



ELSEVIER

Journal of Molecular Catalysis A: Chemical 119 (1997) 245–251

JOURNAL OF
MOLECULAR
CATALYSIS
A: CHEMICAL

Structure and vibrations of adsorption complexes $\text{NH}_3/\text{Ru}(001)$: Density functional model cluster studies

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Received 18 July 1996; accepted 25 October 1996

Abstract

The bonding and the vibrations of isolated NH_3 molecules adsorbed in the on-top and the three-fold hollow positions of a $\text{Ru}(001)$ surface have been studied with the help of a density functional model cluster method. The calculated vibrational frequencies and adsorption energies have been compared to experimental data for the stronger bound α_1 state and for the weaker bound α_2 state of NH_3 on $\text{Ru}(001)$. The density functional results support the assignment of the α_2 state to surface complexes with on-top located adsorbates. The calculated adsorption energy is smaller for NH_3 in the three-fold hollow than in the on-top sites. This finding is at variance with a conceivable assignment of the α_1 state to NH_3 in hcp three-fold hollow sites of $\text{Ru}(001)$.

Keywords: Ammonia; Ruthenium; Vibrations; Adsorption

1. Introduction

The interaction of gas-phase molecules with transition metals is essential for a variety of chemical processes like corrosion, air pollution abatement and catalytic synthesis of chemicals. Among these processes, those with molecules and radicals containing nitrogen, the main component of the earth's atmosphere, play a crucial role in many industrial catalytic reactions. For instance, the synthesis of ammonia from nitrogen and hydrogen on iron catalysts, known as

the Haber–Bosch process, has been widely used since the beginning of the century [1]. There has been a continuous interest in ammonia synthesis on other transition metal surfaces. A great deal of work has been carried out in order to replace iron as a catalyst for the ammonia production by its second-row analogue ruthenium [2].

The interaction of NH_3 with single-crystal $\text{Ru}(001)$ surfaces has been the subject of several experimental studies. The main results of these investigations may be summarized as follows [3–6]. Two chemisorption states α_1 and α_2 , the first one stronger, the second one weaker bound, were found at low temperatures with the thermal desorption observed between 150 and 350 K [3]. Both states are characterized by rather similar vibrational frequencies with one significant difference: the low-frequency feature at

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about 350 cm^{-1} , attributed to the surface-ammonia stretch [4–6], has been recorded for the α_2 state, but has not been observed in the case where only α_1 species are present at the surface. The ammonia molecule is bound to the ruthenium surface via the electron lone pair of the nitrogen atom with the hydrogen atoms pointing away from the surface. The three-fold axis of NH_3 is proposed to be normal to the surface based on HREELS experiments [4,5], but at variance with results of electron-stimulated desorbed ions angular distribution (ESDIAD) measurements suggesting that the three-fold axis of NH_3 in the α_2 state can to some extent be inclined toward the surface [3]. The sites of NH_3 adsorption on Ru(001) are still under discussion. On-top and three-fold hollow geometries of the adsorption complexes, or even both of them depending on coverage, were proposed [3–6] mainly based on the similarity of the observed vibrational frequencies with those measured for amino complexes of known structures.

It is often held that structural information about surface complexes can be successfully provided by vibrational spectroscopy methods drawing on analogies with structurally well characterized coordination or clusters compounds [7]. However, the vibrational data for many adsorption molecular complexes do not fit the familiar frequencies of the inorganic analogues well enough to unequivocally assign the spectral peaks to specific surface structures. Also, the direct transfer of structural features from molecular complexes to surface species has to be invoked with great care, in particular at higher coverages. Indeed, for many adsorption complexes the general reliability of structural assignments based on vibrational spectroscopy has been questioned (see e.g., Refs. [8–13]). It is usually difficult to employ other, more direct and reliable experimental methods to determine the structure and the site of molecular adsorption complexes. On the other hand, modern computational methods of quantum chemistry, especially those based on the density

functional (DF) approach, are known to accurately reproduce observed vibrational frequencies of transition metal compounds and adsorption systems [14,15]. Thus, by comparing vibrational parameters calculated with cluster models of various occupied adsorption sites to the corresponding measured data, one is often able to derive information on the structure of adsorption complexes, at least of those formed in a low-coverage regime.

Our previous model cluster studies of nitrogen-containing adsorbates on transition-metal surfaces [16–19] based on the linear combination of Gaussian-type orbitals density functional (LCGTO-DF) method demonstrated the high efficiency of this theoretical approach for assigning observed vibrational bands of low-coverage adsorption complexes to particular surface structures. In [16] we were able to show for the first time that the rather low vibrational frequency of about 1150 cm^{-1} , observed for NO adsorbed on Ag(111) surface, can be ascribed to surface moieties where the adsorbate molecule is bound to the substrate in a nonclassical fashion, via the oxygen atom. Similarly, we concluded [17] that the unusually oriented ‘oxygen-down’ ON species on Ru(001) surface are manifested by the N–O stretch at 1130 cm^{-1} and by a characteristic photoelectron spectroscopy shift of the NO 4σ level. Also, vibrational features of other NO/Ru(001) complexes [17] as well as vibrational spectra of the NO/Ni(111) adsorption system [18] have been successfully described with the LCGTO-DF calculations. Recently we were able to prove with the help of DF calculations [19] that the vibrational mode observed for the NH/Ru(001) system at about 1350 cm^{-1} is not related to the adsorbed NH species at all. This mode had been assigned to the bending mode of adsorbed NH [6,20,21] and had been employed in ‘fingerprint’ fashion.

The goal of the present article is to examine for the first time within the framework of an accurate DF quantum chemical cluster method which of the two conceivable structures of molecular NH_3 adsorbed on a clean Ru(001)

surface, on-top or hcp threefold hollow, is more consistent with temperature programmed desorption data and with vibrational spectra of the $\text{NH}_3/\text{Ru}(001)$ system.

2. Computational details

A detailed description of the LCGTO-DF cluster method used here has been given elsewhere [14,22,23]. Initially, all-electron nonrelativistic calculations were performed within the local density approximation to the exchange-correlation energy functional suggested by Vosko, Wilk and Nusair (VWN) [24]. Then, once self-consistency was obtained, density gradient corrections to the exchange [25] and to the correlation energy [26,27] (BLYP functional) were computed using the VWN charge density to achieve an improved description of the energetics. This procedure to account for generalized-gradient contributions to the exchange-correlation functional is quite economic and has been found to yield results of adequate accuracy [19,28,29].

For ruthenium, a rather large orbital basis set (17s 11p 8d) [30,31] was augmented to (18s 13p 8d) and contracted in a generalized fashion to (8s 6p 4d) [17] utilizing DF atomic eigenvectors. Orbital basis sets of the type (9s 5p 1d) \rightarrow (5s 4p 1d) [32,33] and (6s 1p) \rightarrow (3s 1p) [32] were used for nitrogen and hydrogen, respectively. The two auxiliary basis sets employed in the LCGTO-DF method to represent the electron charge density and the exchange-correlation potential were constructed from the orbital exponents in a standard fashion [14]. The fractional occupation numbers technique [14] with a level broadening of 0.3 eV was utilized. In this procedure the broadened one-electron spin-up and spin-down states are filled up to the Fermi energy which thus is, together with the resulting spin-polarization of the cluster, determined in a self-consistent way.

The basic cluster models considered in the present work are displayed in Fig. 1. The sub-

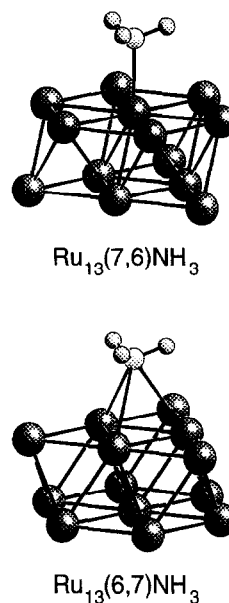


Fig. 1. Cluster models $\text{Ru}_{13}(m_1, m_2)\text{NH}_3$ (point group C_{3v}) for NH_3 species adsorbed on a Ru(001) surface (drawn with the help of program SCHAKAL [41]): (a) model for on-top adsorption, (b) model for three-fold hollow (or μ_3) adsorption. The values m_1 and m_2 ($m_1 + m_2 = 13$) specify the numbers of substrate atoms in the first and second layers of the Ru_{13} moiety. All other cluster models considered are subsystems of the models shown here.

strate part of the clusters was assumed to be unrelaxed and the positions of the metal atoms were determined by the nearest-neighbor distance of hcp bulk ruthenium, 2.70 Å. The N atom of the adsorbate was kept located either in the hcp three-fold hollow site (μ_3 position above the center of a Ru_3 triangle in the top layer of the clusters) or in the on-top site (above a Ru atom in the 'upper' layer of the clusters). The Ru–N distance and all other degrees of freedom of the NH_3 adsorbate were optimized subject to C_{3v} symmetry constraints. Thus, the present cluster models are not suited to address the issue of a possible tilting of the three-fold axes of ammonia relative to the surface normal [3]. At the VWN level, an automatic geometry optimization procedure based on analytical energy gradients was employed.

Harmonic vibrational frequencies have been obtained by diagonalizing the mass-weighted force constant matrix which was calculated from finite differences of VWN total energy gradi-

ents. BLYP and VWN adsorption energies have been computed as differences between the sum of the total energy values determined for the adsorbate (at VWN equilibrium geometry) and the bare substrate cluster (in the fixed bulk-terminated geometry) and the total energy of the adsorption cluster (at VWN geometry). No correction has been applied to eliminate the small basis set superposition error.

3. Results and discussion

Geometric parameters, vibrational frequencies and adsorption energies calculated for various cluster models $\text{Ru}_n(m_1, m_2)\text{NH}_3$ are displayed in Table 1. They are compared to the corresponding available experimental data for $\text{NH}_3/\text{Ru}(001)$ as well as for the observables of free NH_3 molecules. Results obtained for clusters of increasing size representing the same surface sites with adsorbed NH_3 , three-fold hollow or on-top, are listed to demonstrate the rather limited cluster dependence. The systems under consideration exhibit a weak adsorption interaction with flat adsorbate–substrate potential energy curves. Thus, it is not surprising that the largest cluster-size effect has been found for the Ru–N distance, up to 0.2 Å, and for the Ru– NH_3 vibrational frequency, up to 100 cm^{-1} . Adsorption energies computed in the cluster approach are known to be significantly affected by alterations of the size and shape of cluster models (e.g., Ref. [34]). However, it is worth mentioning that the adsorption energy intervals calculated for NH_3 in the two different surface sites do not overlap. In the following we shall only discuss the most accurate data obtained for the largest cluster models $\text{Ru}_{13}(6, 7)\text{NH}_3$ and $\text{Ru}_{13}(7, 6)\text{NH}_3$.

Adsorption-induced alteration of the adsorbate geometry may be taken to reflect the strength of the binding to the substrate. As seen from Table 1, such changes are calculated to be rather small, in general agreement with the observed weak interaction of NH_3 with the

Ru(001) surface [3–6]: upon adsorption the N–H bonds are elongated by less than 0.01 Å and the angles H–N–H are concomitantly increased by $1\text{--}2^\circ$. The metal–nitrogen distance computed for the on-top cluster $\text{Ru}_{13}(7, 6)\text{NH}_3$, 2.156 Å, is somewhat longer than the sum of the metallic radius of Ru and of the covalent atomic radius of N, 2.025 Å, but it fits the metal–ligand bond lengths of 2.15 Å measured in ruthenium complexes with terminal amino ligands [35]. No complexes or cluster compounds are known with the triple-bridge bonded $\mu_3\text{-NH}_3$ moieties to compare their geometry with that of the three-fold hollow cluster model $\text{Ru}_{13}(6, 7)\text{NH}_3$.

A comparison of the adsorption energies calculated for the two $\text{Ru}_{13}\text{NH}_3$ clusters shows that the bonding at the on-top site is stronger than at the three-fold hollow site. The energy difference of 0.5 eV at the VWN level is reduced to about 0.3 eV when density gradient corrections are included at the BLYP level. These differences seem to be meaningful even if one considers possible cluster artifacts. Moreover, the BLYP adsorption energy has been computed repulsive by about -0.2 eV for the three-fold hollow model $\text{Ru}_{13}(6, 7)\text{NH}_3$ whereas a slight bonding of 0.1 eV is calculated for the on-top model $\text{Ru}_{13}(7, 6)\text{NH}_3$. This result is similar to the findings of Hartree–Fock model cluster studies of NH_3 on Cu(111) according to which three-fold hollow adsorption is repulsive [36]; this site has been ruled out in favor of on-top adsorption on copper and other metal surfaces [36]. The present study, too, supports the hypothesis [36] that for most metal surfaces NH_3 binds directly above a substrate atom. Interestingly, the experimentally estimated adsorption energy of NH_3 on Ru(001) 0.92 eV [3] is only slightly below the VWN value for the on-top model of 1.14 eV, but the BLYP energy value of 0.10 eV deviates more significantly. One can expect a small increase of the binding energy if other forms of density gradient corrections to the exchange–correlation potentials are employed [37]. Indeed, preliminary results of DF calculations [38] obtained with the ex-

change-correlation functional of Becke [25] and Perdew [39] (BP) show an increase of the adsorption energies for both on-top and three-fold hollow models compared to the corresponding BLYP values in line with findings for ligand-metal binding energies in a series of metal complexes [40]. At the BP level the three-fold hollow site becomes slightly bound but the energetic preference for the on-top site adsorption by about 0.3 eV computed at the BLYP level remains unchanged.

Frequencies have been calculated only for those vibrational modes which are consistent with the C_{3v} symmetry constraints of the cluster models. These modes comprise the vibration of the whole ammonia molecule against the surface $\nu(\text{Ru-NH}_3)$ (frustrated translation), the symmetric N–H stretch $\nu_s(\text{N-H})$ and the symmetric H–N–H bending $\delta_s(\text{H-N-H})$ (umbrella mode). The corresponding frequencies are presented in Table 1 along with the experimental values. First of all, it should be pointed out that the adsorbate-substrate frequency for the three-fold hollow model, 152 cm^{-1} , is significantly lower than the frequency value of 373 cm^{-1} computed for the on-top model. The former vibration is in a low-frequency region which is hardly accessible experimentally, in agreement with the assumption made in [5]. As mentioned in the introduction, the Ru–NH₃ frequency values represent the most characteristic vibrational spectroscopy difference between the α_1 and α_2 adsorption states: the adsorbate–substrate stretch is observed at about 350 cm^{-1} in the spectra of α_2 moieties (in good agreement with the calculated value for the on-top cluster), but is not found if only α_1 species are present. The other vibrations observed for the α_1 and α_2 states have rather similar frequencies.

Therefore, based exclusively on a comparison of measured and computed frequencies one would be inclined to confirm the tentative assignment [5] of α_1 and α_2 adsorption states to three-fold hollow and on-top complexes of NH₃ on Ru(001), respectively. However, this interpretation is at variance with the observation

[3–6] that the state α_1 is stronger bound (it correlates with higher desorption temperatures) than the α_2 one, because the order of calculated adsorption energies for the three-fold hollow and on-top complexes is the just opposite (Table 1): isolated on-top species are found to be more strongly bound than threefold bridged ones. Of course, one may question how reliable the small calculated energy difference of 0.3 eV is for these two sites. Certainly, much more detailed investigations than the present ones are required to be confident about the ammonia population of the different adsorption sites of Ru(001). Issues to be addressed in further studies are, for example, surface relaxation, lateral adsorbate–adsorbate interaction, energy barriers and local minima for NH₃ at larger distances from the substrate and relativistic effects. Furthermore, alternative adsorption places, not only the bridging μ_2 - or symmetric fcc μ_3 -position, but also asymmetric states of adsorbed NH₃ should be studied. Nevertheless, it seems reasonable to assume that the calculated energy difference under consideration adequately reproduces the experimental situation. This statement is indirectly supported by the finding that calculated frequencies of the NH₃ modes are changed more (larger perturbation of NH₃ by the interaction with Ru(001) surface) for the on-top cluster than for three-fold hollow one. In particular, the bending frequency of ammonia, used previously [5] as an indicator of the adsorption bond strength, is increased upon adsorption by about 90 cm^{-1} for on-top moieties, while the corresponding enhancement in a three-fold hollow case is only 40 cm^{-1} . This discussion shows that the present cluster model results are consistent with the assignment of the state α_2 to the on-top NH₃ species. On the other hand, the α_1 state hardly seems to be related to NH₃ in the hcp three-fold hollow position.

Finally, a few comments on the electronic structure of the adsorption complexes under study and on the bonding mechanism between NH₃ and Ru(001) are in order.

It has been shown that the interaction of NH₃

Table 1

Geometries, vibrational frequencies and adsorption energies calculated for Ru_nNH_3 model clusters^a and measured for $\text{NH}_3/\text{Ru}(001)$ complexes [5]: bond distances $r(\text{Ru}-\text{N})$ and $r(\text{N}-\text{H})$ between N and the nearest Ru atoms and N and H atoms, respectively, angle $\alpha(\text{H}-\text{N}-\text{H})$ in NH_3 , symmetric vibrational frequencies $\nu_s(\text{N}-\text{H})$, $\nu(\text{Ru}-\text{NH}_3)$, and $\delta_s(\text{H}-\text{N}-\text{H})$, and adsorption energy E_b . Calculated and experimental [42] data for free NH_3 molecules are also presented

System	$r(\text{Ru}-\text{N})$ (Å)	$r(\text{N}-\text{H})$ (Å)	$\alpha(\text{H}-\text{N}-\text{H})$ (°)	$\nu(\text{Ru}-\text{NH}_3)$ (cm^{-1})	$\nu_s(\text{N}-\text{H})$ (cm^{-1})	$\delta_s(\text{H}-\text{N}-\text{H})$ (cm^{-1})	E_b^{VWN} (eV)	E_b^{BLYP} (eV)
Three-fold hollow site								
$\text{Ru}_3(3, 0)\text{NH}_3$	2.683	1.033	109	107	3232	947	0.29	-0.49
$\text{Ru}_4(3, 1)\text{NH}_3$	2.912	1.027	109	127	3338	943	0.41	-0.13
$\text{Ru}_{13}(6, 7)\text{NH}_3$	2.736	1.030	109	152	3298	1001	0.64	-0.19
On-top site								
RuNH_3	2.035	1.032	109	434	3265	1054	1.64	1.07
$\text{Ru}_4(1, 3)\text{NH}_3$	2.170	1.029	108	340	3347	1080	1.45	0.76
$\text{Ru}_7(7, 0)\text{NH}_3$	2.042	1.033	111	453	3234	1084	1.30	0.06
$\text{Ru}_{13}(7, 6)\text{NH}_3$	2.156	1.029	110	373	3287	1050	1.14	0.10
Experiment								
$\alpha_1 \text{NH}_3/\text{Ru}(001)$					3170	1110		
$(\alpha_1 + \alpha_2) \text{NH}_3/\text{Ru}(001)$				350	3180	1100		
Free NH_3								
NH_3 calc.		1.023	108		3398	961		
NH_3 exp.		1.016	107		3337	950		

^a Geometries calculated at the VWN level and subsequently utilized to compute the adsorption energy E_b at the BLYP level; harmonic vibrational frequencies computed with the help of VWN analytic energy gradients, assuming an infinitely large mass for the substrate subunit.

with a copper substrate arises mainly from the penetration of the negative end of the adsorbate dipole into the charge cloud of the metal (see Ref. [36] and references therein). There is a favorable electrostatic interaction between dipole moments of the adsorbate and of the polarized metal. π back donation is totally absent and σ donation to the metal is small. This model of the binding rationalizes the preference of NH_3 for occupying on-top positions as being due to the stabilization of the lone pair of ammonia by the positively charged nucleus of the metal atom. The present DF results are consistent with a limited σ charge transfer to the substrate: it amounts to only 0.13 and 0.08 au for $\text{Ru}_{13}(7, 6)\text{NH}_3$ and $\text{Ru}_{13}(6, 7)\text{NH}_3$, respectively, if estimated by the derivative of the dipole moment with respect to the adsorbate height above the surface, $\partial\mu/\partial z$. The adsorption-induced shift of the Fermi level of Ru_{13} (at -4.11 eV) by 0.16 and 0.19 eV upwards is in line with a small charge rearrangement. The Mulliken charges on

NH_3 are computed to 0.28 and 0.20 au for these two adsorption clusters, but this method for assigning charges is known to often be unreliable as a criterion of the charge redistribution, in particular in calculations where, as done here, large basis sets are used.

According to photoelectron spectroscopy measurements for NH_3 on various transition metal surfaces the splitting between the ammonia-derived $3a_1$ (lone pair) and $1e$ levels of about 4.1 eV is significantly smaller than in free NH_3 molecules [3]. The calculated splitting of the corresponding Kohn–Sham one-electron energy levels is considerably reduced in the adsorption models, 3.3 and 3.7 eV for $\text{Ru}_{13}(7, 6)\text{NH}_3$ and $\text{Ru}_{13}(6, 7)\text{NH}_3$, respectively, as compared to free NH_3 (5.4 eV); thus, the calculations qualitatively describe the observations. However, in view of the fact that only very limited charge rearrangement has been calculated, a rationalization [3] of the reduced level splitting based exclusively on a charge transfer

mechanism is not convincing. An electrostatic stabilization of the lone pair of NH_3 by the Ru cores [36] should be at least as important.

In summary, the DF analysis of the bonding and vibrations of NH_3 molecules adsorbed on Ru(001) suggests an assignment of the observed weaker bound adsorption state α_2 to the on-top species. A conceivable interpretation of the stronger bound α_1 state as a manifestation of the NH_3 moieties located in the three-fold hollow position is not supported by the present model cluster DF results. Currently, new experimental and theoretical [38] studies are under way which attempt to rationalize structure and properties of various $\text{NH}_3/\text{Ru}(001)$ surface complexes in more detail than made in this investigation.

Acknowledgements

The authors are grateful to the Deutsche Forschungsgemeinschaft (SFB 338), to the Bayerischer Forschungsverbund Katalyse (FOR-KAT) and to the Fonds der Chemischen Industrie for financial support of this study.

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