

# **3S'85**

**SYMPOSIUM ON  
SURFACE SCIENCE**

## **CONTRIBUTIONS**

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**Obertraun/Austria  
Jan 27 - Feb 2, 1985**

INTERPRETATION OF THE N1S-PHOTOELECTRON SPECTRA OF CHEMISORBED  $N_2$  IN  
TERMS OF LOCAL METAL-MOLECULE INTERACTIONS [1]

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There is at present some controversy concerning the interpretation of core photoelectron spectra for weakly chemisorbed molecules, e.g. CO/Cu and  $N_2$ /Ni. One view<sup>[2,3]</sup> claims that the shape of the surface density of states completely determines the shape of the spectral function while the other view<sup>[4,5]</sup> considers it an indication of the nature of the local metal-molecule interaction. In order to address this problem we present here results of a theoretical ab - initio study including correlation corrections on several electronic states of the neutral and core-ionized (N1s) linear<sup>[1,6]</sup> Ni- $N_2$  cluster using the generalized valence bond method. The structure of the linear complex has been geometry optimized for two states, namely a  $^3\Sigma^+$  and a  $^1\Sigma^+$  state which differ by the electronic configuration of the Ni atom. In the  $^3\Sigma^+$  the Ni is in a  $3d^9 4s^1 ({}^3D)$  in the  $^1\Sigma^+$  in a  $3d^{10} ({}^1S)$  configuration. The lower panel of Fig. 1 shows the potential energy curves for both states. Clearly, the ground state of the system is the  $^1\Sigma^+$  state<sup>[6]</sup>, where the  $N_2$  molecule is coupled to the Ni  $3d^{10}$  configuration. The bond energy gained by interaction between a  $N_2$  molecule and a Ni  $4s 3d^9$  configuration  $^3\Sigma^+$  is by 0.45 eV weaker than the bond energy of the  $^1\Sigma^+$  state. This is mainly due to the strong Pauli repulsion between the  $N_2$  carbon lone pair and the 4s electron of the metal. The resulting bond is not only weaker, but also longer than in the case of the  $^1\Sigma^+$  state. Long bond distances,

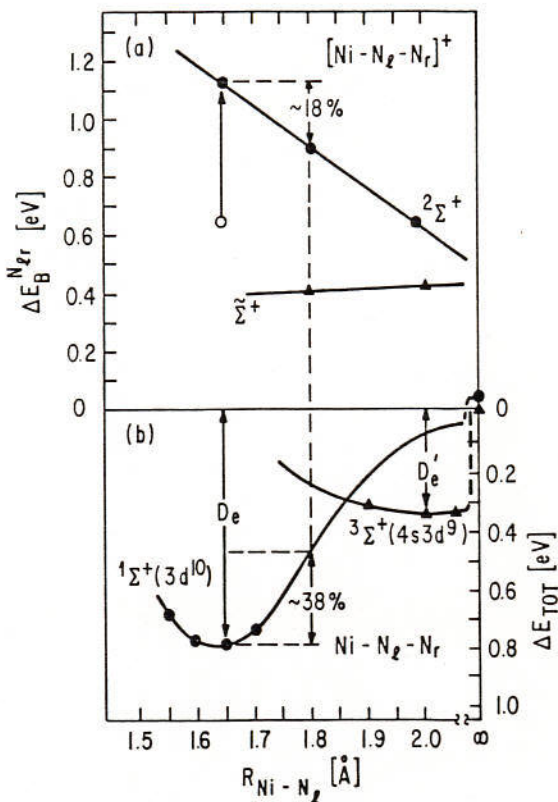


Fig. 1: (a) Upper panel: Binding energy difference between the inequivalent nitrogen atoms  $N_1$  and  $N_r$  as a function of metal molecule separation. ( $\bullet$ ): equivalent core calculations in  $3d^{10}$  configuration, ( $\circ$ ): non equivalent core calculation in  $3d^{10}$  configuration, ( $\blacktriangle$ ): equivalent core calculation in  $4s3d^9$  configuration.

(b) Lower panel: Potential energy curves for the ground state ( $3d^{10}$ ) and the lowest triplet excited state ( $4s3d^9$ ) of neutral  $\text{NiN}_2$ .  $D_e$  and  $D_e'$  denote the heats of adsorption of these states.

consistent with the  $^3\Sigma^+$  state have also been used previously in Hartree-Fock calculations<sup>[7]</sup>. In those calculations the metal configuration was  $4s^1 3d^9$ . Therefore, the  $^3\Sigma^+$  state corresponds to the result of a Hartree-Fock calculation. If we now ionize the system by creating core holes starting from either of the two states we find two important results. i) The difference in N1s binding energy between the two inequivalent nitrogen atoms is rather small for the  $^3\Sigma^+$  state, namely  $\sim 0.3 - \sim 0.4$  eV, and large for  $^1\Sigma^+$  state, namely  $\sim 0.9 - \sim 1.2$  eV respectively (upper panel Fig.1). ii) The binding energy for the N1s ionization of the nitrogen closer to the Ni atom ( $N_1$ ) is larger than for ionization of the more remote nitrogen atom ( $N_r$ ).

Result i) for the  $^3\Sigma^+$  state is consistent with results at the Hartree-Fock level. An estimation of ionization energies based purely on Hartree-Fock calculations would lead to an energetic sequence of binding energies reversed with respect to the present results.

In order to get the result summarized in i) and ii) we had to use the equivalent core approximation to properly account for deficiencies in the basis sets.

Within the equivalent core approximation we can properly account for  $\pi$ -back donation from the metal to the molecule. The distribution of valence electrons in the ion resulting from the  $^1\Sigma^+$  looks like  $Ni^+-NO$  and  $Ni^+-ON$  depending on the position of the hole on the adsorbed molecule. The driving force is the screening of the core hole by metal electrons.

It is the binding energy difference of NO bound with its oxygen or nitrogen end to a Ni ion in the geometry of the neutral ground state that determines the energy separation between the two ion states. The more stable configuration is achieved when "NO" binds with the nitrogen atom to the surface. This qualitative picture is in agreement with result ii).

Corresponding assignments have been put forward, previously<sup>[8,9]</sup>.

Once we know that the proper description is given in terms of the  $^1\Sigma^+$  state we can try the comparison with experiment. Fig. 2 shows a comparison between a convolution of our calculated line spectrum,

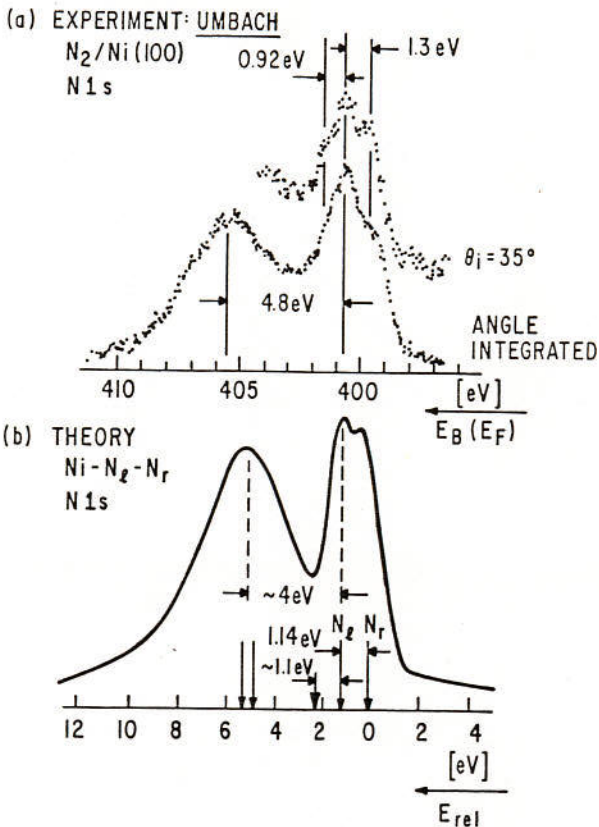


Fig. 2 : Comparison of experimentally observed<sup>[2]</sup> (a)  $N 1s$  spectral functions of  $Ni(100)/N_2$  with the gaussian-convoluted calculated line spectrum of  $NiN_2$  (b). The calculated relative ionization energies are marked by arrows. The full spectrum was taken in an angle integrated mode, while the partially shown spectrum was taken in an angle resolved mode<sup>[2]</sup>.

now including core excited states, and the spectrum of chemisorbed  $N_2$  on Ni(100)<sup>[2]</sup>. In our convolution we used the line widths of the two unscreened components as parameters to fit the experimental spectrum (FWHM: 3.6 eV). The line width of the two screened components were chosen according to the experimental resolution (FWHM: 1.2 eV).<sup>[2]</sup> The physical justification to use different line widths comes from the expected dynamical behaviour (life time) of the screened and unscreened ion states. If one wanted to theoretically describe the different dynamical behaviour of the different ion states properly by an ab-initio calculation one would have to invoke the electronic structure of the extended substrate.

However, given the simplicity of the local model using a single metal atom to describe a transition metal surface we consider the agreement between calculated and measured spectral function, as shown in Fig.2, as excellent, and believe that the essential physics is contained in this approach.

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