African Journal of Advanced Pure and Applied Sciences (AJAPAS)
Online ISSN: 2957-644X
Volume 4, Issue 3, 2025
Page No: 31-37
Website: https://aaasjournals.com/index.php/ajapas/index
ISI 2025: 1.126 **SJIFactor 2024: 6.752** **معامل التأثير العربي: 1.62**

A Study of the Adsorption Structures of Co Molecule on the MgO (001) Surface

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دراسة تراكيب امتزاز جزئ CO على سطح مركب MgO (001)

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Received: May 09, 2025	Accepted: June 30, 2025	Published: July 10, 2025

Abstract:
Using a Monte Carlo simulation model, the results showed that carbon monoxide (CO) molecules stabilize on the magnesium oxide surface (MgO) in either monolayer or multilayer structures. Each of these configurations has distinct thermal characteristics, which differentiate them in terms of unit cell configuration, number of molecules, tilt angles from the surface, vertical height, adsorption energies, and surface coverage ratios.
The simulation results agreed significantly with previously obtained experimental results. At low temperatures, three configurations of type c(4×2) were identified, with each primitive cell containing six CO molecules. The molecules are predominantly adsorbed vertically over Mg^{+2} ions, with a 2:1 ratio of vertical to tilted molecules. The polar angle for tilted molecules was found to be 31°, consistent with Polarization Infrared Reflection Spectroscopy (PIRS) experimental values. Vertical molecules align directly above Mg^{+2} ions, while tilted ones are slightly displaced. The configurations alternate between vertical and tilted molecule rows.
Monte Carlo simulations showed that this configuration remains thermally stable up to approximately 40 **K**. At this temperature, the p(3×2) configuration appears, accompanied by a decrease in coverage due to the replacement of tilted molecules with vertical ones. Only tilted molecules remain in the monolayer configuration at full coverage, while vertical molecules form in the multilayer arrangement.

Keywords: Adsorption, Monte Carlo Simulation, MgO surface, CO molecules, binding energy, surface coverage.

الملخص:
من خلال دراسة نموذج محاكاة باستخدام طريقة المونتي كارلو أظهرت النتائج أن جزيئات أكسيد الكربون تستقر عند درجات حرارة معينة على سطح أكسيد الماغنيسيوم في صورة تراكيب أحادية الطبقة أو متعددة الطبقات، بحيث يكون لكل من هذه التراكيب خصائصها التي تميزها عن غيرها من حيث وحدة الخلية، وعدد جزيئاتها، وزوايا ميلانها عن السطح، وارتفاعها عنه، وطاقات امتزازها الناتجة، ونسب تغطيتها للسطح. وجاءت نتائج المحاكاة التي قمنا بها متوافقة بشكل كبير مع النتائج السابقة المتحصل عليها باستخدام التقنيات التجريبية.
ولقد تبين أن التراكيب في درجات الحرارة المنخفضة تكون من نوع $c(4\times2)$، يعني أن هناك ثلاث جزيئات لكل وحدة خلية بدائية وستة لكل وحدة خلية متمركزة، مواقع الامتزاز مركزة قرب أيونات Mg^{+2} وتحدث بنسبة 2:1 للعمودية مقابل المائلة. الزاوية القطبية في حالة الجزيئات المائلة وجدت 31° لكي تكون متوافقة بشكل جميل مع القيم المقررة من تجارب PIRS.

تستقر الجزيئات العمودية على مستوى السطح مباشرة على قمة أيونات Mg^{+2} لتشكل صفوفاً تشغل كل المواقع. بينما تزاح الجزيئات المائلة من موقع أيون Mg^{2+} إزاحة مقدارها بضعة أعشار الأنجستروم في اتجاه ميلانها لتشكل صفوفاً تشغل بها كل المواقع. جميع هذه الصفوف تتناوب المواقع بحيث يفصل الصف الغير مائل الصفوف المائلة.
وبينت محاكاة MC أن هذا التركيب يكون مستقراً حرارياً حتى درجة حرارة (في حدود **40K**) وبعد هذه الدرجة فتبين المحاكاة حالة عدم الاستقرار للطبقة وتظهر الجزيئات المطرودة من السطح. التغطية تنخفض في التركيب $p(3\times2)$ مع حدوث تبديل مصاحب للجزيئات المائلة بأخرى غير مائلة، ولقد أعطت نتيجة المحاكاة صورة مماثلة للنتائج التجريبية من حيث تحديد التغطية وأعداد الجزيئات المائلة والعمودية.
في الطبقة الأحادية ذات التغطية الكاملة تتواجد الصفوف ذات الجزيئات المائلة فقط، فكل استقرار يتبع التركيب يحدث فيه إضافة صف غير مائل بين الصفوف المائلة عن طريق عمليات الطرد والتحول، لذا يكون التركيب $c(4\times2)$ له صف واحد غير مائل بين الصفوف المائلة، والتركيب $p(3\times2)$ له صفان غير مائلان بين الصفوف المائلة، ..... وهكذا.

الكلمات المفتاحية: امتزاز، محاكاة مونتي كارلو، سطح MgO (001)، جزئ CO، طاقة الربط، تغطية السطح.

Introduction:
Due to significant advancements in experimental techniques and the increasing power of computational systems, the study of molecular adsorption structures on ionic surfaces has garnered considerable interest among physicists. This interest has led to a deeper understanding of the fine details of the behavior of these structures. The use of statistical approaches such as the Monte Carlo method has been instrumental in determining the locations, orientation angles (θ, φ), and phase transitions of adsorbed molecules on ionic surfaces[1-11].
Simulation results showed that at temperatures below 40 **K**, carbon monoxide molecules adsorb physically onto the magnesium oxide surface. A structure with six CO molecules per unit cell ($c(4\times2)$) forms either with vertical or tilted orientation, where the polar tilt angle for tilted molecules is approximately 31°. At higher temperatures, this structure transitions into a $p(3\times2)$ configuration with four molecules per unit cell, and at even higher temperatures, it becomes unstable. A series of transformations involving (n×2)-type structures was observed.

At a surface coverage of 0.625, a second CO layer begins forming on the MgO surface. These findings agree with experimental results from Low Energy Electron Diffraction (LEED), Helium Atom Scattering (HAS), and Polarization Infrared Reflection Spectroscopy (PIRS).

Experimental Section:
In this study, we examine the structure formed by the adsorption of carbon monoxide (CO) molecules on the surface of magnesium oxide (MgO). This allows us to identify key details such as the position, height, and orientation of these molecules relative to the surface, as well as the binding energy associated with their interaction with the substrate.

2.1 Methods and Programs Used:
To simulate the behavior of adsorbed CO molecules on the MgO surface, we employed the Monte Carlo method. We also used supporting visualization programs such as Rasmol for displaying atoms and molecules based on their positions, in addition to software like Maple.
3. Simulation Methods:

3.1 Monte Carlo Method:
In this simulation, we considered a section of the MgO surface and placed N CO molecules on it, where N varies depending on the final configuration. The molecules were allowed to move randomly over a fixed surface without considering any vibrations. The acceptance or rejection of new configurations was determined using the Boltzmann Metropolis criterion[13-14].
We performed 60,000 Monte Carlo steps for each simulation. The initial 30,000 steps were disregarded to ensure that only equilibrium configurations were analyzed.

Simulation Results:

1. **Adsorption of a Single CO Molecule on MgO (001):**

Figure 1 shows top and side views of the final configuration for a single CO molecule adsorbed on the MgO surface after 30,000 Monte Carlo cycles at 1 **K**. The CO molecule is oriented vertically on the surface, with the

carbon atom closer to the Mg^{2+} ion and the oxygen atom positioned upward. The carbon atoms are represented in gray, oxygen in red, Mg^{2+} in purple, and O^{2-} in red.
Figure 2 illustrates the probability density distribution of the polar angle θ. At 1 **K**, the distribution peaks at θ = 0°, indicating a vertical alignment of the molecule without a preferred azimuthal angle.

Figure 3 presents the probability density distribution of the vertical distance (Z) between the CO molecule and the MgO surface. The peak occurs at Z ≈ 2.525 **Å**, corresponding to the equilibrium position of the CO molecule vertically adsorbed on top of a Mg^{+2} ion.

Table 1 summarizes the total energy of the system, the average height of the carbon atom above the Mg^{2+} ion (Z), the average tilt angle θ, and the average binding energy per molecule. The total binding energy per molecule was found to be approximately −3.88 kcal/mol, with the largest contribution from electrostatic interactions.

These results are consistent with previous experimental and theoretical studies, validating the parameters used to calculate the interaction potential between the CO molecule and the MgO surface. This affirms the reliability of the potential model used for further analysis of multi-molecule adsorption configurations.

2. CO Monolayer:

Figure 4 shows top and side views of a 12×12 MgO (001) surface before the addition of CO molecules.

Figure 5 displays the same surface after placing 144 CO molecules, achieving full coverage. A Monte Carlo simulation with 60,000 steps at 1 **K** was conducted to reach equilibrium.

The resulting structure resembles the low-temperature configuration of type p(3×2), where the CO molecules are tilted at an angle of 17° from the surface. This configuration aligns with previous experimental and semi-empirical simulations for similar systems such as CO/NaCl(001) and CO/MgO[12].

Figure 6 illustrates the polar angle distribution, again peaking around 17°, while Figure 7 shows top and side views of the final configuration at 10 **K**. Due to repulsive interactions among CO molecules and differences in lattice constants, the surface cannot accommodate all 144 CO molecules. As a result, some molecules are expelled to form a second layer.

Figure 8 shows that 36 molecules move into the second layer, leaving 108 in the first layer, which corresponds to a surface coverage required for the c(4×2) structure.

Figures 9 and **10** provide the probability density distribution for the polar angle and vertical distance (Z), respectively, further confirming the stability and structural characteristics of the CO monolayer system at low temperatures.

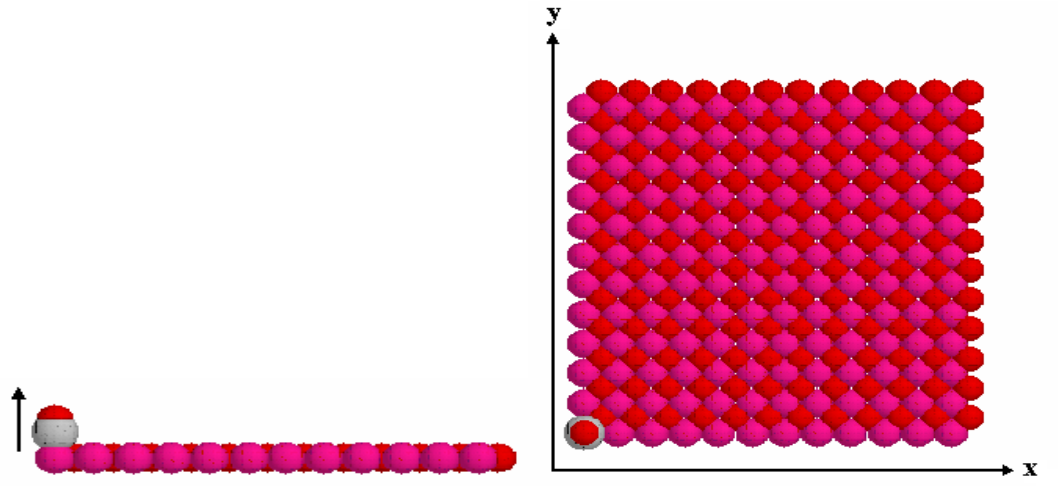

Figure 1: Top and side views of a single CO molecule adsorbed on MgO (001).

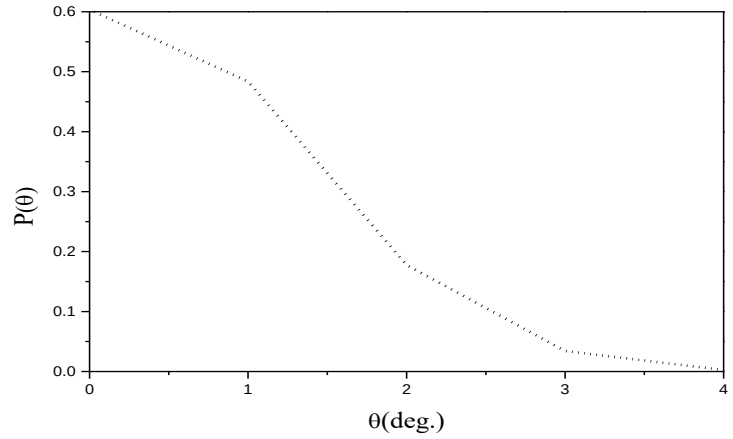

Figure 2: Probability distribution of the polar angle θ at 1 K.

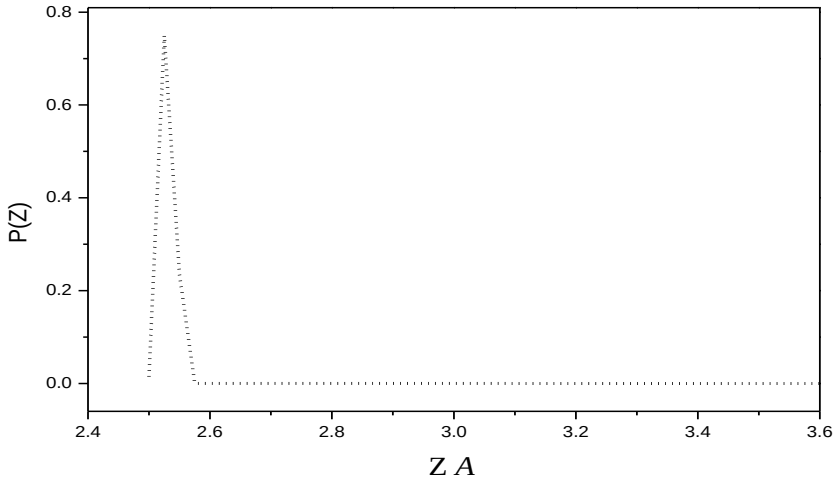

Figure 3: Probability distribution of vertical distance Z at 1 K.

Table 1: Summary of Adsorption Characteristics for CO on MgO (001) at Various Coverages and Structures

Structuare	1 CO	144 CO	108 CO		96 CO		72 CO
CoverageΘ		P(2×1) 1.0	C(4×2) 0.75		P(3×2) 0.66		C(2×2) 0.50
Sites	$CO_{\perp}$	$CO_{\angle}$	$CO_{\perp}$	$CO_{\angle}$	$CO_{\perp}$	$CO_{\angle}$	$CO_{\perp}$
CO molecule	1	144	36	72	48	48	72
$Z_{(C\text{-}Mg)}$ (Å)	2.525	2.588	2.525	2.575	2.525	2.575	2.525
θ °	0	17	0	31	0	31	0
$E_{molecule}$	-3.88	-1.1	-4.27	-3.39	-4.25	-3.4	-4.13
E_{total}	-3.88	-158	-154	-244	-204	-163	-297
E_{layer}	-3.88	-158	-398.6		-367.6		-297
$E_{mol.ave.}$	-3.88	-1.1	-3.69		-3.83		-4.12

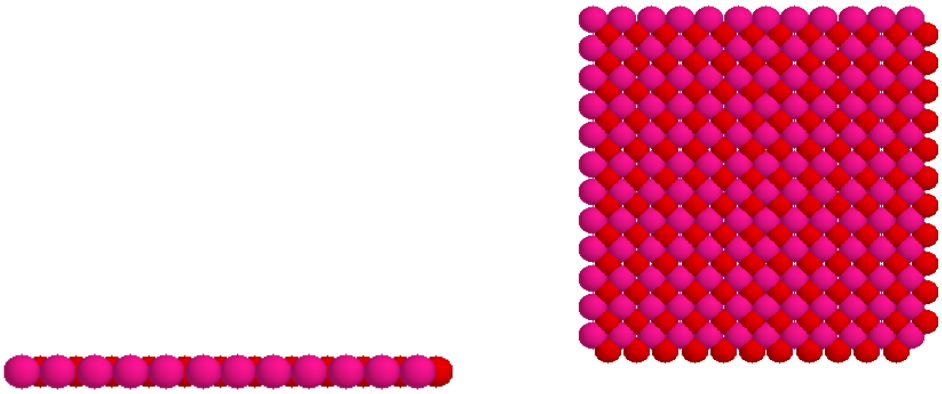

Figure 4: Top and side views of a clean 12×12 MgO (001) surface before CO adsorption.

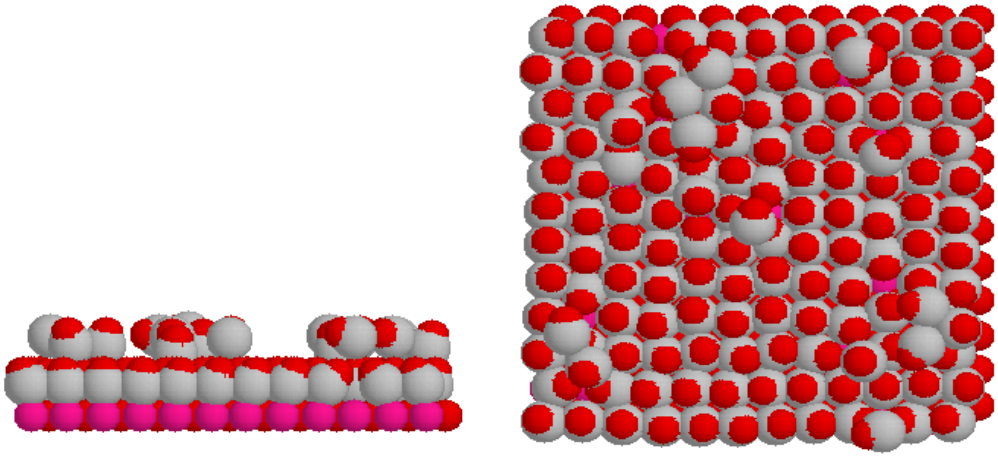

Figure 5: Configuration after placing 144 CO molecules on the MgO surface.

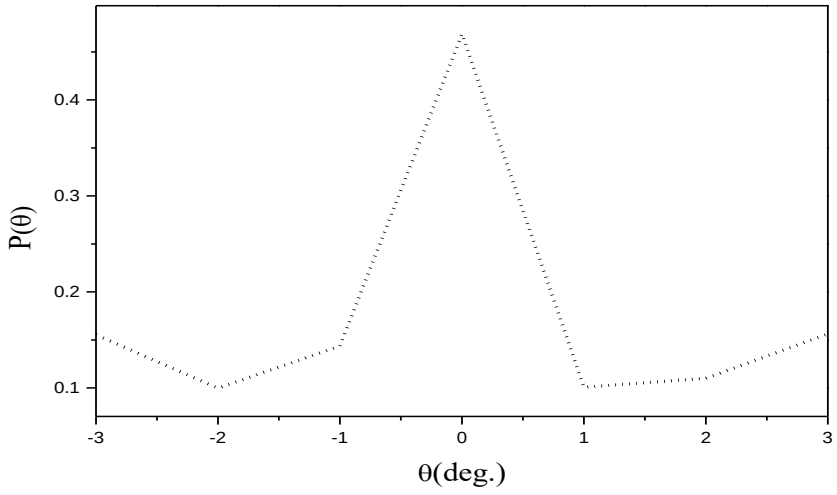

Figure 6: Polar angle distribution of CO molecules at 1 K.

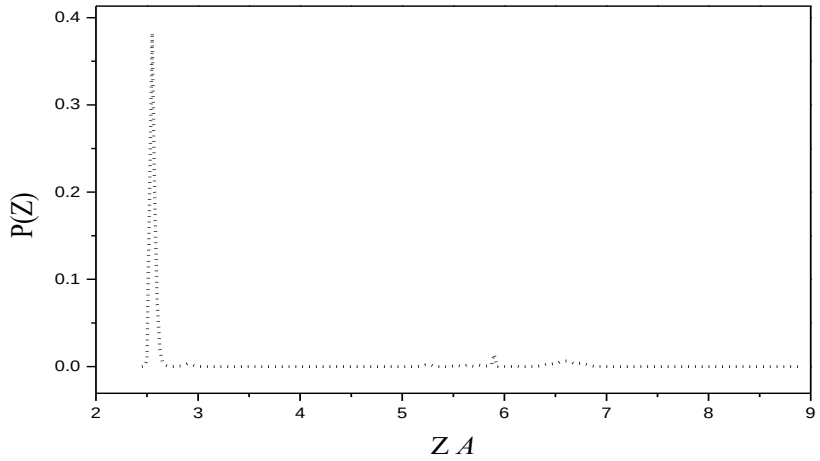

Figure 7: Z-distance probability distribution for monolayer configuration at 1 K.

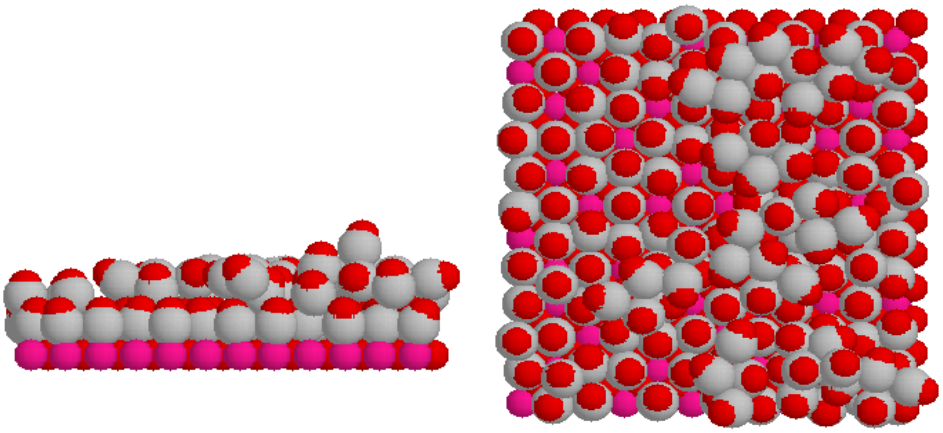

Figure 8: Final configuration at 10 K showing multilayer formation.

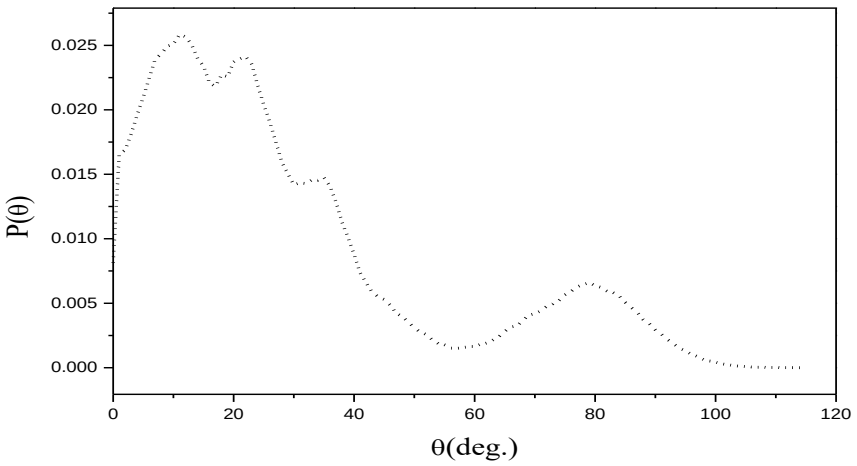

Figure 9: Polar angle distribution confirming monolayer tilt**.**

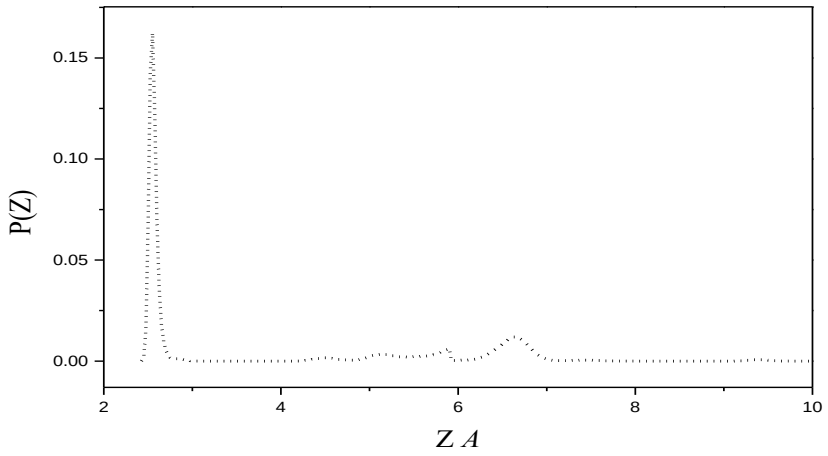

Figure 10: Z-distance probability distribution for monolayer configuration.

Conclusion

This study successfully investigated the adsorption structures of carbon monoxide (CO) molecules on the magnesium oxide (MgO) (001) surface using a Monte Carlo simulation model. The findings demonstrate that CO molecules stabilize on the MgO surface in either monolayer or multilayer configurations, each possessing distinct thermal characteristics, unit cell configurations, molecular counts, tilt angles, vertical heights, adsorption energies, and surface coverage ratios.

The simulation results exhibited significant agreement with previously obtained experimental data, validating the chosen potential model for calculating the interaction between CO and the MgO surface. At low temperatures (below approximately 40 K), the c(4×2) configuration was identified as thermally stable, featuring six CO molecules per primitive cell, predominantly adsorbed vertically over Mg^{2+} ions with a 2:1 ratio of vertical to tilted molecules. The polar angle for tilted molecules was found to be

31∘, which is consistent with experimental values obtained from Polarization Infrared Reflection Spectroscopy (PIRS). Vertical molecules were observed to align directly above Mg^{2+} ions, while tilted ones were slightly displaced. The configurations showed an alternation between rows of vertical and tilted molecules.

As the temperature increased to approximately 40 K, the p(3×2) configuration emerged, accompanied by a decrease in surface coverage as tilted molecules were replaced by vertical ones. The simulations also indicated that at full coverage in the monolayer configuration, only tilted molecules remained, while vertical molecules formed in the multilayer arrangement. The formation of a second CO layer was observed at a surface coverage of 0.625 due to repulsive interactions and lattice constant differences, confirming the dynamic nature of CO adsorption on MgO(001). These detailed insights into the adsorption mechanisms and structural transformations of CO on MgO(001) contribute to a deeper understanding of molecular behavior on ionic surfaces and are in line with various experimental techniques such as LEED, HAS, and PIRS.

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