]	0.19	1.45 [b]	4.88 [c]	0.22
CuS	0.8389	-0.8389	1.0	0.0537	1.322	0.22	4.63	1.48	0.88

[a][34], [b][36] [c][38].

We have also studied bond lengths and frequencies. We report the calculated bond lengths and bond angles in CuO and CuS at equilibrium and compare them with data those obtained by B3LYP correlation function, MP2 and CCSD(T) in Table 2.

It appears that the calculated bond lengths of r for both systems using the interionic force model are excellent agreement with experimental data. Our vibrational frequencies, W, are closer to the experiment then other theoretical results.

Table 2. Geometrical parameters of CuO and CuS. Distances are in Å..

Parameters	Present work	Experiment	B3LYP	MP2	CCSD(T)
r (Cu-O)	1.724	1.724	1.747	1.763	1.757
W (cm^{-1})	636.079	640[a,b],631[c]	616	587	582
r (Cu-S)	2.059	2.051	2.088	2.087	2.102
W (cm^{-1})	415.064	415[d]	393	387	379

[a] [26], [b] [27], [c] [28], [d] [29].

3. 2. Interatomic Interactions and Liquid Structure

Fig. 1 shows the calculated effective pair potentials of CuO and CuS using the interionic force model.

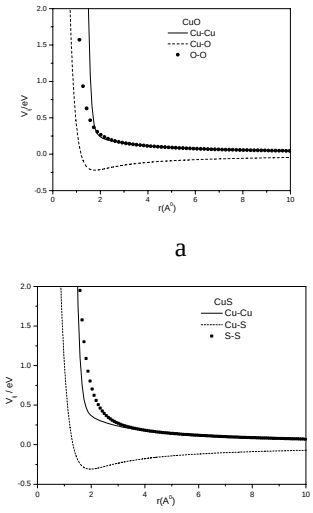

Fig 1. Effective pair potentials for (a) CuO at T = 1540K, ρ = 6.3 g/cm^3 (b) CuS at T = 493K,ρ = 4.6 g/cm^3 thermodynamic states.

It can be seen in Fig. 1 that the calculated pair potentials exhibit similar trends with each other. It is clear that the depth of the primary potential well for different species V_{CuO} and V_{CuS} are deeper than that of others. We note that the contributions to the potentials from van der Waals interaction term are very small, however we will include them in all our calculations. The difference between the size of the positive and negative ions plays an important role at short range. Because of the different values of effective charges, the depth of minima for Cu-O and Cu-S are different.

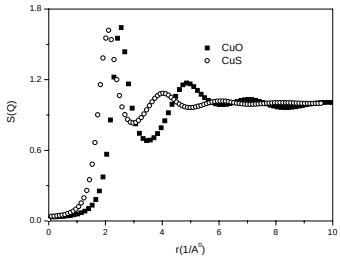

Fig. 2. Total structure factors for CuO and CuS at the same thermodynamic states given Fig.1.

In Fig 2. we have presented the results of total structure factors, within the VMHNC approximation of CuO and CuS using the interionic potentials shown in Fig 1 (a-b). The calculations are carried out at the thermodynamic state for the ionic number density for CuO

ρ=6.3g/cm^3 at T=1540K and for CuS ρ=4.6g/cm^3 at T=493K.

Fig 3. shows the Bhatia-Thornton representations for both CuO and CuS alloys. It appears that the ossillations of each contribution are similar to each other. However the density-density structure factor $S_{NN}(Q)$ in CuO system has a higher peak than CuS. Also the depth of the first minima of two alloy has a high difference. For the concentration fluctuation factors $S_{CC}(Q)$ of both alloy have very small ossilations as we can see and phase-shifted cross term $S_{NC}(Q)$ shows the same ossilations like $S_{CC}(Q)$ but at the medium range both of these factors have negative values.

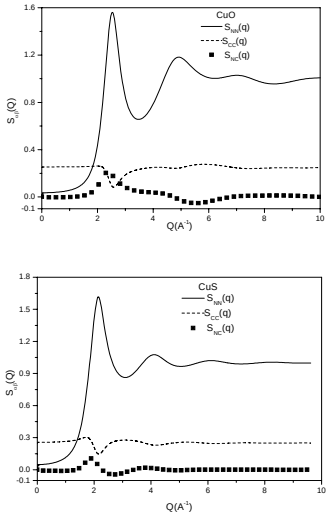

Fig. 3. Bhatia – Thornton partial static structure factors $S_{NN}(Q)$, $S_{NC}(Q)$ and $S_{CC}(Q)$ for (a) CuO and (b) CuS.

4. Conclusions

The equilibrium and structural properties of molten CuO and CuS in their ground state have been studied in detail using the interionic force model. Thus, we can conclude that it is the first time that the molecular structure is shown for these two systems using the interionic force model. The liquid structure of these alloys can be obtained from the interionic force model derived potentials that take into account the effects of the effective valence and the induced polarization. We expect that our results of molecular structure, combined with the results on liquid structure should give a useful first estimate of an ionic model for cupper oxide. We may nevertheless remark that the model parameters for CuS can be redetermined by taking into account for the polarization effect of sulfur. This work will be progressed on this line.

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