

THEORETICAL STUDY OF THE PHYSISORPTION OF CO ON METAL OXIDE SURFACES USING THE KSCED-DFT APPROACH

Nathalie VULLIERMET¹, Tomasz A. WESOLOWSKI^{2,*} and Jacques WEBER³

Department of Physical Chemistry, University of Geneva, 30, quai Ernest-Ansermet, CH-1211 Geneva 4, Switzerland; e-mail: ¹nathalie.vulliermet@chiphys.unige.ch, ²tomasz.wesolowski@chiphys.unige.ch, ³jacques.weber@chiphys.unige.ch

Received June 22, 1998

Accepted June 27, 1998

Dedicated to Professor Rudolf Zahradnik on the occasion of his 70th birthday.

Theoretical studies on structure and stretching frequency of the CO molecule physisorbed on the MgO(100) or ZnO(10 $\bar{1}$ 0) surfaces are reported. The properties of the adsorbed molecule were investigated by means of the recently developed formalism of Kohn–Sham equations with constrained electron density (KSCED). The KSCED method makes it possible to divide a large system into two subsystems and to study one of them using Kohn–Sham-like equations with an effective potential which takes into account the interactions between subsystems. This method (KSCED) was shown to be adequate to study the properties of the CO molecule adsorbed on the MgO(100) surface as reported in a previous paper (Wesolowski *et al.*: *J. Mol. Struct.*, *THEOCHEM*, in press). The effect of the interactions with the surface on the CO stretching frequency and geometry was analyzed for vertically bound (C-down) CO at the Zn-site of the ZnO(10 $\bar{1}$ 0) surface. The ZnO(10 $\bar{1}$ 0) surface was represented using several cluster models: Zn²⁺, (ZnO₃)⁴⁻, or Zn₉O₉ embedded in a matrix of point charges. The KSCED frequency shift of the CO stretching vibration is blue-shifted and in good agreement with experiment.

Key words: Physisorption; Frozen electron density; IR Frequencies; Zinc oxides; Magnesium oxides; Carbon monoxide; Clusters.

The recently developed formalism of Kohn–Sham equations with constrained electron density (KSCED) makes it possible to divide a large system into two subsystems and to study one of them using Kohn–Sham-like equations in which the effective potential takes into account the interactions between the subsystems^{1,2}. The KSCED formalism is closely related to the one proposed by Kohn and Sham³ (KS) and can be seen as a method to minimize the total energy with respect to variations of electron density which are well localized in space.

* The author to whom correspondence should be addressed.

The formalism can be used to obtain the electron density and the energy of the total system *via* the “freeze-and-thaw” cycle⁴ or to obtain the electron density of one subsystem keeping the electron density of the other one frozen^{5–7}. In the latter case, the KSCED formalism can be seen as a theoretical framework for designing the embedding potentials based on density functional theory (DFT).

Previous studies of weak molecular complexes using the KSCED method showed that:

- KSCED calculations using relatively simple expressions for the non-additive kinetic energy functional lead to electron densities which are very similar to the electron densities derived from supermolecule Kohn–Sham calculations^{8,9};
- KSCED results are generally less sensitive to the choice of the approximate functionals than the KS ones owing to the fact that they depend on the accuracy of the sum of the used approximate functionals (E_{xc} and T_s^{nadd}) thus making some error cancellation possible^{10,11}, whereas the KS ones depend on the accuracy of the E_{xc} only;
- The vibrational frequency of the CO molecule physisorbed on the MgO(100) surface calculated using the frozen surface electron density is in good agreement with experimental measurements of the CO frequency shift¹¹.

For CO adsorbed on MgO(100), experimental measurements^{12–15} and the results of several theoretical studies (for comparison of different theoretical methods, see ref.¹⁶; for *ab initio* results, see refs^{17–20}; for density functional theory results, see refs^{21–25}) indicate indeed that CO binds weakly to the MgO(100) surface.

The purpose of this work is to study a similar system, the vertically oriented (C-down) CO molecule adsorbed at the Zn-site of the ZnO(1010) surface. The relatively small experimental shift (59 cm^{–1} ref.²⁶, 47 cm^{–1} ref.²⁷) of the stretching frequency of the CO molecule adsorbed on the ZnO surface and small experimental binding energy (–0.52 eV ref.²⁸, –0.48 eV ref.²⁹) indicate that CO physisorbs at this surface, which was confirmed by several theoretical studies (semi-empirical or *ab initio*)^{30–33}. This system resembles closely the one described in our previous work on the CO adsorption on MgO(100) surface¹¹. Within the framework of the KSCED formalism, the two systems differ only by the terms responsible for the interactions with the surface in the effective potential, the level of quantum mechanical description of the CO molecule being the same.

METHODS

The Kohn–Sham Equations with Constrained Electron Density (KSCED)

The formalism of Kohn–Sham equations with constrained electron density^{1,2} (KSCED) was applied. The description of the KSCED method and the details of its computer implementation can be found elsewhere (see ref.⁹ and references therein).

The KSCED approach allows one to limit the DFT treatment to a selected part of the system (with electron density ρ_1) while taking into account the other part (solvent or

surface, for instance, with electron density ρ_2) by means of an effective potential which takes the following form^{1,2}

$$V_{\text{KSCD}}^{\text{eff}} = \sum_A -\frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} + \int \frac{\rho_2(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' + \int \frac{\rho_1(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' + V_{\text{xc}}(\rho_1(\mathbf{r}) + (\rho_2(\mathbf{r})) + \frac{\delta T_s^{\text{nadd}}[\rho_1, \rho_2]}{\delta \rho_1}, \quad (1)$$

where

$$\rho_1 = \sum_i^{N_i} n_{(1)i} |\Psi_{(1)i}|^2, \quad (2)$$

V_{xc} is conventional exchange-correlation potential ($V_{\text{xc}} = \delta E_{\text{xc}}/\delta \rho$), T_s^{nadd} denotes the non-additive kinetic energy,

$$T_s^{\text{nadd}}[\rho_1, \rho_2] = T_s[\rho_1 + \rho_2] - T_s[\rho_1] - T_s[\rho_2] \quad (3)$$

and the index A runs through the nuclei of subsystem 1 and subsystem 2.

The formalism makes it possible to keep the density of the second part (ρ_2) frozen or to modify it by means of the “freeze-and-thaw” cycle⁴.

The total energy of the system comprising the two subsystems is expressed as:

$$\begin{aligned} E[\rho] = E[\rho_1 + \rho_2] = & T_s[\rho_1] + T_s[\rho_2] + T_s^{\text{nadd}}[\rho_1, \rho_2] + \\ & + \frac{1}{2} \iint \frac{(\rho_1(\mathbf{r}') + \rho_2(\mathbf{r}'))(\rho_1(\mathbf{r}) + \rho_2(\mathbf{r}))}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' d\mathbf{r} + \\ & + \sum_A \int \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} (\rho_1(\mathbf{r}) + \rho_2(\mathbf{r})) d\mathbf{r} + E_{\text{xc}}[\rho_1 + \rho_2] \end{aligned} \quad (4)$$

In the absence of strong chemical interactions between the adsorbate and the surface, it is natural to use the electron density of the adsorbate as ρ_1 and electron density of the surface as ρ_2 . With such a partition of the electron density, one can consider the adsorbed molecule as a quantum mechanical system in an effective potential which depends on ρ_2 . The electron density ρ_2 , the position and charges of atomic nuclei of the surface enter as parameters into the expression of the effective potential. It is possible, therefore, to calculate the total energy of the system assuming a given position of the

surface atoms as well as a given electron density of the surface. Such calculations in which ρ_2 does not depend on the position of the adsorbate introduce an additional approximation, namely, neglecting the relaxation of the surface electron density. The KSCED results obtained using frozen ρ_2 density calculated for the surface without adsorbed molecules will be referred to as KSCED(1). The KSCED formalism makes it also possible to relax the surface electron density by means of the “freeze-and-thaw” cycle in which the electron densities of the surface and of the adsorbed molecule invert their roles in a series of subsequent KSCED calculations⁴. Such calculations will be referred to as KSCED(n) where n denotes the corresponding number of swaps in the “freeze-and-thaw” cycle.

All results presented were obtained using the surface model comprising the cluster (with frozen electron density in most cases) embedded in an array of point charges.

Description of the Cluster Models

Scarano *et al.*²⁷ studied ZnO microcrystals by means of high resolution transmission electron microscopy; it was found that the dominant face is (10 $\bar{1}$ 0). Based on the IR spectra, the authors deduced that CO adsorbs on this face at the Zn-sites forming a linear structure. According to the photoelectron spectroscopy studies²⁸ of CO bound on clean terrace (10 $\bar{1}$ 0) sites of ZnO surface, CO molecules are adsorbed at the Zn-sites and are tilted by 30° off the surface normal.

In this work, the ZnO(10 $\bar{1}$ 0) surface was represented as a cluster (Zn²⁺, (ZnO₃)⁴⁻, or Zn₉O₉) with frozen electron density embedded in an array of point charges (+2e for Zn and -2e for O atoms), or, for reference purposes, by means of point charges only. In all cases, the total system boundaries were defined by a 13 × 13 × 4 matrix.

The following clusters embedded in the 13 × 13 × 4 array of point charges were used (see Fig. 1): (i) cluster 0: point charges only; (ii) cluster 1: Zn²⁺ atom; (iii) cluster 2: (ZnO₃)⁴⁻; (iv) cluster 3: Zn₉O₉. Cluster 0 was used for reference purposes to separate the effect of the electrostatic interactions from short-range contributions. Cluster 1 includes only the nearest atom of the surface whereas the largest one (cluster 3) was used to model the ZnO(3 × 3 × 2) section of the surface. The structure of the cluster was defined by the (10 $\bar{1}$ 0) cleavage of the ideal crystal structure at 22 °C (ref.³⁴). The calculations were made for the C-down orientation of the CO molecule adsorbed at the Zn-site of ZnO(10 $\bar{1}$ 0) (see Fig. 1). A vertical orientation of the adsorbed CO molecule and a rigid non-relaxed surface structure were assumed for sake of simplicity.

The choice of the clusters in this study was based on previous investigations of the CO adsorption at the Mg-site of the MgO(100) surface, where the following clusters embedded in an array of point charges were used: (MgO₅)⁸⁻ and Mg₉O₉ (representing MgO(3 × 3 × 2), ref.¹¹) embedded in a 13 × 13 × 4 array of point charges (+2e on Mg and -2e on O atoms, respectively).

Numerical Details

The program deMon³⁵ was modified to perform the KSCED calculations. Gaussian basis sets were used to expand one-electron orbitals and to fit (auxiliary functions) the electrostatic and exchange-correlation potentials. The orbitals were constructed using atomic basis sets with the following contraction patterns: (621/51/1*) for carbon³⁶, (621/41/1*) for oxygen³⁶, and (621/41/1*) for zinc³⁷, which were developed specifically for Kohn–Sham calculations. The coefficients of the auxiliary functions were taken from ref.³⁶ (4,3;4,3) for carbon and oxygen³⁶, and from ref.³⁷ (5,5;5,5) for zinc. Additionally, other sets of auxiliary basis functions were used to fit the non-additive kinetic energy term in the effective potential. They were constructed by multiplying all exponents of the standard exchange-correlation auxiliary functions by factor two. This simple procedure is justified by the fact that the exchange-correlation potential is proportional to $\rho^{1/3}$ whereas applied functionals used to derive $\delta T_s^{\text{nadd}}[\rho_1, \rho_2]/\delta \rho_1$ lead to terms proportional to $\rho^{2/3}$. The applied construction scheme proved to be numerically very stable in several test cases³⁸.

The expansion of the electron density of CO using atom-centered Gaussians involved only CO atoms. Similarly, the expansion of the surface electron density involved only Gaussians centered on the surface atoms. Such an expansion of the electron density, referred to as KSCED(*m*) (in ref.⁹) where *m* stands for monomer implies that the expansion of the electron density of a given fragment uses the same basis functions regardless of the mutual orientation of interacting fragments. It is, therefore, free from the usual basis set superposition error of quantum mechanical results derived from the supermolecule calculations³⁹.

The PW91 exchange-correlation (E_x and E_c proposed by Perdew and Wang⁴⁰) functional was used. The PW91K functional was employed to approximate the non-additive

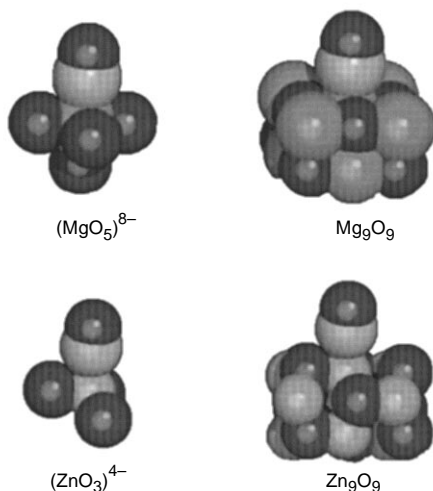


FIG. 1

The geometries of studied clusters

kinetic energy and the associated functional derivative⁴¹. The choice of the PW91 functionals for the present study was based on the study of the adsorption of CO on the MgO(100) surface reported previously¹¹ and our studies on other weak complexes^{10,42}.

Aiming at reducing the computational effort needed to study physisorbed molecules on chemically inert surfaces, the electron density of the surface was frozen. Therefore, the major part of calculations presented here were made at the KSCED(1) level. This approximation was discussed in ref.¹¹ where it was shown that allowing the surface electron density to relax upon adsorbing the CO molecule did not lead to significant changes of neither the CO stretching vibration frequency nor the interaction energy.

At all considered C–Zn distances, the CO stretching frequency was calculated by fitting a third-order polynomial to the potential energy curve corresponding to the atomic displacements as in the stretching vibrational mode of the isolated CO molecule (11 points at $3.8 \cdot 10^{-4}$ Å intervals).

RESULTS

CO Adsorption Energies

The frozen surface calculations (KSCED(1)) neglect the effect of the surface's electron density relaxation. To study its importance the “freeze-and-thaw” calculations were made. The effect of the relaxation of the electron density of the surface on the binding energies was analyzed for the $(\text{ZnO}_3)^{4-}$ cluster (cluster 2). Both the frozen (KSCED(1)) and the relaxed (KSCED(2)) surface density results are presented in Fig 2. Freezing the electron density of the surface, which proved to be a good approximation in the MgO(100) case leads to small binding energy errors also in the ZnO(10 $\bar{1}$ 0) case. The KSCED(1) and KSCED(2) potential energy curves are almost undistinguishable at intermediate C–Zn distances whereas at shorter distances the relaxation of the surface electron density lowers slightly the total energy. The KSCED(2) binding energy amounts -0.14 eV at $R_{\text{C-Zn}} = 2.5324$ Å.

The test calculations with more “freeze-and-thaw” iterations show that the “freeze-and-thaw” cycle converges rapidly (the KSCED(2) and KSCED(5) energies differ less than 0.001 eV).

As expected, the point charge model leads to qualitatively wrong trends for short C–Zn distances. The use of even the smallest cluster possible (the Zn^{2+} atom) reverses these trends and leads to a strong repulsion at short C–Zn distances.

The C–Zn distance at the minimum of the KSCED potential energy curve is equal to 2.71 Å for cluster 2 and the interaction energy amounts -0.16 eV. The KSCED interaction energies lie above both the experimental binding energies (-0.48 eV (ref.²⁹) and -0.52 eV (ref.²⁸)) and the ones derived from theoretical calculations (semi-empirical: from -1.35 to -1.84 eV (ref.³²) at $R_{\text{C-Zn}}$ between 1.988 Å and 2.137 Å or *ab initio*: -0.41 eV (ref.³¹) at $R_{\text{C-Zn}} = 2.705$ Å). As it was shown by Jaffe *et al.*³⁰ the structure of

the ZnO(10 $\bar{1}$ 0) surface differs from that of the bulk crystal. The prerequisite for the accurate prediction of the binding energy is the knowledge of the relaxation of the ZnO(10 $\bar{1}$ 0) surface. The determination of the surface of ZnO(10 $\bar{1}$ 0) is beyond the scope of this work. As the main object of the present work studies is the prediction of the CO stretching frequency, the absolute values of the binding energy are of lesser importance.

The CO–ZnO interaction energy is significantly lowered, however, if the CO molecule approaches the surface not vertically but tilted by 30° (as indicated by the experimental measurements²⁷). The interaction energy calculated using cluster 2 for non-vertical orientation of CO amounts –0.45 eV at C–Zn distance equal to 2.5324 Å which is in a very good agreement with experiment.

The relaxation effect on the CO frequencies was negligible in the previously studied case of CO on MgO. It was, however, more important for the KSCED energies being rather small (less than 0.001 eV) compared to the adsorption energy (about –0.4 eV). The position of the minimum of the potential energy curve was also not significantly affected ($R_{\text{C-Mg}} = 2.35$ Å and 2.33 Å for frozen surface density and “freeze-and-thaw” calculations, respectively). The CO–MgO interaction energies obtained using two different cluster models ((MgO₅)⁸⁻ and Mg₉O₉ embedded in the 13 × 13 × 4 array of point charges) are listed in Table I. Near the minimum of potential energy curve, the effect of the cluster size on the interaction energy was small compared to the absolute values of the interaction energy. At shorter C–Mg distances, the difference between the KSCED(1) energies derived using different clusters increases.

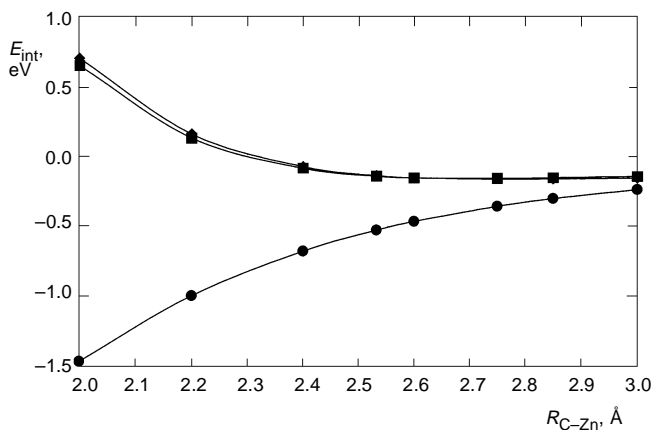


FIG. 2

CO binding energy to the ZnO(10 $\bar{1}$ 0) surface obtained using different embedded cluster models of the surface for several $R_{\text{C-Zn}}$ distances (13 × 13 × 4 matrix of point charges, C-down orientation, Zn binding site) (for description of clusters, see the text); ● cluster 0, ◆ KSCED(1) energies for cluster 2, ■ KSCED(2) energies for cluster 2

CO Bond Length

The same cluster models as the ones described in the previous section were applied to optimize the CO bond length and to calculate the CO-stretching vibrational frequency. Figure 3 shows the CO bond length calculated for different C–Zn distances for the vertically oriented CO molecule.

The CO bond lengths derived from KSCED(1) calculations are shorter than the free-CO bond length (the corresponding Kohn–Sham calculations lead to R_{CO} equal to 1.1515 Å) for all clusters including at least one surface atom. At a C–Zn distance equal to 2.5234 Å, the KSCED(1) CO bond lengths are shorter by 0.005, 0.004, and 0.006 Å, for the Zn^{2+} , $(\text{ZnO}_3)^{4-}$, and Zn_9O_9 clusters, respectively. At smaller C–Zn distances, the CO bond length shortens even more. The same trends were found previously for CO adsorbed on the MgO(100) surface (see Table II). The CO bond length shortens by about 0.003 Å at $R_{\text{C-Mg}}$ equal to 2.42 Å (ref.¹¹).

The point charge model of the ZnO surface does not lead to significant changes in the CO bond length compared to free CO. The CO bond length change being rather small does not vary significantly with the C–Zn distance.

CO Stretching Frequency

High Resolution Electron Energy Loss Spectroscopy (HREELS) was used by D'Amico²⁶ to study the interaction of CO with the ZnO(10 $\bar{1}$ 0) surface. The symmetrical loss feature at 2 202 cm^{-1} was assigned to the carbon–oxygen stretching mode of the adsorbed CO. Compared to the free-CO IR spectrum, the blue-shift of the frequency

TABLE I

Intermolecular distance ($R_{\text{C-Mg}}$) and binding energy (E_{int}) calculated for two embedded cluster models of the MgO(100) surface ($(\text{MgO}_5)^{8-}$ or Mg_9O_9 , $13 \times 13 \times 4$ array of point charges, vertical orientation, C-down, Mg binding site). For description of applied methods and functional parametrizations, see text

$R_{\text{C-Mg}}$, Å	E_{int} , eV	
	$(\text{MgO}_5)^{8-}$	Mg_9O_9
2.1	–0.178	0.061
2.2	–0.234	–0.129
2.3	–0.259	–0.288
2.45	–0.265	–0.270
2.6	–0.234	–0.236
2.8	–0.173	–0.188

amounts 59 cm^{-1} . More recently, Scarano²⁷ obtained an IR peak at $2\,190\text{ cm}^{-1}$, at the low coverage limit which was assigned to CO bonded linearly at the Zn site ($\Delta\omega_{\text{CO}} = 47\text{ cm}^{-1}$).

In this work, the stretching frequency of CO adsorbed on the $\text{ZnO}(10\bar{1}0)$ surface is compared with the free-CO stretching frequency derived from KS(PW91) calculations ($2\,113.1\text{ cm}^{-1}$). The frequency shifts ($\Delta\omega_{\text{CO}} = \omega_{\text{CO(adsorbed)}} - \omega_{\text{CO(free)}}$) obtained using different models of the surface and the KSCED(1) approach are presented in Fig. 4 for several C–Zn distances.

TABLE II
Intermolecular distance ($R_{\text{C-Mg}}$) and C–O bond length calculated for the two embedded cluster models of the $\text{MgO}(100)$ surface ($(\text{MgO}_5)^{8-}$ or Mg_9O_9 , $13 \times 13 \times 4$ array of point charges, vertical orientation, C-down, Mg binding site). For description of applied methods and functional parametrizations, see text

$R_{\text{C-Mg}}, \text{\AA}$	$R_{\text{C-O}}, \text{\AA}$	
	$(\text{MgO}_5)^{8-}$	Mg_9O_9
2.3	1.1469	1.1464
2.375	1.1479	1.1468
2.45	1.1484	1.1483
2.6	1.1487	1.1491
2.8	1.1488	1.1499
∞	1.1515	

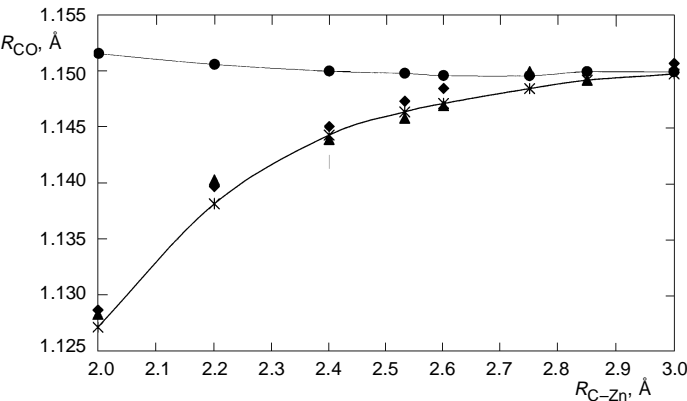


FIG. 3
CO bond length calculated as a function of C–Zn distance for different cluster models (for description of clusters, see the text); ● cluster 0, * cluster 1, ◆ cluster 2, ▲ cluster 3

The equilibrium C–Zn distance was not determined experimentally. Different theoretical *ab initio* studies using cluster models of the surface lead to the energy minimum at C–Zn distance ranging from 2.3 to 2.7 Å (refs^{31,33}). At C–Zn distances in the $R_{\text{C-Zn}} = 2.4\text{--}2.75$ Å range, the frequency shift varies within the following limits: (i) 71.8 to 26.9 cm⁻¹ for cluster 1 (Zn²⁺), (ii) 70.7 to 17.1 cm⁻¹ for cluster 2 ((ZnO₃)⁴⁻), and (iii) 68.9 to 25.4 cm⁻¹ for cluster 3 (Zn₉O₉). At the minimum energy C–Zn distance amounting 2.5324 Å, derived from supermolecule Kohn–Sham calculations for cluster 3, the frequency shifts equal to 50.0, 42.1, and 38.5 cm⁻¹ for clusters 1–3, respectively. These results are in line with experimental measurements (47 cm⁻¹ (ref.²⁷) and 59 cm⁻¹

TABLE III

Intermolecular distance ($R_{\text{C-Mg}}$) and $\Delta\omega_{\text{CO}}$ frequency shift (relative to that of free CO derived from KS(PW91) calculations $\omega_{\text{CO(free)}} = 2\,113.1$ cm⁻¹) calculated for two embedded cluster models of the MgO(100) surface ((MgO₅)⁸⁻ or Mg₉O₉, 13 × 13 × 4 array of point charges, vertical orientation, C-down, Mg binding site). For description of applied methods and functional parametrizations, see text

$R_{\text{C-Mg}}$, Å	$\Delta\omega_{\text{CO}}$, cm ⁻¹	
	(MgO ₅) ⁸⁻	Mg ₉ O ₉
2.3	53.2	53.2
2.45	36.0	33.6
2.6	20.5	25.7
2.8	7.1	3.0

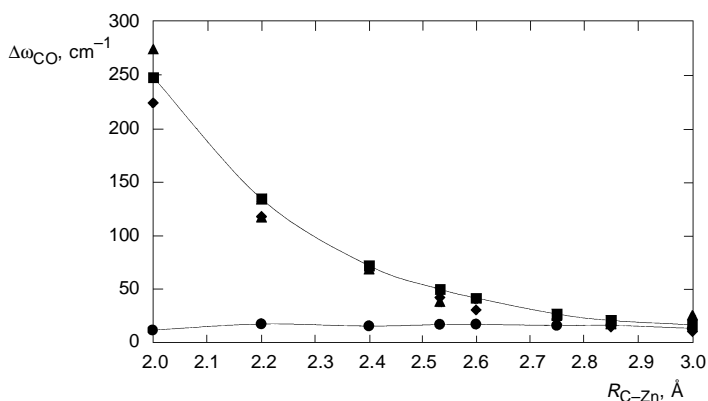


FIG. 4

CO stretching frequency shift ($\Delta\omega_{\text{CO}}$ relative to that of free CO derived from KS(PW91) calculations $\omega_{\text{CO(free)}} = 2\,113.1$ cm⁻¹ (for description of clusters, see the text); ● cluster 0, ■ cluster 1, ◆ cluster 2, ▲ cluster 3

(ref.²⁶). In the same range of C–Zn distances, the point charges model (cluster 0) leads to a value lying between 15.5 and 16.9 cm⁻¹. The point charges model leads to a small frequency shift which does not vary significantly with the C–Zn distance (see Fig. 4). This is in line with the results of the analysis of the contributions to the $\Delta\omega_{\text{CO}}$ of CO adsorbed on MgO surface by Pacchioni *et al.* (see, *e.g.*, ref.²⁰) which indicated that the electrostatic effects are far less significant than the ones identified as “wall effect” due to the Pauli repulsion.

The cluster size effect on the KSCED(1) results is rather small. At intermediate C–Zn distances, the frequencies of the adsorbed CO molecule calculated using three applied clusters agree within 11 cm⁻¹.

A similar agreement between the experimental frequency shift with the one derived from the KSCED(1) calculations was reported previously for CO on MgO(100) in the C-down orientation¹¹ and listed in Table III. The shifts at $R_{\text{C-Mg}} = 2.42 \text{ \AA}$ (with (MgO₅)⁸⁻ cluster as a model of the surface), which corresponds to the minimum of the KS(PW91) potential energy curve, amount 35 cm⁻¹ (KSCED(1)) and 36 cm⁻¹ (KSCED(conv.)), in excellent agreement with experiment ($\Delta\omega_{\text{CO}} = 35 \text{ cm}^{-1}$, ref.¹³).

CONCLUSIONS

The interaction energy as well as the CO stretching frequency for the C-down orientation of the CO molecule are not significantly affected by the choice of the cluster size used to model the MgO(100) or the ZnO(1010) surface.

The frequency shift obtained using the frozen surface KSCED calculations is in a good agreement with the experimental measurements. The physisorbed CO interacts very locally with the ZnO(1010) surface as evidenced by the small influence of the cluster size on both the CO geometry and the stretching frequency. Good qualitative results were obtained using even the smallest considered cluster (consisting of only the Zn²⁺ ion) whereas larger clusters led to a good agreement with experiment. The fact that the long-range electrostatic interactions do not influence significantly the CO stretching frequency, which is determined by local interactions with the surface, supports the applied model in which the surface structure relaxation was neglected and the vertical adsorption was assumed.

Our results together with the ones presented previously for the MgO surface¹¹ indicate that the dominant contribution to the CO stretching frequency shift accompanying the physisorption of CO on such inert chemically metal oxide surfaces originates from Pauli repulsion and not from electrostatic long-ranged interactions. This conclusion is in line with the analysis performed by Pacchioni *et al.*²⁰ of the contributions to the CO frequency shifts upon adsorption on the MgO(100) surface. These studies showed that the dominant contribution is due to the “wall effect” which is represented in the model applied in the present work by the non-additive kinetic energy component of the effective potential.

The authors are greatly indebted to Prof. P. Bagus for stimulating discussions which inspired this work. The authors are grateful to Prof. D. R. Salahub for providing a copy of the deMon program, which was used to perform the Kohn–Sham calculations and into which the KSCED formalism was implemented. Financial support by the Federal Office for Education and Science, acting as Swiss COST office, is greatly acknowledged. This work is also a part of Project 20-49037.96 of the Swiss National Science Foundation.

REFERENCES AND NOTES

1. Cortona P.: *Phys. Rev. B: Condens. Matter* **1991**, 44, 8454.
2. Wesolowski T. A., Warshel A.: *J. Phys. Chem.* **1993**, 98, 5183.
3. Kohn W., Sham L. J.: *Phys. Rev. A* **1965**, 140, 1133.
4. Wesolowski T. A., Weber J.: *Chem. Phys. Lett.* **1996**, 248, 71.
5. Wesolowski T. A., Warshel A.: *J. Phys. Chem.* **1994**, 98, 5183.
6. Stefanovitch E. V., Truong T. N.: *J. Chem. Phys.* **1996**, 104, 2946.
7. Wesolowski T. A., Muller R., Warshel A.: *J. Phys. Chem.* **1996**, 100, 15444.
8. Wesolowski T. A., Chermette H., Weber J.: *J. Chem. Phys.* **1996**, 105, 9182.
9. Wesolowski T. A.: *J. Chem. Phys.* **1997**, 106, 8516.
10. Wesolowski T. A., Ellinger Y., Weber J.: *J. Chem. Phys.* **1998**, 108, 6078.
11. Wesolowski T. A., Vulliermet N., Weber J.: *J. Mol. Struct., THEOCHEM*, in press.
12. Henry C. R., Chapon C., Duriez C.: *J. Chem. Phys.* **1991**, 95, 700.
13. He J.-W., Estrada C. A., Corneille J. S., Wu M. C., Goodman D. W.: *Surf. Sci.* **1992**, 261, 164.
The value of $\Delta\omega_{\text{CO}} = 35 \text{ cm}^{-1}$ was confirmed in recent IR experiments by F. Vanolli *Ph.D. Thesis*. Universite de Lausanne 1997.
14. Scarano D., Spoto G., Bordiga S., Coluccia S., Zecchina A.: *J. Chem. Soc., Faraday Trans.* **1992**, 88, 291.
15. Marchese L., Coluccia S., Martra G., Zecchina A.: *Surf. Sci.* **1992**, 269, 135.
16. Jug K., Geudtner G.: *J. Chem. Phys.* **1996**, 105, 5285.
17. Pacchioni G., Cogliandro G., Bagus P. S.: *Int. J. Quantum Chem.* **1992**, 42, 1115.
18. Mejias J. A., Marquez A. M., Fernandez-Sanz J., Fernandez-Garcia M., Ricart J. M., Sausa C., Illias F.: *Surf. Sci.* **1995**, 327, 59.
19. Nygren M., Petterson L. G. M.: *J. Chem. Phys.* **1996**, 105, 9339.
20. Pacchioni G., Ferrari A. M., Marquez A. M., Illias F.: *J. Comput. Chem.* **1997**, 18, 617.
21. Neyman K. M., Rosch N.: *Ber. Bunsen-Ges. Phys. Chem.* **1992**, 96, 1711.
22. Neyman K. M., Rosch N.: *Chem. Phys.* **1992**, 168, 267.
23. Neyman K. M., Rosch N.: *Chem. Phys.* **1993**, 177, 561.
24. Neyman K. M., Ruzankin S. P., Rosch N.: *Chem. Phys. Lett.* **1995**, 246, 546.
25. Kobayashi H., Salahub D. R., Ito T.: *Catal. Today* **1995**, 23, 357.
26. D'Amico K. L., McFeely F. R., Solomon E. I.: *J. Am. Chem. Soc.* **1983**, 105, 6380.
27. Scarano D., Spoto G., Zecchina A.: *Surf. Sci.* **1989**, 211–212, 1012.
28. Gay R. R., Nodine M. H., Henrich V. E., Ziegler H. J., Solomon E. I.: *J. Am. Chem. Soc.* **1980**, 102, 6752.
29. Bolis V., Fubini B., Giamello E., Reller A.: *J. Chem. Soc., Faraday Trans. 1* **1989**, 85, 855.
30. Jaffe J. E., Harrison N. M., Hess A. C.: *Phys. Rev. B: Condens. Matter* **1994**, 49, 11153.
31. Jaffe J. E., Hess A. C.: *J. Chem. Phys.* **1996**, 104, 3348.
32. Martins J. B. L., Longo E., Andres J., Taft C. A.: *J. Mol. Struct., THEOCHEM* **1996**, 363, 249.
33. Martins J. B. L., Longo E., Taft C. A., Andres J.: *J. Mol. Struct., THEOCHEM* **1997**, 397, 147.

34. Villars P., Calvert L. D.: *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, Vol. 4, p. 4794. ASM International, Materials Park, OH 1991.
35. St-Amant A.: *Ph.D. Thesis*. Universite de Montreal, Montreal 1992.
36. Godbout N., Salahub D. R., Andzelm J., Wimmer E.: *Can. J. Chem.* **1992**, 70, 560.
37. The contraction coefficients distributed with the program deMon (D. R. Salahub, Montreal) constructed as proposed by Godbout N.: Ref.³⁶.
38. Wesolowski T. A.: Unpublished results.
39. Boys S. F., Bernardi F.: *Mol. Phys.* **1970**, 19, 553.
40. Perdew J. P., Wang Y. in: *Electronic Structure of Solids' 91* (P. Ziesche and H. Eschrig, Eds), p. 11. Akademie Verlag, Berlin 1991.
41. The T^{PW91} kinetic energy functional is obtained from the PW91 exchange functional (ref.⁴⁰) using the route proposed by Lee H., Lee C, Parr R. G.: *Phys. Rev. A: At., Mol., Opt. Phys.* **1991**, 44, 768.
42. Wesolowski T. A., Parisel O., Ellinger Y., Weber J.: *J. Phys. Chem. A* **1997**, 101, 7818.