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The structure of self-assembled N_2O multilayers

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ABSTRACT

Based on the structure of the monolayer, the structure of multilayered nitrous oxide (N_2O) was determined by applying the first-principle technique. Several potential structures of the N_2O multilayer were evaluated. The results showed that the multilayer consisted of many layers and that the distance between neighboring layers was equal to 4.1 Å.

1. Introduction

Molecular self-assembly is the spontaneous organization of molecules under thermodynamic equilibrium conditions into well-defined arrangements via cooperative effects between chemical bonds and weak noncovalent interactions [1]. Molecules undergo self-association without external instruction to form hierarchical structures. Molecular self-assembly is ubiquitous in nature and has been recently emerged as a new strategy in chemical biosynthesis, polymer science and engineering [2–7]. Molecular self-assembly is the basis of the early stages of polymer synthesis and occurs prior to polymerization.

In the gas phase, nitrous oxide (N_2O) is a linear triatomic molecule and is considered asymmetric because the two nitrogen atoms are located in different chemical environments. Specifically, the center (N_C) and terminal (N_T) nitrogen atoms can be clearly distinguished by core level spectroscopy [8]. Due to the intense interest in surface science and its important applications in environmental protection strategies, interactions between N_2O and solid surfaces have been extensively investigated, and studies on N_2O surface oxidation and surface photochemistry have been conducted [9–14]. The local structure of N_2O multilayers has been described in the literature [15]; however, the proposed structure is relatively coarse. The structure of monolayered N_2O has been identified by applying the first-principle theory [16]. Thus, in the present article, the first-principle calculations were adopted to determine the structure of N_2O multilayers.

2. Details of the calculations

Electronic structure calculations are based on the density functional theory, and exchange-correlation functional is the most popular Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) [17]. Moreover, interactions between core electrons and valence electrons can be described by ultrasoft pseudopotentials. In the present study, the potential structures of N_2O multilayers were calculated based on the structure of the N_2O monolayer described in the literature [16], in which the original cell contains two N_2O molecules, as shown in Fig. 1. Three edges labeled L_{OA}, L_{OB} and L_{OC} meet at the origin (O) of the unit cell, and their lengths are represented as a, b and c, respectively. The face angles of the cell $\angle$BOC, $\angle$AOC and $\angle$AOB are represented as α, β and γ, respectively. Based on the results presented in the literature [16], the length of edges L_{OA} and L_{OC} were set to 4.1 Å, and the face angles α, β and γ were set to 90°. Moreover, the original angle between the molecule and the substrate (labeled as φ) was set to 42°. To identify the structure of multilayered N_2O, only the edge L_{OB} of the unit cell was determined.

To avoid costly calculations, a planewave cutoff energy of 380 eV was employed, and satisfactory results were obtained. The following convergence criteria for the energy minimization were applied: the Hellmann–Feynman forces were less than 0.01 eV/Å, and the energies and displacements converged to 0.000005 eV and 0.0005 Å, respectively. Brillouin zone integration was performed on a suitable ***k***-point mesh to maintain energy convergence, and the ***k***-point meshes were taken as $6\times3\times6$. The results were calculated using CASTEP codes [18,19], which were implemented in the Materials Studio environment [20].

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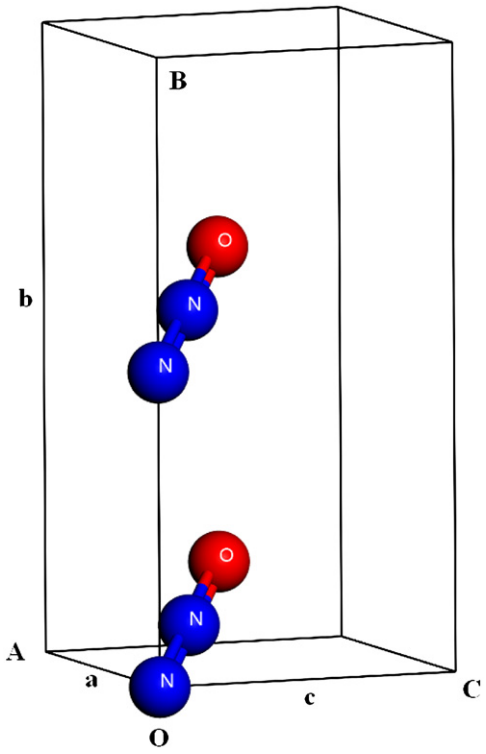

Fig. 1. Original cell of the potential structure of the N_2O multilayer. The N_T atom is the vertex of the unit cell.

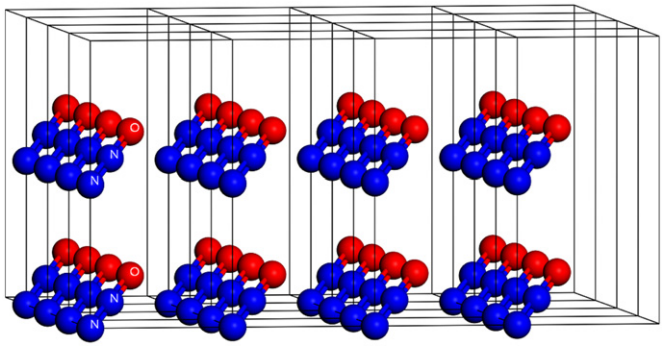

Fig. 2. Schematic depiction of the structure of the N_2O multilayer.

3. Results and discussion

3.1. Structure of the N_2O multilayer

Fig. 2 displays a schematic depiction of the structure of the N_2O multilayer. As shown in the figure, the multilayer consisted of two identical layers. CASTEP calculations were performed on the multilayer, and the height (h) between the neighboring layers varied from 3.3 to 5.3 Å. Table 1 lists the calculated total energy (E), relative energy (E_r) and probability of multilayer configuration. According to the literature [16], when edges L_{OA} and L_{OC} are set to 4.1 Å, the energy of the N_2O monolayer is equal to −979.673 eV. Thus, the energy of the two layers (E_0) is 1959.346 eV. The energy of each model was established relative to the energies (E_0 and E_r) of the other configurations, which were defined by comparing their total energies to E_0. Clearly, as the height (h) increased (see Fig. 3), the energy of the multilayer decreased and then increased slowly. When the relative energy between the monolayer and multilayer is equal to 0.030 eV,

Table 1
Total energy (E), relative energy (E_r), the probability for the potential configurations of the multilayer as the height h between the neighbor monolayers from 3.3 to 5.3 Å.

Code	h (Å)	E (eV)	E_r (eV)	Probability
1	3.3	−1959.293	−0.053	
2	3.5	−1959.347	0.001	Good
3	3.7	−1959.367	0.021	Good
4	3.9	−1959.378	0.032	Best
5	4.1	−1959.381	0.035	Best
6	4.3	−1959.380	0.034	Best
7	4.5	−1959.375	0.029	Good
8	4.7	−1959.369	0.023	Good
9	4.9	−1959.364	0.018	Good
10	5.1	−1959.360	0.014	Good
11	5.3	−1959.356	0.010	Good

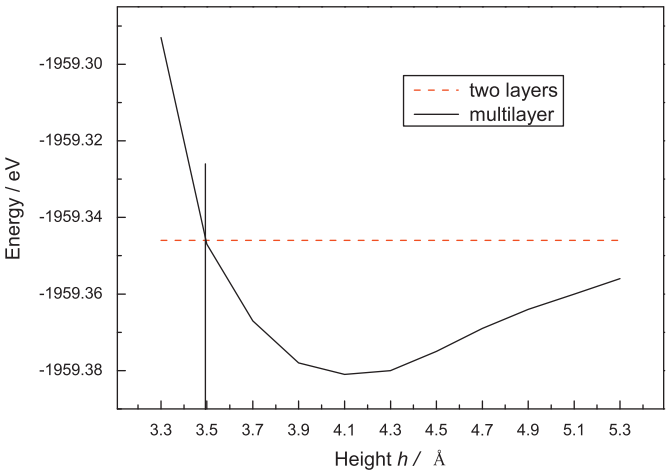

Fig. 3. Total energy of the potential multilayer at heights (h) ranging from 3.3 to 5.3 Å. The dotted line represents the energy of two layers.

several layers combine to form a stable multilayer. Thus, the height between the neighboring layers in the multilayer is equal to 4.1 ± 0.1 Å.

Fig. 4 shows the planforms of the probable structures of the multilayer. The models are labeled as 1*a*, 2*a*, 3*a*, 1*b*, 2*b*, 3*b*, 1*c*, 2*c* and 3*c*, and model 1*a* is shown in Fig. 2. The label 1 indicates that the second layer is identical to the first, and the number 2 indicates that the second layer is oriented at a 90° angle with respect to the first layer. Alternatively, the number 3 indicates that the second layer is oriented at a 180° angle with respect to the first layer. In models *a*, *b* and *c*, the N_T atom in the second layer is the top site, bridge site and hollow site, respectively.

Table 2 lists the calculated total energy (E) of the nine potential configurations as the height (h) varied from 3.7 to 5.1 Å. A contour plot of the total energy (E) of the N_2O multilayer is shown in Fig. 5. As shown in the figure, as the height increased, the total energy of the models decreased and then increased slowly. Models *a*, *b* and *c* presented the lowest energy; however, models *b* and *c* are not stable. Alternatively, models *b* and *c* are metastable models of the multilayer.

We hypothesized that many layers combine to form a stable multilayer when the relative energy between the two layers and the multilayer is equal to 0.028 eV. Thus, we can conclude that the multilayer consists of many layers, and the height (h) is equal to 4.1 ± 0.3 Å. Interestingly, the height is the same as the length of the edges of the monolayer, and both parameters possess the same characteristics.