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# Density functional calculations on cation-induced changes in the adsorption of sulphur on Ir<sub>4</sub> clusters

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In this paper we present the results of density functional calculations, including relativistic effects, for sulphur adsorption on a tetrahedral Ir<sub>4</sub> cluster. We used a Vosko–Wilk–Nussair exchange–correlation potential with Stoll and Becke non-local correction. The S atom is found to prefer a twofold coordination. Introducing a Mg<sup>2+</sup> ion at the opposite side of the Ir<sub>4</sub> cluster lowers the adsorption energy for the onefold geometry, but increases it for the threefold geometry. The twofold geometry is influenced only slightly. We analyse the results in terms of the steric repulsion and orbital interactions, as a function of the electronic configuration and the distance between sulphur and the cluster.

## 1. Introduction

The chemical reactivity of small metal clusters is of considerable fundamental as well as practical interest. When dispersed in the micro cavities of zeolites, they form active hydrocarbon conversion catalysts. A common problem in these processes is the rapid poisoning of the catalyst when converting reactants containing traces of sulphur. The resistance against this poisoning, as well as the catalytic activity of the catalyst, has been reported to be a strong function of the cation charge [1–3]. Quantum chemical methods have reached a stage that the basis of this phenomenon can be studied using chemically relevant model systems. Earlier we reported the results of LDA calculations using the X $\alpha$  potential, on the adsorption of H<sub>2</sub>, CO and H on iridium clusters [4–7]. When introducing a cation we found changes in the geometry, the adsorption energy and the stretch frequencies.

The X $\alpha$  method has been shown to give reasonably accurate results for diatomic molecules. But in general, it is found to overestimate the bond energy for carbonyl complexes, whereas bond lengths are predicted somewhat too short. Various improvements have been suggested, mainly concerning a better description of the exchange–correlation potential.

In the calculations we are reporting, we have incorporated some of these.

We studied the adsorption of sulphur on a cluster in three different adsorption geometries and in the presence or absence of the Mg<sup>2+</sup> cation on the opposite side of the cluster. That Mg<sup>2+</sup> will influence the adsorption of sulphur is due to the fact that it will polarize the cluster [5]. Negative charge will develop on the Ir atoms close to the cation, and a reduction of the electron density between the cluster and the adsorbate will result. The way this influences the strength of the bond between adsorbate and the cluster, depends on the extent in which repulsive and interactive forces are affected by the cation. LDA gives us a powerful tool to analyze these often competing changes.

## 2. Method

We have performed restricted calculations using the local density approximation. We used the Amsterdam density functional (ADF) program suite developed by Baerends and coworkers, which is an implementation of the Kohn–Sham equations [8–10]. For the adsorption of sulphur, we followed an approach that differed slightly from our first LDA

calculations. We used the Vosko–Wilk–Nussair (VWN) potential [11], based on homogeneous electron gas calculations, to describe the exchange–correlation energy. Since VWN is known to underestimate the exchange energy and to overestimate the correlation energy, we used the non-local corrections as proposed by Stoll [12], to repair the correlation error, and by Becke [13] to repair the exchange error. Another point where our calculations differ from the former ones is that relativistic effects have been included [14,15]. We used a relativistic frozen core, obtained by Dirac–Slater calculations, and included relativistic effects on the valence electrons as perturbation to first order.

The molecular orbitals are represented as linear combinations of atomic Slater type orbitals. Integrals are computed numerically, using the te Velde integration [16]. Adsorption energies are computed with the Ziegler transition state method [17]. For magnesium the 1s orbital is kept frozen, for sulphur the 1s, 2s, and 2p orbitals, and for iridium electrons up to the 4f. The exponents of the STO basis set for sulphur are shown in table 1. The basis sets for iridium and magnesium can be found in earlier reports [4,5]. The basis sets we used are of double  $\zeta$  quality with a triple  $\zeta$  5d for iridium. Polarization functions have been added for iridium and sulphur. Fig. 1 shows the three Ir<sub>4</sub>–S clusters studied.

The distance between two iridium atoms is taken equal to the nearest neighbour distance in the bulk, 2.71 Å [18]. We found that this is very close to the distance for the geometry optimized Ir<sub>4</sub> cluster. The distance between the iridium atoms and the Mg<sup>2+</sup> ion is taken to be equal to the ionic radius (0.66 Å [19]) plus half the Ir–Ir distance (1.36 Å). With this distance we tried to compromise between a maxi-

Table 1  
Exponential coefficients for basis functions of sulphur

Type	Exp
1s	13.25
2s	5.35
2p	6.25
3s	1.60
3s	2.60
3p	1.15
3p	2.15
3d	2.20

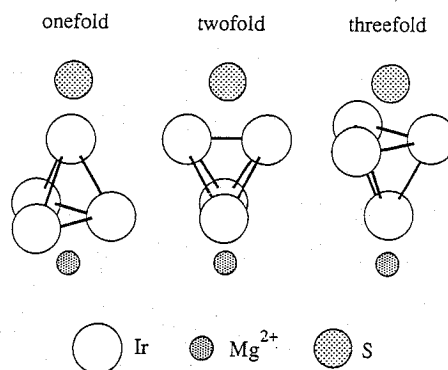


Fig. 1. Structures of the three Mg<sup>2+</sup>Ir<sub>4</sub>–S systems that have been studied. The structures of the Ir<sub>4</sub>–S systems are the same except for the Mg<sup>2+</sup> ion which is absent.

imum influence on the S adsorption and still retaining the ionic character of Mg<sup>2+</sup>. The distance between the S atom and the cluster has been optimized. The Mg<sup>2+</sup> ion is located on the opposite side of the cluster where the sulphur is adsorbed. Earlier we reported that we had to reckon with a numerical error in the calculations of about 0.1 eV.

### 3. Results and discussion

Before discussing the Ir<sub>4</sub>–S results we will briefly address the results of the calculations on single Ir atoms to show the changes related with the new exchange–correlation potentials and the relativistic corrections. We found that a non-relativistic calculation gave d<sup>9</sup> as ground state (which was also found in X $\alpha$  calculations [5]), whereas the calculations with the relativistic corrections show a preference for a d<sup>8</sup>s<sup>1</sup> state (which was 0.7 eV lower in energy than d<sup>7</sup>s<sup>2</sup>, the true ground state). When doing an unrestricted calculation for iridium we found that the energies of d<sup>7</sup>s<sup>2</sup> and d<sup>8</sup>s<sup>1</sup> are very close. LDA with non-local and relativistic corrections seems to give a better description of a single iridium atom than calculations with the X $\alpha$  potential. An unrestricted calculation for the S atom shows an energy of –0.72 eV with respect to the restricted state. We observed no significant changes in unrestricted calculations for the closed shell fragments Ir<sub>4</sub> and Mg<sup>2+</sup>. We found that relativistic corrections for sulphur and magnesium are much smaller than for iridium, as expected.

We incorporated the relativistic corrections for all atoms.

Table 2 summarizes the results of sulphur adsorption for the optimized geometries with the electron configuration of the ground state. The adsorption energies are defined as

$$\Delta E_{\text{ads}} = E(\text{Ir}_4\text{S}) - E(\text{S}),$$

for the calculation without the  $\text{Mg}^{2+}$  ion, and as

$$\Delta E_{\text{ads}} = E(\text{Mg}^{2+} - \text{Ir}_4\text{S}) - E(\text{Mg}^{2+} - \text{Ir}_4) - E(\text{S}),$$

for the calculation with the  $\text{Mg}^{2+}$  ion. The difference between restricted and unrestricted sulphur has been included in the tables in  $\Delta E_{\text{ads}}$ , but not in its decomposition, which is with respect to the restricted state. We see that the S atom has a preference for the twofold adsorption site. The adsorption energies for the onefold and the threefold position are very close, however.

We see for the onefold geometry that the ion is destabilizing the bond. For the twofold geometry we see no change in adsorption energy, whereas we can see for the threefold geometry that  $\text{Mg}^{2+}$  is stabilizing the bond. We also see that for the two- and the three-fold geometry the distance between the cluster and the S atom is decreased by approximately 0.12 Å. For the onefold geometry the adsorption distance is changed only slightly.

We also calculated  $\text{Ir}_4$ -S stretch frequencies. For all geometries we found that the stretch frequency decreases upon introduction of the  $\text{Mg}^{2+}$  ion, as was also found for  $\text{H}_2$  and CO. We did not find experi-

mental values for these vibrations. However, our values are of comparable magnitude as calculated S stretch frequencies on nickel clusters [20].

In order to understand the site dependence and the effect of  $\text{Mg}^{2+}$  we have decomposed the adsorption energy into two main contributions [21]:

$$\Delta E_{\text{ads}} = \Delta E_{\text{steric}} + \Delta E_{\text{int}}.$$

Here  $\Delta E_{\text{steric}}$  is defined as the energy change due to superposition of  $\text{Ir}_4$  and S without changing their molecular orbitals. It can be split in an electrostatic and an exchange repulsion contribution

$$\Delta E_{\text{steric}} = \Delta E_{\text{elstat}} + \Delta E_{\text{xrep}} + \Delta E_{\text{rest}}.$$

The term  $\Delta E_{\text{rest}}$  contains the non-local Becke correction, which is for the systems studied almost constant. The second term in the decomposition of  $\Delta E_{\text{ads}}$  is the interaction energy, which gives the energy change due to orbital relaxation. It can be split into various symmetries

$$\Delta E_{\text{int}} = \Delta E_{\sigma} + \Delta E_{\pi} + \Delta E_{\delta} + \Delta E_{\text{rest}}.$$

The point group symmetry is  $C_{3v}$  for the one- and the three-fold geometry, and is  $C_{2v}$  for the twofold geometry. With  $\sigma$  we mean  $a_1$ , and with  $\delta$  we mean  $a_2$  for both point group symmetries. With  $\pi$  we mean e symmetry in  $C_{3v}$  and  $b_1$  and  $b_2$  in  $C_{2v}$  (in that case we will refer to it as  $\pi_1$  and  $\pi_2$ , respectively). The Becke correction ( $\Delta E_{\text{rest}}$ ) is again almost constant.

The decomposition of the adsorption energy for the ground state of the geometry optimized systems is shown in columns II and V of tables 3, 4 and 5.

Table 2

Calculated properties for  $\text{Ir}_4$ -S and  $\text{Mg}^{2+}\text{Ir}_4$ -S: electronic configuration of the ground state, geometrical parameters, adsorption energies, and  $\text{Ir}_4$ -S stretch frequencies. Energies include Becke, Stoll and relativistic corrections, and the difference between restricted and unrestricted sulphur (0.72 eV)

		Geometry		
		onefold	twofold	threefold
$\text{Ir}_4$ -S	electronic configuration	$a_1^{13}a_2^1e^{28}$	$a_1^{16}a_2^6b_1^{10}b_2^{10}$	$a_1^{12}a_2^2e^{28}$
	$d(\text{Ir-S})$ (Å)	2.15	2.37	2.54
	$\Delta E_{\text{ads}}$ (eV)	-3.07	-3.47	-2.94
	$\omega$ ( $\text{cm}^{-1}$ )	550	710	355
$\text{Mg}^{2+}\text{Ir}_4$ -S	electronic configuration	$a_1^{17}a_2^3e^{31}$	$a_1^{20}a_2^6b_1^{12}b_2^{12}$	$a_1^{18}a_2^3e^{30}$
	$d(\text{Ir-S})$ (Å)	2.12	2.25	2.42
	$\Delta E_{\text{ads}}$ (eV)	-2.60	-3.47	-3.88
	$\omega$ ( $\text{cm}^{-1}$ )	480	310	305

Table 3

Onefold geometry: decomposition of steric repulsion and interaction energy into various symmetries as defined in the text (in eV). Energies include Stoll and relativistic corrections.  $\Delta E_{\text{steric}}$ ,  $\Delta E_{\text{int}}$ , and  $\Delta E_{\text{ads}}$  also include Becke correction and the difference between restricted and unrestricted sulphur

	Without Mg <sup>2+</sup>		With Mg <sup>2+</sup>		
	I	II	III	IV	V
electronic configuration	$a_1^{13.33} a_2^{26.67}$	$a_1^{13} a_2^{28}$	$a_1^{17.33} a_2^{30.67}$	$a_1^{17} a_2^{31}$	$a_1^{17} a_2^{31}$
$d(\text{Ir-S})$ (Å)	2.15	2.15	2.15	2.15	2.12
$\Delta E_{\text{elstat}}$	-6.46	-6.46	-4.94	-4.94	-5.43
$\Delta E_{\text{xrep}}$	9.79	9.79	7.82	7.82	8.68
$\Delta E_{\text{steric}}$	4.44	4.44	3.93	3.93	4.33
$\Delta E_{\sigma}$	-4.03	-2.48	-3.41	1.48	1.37
$\Delta E_{\pi}$	-4.99	-10.04	-4.41	-9.24	-9.53
$\Delta E_{\delta}$	0.00	3.96	0.00	0.00	0.00
$\Delta E_{\text{int}}$	-8.45	-8.23	-7.30	-7.23	-7.65
$\Delta E_{\text{ads}}$	-3.29	-3.07	-2.66	-2.59	-2.60

Table 4

Twofold geometry: decomposition of steric repulsion and interaction energy as in table 3

	Without Mg <sup>2+</sup>		With Mg <sup>2+</sup>		
	I	II	III	IV	V
electronic configuration	$a_1^{17.33} a_2^6 b_1^{9.33} b_2^{9.33}$	$a_1^{16} a_2^6 b_1^{10} b_2^{10}$	$a_1^{21.33} a_2^6 b_1^{13.33} b_2^{13.33}$	$a_1^{20} a_2^6 b_1^{12} b_2^{12}$	$a_1^{20} a_2^6 b_1^{12} b_2^{12}$
$d(\text{Ir-S})$ (Å)	2.37	2.37	2.37	2.37	2.25
$\Delta E_{\text{elstat}}$	-10.44	-10.44	-8.35	-8.35	-11.78
$\Delta E_{\text{xrep}}$	16.53	16.53	13.79	13.79	19.76
$\Delta E_{\text{steric}}$	7.47	7.47	6.79	6.79	9.53
$\Delta E_{\sigma}$	-5.38	-0.76	-5.26	12.57	11.26
$\Delta E_{\pi_1}$	-3.60	-6.26	-3.51	-12.61	-13.57
$\Delta E_{\pi_2}$	-2.26	-4.97	-2.05	-11.33	-11.84
$\Delta E_{\delta}$	-0.20	-0.21	-0.15	-0.15	-0.26
$\Delta E_{\text{int}}$	-10.89	-11.66	-10.34	-10.86	-13.72
$\Delta E_{\text{ads}}$	-2.70	-3.47	-2.83	-3.35	-3.47

Apart from the steric repulsion and the orbital relaxation these columns also contain the effect of a change in the electronic configuration when the S atom is brought close to the cluster. This leads to  $\Delta E_{\delta} = 3.96$  eV for the onefold adsorption without Mg<sup>2+</sup>, even though no orbitals of  $\delta$  symmetry form chemical bonds. Moreover, when comparing systems with and without Mg<sup>2+</sup> we have an effect of the change in the Ir-S distance.

In order to split off these effects we performed calculations on intermediately configured systems. Columns I show the results for the system without

the cation, that differs from the optimized system only in that it has the electronic configuration of the ground state for S at infinity. For example, for the onefold geometry we did a calculation with the configuration  $a_1^{13.33} a_2^{26.67}$ , being the combined configuration of Ir<sub>4</sub> ( $a_1^{10} a_2^{24}$ , which is derived from  $a_1^4 e^8 t_1^6 t_2^8$  in T<sub>d</sub> symmetry by reducing the representations), and sulphur ( $a_1^{3.33} e^{2.67}$ , which is derived from  $s^2 p^4$ ). Although it does not comply completely with the basic idea of Kohn and Sham, it can be very instructive to work with fractional occupation numbers. We have separated now the effects of the shifts

Table 5

Threefold geometry: decomposition of steric repulsion and interaction energy as in table 3

	Without Mg <sup>2+</sup>		With Mg <sup>2+</sup>		
	I	II	III	IV	V
electronic configuration	a <sub>1</sub> <sup>13.33</sup> a <sub>2</sub> <sup>2</sup> e <sup>26.67</sup>	a <sub>1</sub> <sup>12</sup> a <sub>2</sub> <sup>2</sup> e <sup>28</sup>	a <sub>1</sub> <sup>18.33</sup> a <sub>2</sub> <sup>2</sup> e <sup>29.67</sup>	a <sub>1</sub> <sup>18</sup> a <sub>2</sub> <sup>2</sup> e <sup>30</sup>	a <sub>1</sub> <sup>18</sup> a <sub>2</sub> <sup>2</sup> e <sup>30</sup>
d(Ir-S) (Å)	2.54	2.54	2.54	2.54	2.42
ΔE <sub>elstat</sub>	-9.22	-9.22	-8.08	-8.08	-11.57
ΔE <sub>xrep</sub>	14.79	14.79	14.19	14.19	20.39
ΔE <sub>steric</sub>	7.02	7.02	7.50	7.50	10.45
ΔE <sub>σ</sub>	-4.31	0.21	-5.41	-1.54	-2.76
ΔE <sub>π</sub>	-6.28	-11.53	-6.44	-10.98	-12.85
ΔE <sub>δ</sub>	-0.03	-0.03	-0.02	-0.02	-0.05
ΔE <sub>int</sub>	-9.94	-10.68	-11.32	-11.97	-15.05
ΔE <sub>ads</sub>	-2.20	-2.94	-3.10	-3.75	-3.88

of the molecular orbital levels on the one hand (columns I), and the effect of electron transfer on the other (change from columns I to II). The decomposition shows clearly the various symmetry contributions to the interactions. We see in columns I that for the Ir<sub>4</sub>-S system the interactions are, as expected, predominantly with the σ and π orbitals for all geometries; with the π interactions somewhat stronger. The change in electronic configuration lowers ΔE<sub>ads</sub> only substantially for high coordination sites. For the onefold adsorption the configuration with fractional occupation number is slightly more stable. This is a consequence of the fact that we use an approximation for the exchange-correlation potential [22]. We conclude that the optimization of the electronic configuration for onefold adsorption has little effect. The steric repulsion in columns I and II are necessarily the same as they relate only to the orbitals of the Ir<sub>4</sub> and the S atom, and not to the final orbitals.

For the systems with Mg<sup>2+</sup> we did comparable calculations. Columns III show results of calculations that differ from the ones in columns IV only in electronic configuration. For the onefold geometry we did a calculation with the configuration a<sub>1</sub><sup>17.33</sup>a<sub>2</sub><sup>2</sup>e<sup>30.67</sup>, being the combined configuration of the ground state of fragment Mg<sup>2+</sup>Ir<sub>4</sub> (a<sub>1</sub><sup>14</sup>a<sub>2</sub><sup>2</sup>e<sup>28</sup>) and sulphur (a<sub>1</sub><sup>3.33</sup>e<sup>2.67</sup>). The Ir-S distance in columns III and IV is the same as in the systems without Mg<sup>2+</sup>. Again we see (columns III) that the interaction is with the π orbitals, and to a somewhat lesser extent with the σ orbitals. The effect of the change of the

electronic configuration is the same as without Mg<sup>2+</sup>.

The difference between columns IV and V is the relaxation of the Ir-S bond, which lowers the adsorption energy for the twofold and threefold geometry by approximately 0.1 eV, involving a decrease of the bond length of about 0.12 Å. Such a reduction in adsorbate-metal distance has also been found before for H<sub>2</sub>, resulting from the reduction in electron density between adsorbate and metal atom [4]. For onefold geometry these changes are almost negligible. The contribution to the adsorption energy from the optimization of the bond length is rather small; the decomposition, however, changes a lot. As expected the steric repulsion increases, but this is compensated by a more favourable interaction of especially the π orbitals.

Fig. 2 shows sulphur s, p<sub>σ</sub>, p<sub>π</sub> local density of states (LDOS) for the threefold geometries. We see that there is only one large peak for sulphur s orbitals, whereas the p<sub>σ</sub> and p<sub>π</sub> orbitals show a broad band. These plots are characteristic for all geometries. They indicate that the bonding is mainly a result of interaction with the sulphur p<sub>σ</sub> in combination with the sulphur p<sub>π</sub> orbitals. For twofold adsorption the plots for the two p<sub>π</sub> orbitals differ. This is because the p<sub>x</sub>, which points in the direction of the two closest iridium atoms, interacts strongly. The p<sub>y</sub> orbital on the other hand, perpendicular to the line connecting the two closest iridium atoms, interacts less.

As the change in Ir-S distance when Mg<sup>2+</sup> is added has only a small effect on the adsorption energy we

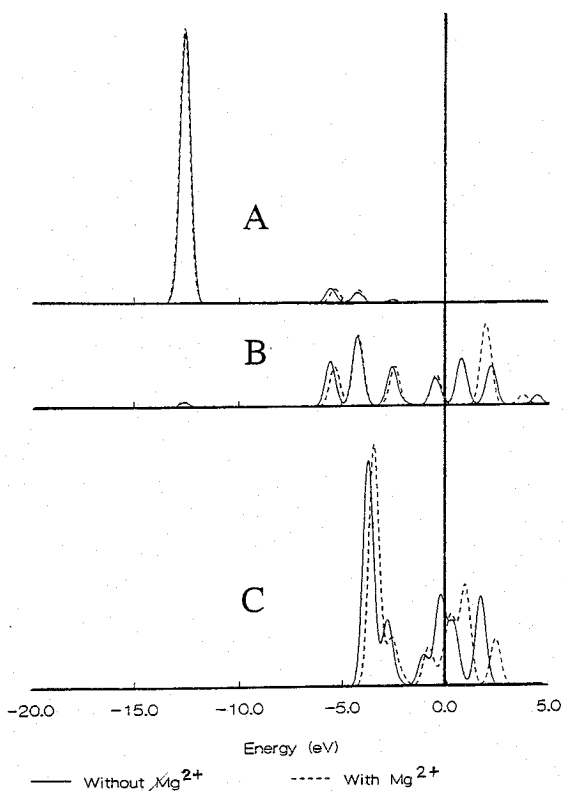


Fig. 2. Local density of states plots for the threefold geometry: LDOS of the sulphur s orbital (A), of the  $p_z$  orbital (B), and of the  $p_x$  orbitals (C). Energies are with respect to the Fermi level.

look at the effect of  $Mg^{2+}$  by comparing columns II and IV. For one- and two-fold adsorption we see the same trend as we found in previous studies [4–7]. The cation polarizes the  $Ir_4$  cluster, thus decreasing the electron density at the site where the S atom adsorbs. This reduces the steric repulsion, but also the interaction between the cluster and the S atom. The two effects tend to cancel. This is indeed the case for the twofold adsorption. For onefold adsorption the interaction energy is reduced more than the steric repulsion so that the net effect is a smaller adsorption energy. The relative importance of the  $\sigma$  and  $\pi$  interactions does not change.

The threefold adsorption is different. The steric repulsion increases. As for the other sites it changes, because the exchange repulsion and the electrostatic interaction both decrease in absolute value. Usually the effect in the exchange repulsion dominates, but for threefold adsorption the electrostatic change is

more important. At the same time the interaction energy increases; primarily via the  $\sigma$  orbitals. The net effect is an increased adsorption energy. Such an increase we have found before for  $H_2$  adsorption [4]. However, there this increase was accompanied by a large change in geometry. Apparently, the effect of  $Mg^{2+}$  for threefold adsorption is not just electrostatic, but the cation also changes the chemical bond between  $Ir_4$  and S in a qualitative way.

Additional information on the nature of the bonding is given by density difference plots. The plots for the twofold geometry with and without the cation are shown in figs. 3 and 4. We see in fig. 3 an increase of the electron density in the region of the sulphur  $p_\pi$  orbitals, and a decrease just below the S atom. The increase in the  $p_\pi$  region indicates the formation of bonding orbitals of the  $p_x$  orbital. The decrease just below the S atom points to a reduction of the steric repulsion between the partially filled  $p_z$  orbital and filled cluster orbitals. Such an effect we found previously for CO adsorption [5,7]. In fig. 4 we do not see the decrease just below the S atom because

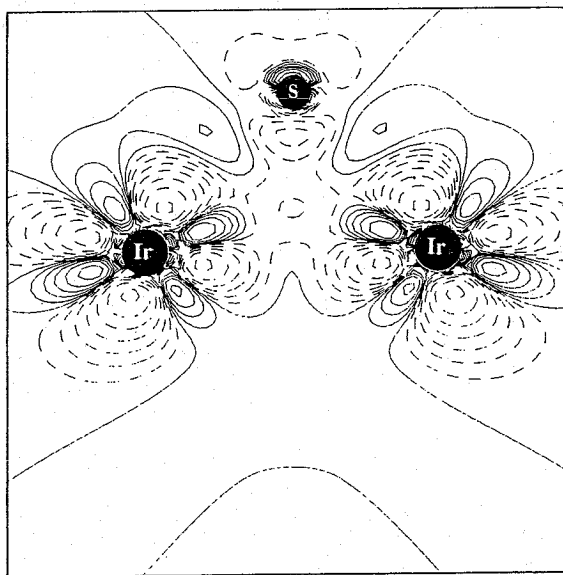


Fig. 3. Contour plot of the electron density difference  $\rho(Ir_4-S) - \rho(Ir_4) - \rho(S)$  for twofold adsorption. Dashed lines show a decrease and solid lines an increase of the electron density, except for the solid lines near the dashed lines which depict nodal surfaces. Subsequent contours correspond to  $\pm 0.020$ ,  $\pm 0.041$ ,  $\pm 0.081$ ,  $\pm 0.128$ ,  $\pm 0.223$ ,  $\pm 0.365$ ,  $\pm 0.601$ ,  $\pm 0.993$ ,  $\pm 1.641$  electrons/ $\text{\AA}^3$ .

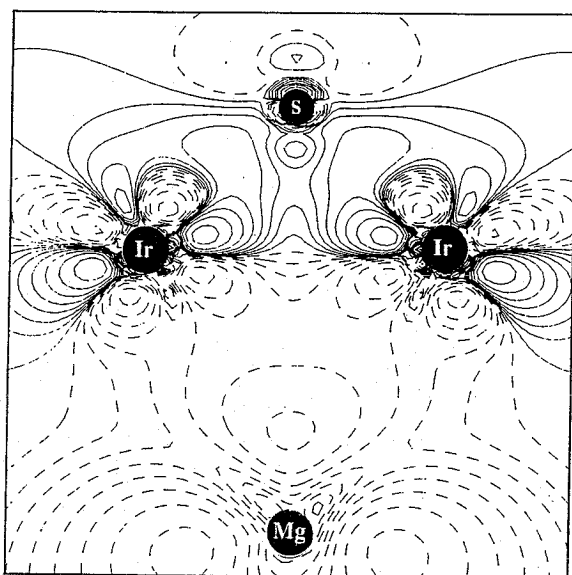


Fig. 4. Contour plot of the electron density difference  $\rho(\text{Mg}^{2+}\text{Ir}_4\text{-S}) - \rho(\text{Mg}^{2+}\text{Ir}_4) - \rho(\text{S})$  for twofold adsorption. Values at the contours as in fig. 3.

the cation polarizes the cluster, thus decreasing the electron density and the steric repulsion at the site where the S atom adsorbs. The interaction with the metal d orbitals is also very clear from the cloverleaf structure in this picture. The polarization due to the cation is substantial, as can be seen by comparing the two figures.

Another way to analyze the adsorption is to pro-

mote fragments so that electrons already occupy orbitals of the same symmetry as in the final system. The main advantage of this analysis is that the decomposition of the interaction energy directly reflects the orbitals that form chemical bonds. Misleading results as  $\Delta E_{\delta} = 3.96$  eV for onefold  $\text{Ir}_4\text{-S}$  are not found. The results for the threefold geometry for the systems without and with the cation are given in table 6. We promoted the fragments by primarily rearranging the degenerate sulphur p electrons, thus keeping the promotion energy minimal. For the system without the cation we promoted the S atom from  $a_1^{3.33}e^{2.67}$  to  $a_1^2e^4$ , which combines with  $\text{Ir}_4$  ( $a_1^{10}a_2^2e^{24}$ ) to the ground state configuration of  $\text{Ir}_4\text{-S}$  ( $a_1^{12}a_2^2e^{28}$ ). The corresponding energy cost was 0.72 eV. For the system with the cation, the sulfur was promoted to  $a_1^3e^3$ , which costed only 0.04 eV. We see that the steric repulsion and its decomposition change, because of the different fragment electron configuration. The steric repulsion of the system with  $\text{Mg}^{2+}$  is much larger than for the system without  $\text{Mg}^{2+}$ , because the  $p_{\sigma}$  orbital of S is (partially) occupied. The system with  $\text{Mg}^{2+}$  shows also a much larger  $\pi$  interaction. As  $\text{Ir}_4\text{-S}$  has one more  $\pi$  electron, the smaller  $\pi$  interaction indicates that this electron occupies on anti-bonding orbital. Consequently, the interaction must be with filled  $\text{Ir}_4$   $\pi$  orbitals. This result is less important for one- and two-fold adsorption, because of the smaller overlap of the  $\pi$  orbitals. This may explain the difference between one- and two-fold adsorption on the one, and three-

Table 6

Threefold geometry: decomposition of steric repulsion and interaction energy into various symmetries for optimized systems from table 5, built from promoted fragments (in eV). Results for systems from columns II and IV from table 5, which are built from ground state fragments, are given for comparison

	Without $\text{Mg}^{2+}$		With $\text{Mg}^{2+}$	
	promoted fragments with ( $\text{S}a_1^2e^4$ )	ground state fragments	promoted fragments with ( $\text{S}a_1^3e^3$ )	ground state fragments
$\Delta E_{\text{elstat}}$	-7.34	-9.22	-7.55	-8.08
$\Delta E_{\text{xrep}}$	9.98	14.79	13.55	14.19
$\Delta E_{\text{steric}}$	4.14	7.02	7.39	7.50
$\Delta E_{\sigma}$	-6.83	0.21	-6.65	-1.54
$\Delta E_{\pi}$	-2.44	-11.53	-5.83	-10.98
$\Delta E_{\delta}$	-0.05	-0.03	-0.03	-0.02
$\Delta E_{\text{int}}$	-8.47	-10.68	-11.89	-11.97
$\Delta E_{\text{ads}}$	-3.60	-2.94	-3.78	-3.75



fold adsorption on the other hand.

We finally want to make some comparisons between our results and experimental results. Chan and Weinberg [23] found with LEED spectroscopy an Ir-S bond length of 2.28 Å for a threefold coordinated position. McCarty and Wise [24] published heats of adsorption from equilibrium measurements and found for sulphur on alumina-supported iridium  $\Delta H_f^\theta = -219$  to  $-149$  kJ mol<sup>-1</sup>. In view of the probable differences between the experimentally studied system and ours we think that our results are in good agreement with these results.

#### 4. Conclusions

We have performed density functional calculations using the Vosko-Wilk-Nussair exchange-correlation potential, including non-local and relativistic corrections, on the adsorption of sulphur on a tetrahedral Ir<sub>4</sub> cluster. We have studied the influence of a Mg<sup>2+</sup> ion at the opposite end of the cluster with the S atom adsorbed in three different geometries. We analyzed the results in terms of the steric repulsion and orbital interactions, as a function of the electronic configuration and the distance between sulphur and the cluster. This gave us a tool to obtain from the decomposition of the interaction energy the contributions of orbitals of the various symmetries.

We have found adsorption energies for the cluster without the cation between  $-3.0$  eV for one- and three-fold geometries and  $-3.5$  eV for the twofold geometry. These values are in good agreement with values found from equilibrium measurements [24]. The bonding between the metal cluster and the S atom is found to be mainly caused by interaction with the p orbitals of sulphur; the interaction of p<sub>π</sub> is slightly stronger than p<sub>σ</sub>. The s orbitals do not play a role in the bond formation. The effect of introducing the Mg<sup>2+</sup> is geometry dependent. The bond strength of the onefold geometry is weakened, whereas that of the threefold geometry is strengthened. The effect on the adsorption energy of the twofold geometry is small. For the two- and three-fold geometries the distance between the S atom and the metal is decreased by approximately 0.12 Å. For the onefold geometry the bond length remains almost unchanged.

In previous papers, studying the adsorption of H<sub>2</sub>, CO, and H, we have explained the changes in the adsorption due to Mg<sup>2+</sup>, with a relatively simple electrostatic model. We could do this because the Mg<sup>2+</sup> electrostatic field was dominating the changes. In the present study of sulphur the influence of the cation appears to be very similar for the one- and the twofold geometry. For the threefold geometry however, chemical bonding effects are more important, which forced us to a more extensive analysis. The changes for threefold adsorption can be explained using a promoted S atom which has for this geometry a more favourable π interaction with Ir<sub>4</sub> when Mg<sup>2+</sup> is present. The overall finding is that the S bondstrength increases when a cation is added. This is compatible with the observed larger S sensitivity for metal particles in close contact with Ba<sup>2+</sup> ions [3].

#### References

- [1] M. Boudart and G. Djega-Mariadassou, in: Proceedings of the 3rd International Congress on Catalysis, Vol. 2, eds. W.M.H. Sachtler, G.C.A. Schuit and P. Zwietering (North-Holland, Amsterdam, 1965).
- [2] P. Gallezot, *Catal. Rev. Sci. Eng.* 20 (1979) 121.
- [3] T.R. Hughes, W.C. Buss, P.W. Tamm and R.L. Jacobson, in: Proceedings of the 7th International Zeolite Conference, eds. Y. Murakami, A. Iijima and J.W. Ward (Elsevier, Amsterdam, 1986).
- [4] E. Sanchez Marcos, A.P.J. Jansen and R.A. van Santen, *Chem. Phys. Letters* 167 (1990) 399.
- [5] A.P.J. Jansen and R.A. van Santen, *J. Phys. Chem.* 94 (1990) 6764.
- [6] W. Biemolt, A.P.J. Jansen and R.A. van Santen, *Chem. Phys. Letters* 180 (1991) 95.
- [7] A.P.J. Jansen and R.A. van Santen, in: Structure activity relationships in heterogeneous catalysis, eds. R.K. Grasselli and A.W. Sleight (Elsevier, Amsterdam, 1991).
- [8] E.J. Baerends, D.E. Ellis and P. Ros, *Chem. Phys.* 2 (1973) 41.
- [9] P.M. Boerrigter, G. te Velde and E.J. Baerends, *Int. J. Quantum Chem.* 33 (1988) 87.
- [10] G. te Velde and E.J. Baerends, *J. Comput. Phys.*, in press.
- [11] S.H. Vosko, L. Wilk and M. Nussair, *Can. J. Phys.* 58 (1980) 1200.
- [12] H. Stoll, C.M.E. Pavlidou and H. Preuss, *Theoret. Chim. Acta* 49 (1978) 143.
- [13] A.D. Becke, *Phys. Rev. A* 38 (1988) 3098.
- [14] J.G. Snijders and E.J. Baerends, *Mol. Phys.* 36 (1978) 1789.
- [15] J.G. Snijders, E.J. Baerends and P. Ros, *Mol. Phys.* 38 (1979) 1909.

- [16] G. te Velde, Ph.D. Thesis (Free University of Amsterdam, Amsterdam, 1990).
- [17] T. Ziegler and A. Rauk, *Theoret. Chim. Acta* 46 (1977) 1.
- [18] R.W.G. Wychoff, *Crystal structures*, Vol. 1, 2nd Ed. (Wiley, New York, 1963).
- [19] R.C. Weast, ed., *Handbook of Chemistry and Physics*, 64th Ed. (CRC Press, Boca Raton, 1983).
- [20] T.H. Upton and W.A. Goddard III, *CRC Crit. Rev. Solid State Mater. Sci.* 10 (1981) 261.
- [21] D. Post and E.J. Baerends, *J. Chem. Phys.* 78 (1983) 5663.
- [22] J.P. Perdew, in: *Density functional methods in physics*, eds. R.M. Dreizler and J. da Providencia (Plenum Press, New York, 1985).
- [23] C.-M. Chan and W.H. Weinberg, *J. Chem. Phys.* 71 (1979) 3988.
- [24] J.G. McCarty and H. Wise, *J. Catal.* 94 (1985) 543.