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Adsorption and transformation mechanism of NO_2 on NaCl(100) surface: A density functional theory study

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HIGHLIGHTS

- NO_2 is vertically located at the Na–Na bridge site.
- Three ways can spin pair the orbitals of two NO_2 to make a closed-shell dimmer.
- The isomerization step consists of reciprocal transformation and mutual conversion.
- The reactions of H_2O with three N_2O_4 isomers are considered.

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ABSTRACT

To understand the heterogeneous reactions between NO_2 and sea salt particles in the atmosphere of coastal areas, the absorption of an NO_2 molecule on the NaCl(100) surface, the dimerization of NO_2 molecules and the hydrolysis of N_2O_4 isomers at the (100) surface of NaCl are investigated by density functional theory. Calculated results show that the most favorable adsorption geometry of isolated NO_2 molecule is found to reside at the bridge site (II-1) with the adsorption energy of −14.85 kcal/mol. At the surface of NaCl(100), three closed-shell dimers can be identified as *sym*-O_2N–NO_2, *cis*-ONO–NO_2 and *trans*-ONO–NO_2. The reactions of H_2O with *sym*-O_2N–NO_2 on the (100) surface of NaCl are difficult to occur because of the high barrier (33.79 kcal/mol), whereas, the reactions of H_2O with *cis*-$ONONO_2$ and *trans*-$ONONO_2$ play the key role in the hydrolysis process. The product, HONO, is one of the main atmospheric sources of OH radicals which drive the chemistry of the troposphere.

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1. Introduction

Sea salt particles containing NaCl are the largest source of tropospheric aerosol particulate matter with 10^{12} kg introduced into the atmosphere from wave action over the oceans each year (Weis and Ewing, 1999). NO_2 is one of the major pollutants in vehicle exhaust (Lawrence and Crutzen, 1999). In coastal cities with severe vehicle exhaust pollution, considerable attention has been paid to heterogeneous reactions between NaCl and NO_2, and their possible roles in atmospheric chemistry (Finlayson-Pitts and Hemminger, 2000; Karlsson and Ljungström, 1995; Rossi, 2003). The heterogeneous reaction of NO_2 on the surface of NaCl has been an intense research area of recent physical chemistry using X-ray photoelectron spectroscopy (Laux et al., 1996), infrared spectroscopy (Finlayson-Pitts, 1983; Vogt and Finlayson-Pitts, 1994; Weis and Ewing, 1999; Ye et al., 2010; Yoshitake, 2000) and Raman spectroscopy (Scolaro et al., 2009). All kinetic studies clearly show that the reaction is second order with respect to NO_2, but there remains the issue of whether the reactive molecule is NO_2 or its dimer, N_2O_4.

In many cases with NO_2 as reactant, it is not NO_2 monomer itself that directly participates in reactions, but its dimer (Finlayson-Pitts, 2003; Koda et al., 1985; Njegic et al., 2010; Raff et al., 2009; Schroeder and Urone, 1974). It has been known that dinitrogen tetroxide (N_2O_4) exists in substantial concentrations in chemical equilibrium at room temperature and atmospheric pressure. The formation process of N_2O_4 from NO_2 has been investigated by many scientists (Liu and Goddard, 2012; Pimentel et al., 2007a). The pathways of forming such dimers on the surface of NaCl, however, have no previous study.

In the marine environment, there are large amounts of water vapor in the air. Therefore, simulation of the heterogeneous reaction in the presence of water vapor much more resembles the real atmospheric environment than a dry one. Yoshitake (2000) proposed that the NO_2/H_2O/NaCl reaction is thought to keep the following mechanism:

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$$2NO_2 + H_2O \rightarrow HNO_3 + HONO \quad (1)$$

$$HNO_3 + NaCl \rightarrow HCl + NaNO_3. \quad (2)$$

Reaction (2) is likely fast enough to make reaction (1) rate-determining. Reaction (1) is the main source of HONO, which is one of the main atmospheric sources of OH radicals that drives the chemistry of the troposphere (Stockwell and Calvert, 1983; Stutz et al, 2004). In heavily polluted regions, HONO photolysis accounts for about 50% of the total OH production during the early morning. Finlayson-Pitts (2003) and Miller et al. (2009) indicated that the asymmetric dimer (ONO–NO_2) on surfaces plays a key role in NO_2 hydrolysis to form HONO and HNO_3. There are some data on the heterogeneous reaction of NO_2/H_2O/NaCl (Finlayson-Pitts, 1983; Finlayson-Pitts and Hemminger, 2000; Weis and Ewing, 1999; Ye et al., 2010). Unfortunately, the chemical and physical interactions on the surface of NaCl are not well understood on a molecular scale.

Theoretical calculation can provide information for the reaction intermediates and pathways. In this work, the density functional theory (DFT) calculation (Payne et al., 1992) was carried out to investigate the possible absorption of an NO_2 molecule at the NaCl(100) surface, the dimerization of NO_2 molecules and the N_2O_4–H_2O intermolecular potential at the same surface.

2. Computational method

All calculations were performed with the program package of CASTEP in Materials Studio (version 5.5) of Accelrys Inc. (Segall et al., 2002), implementing the Perdew–Wang 1991 (PW91) version of the general gradient approximation (GGA) (Perdew et al., 1992; Perdew and Wang, 1992). The energies of three important crystallographic surfaces (100), (110) and (111) were calculated, and the stability order of this three surfaces of NaCl was found to be (100) > (110) > (111) (Khan and Ganguly, 2013). Thus, in this study, we used a (2 × 2) supercell with a slab of four layers to represent the NaCl(100) surface. Cabrera-Sanfelix et al. (2006) verified that this was enough thickness to produce consistent adsorption properties. The vacuum gap along the normal to the surface was 12 Å. This has proven to be sufficient to prevent any significant overlap of the electronic densities corresponding to different periodic images of the slab. During geometry optimization, the bottom of two NaCl layers was fixed, and the atoms in the two topmost layers as well as the NO_2 were allowed to relax. All other degrees of freedom were allowed to relax until all the components of the forces were smaller than 0.01 eV/Å. We used a plane-wave cutoff of 330 eV and a $2 \times 2 \times 1$ Monkhorst–Pack k-point sampling, and the cutoff energy and k-point sampling were used throughout our calculations. The tolerance of self-consistent field (SCF) convergence was 1×10^{-6}.

The adsorption energy E_{ads} is defined as the energy difference between the optimized system and those of the relaxed NaCl(100) surface and the isolated NO_2 molecule.

$$E_{ads} = E_{(NO_2/slab)} - \left[E_{(NO_2)} + E_{(slab)}\right]$$

where the first term is the total energy of the slab with the adsorbed NO_2 on the surface, the second term is the total energy of free NO_2, and the third term is the total energy of the bare slab of the surface. According to the above definitions, a negative E_{ads} value corresponds to an exothermic adsorption, and the more negative is the E_{ads}, the stronger is the adsorption between NO_2 and NaCl.

In order to determine accurate activation barriers of the reaction, we chose the complete LST/QST approach to search for transition states of the reactions (Halgren and Lipscomb, 1977). In this method, the linear synchronous transit (LST) maximization was performed, followed by an energy minimization in directions conjugating to the reaction pathway to obtain an approximated transition state (TS). The approximated TS was used to perform quadratic synchronous transit (QST) maximization, and then another conjugated gradient minimization was performed. The cycle was repeated until a stationary point was located. The reaction energy (E_r) and energy barrier (E_b) of an elementary reaction on NaCl(100) surface were calculated based on the following formulas:

$$E_r = E_{Product} - E_{Reactant}$$

$$E_b = E_{TS} - E_{Reactant}.$$

3. Results and discussion

3.1. Tests of computational conditions

To confirm the reliability of the methods, we compared the bond distances (in Å) and bond angle (°) for H_2O, NO_2 and N_2O_4 with available experimental values in Table 1. We take here the energy of the H_2O, NO_2 and N_2O_4 molecules in a large unit cell of 10 Å × 10 Å × 10 Å. The calculated bond length and bond angle are in good agreement with the experimental values (Pimentel et al., 2007b). All of the calculated bond lengths are within 2% of experimental ones, and the calculated bond angles are within 1°.

3.2. NO_2 adsorption on the (100) surface of NaCl

The $^2A_1$ ground state of NO_2 has a bent structure with the unpaired electron residing on the N atom, which has three different adsorption sites on the NaCl(100) surface: the top site (I), the bridge site (II) and the 3-fold hollow site (III). Resulting NO_2/NaCl(100) structures are shown in Fig. 1.

As shown in Fig. 1 and Table 2, NO_2 could either weakly adsorb at the Na top site on NaCl(100) surface with the adsorption energy of below −10 kcal/mol, or adsorb at the Cl top site on NaCl(100) surface with the adsorption energy of above −9.5 kcal/mol. According to the definitions of E_{ads}, the more negative is the E_{ads}, the stronger is the adsorption between NO_2 and NaCl. Thus, the Na–NO_2 interaction is much stronger than the Cl–NO_2 interaction, possibly because Na is an electron donor.

For the bridge site, NO_2 is vertically located at Na–Na bridge site, Na–Cl bridge site and Cl–Cl bridge site. On the whole, the NO_2 at Na–Na bridge sites (II-1, II-4, and II-7) are the most energetically favorable among the all structure, and then the Na–Cl bridge sites (II-2, II-5, II-8 and II-9) and Cl–Cl bridge sites (II-3, II-6, and II-10).

For the 3-fold hollow sites, there are two different adsorption forms: the first one is that O atom is bound to the surface of Na atom whereas the N atom was bound to the Cl atom, and the second one is that the O atom is bound to the surface of Cl atom whereas the N atom is bound to the NaCl atom. The first adsorption form is more stable.

In all the structures, the most stable adsorption of the NO_2 on NaCl(100) surface is found to reside at the bridge site (II-1) with the adsorption energies of −14.85 kcal/mol which is taken for example in the subsequent reactions.

Table 1
The bond distances (in Å) and bond angle (°) for H_2O, NO_2 and N_2O_4.

Molecule	Parameter	Calculated value	Experimental value[a]
H_2O	O–H	0.975	0.958
	∠HOH	104.6	104.5
NO_2	N–O	1.231	1.193
	∠ONO	133.5	134.1
N_2O_4	N–N	1.807	1.782
	N–O	1.222	1.190
	∠ONO	135.4	135.4

[a] Lide, D. R. *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, 1996.

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