Theoretical Study of the Interaction of N_2O with Pd(110)

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N_2O has been found from experimental and theoretical considerations to bind on-top to the Pd(110) surface in a tilted end-on fashion *via* its terminal N atom. We use a frontier orbital description of the bonding interactions in the Pd-N_2O system to obtain molecular insight into the catalytic mechanism of the activation of N_2O by the Pd(110) surface giving rise to the formation of N_2 and O on the surface. For the tilted end-on N_2O binding mode, the LUMO 3π of N_2O has good overlap with the Pd d_σ and d_π orbitals which can serve as the electron donors. The donor-acceptor orbital overlap is favorable for electron transfer from Pd to N_2O and is expected to dominate the surface reaction pathway of N_2O decomposition.

Key Words : Extended Hückel calculations, Palladium, Nitrous oxide

Introduction

N_2O decomposition on transition metal surfaces has attracted much attention because of the environmental problems connected with the release in the atmosphere of this molecule in industrial processes, like production of fertilizers or polymer fibers, or from car exhausts.[1,2] Furthermore, N_2O itself is harmful and yields a remarkable greenhouse effect, and also contributes to stratospheric ozone depletion. Besides this environmental point of view, the enzyme nitrous oxide reductase (N_2OR) catalyzes the reduction of N_2O to N_2 and H_2O in the final step of the bacterial denitrification process.[3-6] This process is also of great importance from an interest in N_2O reduction and protonation originating from bioinorganic chemistry. Hence, the properties of nitrous oxide and its reactivity are not only of global importance, but also of interest for bioinorganic chemistry. Many catalytic systems have been employed for N_2O decomposition, including metals, pure and mixed oxides, supported metals, and zeolites.[1] The reaction is initiated by the bonding of the N_2O molecule to the active metal center, followed by its decomposition, resulting in the formation of N_2 and O on the surface. The formation of NO upon interaction of N_2O with catalyst surfaces has not been reported in the literature. In the asymmetric N-N-O molecule the N-N bond order is larger (~2.7) than that of N-O (~1.6) and therefore one would expect catalytic decomposition yielding N_2+O to be energetically favored.

The principal catalytic model proposed for the reaction mechanism is the electron transfer process.[7-9] During the reaction, an electron transfer occurs from the metal atom to the N_2O LUMO state, resulting in a distinctive weakening of the N-O bond and thus a lowering of the activation energy. Fontijn and co-workers[10] have advanced a resonance interaction model to predict the rate constants for metal atoms reacting with N_2O. According to this model, the activation barriers should vary with the sum of the ionization potential and s-p promotion energy of the metals. This could indeed explain the observed trend for the rate constants k(Sc) > k(Mo) > k(Rh) > k(Cu). Many metals have been studied in reactions with N_2O and this model appears to describe the activation barriers for these reactions reasonably well. A density functional study on the reaction mechanism of transition metals Sc, Ti, and V with N_2O presented that the energy barriers for these reactions should be very low (within 3-5 kcal/mol).[11] The calculations indicated that electron transfer from the metal atoms to N_2O is an essential element of the reaction mechanism.

Experimental studies have been published on the adsorption and decomposition of N_2O on well-defined metal surfaces.[12-31] The reactivity of N_2O appears to depend strongly on the nature of metals and their surface structure. Li and Bowker[12] reported that N_2O decomposes to produce N_2 at low temperature on Rh(111) and Rh(110). Matsushima et al. confirmed, through the analysis of the angular distribution of desorbing N_2 by means of angle-resolved thermal desorption, that N_2O adsorbed on Rh(110) yielded N_2 in the surface temperature range of 100-180 K.[24,25] N_2O(ads) is desorbed at 90-120 K on Pt(111),[14] Ir(111),[15] Ni(111),[17] and Ag(111)[26] without dissociation. On Pd(110),[21] Ru(001), W(110),[27] Cu(110),[28] and stepped Ni(557),[29] it dissociates below 170 K, yielding N_2. Incident N_2O was decomposed on Ni(110), Ni(100), and Rh(110) below 200 K,[18,30] but not on Rh(111).[31]

Theoretical studies of N_2O adsorption on metal surfaces are very scarce. To our knowledge, only the adsorptions of N_2O on Pd(110),[23,32,33] Rh(110),[34] Ni(755),[35] and Pt(111)[36] have been investigated. Both experimental[19-22] and density functional theory[23,32,33] studies of N_2O decomposition have been carried out on a Pd(110) surface. They found that N_2O is preferentially adsorbed in a tilted form *via* its terminal N atom on the on-top site and it lies on the surface prior to decomposition. Since very little is known the nature of the bonding and activation of N_2O to the metal surface, we need to discuss in depth the electronic factors that govern the adsorption phenomenon.

This work was undertaken to obtain an MO theoretical understanding of the adsorption and reactivity of N_2O over Pd(110). All calculations were carried out within the

Table 1. Extended Hückel parameters

atom	orbital	H_{ii}(eV)	ζ_1^a	C_1^a	ζ_2	C_2
Pd	5s	−6.82	2.190			
	5p	−3.25	2.152			
	4d	−10.52	5.983	0.5264	2.613	0.6373
N	2s	−26.0	1.95			
	2p	−13.4	1.95			
O	2s	−32.3	2.275			
	2p	−14.8	2.275			

[a]Exponents and coefficients in a double-ζ expansion of the 3d orbital.

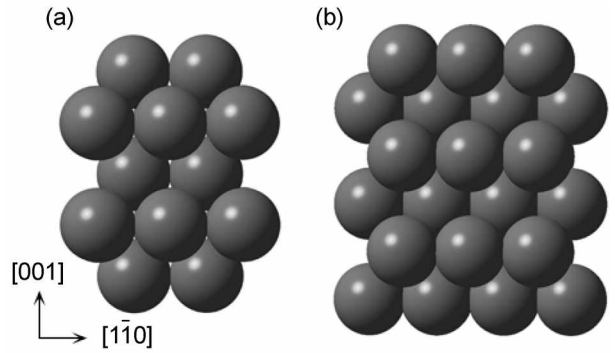


Figure 1. Three-layer cluster (a) and slab (b) models of N_2O/Pd(110) adsorption system. In the slab model, a p(2×2) supercell containing four Pd atoms per layer and three layers in the [110] direction was used.

framework of extended Hückel theory (EHT).[37] The atomic parameters are listed in Table 1. Since this method does not allow geometrical optimization, we adopt the adsorption structures of N_2O on Pd(110) from DFT study.[33] The Pd(110) surface was modeled using both the cluster of 18 atoms arranged in three layers and periodic three-layer slabs with a p(2×2) unit cell, as seen in Figure 1. The experimental lattice parameter of bulk palladium (3.89 Å) was used in the calculations.[38] The Pd-Pd distances were kept fixed with the Pd-Pd nearest neighbor distance equal to that obtained from the bulk lattice parameter. The bond distances of the gas-phase N_2O molecule were taken as 1.14 Å for N-N and 1.21 Å for N-O. The adsorption energy (E_{ads}) was calculated according to $E_{ads} = E_{sub} + E_{N2O} - E_{N2O/sub}$, where E_{sub}, E_{N2O}, and $E_{N2O/sub}$ are the energies of the naked substrate, the isolated N_2O molecule, and the composite system of the two, respectively. Positive adsorption energy indicates a stable adsorption process.

The purpose of this paper is to investigate the activation of nitrous oxide adsorbed on-top on Pd(110) surface and to identify the orbital interactions involved in this process through the frontier orbital concept.[39] The theoretical tool we use is perturbation theory.[40,44,45] The principal mechanism by which the nitrous oxide can be decomposed involves an electron transfer (ET). The transition metal atoms act as the surface electron donor centers, giving rise to reductive activation of the N_2O molecule. A molecular pathway for the electron transfer process occurring at catalytic surfaces consists in electron movement between relevant orbitals. Interaction between the occupied donor and unoccupied acceptor orbitals plays a vital role. Both the energy compatibility and symmetry match of these redox orbitals are important for effective orbital overlap. On-top adsorption of nitrous oxide on Pd(110) leads to ET-induced activation which produces N_2 and O species. A π-type overlap between HOMO (2π) and LUMO (3π) of N_2O and Pd d_π orbitals and a σ-type interaction between 7σ (N_2O) and z^2 (Pd) orbitals are important. Since Pd has a d^{10} electron configuration, however, σ and π donations of N_2O into the Pd d functions are not significant in the linear Pd-NNO geometry. The σ-type interaction is decisive to favor the tilted adsorption of N_2O. Therefore, a stable metal-NNO bond is primarily achieved by π back-bonding interaction, which provides a pathway for the electron transfer process from the d_π donor orbitals of palladium toward the antibonding 3π acceptor orbitals of N_2O with formation of a transient $N_2O^{\delta-}$ species. This leads to a severe bending of the $N_2O^{\delta-}$ intermediate which activates the N_2O molecule toward N-O bond dissociation. This observation is consistent with the result of the dissociation energies $D(NN\text{-}O^-) = 0.4$ eV and $D(N\text{-}NO^-) = 5.1$ eV, determined from beam-collision chamber experiments.[41] In order to rationalize this mechanism, thorough considerations of orbital interaction between metal and N_2O are required. The general implications of these results are discussed below.

Results and Discussion

General features of the interaction. The main feature of our study is manifested by the formation of a Pd(N_2O) compound from the end-on bonding of a linear N_2O to a metal atom. A study of linear *vs.* bent N_2O is approached by the construction of an interaction diagram between the metal fragment and the nitrous oxide. Since we are working in a molecular orbital representation, what matters to us is the symmetry type and relative energy of the orbitals contributed on one hand by the metal and on the other hand by the nitrous oxide. The orbitals of the N_2O and the metal fragment are well-known.[42] The important MO contour diagram of free N_2O is shown in Figure 2a. The bonding properties of this molecule are evaluated. The LUMO, 3π, is a π^* orbital with antibonding character for both the N-O and N-N bonds. The HOMO, 2π, is almost nonbonding π orbital which is antibonding with respect to the N-O bond but bonding for the N-N bond. Next in energy is the weakly N-N and N-O σ bonding orbital 7σ, which mostly has lone pair character on the terminal nitrogen. This orbital could therefore act as a σ donor. However, since this orbital is located at even lower energy than the d_{z^2} orbital of Pd, the σ donor ability of N_2O should be weak.

We begin with the linear geometry of a hypothetical Pd(N_2O) compound with Pd-N distance of 2.03 Å, which is the model structure of the N_2O-Pd surface complex where nitrous oxide is bound on-top through its terminal nitrogen

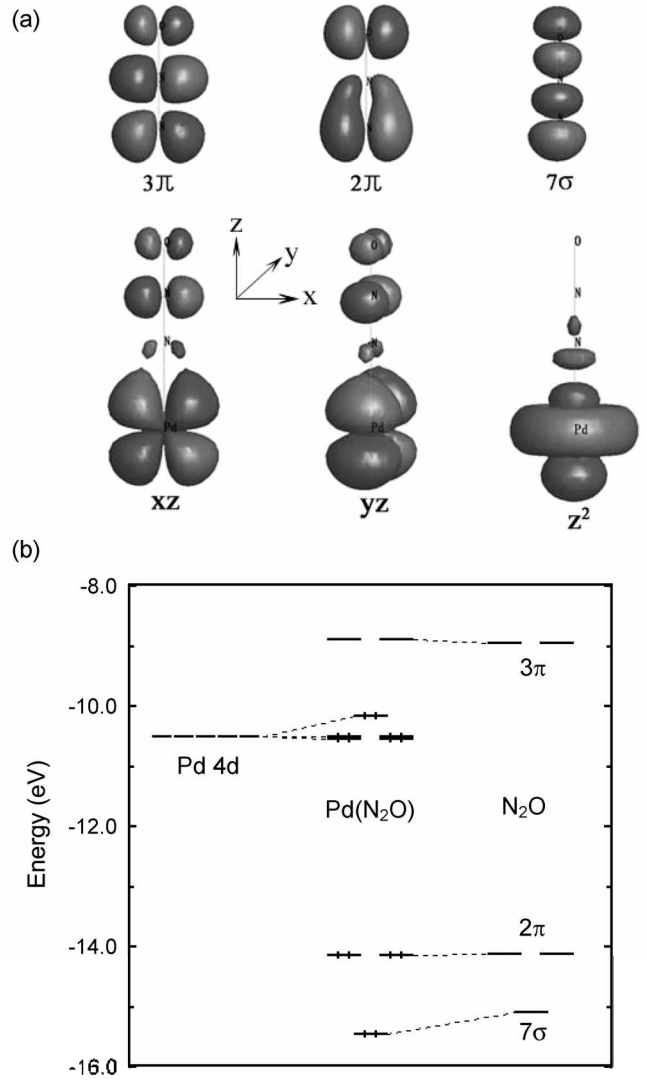


Figure 2. (a) The orbitals formed from the metal and N_2O orbitals in appropriate linear combinations and the important orbitals of an N_2O molecule. (b) Interaction diagram for a linear Pd-N_2O system.

atom. The MO correlation diagram of this model structure is shown in Figure 2b. In the discussion of the interaction between the metal fragment and N_2O, we omitted the following orbitals: (1) the x^2-y^2 and xy orbitals of Pd, because in the linear Pd(N_2O) complex there is no orbital of symmetry to interact with them; (2) the higher 8σ, 9σ, and the lower 4σ, 5σ, 6σ, and 1π orbitals of the N_2O, because these orbitals are too high or too low in energy to interact significantly with d orbitals of the metal fragment. We thus are left with xz, yz, and z^2 orbitals of Pd to interact with the 2π, 3π, 7σ orbitals of the N_2O. The nitrous oxide molecule is here reduced to its essentials-the donor orbital 7σ, a lone pair on N, somewhat delocalized, and the pairs of donor 2π and acceptor 3π orbitals. The energy of these π orbitals relative to the metal d levels will be seen later to be a crucial matter, but let us initially notice that d levels are in between 2π and 3π. Two strong interactions occur-the σ mixing between 7σ and z^2 and the π interaction between degenerate 3π (π^*) and metal xz and yz. This is shown schematically in Figure 2a together with the coordinate system that is used in the following discussion. The strength of the interactions between two fragment orbitals depends on the magnitude of overlap between the orbitals and the compatibility of the orbital energies. The highest occupied z^2 orbital of Pd(N_2O) is a metal z^2-N_2O 7σ antibonding combination, with some mixing of metal s and z orbital. Since the z^2 of Pd is the filled orbital that strongly interacts with the lower-lying 7σ of a N_2O, the z^2-7σ interaction is a four-electron, closed-shell, destabilizing interaction. On the basis of the compatibility of orbital energies, the interactions between 3π (π^*) of N_2O and d_π (xz and yz) orbitals of Pd are significant enough to be considered. The xz and yz orbitals begin with weak π bonding with the 3π (π^*) orbitals of the nitrous oxide as a result of mixing of 2π in an antibonding way. The xz, yz-π^* interaction is only slightly stabilizing, therefore, with the increased N-O antibonding interaction due to the mixing of 2π into it, which is discussed in a later section.

Now suppose the PdNN angle is lowered from 180°, the N_2O group moving in the xz plane. The z^2 orbital in the linear geometry is localized on the metal, but with some N_2O 7σ mixed in an antibonding way. As the N_2O bends, z^2 will decrease its antibonding interaction with 7σ, which is no longer collinear with the Pd-N bond. At the same time z^2 begins to interact more and more with $\pi^*(x)$ on N_2O, leading to a favorable stabilizing pseudo-σ bonding interaction with it. The latter interaction is symmetry forbidden in the linear coordination. These points are shown in **1**. In the course of the same bending the metal xz orbital goes up in energy because its π bonding with $\pi^*(x)$ decreases, while its antibonding interaction with 7σ, absent in the linear geometry, is now turned on. This is illustrated in **2**. As the nitrous oxide bends, the interaction of xz orbital is gradually weakened, but the yz-$\pi^*(y)$ interaction is maintained. The essential features of a Walsh diagram in Figure 3 corroborate our qualitative conclusions for bending of a nitrous oxide in the model Pd(N_2O) complex. Whether a nitrous oxide group is bent or not depends on two opposing factors: the slope of

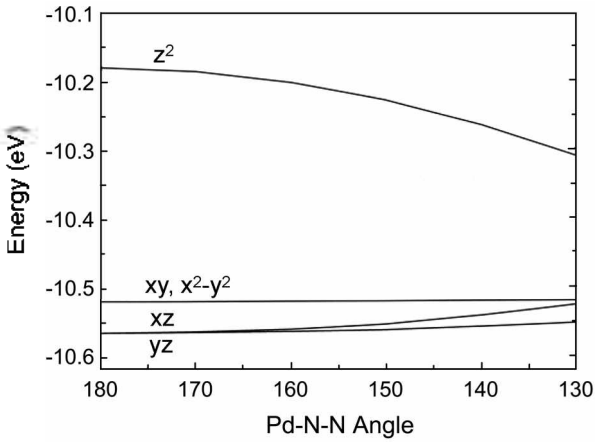
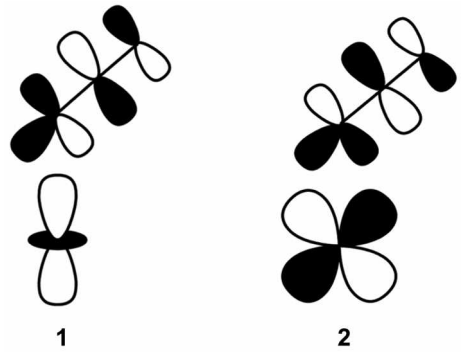


Figure 3. Calculated energy levels of Pd(N_2O) as a function of the Pd-N-N angle. The labels identify the primary character of the MO, even though these orbitals are to some extent delocalized.



the z^2 level, which favors bending, and the slope of xz level, which favors linearity. Since the z^2 level is filled and it is the main stabilizing interaction which causes the bending, we would expect the Pd(N_2O) system to be bent. The back-bonding interaction between z^2 and $\pi^*(x)$ as well as d_π and π^* in the bent geometry makes the nitrous oxide become more negative by populating a N_2O π^* orbital, with much density on centered N and O and the resultant weakened N-O bond. On the basis of this orbital scheme some considerations will be made on the nature of the surface-N_2O bonding and the N_2O activation in the subsequent sections.

Bonding of nitrous oxide to Pd(110). There existed some debate as to the end-on orientation of the N_2O on the metal surface *via* either the oxygen or the terminal nitrogen atom. The adsorption of N_2O *via* either O or N atom can not be discriminated on the basis of the results of the EH calculations, but experimental and theoretical investigations seem to favor N_2O attached by nitrogen. This result can be explained in terms of the coefficients of the relevant orbitals of the N_2O. Because of the different electronegativities of N and O, the coefficients of orbitals on the N side of NNO are larger than those of the O side for 3π and 7σ orbitals of N_2O in Figure 2a. Larger coefficient, *i.e.*, spatial extension at the N side for these orbitals leads to larger overlap with the surface orbitals. Thus the adsorption of N_2O *via* its terminal N atom is strongly preferred. The binding of nitrous oxide molecule to the Pd(110) surface was evaluated using density functional calculations by Kokalj and co-workers.[23,32,33] According to their conclusions, only *via* the terminal N, in a tilted configuration, N_2O at 0.5 monolayer coverage adsorbs on-top on Pd(110) with its geometry remaining linear.

As reported by Kokalj *et al.*, several adsorption modes are possible on the Pd(110) surface. The adsorption is modeled by attaching the N_2O molecule with the terminal nitrogen to the surface in either *linear* or *tilted* form and by placing the

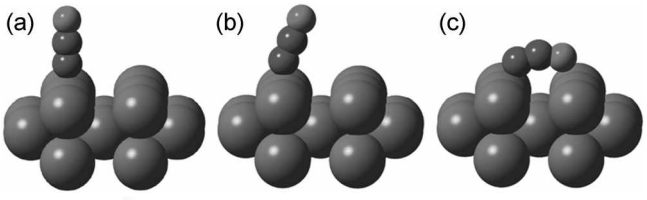


Figure 4. Different adsorption modes of N_2O on Pd(110): (a) linear on-top, (b) tilted on-top, and (c) flat on-top adsorption.

molecule horizontally on the surface in the [001] direction so that its terminal N and O atoms are interacting with the metal atoms (hereafter designated as *flat* form). Our calculations were performed with the three-layer cluster model of the surface in Figure 1a. The adsorption energies as well as all important geometrical parameters (see Figure 4 for views of structures) are presented in Table 2. The adsorption energies were calculated to be relatively small. The adsorption through the terminal N atom in a tilted form on top of one Pd atom yields an adsorption energy of 0.86 eV. This tilted adsorption mode is only slightly more stable than the terminal N on-top linear adsorption mode. The flat form lying horizontally on the surface is the most stable adsorption mode of N_2O that is rearranged to a bent structure with the terminal N and O atoms pointing toward the surface. The geometry of the adsorbed molecule is very different from that of the gas phase. The N-N-O angle is 156° and the N-N (1.17 Å) and N-O (1.24 Å) distances are larger compared to those in gas-phase N_2O. An adsorption energy of 1.06 eV is calculated when the two terminal atoms are oriented in top positions along the [001] direction. We find that at low coverages on Pd(110) the flat form is more stable by 0.20 eV than the tilted one. This result is in agreement with DFT studies by Kokalj and co-workers.[32]

In order to describe the interaction of N_2O with the Pd(110) surface effectively it is necessary to consider the bonding role of the frontier orbitals on N_2O and the metal d orbitals. Chemisorption involves not only the bond formation between the N_2O molecule and the surface but also a variation in the strength of the N-O bond within N_2O. From our earlier examination of the bonding contributions to the metal due to the individual N_2O orbitals it is important to note that most of the interaction comes from the 7σ, 2π, and 3π N_2O orbitals. Since Pd has a d^{10} electron configuration, the d orbitals are fully occupied. Consequently, σ and π donations from the N_2O 7σ and 2π are not expected to be significant and hence their interactions do little contribute to

Table 2. Calculated adsorption energies (E_{ads}) and geometrical parameters used in the calculations[a]

System	E_{ads}	d_{PdN}	d_{NN}	d_{NO}	d_{PdO}	∠PdNN	∠NNO	∠NOPd
Linear on-top	0.84	2.09	1.14	1.21		180	180	
Tilted on-top	0.86	2.09	1.14	1.21		157	180	
Flat on-top	1.06	2.10	1.17	1.24	2.33	130	156	116
N_2O (g)			1.14	1.21			180	

[a]Taken from Reference 33. The labels d_{PdN}, d_{NN}, d_{NO}, and d_{PdO} stand for the distances between the corresponding atoms and the labels ∠PdNN, ∠NNO, and ∠NOPd for the angles. Adsorption energies are in eV, distances in Å, and angles in degrees.

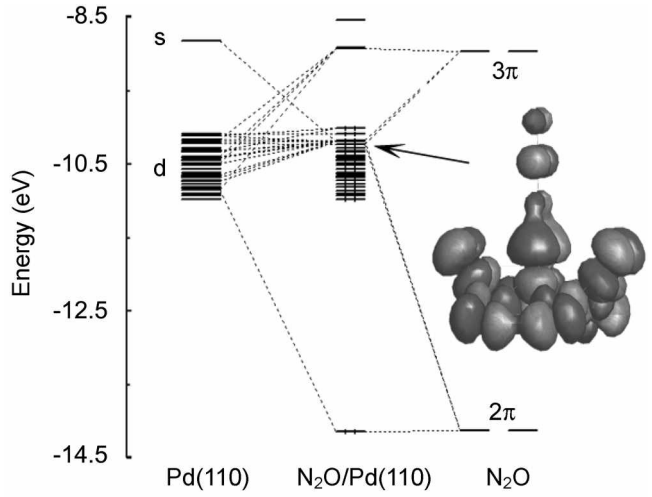


Figure 5. Schematic representation of orbital interactions in the N_2O/Pd(110) adsorption system.

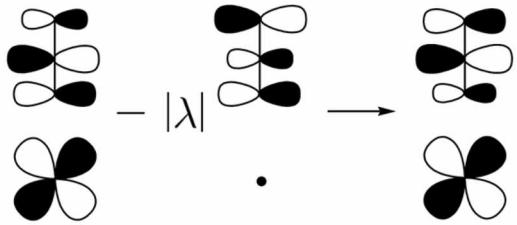
the surface-N_2O bonding. Back-bonding from the surface to the N_2O 3π orbital is clearly a major contributor to the surface-N_2O bonding. Our focus here is on the π bonding and in particular on the roles played the N_2O 2π and 3π orbitals.

Mixing of the 2π orbitals into the bonding combinations, xz-π^*(x) and yz-π^*(y), between dπ and 3π can be analyzed within the framework of perturbation theory. The consequence of second-order perturbation theory is that if the two orbitals mix, the energetically higher orbital of the two mixes into itself the lower one in a bonding way. Conversely, the energetically lower orbital mixes into itself the higher level in an antibonding way. We proceed by first interacting the 3π and the metal d_π orbitals for the on-top linear adsorption structure of N_2O *via* the terminal N atom. We mix metal dπ with the N_2O 3π. Since the 3π orbital is higher in energy than the Pd dπ orbital, the bonding combinations xz-π^*) and yz-π^*(y) of the back-donation interaction are occupied and composed mainly of metal d_π with the contribution from N_2O 3π. The corresponding antibonding counterparts are empty and consist of N_2O 3π orbital with metal dπ mixed in out-of-phase. We now mix N_2O 2π into the bonding combinations between d_π and 3π. The phase with which 2π mixes in will be controlled by the d_π-2π interaction, because the metal d_π orbital is the major contributor to the orbital in question. The metal d_π orbital is located higher in energy than 2π, hence 2π will mix in an antibonding way. The phase is illustrated schematically in **3** (λ is an MO mixing coefficient). The net result is drawn on the right of the arrow (**3**). We note the reduction and increase in orbital coefficients on the terminal nitrogen and the other two atoms of N_2O, respectively. This produces a somewhat smaller Pd-N_2O bonding and a sizable N-O antibonding interaction. The calculated Pd-N_2O overlap population of 0.34 shows that nitrous oxide is weakly bound. The latter interaction provides key information on how the activation of nitrous oxide by the surface works on a molecular level. Schematic representation of the orbital interaction in the

Table 3. Bonding characteristics for tilted N_2O adsorption on Pd(110)

	N_2O	N_2O/Pd(110)
Occupations		
3π	0	0.26
2π	4	3.99
7σ	2	1.89
Overlap populations		
N-N	1.55	1.49
N-O	0.91	0.88
Pd-N	0	0.33
Pd1[a] charge		0.11

[a]The palladium atom here is the closest to the nitrous oxide molecule under consideration.



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N_2O/Pd(110) adsorption system is shown in Figure 5. Importantly, the nitrous oxide molecule is activated for N-O dissociation by the population of 3π through back-donation from the metal, which will explain later the observed weakening of the N-O bond upon adsorption of N_2O.

What happens when the nitrous oxide molecule is tilted with respect to the surface? A qualitative bonding model of the tilted N_2O adsorption on Pd(110) invokes simultaneous electron back-donation from the z^2 and the d_π orbitals on the metal surface to the lowest unoccupied 3π orbitals on N_2O. A considerable amount of electron density is transferred from Pd to N_2O through the π system. The strength of the back-bonding interactions is reflected by the occupations of the N_2O fragment orbitals 3π (0.26 e^-). Besides this strong back-bonding, there is also a Pd z^2-N_2O σ bonding mediated by the 7σ orbital, which corresponds to a weak interaction because the antibonding combination is mostly occupied. This bonding description is represented by the calculated charges, electron densities, and overlap populations given in Table 3. As a consequence of the population of the 3π, a marked N-O bond activation would be expected. The potential reactivity of end-on bound N_2O for N-O cleavage mediated by σ and π back-donation is explored in the next section.

Reactivity of end-on terminally N-bound N_2O. In the gas phase, the N_2-O cleavage generates N_2 and a triplet O atom, which is energetically uphill (ΔH of *ca.* 40 kcal/mol) and has a high activation barrier of 59 kcal/mol.[43] In order to overcome this reaction barrier, transition metals are used as activation centers to donate electron density to N_2O. Scheme **4** shows the activation process of end-on terminally N-

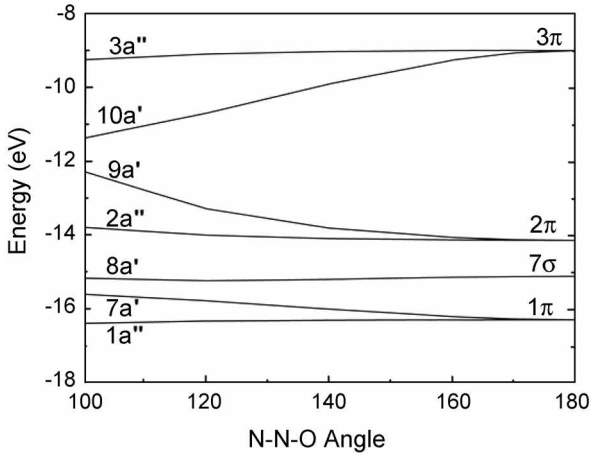
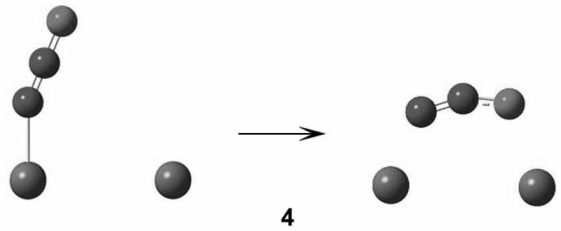


Figure 6. Orbital energies of NNO as a function of the N-N-O angle.



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bound N_2O into the N-O dissociation considered in this study. Adsorption on the Pd(110) surface occurs *via* the terminal N atom on the atop site, by tilting of the molecule toward the surface. In order for N_2O to decompose, the molecule must lie on the surface in the [001] direction, thereby enabling the oxygen atom to bond with a surface Pd atom. A charge transfer of 0.26 e^- occurs at the initial stage of the adsorption from the surface to the LUMO (3π) of N_2O. Population of this orbital favors a bent geometry of the N_2O molecule, because the N_2O^- ion is bent with destabilized N-O and N-N bonds. The formation of a bent N_2O^- ion is favorable process, as illustrated by the Walsh diagram in Figure 6. According to Walsh rules, the geometrical configuration of many polyatomic molecules depends, to a reasonably good approximation, on the number of valence electrons. The geometry of N_2O^- ion will differ significantly from that of the corresponding neutral molecule. The neutral N_2O in its ground state favors the linear configuration of the nuclei. However, in the case of the N_2O^- species the unpaired electron occupies the orbital 10a' (derived from 3π) which is strongly stabilized upon bending as can be inferred from the Walsh diagram in Figure 6. The N_2O^- is thus bent whereas the neutral N_2O is linear. Therefore, the metal-to-N_2O electron transfer should cause a strong angular distortion of transient N_2O in the proposed surface reaction mechanism to account for the N_2O decomposition.

The very bent geometry of N_2O causes a splitting of the degenerate 3π of N_2O into two nondegenerate π^* orbitals and stabilizes the resultant in-plane 3π (10a') due to loss in antibonding character. This shifts the 10a' closer to the fully occupied d band of the Pd cluster and makes the N_2O molecule a better electron acceptor. In the linear N_2O geometry of tilted adsorption form the acceptor orbital 3π (E = −8.98 eV) is situated distinctly above the top of the palladium d band (E = −10.0 eV), whereas in the bent geometry the energy of the 10a' orbital is lowered close to the d band. Remarkable shift down in the energy of this acceptor orbital upon bending opens the pathway for making the electron transfer energetically favorable. Although the symmetry of N_2O is reduced on bending and the π orbitals are split into corresponding a' and a" states, the notation of σ and π orbitals of linear N_2O will be used for the convenience of discussion. The variation in the population of 3π at different bending angles of N_2O toward the surface in the tilted form is presented in Table 4. It is noted that the electron population of 3π rises as the NNO angle is decreased from 180°. The decrease of the N_2-O bond strength due to the cooperative action of the more donative pseudo-σ and π back-bonding to N_2O 3π orbital will facilitate the activation process of a bent N_2O into the N-O dissociation.

Table 4. Electron occupation of 3π at different bending angles of N_2O adsorbed in the tilted form on Pd(110)

∠NNO	3π occupation
180°	0.26
170°	0.30
160°	0.41
150°	0.71

The electronic structure calculations for the surface complex of the flat form result in a distinctively weakened N-O bond with overlap population of 0.73 (compared to 0.91 for the gas-phase N_2O). Overlap population between atoms N and O measures the electron density in the N-O bond. It is an indication of the bond order and can also be used to evaluate the strength of the bond. The 3π occupation rises dramatically to 1.15 in the flat form, compared to 0.26 in the tilted one (Table 3). This finding is the result of an increased transfer of electron density on the surface into the unoccupied set of 3π orbitals of N_2O through the back-bonding with the occupied z^2 and d_π orbitals of Pd. The Mulliken electron charge of N_2O and the Pd atom closest to it in the flat form is around −0.93 and 0.70, respectively, indicating a very substantial back-donation from the Pd d orbitals to the 3π orbitals. The large charge transfer from the Pd surface to N_2O upon adsorption plays a crucial role in N_2O activation, since the 3π population gives rise to a relevant decrease of the N-O bond order. It is clear that N_2O binding in a bent flat form to the metal surface is most efficient for the strong back-bonding interaction from metal and thereby increased charge transfer to the N_2O antibonding states favors N-O bond breaking. As illustrated in scheme **3** and Figure 5, mixing of the 2π orbital into the bonding combination between the 3π and the d_π orbitals results in increased N-O π antibonding. The occupancy of this orbital promotes N_2-O bond dissociation upon adsorption, giving rise to reduced N-O bonding. Thus we conclude

Table 5. Calculated activation barriers (E_a) for M + N_2O reactions and ionization potentials (IP) of transition metals (M), all in kJ/mol

Transition metal	E_a (calc)[a]	IP[a]
Sc	4.5 (7.7)	631
Ti	8.0 (10.1)	658
Zr	2.6	640
Co	31.5	759
Ni	32.7	737
Mo	28.1 (~28)	684
Rh	33.2	720
Cu	39.6 (39.6)	745
Pt	46.2	865
Au	56.4	890
Zn	51.7	906

[a]Reference 10. In parentheses are given the experimental values.

that the bridging flat form with a bent N_2O moiety is the favorable precursor structure of the N_2O decomposition and the degree of activation depends on the extent of electron population in N_2O 3π orbitals.

These results offer a great deal of information on how transition metals can mediate the decomposition of nitrous oxide and what the potential reaction mechanism is. From a more general viewpoint, if more charge is put on N_2O in the surface-N_2O complex, the degree of activation of N_2O would be increased. One would also expect that the charge transferred from the metal to N_2O increases when the ionization potential decreases. The higher-lying in energy the metal d orbitals are, the larger the metal-to-3π back-donation is, *i.e.*, a higher reduction of the N-O bond order is expected. This may be achieved through adsorption of N_2O on metals of lower effective nuclear charge than Pd lying on the left-hand side of the transition metal series. A correlation between the activation barrier of N_2O and the ionization potential of the transition metals is presented in Table 5.

Band electronic structure of adsorbed N_2O. Further insights into the bonding interaction and electronic properties of adsorbed N_2O can be obtained using the projected density of states (PDOS) of the different systems. For proper comparison between cluster and slab results, the band calculations were also performed with three-layer slab model of the surface. The electronic structure of the N_2O/Pd(110) slab model is similar to that of the N_2O/Pd_{18} cluster model. Figure 7 shows the PDOS curves on the N_2O molecule for the tilted on-top and the flat on-top p(2×2) N_2O/Pd(110) structures. We see that the most noticeable difference in the molecular PDOS of the flat structure compared to the tilted structure is the downshift and splitting of 3π orbitals. For the on-top tilted adsorption mode, the 7σ and 2π orbitals are slightly shifted down in energy (0.34 and 0.02 eV, respectively) with respect to those of the free molecule and there is only a relatively small contribution of the metal states at the corresponding energies. The 3π orbital is upshifted (0.05 eV), indicating the presence of back-donation. On the contrary, for the flat adsorption mode, the downshift of the 3π orbitals with respect to those of the tilted one is

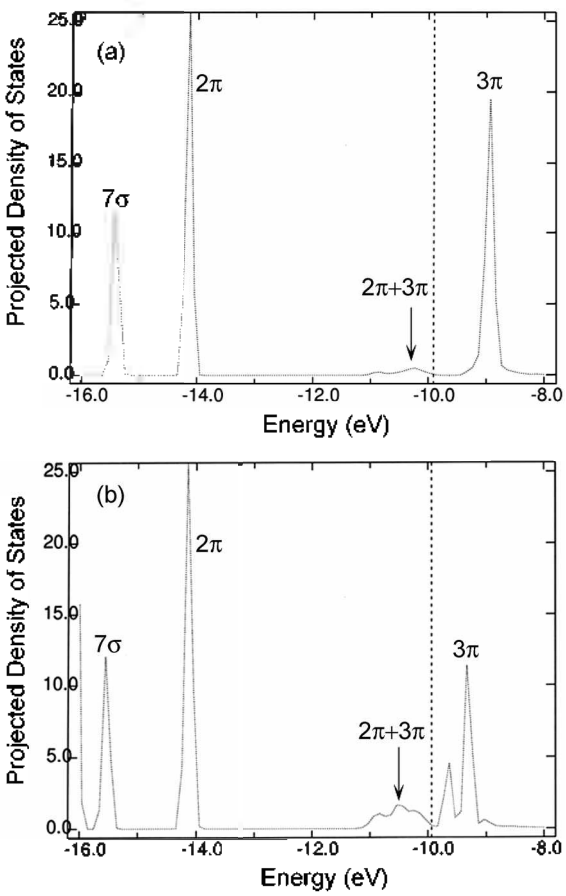

Figure 7. Projected density of states on N_2O for (a) on-top tilted adsorption mode and (b) flat adsorption mode.

significant. The 3π orbitals become split closer to the d band and they also mix together to give a fairly broad range of enhanced molecular peaks immediately below the Fermi level (in fact, the distortion of the molecule disables a strict classification between σ and π interactions), thus indicating a stronger interaction of the π system with the surface. This contribution is composed of molecular states of the 2π and 3π orbitals that are coupled with the surface $d_{\sigma,\pi}$ states. The 3π-related bonding features present in just below the Fermi level are a clear indication of the substrate back-donation into the molecular 3π orbitals. As the 3π-related orbital is strongly antibonding between central N and O atoms, its substantial population leads to a distinct weakening of the N-O bond which nicely prepares for N-O bond breaking.

Recent DFT calculations by Kokalj *et al.* have shown that the most stable adsorption mode at high coverage is the on-top tilted adsorption by the terminal nitrogen atom.[23,32,33] On the basis of the experimentally observed inclined desorption of product N2 in the thermal decomposition of N_2O adsorbed on Pd(110) surface, the flat form of N_2O lying in the [001] direction is preferred as the precursor for N_2O dissociation as it may result in the inclined N_2 desorption.[19-22] This form of N_2O is bent with its O atom pointing to the surface and the oxygen atom is easily released to the surface. The substrate back-donation into the N_2O 3π orbitals induces the nitrous oxide to rearrange to a bent structure

prior to further decomposition. Consequently, the precursor state for N_2O decomposition can be achieved by the transformation of a tilted adsorption into the flat adsorption mode of N_2O with a bending configuration (see Fig. 4c). The dissociation is expected to proceed *via* elongation of the N-O bond in the **[001]** direction (*i.e.*, the direction of N_2 desorption after the N-O bond is broken).

Conclusion

In order to explore the mechanism of N_2O dissociation in the terminally N-bound N_2O adsorption in a tilted form on Pd(110), we applied EHMO calculations to the model complex of Pd_{18}-N_2O. An MO analysis of the NN-O bond scission was made in terms of interactions of N_2O 2π and 3π orbitals with Pd d_π orbitals. It was shown that the metal centers primarily interact with the LUMO 3π orbitals of the N_2O to form two metal-N_2O π bonding MOs, leading to a significant charge transfer from the metal to the N_2O 3π. In addition, a pseudo-σ interaction occurs between the metal z^2 and the in-plane N_2O 3π.

The electron transfer due to the orbital overlap in the tilted geometry also forces the nitrous oxide to rearrange to a bent structure, which is a prerequisite for the N_2-O dissociation. The bent geometry of this N_2O precursor may play a crucial role in the overall reaction mechanism. The σ and π interactions of a metal center with the 3π of a bent N_2O lead to a further electron delocalization from the filled 3d orbitals on the metal into the empty N_2O 3π. This back-donation results in a severe weakening of the N-O bond which would be favorable for its activation toward dissociation upon adsorption of N_2O. This can be explained in terms of the mixing of the lower-lying N_2O 2π into the bonding combinations 3π-d_π of the π back-bonds leading to a strongly antibonding N-O character.

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