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# N<sub>2</sub> Abstraction during the Chemisorption of N<sub>2</sub>O on Cs Films<sup>†</sup>

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The interaction of N<sub>2</sub>O molecules with Cs atoms deposited on Ru(0001) has been investigated by the means of the molecular beam scattering technique (MBS) and the ultraviolet photoelectron spectroscopy (UPS) as well as thermal desorption spectroscopy (TDS). The dissociative chemisorption of N<sub>2</sub>O molecules is accompanied by an intense N<sub>2</sub> emission. The emission yield strongly depends on the Cs load predeposited on the surface. For a thick Cs film the reaction kinetics is governed by the diffusion of Cs atoms through the oxidized layer. For Cs coverage lower than one monolayer two kinetic components can be distinguished. The initial component is related to the formation of the Cs<sub>ad</sub>–O<sub>ad</sub> bond, and the later one mirrors the formation of CsO<sub>x</sub> oxide-like surface aggregates. Both behave independently of the work-function course, which implies a minor role of the harpooning-mediated abstraction channel. The initial intensity as well as the total abstraction yield reach maximum values for a low Cs coverage ( $\Theta < 0.6$  ML), where Cs adatoms become accessible for N<sub>2</sub>O molecules via the adsorption on the Ru substrate. The lateral delocalization of Cs-6s electrons as accompanying the formation of densely packed Cs layers ( $\Theta > 0.6$  ML) blocks the substrate-mediated reaction channel and consequently is responsible for the observed lowering of the reaction probability per one adatom.

## Introduction

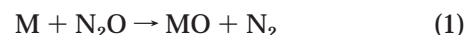
The emission of charged particles observed during the interaction of molecules with metallic surfaces has been recognized to be a convenient tool to investigate the dynamics of the chemisorptive event (e.g. refs 1–3 and references therein). In particular slow electrons emitted during the chemisorption of electronegative molecules reveal nonadiabatic steps of the chemisorptive cascade.<sup>2,3</sup> It has also been shown that the negatively charged ions accompanying the dissociation of chemisorbing oxygen molecules signalize the molecular steering at surfaces which have been strongly structured by deposited atoms.<sup>4</sup> The emission of neutral fragments resulting from the chemisorption-conditioned decomposition of impinging molecules has been investigated not so intensively as this was the case for reactions between corresponding gas-phase species.<sup>5–7</sup> Consequently, the role of the surface on the elemental reaction steps still remains a subject for further investigations.<sup>8,9</sup> The declared goal of these efforts is to apply the emission of neutral products as an additional tool for the study of the dynamics of the chemisorptive event.

This work focuses on the emission of N<sub>2</sub> molecules as observed during the dissociative chemisorption of N<sub>2</sub>O molecules on Cs layers deposited on Ru(0001). This particular choice is motivated by several aspects: Nitrous

oxide is known as an environment pollutant which contributes to the destruction of the stratospheric ozone. This process might be drastically slowed by applying high-duty catalysts for the decomposition of nitrous oxides. Currently, alkali atoms are considered as ingredients which should raise the decomposition yield high above the level reached by using traditional transition-metal supported catalysts.<sup>10,11</sup>

A second motivating aspect is the fact that a detailed knowledge of the electronic and geometric structure of Cs layers deposited on Ru(0001) has been achieved during the past decade. This fact allows one to relate some elementary steps of the postulated reaction mechanism more precisely to the specific properties of the Cs/Ru target.<sup>12–14</sup> Moreover, in contrast to the chemisorption of diatomic molecules (O<sub>2</sub> or Cl<sub>2</sub>), in the case of N<sub>2</sub>O the possible dissociation products, N<sub>2</sub> and O, are easily detectable and distinguishable from the primary molecules by conventional mass spectrometry.

The gas-phase reactions of nitrous oxides with alkali metals (M) are highly exothermic and proceed according to the scheme



with rate constants higher than  $10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>5,7</sup> The abstracted N<sub>2</sub> molecules reach hyperthermal kinetic energies. The same reaction conducted at alkali metal surfaces proceeds with a much higher probability (roughly estimated value of the initial sticking coefficient is about 0.5) and is accompanied by an intense emission of low-energy electrons.<sup>15</sup>

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It has been demonstrated that the N<sub>2</sub> emission as accompanying the scattering of N<sub>2</sub>O molecules at a homogeneous Cs layer depends on the orientation of the NN–O bond in respect to the surface normal.<sup>16,17</sup> A significantly higher N<sub>2</sub> emission was observed when the impinging N<sub>2</sub>O molecules were directed with the O end toward the surface.

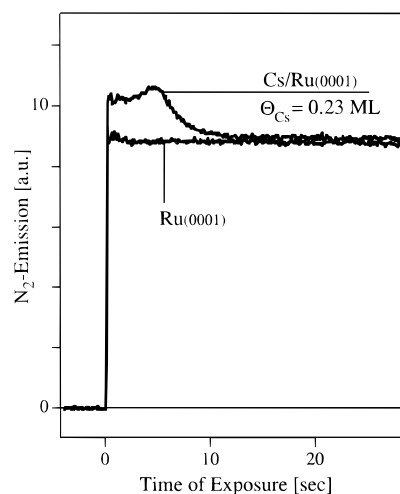
In the present work it will be shown how the electronic structure of the metal surface, strongly varied by adsorbed Cs atoms, influences the N<sub>2</sub> abstraction. In contrast to the N<sub>2</sub>O-induced exoemission which reflects mainly the gas-phase harpooning process,<sup>15</sup> the N<sub>2</sub> emission reveals the event of Cs<sub>ad</sub>–O bond formation as the decisive step in the chemisorptive path.

### Experimental Section

The experiments were performed in an ultrahigh vacuum chamber at a base pressure lower than 10<sup>−10</sup> mbar. The Ru crystal has been cleaned by applying sputtering and annealing cycles according to the procedure described by Madey et al.<sup>18</sup> The achieved cleanliness of the Ru surface was controlled by applying the ultraviolet photoelectron spectroscopy (UPS). The chamber was connected to a molecular beam apparatus which provided a nearly monoenergetic molecular flux by supersonic gas expansion through a nozzle with a diameter lower than 10 μm at a stagnation pressure up to 12 bar. Under such conditions the molecular flux reached a level of 10<sup>13</sup> molecule cm<sup>2</sup> s<sup>−1</sup> with the beam cross section covering more than 90% of the sample surface. The N<sub>2</sub>O beam was scattered under 45° at the surface, and the flux of escaping N<sub>2</sub> molecules was monitored by a mass spectrometer mounted along the surface normal. All experiments were performed with thermal molecules, i.e., with a nozzle kept at room temperature. The molecular flux has been determined by measuring the oxygen load reached by exposing the clean Ru surface to the N<sub>2</sub>O beam and comparing this value with the one obtained by performing the oxygen deposition once more by flooding the chamber with N<sub>2</sub>O up to several pressures in the region of 10<sup>−8</sup>–10<sup>−7</sup> mbar. The resulting oxygen coverage has been determined by taking the O<sub>2</sub> thermal desorption spectra and relating the integral of the TD traces to the spectrum which represents the saturated layer of chemisorbed oxygen (1 ML (monolayer) = 1.58 × 10<sup>15</sup> cm<sup>−2</sup>).<sup>19</sup> Cs films have been deposited by an evaporation from the SAES getter source onto the Ru sample kept at 250 K. The resulting Cs load has been determined by taking thermal desorption spectra of the deposited Cs atoms and comparing the integral intensity to the one obtained for a saturated Cs monolayer (1 ML = 5.3 × 10<sup>14</sup> atom/cm<sup>2</sup>). Cs submonolayers were prepared via thermal desorption of a predeposited thick Cs film up to a certain sample temperature *T*<sub>cov</sub> which defines the remaining Cs coverage, Θ<sub>Cs</sub>. The relationship between Θ<sub>Cs</sub> and *T*<sub>cov</sub> has previously been precisely determined by combining the TDS, Auger, and LEED studies.<sup>13–15</sup>

### Results and Discussion

Figure 1 shows the N<sub>2</sub> signal as measured by the mass spectrometer during the exposure of the clean Ru surface and the Cs layer of 0.23 ML to a N<sub>2</sub>O beam of 4.8 × 10<sup>13</sup> molecules cm<sup>−2</sup> s<sup>−1</sup>. For the clean Ru surface the intense signal is caused by a very efficient dissociation of N<sub>2</sub>O molecules approaching the hot filament in the mass spectrometer. The response is only slightly affected by the progressing adsorption at the beginning of the exposure where the initial probability for dissociative sticking remains still measurable. The presence of Cs atoms covering the surface considerably raises the initial N<sub>2</sub>



**Figure 1.** N<sub>2</sub> signal from the mass spectrometer taken during exposing the clean and with Cs precovered Ru(0001) surface to the N<sub>2</sub>O beam, lower and upper curves, respectively. The sample temperature during Cs deposition as well as during the exposure to N<sub>2</sub>O was kept constant at 250 K.

signal. This drastic increase cannot be attributed to the higher reflectance of the Cs layers for scattered N<sub>2</sub>O molecules because of the known high exothermicity of the N<sub>2</sub>O + M reaction which implies a rather high sticking probability for impinging N<sub>2</sub>O molecules.<sup>5,6</sup> Thus, the comparison of the two traces clearly indicates the role of the deposited Cs atoms as efficient dissociation centers. Here, the difference of the two traces will be taken as a measure of the Cs-conditioned N<sub>2</sub> emission. The N<sub>2</sub> flux emitted can be roughly estimated when knowing the initial sticking coefficient and assuming that the dissociative N<sub>2</sub>O sticking is the dominating chemisorption channel. Recent N<sub>2</sub>O-beam scattering experiments revealed that the initial sticking probability only weakly depends on the Cs coverage. It ranges from 0.4 to 0.55.<sup>32</sup> Thus the initial N<sub>2</sub> flux reaches a value about 2.4 × 10<sup>13</sup> molecule cm<sup>−2</sup> s<sup>−1</sup>.

In the following the intensity and the kinetics of this emission will be related to the electronic structure of the Cs layers.

For Cs coverages beyond one monolayer the influence of the Ru substrate on the electronic structure of the topmost Cs layer appears to be negligible; i.e., the electronic properties of the topmost Cs layer remain independent of the film thickness. Figure 2 shows the N<sub>2</sub> emission observed during the exposure of three Cs layers (0.9, 2.4, and 6.2 ML) to the same N<sub>2</sub>O flux. The total yield for this emission increases with the Cs load deposited on the surface. Whereas the initial intensity varies only slightly, the kinetics of this emission changes drastically

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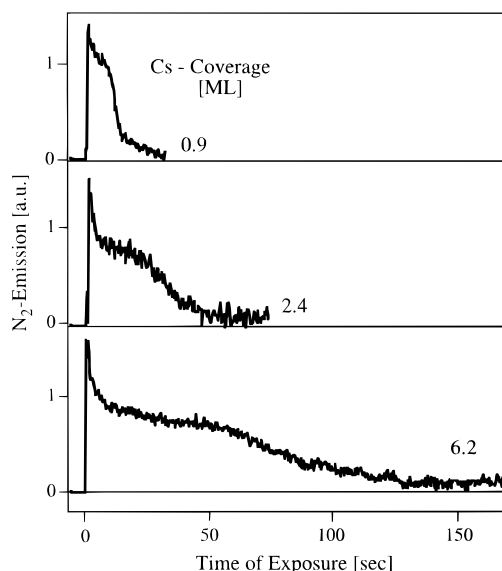
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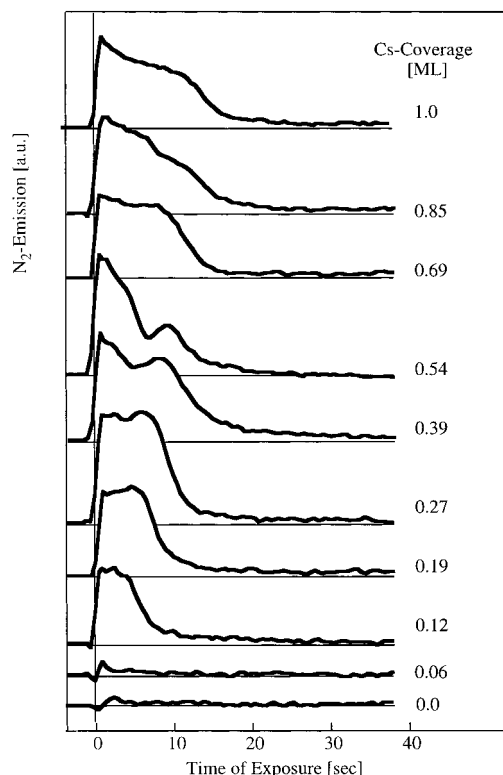


**Figure 2.** Kinetics of the N<sub>2</sub> emission as observed during the exposure of different thickness Cs layers to the same N<sub>2</sub>O flux of  $4.3 \times 10^{13}$  molecules cm<sup>-2</sup> s<sup>-2</sup>. The samples differed by the thickness of the deposited Cs layers as indicated in the figure.

with the thickness of the layer. The duration of this emission increases with the thickness of the Cs film. Considering the sample as a 2D target for impinging molecules, one might expect a kinetics which mirrors the Langmuir-like dissociative chemisorption of the N<sub>2</sub>O molecules, i.e., a continuously decaying N<sub>2</sub> emission. Evidently this is not the case. Rather a steplike evolution is observed; i.e., the short initial decay is followed by a long-time period with an almost constant emission intensity. Afterward the emission quickly disappears. This characteristic evolution can be qualitatively reconstructed when considering the emission as the result of two coupled processes, the surface-molecule electron transfer and the Cs diffusion. The incorporation of all possible chemisorption fragments (O, N<sub>2</sub>, NO, etc.) into the Cs film leads to the formation of an insulating layer. At a certain thickness this layer diminishes considerably the rate of the electron transfer to the impinging molecules and it substantially hinders the diffusion-conditioned Cs appearance at the top of the surface. This scenario is supported by a study of the electron emission observed during the oxidation of thick Cs layers.<sup>20</sup> The temperature dependence of this emission allowed us to determine the activation barrier for the Cs penetration through the growing oxide layer.

In contrast to thick layers, the electronic structure of the target, Cs/Ru(0001), changes dramatically when varying the density of Cs adatoms within the submonolayer region, i.e., for  $\Theta_{\text{Cs}} < 1$  ML.<sup>12–14</sup> The chemisorptive bond varies with increasing Cs coverage what is reflected mainly by the reduction of the work function from 5.3 to 1.7 eV.<sup>14,15</sup> The strong ionic Cs–Ru bond of a single adatom becomes weaker for higher coverages due to the lateral dipole–dipole interaction of adjacent atoms. For coverages higher than 0.6 ML the Cs → Ru electron transfer becomes incomplete and the Cs layer exhibits metallic properties.<sup>12–14</sup> We utilize here this behavior to show how the N<sub>2</sub> emission is affected by the electronic nature of the Cs–Ru bond.

Figure 3 shows N<sub>2</sub> kinetics recorded during the exposure of several submonolayers differing by the Cs coverage to the same N<sub>2</sub>O flux. As in the case of thick Cs films, the reaction kinetics surprises somewhat. The Cs submonolayers offer finite numbers of adsorption sites for chemi-

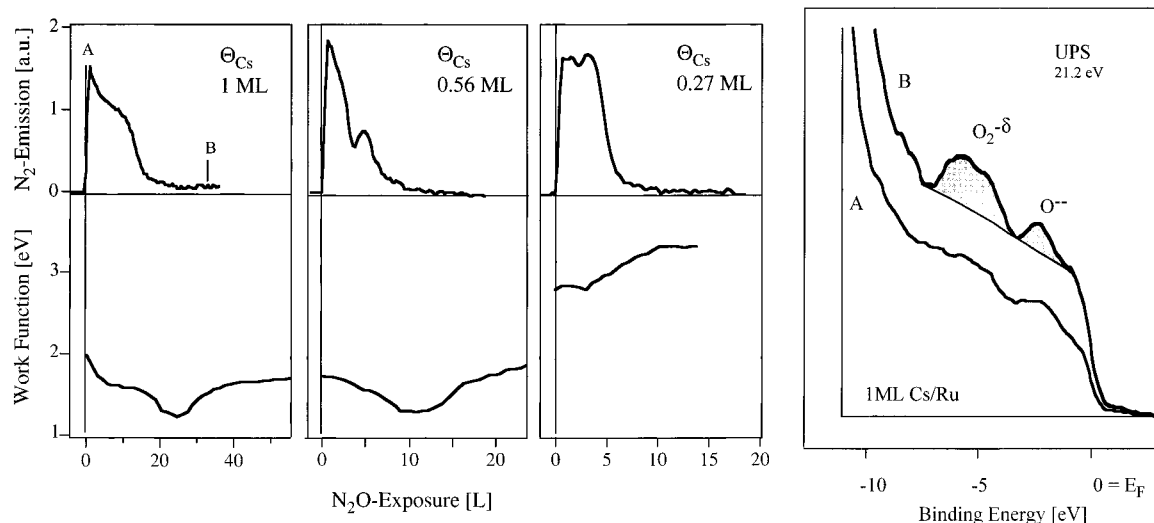


**Figure 3.** Kinetics of the N<sub>2</sub> emission from several Cs submonolayers as observed during exposing them to a constant N<sub>2</sub>O flux. The Cs coverage varied from 0 to 1 ML.

sorbing N<sub>2</sub>O molecules. The progressing chemisorption continuously reduces the number of available adsites, and consequently, the dissociation conditioned N<sub>2</sub> emission is expected to decay in the same manner. Instead, some of the kinetics exhibit a second, well-distinguishable maximum appearing in the late chemisorption stage. For samples covered by more than about 0.12 ML of Cs this maximum separates itself well from the initial emission. This separation time becomes longer with an increasing Cs coverage up to 0.7 ML where the sample is characterized by the minimum of the work function. For even higher coverages the buried second maximum can no longer be subtracted from other components. Both the most intense initial emission and the late maximum coincide with the so-called *ionic coverage range* where the Cs-6s electrons are localized at the adatom–substrate interface and consequently form strong dipoles. In this case the adatoms are separated from each other by many adsites on the Ru substrate.<sup>12,13</sup> For instance, for a sample covered by 0.7 ML of Cs the mean distance of adjacent adatoms does not exceed the value known as the lattice constant of a Cs crystal, i.e., it is lower than 5.38 Å.<sup>22</sup> In this coverage range, the two Cs neighbors are separated by at least one Ru adsite.

The kinetics can be qualitatively reconstructed when considering two electronic processes which can cause the dissociation of the sticking molecules. The very initial maximum intensity might be attributed to the situation when the impinging molecule hits the Cs adatom directly, which immediately leads to the formation of a Cs<sup>+</sup>–O<sup>−</sup> bond at the surface and to simultaneous N<sub>2</sub> emission into the gas phase. The second maximum can be attributed to the lateral electron transfer between Cs adatoms and the N<sub>2</sub>O molecules preadsorbed on Ru substrate. Both dissociative phenomena result from the short-distance electron transfer, initiated by overlapping wave functions of the reactants. Obviously, the probability that the N<sub>2</sub>O

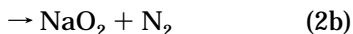
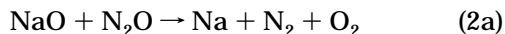




**Figure 4.** N<sub>2</sub> emission from three different Cs submonolayers in comparison to the corresponding evolution of the work function as induced by a progressing oxidation. The work function has been measured by following the onset of the UP (21.2 eV) spectra taken during the exposure to N<sub>2</sub>O with a time resolution of 6 s.

molecules occupying adsorption sites on the Ru substrate may reach the Cs adatoms via lateral migration is limited by its rather short residence time. But this restriction may be overcome by the usually high mobility of molecules in the precursor state.<sup>21</sup> Most likely the lateral electron-transfer conditioned N<sub>2</sub> abstraction follows the event of bond formation between the partly occupied Cs-6s orbital and the N<sub>2</sub>O or N<sub>2</sub>O<sup>δ</sup> species preadsorbed on the Ru substrate. In this picture, both the initial and the late N<sub>2</sub> emission represent two possible electron-transfer mediated channels for the formation of a Cs–O bond.

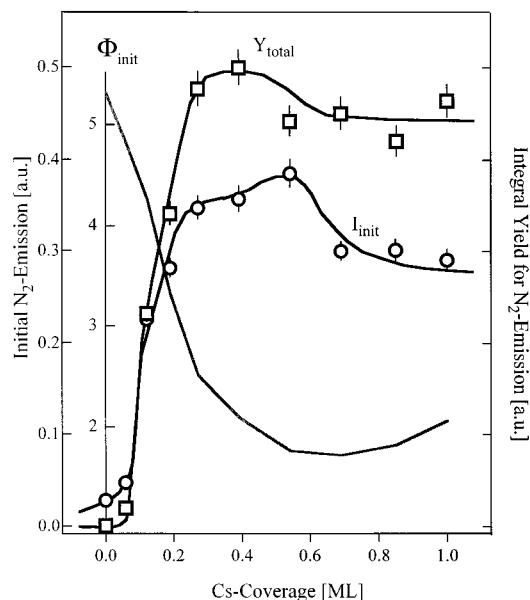
The fact that a second local maximum in the N<sub>2</sub> emission appears at late oxidation stages remains still intriguing (samples 0.2–0.6 ML). In fact, it reveals a kind of reactivation of the initial capacity of the sample for the dissociation of sticking molecules. A possible explanation is based on the decomposition of nitrous oxides as occurring during their interaction with alkali-metal oxides in the gas phase.<sup>23</sup> For instance, it has been demonstrated that the reaction of NaO with N<sub>2</sub>O has two exothermic product channels:



The common step is the N<sub>2</sub> abstraction which in the temperature range below 300 K proceeds several orders of magnitude slower than reaction 1. Path b represents the dominating reaction channel with an upper limit of the rate constant less than  $2 \times 10^{-15} \text{ cm}^3/(\text{molecules} \cdot \text{s})$ . Thus, it cannot be definitely excluded that the surface-modified version of this reaction path might be also responsible for the late maximum observed in the N<sub>2</sub> abstraction kinetics (Figure 3). Despite the rather low reaction rate in the gas phase, the surface path of this reaction might be quite efficient due to the high concentration of the reactants achievable in course of the chemisorption. This alternative is nicely supported by recent studies of the N<sub>2</sub>O interaction with the CaO(100) surface.<sup>24</sup> The calculations reveal the dissociation of nitrous oxide as taking place over the O<sup>2-</sup> sites when the approaching molecule sticks with the O end. The O–O<sup>2-</sup>  $\sigma$ -bond is formed as a kind of peroxy species created when the N<sub>2</sub>–O  $\pi$ -bond is broken and the N<sub>2</sub>–O  $\sigma$ -bond is getting weaker. A similar situation can occur when the charge

state of oxygen in the [Cs–O–Ru]<sub>ad</sub> aggregate tends to reach 2e. Indeed, this is the case for a low coverage of alkali metal atoms (<0.5 ML), where the coadsorbed oxygen is surrounded by M<sup>+</sup> but it is strongly bound directly to the Ru substrate as O<sup>2-</sup> ad species.<sup>25</sup> The maximum N<sub>2</sub> emission is observed within the same coverage range. At present both alternative explanations have to be considered as possible reaction channels. Further experimental work is needed to indicate the dominating channel.

An additional support for the postulated scheme for N<sub>2</sub> emission can be gained when the contribution of the long-range harpooning process as a possible step responsible for the intense N<sub>2</sub> emission could widely be excluded. It is well-known that the probability for harpooning exponentially depends on the difference between the Fermi level  $E_F$  of the sample (work function) and the affinity level of the chemisorbing molecule  $E_a$ ; i.e., this process becomes very efficient for low work function surfaces. Thus, the purpose of the next experiment was to answer the question whether the ability of emitting N<sub>2</sub> molecules is affected by the work function of the surface. The work function was measured by recording the low energy cut off in the UP (21.2 eV) spectra during the exposure of the surface to N<sub>2</sub>O. Figure 4a shows three examples differing by the Cs coverage which illustrate the expected correlation between the N<sub>2</sub> emission and the work function. The message of this figure is clear: Whereas the values of the initial work function differ by more than 1 eV ( $\Theta_{\text{Cs}} = 1$  and 0.27 ML), the corresponding emission remains unchanged. Moreover, the emission kinetics does not follow the evolution of the work function. In particular the oxidation-conditioned local minimum work function terminates the N<sub>2</sub> emission. Hence, the long-distance surface harpooning as the work function dependent process cannot be responsible for the observed N<sub>2</sub> abstraction. This finding indicates that the abstraction event rather results from the short-range Cs–N<sub>2</sub>O interaction. Figure 4b shows two valence band UP spectra of a Cs monolayer before and after exposing it to about 10 L N<sub>2</sub>O, spectra A and B, respectively. The spectrum of an oxidized layer exhibits three characteristic oxygen derived states at binding energies of 1.8, 4.7, and 5.4 eV. These spectral features are characteristic for the O-2p photoionization triplet which reveals the formation of surface oxides.<sup>31</sup> The



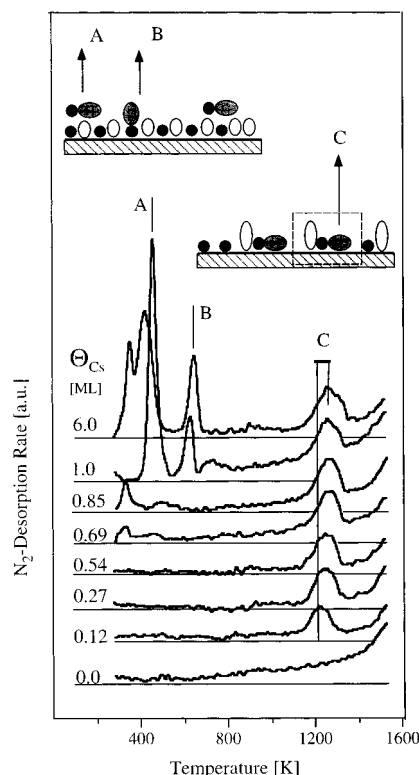
**Figure 5.** Integral yield for the  $N_2$  emission and the probability for the initial  $N_2$  emission versus Cs coverage, squares and circles, respectively. For comparison the work function versus Cs coverage is added (gray line).

intense  $N_2$  emission disappears before the intensities of the three features saturate; i.e., it reflects the initial formation of Cs–O bonds.

Figure 5 presents the intensity of the initial  $N_2$  emission,  $I_{init}$  (circles), and the integral emission yield,  $Y_{total}$  (squares), both versus the Cs coverage. The initial work function,  $\Phi_{init}$ , versus Cs coverage is added as the simplest macroscopic parameter characterizing the electronic properties of the sample. The emission yield (integral of the kinetics traces shown in Figure 3) does not depend linearly upon the Cs content deposited at the surface. The  $Y_{total}(\Theta_{Cs})$  function can roughly be approximated by a straight line only within the coverage range between 0.05 and 0.2 ML, i.e., in the region where the Cs atoms are separated from each other by several Ru adsites and exhibit large dipole moments.  $Y_{total}(\Theta_{Cs})$  reaches a maximum for Cs coverages around 0.3 ML and becomes significantly reduced by a further increasing Cs coverage where the sample exhibits metallic features. The low-coverage samples ( $\Theta_{Cs} < 0.3$  ML) exhibit a surprisingly high  $N_2$  emission in comparison with the one observed for metallic layers ( $\Theta_{Cs} > 0.6$  ML). This effect becomes more pronounced when considering the contribution of a single Cs atom to the  $N_2$  abstraction ( $Y_{total}/\Theta_{Cs}$ ). For instance, when the samples are compared, 0.2 and 1 ML, representing the ionic and the metallic regions, respectively, both show nearly the same emission yield but differ by the factor of 5 in the number of Cs atoms. These comparisons imply that the lateral delocalization of Cs 6s electrons associated with the formation of the metallic Cs layer ( $\Theta_{Cs} > 0.6$  ML) reduces the ability of a single adatom to dissociate the sticking  $N_2O$  molecules.

Thus, Figure 5 shows clearly that neither  $Y_{total}$  nor  $I_{init}$  exhibits any correlation with the course of the  $\Phi(\Theta_{Cs})$  function. This finding implies that the  $N_2$  emission is governed rather by the short-range  $N_2O \leftrightarrow Cs_{ad}$  interaction and the long-distance harpooning, as the main initiator of the electron emission,<sup>15</sup> represents only a minority path in the chemisorption.

As shown in Figure 4a, the oxidation of cesiated surfaces is not completed with the decay of the  $N_2$  emission. The subsequently increasing work function signals that the



**Figure 6.** Thermally induced emission of  $N_2$  molecules monitored during the heating of several Cs layers after exposing them to the  $N_2O$  beam for 300 s.

capacity of the Cs layer to accommodate  $N_2O$  molecules or their fragments is not limited by the formation of a 2D layer of  $Cs_xO_y$ . It is extended by a further adsorption on top of the already oxidized 2D layer. This oxidation stage is only accompanied by a spurious emission of  $N_2$  molecules (below the sensitivity of our detection system,  $I < I_{init}/10$ ); i.e., the chemisorption is dominated by the nondissociating reaction channel.

This sticking path is governed by the electron tunneling from the Ru substrate through the  $Cs_xO_y$  insulating layer. The simplest way to identify a stable species deposited on top of a layer is to monitor the particles escaping the surface during the thermal desorption scan. No emission of  $N_2O$  molecules could be detected during heating the surface up to 1700 K, where all possible constituents were entirely removed from the Ru surface. Only the  $N_2$  emission can be taken as a fragment indicating the presence of adsorbed  $N_2O$  molecules. Figure 6 shows the thermal emission of  $N_2$  observed during the heating of several Cs submonolayers oxidized by exposing it to a  $N_2O$  beam for 300 s. A clean Ru surface exposed to  $N_2O$  exhibits no emission of any  $N_2$  molecules. For samples covered with Cs up to about 0.6 ML, i.e., within the ionic region of the Cs adsorption, only one desorption peak at 1250 K is observed (peak C). The desorption region overlaps with the temperature region where both the endmost Cs atoms, characterized by the highest possible dipole moment as well as the CsO molecules, leave the surface.<sup>26,27</sup> For more densely packed layers the intensity of this peak slightly increases and its center gradually shifts toward higher desorption temperature. The coincidence between the desorption of strongly polarized Cs atoms and  $N_2$  molecules suggests that they form a stable molecular aggregate at the surface, as shown schematically in the lower inset in Figure 6 (species C). Such aggregates start to decompose at surface temperatures above 1100 K leaving behind strongly bound oxygen atoms

which can escape from the surface only via recombinative desorption as oxygen molecules. However, it cannot be excluded that a fraction of these aggregates decomposes only when reaching the hot filament of the mass spectrometer.

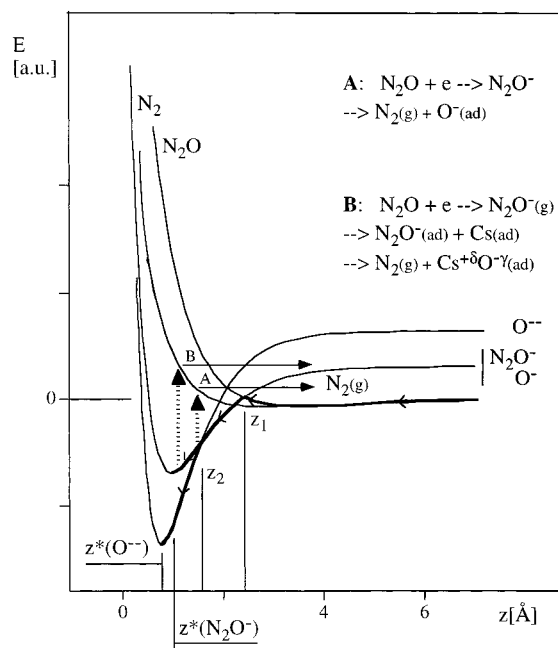
For metallic submonolayers,  $\Theta_{\text{Cs}} > 0.6$  ML, additional peaks appear in the low-temperature desorption region between 300 and 700 K. Peak A appears around 400 K and reaches a maximum for the completed Cs monolayer (upper inset in Figure 6). It can be attributed to the decomposition of the N<sub>2</sub>O<sup>-</sup> molecular ions deposited on top of the already oxidized layer. In this case a considerably reduced binding energy resulting from the weakened image attraction is expected. This bond should be lower when the thickness of the insulating spacer increases. Exactly this occurs when oxidizing a thick Cs film; a 3D oxide multilayer is created, and the N<sub>2</sub>O<sup>-</sup> molecular ions are kept at this surface by a considerably lower image potential than was the case for an insulating monolayer (see TD spectra of the 6 ML). The third TD feature, peak B, appears only for Cs loads higher than a monolayer. It can be merely tentatively attributed to thermal decomposition of a molecular aggregate composed of the N<sub>2</sub>O<sup>-β</sup> with its O end surrounded by Cs<sup>+δ</sup> like an anchor and the N<sub>2</sub> end aligned toward the vacuum (see top inset in Figure 6).

The concept of negatively charged molecular species which terminate the oxidation of thin metallic films was proposed by Grobceker et al.<sup>29</sup> It has been demonstrated that the metastable peroxy oxygen stored on top of a partly oxidized layer can be incorporated into the Cs layer as O<sup>2-</sup> via the thermally activated dissociation. The N<sub>2</sub>O<sup>-</sup> molecular ions terminating the oxidized Cs layer represent a further example for this kind of metastable species.

In summary, the adsorption of negative molecular ions takes place during the late reaction stage. It manifests itself by a pronounced increase of the work function as well as by the intense thermal desorption of N<sub>2</sub> (peak A).

Now, we turn to the ability of a surface covered by Cs atoms to accommodate oxygen due to the dissociative chemisorption of N<sub>2</sub>O. The oxygen load achieved by exposing the Ru(0001) surface to N<sub>2</sub>O has been determined by Shi et al.<sup>19</sup> Under typical UHV conditions the saturating oxygen coverage has been found to be two times lower than the one reached when exposing the surface to O<sub>2</sub>. The maximum coverage reached was solely around 0.25 ML. In our experiment the O<sub>2</sub> TD spectra have been taken after exposing Cs submonolayers to the N<sub>2</sub>O beam for 300 s. The resulting TD spectra resemble the ones known for oxygen chemisorbed on a clean Ru surface.<sup>18,28</sup> The capacity of Cs layers as a kind of storage for oxygen was measured as the integral of O<sub>2</sub> TD spectra.<sup>26</sup> The resulting oxygen content increases nearly linearly with the increasing Cs load deposited. It reaches a maximum of about 0.6 ML for a Cs monolayer. Thus, Cs submonolayers considerably raise the capacity of the Ru substrate to accommodate oxygen. Moreover, this linear relationship between the oxygen load and the Cs coverage nicely supports the concept of short-distance Cs<sub>ad</sub> ↔ N<sub>2</sub>O interaction postulated here as the only responsible for the observed N<sub>2</sub> emission.

Obviously the presented kinetic measurements gain only time-unresolved data which cannot be used for reconstruction of the chemisorptive events taking place on the time scale of several picoseconds. Thus, merely a qualitative scheme illustrating the proposed chemisorption path is given in Figure 7. It shows the interaction potentials of N<sub>2</sub>, N<sub>2</sub>O, O<sup>-</sup>, and O<sup>2-</sup> with a low work-function metal surface corresponding to a Cs monolayer deposited



**Figure 7.** Postulated, qualitative scheme of the interaction potentials for all actors involved in the interaction of N<sub>2</sub>O molecules with the Cs monolayer deposited on Ru(0001) (explanations in text).

on Ru(0001). The most probable trajectory is marked by arrows. Around the distance  $z_1$  where the potentials  $V(\text{N}_2\text{O})$  and  $V(\text{N}_2\text{O}^-)$  cross each other the impinging molecules become negatively charged due to the long-distance harpooning. Within the distance interval between  $z_1$  and  $z_2$  they undergo an acceleration in the image potential and can dissociate, which results in the N<sub>2</sub> abstraction and in the landing of the O<sup>-</sup> ion on the surface (channel A). The final ionic state of the sticking oxygen depends on the local electronic structure of the stroked adsorption site. On the other hand, the dissociation transfers the N<sub>2</sub> molecule onto the repulsive flank of the physisorption potential  $V(\text{N}_2)$ , which guaranties that this molecule can easily overcome the potential well with hyperthermal energies. This process is assumed to be only slightly dependent on the local structure of the adsorbed Cs atoms because of the long distance to the surface. Instead, it strongly depends on the vibronic state of the N<sub>2</sub>O molecule as was convincingly demonstrated for "hot" N<sub>2</sub>O in the gas-phase reaction.<sup>7,16,30</sup> The N<sub>2</sub>O<sup>-</sup> ions occupying the ground vibronic state can continue this path until  $z^*(\text{N}_2\text{O}^-)$ ; i.e., where the short-distance electron transfer takes place and the Cs<sup>+δ</sup><sub>ad</sub>-O<sup>-γ</sup> bond can be formed, where  $\gamma > 1$  (channel B). The position  $z^*(\text{N}_2\text{O}^-)$  marks the potential minimum which is presumably located inside the plane of Cs adatoms. This state represents the substrate mediated dissociation which results in an enhanced abstraction observed for low Cs densities ( $\Theta_{\text{Cs}} < 0.3$  ML). The Cs<sup>+δ</sup><sub>ad</sub>-O<sup>-γ</sup> bond formation occurs closer to the Ru substrate, which implies that the N<sub>2</sub> is suddenly transferred into an energy state high above the well of the potential  $V(\text{N}_2)$  and consequently can escape the surface with a rather high kinetic energy. Therefore, the energy gained by the N<sub>2</sub> molecules abstracted via paths A and B is expected to differ considerably. It is planned to follow this prediction and to distinguish the two channels by measuring the kinetic-energy distribution of the emitted N<sub>2</sub> molecules.

### Summary

It has been demonstrated that the interaction of nitrous oxides with the Ru(0001) surface precovered with Cs is accompanied by an intense abstraction of N<sub>2</sub> molecules. The efficiency of this process depends strongly on the electronic properties of the adsorbed Cs layer. For samples with a low Cs coverage the N<sub>2</sub> emission is dominated by the substrate-mediated chemisorption path in which the N<sub>2</sub>O molecules only dissociate when a bond with strongly polarized Cs<sub>ad</sub> atoms is created. For metallic Cs layers, for which the substrate-mediated channel is blocked, only a considerably lower yield for N<sub>2</sub> emission has been observed. The nondissociative chemisorption path of nitrous oxides has been found to be a dominating reaction

channel in the late oxidation stage of metallic Cs layers ( $\Theta_{\text{Cs}} > 0.6$  ML). It represents a considerable extension of the capacity of the Cs layer for oxygen accommodation. The nitrous oxides are deposited in the form of various molecular aggregates Cs<sub>x</sub>N<sub>2</sub>O stable at room temperature. The thermal decomposition of these aggregates proceeds mainly via N<sub>2</sub> abstraction in the temperature range of 350–700 K.

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