Unimportance of the Surrounding Lattice in the Adsorption of CO on Low-Coordinated Mg Sites of MgO

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The frequency shifts and binding energies of CO adsorbed on three-coordinated (3c) and four-coordinated (4c) Mg sites of MgO via the C-end are computed using bare, stoichiometric cluster models of progressively increasing size: $CO \cdot Mg_n O_n$, $n = 4, 10, 13, 19$ for the Mg_{3c} site and $n = 6, 10, 12, 20$ for the Mg_{4c} site. Calculations are performed by the SCF and DFT methods with a combined basis set which effectively provides the 6-311+G(2df) level of treatment. No marked dependence of the calculated properties on the model size is found. All the bare cluster models reproduce the related experimental frequency shifts and binding energies of CO on MgO to about the same accuracy as the embedded cluster models based on the total ion ab initio model potential (AIMP) formalism [Nygren, M. A.; Pettersson, L. G. M. *J. Chem. Phys.* **1996**, *105*, 9339]. Unlike the common assumption that the surrounding lattice makes a significant contribution to the adsorption characteristics of CO on Mg_{3c} and Mg_{4c} sites of MgO, these results suggest its role to be unimportant. The analysis of the electric field (EF) in the adsorption region of these sites of the bare MgO clusters allows us to conclude that, due to the very steep decrease of the EF on moving away from the surface, both the frequency shift and binding energy of CO are mainly defined by the EF in the CO lone pair subregion nearby the adsorbing Mg. This finding justifies the adequacy of the bare cluster models: as the EF in the vicinity of the adsorbing Mg should be dominated by the smallest stoichiometric cluster including the Mg and its nearest surroundings, the effect of the residual lattice is insignificant.

Introduction

Recently we postulated[1] that *the interactions responsible for the frequency shifts of probe molecules on active sites of oxides are so local in nature that in most cases they are nearly identical to the analogous interactions in molecular complexes.* The experimental CO and CN stretching frequency shifts of nine CO and CD_3CN surface complexes on different oxides, namely, $CO \cdot X$ (X = $\equiv POH$ (AlPO₄), $\equiv SiOH$ (silica), $\equiv SiO(H)Al\equiv$ (zeolites), $\equiv Al$ (zeolites), Mg_{3c} (MgO), and Mg_{4c} (MgO)) and $CD_3CN \cdot Y$ (Y = $\equiv SiOH$ (silica), $\equiv Al$ (zeolites), and Mg_{3c} (MgO)), were accepted as the reference data for checking this hypothesis. This choice was mainly on the basis of three criteria: (i) the structure of the reference complexes should be generally accepted, (ii) the examined frequencies should be conclusively assigned, and (iii) the theoretical description of the frequency shifts should be simple enough to allow their prediction for the molecular analogues to an accuracy of a few cm^{-1}. The result of our calculations was striking: the frequency shifts of $CO \cdot X'$ (X' = $OP(OH)_3$, $Si(OH)_4$, $SiAL(OH)_7$, $Al(OH)_3$, Mg_4O_4, Mg_6O_6) and $CD_3CN \cdot Y'$ (Y' = $Si(OH)_4$, $Al(OH)_3$, and Mg_4O_4) molecular complexes were equal within $\sim$2 cm^{-1} to the frequency shifts of the related surface complexes (Figure 1). According to the available literature, such a good quantita-
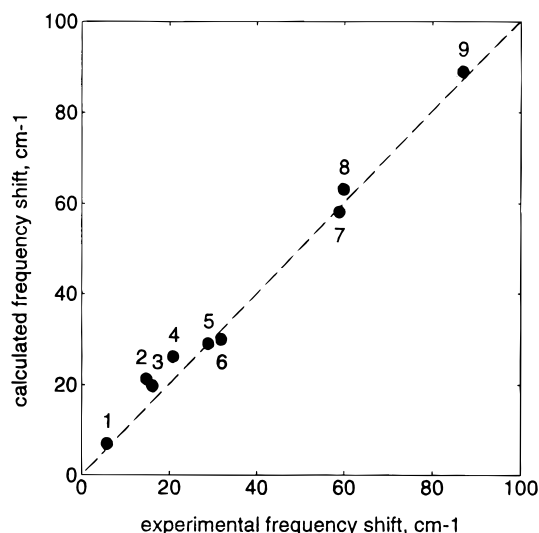

Figure 1. Correlation between calculated and experimental CO and CN stretching frequency shifts of CO and CD_3CN on active sites of oxides: $CD_3CN \cdot HOSi\equiv$ (1), $CO \cdot HOSi\equiv$ (2), $CO \cdot Mg_{4c}$ (3), $CD_3CN \cdot Mg_{3c}$ (4), $CO \cdot HOP\equiv$ (5), $CO \cdot (\equiv SiO(H)Al\equiv)$ (6), $CO \cdot Mg_{3c}$ (7), $CD_3CN \cdot Al\equiv$ (8), and $CO \cdot Al\equiv$ (9).

tive agreement with experimental frequency shifts, for so large a series of surface complexes, and within the same theoretical approximation was reached for the first time. An important

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conclusion follows from this fact regarding the conflicting standpoints of different authors on the extent to which the adsorption properties of active sites of oxides depend on the surrounding lattice.[1-9] Namely, our result suggests that the importance that is frequently given[5-9] to the lattice is strongly exaggerated. Considering the increasing interest in the modeling of oxides, the check of this point is very important for choosing the best strategy to follow. It is even more important to understand why small molecular models, which completely neglect the oxide lattice, are sufficient for reproducing the frequency shifts of probe molecules to such a high accuracy.[1,3,10-15] To these aims, in the present paper we examine the difference in adsorption properties between Mg_{3c} and Mg_{4c} sites of stoichiometric cluster models of MgO and those of the MgO surface. Our choice of these two sites allows us to directly check the general assumption[5-9] that the adsorption properties of strongly ionic magnesium oxide should be highly responsive to the neglect of the lattice. The Mg sites are characterized by the frequency shift and binding energy of CO adsorbed on these sites via the C-end. Particular importance is given for the computed results for the cluster models to correspond to the theory limit. Experimental IR[16] and TPD[17] data and results of AIMP embedded cluster calculations[18] are used as reference data for the Mg_{3c} and Mg_{4c} sites of the MgO surface.

It is currently assumed (ref 19 and references therein) that the interaction of neutral molecules with non-d cations at oxide surfaces is predominantly electrostatic in nature. Therefore we examined the EF at these sites of the MgO clusters to elucidate the role of the surrounding lattice in the frequency shift and binding of CO on Mg_{3c} and Mg_{4c} sites.

The convergence of the computed frequency shift and binding energy of CO on the MgO surface with respect to the cluster size has been investigated in many theoretical studies[20-27] for the embedded cluster approach. As far as we know, there has been no attempt to check this convergence for the case of the bare cluster models of MgO.

Details of Calculations

Calculations were performed with the GAUSSIAN-94 package.[28] For the geometry optimization and the frequency calculations the SCF method was employed. The binding energies were computed by a DFT method using the hybrid B3LYP functional as implemented in GAUSSIAN-94,[29] which is a parametrized combination of the Becke's exchange functional,[30] the Lee, Yang, and Parr's correlation functional,[31] and the exact exchange. A variety of combined basis sets were used. For convenience their specifications are given below when discussing particular problems. Corrections to the binding energies for the basis set superposition error (BSSE) were estimated by the counterpoise method.[32]

The C-O bond of CO and its position with respect to MgO models were fully optimized within the adopted symmetry constraints. In the MgO clusters only the position of the adsorbing Mg was optimized, while the positions of all the other Mg and O atoms correspond to those in magnesium oxide (R_{MgO} = 3.97 bohr). This is in line with the generally accepted methodology of the molecular modeling for ionic oxides.[1,23-27]

As the interaction between CO and the MgO surface is very weak compared with the strength of the C-O bond, the mixing of the CO internal mode with the other vibrational modes is negligible.[33] Therefore we treated the adsorbed CO as a kinematically independent oscillator, the distance of the CO center of mass from the surface being fixed at the optimal position.[8,9,33] When computing the harmonic CO frequency,

TABLE 1: Harmonic HF Frequency Shift, $\Delta\tilde{\nu}$ (cm^{-1}), Anharmonic Frequency Shift, $\Delta\nu$ (cm^{-1}), and Binding Energy, E_b (kcal/mol), of CO Adsorbed on Mg_{3c} and Mg_{4c} Sites

basis set[a]	Mg_{3c} (**1a**)				Mg_{4c} (**1b**)			
				E_b[d]				E_b[d]
	$\Delta\tilde{\nu}$[b]	$\Delta\nu$[c]	SCF	B3LYP// SCF	$\Delta\tilde{\nu}$[b]	$\Delta\nu$[c]	SCF	B3LYP// SCF
A	58		6.5	8.8	20		1.6	3.5
B	59		6.2	7.8	19		1.6	3.9
C	58		5.5	7.2	10		0.9	2.8
D	60		6.3	7.4	15		2.0	3.4
E	57	51	6.0	8.1(8.5)	13	12	1.8	3.9(4.2)
F	61		6.4	7.6	17		2.0	3.7
AIMP[e]	55			11.1	24			4.2
expt[f]		59		9.7		16		

[a] A, 6-31G(d); B, 6-31G(d) for CO and adsorbing Mg, 3-21G for the rest; C, 6-311+G(d) for CO, 6-31G(d) for adsorbing Mg, 3-21G for the rest; D, 6-311+G(d) for CO and nearest oxygen surroundings of the adsorbing Mg, 6-31G(d) for this atom, 3-21G for the rest; E, 6-311+G(D) for CO, 6-31G(d) for adsorbing Mg, 6-311+G(2df) for nearest oxygen surroundings of this atom, 3-21G for the rest; F, 6-311+G(2df) for CO and nearest oxygen surroundings of adsorbing Mg, 6-31G(d) for this atom, 3-21G for the rest. [b] With respect to ν = 2439 (A and B), 2432 (C, D, and E), 2429 (F), and 2166[18] (AIMP) cm^{-1} frequencies of free CO. [c] SQMFF-corrected harmonic HF frequencies. [d] BSSE-corrected E_b = E(complex) − [E(substrate) + E(adsorbate)]. Numbers in parentheses are B3LYP values. [e] Reference 18. [f] References 16 and 17.

$\tilde{\nu}$, the C-O force constant was determined by a two-degree polynomial fit to three points around the C-O minimum.

Anharmonic CO frequencies, ν, were calculated by fitting the Morse function

$$U = D\{1 - \exp[-a(R - R_{CO}^{\circ})]\} \quad (1)$$

where D and a are constants and R_{CO}° is the equilibrium C-O bond length, to five points around the C-O minimum. For the Morse C-O potential curve the ν frequency can be expressed[34] as

$$\nu = \tilde{\nu} - 2\chi\tilde{\nu} \quad (2)$$

where

$$\chi = a^2\hbar/(4\pi c\mu\tilde{\nu}) \quad (3)$$

is the anharmonicity constant and μ is the reduced mass of the C-O oscillator. This method has been successfully used for computing anharmonic stretching frequencies of free and interacting molecules at the HF level of theory.[35,36]

The EF was plotted in the adsorption region of the MgO clusters along the symmetry axis on which the adsorbed CO should lie. The GAUSSIAN-94 CUBE option was used for this procedure.[29] The adsorption region was defined as that of 8.0 bohr above the ion radius of the adsorbing Mg (1.4 bohr). Considering the average distance between the Mg and C atom for the CO on Mg_{3c} and Mg_{4c} sites (~4.7 bohr[18]), the length of the C-O bond (~2.1 bohr), and the van der Waals radius of the O atom (2.6 bohr), the adsorbed CO should fully fall in this region.

Results and Discussion

1. Smallest Bare Stoichiometric Cluster Models of CO on Mg_{3c} and Mg_{4c} Sites. In Table 1 we report the computed $\Delta\tilde{\nu}$ frequency shifts and E_b binding energies of CO on the Mg_{3c} site of the Mg_4O_4 cluster (**1a**, Figure 2) and on the Mg_{4c} site of
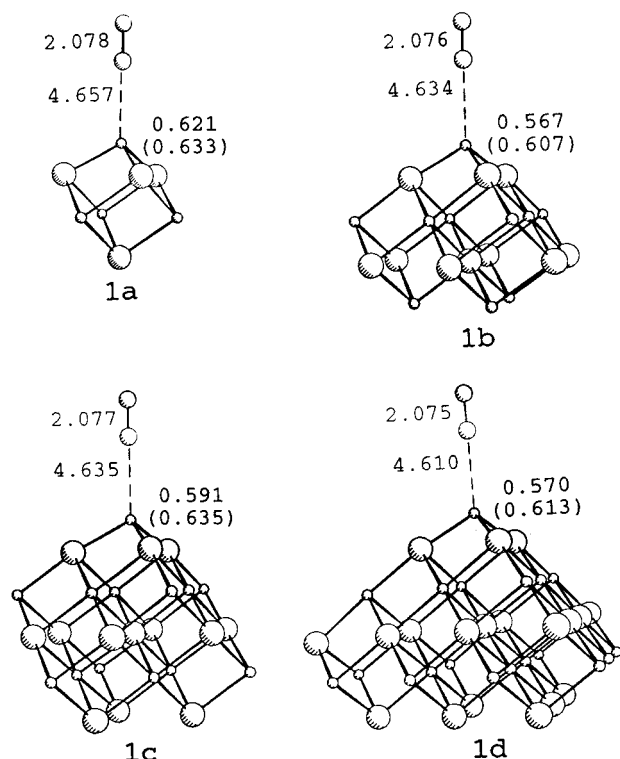
Figure 2. Bare cluster models of CO adsorbed on the Mg_{3c} site of MgO: $CO \cdot Mg_4O_4$ (**1a**), $CO \cdot Mg_{10}O_{10}$ (**1b**), $CO \cdot Mg_{13}O_{13}$ (**1c**), and $CO \cdot Mg_{19}O_{19}$ (**1d**). Bond lengths and inward displacements (in bohr) of the adsorbing Mg_{3c} cation with and without (in parentheses) adsorbate.

Figure 3. Bare cluster models of CO adsorbed on the Mg_{4c} site of MgO: $CO \cdot Mg_6O_6$ (**2a**), $CO \cdot Mg_{10}O_{10}$ (**2b**), $CO \cdot Mg_{12}O_{12}$ (**2c**), and $CO \cdot Mg_{20}O_{20}$ (**2d**). Bond lengths and inward displacements (in bohr) of the adsorbing Mg_{4c} cation with and without (in parentheses) adsorbate.
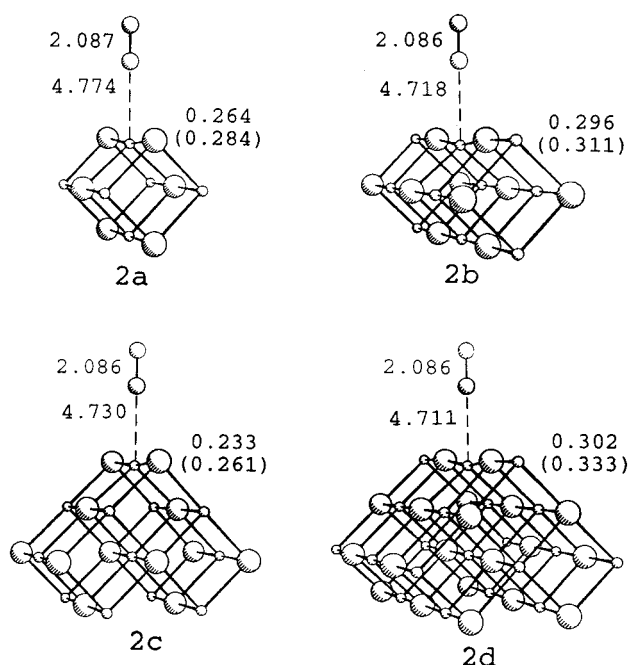
the Mg_6O_6 cluster (**2a**, Figure 3). These clusters represent the smallest bare, stoichiometric models of Mg_{3c} and Mg_{4c} sites of MgO. The frequency shifts were calculated with six basis sets, designated as A, B, C, D, E, and F. The details of these basis sets are reported in Table 1. The examination of these data suggests that the reduction of the basis set from the 6-31G(d) to the 3-21G for all the atoms of Mg_4O_4 and Mg_6O_6

clusters, excluding the adsorbing Mg and its first coordination sphere, marginally affects the $\Delta\tilde{\nu}$ shifts (cf. A and B). In line with our analysis of the basis set effect on the CN stretching frequency shift of CD_3CN on the Mg_{4c} site of the Mg_6O_6 cluster,[37] this result suggests that the CO frequency shifts slightly depend on the quantum chemical description out of "the center" of the clusters. The gradual extension of the basis set, from the 6-31G(d) to the 6-311+G(2df), on CO and the first coordination sphere of the adsorbing Mg (cf. B, C, D, E, and F) also insignificantly changes the frequency shifts. Therefore in the following we use basis set E, suggesting that the SCF/E $\Delta\tilde{\nu}$ frequency shifts represent the best results that can be achieved in a HF harmonic treatment.

Pulay et al.,[38] Blom et al.,[39] and Botschwina et al.[40] showed that the HF method, despite its shortcomings which lead to nonnegligible errors, correctly describes the difference in the force fields of similar fragments in different chemical environments, as the errors in the computed force constants are *quantitatively systematic*. This feature of the HF approximation has been successfully used for developing the scaled quantum mechanical force field (SQMFF) methodology for the quantitative description of vibrational frequencies of molecules[38−40] and molecular complexes.[41] We employ the SQMFF approximation to correct the harmonic HF CO frequencies.

For CO molecule and CO complexes the C−O oscillator is kinematically independent to a high accuracy.[33] In this case the SQMFF correction to the harmonic HF frequency for the basis set incompleteness and the electron correlation neglect is equivalent to the scaling procedure

$$\tilde{\nu}^{SQMFF} = k_{CO}\tilde{\nu} \tag{4}$$

where $\tilde{\nu}^{SQMFF}$ is the SQMFF-corrected frequency and k_{CO} is the scale factor. At the SCF/E level k_{CO} is equal to 0.8923, being defined as the k_{CO} fitting the computed harmonic frequency of free CO, 2432 cm^{-1}, to the experimental one, 2170 cm^{-1}.[34] Thus, within the SQMFF SCF/E approximation

$$\Delta\tilde{\nu}^{SQMFF} = 0.8923\Delta\tilde{\nu} \tag{5}$$

The errors due to BSSE and anharmonicity should be taken into account too. To estimate the BSSE effect, we recomputed the ν frequencies of CO on Mg_{3c} and Mg_{4c} sites, correcting each point in the C−O potential energy curve for the BSSE. The correction turned out to be very small ($\sim$1 cm^{-1}), close to an analogous result by Pettersson et al.[42] Therefore in the following consideration we neglect the BSSE effect on the frequency shifts. The corrections for anharmonicity were found to be −25 cm^{-1} for the free CO (in excellent agreement with experimental data, −27 cm^{-1} [34]) and −24 cm^{-1} for the CO on both Mg_{3c} and Mg_{4c} sites. Thus, also the anharmonicity effect on the frequency shifts of CO is negligible. On the basis of these results, we take the SQMFF-corrected SCF/E $\Delta\tilde{\nu}$ frequency shift of CO (Table 1) to correspond to the theory limit for the anharmonic approximation

$$\Delta\nu = \Delta\tilde{\nu}^{SQMFF} \tag{6}$$

As the SCF method strongly undervalues the electron density on the CO lone pair, the binding energies were computed by the DFT method. The calculations were performed at the B3LYP/E, B3LYP//SCF/E, B3LYP//SCF/A, and B3LYP//SCF/B levels. The comparison of the B3LYP/E and B3LYP//SCF/E results (Table 1) suggests that the optimization of the geometry at the DFT level increases the binding effect by 0.3−0.4 kcal/mol only. Therefore, to reduce the computational cost,

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TABLE 2: Anharmonic Frequency Shift, $\Delta\nu$ (cm^{-1}), and Binding Energy, E_b (kcal/mol), of CO Adsorbed on Mg$_{3c}$ and Mg$_{4c}$ Sites[a]

Mg$_{3c}$			Mg$_{4c}$		
model	$\Delta\nu$[b]	E_b[c]	model	$\Delta\nu$[b]	E_b[c]
1a	51	8.1	**2a**	12	3.9
1b	56	10.6	**2b**	14	3.0
1c	53	10.1	**2c**	13	3.9
1d	61	11.3	**2d**	15	4.4
AIMP[d]	56[e]	10.1[e]	AIMP[d]	24	4.2
expt[f]	59	9.7	expt[f]	16	

[a] E basis set. [b] For cluster models $\Delta\nu$ frequency shifts are SQMFF-corrected SCF/E $\Delta\tilde{\nu}$ frequency shifts. SCF/E $\tilde{\nu}$ frequency shifts are computed with respect to free CO $\tilde{\nu} = 2432$ cm^{-1} (E). [c] BSSE-corrected B3LYP//SCF $E_b = E$(complex) $-$ [E(substrate) $+$ E(adsorbate)]. [d] Reference 18. [e] Calculations were performed without relaxation of the Mg$_{3c}$ site. [f] References 16 and 17.

we examined the binding energy within the B3LYP//SCF/E approximation. As the binding of CO on positively charged non-d sites is basically related to electrostatic interactions,[19] the increase of electron density on the C-end of CO on going from the SCF to DFT approximation increases the binding energies by $\sim$2 kcal/mol (Table 1). Like for the frequency shifts (Table 1), neither the reduction of the basis set on "the outer part" of the Mg$_4$O$_4$ and Mg$_6$O$_6$ clusters (cf. A and B) nor the extension of the basis set on CO and the first coordination sphere of the adsorbing Mg (cf. B and E) influences significantly the binding energies. Therefore we regard the B3LYP//SCF/E binding energies as those approaching the theory limit.

In agreement with our hypothesis,[1] the frequency shifts and binding energies of CO coordinated with Mg$_{3c}$ and Mg$_{4c}$ sites on bare Mg$_4$O$_4$ and Mg$_6$O$_6$ clusters are very close to those on the MgO surface[16-18] (Table 1). Our ideas[1] also suggest that these adsorption properties should slightly depend on the cluster size. To verify this suggestion, below we examine the cluster-size effect on these characteristics.

2. Effect of Cluster Size on Frequency Shift and Binding Energy of CO on Mg$_{3c}$ and Mg$_{4c}$ Sites. In Table 2 we report the calculated frequency shifts and binding energies of CO on Mg$_{3c}$ and Mg$_{4c}$ sites, obtained with {**1a**, **1b**, **1c**, **1d**} (Figure 2) and {**2a**, **2b**, **2c**, **2d**} (Figure 3) sets of models, respectively. For all the extended models the frequency shifts and the binding energies were calculated in the SQMFF SCF/E and B3LYP//SCF/E approximations, respectively, as for the minimum **1a** and **1b** models. Figures 4 and 5 present the dependence of the $\Delta\nu$ shifts and E_b energies on parameter n in the series of the CO·Mg$_n$O$_n$ models. No pronounced dependence of these characteristics on the cluster size is found, in agreement with our hypothesis.[1] One can note that the **1a** model somewhat underestimates both the frequency shift and the binding energy compared with the larger models of CO on the Mg$_{3c}$ site. However, all the bare cluster models reproduce the related experimental data to about the same accuracy as the most advanced embedded cluster method based on the AIMP formalism.[18]

To give a theoretical interpretation of this result, below we analyze the EF in the adsorption region of Mg$_{3c}$ and Mg$_{4c}$ sites of the examined models.

3. Analysis of Electric Field at Mg$_{3c}$ and Mg$_{4c}$ Sites. Figure 6 shows a one-dimensional plot of the EF in the adsorption region of Mg$_{3c}$ and Mg$_{4c}$ sites of Mg$_4$O$_4$ and Mg$_6$O$_6$ clusters, respectively. The most important feature to note is that the EF sharply decreases on moving away from the surface, the EF in the 5σ lone pair subregion being much larger than
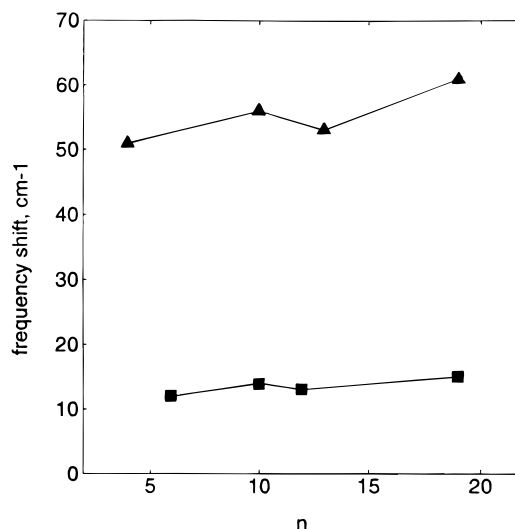
Figure 4. Dependence of the computed frequency shift of CO on Mg$_{3c}$ (▲) and Mg$_{4c}$ (■) sites of bare Mg$_n$O$_n$ clusters on parameter n.
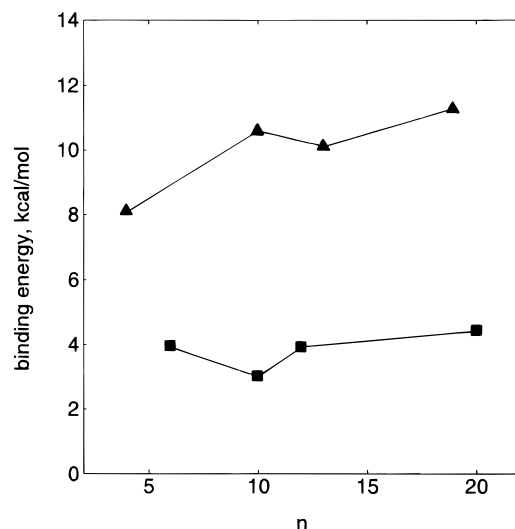
Figure 5. Dependence of the computed binding energy of CO on Mg$_{3c}$ (▲) and Mg$_{4c}$ (■) sites of bare Mg$_n$O$_n$ clusters on parameter n.

that in the residual part of the adsorption region. This result suggests that the main contribution to the adsorption characteristics should be due to the EF at the C-end close to the adsorbing Mg. The comparison of the EF at $z = 3$, 6, and 8 bohr distances from Mg$_{3c}$ and Mg$_{4c}$ sites of the cluster models (Table 3) verifies this suggestion. (We take the EF at these three points as characteristic of the EF in three subregions of the CO charge distribution, namely, the C-end ($z = 3$ bohr), the center ($z = 6$ bohr), and the O-end ($z = 8$ bohr).) When increasing the model size, the change in EF at $z = 6$ and 8 bohr is comparable with the EF itself. However the frequency shift and the binding energy slightly change in the examined series of models (Table 3). This fact implies that these characteristics have no significant relation to the EF produced by the surface at both the center and O-end of the molecule. The adsorption properties being insensitive to the model size can be accounted for only by the predominant role of the EF at the C-end: the change in EF at $z = 3$ bohr is about the same as at $z = 6$ and 8 bohr (Table 3), but it is small in comparison with the EF itself. This finding explains why the bare, stoichiometric cluster models of MgO reproduce the frequency shifts and binding energies of CO on Mg$_{3c}$ and Mg$_{4c}$ sites to quantitative accuracy. As the EF in the vicinity of an adsorbing
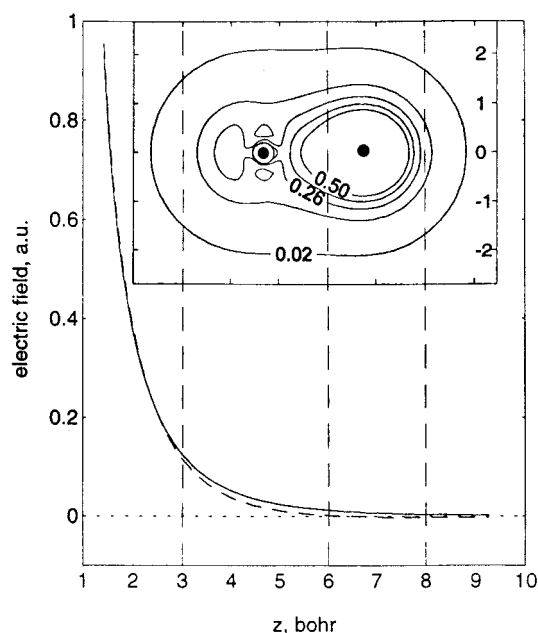
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Figure 6. One-dimensional plot of the EF at Mg_{3c} (solid line) and Mg_{4c} (dotted line) sites of bare Mg_4O_4 and Mg_6O_6 clusters, respectively. The EF is given along the symmetry axis of the clusters on which the adsorbed CO should lie. The inset shows the electron density map of the adsorbed CO; electron density in au. The distance between the adsorbing Mg and the CO center of mass is 5.9 bohr, which corresponds to the average value for the adsorption on Mg_{3c} and Mg_{4c} sites. The vertical dotted lines are plotted at $z = 3$, 6, and 8 bohr; the EF at these points is chosen to characterize the EF in the C-end, center, and O-end subregions of the adsorbed CO.

TABLE 3: Electric Field, EF (au), at Various Distances, z (bohr), from Mg_{3c} and Mg_{4c} Sites of Mg_4O_4 and Mg_6O_6 Clusters and Its Difference, EFD (au), from That of Extended Clusters

	$z = 3$		$z = 6$		$z = 8$	
cluster	EF	EFD	EF	EFD	EF	EFD
Mg_4O_4	0.1219		0.0118		0.0036	
$Mg_{10}O_{10}$		0.0046		0.0027		0.0020
$Mg_{13}O_{13}$		0.0038		0.0027		0.0022
$Mg_{19}O_{19}$		0.0070		0.0043		0.0031
Mg_6O_6	0.1127		0.0015		−0.0025	
$Mg_{10}O_{10}$		−0.0001		0.0008		0.0014
$Mg_{12}O_{12}$		0.0015		0.0003		−0.0003
$Mg_{20}O_{20}$		0.0005		0.0012		0.0019

Mg site is mainly determined by the minimum neutral cluster including the Mg and its nearest surroundings (Table 3), the effect of the residual lattice is small. Our result also suggests that the approximation of a strongly nonuniform EF at surface cations by a uniform EF when treating the CO adsorption, the strength of the uniform EF being equal to that of the nonuniform EF at the center of the CO,[33,46,47] has to be critically reexamined.

Conclusion

The bare $CO \cdot Mg_4O_4$ and $CO \cdot Mg_6O_6$ cluster models of CO on Mg_{3c} and Mg_{4c} sites of MgO reproduce the related experimental frequency shifts and binding energies of CO to quantitative accuracy. This result suggests that the influence of the neglected lattice on the adsorption properties of these sites is unimportant. The check of the cluster-size effect on these adsorption characteristics validates this suggestion: no significant change in calculated results is found upon gradual

increase of the minimum models of Mg_{3c} and Mg_{4c} sites up to $Mg_{19}O_{19}$ and $Mg_{20}O_{20}$, respectively.

The analysis of the electric field in the adsorption region of Mg_{3c} and Mg_{4c} sites of the examined MgO clusters shows that the electric field produced by the surface in the central and O-end subregions of the adsorbed CO does not play a significant role in both the frequency shift and the binding effect. These characteristics are mainly defined by the electric field in the CO lone pair subregion close to the adsorbing Mg. This result explains why the small, stoichiometric cluster models of MgO are adequate for describing the adsorption properties of these Mg sites: the electric field close to the adsorbing Mg is dominated by a small neutral cluster including the Mg and its nearest surroundings.

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