Gas Sensing Properties of the Adsorption of NO on WO₃ Cubic Structures of Different Bond Lengths

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Abstract

Nitric oxide is a pollutant linked to the production of smog and acid rain in the environment. Due to the increase in production of nitric oxide, scientists have attempted to increase methods to detect the pollutant at low and high concentrations. Scientists have investigated gas sensors because of their low cost, sensitivity to gases at low concentrations, and fast response time. WO_3 gas sensing properties make it an excellent candidate to observe the absorption of NO. In this study, WO_3 and NO have been created in a molecular dynamics simulation via the program LAMMPS at temperatures between 10 K-500 K to create an N-W bond. The results showed that the highest pairwise energy of N-W was induced at 14.5eV with a bond length of 1.69 Angstrom. This simulation investigates the change of pairwise energy based on the change of bond length and energy. Two NO structures are adsorbed on the cubic structure of WO_3 on a silicon substrate. The N-W bonds were created at bond energies of 13.8 eV and 14.5 eV with bond lengths of 1.69, 1.67, and 1.65 Angstrom, respectively. The results show that the second NO structure produced the greatest pairwise energy for the N-W bond at 14.5 eV and 1.69 Angstrom. The results confirm that for bond energies of 14.5 eV and 13.8 eV the second NO structure produced the strongest bond energy at 1.69 Å. This doesn't correspond to the results for the first NO structure. Due to the major differences in pairwise energy between the NO structures, the development of a Si substrate was pursued in order to determine its impact on the pairwise energy for future research.

1. Introduction

The EPA has raised multiple concerns about the pollutant NO_x due to its negative impact to environmental health.[10] NO_x is a toxic gas released into the air due to combustion processes linked to cars and other fume exerting devices.[10] Even with the use of the Clean Air Act enacted in 1970, the production of NO_x has increased by ten percent between 1970 and 1998.[10] To compact this severe environmental issue, scientist have looked to the development of gas sensors. Gas sensors are a cheap and efficient way to detect low to high concentrations of harmful gases. [10]

Tungsten trioxide gas sensor is being investigated in this study due to its interesting chemical and physical properties. For example, different structures of tungsten oxide can produce W^{+6} and W^{+5}.[13] With this change in oxidation numbers, NO is able to absorb to the surface of WO_3 more easily. [13]

Nitric oxide's influence on tungsten oxide with a silicon substrate is being observed over different temperatures with the use of Raman spectroscopy. In this investigation, it is being modeled in a molecular dynamics simulation. Molecular dynamics simulation provides a visual means to observe the adsorption impact of nitric oxide on the tungsten oxide surface.

The purpose of the current approach is to develop different structures of tungsten oxide for nitric oxide adsorption with a silicon substrate using molecular dynamics simulations via the program LAMMPS. Bonds will be induced between N-W at 13.8 eV and 14.5 eV with bond lengths of 1.65, 1.67, and 1.69 Angstrom. The output of the simulations will be used to determine the effect of pairwise energy between the N-W bond as the energies and bond lengths change. [6]

2. Computational Details
a. Overview of simulation

The simulations were created with the assistance of LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulation). [12] The simulation begins with the creation of a data file composed of W,O, and N atoms at different x, y, z coordinates in a atomic/molecular format. The box composed of the various atoms was <-6,-6,-6> to <12, 12, 12>. A Si substrate was created with the dimensions <-6,-6, 3.905> to <12, 12, 12>. For the boundary constraints, the simulation was periodic in all directions. While interacting with each atom in the system, the species can enter and exit the simulation box from the corresponding dimension. [12]

To initiate motion of the atoms, I used the Nosé–Hoover thermostat, which maintains constant the number of particles, volume, and temperature of the system.[11] The output from this algorithm is determined using metal units.[12] The necessary units for temperature, energy, and volume are K, eV, and Angstrom, respectively. [12]

b. Potentials for the simulation

To create the bonds between the W, O, N, and Si atoms, potentials such as Buckingham, 12/6 Lennard-Jones, and Morse were used to create the interatomic forces between the atomic bonds. The parameters between the atoms are defined in Tables 1-3. [1-7]

Table 1. Parameters of Buckingham Potential in units eV and Å.

	A (eV)	ρ (Å)	$C(eV\text{Å}^6)$
O-O-W	2023.0	0.2674	13.83
W-O	767.43	0.4386	0.000
W-W	200.00	3.7200	0.000
N-Si	7583.9	0.2583	207.1801

Table 2. Parameters of Lennard Jones Potential in units eV and Å.

	ϵ (eV)	σ(Å)
N-O-W	0.007562	3.2234
Si-O-W	0.013053	3.2700
W-N	14.50000	1.6500
N-N	0.008672	3.2963
O-O-N	0.008353	2.8750
Si-Si	0.025325	3.3900

Table 3. Parameters of Morse Potential in units eV and Å.

|	D_0(eV)	α (Å^{-1})	R_0(Å)
W-O-O-N	5.214	2.654	1.208
W-Si	0.8327	3.316	2.000

c. Temperature Effects

The investigation of the change of pairwise energy due to temperature was analyzed with the assistance of the Nosé–

Hoover thermostat algorithm without the Si substrate. Two NO molecules are bonded to the surface of WO_3 over the change of temperature to create N-W bonds. For each simulation, the temperature was initialized at 10 Kelvin. Over the change of temperature, the bond length of the N-W bond was changed at constant bond energy.

For the first simulation, the bond energy between the N-W bonds was fixed at 13.8 eV. The bond length was set at 1.69 Å over the temperature range 10-500K. The simulation was repeated with bond lengths of 1.67 Å and 1.65 Å. An image of the simulation is displayed in Figure 1. The simulation was recreated with the bond energy equivalent to 14.5 eV. With the change in temperature over the varying bond lengths, the N-W(1) pairwise energy of the structure was highest with the bond length

Figure 1. The W,O-W, N, and N-O atoms are represented by blue, purple, green, and pink colors, respectively. In the following graphs, the first N-W bond is represented by the left NO molecule, and the second N-W bond is represented by the NO molecule to the right
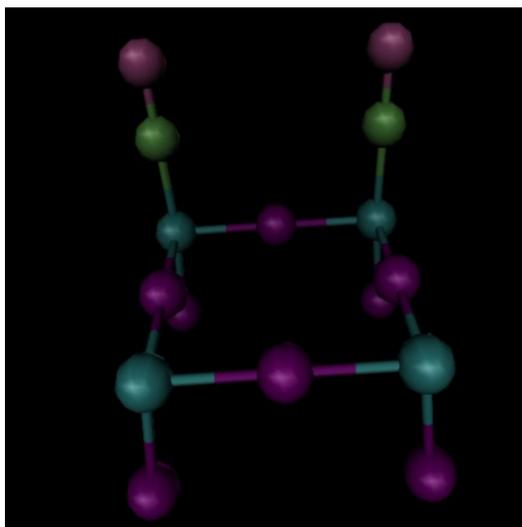
of 1.67 Å at the bond energy of 13.8 eV. With bond energy of 14.5 eV, the strongest N-W bond produced was at a bond length of 1.69 Å. For the N-W (2) under the same conditions, the strongest bond was produced at a bond length of 1.69 Å at 13.8 eV and 14.5 eV.

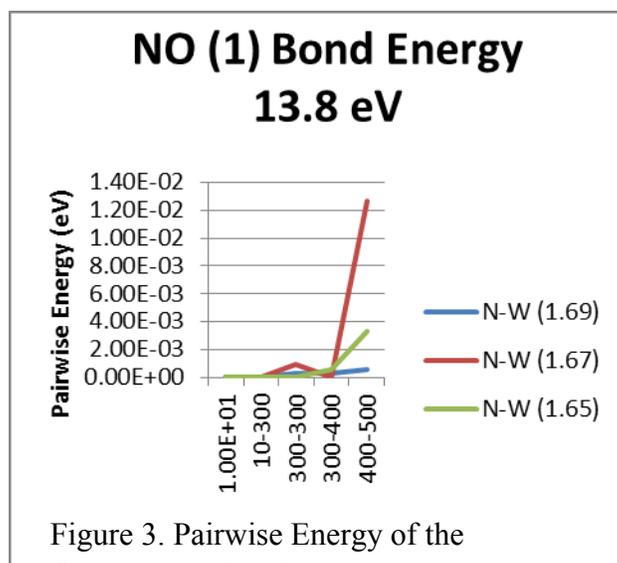Figure 2. Pairwise Energy of the first N-W (1) bond over 10-500K.

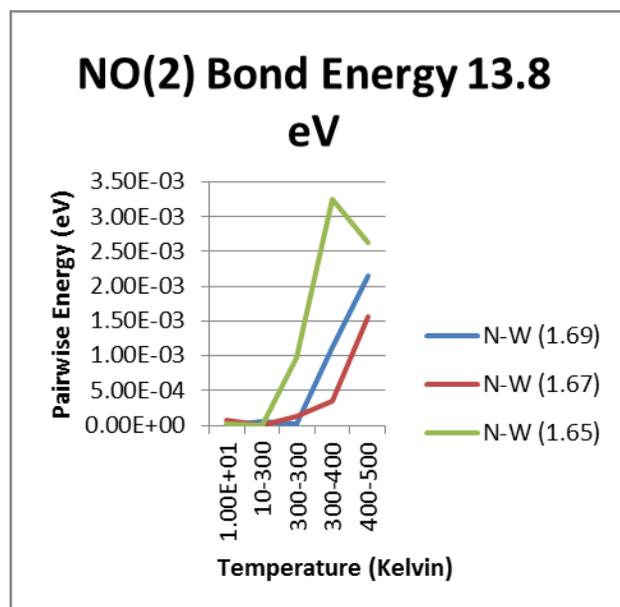Figure 3. Pairwise Energy of the first N-W (2) bond over 10-500 K.

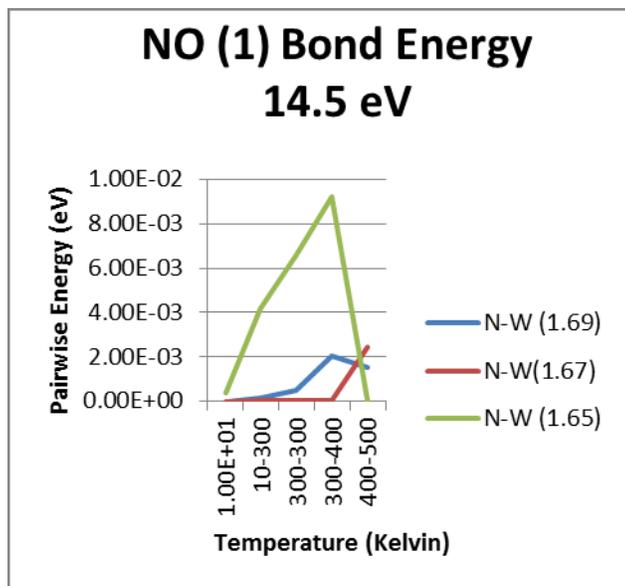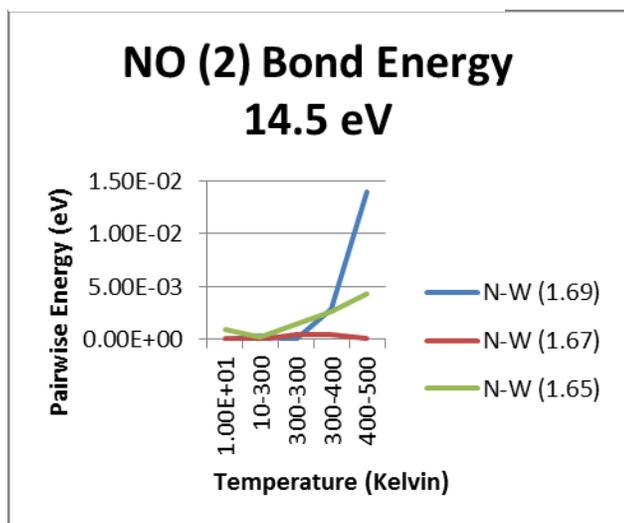Figure 4. Pairwise Energy of the first N-W (1) bond over 10-500 K.

NO (1) Bond Energy 14.5 eV

Figure 5. Pairwise Energy of the first N-W (2) bond over 10-500 K

NO (2) Bond Energy 14.5 eV

3. Conclusion

It is uncertain as to why the pairwise energies between the N-W bonds are not similar. The difference in x y z coordinates should not play a major role in the difference, since the absolute value of each coordinate is the same. To further investigate this observation, simulations of the structure on Si substrate have been constructed. At this point, however, it remains inconclusive as to the exact reasons for the differences in pairwise energy between the different NO structures.

4. Acknowledgments

5. References

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