

# $\text{N}_2$ chemisorption to $\text{W}_n^-$ nanoclusters: molecular versus dissociative chemisorption

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## Abstract

Comparative studies on adsorption of atomic and molecular nitrogen indicate that in contrast to the previous results from tungsten bulk crystals, molecular chemisorption of  $\text{N}_2$  is more stable than dissociative ones on tungsten anion clusters consisting of 8 atoms or less. Our result provides a new aspect in chemisorption on metal clusters, namely the energetically preferred channel of chemisorption – dissociative versus molecular – might be different for metal clusters and bulk surfaces.

A long-standing question in surface science is how to overcome the gap between model and real catalysts. Real catalysts consist of metal particles with confined sizes on support materials, showing much different chemical properties in comparison to the model systems, which are generally metal single crystals [1–3]. To overcome this ‘material gap’, information on size-dependent changes of the chemical properties should be obtained. In this context, it is worthwhile mentioning that efforts to characterize chemical properties of mass-selected clusters in the gas phase provide important information [4–22], which is helpful to better understand ‘real catalysis’.

Besides the ‘material gap’, scientists often confront the ‘pressure gap’ [23]: chemisorption experiments under vacuum conditions can end up with a metastable state, when further transitions to other metastable states or to the ground state are kinetically hindered. Thus, the determination of the ground state for the chemisorption based on experimental observations can be misleading. For example, dissociation of nitrogen molecules on metal surfaces, which is the rate determining step of the ammonia synthesis, can involve large activation barriers, and therefore, only molecular chemisorption can be detected in the ultrahigh vacuum experiments, even though dissociation is energetically more favorable with respect to the molecular chemisorption [24]. Under conditions of real catalysis (higher pressures, higher temperatures), high activation barriers can be easily overcome, and consequently chemical species, which

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are not identified in scientific experiments, can form on the surface, opening unexpected reaction channels. To overcome the ‘pressure gap’, information on complete energetics of chemisorption is required, which can be obtained by developing new experimental techniques to facilitate the kinetically hindered reactions steps.

Experiments using atomic and molecular hydrogen, oxygen or nitrogen have been widely carried out in surface science studies to promote the dissociative chemisorption with high kinetic barriers. The present work provides experimental results for the comparative studies on the adsorption of atomic and molecular species of a diatomic molecule on mass-selected metal clusters. Using time-of-flight (ToF) mass spectroscopy and ultraviolet photoelectron spectroscopy (UPS), interactions of tungsten anion clusters with atomic and molecular nitrogen were compared. Dissociation of nitrogen is suggested to be less stable with respect to the molecular chemisorption on  $W_n^-$  for  $n < 9$ , which is completely different from the results for tungsten bulk crystals [25,26].

Tungsten clusters are produced with a Pulsed Arc Cluster Ions Source (PACIS) in which tungsten is evaporated by a pulsed electric arc within a carrier gas (He) injected using a pulsed valve [27]. A He gas pulse flushes the evaporated material through a 10 cm long channel (extender) into vacuum. In the extender, the plasma generated by the arc cools down to about room temperature, and tungsten clusters grow.  $W_nN_m$  clusters can be generated by two different ways: a pulse of  $N_2$  gas is injected 2–3 cm downstream into the He flow and  $N_2$  molecules react with the clusters. Alternatively, a pulse of  $N_2$  gas is inserted into the source before the He valve opens to allow  $N_2$  being present in the electric arc, leading to the dissociation of large fraction of the  $N_2$  molecules into atomic nitrogen. The mass of the clusters can be selected using a reflectron time-of-flight spectrometer (mass resolution  $m/\Delta m = 400$ ). A mass-selected bunch is irradiated by a UV laser pulse ( $h\nu = 4.66$  eV), and the kinetic energies of the detached electrons are measured using a ‘magnetic bottle’-type time-of-flight electron spectrometer. The peaks in the photoelectron spectra correspond to vertical transitions from the anionic ground

state to the allowed states of the neutral having the same geometry as the anion. Vibrational fine structures of the feature at the lowest binding energy corresponding to the transition into the neutral ground state can be assigned to vibrational modes of the neutral species in the geometry of the anion.

Mass spectra for the tungsten anion clusters taken before and after reaction with molecular nitrogen ( $N_2$ ) are illustrated in Fig. 1. As the background pressure of  $N_2$  increases, concentrations of some pure tungsten clusters decrease, and concomitantly new peaks for  $W_nN_m^-$  appear. It is important to note that the formation of  $W_nN_m^-$  with  $m = \text{odd numbers}$  is not observed, suggesting that the concentration of atomic nitrogen in the cluster source was negligibly low in this experiment.

Fig. 2 shows the mass spectra of tungsten anion clusters taken before and after reaction in atomic nitrogen (N) environments. Here,  $W_nN_m^-$  with  $m = \text{odd numbers}$  as well as even numbers are observed. For the low N pressures, the  $W_nN^-$  peak intensities are higher than those of the respective  $W_nN_2^-$  peaks, indicating that the majority of tungsten clusters actually reacted with atomic nitrogen.

The question arises whether structures of  $W_n$   $N_2$ -generated by atomic nitrogen are different with

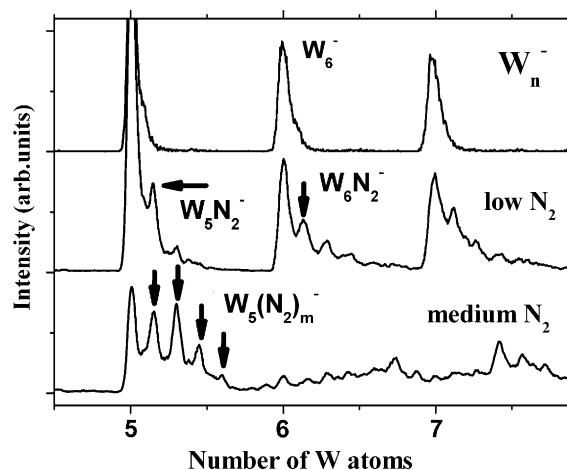


Fig. 1. Mass spectra of tungsten anion clusters before (top trace) and after reaction with molecular nitrogen at two different background pressures of  $N_2$ .

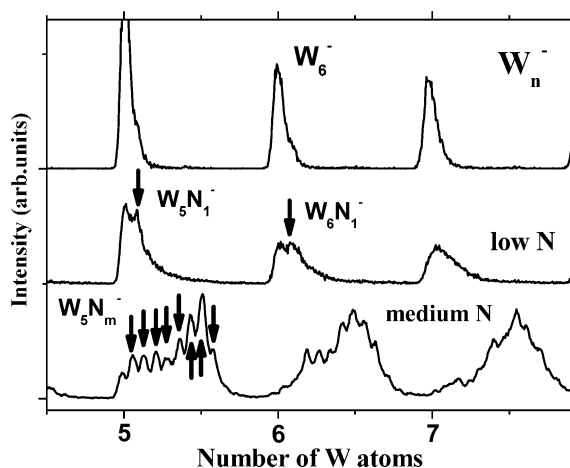


Fig. 2. Mass spectra of tungsten anion clusters before (top trace) and after reaction with atomic nitrogen at different background pressures of N.

respect to those produced in molecular nitrogen environments. In the presence of a high activation barrier for the dissociative adsorption, one may expect that the reaction with atomic nitrogen ends up with dissociatively bound N–W<sub>n</sub>–N-type structure, whereas reactions with molecular N<sub>2</sub> result in molecularly bound N<sub>2</sub> (W<sub>n</sub>–(N<sub>2</sub>)-type structure). Two dissimilar species with a same mass can be distinguished by vibrational spectroscopy. For the molecularly bound N<sub>2</sub>, a stretching frequency of N<sub>2</sub> in the frequency range between 150 and 300 meV should be observed, whereas dissociative chemisorption should yield much lower frequencies corresponding to W–N stretching.

As a first example, the photoelectron spectrum of the reacted monomer W<sup>–</sup>(N<sub>2</sub>) is displayed in Fig. 3. The spectrum does not depend on the method of synthesis, i.e., the same spectrum is obtained by using molecular or atomic nitrogen. A broad feature with rich vibrational fine structure is observed between 0.5 and 2.5 eV binding energy. A spacing of 290 ± 20 meV between the main peak A and B is slightly lower than the stretching frequency of free N<sub>2</sub>. We tentatively assign feature A to the 0 ← 0 and feature B to the 1 ← 0 vibrational transitions of N–N stretching mode, implying the non-dissociative adsorption of N<sub>2</sub>. Since the intensity of the 1 ← 0 transition is higher than the one of the 0 ← 0 transition, further transitions into

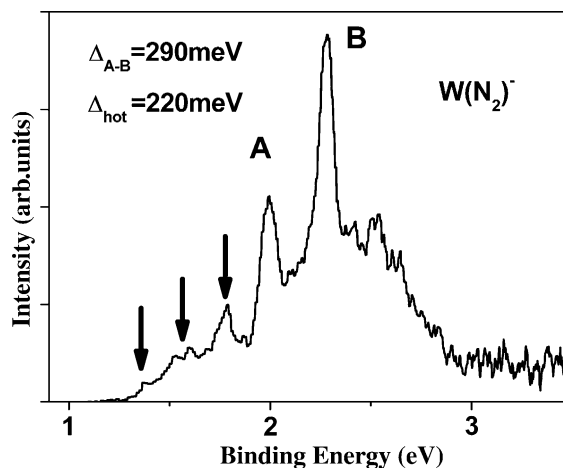


Fig. 3. UPS spectrum of WN<sub>2</sub><sup>–</sup> obtained with a photon energy of 4.66 eV. The intensities and positions of the main features in the spectrum do not depend on the method used for generation (reaction with molecular or atomic nitrogen). The spacing of the main peaks A and B is 290 ± 20 meV and the spacings between the weak peaks observed at binding energies below 2 eV (marked by arrows) is 220 ± 40 meV.

higher vibrational states of the neutral are expected corresponding to the ‘normal’ Franck–Condon profile. However, the higher vibrational state is not detected in Fig. 3, most likely, due to the fact that the higher vibrationally excited states are not bound and undergo vibrational predissociation. This process is extremely fast, leading to the observation of broad vibrational transitions without discrete peaks.

Some weak ‘hot bands’ are observed in Fig. 3 (marked by arrows at binding energies below 2 eV), which are tentatively assigned to transitions from excited vibrational levels of the anion. This frequency is significantly lower than that of the neutral WN<sub>2</sub>, indicating that the N–N bonding is more activated in the anionic state with respect to the neutral one. In contrast to the bulk W surface, chemisorption of vibrationally excited N<sub>2</sub> to a W atom does not allow quenching of the vibrational excitation. The vibrational quantum of N<sub>2</sub> is so large that cooling in the extender by collisions with He atoms can become ineffective. This explains our observation for the highly excited anions, although the vibrational temperature of anionic clusters created in our cluster source is usually estimated to be room temperature, which was estimated by the

linewidths of the UPS spectra of metal anion clusters [28].

According to the qualitative analysis of the photoelectron spectra of  $W(N_2)^-$  described above, nitrogen is molecularly bound to the W anion. Because of the pronounced vibrational progression observed, the additional electron most likely occupies an orbital with a strong contribution of the antibinding  $2\pi^*$  orbital of  $N_2$ . Detachment from such an orbital should result in excitation of the  $N_2$  stretching mode, in line with our observations. Accordingly, the additional electron of the anion further activates the  $N_2$ -bond. From these considerations, it is reasonable to conclude that the propensity of the anions towards dissociative chemisorption should be stronger than that of the neutral counterpart, implying that a molecularly bound  $N_2$  is the most stable configuration not only for the anionic  $W(N_2)^-$ , but also for the respective neutral species.

To shed light on structural properties of chemisorbed nitrogen on tungsten anion clusters, various  $W_nN_2^-$  ( $n = 6-8$ ) clusters synthesized by exposing tungsten clusters to atomic nitrogen as well as molecular nitrogen were investigated using UPS (Fig. 4). The photoelectron spectra of the  $W_nN_2^-$  clusters with  $n = 6-8$  prepared using molecular nitrogen show vibrational fine structures, corresponding to about 200 meV, which are absent for the pure tungsten clusters (Fig. 4). For  $W_8^- + N_2$ , a spectrum with sufficient signal-to-noise ratio to allow unambiguous assignment could not be recorded. Note that for larger clusters, separation of  $W_nN_2^-$  from the bare  $W_n$  is very difficult due to broader isotope distributions. 200 meV is attributed to the stretching frequency of chemisorbed  $N_2$  molecules based on previous high resolution electron energy loss spectroscopy (HREELS) data for nitrogen adsorption on tungsten single crystal surfaces [25], indicating that nitrogen is molecularly adsorbed on these clusters. These results are different from those obtained with  $W(100)$ , on which dissociative chemisorption of nitrogen takes place at room temperature [25,26].

Considering that minor differences in the UPS spectra can originate from different vibrational temperatures of clusters, the positions and inten-

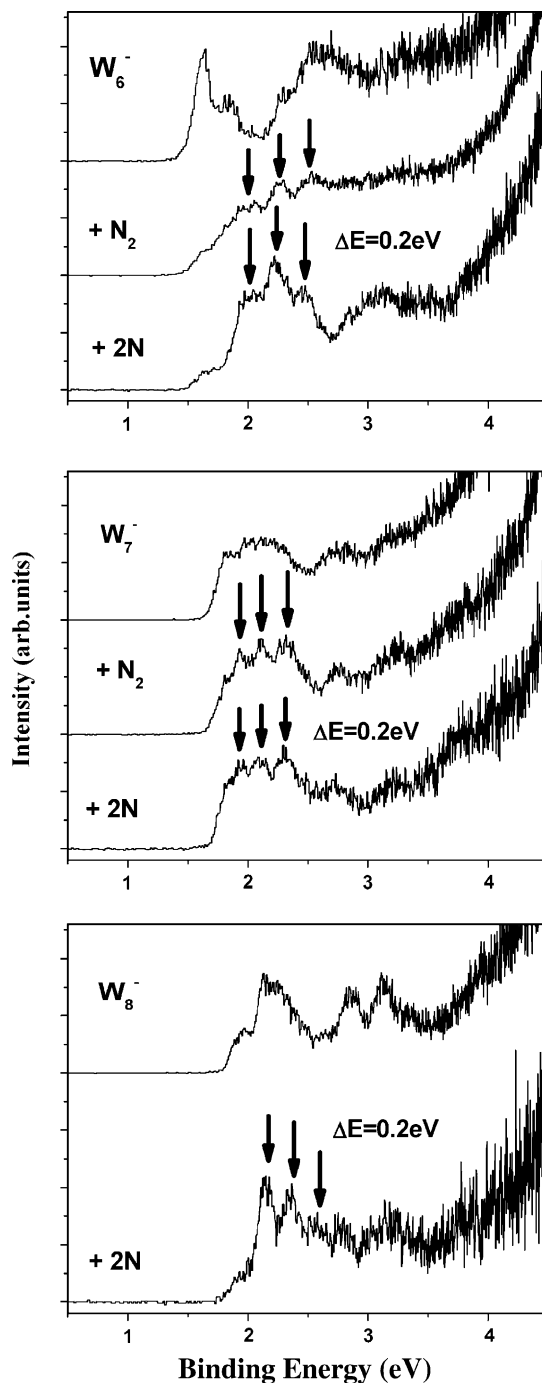


Fig. 4. UPS spectra of various  $W_n^-$  and  $W_nN_2^-$  clusters ( $n = 6-8$ ) obtained with a photon energy of 4.66 eV.  $W_nN_2^-$  clusters were created by exposing tungsten clusters to atomic (+2N) or molecular (+ $N_2$ ) nitrogen. For  $W_8^-$  we did not succeed in recording a spectrum for reaction with molecular  $N_2$  because of too low anion intensities.

sities of the features in the UPS spectra of  $W_nN_2^-$  ( $n = 6, 7$ ) created by different methods are almost identical. In contrast, for  $W_nN_2^-$  with  $n = 2-5$  a strong dependence on the method of production was found in the UPS spectra. In this Letter, we focus on the  $W_nN_2^-$  clusters, for which identical UPS spectra were observed by using atomic and molecular nitrogen, and therefore results for  $W_nN_2^-$  with  $n = 2-5$  are out of scope of this Letter. Detailed explanation for  $n = 2-5$  is going to be provided in our forthcoming Letter.

Fig. 4 demonstrates that di-nitrogen species are formed, even if atomic nitrogen is provided, i.e., two nitrogen atoms adsorbed on these clusters spontaneously recombine to form di-nitrogen species. We conclude that molecular adsorption of  $N_2$  is energetically more stable than dissociative chemisorption, and the mobilities of nitrogen atoms on these clusters are quite high. These results are much different from those found for tungsten bulk crystals, on which dissociation of nitrogen is thermodynamically more favored with respect to the molecular chemisorption [25,26]. We cannot rule out the possibility that tungsten clusters did not react with atomic nitrogen but only with molecular nitrogen, existing in atomic nitrogen environments. If dissociative chemisorption was energetically more favorable than molecular one, the tungsten clusters would react better with atomic nitrogen than molecular nitrogen. That the tungsten clusters preferentially react with molecular nitrogen ( $N_2$ ) is an evidence for the molecular chemisorption of nitrogen being energetically more stable than dissociative nitrogen. Therefore, within this scenario, our main conclusion that molecular chemisorption of  $N_2$  is the energetic ground state is still valid.

As we have already discussed for  $WN_2$ , the excess electron in the anionic state further activate the N–N bonding, and therefore, the dissociation of  $N_2$  is more probable for the anions in comparison to the case of the neutral counterpart. Considering this, we conclude that molecular  $N_2$  chemisorption is the energetically most favorable chemisorption channel for neutral  $W_n$  clusters as well as for the anionic clusters.

Cluster size-dependent changes of chemical reactivities have been often interpreted in terms of

the activation barriers for the dissociation, whereas no attention has been paid to the thermodynamics, i.e., whether molecular or dissociative chemisorption is the most stable bonding mechanism [17]. Even though our discussion and assignments need support by further calculations, experimental evidences provided in the present work demonstrate strong indications for the size-dependent changes of the chemisorption mechanism: for small  $W_n^-$  clusters  $N_2$  binds molecularly to W, whereas for the bulk tungsten surfaces  $N_2$  dissociates at room temperature. Our results may reconcile the previous work from Ros en et al. [20], reporting drastic jump of  $N_2$  adsorption reactivities of  $W_n$ -clusters as the number of W atoms in a cluster exceeds 15. We found molecular chemisorption to be the most stable channel for the small  $W_n$  clusters, whereas dissociative chemisorption is the most stable state for bulk surfaces. Therefore, a transition from dissociation to non-dissociation for the chemisorption ground state should exist as a function of clusters size. It is possible that Ros en et al. observed this transition at  $n = 15$ , although a different interpretation for their data was provided in [20].

Regarding the driving force of such a transition, we cannot rule out geometry effects. However, it should be noted that the tungsten clusters are not expected to have size-dependent structural changes analogous to carbon or gold clusters. Most likely, W clusters exhibit compact three-dimensional structures from the tetramer, analogous to other transition metals such as Ni, Co, and Nb clusters [17,29]. Taking this into account, our result in Fig. 4 is not completely rationalized by a geometric effect alone. It is important to note that continuous change of the electronic structure is generally observed with increasing cluster size, especially for the metal d-orbitals [5]. The energy necessary to remove a charge from a metal d-orbital depends on the number of the directly neighboring metal atoms. This is evident from various experimental studies such as photoionization and photoemission experiments, in which the so-called final state effect plays an important role for the shift of the electron binding energy as a function of particle size [30]. For larger particles, the positive hole created by photoionization is

immediately screened by the electrons from the neighbors, lowering the energy cost required to remove an electron. In contrast, lower average coordination numbers of smaller clusters reduce this screening process, increasing the energy cost for removing an electron. Similar effect can play a crucial role for the charge donation from the metal d-orbital to the valence orbitals of adsorbate ( $2\pi^*$  orbital of  $N_2$ ). With increasing number of nearest neighbors in a metal cluster, the charge transfer from the metal to the adsorbate can become easier, i.e., the d-orbitals are 'softened' due to the hybridization. Above a certain cluster size, the charge transfer become sufficient to break the N–N bonding, allowing dissociative chemisorption being the most stable state. It is worth mentioning that this charge transfer model also explains the higher vibrational frequency of the  $N_2$  adsorbed to a single W atom with respect to larger W clusters.

It is likely that besides tungsten, other metal clusters undergo similar non-dissociation  $\rightarrow$  dissociation transitions, for example,  $H_2$  on  $Ti_n^-$  and  $O_2$  on  $Au_n^-$  experience the  $2H \rightarrow H_2$  (or  $O_2 \rightarrow 2O$ ) transition with varying cluster size [21,22], most likely as a result of the switch of the metastable and ground state in the chemisorption. An important consequence of the change of the ground state in the chemisorption energetics is that new reaction channels are opened on the nanoclusters, which are not present on the bulk materials [21]. Further comparative studies for the chemisorption of atomic and molecular species on various nanoclusters will contribute to discover new reaction mechanisms on nanoclusters.

In summary, for the tungsten anion clusters smaller than  $W_9^-$ , molecular adsorption of  $N_2$  was found to be thermodynamically more stable with respect to the dissociative chemisorption. In contrast to our results, dissociative adsorption of nitrogen is energetically more favorable than molecular adsorption on tungsten single crystal surfaces [25,26], suggesting that the ground state of nitrogen chemisorption undergoes transition from molecular to dissociative adsorption ( $N_2 \rightarrow 2N$ ) with increasing number of tungsten atoms ( $n$ ). Comparative studies on atomic and molecular species of gas molecules on metal clusters can be used to characterize the complete

chemisorption energetics on nanoclusters, which will contribute to bridge the gap between model and real catalysts.

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