

**QUANTUM CHEMICAL STUDY OF
CHEMISORPTION OF NITRIC OXIDE
AND CARBON MONOXIDE
ON ALUMINUM (111) SURFACE**

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ALUMINUM (111) SURFACE**

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DECLARATION BY THE CANDIDATE

I do hereby declare the work described in this thesis was carried out by me under the supervision of Dr. W.S.J. Silva and a report on this thesis has not been submitted in whole or part to any university or any other institution for another Degree/Diploma.

Date 24/09/2007


Signature of Candidate

DECLARATION BY THE SUPERVISOR

I certify that the above statement made by the candidate is true and that thesis is suitable for submission to the university for the purpose of evaluation

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UNIVERSITY OF SRI JAYEWARDENEPURA, SRI LANKA

FACULTY OF GRADUATE STUDIES

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GUNASINGHAM PARTHIBAN

ABSTRACT

The interaction of NO and CO with Al (111) surfaces including slabs and clusters has been studied by means of the semi-empirical and ab initio DFT methods. Metal cluster models (up to 51 atoms) with different size and geometry and slab of Al₄, Al₉ and Al₅(4,1) have been used to describe the atop, bridge and three-fold sites. The binding energies of N (1s), 4σ 5σ and π and electrons C (1s), 4σ 5σ and π electrons are calculated and compared with the results from the previous study and the experimental data available. GAMESS and OpenMX quantum chemical programs compute the binding energy of the system and the geometrical properties of the initial and optimized clusters obtained from MOLDEN and RasMol packages respectively. The NO and CO tilted upright with respect to the surface normal axis when adsorbed on top, bridge and three-fold sites and nitrogen and carbon atoms are pointing towards the surface. The cluster model approach is discussed in terms of its reliability to determine the adsorption energies and the favored site of adsorption.

1. CHAPTER 1: INTRODUCTION

Developing a theoretical understanding of adsorbates interacting with surfaces has applications in wide areas of quantum chemistry. Two computational strategies have commonly been used, cluster and slab⁽¹⁾ calculations. The cluster calculations regard the adsorbate-surface interaction to be mainly local in nature and perform standard quantum chemistry calculations on fragments of the extended substrate. The slab calculations incorporate more of the long-range effects of the adsorption process by performing calculations on multilayer structures with two-dimensional periodicity.

1.1 Adsorption

A quantitative measure of adsorption may be, and usually is, based on adsorption of one or more of the components, at one or more of the phase boundaries of a multicomponent, multiphase system, is said to occur if the concentrations in the interfacial layers are different from those in the adjoining bulk phases, so that the overall stoichiometry of the system deviates from that corresponding to a reference system of homogeneous bulk phases.

In the molecular adsorption state the interaction between the molecule and the surface is relatively weak. Molecules aligned such that the internuclear axis is parallel to the surface plane may bond to a single metal atom of the surface via both

1. σ -donor interaction, in which the charge transfer is from the occupied molecular π -bonding molecular orbital of the molecule into vacant orbitals of σ -symmetry on the metal (i.e. Metal \leftarrow molecule), and

2. π -acceptor interaction, in which an occupied metal d -orbital of the correct symmetry overlaps with empty π^* orbitals of the molecule and the charge transfer is from the surface to the molecule (i.e. Metal \rightarrow molecule)

If the molecule or its fragments are bound to the surface, they are known as adsorbates. The reverse process is called desorption. Understanding adsorption and adsorbates is essential for gaining insight into catalysis, e.g. exhaust gas purification by catalysts, where different toxic gases adsorb on the catalyst, undergo a reaction on the surface and the reaction products (non-toxic gases) desorb from the surface. This molecular state might be either a chemisorption or physisorption state.

1.2 Chemisorption

Chemisorption arises when a chemical bond is created between the adsorbate and the surface. In this case, the strong interactions with the surface will alter the molecular electron structure. Typically in these states there is a charge transfer between the metal and the molecule during chemisorption.

1.3 Physisorption

Physisorption is an adsorption process in which the forces involved are intermolecular forces (van der Waals forces) of the same kind as those responsible for the imperfection of real gases and the condensation of vapours, and which do not involve a significant change in the electronic orbital patterns of the species involved. The term *van der Waals* adsorption is synonymous with physical adsorption, but its use is not recommended.

1.4 Dissociation

The molecule-surface interactions might break the molecular bond, leading to dissociation of the molecule. One mechanism behind the dissociation process is that electrons from the surface are transferred to the antibonding orbitals of the molecule. After dissociation, the atom fragments might diffuse along the surface or into the substrate.

1.5 NO molecule

Nitric oxide (NO) is a heteronuclear diatomic molecule. The NO molecule has a singly occupied π^* molecular orbital; therefore, it is more reactive and the chemical properties of adsorbed NO are quite different from other diatomic molecules. The electronic configuration of NO molecule is $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \pi_{2p}^4 \pi_{2p}^{*1}$ (Figure 1.1)

1.6 CO molecule

Carbon monoxide (CO) is also a heteronuclear diatomic molecule. The CO molecule possesses an even number of electrons; therefore, it is a closed shell molecule. Electronic configuration of CO is similar to that of NO, but the only difference is that there are no electrons in its antibonding molecular orbitals. The electronic configuration of CO molecule is $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \pi_{2p}^4$ (Figure 1.1)