Theoretical Study of NO Adsorption and Decomposition on Si(100) Surfaces

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Using hybrid density functional theory (DFT), we analyzed NO adsorption on a clean Si(100) surface and on Si(100) surfaces modified by an oxygen atom or molecule. The estimated vibrational frequencies for the N-O stretching mode of chemisorbed NO molecules on both the clean and the modified surfaces were 1500-1550 cm\(^{-1}\) for the N-end-down configuration and 1610 cm\(^{-1}\) for the O-end-down configuration. NO dissociated easily from the clean surface via a NO dimer with a Si-NO-NO configuration, and the activation energy for the dissociation was small. [DOI: 10.1380/ejssnt.2006.624]

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I. INTRODUCTION

For recent decades, nitric oxide (NO) adsorption on silicon surfaces has been of interest not only in fundamental scientific fields but also in terms of the development of electronic devices, because Si-oxyxnitrde is a leading candidate for use as a material for ultrathin gate dielectric films and tunnel dielectric films [1]. Much of the research has led to the consensus that the concentration of nitrogen atoms resulting from the deposition of NO is higher than the concentration resulting from the deposition of N\(_2\)O, and that oxynitridation with NO is superior to that with N\(_2\)O [2]. However, the initial adsorption state of NO on Si(100) surfaces is still a matter of controversy. A high-resolution electron energy loss spectroscopy (HREELS) study has not confirmed a N-O stretching mode at room temperature [3], and the authors of the study stated that, if the molecular species was present, it was minor [4]. Similarly, photoemission experiments [5-7] have indicated that NO is completely dissociated, even at low temperatures. In contrast, a molecularly adsorbed species was observed by means of photodesorption experiments [8] and an Auger electron spectroscopy (AES) study [9] at room temperature. Theoretical studies of NO adsorption on surfaces have also afforded both dissociative [10, 11] and molecular [12] adsorption. More recently, Kato, et al. [13] used density functional theory (DFT) calculations to estimate the activation barrier for NO dissociation to be 0.07-0.61 eV higher than the energy of the reactants. Kato, et al. concluded that NO is molecularly chemisorbed but is occasionally dissociated. A similar conclusion has also been reached by means of X-ray photoelectron spectroscopy (XPS) and electron-stimulated desorption (ESD) measurements [14]. In these experiments, the researchers observed desorption of NO\(^+\) ion and N(1s) peaks for molecularly adsorbed species at 90 K, in addition to dissociated species. Although there have been several reports of molecular species, the vibrational frequency of the N-O stretching mode has never been reported. Theoretical analysis of this fingerprint may give vital information about the complex surface reaction and surface structure involved in the adsorption of NO on Si(100) surfaces. Therefore, we focused on predicting the vibrational frequency (\(\nu_{\text{N-O}}\)) for molecularly adsorbed NO molecules on Si(100)-(2\times1) surfaces using hybrid DFT calculations. We also report an effective NO dissociation pathway via the formation of a NO dimer.

II. COMPUTATIONAL DETAILS

The details of the computational methods have been described elsewhere [15], but we will briefly describe the methodology here. We used a four-layer cluster model that includes a single surface-dimer and bulk Si atoms terminated with H atoms (Si\(_9\)H\(_{12}\)) as the clean surface. We employed two types of oxidized surfaces: one with an adsorbed oxygen atom (O-mod) and one with an adsorbed oxygen molecule (dissociative adsorption; O\(_2\)-mod).

All calculations were performed using the GAUSSIAN 98 package. The Berny algorithm was used during geometry optimization [16]. Both the surfaces and a NO molecule were fully optimized at the unrestricted B3LYP/6-31G(d) level [17-20]. For vibrational analysis, scaling factors of 0.9614 and 0.9806 were used for vibrational frequencies and zero-point energy, respectively [21]. Adsorption energies (\(E_{\text{ad}}\)) were estimated from Eq. (1):

\[
E_{\text{ad}} = E_C - (nE_A + E_S), \quad (n = 1, 2)
\]

where \(E_C\), \(E_A\), and \(E_S\) represent the total energies of the complex, the isolated adsorbate, and the surface, respectively, and \(n\) denotes the number of adsorbates. From these definitions, negative values of \(E_{\text{ad}}\) represent a stable adsorbed state.

III. RESULTS AND DISCUSSION

A. Models of Si(100) Surfaces and the Free NO Molecule

Figure 1 shows the surface models employed in this study. For the clean surface, the bond length of the surface dimer was 2.224 Å, which is in excellent agreement with the experimentally observed value of 2.24 ± 0.08 Å [22].
FIG. 1: Optimized structures for (a) the clean Si(100) surface and for the surface modified by (b) an oxygen atom and (c) an oxygen molecule. (Bond lengths and bond angles are given in Å and degrees, respectively.)

When an oxygen atom was adsorbed on the clean surface, a Si-O-Si bridge was formed [Fig. 1(b)]. The Si-O-Si bond angle of 82.9° is smaller than the usual angle for sp²- and sp³-hybridized orbitals. When an oxygen molecule was adsorbed on the clean surface, the modified surface had a structure in which an oxygen atom was inserted between the atoms of the cleaved surface-dimer [Fig. 1(c)]. The Si-O-Si bond angle of 145° is in excellent agreement with the experimental [23] and theoretical [24] value of 144° for oxides.

The calculated bond length of an isolated NO molecule with a doublet ground state was 1.159 Å. This value agrees with the experimental value of 1.151 Å [25].

B. Adsorption of a NO Molecule on Clean Si(100)-(2 × 1)

Optimized structures, S₁ and S₂, of the clean Si(100) surface with an adsorbed NO molecule are shown in Fig. 2, along with the adsorption energies, relevant geometrical parameters, and spin densities. In both structures, the NO molecule strongly interacted with the surface dimer in an on-top configuration. The adsorption energy was approximately -15 kcal/mol for both structures. The \( <S^2> \) value was 0.754, which indicates that the contribution of spin contamination upon NO adsorption was small for both structures. The Si-N bond lengths for S₁ and S₂ were 1.910 and 1.875 Å, respectively. The N-O bond of the chemisorbed NO was 0.05 Å longer than the bond in isolated NO.

C. Adsorption of Two NO Molecules on Clean Si(100)-(2 × 1)

When we calculated the simultaneous adsorption of two NO molecules on the clean surface, we obtained N-end-down and O-end-down configurations, as well as NO dimers [D₁-D₆; Fig. 3(a)-(f)]. These structures can be classified into three groups: (i) structures in which both NO molecules are in the N-end-down configuration (D₁, D₂); (ii) structures in which one of the NO molecules is in the N-end-down configuration and the other is in the O-end-down configuration (D₃, D₄); and (iii) dimerized structures (D₅, D₆).

The first group had tilted structures with adsorption energies of approximately -37 kcal/mol and NO-surface-dimer bond lengths of 1.91-1.93 Å. The intramolecular N-O bonds were 0.05 Å longer than those in the case of a NO adsorption. The second group also showed tilted structures. The two NO molecules in structures D₃ and D₄ are arranged trans and cis, respectively, with respect to the plane perpendicular to the surface dimer. These structures showed low adsorption energies of approximately -7 kcal/mol. The length of the Si-N bond was approximately 1.92 Å for both structures; this value is similar to the value observed for the first group of structures. In contrast, the Si-O bond length was more than 2.2 Å for both structures. However, the Kohn-Sham (KS) orbitals indicated a bonding orbital between the O and Si atoms.

We also obtained an optimized structure in which both NO molecules were in O-end-down configurations. The adsorption energy of this structure was positive (22 kcal/mol). This result clearly shows that the O-end-down configuration is unstable with respect to the adsorption energy, as is the case for Si(111) surfaces [26].

The third group of structures, the NO dimers, were very stable. These structures had covalent N-N (1.386 Å) and N-O (1.466 Å) bonds between the two NO molecules (D₅ and D₆, respectively). The most stable structure was an ON-NO dimer (D₅), which had an adsorption energy of about -50.13 kcal/mol and a Si-N bond length of 1.874 Å. The two N-O bonds were stretched by approximately 0.08 Å compared to the bond in an isolated NO molecule. The D₆ structure, which had an adsorption energy of -32.57 kcal/mol, had a three-membered ring between the surface dimer and the adjacent N atom. The SiN-ONO bond (hereafter called the first NO bond) was greatly stretched (by more than 0.2 Å), whereas the SiNON-O bond (the second NO bond) was stretched by only 0.018 Å.

The formation of NO dimers has been experimentally confirmed on Si(111) surfaces [27] and on Si thin films [28]. The results of these experiments indicated that formation of the NO dimer precedes N₂O desorption (surface oxidation) [27, 28]. The computational study [26] also indicated that elimination of N₂ from dimeric structures is exothermic. In addition, the authors noted that dimeric...
FIG. 2: Optimized structures for NO adsorption on the clean surface (hydrogen atoms omitted). The values in parentheses and the underlined values represent adsorption energies and atomic spin densities, respectively. (Adsorption energies and bond lengths are given in kcal/mol and Å, respectively.)

FIG. 3: Optimized structures for adsorption of two NO molecules on the clean surface (hydrogen atoms omitted). The values in parentheses represent adsorption energies. (Adsorption energies and bond lengths are given in kcal/mol and Å, respectively.)

adspecies should undergo further decomposition to eliminate N₂ or N₂O. However, to our knowledge, there have been no experimental or theoretical studies reporting the formation of NO dimers on Si(100) surfaces. Because our calculations afforded two types of NO dimers, we can discuss the possibility of NO dissociation and N₂O formation via the dimers. We considered the following processes from D₆ only:

\[
\begin{align*}
\text{Si-N-ONO(a)} & \rightarrow \text{Si-N(a)} + \text{NO}_2(g) \quad (2) \\
\text{Si-NO-NO(a)} & \rightarrow \text{Si-NO(a)} + \text{NO(g)} \quad (3)
\end{align*}
\]

where Eqs. (2) and (3) denote surface nitridation and oxynitridation, respectively. Although N₂O and N₂ formation via an ON-NO dimer on Si(111) [26] and Ag(111) [29, 30] surfaces have been reported, the formation of such products from D₅ is difficult.

Figure 4 shows the potential-energy surface (PES) for NO dissociation via NO dimer D₆, along with the structures of the stationary points. When the first NO bond was stretched by about 1.0 Å along the bonding direction, we obtained a transition state (TS) structure with an activation barrier of approximately 11 kcal/mol relative to the energy of D₆. The imaginary vibrational frequency of the TS vector was 100.9i cm⁻¹. When the N-O bond was further elongated to 2.75 Å, we obtained a very sta-
The transition state is not excessive for this pathway, NO dissociation via NO dimer, with structures of stationary points. (Relative energies and bond lengths are given in kcal/mol and Å, respectively.)

In the D7 structure, which has a large adsorption energy (-97.7 kcal/mol), the NO adsorption was calculated to be 1.759 Å, and the N-Si-N-Si angle was 139.2°, which is slightly smaller than the Si-O-Si angle for the O2-mod surface. From the D7 structure, we tried to trace the NO and NO2 desorption processes [Eqs. (2) and (3)]. However, exchange of Si-O bonds, such as Si-O(1)NO(2) to Si-O(2)NO(1), could occur without any prohibitive barriers only for the process illustrated in Eq. (2). In the process illustrated in Eq. 3, the desorbed NO brought about two problems: a hydrogen atom was abstracted from the surface, and the desorption angle of NO was lower than the surface plane without any constraints, respectively. We could not correctly elucidate the process illustrated in Eq. (3) at this cluster size. Studies with larger cluster models are now in progress.

Because the relative energy of the reactants and the transition state is not excessive for this pathway, NO dissociation via dimerized NO is clearly one effective pathway for this process.

D. NO Adsorption on a Partially Oxidized Surface

Investigating the behavior of NO on partially oxidized surfaces is worthwhile because production of oxyxnitride surfaces is known to be more effective by means of NO adsorption than by means of N2O adsorption, as stated above, and no information about its formation processes on partially oxidized Si(100) surface is available yet.

We found three weakly adsorbed structures on the O-mod surface, with small adsorption energies, less than -2.0 kcal/mol (OA1-OA3; Fig. 5). The contribution of spin contamination was small, < S2 > <= 0.753, for the structure. In these three structures, the intermolecular distance between NO and adjacent surface atoms was 2.7-3.5 Å, which is as large as the value for N2O adsorbed (2.8 Å) on the same surface. The N-O bond was slightly stretched (by only 3 mÅ) compared to the same bond in a free NO molecule. Because no bonding orbitals were formed between NO and the surface, we concluded that, on this surface, NO was physisorbed by electrostatic interactions alone.

When a NO molecule was adsorbed on the Si(100) surface modified with an oxygen molecule, NO chemisorbed only in the N-end-down configuration (Fig. 6). The adsorption energy was -20.74 kcal/mol, and the contribution of spin contamination was small, < S2 > <= 0.759. The length of the intermolecular bond between the N atom and the adjacent Si atom was 1.893 Å, and the N-O bond was stretched by 0.06 Å. There was no significant difference between the O2-mod surface and the clean surface with respect to adsorption energy or optimized geometry.

E. Vibrational Analysis of Adsorbed NO Molecules

In this final section, we compare calculated and experimental values for the NO vibrational frequency (νNO). Because molecular adsorption of NO on Si(100) has not been confirmed correctly, we used vibrational frequencies for NO on Si(111) and various transition-metal surfaces as experimental values. We believe that our analysis makes sense chemically, because no report with respect to the vibrational analysis of NO on any modified surfaces has been published.

The calculated vibrational frequency for free NO was calculated as 1914 cm−1, which is in good agreement with the experimental value of 1904 cm−1 [25]. For NO chemisorbed on the clean Si(100) surface, the calculated vibrational frequency was strongly red-shifted to 1542 and 1497 cm−1 for S1 and S2, respectively. For adsorption of two NO molecules, we theoretically predicted that the frequencies would be strongly red-shifted, by more than 360 cm−1. For each NO molecule, the frequencies were split into two modes around 1530-1550 cm−1. The calculated frequencies were 1529 and 1549 cm−1 for D1 and 1536 and 1546 cm−1 for D2. These two modes were assigned to the asymmetric and symmetric stretching modes, respectively. The symmetric stretching mode involves vibration in which both NO molecules stretch in the same direction, and the asymmetric stretching mode involves vibration in which the two NO molecules stretch in opposite directions simultaneously.

Furthermore, we theoretically predicted that there would be a significant difference in νNO for the two NO configurations designated D3 and D4. For the N-end-down configuration, νNO was 1537 cm−1 for both structures. In contrast, for the O-end-down configuration, the νNO values were 1605 cm−1 for D3 and 1608 cm−1 for D4. The calculated νNO values for D3 were 1397 and 1421 cm−1 for the asymmetric and symmetric modes, respectively. These were more red-shifted (by more than 100 cm−1) than the values for the other two NO adsorption structures, correlated with its adsorption energy. The calculated νNO for the D5 structure was 1684 cm−1 for the second NO bond. Unfortunately, we could not assign the νNO for the first NO bond or for the coupling between the first NO bond and the second NO bond, because of overlap with other vibrational modes.

For structures OA1-OA3, the calculated vibrational frequency of the NO molecule indicated a small interaction: the frequency was slightly red-shifted (by 33 cm−1).
FIG. 5: Optimized structures for NO adsorption the O-mod surface (hydrogen atoms omitted). Values in parentheses and in italics represent adsorption energies and atomic charges, respectively. (Adsorption energies and bond lengths are given in kcal/mol and Å, respectively.)

FIG. 6: Optimized structure for NO adsorption on the O$_2$-mod surface (hydrogen atoms omitted). The values in parentheses and the underlined values represent adsorption energies and atomic spin densities, respectively. (Adsorption energies, bond lengths, and the Si-O-Si angle are given in kcal/mol, Å, and degrees, respectively.)

for OA$_1$ and by 5 cm$^{-1}$ for OA$_2$, whereas the frequency was slightly blue-shifted (by only 1 cm$^{-1}$) for OA$_3$, as compared to the value for the free NO molecule.

For the O$_2$-mod surface, the calculated vibrational frequency also showed similar tendency as the clean surface; that is, the frequency was strongly red-shifted, by about 380 cm$^{-1}$ (to 1535 cm$^{-1}$) relative to that of the free NO molecule.

Experimental results indicate that the $\nu_{SO}$ values for bridge and on-top sites on the Si(111) surface are 1807 and 1516 cm$^{-1}$, respectively [27]. A previous theoretical analysis showed a band for $\nu_{SO}$ at 1516-1557 cm$^{-1}$ [26]. Both results are in quite good agreement with our results. Furthermore, NO adsorbed on transition-metal surfaces shows bands in the 1370-1850 cm$^{-1}$ range. This result supports our proposal that these surfaces give values that are valid for Si(100), although EELS measurement (at room temperature) suggests that molecular species on the Si(100) surface would be minor, if they were present at all [4]. We believe that additional EELS or IR measurements should be able to clearly show whether NO adsorbs molecularly or not on Si(100) at low temperatures (below 90 K), although NO dissociation has already been observed at 20 K in a photoemission experiment [7].

IV. CONCLUSIONS

Using the hybrid DFT method, we calculated the optimized structures and vibrational frequencies of NO adsorbed on a clean Si(100) surface and on surfaces modified by an oxygen atom or molecule. Our results clearly showed a significant difference between chemisorbed and physisorbed species with respect to the vibrational frequencies. The estimated frequencies for the N-O stretching mode of chemisorbed NO on either the clean surface or the surface modified by an oxygen molecule were 1500-1550, 1610, and 1400-1420 or 1680 cm$^{-1}$ for the N-end-down, O-end-down, and dimerized-NO structures, respectively. In contrast, the frequencies for physisorbed NO were slightly red- or blue-shifted to 1870-1915 cm$^{-1}$ on the surface modified by an oxygen atom.

We found that a new NO dissociation process via dimerized-NO structures could proceed easily with a small activation energy, although no desorbing species (NO or NO$_2$) were observed. Theoretical investigation of the reaction pathway is important for the design of novel functional materials and for the control of surface reactions.

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