Effect of surface relaxation and rumpling on the vibrational spectrum of NO adsorbed on a Cu_2O surface

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Abstract

We report theoretical results for the bonding of NO to a singly coordinated Cu^+ cation of the $Cu_2O(111)$ surface. The effect of the surface relaxation and of the rumpling of coordinatively unsaturated cations on the energy and bonding nature of the interaction and on the vibrational spectrum has been analyzed by using the constrained space orbital variation, CSOV, technique. We found that the bonding is always electrostatic in nature with negligible electron transfer between adsorbate and surface. Surface relaxation phenomena alter the balance among the significant contributions (electrostatic, Pauli repulsion and NO polarization) to the N–O stretch frequency, suggesting that these effects, rather than charge transfer ones, may be in the physical origin of the red shift experimentally observed on NO/Cu_2O systems.

Keywords: Copper oxide; Nitric oxide; Bonding; Vibrational spectrum

1. Introduction

The interaction of nitric oxide with reduced and oxidized copper surfaces is a theme of constant interest due to its technological implications. Copper-based catalysts have been actively studied in recent years as potential systems for the catalytic reduction of NO emissions in vehicles and industrial boilers [1,2]. The active form of this element during reaction depends on the nature of the reductant molecule and the experimental conditions. When CO is used as reductor in stoichiometric proportion conditions (1:1 molar NO:CO ratio), it has been shown that Cu^+ centers are the ones involved on the slow rate step of the reaction [3]. When other reductants, like hydrocarbons, are used in net oxidizing conditions there is not a clear indication about the active form [4] although very recent experiments seem to favor Cu^{2+} [5,6]. Therefore, there is an evident necessity to explore and understand the NO interaction with Cu^{1+}/Cu^{2+} surfaces. In this context, we have recently initiated the theoretical study of the NO adsorption process on the $Cu_2O(111)$ surface [7,8]. In these works we showed that, at least on a perfect surface, the NO/Cu_2O interaction is electrostatic in nature. In reference [7], based in

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the analysis of the N–O stretch frequency, we were also able to show that the NO molecule experimentally observed at low coverages is adsorbed over a singly coordinated Cu^+ cation with an up-right, O-down orientation. Obviously, due to the electrostatic nature of the adsorption process, it does not significantly activate the N–O bond. This is in apparent contradiction with the normal belief that interprets the N–O stretch red shift observed by IR spectroscopy in NO/Cu_2O systems as originated from a $Cu^{1+} \rightarrow 2\pi^* NO$ charge transfer process [9]. To gain insight into the interpretation of the vibrational spectrum of NO/Cu_2O systems, here we present a detailed study of the effects of the bonding nature on the vibrational spectrum of NO adsorbed on $Cu_2O(111)$. Our main goal will be the analysis of the effect that surface relaxation and rumpling processes may have on both the bonding nature and the vibrational observables.

2. Surface models and computational details

Cu_2O has a cubic structure, with O^{2-} ions arranged in a bcc lattice and Cu^+ at the midpoints of the shortest O–O distance, resulting in a tetrahedral environment of Cu^+ cations around O^{2-} anions and a two-fold linear coordination of O^{2-} anions around Cu^+ cations, the Cu–O distance being 1.85 Å. The non-polar $Cu_2O(111)$ surface is known to exist without reconstruction [10]; it can be described as a stacking of slabs, each one formed by three atom planes which contain respectively one O^{2-}, four Cu^+ and one O^{2-} ions per surface unit cell. Thus, in this symmetric sandwich structure no single atomic layer contains both cations and anions. Therefore, a three-plane unit (O–Cu–O) is necessary to satisfy stoichiometry and charge neutrality at the surface. In this unit, the outermost atomic layer contains three-coordinated oxygens and the second layer, located 0.616 Å below, con-

tains both singly and doubly coordinated Cu^+ cations (in a 1:3 ratio).

In a previous study [7] we showed that the singly coordinated Cu^+ cations constitute the preferential adsorption site for the NO molecule, which bonds to the surface through its O atom. This adsorption site is here modeled by a $[CuO_4]^{7-}$ cluster (Fig. 1) embedded in an array of 441 point charges (PCs). This array consists of a 6-layer thick slab (two three-layer units) in which the PC values of fully coordinated ions have been fixed to the formal ones, +1 for Cu cations and −2 for O anions. Partially coordinated edge ions have PC values corresponding to the fractional occupation of their first coordination shell in order to satisfy charge neutrality, minimize possible border effects and enhance the convergence of the Madelung potential (see references cited in [8]). All the above mentioned choices assume that Cu_2O is an ionic solid, as it has been demonstrated in previous studies [11]. The Madelung potential calculated at the Cu^+ central cation (0.550604 a.u.) is reproduced within a 7% of error. Also, the PC array used is large enough to properly account for the long-range Coulombic term of the adsorbate-surface interaction [8]. To correctly handle short-range adsorbate-surface Coulombic interactions as well as to account for quantum lattice effects (other than the Madelung potential), all ions directly coordinated to those in the cluster have been
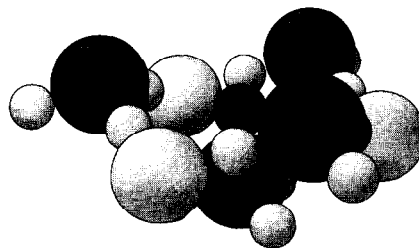

Fig. 1. Representation of the $[CuO_4]$ cluster and nearest neighboring ions. Smaller spheres represent copper cations and larger ones oxide anions. Dark spheres represent ions explicitly included in the calculations and light spheres correspond to ions simulated as TIPs.

replaced by total ion potentials (TIPs) [7]. A total of 15 TIPs, 12 Cu^+ with the spatial extent of a copper $3d^{10}$ shell and 3 O^{2-} with that corresponding to a $2p^6$ shell were introduced on the surface model (see Fig. 1). Since previous results on other adsorbate-surface systems with electrostatic interaction show that the finite size of surface ions located near the adsorbate should be considered in order to properly describe the shape of the potential energy surface [12], selected calculations were repeated using a model with 80 (15 + 65) TIPs, but no significant differences were observed with respect to the 15 TIPs model, showing that the latter has enough ions simulated as TIPs to correctly account for this effect.

Solid termination at the (111) surface of the Cu_2O material can produce two kinds of different displacements from bulk positions: 'rumpling' of the singly coordinated cations (i.e. displacement from the plane defined by the two-coordinated Cu^+ cations) and relaxation of the superficial layers (i.e. change in the interlayer distances). Using the above mentioned surface model, relaxation of the atomic layers and rumpling of the unsaturated Cu^+ cations were studied. For comparative purposes, three different simulations of the surface are included in the calculations. The first one is an ideal surface (model I) without relaxation/rumpling. The second one takes into account the 'local' surface rumpling of the Cu^+ cation in direct contact with the NO (model R), which becomes displaced outwards by about 10% of the inter-layer distance, and it is introduced to allow comparison with the results of reference [7]. The third one introduces both relaxation and rumpling (model RR); this model shows a substantial outwards displacement of the outer oxygen ions (about 60% of the interlayer distance) and of the second copper layer (about 20%). In this case, singly coordinated Cu^+ cations show a somewhat lower (about 15%) outwards displacement (i.e. 5% negative rumpling). The important displacements observed for the RR model indicate that our representation of the relaxation process should be considered only as qualitative, although it is known that geometrically related surfaces (e.g. (111) in fluorite or anti-fluorite structures) also show important displacements of the atomic layers [13]. This is by no means a surprise due to the intrinsic limitations of the cluster representation of a surface. On the other hand, the low density of the ionic layers in Cu_2O (111) may explain the important displacements here obtained. When the adsorbate is included in the calculations, all the real ions, TIPs and PCs except the singly coordinated Cu^+ cation of the $[CuO_4]^{7-}$ cluster were kept frozen at the adjusted Cu_2O cluster positions. The presence of NO reduces the Cu^+ rumpling to about 7%. A schematic view of the equilibrium geometries for the relaxed R and RR structures is presented in Fig. 2.

For these Cu_2O models we have obtained valence ab initio SCF wave functions. Non-empirical pseudopotentials [14] were used for the [Ar] core of Cu and [He] core of N, O atoms.
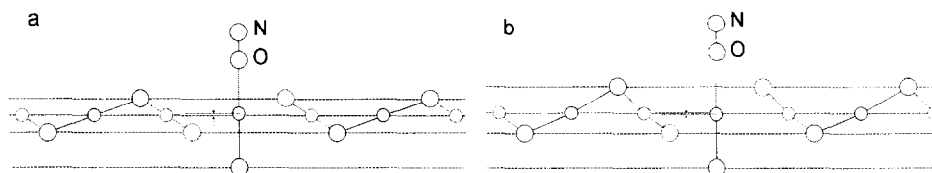

Fig. 2. Sketch of the adsorption site and its environment for $NO/Cu_2O(111)$: (a) R model, (b) RR model. In the figure, [111] direction is vertical and [0, −1, 1] is normal to the plane. Small circles represent Cu^+ and larger ones O^{2-}. Full and broken line symbols indicate structural elements (atoms and bonds) located respectively in and out of the figure plane. A horizontal line has been drawn through the central Cu^+ cation in order to highlight the rumpling phenomenon.

Gaussian-type atomic basis sets, CGTOs, of (3s3p5d/2s1p2d) and (5s5p/3s3p) qualities were used for Cu^+ and O^{2-} ions, respectively. N, O atoms of the NO molecule were represented by a double zeta plus polarization (4s4p1d/2s2p1d) basis set. These basis sets have been shown to allow a correct description of the system [7]. NO was assumed to be adsorbed through its O atom [7]. Optimized geometries were obtained by independently varying the surface–NO and N–O distances. The tilting of the NO molecule away from the normal orientation was found always unfavorable. The high and low frequency separation method [15] has been used to obtain the frequencies of the N–O and surface–ON stretching vibrations at the equilibrium geometries. This uncoupled approach yields almost the same result that a normal coordinate analysis due to the fact that the calculated values for these two frequencies differ by one order of magnitude. The vibrational frequencies have been obtained from a quadratic or cubic polynomial fitted to five points around the minimum of the corresponding energy curve.

In all of the systems studied we have characterized the nature of chemical bonding by means of the constrained space variation technique (CSOV) [16]. This technique introduces stepwise the orbital subspaces of the interacting fragments in the variational space allowing to quantify the importance of the different contributions to any observable (here, the energy and the vibrational frequency). At each step of the CSOV procedure, the interaction energy, E_{int}, is given as

$$E_{int}(\text{CSOV step } n)$$

$$= E(NO) + E(Cu_2O)$$

$$- E(NO/Cu_2O; \text{CSOV step } n)$$

The sign is such that a positive E_{int} indicates a net binding NO–Cu_2O interaction. The change in E_{int} between CSOV step n and the preceding step $n - 1$, ΔE_{int}, represents the energetic importance of the new variational freedom allowed

at step n. A similar analysis is carried out for the N–O stretch frequency shift (respect to free NO).

3. Results and discussion

In Table 1 we report the geometric and energetic parameters of the equilibrium minima found. The NO interaction with our three models is weak, of the order of 0.2–0.1 eV. This is in (qualitative) agreement with the weak interaction experimentally observed [17]. The low value of the interaction energy is an indication of the electrostatic nature of the bonding. To analyze the importance of electrostatic and chemical bonding contributions to the NO bond on the three models of the $NO/Cu_2O(111)$ system, we have obtained the cluster wave functions following the mentioned constrained space orbital variation, CSOV, technique. Results from the CSOV analysis can be seen in Table 2. In this table, V(A, B) represents a CSOV step at which variational change (additionally to that introduced in previous steps) is allowed to occur, where A means the fragment orbitals which are to be varied and B the orbital subspace in which the orbital variation is carried out.

The first step, 1A, of the CSOV considers the simulation of the ionic surface (including the $[CuO_4]^{7-}$ cluster) by an array of PCs only. It should be pointed out that this only yields a crude estimate of the electrostatic interaction because it ignores the nonsphericity of the surface ion electronic clouds, i.e., the effect of the

Table 1
SCF results for NO adsorbed on a cluster model of a singly coordinate Cu^+ position of the $Cu_2O(111)$ surface; equilibrium distances for Cu^+–NO center of mass and N–O, d, in Å, adsorption energy, D_e, in eV

Model	d_{Cu-NO}	d_{N-O}	D_e
I	2.85	1.122	0.11
R	2.74	1.126	0.15
RR	2.72	1.124	0.21

Table 2
CSOV analysis of the different contributions to the interaction energy (eV) for NO adsorbed on cluster models of a singly coordinated Cu^+ position of the $Cu_2O(111)$ surface (for meaning of the different symbols see text)

CSOV step	Model		
	I	R	RR
(1A) Electrostatic int.	0.10	0.15	0.21
(1B) Pauli repulsion	−0.21	−0.27	−0.35
(2) V(NO; NO)	0.03	0.05	0.08$_5$
(3) V(NO; all)	0.05	0.07	0.07$_5$
(4) V(Cu$_2$O; Cu$_2$O)	0.07	0.06	0.10
(5) V(Cu$_2$O; all)	0.06	0.07	0.07
(6) V(op; cl)	0.01	0.01	0.02
(7) Full SCF	$< 10^{-2}$	0.01	$< 10^{-2}$

ligand field in the electronic distribution of the ions [12,18]. In spite of this limitation, it can be seen that the electrostatic contribution grows as we approach to more 'realistic' (i.e. relaxed) models of the surface. This contribution seems to be a rather complex function of the ion positions. The Pauli repulsion, introduced in step 1B by including now the TIPs and the $[CuO_4]^{7-}$ cluster but keeping all orbitals frozen as in the separate fragments, also increases its value in the same direction due to the fact that ions move (in R and RR models) outwards, decreasing the NO-ion distances. Polarization of the adsorbate, singled out in step 2, follows the same trend, in response to the Pauli repulsion. Cu_2O polarization (step 4) and NO and Cu_2O donations (steps 3 and 5, respectively) are nearly equal in all models. In our previous study, we showed that the values obtained at steps 3 and 5 are mainly due to BSSE, and that chemical contributions, i.e. charge transfer processes, are not of significant magnitude [7]. With the mixing of the closed and open shells, step 6, it can be seen that the SCF energy (step 7) is almost completely recovered, indicating that all important bonding mechanisms have been accounted for in previous orbital variations. In short, the CSOV analysis evidences that the main contributions to the bond are the electrostatic and

Pauli repulsion, the latter being almost exactly overcome by the combination of the electrostatic and polarization terms of the interaction energy. All of these terms grow from the I model to the RR one but the overall result is that the electrostatic nature of the bonding remains unaltered among the models studied.

The surface–ON and N–O stretch frequencies for the equilibrium geometries of Table 1 are reported in Table 3. The latter could be compared with the experimental shift (between -50 to -90 cm^{-1}) observed for the adsorption of NO on polycrystalline Cu_2O surfaces [17]. A moderate increase of the surface–ON stretch is observed in parallel with the increase of the computed interaction energy. The N–O stretching shift respect to that of the free molecule is close to zero for the I model, while the other models present negative shifts. Results for the R model are very similar to those reported in reference [7] (the small differences come from differences in the method used to represent TIPs). The CSOV analysis of the N–O stretch frequency shift is presented in Table 4. Again, we must point out that the values of the step 1A are only a qualitative estimate of the electrostatic contribution. In any case, model I shows a lower contribution, by a factor of two, than the remaining models. The effect of the Pauli repulsion, step 1B, grows in the same direction as the energy, showing mainly the big impact of the superficial O^{2-} movement, which can be ex-

Table 3
Vibrational frequencies (cm^{-1}) of the N–O, ω_e(N–O) [a], and surface–NO, ω_e(S–NO), stretching modes for the equilibrium geometries described in Table 1

Model	ω_e(N–O) [a]	ω_e(S–NO)
I	−8	107
R	−56	128
RR	−38	155

[a] This frequency is expressed as a shift with respect to the corresponding calculated vibrational mode of the free NO molecule, ω_e(N–O)$_{free}$ = 2297 cm^{-1}.

Table 4
CSOV analysis of the different contributions to the N–O stretch frequency shift (cm^{-1}) for NO adsorbed on cluster models of a singly coordinated Cu$^+$ position of the Cu$_2$O(111) surface

CSOV Step	Model		
	I	R	RR
(1A) FO. electrostatic int.	−13	−53	−37
(1B) FO. Pauli repulsion	30	35	51
(2) V(NO; NO)	−4	−18	−20
(3) V(NO; all)	−6	−3	−10
(4) V(Cu$_2$O; Cu$_2$O)	−7	−8	−9
(5) V(Cu$_2$O; all)	−6	−6	−8
(6) V(op; cl)	−1	−1	−4
(7) Full SCF	−1	−2	−1

plained because the outer layer displacement is the biggest one among the calculated and involves very (spatially) extended ions. This result evidences the larger influence of the relaxation phenomenon, in comparison to that of rumpling of singly coordinated cations, on the repulsive Pauli contribution. Polarization of the NO electronic cloud (step 2) is again smaller in the I model. The remaining bonding components contribute to a lesser extent to the shift of the N–O stretch frequency. From the CSOV analysis we can see that both superficial phenomena, relaxation and rumpling, affect the N–O stretch frequency shift in a similar way, decreasing the frequency respect to unrelaxed models through the electrostatic and NO polarization contributions. However, these phenomena also affect the Pauli repulsion, partially counteracting the mentioned decreasing effect of the bonding or positive contributions. It is important to note, in any case, that the steps where electron donation is allowed (3 and 5) are clearly not those which most significantly contribute to the computed red shift.

In summary, the results outlined above show that the relaxation/rumpling phenomena do not alter the nature of the bonding although they may be a key factor to explain the red shift experimentally observed in the N–O stretch frequency for NO/Cu$_2$O systems [17]. This fre-

quency shift would appear because these surface phenomena change the balance between the Pauli repulsion and the positive contributions to the bond along the potential energy curves. The trade-off between positive and negative (Pauli) contributions is very complex, and because of the intrinsic limitations of the cluster representation of a surface used, it can only be obtained here in a qualitative basis. However, the presented data suggest that the physical origin of the red shift may be the result of short adsorbate-ion distances (observed in relaxed models respect to unrelaxed or bulk-terminated ones), rather that of the presence of a net charge transfer between surface and adsorbate.

Acknowledgements

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