

Bromine and Iodine Adsorption on an Fe(100) Surface

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Abstract

We studied bromine and iodine adsorption on an Fe(100) surface in the temperature range of 110 K to 700 K. In this communication we compare core-level binding energies of dissociatively and molecularly adsorbed halogen species as a function of coverage. Our valence band photoemission data suggest that bromine and iodine adsorption at 300 K is always dissociative. At 110 K, initial dissociative adsorption is followed by condensation of molecular halogens. At 300 K the core-level binding energies E_B^F of bromine and iodine decrease as a function of coverage by 0.2 eV and 0.7 eV, respectively. The E_B^F values found for the condensed molecular species are identical to or even lower by 0.3 eV than for the room temperature saturated bromine and iodine overlayers, respectively.

1. Introduction

The question has been discussed in the literature, whether LEED superstructures observed with halogen adsorption at 300 K on iron or tungsten surfaces are most reasonably explained by dissociative or by molecular adsorption [1, 2]. Our He I and He II UPS results indicate that bromine and iodine are dissociatively adsorbed at 300 K. At $T < 150$ K for bromine and $T < 210$ K for iodine molecular multilayer formation was observed for both halogens following initial dissociative adsorption. As will be shown, the E_B^F values for the molecular species are found to be somewhat smaller than the E_B^F values for the respective atomic species. These rather surprising results can, however, be explained on the basis of a thermodynamic Born-Haber cycle making use of the equivalent cores approximation.

2. Experimental

A full account of the experimental procedures is given elsewhere [3, 4]. The core-level spectra shown here was taken with AlK $_{\alpha}$ radiation and electron binding energies are referred to the Fermi level of the substrate. The experimental resolution in the XPS experiments was ~ 1.1 eV. Exposures given here are not corrected for the different ion-gauge sensitivities S of bromine or iodine, i.e., $S_{Br_2}/S_{N_2} = 1$ and $S_{I_2}/S_{N_2} = 1$.

3. Results

XPS data were taken for the Br 3d, Br 3p $_{3/2}$, Br 3p $_{1/2}$ and Br 3s core levels. Their behaviour as a function of coverage at a given substrate temperature was found to be the same within our experimental resolution. In Fig. 1 the results for the bromine 3p $_{3/2}$ core level binding energy E_B^F and FWHM are shown

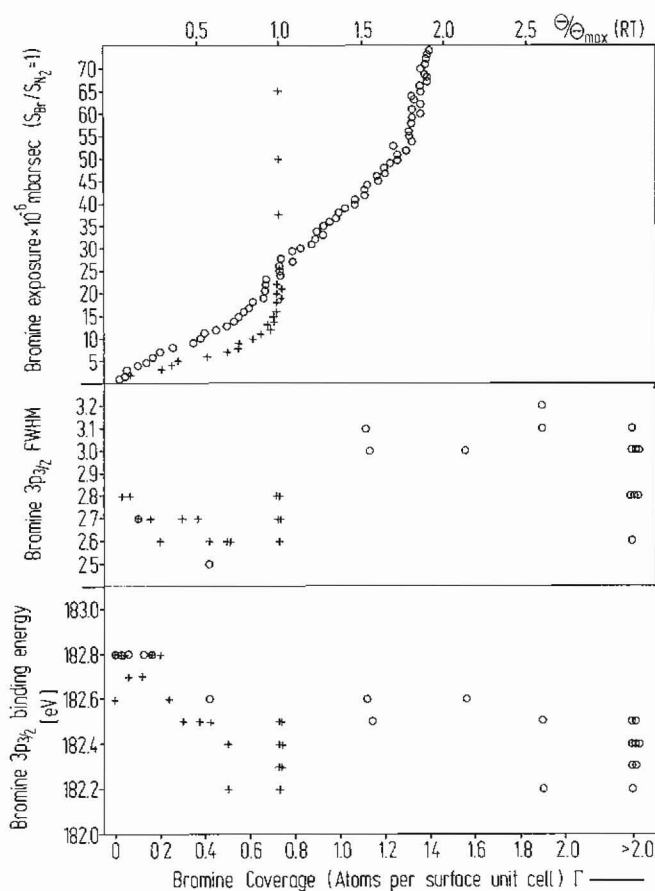


Fig. 1. The upper part of the figure shows bromine coverage at 300 K (+) and 110 K (o) as a function of exposure. In the lower half, the Br 3p $_{3/2}$ core level FWHM and binding energy are displayed as a function of bromine coverage. $\theta/\theta_{max}(RT) = 1$ refers to the room temperature saturated surface, Γ is the bromine coverage in terms of atoms per surface unit cell.

as a function of bromine coverage at 300 K (+) and 110 K (o). In the upper part of the figure, the bromine coverage at 300 K and 110 K as a function of exposure (measured by the Br 3p $_{3/2}$ intensities) is displayed for exposures up to 70×10^{-6} mbar \cdot s. This unusual way of displaying the adsorption curves was chosen to allow a direct comparison between exposure, coverage and core level data. As for the iodine data shown below, the coverage in terms of bromine atoms per surface unit cell was derived from published LEED data [5, 6] and was found to be in good agreement with estimates based on relative core-level intensities. The bromine uptake curve at 300 K

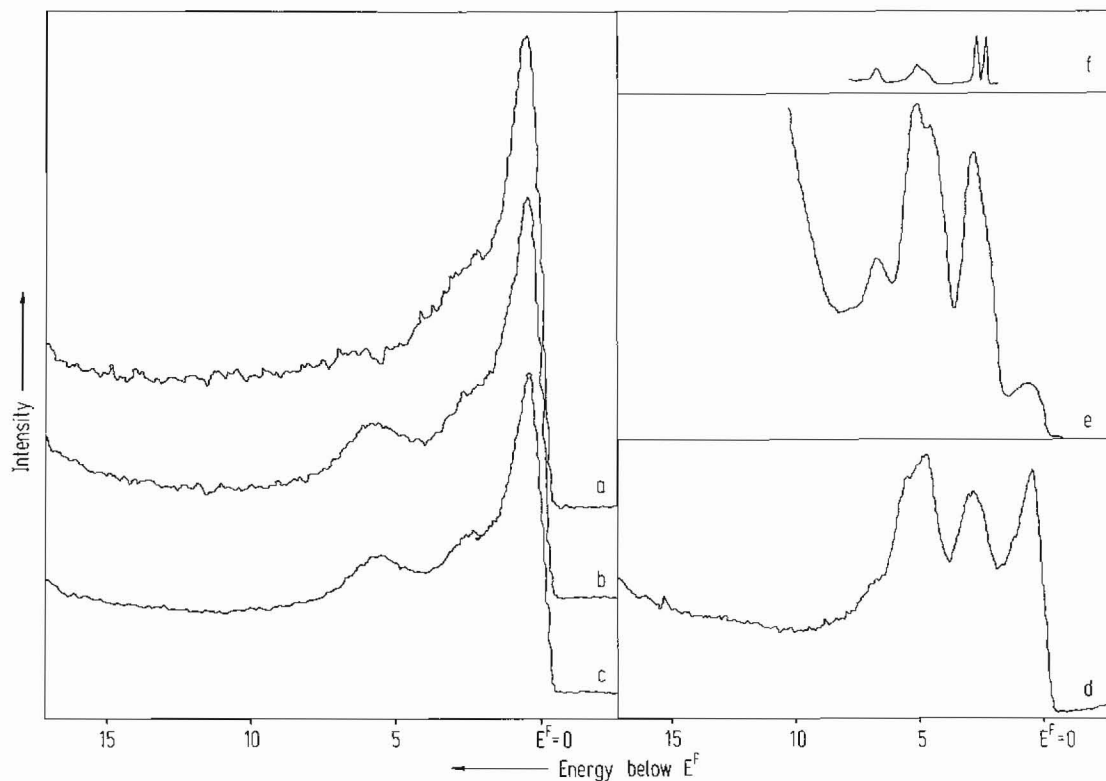


Fig. 2. He II and He I UPS-data for bromine adsorption on Fe(100). (a) Clean Fe(100) surface, (He II). (b) $\theta/\theta_{\max} = 1$ for adsorption at 300 K (He II). (c) $\theta/\theta_{\max} = 1$ for adsorption at 110 K (He II). (d) He II –

spectrum for $\theta/\theta_{\max} = 3$, $T = 110$ K. (e) He I – spectrum for $\theta/\theta_{\max} = 3$, $T = 110$ K. (f) He I – gas phase spectrum of bromine.

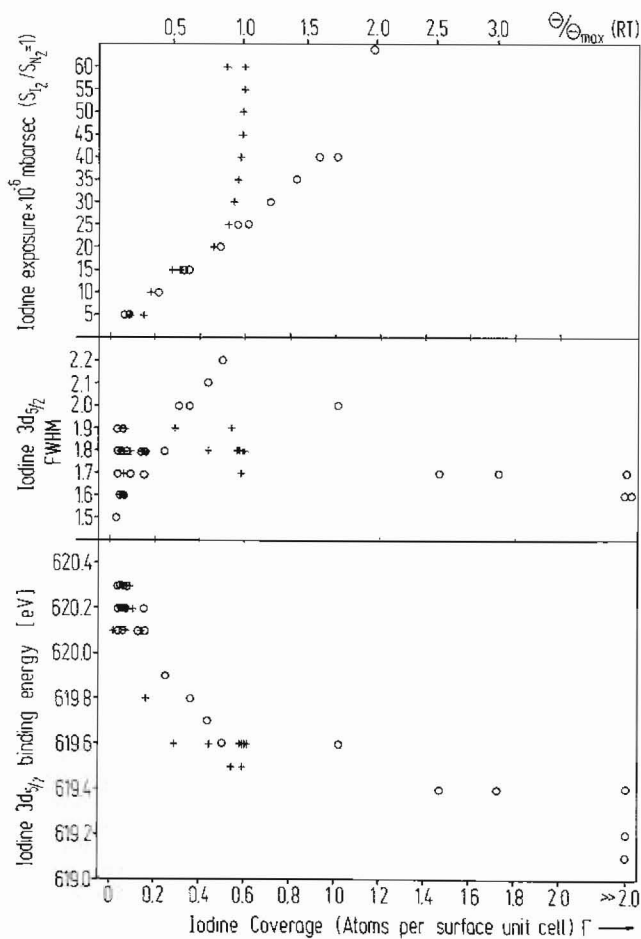


Fig. 3. Iodine uptake curve, iodine $3d_{5/2}$ core level FWHM and binding energy as a function of coverage at 300 K (+) and 130 K (o). $\theta/\theta_{\max}(RT) = 1$ refers to the room temperature saturated surface, Γ is the iodine coverage in terms of atoms per surface unit cell.

is linear almost up to saturation coverage at 300 K ($\Gamma_{\text{sat}} = 0.73 \pm 0.01$) indicating that adsorption proceeds via a mobile precursor state. At 110 K we observe a smaller initial sticking coefficient than for adsorption at 300 K which decreases further when adsorption continues above monolayer coverage. The FWHM for the $\text{Br } 3p_{3/2}$ emission are, within the experimental uncertainties, identical at $\theta/\theta_{\max} < 1$ for adsorption at 300 K and 110 K. Also there is no apparent difference in the slight decrease of the E_{B}^{F} values at 300 K and 110 K for $\theta/\theta_{\max} < 1$. Increasing the coverage above $\theta/\theta_{\max} = 1$ at 110 K seems not to change the core-level binding energy or the FWHM further within our experimental accuracy.

In Fig. 2 we show some representative He II and He I UPS data. Spectrum 2a of the clean Fe(100) surface was taken prior to adsorption at 300 K. Spectrum 2b and 2c both correspond to $\theta/\theta_{\max} = 1$, taken after adsorption at 300 K and 110 K, respectively. Clearly, there is no obvious difference in the two He II-spectra (the same is true for the respective He I data and the difference spectra with respect to the clean surface). This suggests that at both temperatures the chemical state of most of the adsorbate is identical. We identify the single band at 5.3 eV below E_{F} as arising from the bonding (with respect to the surface) $4p_z$ orbital of atomic bromine. Contrary to results obtained on other metal surfaces [7, 8], we cannot detect emission from the $4p_{x,y}$ orbital of the adsorbed bromine atoms. Further exposure at 110 K then leads to the appearance of additional features in the He I and He II data which are easily identified by comparison to gas-phase data as arising from condensed molecular bromine (Fig. 2d, e, f).

The $13d_{5/2}$, $13d_{3/2}$, $14d_{5/2}$ and $14d_{3/2}$ core level emission was followed as a function of coverage. Again, the relative changes in FWHM and E_{B}^{F} are identical for these core-levels and therefore only data for the $13d_{5/2}$ emission are shown in Fig. 3. Contrary to bromine adsorption, the sticking coefficient

is the same for adsorption at 300 K and 130 K up to $\theta/\theta_{\max} = 0.9$. The FWHM is constant over the whole coverage region at 300 K, yet there is a substantial decrease in E_B^F of 0.6 ± 0.1 eV with increasing surface iodine density. The behaviour of the $13d_{5/2}$ binding energy as a function of coverage at 130 K follows the behaviour observed for $\theta/\theta_{\max} < 1$ at 300 K and only decreases slightly further upon multilayer formation. However, we note that for $\theta/\theta_{\max} = 1$ at 130 K the FWHM is ~ 0.4 eV larger than at 300 K and then decreases again with ongoing condensation. This indicates that for adsorption at 130 K molecular iodine species, which have a ~ 1 eV smaller core-level binding energy, are present on the surface at $\theta/\theta_{\max} < 1$ and the increase in FWHM is due to the overlap of two distinct bands separated by ~ 1 eV.

In the UPS data (not shown here) there is no clear difference between an iodine saturated surface at 300 K and at 130 K indicating that the concentration of condensed species is relatively small compared to the atomic species. We are, however, aware of the possibility that a π -bonded bromine or iodine molecule adsorbed on the clean surface might, contrary to the condensed halogens, exhibit UPS-spectra at normal emission which are similar to the spectra of atomic species [9].

4. Discussion

We discuss here the changes in core level binding energies of bromine and iodine with coverage at the two different adsorption temperatures. The general adsorption behaviour of the two halogens is detailed elsewhere [3, 4].

First we address the core-level binding energies observed at 300 K as a function of coverage. The valence-band photoemission data together with other experimental evidence [3, 5, 6] indicate strongly that both bromine and iodine adsorption over the whole coverage range at 300 K is dissociative. The conclusion that only one distinct halogen species populates the surface is also supported by the constant FWHM for adsorption at 300 K. The core level binding energies of bromine and iodine decrease, where for the latter the magnitude of the changes in E_B^F is unique compared to other adsorption systems. From the LEED data it is known that for bromine adsorption a sharp $c(2 \times 2)$ structure is formed at very low coverages [5], while for iodine a sharp $c(2 \times 2)$ overlayer structure is seen only at $\Gamma = 0.5$ [6]. Thus, bromine atoms are in essentially the same

chemical environment at $\Gamma \leq 0.5$ (island formation) while for the iodine atoms the local chemical environment changes continuously until the $c(2 \times 2)$ structure is completed.

The decrease in E_B^F of bromine and iodine with increasing coverage could therefore reflect changes in total initial state energy (see the following discussion of the Born-Haber cycle) or increasing final state screening. This effect will be more pronounced for iodine ($\Delta E_B^F \sim 0.6$ eV) due to the continuous change in interatomic separation at $\Gamma < 0.5$. For bromine, where, as concluded from the LEED data, the atoms seem to be essentially in the same geometric arrangement for $\Gamma \leq 0.5$, a "chemical shift" of the core levels is expected to be absent or less pronounced. In this respect we also note that the core level binding energies for the compressed atomic halogen overlayers are identical to or even lower than the E_B^F values for molecular adsorbed bromine and iodine, respectively. This would be expected if increasing interatomic final state screening is causing the decrease in E_B^F with increasing coverage at 300 K.

The small difference in the core level binding energies for atomically adsorbed bromine and iodine as compared to the molecular multilayers can be explained by a Born-Haber cycle using thermodynamic data and the "equivalent cores" approximation. We have discussed the application of the equivalent cores approximation to adsorbates in detail elsewhere before [10, 11] and therefore give only a brief summary here.

In order to obtain core level binding energies of adsorbates within the equivalent cores approximation, a thermodynamic cycle (Born-Haber cycle) has to be set up for calculating the total initial state and final state energy of the system. Starting from the initial state, which, for atomically adsorbed bromine is a chemisorbed bromine atom, we have to overcome first the adsorption energy E_{chem}^i . Next, the gaseous bromine atom is core-ionized and within the equivalent cores approximation the final state of the ion (Br^*) is replaced by a valence ionized krypton atom (Kr^+). For an adsorbed bromine atom the fully screened final state would be Br^{*-} (core hole plus screening electrons) = Kr (neutral). Thus, in order to neutralize the Br^{*-} ion the ionization energy $I_{(\text{Kr})}^0$ of krypton is released. Finally the krypton atom is adsorbed onto the surface thereby gaining the adsorption energy of krypton. An analogous cycle can be set up for molecular bromine where in the initial state, in addition to the condensation energy, the dissociation energy of molecular bromine has to be taken into account. The final

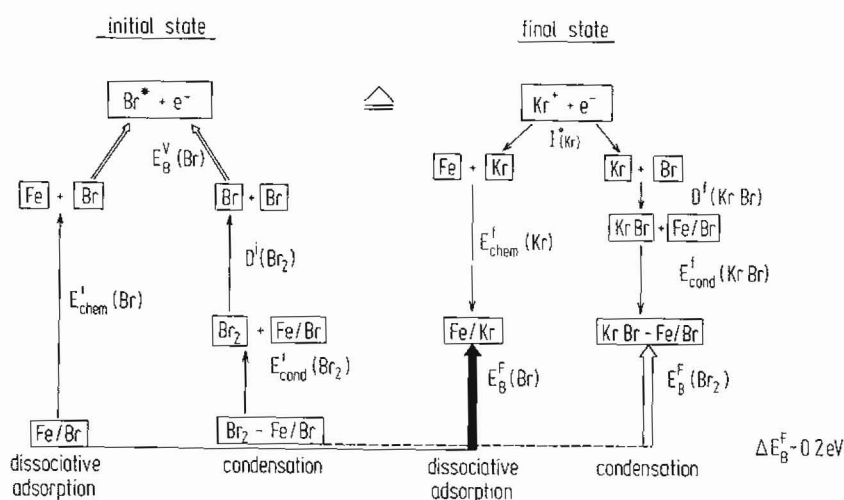


Fig. 4. Born-Haber cycle for dissociative adsorption and condensation of bromine on an Fe(100) surface. Both cycles assume complete screening in the final state.

Table 1. Thermodynamic values used to calculate differences in core-level binding energies of dissociatively and molecularly adsorbed bromine and iodine (energies in eV)

System	E_{chem}^i	E_{cond}^i	D^i	I^0	D^f	E_{chem}^f	E_{cond}^f	
Fe/Br	2.56 ^a			14.0		0.18 ^d		
Fe/Br-Br ₂		0.51 ^b	2.01	14.0	0.2 ^c		0.1 ^f	$\Delta E_{\text{B}}^{\text{F}} \sim 0.2$
Fe/I	2.51 ^a			12.2		0.32 ^e		
Fe/I-I ₂		0.64 ^b	1.58	12.2	0.2 ^c		0.2 ^f	$\Delta E_{\text{B}}^{\text{F}} \sim 0.4$

^a We use the bond strength of an FeBr and FeI molecule [12, 13] as an estimate for E_{chem}^i . Similar values are derived from desorption data [3] for small coverages.

^b Ref. [3].

^c Estimate from $D(\text{ArAr}) = 0.01$ eV and $D(\text{FXe}) = 0.48$ eV.

^d Ref. [14].

^e Ref. [15].

^f Estimates.

state situation for the condensate thus also includes the dissociation energy of a hypothetical KrBr-molecule. The Born-Haber cycle for dissociative bromine adsorption is shown together with the cycle for condensed bromine in Fig. 4.

From Fig. 4 it follows then that with the assumption of complete final state screening the core-level binding energies of dissociatively and molecularly condensed bromine are given by

$$E_{\text{B}}^{\text{F}}(\text{Br}) = E_{\text{chem}}^i(\text{Br}) + E_{\text{B}}^{\text{V}}(\text{Br}) - I^0(\text{Kr}) - E_{\text{chem}}^f(\text{Kr}) \quad (1)$$

and

$$E_{\text{B}}^{\text{F}}(\text{Br}_2) = E_{\text{cond}}^i(\text{Br}_2) + D(\text{Br}_2) + E_{\text{B}}^{\text{V}}(\text{Br}) - I^0(\text{Kr}) - D(\text{KrBr}) - E_{\text{cond}}^f(\text{KrBr}) \quad (2)$$

Thus, the difference $\Delta E_{\text{B}}^{\text{F}} = E_{\text{B}}^{\text{F}}(\text{Br}) - E_{\text{B}}^{\text{F}}(\text{Br}_2)$ can be calculated if the respective thermodynamic values are known. The knowledge of $E_{\text{B}}^{\text{V}}(\text{Br})$ is not required, since this value cancels in the difference of the two binding energies.

Using the thermodynamic values listed in Table I, we find that the core-level binding energies of molecular bromine should be lower by ~ 0.2 eV than the core-level binding energies of an adsorbed bromine atom. For iodine, an analogous cycle via an $I^* \rightarrow \text{Xe}^+$ core exchange predicts a decrease in binding energy of ~ 0.4 eV between an adsorbed iodine atom and a condensed iodine molecule (see Table I).

The agreement between experiment and thermodynamic prediction is good and we therefore conclude that the reason for the unexpected slight decrease in E_{B}^{F} between atomic and molecular species is due to only a small difference in total initial and final state energies for atomic and condensed species in these two adsorption systems.

With reference to the change in E_{B}^{F} with coverage at 300 K we note that a decrease in adsorption energy E_{chem}^i at constant or nearly constant final state adsorption energy E_{chem}^f would result in a decrease in E_{B}^{F} . Unfortunately, the heats of adsorption of bromine, iodine, krypton or xenon as a function of coverage are not known accurately enough to verify such an interpretation.

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