

## THERMODYNAMIC INTERPRETATION OF CORE-LEVEL BINDING ENERGIES IN ADSORBATES

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Using the “equivalent cores” approximation in combination with a Born–Haber cycle we calculate core-level binding energies for adsorbates on metal surfaces. Since accurate thermodynamic data are required for the molecule both in the initial and in the final state, we restrict our discussion to adsorbed carbon monoxide, surface species that contain nitrogen and the halogens bromine and iodine. Reasonable agreement between theoretical and experimental values is achieved for adsorbates for which the adsorption energies are accurately known and complete final state screening for the adsorbate is expected.

### 1. Introduction

Recent high resolution results on core-level electron binding energies of alloys and mixed valence compounds have led to the rediscovery of the “equivalent cores” approximation for calculating core-level photoelectron binding energies. This approximation dates back to Skinner [1] in 1932 and was used extensively by Jolly and coworkers [2] to improve predictions on “chemical shifts” in inorganic molecules and solids and to estimate thermodynamic energies from ESCA data [3]. The general idea is to exchange the core ionized  $Z^*$  final state of the ion with the valence ionized state of the  $(Z + 1)^+$  atom. It is assumed that this exchange requires no energy, an approximation which is only valid for the core levels of the light elements. Following the general procedure outlined by Jolly [2] and Johansson and Mårtensson [4] we construct a Born–Haber cycle to calculate the total energies of the initial and the final

states of adsorbates thus giving a theoretical estimate for the respective core-level electron binding energies [5].

In this communication we summarize the theoretical model and report results for CO, NO, N<sub>2</sub> and NH<sub>3</sub> on various metal surfaces and for Br, Br<sub>2</sub>, I, I<sub>2</sub> on a Fe(100) surface. Our theoretical estimates agree with experimental data in those systems where complete final state screening can be assumed.

## 2. Calculation of binding energies in adsorbates

The experimental binding energy of a core electron in a molecule or atom is equal to the difference in total energy of the initial neutral state and the final ionized state of the system. The valence electrons relax towards the core hole in an attempt to screen it. In general, more than one discrete final state is possible, thus leading to more than one observed binding energy. For a molecule adsorbed on a metal, the final state for a core transition with the lowest energy may correspond to a situation where an electron is effectively transferred from the metal Fermi level  $E_F$  to an available empty valence orbital of the adsorbed molecule lying below  $E_F$ . In this “fully screened final state” the adsorbed molecule is essentially neutral. This situation can be treated most easily, because the energy released in the screening process corresponds to the energy difference of two discrete electronic states.

In order to obtain core-level binding energies within the “equivalent cores” approximation for adsorbates, a thermodynamic cycle (Born–Haber cycle) has to be set up for calculating the total initial and final state energy. As an example, in fig. 1 we show the appropriate cycle for the calculation of the C 1s binding energy in carbon monoxide chemisorbed on a metal surface. Starting from the initial state, which is a chemisorbed CO molecule, we have to

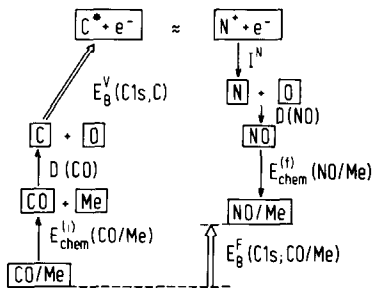


Fig. 1. Born–Haber cycle for the calculation of the C 1s core-level binding energy in a CO molecule adsorbed on a metal surface. The binding energy  $E_B^F$  (C 1s; CO/Me) is given with respect to the Fermi energy of the substrate and corresponds to a fully screened final state. The construction of the cycle is discussed in the text.

Table 1

Core-level binding energies in adsorbates (energies in eV)

System	$E_{\text{chem}}^{(i)}$	$E_{\text{chem}}^{(f)}$	Excited level	$E_{\text{B}}^{\text{F}}(\text{theor.})$	$E_{\text{B}}^{\text{F}}(\text{exp.})$
CO/Pt(111) <sup>a)</sup>	1.12 <sup>b)</sup>	1.45 <sup>c)</sup>	C 1s	285.3	285.8 <sup>b)</sup>
CO/Pt(111) <sup>d)</sup>	1.16 <sup>b)</sup>	0.61 <sup>c)</sup>	C 1s	286.2	286.8 <sup>b)</sup>
CO/Pt(100)	1.37 <sup>e)</sup>	1.73 <sup>c)</sup>	C 1s	285.2	284.4 <sup>f)</sup>
CO/Pd(111)	1.31 <sup>g)</sup>	1.34 <sup>h)</sup>	C 1s	285.6	285.8 <sup>i)</sup>
CO/Ni(111) <sup>j)</sup>	1.13 <sup>k)</sup>	1.08 <sup>l)</sup>	C 1s	285.7	285.4 <sup>m)</sup>
CO/Rh(110)	1.29 <sup>i)</sup>	1.13 <sup>n)</sup>	C 1s	285.8	285.4 <sup>i)</sup>
CO/W(110) <sup>o)</sup>	~ 0.26 <sup>o)</sup>	≥ 0.4 <sup>p)</sup>	C 1s	≤ 285.9	285.9 <sup>o)</sup>
NO/Pt(100)	1.73 <sup>c)</sup>	< 0.38 <sup>q)</sup>	N 1s	> 400.0	401.0 <sup>f)</sup>
N <sub>2</sub> /Ni(110)	0.5 <sup>r)</sup>	1.1 <sup>l)</sup>	N 1s	400.1	400.2 <sup>r)</sup>
N <sub>2</sub> /W(110)	0.5 <sup>s)</sup>	≥ 0.4 <sup>p)</sup>	N 1s	≤ 400.8	400.5 <sup>s)</sup>
NH <sub>3</sub> /W(110)	0.5 <sup>s)</sup>	~ 0.7 <sup>s)</sup>	N 1s	~ 400.9	400.9 <sup>t)</sup>
Br/Fe(100) <sup>u)</sup>	2.56 <sup>v)</sup>	0.18 <sup>w)</sup>	Br 3d Br 3p <sub>3/2</sub> Br 3p <sub>1/2</sub> Br 3s	$E_{\text{B}}^{\text{V}}(\text{Br})$ - 11.6	$\left\{ \begin{array}{l} 69.0 \text{ }^{\text{x})} \\ 182.7 \text{ }^{\text{x})} \\ 189.1 \text{ }^{\text{x})} \\ 256.2 \text{ }^{\text{x})} \end{array} \right.$
Br <sub>2</sub> /Fe(100) <sup>y)</sup>	0.51 <sup>z)</sup>	0.1	Br 3d Br 3p <sub>3/2</sub> Br 3p <sub>1/2</sub> Br 3s	$E_{\text{B}}^{\text{V}}(\text{Br})$ - 11.8	$\left\{ \begin{array}{l} 68.8 \text{ }^{\text{x})} \\ 182.4 \text{ }^{\text{x})} \\ 188.8 \text{ }^{\text{x})} \\ 255.9 \text{ }^{\text{x})} \end{array} \right.$
I/Fe(100) <sup>u)</sup>	2.52 <sup>aa)</sup>	0.32 <sup>bb)</sup>	I 4d <sub>5/2</sub> I 4d <sub>3/2</sub> I 5d <sub>5/2</sub> I 3d <sub>3/2</sub>	$E_{\text{B}}^{\text{V}}(\text{I})$ - 10.0	$\left\{ \begin{array}{l} 50.1 \text{ }^{\text{x})} \\ 51.4 \text{ }^{\text{x})} \\ 620.2 \text{ }^{\text{x})} \\ 631.8 \text{ }^{\text{x})} \end{array} \right.$
I <sub>2</sub> /Fe(100) <sup>y)</sup>	0.64 <sup>z)</sup>	0.2	I 4d <sub>5/2</sub> I 4d <sub>3/2</sub> I 5d <sub>5/2</sub> I 3d <sub>3/2</sub>	$E_{\text{B}}^{\text{V}}(\text{I})$ - 10.4	$\left\{ \begin{array}{l} 48.9 \text{ }^{\text{x})} \\ 50.6 \text{ }^{\text{x})} \\ 619.3 \text{ }^{\text{x})} \\ 630.8 \text{ }^{\text{x})} \end{array} \right.$

## Notes to table 1

a) "Bridge" bonded (low  $\theta$ ).

b) Ref. [6].

c) Ref. [7].

d) "Linear" bonded (high  $\theta$ ).

e) Ref. [9].

f) Ref. [8].

g) Ref. [11].

h) Ref. [12].

i) Ref. [10].

j) Saturation coverage.

k) Ref. [13].

l) Ref. [15].

m) Ref. [14].

n) Ref. [16].

o)  $\alpha$ -CO (molecular) [17].p) NO dissociates even at 100 K on W(110) [18]. We therefore assume  $E_{\text{chem}} > E_{\text{diss}}$ .q) Ref. [19] corresponding to a flat-lying O<sub>2</sub>, in contrast to the initial state geometry.

r) Ref. [31].

s) Ref. [5].

t) Ref. [5] ( $\theta = 0.2$  value).u) Dissociatively adsorbed species on the substrate (low  $\theta$ ).

v) Estimated from thermodynamic data for diatomic molecules [20].

w) Ref. [21].

x) Refs. [22] and [23].

y) Condensed phase (molecular adsorption at high  $\theta$ ).

z) Ref. [23].

aa) Calculated from thermodynamic gas-phase data [32].

bb) Ref. [24].

overcome first the adsorption energy  $E_{\text{chem}}^{(i)}$  (CO/metal) to desorb CO and then the dissociation energy  $D(\text{CO})$  to obtain isolated atoms. Next, the gaseous C atom is core ionized. Within the “equivalent cores” model, the final state of the core ionized  $Z^*$  atom (here,  $Z$  denotes the atomic number and the asterisk stands for a core vacancy) has the same energy as that of a  $(Z + 1)^+$  ion with its core electrons all present, but its highest-lying valence electron removed. Thus, the  $\text{C}^*(1s \text{ hole})$  atom is replaced by a  $\text{N}^+(2p \text{ hole})$  ion. For a C atom in the adsorbed CO the fully screened final state would be  $\text{C}^{*-}(1s \text{ hole, plus screening electrons}) = \text{N}(\text{neutral})$ . Thus, in order to neutralize the  $\text{N}^+$  ion on the right-hand side of the Born–Haber cycle the ionization energy  $I^{\text{N}}$  of N is released. Next, the dissociation energy  $D(\text{NO})$  is released when N combines with the oxygen atom. Finally, NO is adsorbed on the surface thereby gaining the adsorption energy  $E_{\text{chem}}^{(f)}$  (NO/metal) of a NO molecule.

From this cycle, the C 1s binding energy of a carbon core electron in an adsorbed CO molecule can be calculated as

$$\begin{aligned}
 E_{\text{B}}^{\text{F}}(\text{C } 1s; \text{CO/metal}) &= E_{\text{chem}}^{(i)}(\text{CO/metal}) \\
 &+ D(\text{CO}) + E_{\text{B}}^{\text{V}}(\text{C } 1s; \text{C}) - I^{\text{N}} - D(\text{NO}) \\
 &- E_{\text{chem}}^{(f)}(\text{NO/metal}).
 \end{aligned} \tag{1}$$

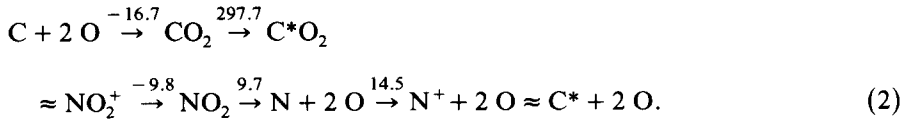
The Born–Haber cycle described above gives the binding energy with reference to  $E_{\text{F}}$  and allows a direct comparison with experiment. A similar thermodynamic cycle can be set up for other adsorption systems, provided the individual energies are known.

In table 1 we present a compilation of thermodynamic data used to calculate  $E_{\text{B}}^{\text{F}}$  in adsorbed carbon monoxide, nitrogen containing species and halogens according to eq. (1). Although no atomic rearrangement takes place during the core excitation (Franck–Condon principle), to a good approximation equilibrium data of the  $(Z + 1)$  molecule may be used for the dissociation and chemisorption energies in the final state. Tabulated experimental core-level binding energies always correspond to a completely screened final state.

## 2.1. Carbon monoxide

For calculating the C 1s binding energy values in CO adsorbed on different metal substrates, we used the values [20]  $D(\text{CO}) = 11.2 \text{ eV}$ ,  $I^{\text{N}} = 14.5 \text{ eV}$ ,  $D(\text{NO}) = 6.5 \text{ eV}$  and the chemisorption energies given in table 1. At present, no reliable data exist for the C 1s binding energy in an isolated C atom. We estimated this energy to be  $E_{\text{B}}^{\text{V}}(\text{C } 1s; \text{C}) = 295.4 \text{ eV}$  from an independent thermodynamic cycle, using experimental data for reaction energies [20] and

the C 1s binding energy [25] in gaseous CO<sub>2</sub> (all energies in eV):



Hence, from eq. (1),

$$E_{\text{B}}^{\text{F}}(\text{C 1s}; \text{CO/metal}) = E_{\text{chem}}^{(\text{i})}(\text{CO/metal}) - E_{\text{chem}}^{(\text{f})}(\text{NO/metal}) + 285.6 \text{ eV}. \quad (3)$$

Note the surprisingly good agreement with experimental data in table 1 (generally within 0.3 eV) despite the numerical uncertainties, especially for chemisorption energies.

## 2.2. Nitrogen containing species

We use an obvious modification of eq. (1) for NO, N<sub>2</sub> and NH<sub>3</sub> with the dissociation energies [20]  $D(\text{NO}) = 6.5 \text{ eV}$ ,  $D(\text{O}_2) = 5.2 \text{ eV}$ ,  $D(\text{N}_2) = 9.8 \text{ eV}$ ,  $D(\text{NH}_3) = 12.1 \text{ eV}$  and  $D(\text{OH}_3) = 8.5 \text{ eV}$  [8]. The ionization potential of O is [20]  $I^{\text{O}} = 13.6 \text{ eV}$  and the N 1s binding energy in isolated nitrogen has been estimated [5], similar to carbon, to be  $E_{\text{B}}^{\text{V}}(\text{N 1s}; \text{N}) = 411.0 \text{ eV}$ . Again, we find a very good agreement between the calculated and the experimental binding energies as demonstrated in table 1.

## 2.3. Halogens

In the last section of table 1 we present results for core-electron binding energies in bromine and iodine chemisorbed on Fe(100) both at low coverage  $\theta$  (dissociatively adsorbed Br, I) and at high  $\theta$  (molecularly adsorbed Br<sub>2</sub>, I<sub>2</sub>). In these adsorption systems it was found that the molecular condensed halogens show smaller core-level binding energies than the dissociatively adsorbed atoms at low coverage [22]. In the Born–Haber cycle we use the tabulated values [6]  $D(\text{Br}_2) = 2.0 \text{ eV}$ ,  $D(\text{I}_2) = 1.6 \text{ eV}$ ,  $I^{\text{Kr}} = 14.0 \text{ eV}$  and  $I^{\text{Xe}} = 12.2 \text{ eV}$ . The dissociation energies of BrKr and IXe have been estimated to be  $D(\text{BrKr}) \approx D(\text{IXe}) \approx 0.2 \text{ eV}$ . Note that at high coverage the  $E_{\text{chem}}$  data correspond to a heat of condensation. Unfortunately it is not possible to obtain core-level binding energies in isolated I and Br atoms from a thermodynamic cycle. This quantity, however, cancels in the binding energy difference for the molecularly and dissociatively adsorbed halogens. Using data for the heats of adsorption (condensation) from table 1, we obtain

$$E_{\text{B}}^{\text{F}}(\text{Br}; \text{Br/Fe(100)}) - E_{\text{B}}^{\text{F}}(\text{Br}; \text{Br}_2/\text{Fe(100)}) = 0.2 \text{ eV}, \quad (4)$$

for all deep-lying Br levels, in excellent agreement with the experimental results. Thus, molecular and atomic bromine are not easily distinguishable in XPS experiments.

Similarly, the binding energy difference between the dissociatively adsorbed and the condensed iodine can be obtained from table 1 as

$$E_{\text{B}}^{\text{F}}(\text{I}; \text{I}/\text{Fe}(100)) - E_{\text{B}}^{\text{F}}(\text{I}; \text{I}_2/\text{Fe}(100)) = 0.4 \text{ eV}. \quad (5)$$

This is not a bad estimate of the experimental value of the binding energy difference between atomic and molecular iodine ( $\approx 1 \text{ eV}$ ) considering the uncertainties in the thermodynamic data used.

### 3. Discussion

In this communication we calculated core-level binding energies in different adsorbates within a Born–Haber cycle, using the “equivalent cores” approximation. In the following we discuss the limitations of such a description.

First, a complete set of reliable thermodynamic data is required in order to calculate binding energies in a given system. Although the thermodynamic cycle presented in fig. 1 has been developed for a fully screened final state, it can be extended for the case of incomplete screening [5]. In this case, however, large error bars are imposed on the predicted binding energy values [5].

The “equivalent cores” approximation is valid for the deep lying and localized core electrons of the light elements. Although it is expected to give best results in isolated atoms, it has been found that the heat of core exchange  $\text{C}^* \rightarrow \text{N}^+$  is constant also in a large number of carbon containing molecules [28], e.g.  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{CO}_2$ , ... In some other molecules [28] like  $\text{CO}$  and  $\text{CF}_4$ , however, the “equivalent cores” approximation works less satisfactorily. A condition for the energetic equivalence of a  $\text{Z}^*$  and a  $(\text{Z} + 1)^+$  atom in a gaseous  $\text{Z} - \text{R}$  molecule is that the charge distribution in the relaxed  $(\text{Z}^* - \text{R})$  molecule is the same as in the final state valence ionized  $((\text{Z} + 1) - \text{R})^+$  molecule. This seems not to be the case for  $\text{CO}$ , where the calculated core level binding energy turns out to be  $\approx 1 \text{ eV}$  larger than the experimental value. We therefore performed the core exchange on an isolated carbon atom, as shown in fig. 1. This, however, requires knowledge of the atomic  $\text{C } 1\text{s}$  binding energy. We estimated this value to yield  $E_{\text{B}}^{\text{V}}(\text{C } 1\text{s}; \text{C}) = 295.4 \text{ eV}$  from a thermodynamic cycle in eq. (2), where the core exchange has been performed in the  $\text{CO}_2$  molecule, as  $\text{C}^*\text{O}_2 \rightarrow \text{NO}_2^+$ . Note that a similar value would be expected from an analogous cycle in other carbon containing molecules (once the relevant thermodynamic data are known) except in those for which the “equivalent cores” approximation breaks down [28,30] (e.g.  $\text{CO}$ ,  $\text{CF}_4$ ). A direct estimate of  $E_{\text{B}}^{\text{V}}(\text{C } 1\text{s}; \text{C})$  can be obtained from the electron binding energy in solid carbon, which has to be corrected for the change of the reference level from  $E_{\text{F}}$  to  $E_{\text{V}}$ . Using experimental data [29] for  $E_{\text{B}}^{\text{F}}(\text{C } 1\text{s}; \text{C solid}) = 284.0 \text{ eV}$  and the ionization potential [20]  $I^{\text{C}} = 11.3 \text{ eV}$ , we estimate the atomic value to be  $E_{\text{B}}^{\text{V}}(\text{C } 1\text{s}; \text{C}) = 295.3 \text{ eV}$ . This is in excellent, but somewhat accidental, agreement with the value obtained from eq. (2).

The agreement between theoretical and experimental binding energies in adsorbed CO justifies the “equivalent cores” approximation in isolated C atoms and the procedure presented above to obtain C 1s binding energies in isolated C atoms. A similar good agreement for the  $E_B^F(\text{N } 1s)$  values in nitrogen containing adsorbates has been discussed extensively elsewhere [5].

It seems surprising that one obtains nearly the same core-level binding energies in dissociatively adsorbed and in condensed halogens on a metal surface (see table 1), once the different bonding and screening mechanisms are taken into account. However, this fact can easily be understood using the Born–Haber cycle, since the sum of the heat of condensation and the dissociation energy for the condensed species is nearly identical to the chemisorption energy of the dissociatively adsorbed species both in the initial and final state. The relatively good agreement of the binding energy difference in theory and experiment suggests that the same complete final state screening occurs both in the dissociatively chemisorbed and the condensed species. No thermodynamic estimate could be made for the core-level binding energy of halogen atoms due to the lack of thermodynamic data (especially for noble gas compounds) required in a cycle similar to that in eq. (2). In order to be able to compare absolute values for the core-level binding energies in adsorbed halogens a direct measurement in the atomic species would be desirable.

In conclusion, the good agreement between theory and experiment suggests that the use of a thermodynamic Born–Haber cycle, based on the “equivalent cores” approximation, is an adequate tool to calculate core-level binding energies in adsorbates.

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