CALCULATION OF PHYSISORPTION ENERGIES OF DIPOLAR MOLECULES ON α-Fe_2O_3 (III) SURFACE USING A CRYSTAL FIELD CLUSTER MODEL

A. Uzairu* and G.F.S. Harrison
Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria

ABSTRACT

A complete electrostatic intermolecular potential

$$U(R,\beta,r,\theta,\phi)=-\sum_{k=0}^{\infty}\sum_{j}\left(\frac{\mu C_k(R,r_j,\theta_j,\phi_j)}{R^2}\cos\beta+\frac{\mu\mu_k(R,r_j,\theta_j,\phi_j)}{R^3}\sin\beta\right)$$
$$+\sum_{k=0}^{\infty}\sum_{j}\frac{\mu Q_k(R,r_j,\theta_j,\phi_j)}{R^4}f_k(R,r_j,\theta_j\phi_j)\cos\beta$$

has been developed from a single zero-overlap physical theory, without recourse to adhoc procedures or invocation of 'chemical' interaction to account for the repulsive part, for use in the calculation of physisorption energies of dipolar molecules on ionic solid surfaces. The second sum is the zero-overlap repulsion energy term; this potential has been used to calculated the H_2O^+, H_2O, HO^- and NH_3 physisorption energies at an oxygen vacant site on the (III) surface of α-Fe_2O_3. The values obtained are found to be satisfactory.

INTRODUCTION

Adsorption on transition metal oxide surfaces is of considerable interest in industry and theoretical calculations of chemisorptive and physisorptive binding energies on the surfaces of these oxides have been done[1-2]. However, inspite of its industrial importance α-Fe_2O_3 surface has received relatively little attention. In addition, the treatment of physisorption on solid surfaces, especially the surface - adsorbate van der Waals interaction potential, is unsatisfactory in some respect. A potential of the form

$$\Delta U(R)=\Delta E_{lr,pair}(R)+\phi(R) \quad \ldots(1)$$

has been in common use for van der Waals type interactions. $\Delta E_{lr,pair}(R)$ is the long-range attractive part that consists of electrostatic (ΔE_{es}), induction (ΔE_{ind}), and dispersion (ΔE_{disp}) energy terms. Thus

$$\Delta E_{lr,pair}(R)=\Delta E_{es}(R)+\Delta E_{ind}(R)+\Delta E_{disp}(R) \quad \ldots\ldots(2)$$

The long-range attractive components in (2) have firm theoretical basis[3-8]. The repulsive term $\phi(R)$, i.e. second term in (1), has been more difficult to represent without recourse to specific models. Even in the more recent treatments[9-11] of van der Waals potential, a unified treatment of the attractive and repulsive parts of the physisorptive forces was not presented. However the repulsive term $\phi(R)$ has been treated by various workers phenomenologically and quantum mechanically in the literature. A good summary of the semi-empirical analytic forms for $\phi(R)$ may be found in a paper by Kumar and Shanker[12]. Quantum mechanically, it has been shown[9-11,13] that $\phi(R)$ could arise as a result of electronic exchange between the surface and adsorbate at short distances. Such calculations are not yet readily available for surface-adsorbate interactions.

The Problem of the calculation of the repulsive part, $\phi(R)$, of the physisorptive forces also entails assumptions about the solid. Of the two main models of solids, band and localized models, the latter is of greater importance to us since magnetic electrons in ionic solids such as α-Fe_2O_3 are now generally recognized as localized[14-15]. For the present, it is sufficient to remark that there are a variety of models for the description of such localized electrons and discrimination between these appears to be a matter of convenience and taste. Our preference is for a cluster model of ions in a crystalline solid in which the metal ion with the nearest anion neighbours as ligands is a natural cluster. For physisorption, the adsorbate is considered as one of the ligands.

The choice of a cluster model for physisorption problem raises questions about the theoretical definition of physisorption energy, a quantity of interest to us here. It seems to us more reasonable, in the case of the transition metal oxides, to define the physisorption energy in terms of the effects of the adsorbates in the crystal field of a *surface cluster*. This takes full account of the local symmetry at the adsorption site. Having chosen a crystal field model, for the surface cluster, there is no longer any

* *Author for correspondence*

necessity to make separate calculations of the surface dipoles or arbitrarily fix a distance of approach of the admolecule to the surface.

As regards the problem of the repulsive part of the adsorption potential, we think it has arisen because the expansion of the pair electrostatic interaction is truncated by the classical simulation of the interaction but it may naturally arise through semi-quantum mechanical treatment of the admolecule - surface electrostatic interaction. For the physisorption of molecules with permanent dipole moment it is reasonable, in our opinion, to represent the admolecule by a classical dipole so as to avoid overlap of the admolecule and solid wave functions. This way the repulsion energy part, in addition to the well known attractive terms, of the admolecule-surface pair electrostatic potential, arises naturally from a single zero-overlap physical theory as we shall show.

The crystal field cluster physisorption model

As shown in Figure 1, the adsorbate physisorbs on a surface FeO_5^{7-} cluster site. This choice of cluster naturally assumes an oxygen vacancy at the physisorption site and the adoption of at least three top [111] planes of atomic layers as the surface region. FeO_5^{7-} cluster is inside a truncated rhombohedral unit cell, the C_4 axis of the cluster being taken as the z-axis.

The adsorbate approaches the physisorbing surface - (111) surface, along the C_4 axis of the FeO_5^{7-} cluster giving a FeO_5^{7-}.adsorbate 'physisorption cluster' with the structure of a distorted octahedron of at most C_{4v} point group symmetry. Adsorbates are considered as classical dipoles. Furthermore, adsorbate distance from Fe^{3+} is variable but no reconstruction of the (111) surface is allowed for.

The FeO_5^{7-}.adsorbate cluster Hamiltonian

It is convenient to choose an effective Hamiltonian for the $3d^5$ valence electrons of the Fe^{3+} ion of the FeO_5^{7-}.adsorbate cluster. All the O^{2-} as well as Fe^{3+} ions other than those at the site of physisorption provide and 'external' electrostatic field so that the only core electrons are those of the Fe^{3+} at the site of physisopriton, i.e. the FeO_5^{7-}.adsorbate cluster on the (111) surface is surrounded by the rest of the solid whose effect is only to provide a constant 'external' electric field.

Neglecting the effect of the rest of the solid, the effective Hamiltonian for the FeO_5^{7-}.adsorbate cluster is

$$H_{eff}=H_{eff}^{(o)}+H_{cf}^{(o)}+H_{so}+H_{ad} \quad (3)$$

where $H_{eff}^{(o)}$ is the effective Hamiltonian for the 3d-electrons; $H_{cf}^{(o)}$ is the crystal field approximated to that due to the five O^{2-} ligands taken as point charges; H_{so} is the spin-orbit coupling energy for the $3d^5$ electrons and H_{ad} is the potential energy due to the adsorbate dipole. For the physisorption energy calculations, only H_{so} and H_{ad} are considered as perturbations so that H_{eff} may be expanded as

$$H_{eff} = H_{eff}^{(1)} + H_{so} + H_{ad}, \quad (4)$$

where $H_{eff}^{(1)}$ is equal to the sum of $H_{eff}^{(o)}$ and $H_{cf}^{(1)}$ .H_{ad} is usually much smaller than H_{so}, spin-orbit coupling in the transition series being of the order of 8000 cm^{-1} and less while physisorption energies range from 100 to 1000 cm^{-1}. There is therefore some justification for treating the two terms differently.

H_{ad} is taken as function of the separation between the adsorbate and the (111) surface, a kind of potential, and the physisorption energy derived from such a potential. Since the spin-orbit coupling is independent of the adsorbate-(111) surface separation, we may therefore drop it in the physisorption energy calculations.

The potential energy U due to the admolecule dipole

The physisorption energy is then to be calculated as the van der Waals interaction energy between the FeO_5^{7-} cluster (site) on the (111) surface and the admolecule dipole. Figure 2 shows the interaction between the admolecule dipole and the FeO_5^{7-} cluster. We consider the interaction of the admolecule dipole with the 3d-electrons of the Fe^{3+} ion as an approximate measure of admolecule-surface potential energy. To calculate this energy, the Fe^{3+} ion is taken as being subjected to an electric field originating from the admolecule dipole. The potential energy provided by the admolecule dipole is given by

$$U(TP,\beta) = \pm \frac{\sum (j)\, e_j q}{TP} \cdot \left(\frac{1}{(1+K_1)^{1/2}} - \frac{1}{(1+K_2)^{1/2}} \right) \quad (5)$$

where

$$K_1 = \frac{l^2}{4TP^2} - \frac{l\cos(\beta - a)}{TP}; \quad (6)$$

$$K_2 = \frac{l^2}{4TP^2} + \frac{l\cos(\beta - a)}{TP} \quad (7)$$

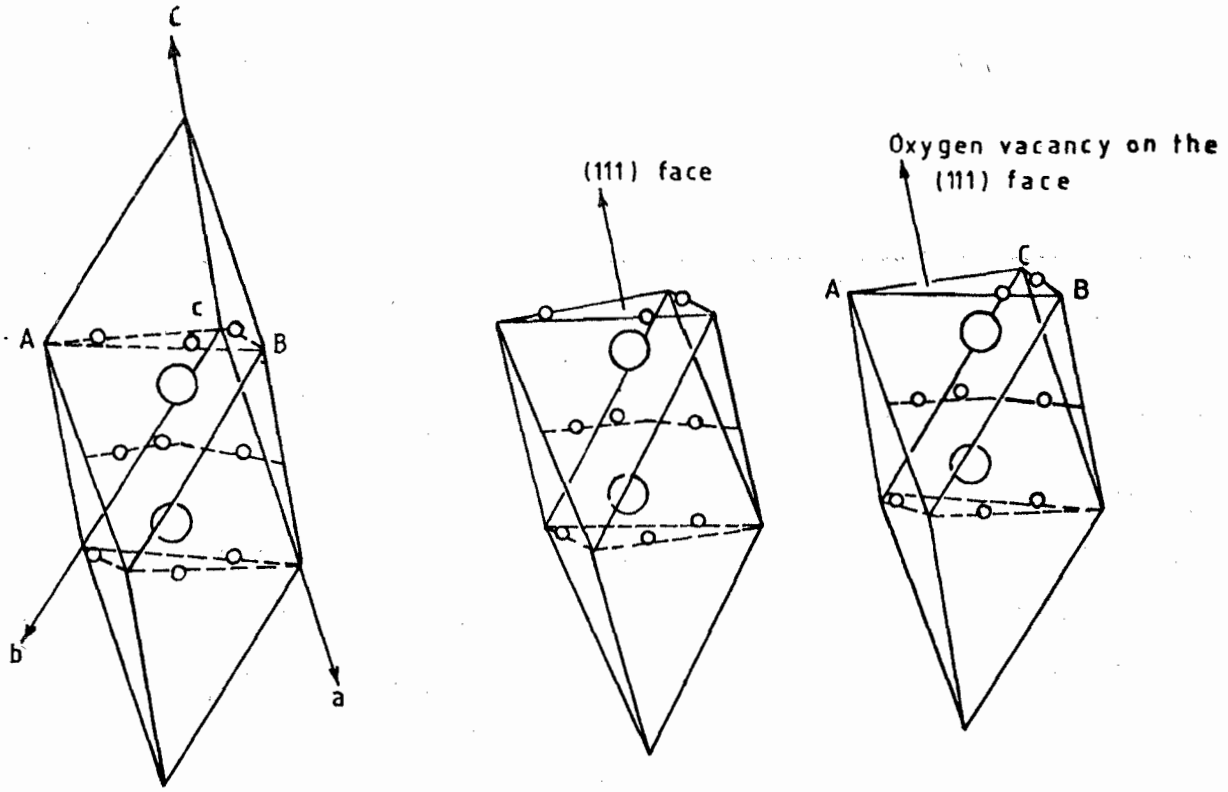

Figure 1(a). Diagrams showing the unit cell, (111) face and an oxygen vacancy at the (111) face of α-Fe_2O_3 solid; Large circles represent Fe^{3+} ions whereas small circles represent O^{2-} ions.

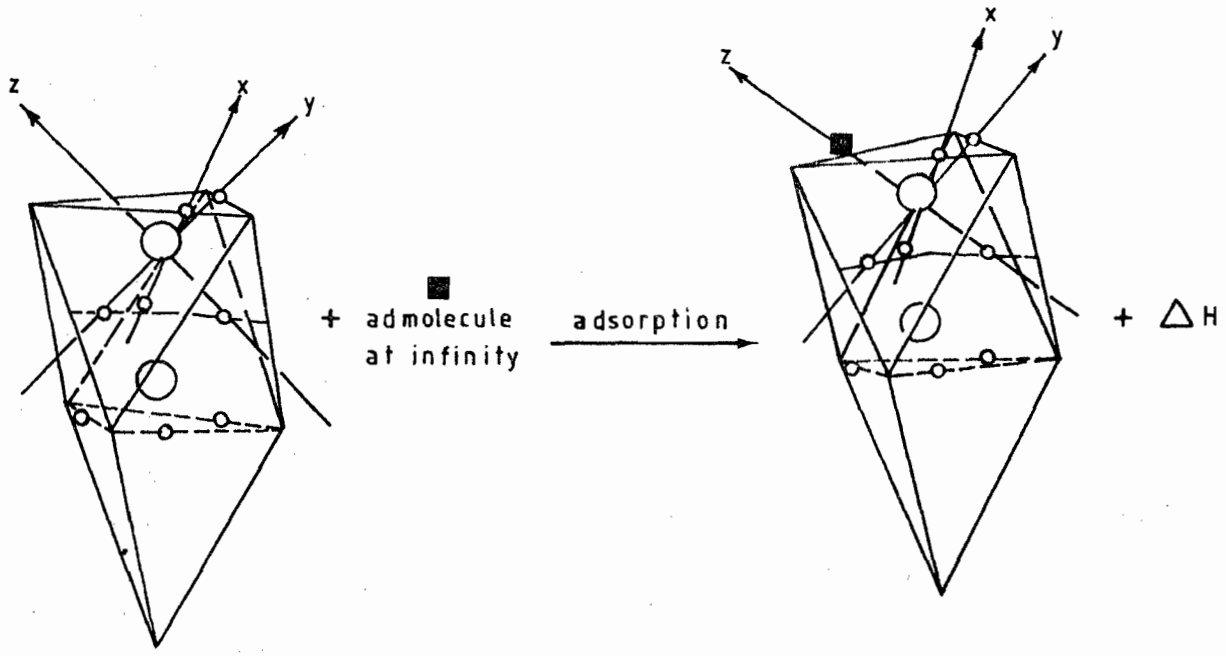

Figure 1(b). Adsorption at an oxygen vacancy on α-Fe_2O_3 (111) face.

and the summation $\Sigma(j)$ is over all 3d-electrons of the Fe^{3+} ion. Assuming that K_1, $K_2 << 1$, equation (5) beomes

$$U(TP,\beta) = \frac{\sum (j)\, e_j}{TP}\left(\frac{\mu\cos(\beta-a)}{TP} + \frac{3}{8}\frac{\eta}{TP^3}\left[\frac{5}{3}\cos^3(\beta-a) - \cos(\beta-a)\right] + \frac{15}{128}\frac{\xi}{TP^5}\left[\frac{21}{5}\cos^5(\beta-a) - \frac{28}{3}\cos^3(\beta-a) + \cos(\beta-a)\right] + \text{higher terms} - \right) \quad \ldots\ldots\ldots\ldots\ldots (7)$$

where μ, η, ξ etc. are the admolecule permanent dipole, octopole, and odd higher multipole moments defined as

$$\mu = ql;\ \eta = ql^3;\ \xi = ql^5;\ \text{etc} \quad \ldots\ldots\ldots\ldots\ldots (8)$$

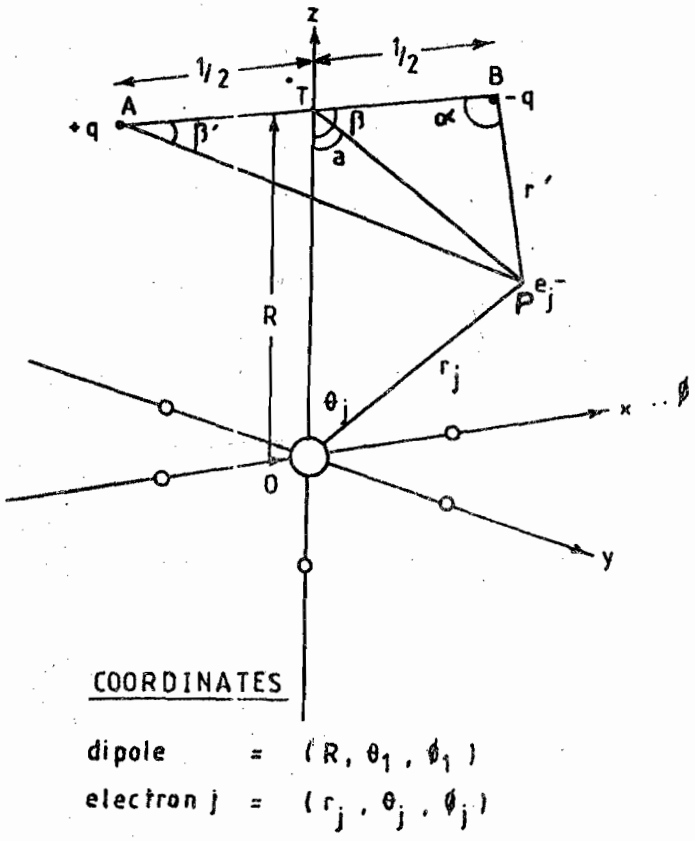

Fig. 2. The interaction of admolecule dipole with the Fe^{3+} ion electrons as simulated by Fig. 1(b) where large circle represents Fe^{3+} ion and small circles represents O^{2-} ions

Also in arriving at equation (7) we have chosen the negative sign in equation (4).

In dipole approximation, the higher multipole terms in (7) are not important. Thus only the first term in the factor multiplying $\Sigma(j)$ over all 3d-electrons is retained

$$U_\mu(TP,\beta) = -\frac{\mu\sum (j)\, e_j\cos(\beta-a)}{TP^2} \quad \ldots\ldots\ldots\ldots (9)$$

dropping all higher permanent odd multipole terms. From ΔTOP (Fig.2) assuming that $1 >> r_j^2\sin^2\theta_j/TP^2$, it can be shown that

$$Cos(\beta-a) = \left(1 - \frac{r_j^2\sin^2\theta_j}{TP^2}\cdot f(TP, r_j, \theta_j)\right) \cdot Cos\beta + \frac{\sin\beta\,.\,r_j\sin\theta_j}{TP} \quad \ldots\ldots (10)$$

where $f(TP, r_j, \theta_j)$ is an exponential function given by

$$f(TP, r_j, \theta_j) = \sum_{n=0}^{\infty} C_n\left(-\frac{r_j^2\sin^2\theta_j}{TP^2}\right)^n \quad \ldots\ldots\ldots (11)$$

with the coefficients C_n in (11) given by

$$C_n = \left(\frac{1}{2}-0\right)\cdot\left(\frac{1}{2}-1\right)\ldots\left(\frac{1}{2}-r\right)\ldots\left(\frac{1}{2}-n\right)\cdot\frac{1}{(n+1)!} \quad \ldots\ldots\ldots\ldots (12)$$

Using the value of cos (β-a) from equation (10), we have

$$U_\mu(TP,\beta,r,\Theta) = \left[\frac{\mu\sum (j)\, e_j}{TP^2} + \mu\frac{\sum (j)\, e_j\sin^2\theta_j r_j^2}{TP^4}\cdot f(TP, r_j, \theta_j)\right]\cos\beta\,.\,\frac{\mu\sum (j)\, e_j\sin\theta_j\,.\,r_j}{TP^3}\sin\beta \quad \ldots\ldots\ldots\ldots (13)$$

From Δ TOP in Figure 2, it is easy to see that, using cosine rule,

$$\frac{1}{TP} = \frac{1}{R}\sum_{k=0}^{\infty} C_k^o \left(\frac{r_j}{R}\right)^k Y_k^o(\theta_j, \phi_j)$$

..... (14)

where $C_k^o = \{4\Pi/(2k+1)\}\, Y_k^{o*}(\theta_1, \phi_1)$. Substituting for the value of 1/TP in (13) we obtain for the admolecule dipole the potential energy

$$U_\mu(R, \beta, r, \Theta, \phi) = \sum_{k=o}^{\infty}\sum_{j} [-\frac{\mu C_k(R, r_j, \theta_j, \phi_j)}{R^2} + \frac{\mu Q_k(R, r_j, \theta_j, \phi_j)}{R^4} . f_k(R, r_j, \theta_j, \phi_j)]\cos\beta - \sum_{k=o}^{\infty}\sum_{j} \frac{\mu\mu_k(R, r_j, \Theta_j, \phi_j)}{R^3}\sin\beta$$

.....(15)

where C_k, μ_k and Q_k are contributions by the jth Fe^{3+} valence electron to the induced electronic-monopole, -dipole and -quadrupole moments on Fe^{3+}. Thus

$$C_k(R, r_j, \Theta_j, \phi_j) = e_j g_k(R, r_j, \Theta_j, \phi_j)$$

.....(16)

$$u_k(R, r_j, \Theta_j, \phi_j) = e_j [g_k(R, r_j, \Theta_j, \phi_j)]^{\frac{3}{2}} \sin\theta_j . r_j \ldots\ldots\ldots\ldots (17)$$

$$Q_k(R, r_j, \Theta_j, \phi_j) = e_j [g_k(R, r_j, \Theta_j, \phi_j)]^2 \sin^2\theta_j . r_j^2 \ldots\ldots (18)$$

Also, the kth exponential function in (15) is given by

$$f_k(R, r_j, \Theta_j, \phi_j) = \sum_{n=o}^{\infty} C_k (-\frac{r_j^2 \sin^2\Theta_j}{R^2} . (g_k(R, r_j, \theta_j, \phi_j))^n \ldots\ldots (19)$$

where the g_k function is defined as

$$g_k(R, r_j, \Theta_j, \phi_j) = [C_k^o Y_k^o(\Theta_j, \phi_j)]^2 . (\frac{r_j}{R})^{2k} \ldots\ldots\ldots (20)$$

It is to be noted that the last term in (15) is the admolecule dipole-surface dipole interaction potential and we represent it as $U_{\mu\mu}$,

$$U_{\mu\mu}(R, r, \Theta, \phi) = - \sum_{k=0}^{\infty}\sum_{j} \frac{\mu\mu_k(R, r_j, \theta_j, \phi_j)}{R^3} \ldots (21)$$

The other part consists of admolecule-surface monopole (charge) and admolecule dipole-surface quadrupole potentials. These we represent as $U_{\mu s}$,

$$U_{\mu s}(R, r, \Theta, \phi) = \sum_{k=0}^{\infty}\sum_{j} (-\frac{\mu C_k(R, r_j, \theta_j, \phi_j)}{R^2} + \frac{\mu Q_k(R, r_j, \theta_j, \phi_j)}{R^4} . f_k(R, r_j, \theta_j, \phi_j)) \ldots (22)$$

Thus, the total interaction potential U_μ can be written in terms of the $U_{\mu\mu}$ and $U_{\mu s}$ potential energy terms

$$U_\mu(R, \beta, r, \Theta, \phi) = U_{\mu s}(R, r, \Theta, \phi) . \cos\beta + U_{\mu\mu}(R, r, \theta, \phi)\sin\beta \ldots . (23)$$

Dipolar ligands such as H_2O^+, H_2O, HO^- and NH_3 always bind to metal ions with their negative end to the metal[16], that is Fe^{3+} .....O^{q-}_____$(H)_2^{q+}$, Fe^{3+}..... N^{q-}_____$(H)_3^{q+}$ etc. This implies that dipole orientation is along the line joining its centre to the Fe^{3+} ion and automatically puts $\beta=0$. Under this condition the potential energy (23) reduces to

$$U_\mu(R, r, \Theta, \phi) = U_\mu(R, O^o r, \Theta, \phi) = U_{\mu s}(R, r, \Theta, \phi) \ldots . (24)$$

and the dipole-dipole interaction term simply vanishes.

Physisorption energy of the admolecules

In order to study the stability of the admolecule dipole-surface entity, we shall consider the potential energy $U_\mu(R,r,\theta,\phi)$ in equation (24). For now, $U_\mu(R,r,\theta,\phi)$ is the perturbation operator H_{ad} of (3) whose matrix elements over the appropriate electronic state of the Fe^{3+} in the admoleule dipole - FeO_5^{7-} surface complex are required. Beause tetragonal distortion causes low spin configuration in the octahedral FeO_6^{9-} complex[17], we have assumed a low spin configuration for the Fe^{3+} ion in the FeO_5^{7-}.dipole complex. With such a configuration, an ^2E electronic term in the C_{4v} point group is chosen for the calculation of the perturbation matrix element.

But first of all, $U_\mu(R,r,\theta,\phi)$ must transform as the totally symmetric representation of C_{4v} point group of FeO_5^{7-}.dipole ($\beta=0$) complex. Let us take C_4 axis as our axis of quantization, this being the z-axis as in Figure 2. Then C_4 implies

$$C_4 Y_k^o(\Theta,\phi) = Y_k^o(\Theta,\phi)$$
$$\text{all } k \text{ values} \ldots (25)$$

So that $U_\mu(R,r,\theta.\phi)$ is already symmetric.

The first order perturbation $\Delta U_\mu(R)$ is then given by

$$\Delta U_\mu(R) = \langle \psi(^2E) / U_\mu(R, r\Theta, \phi) / \psi(^2E) \rangle \ldots\ldots (26)$$

From equation (24), we see that $\Delta U_\mu(R)$ breaks into attractive and repulsive terms thus

$$\Delta U_\mu(R) = \sum_{k=o}^{\infty} \left(-\frac{\mu \langle \psi(^2E) / \sum (j) C_k(R, r_j, \theta_j, \phi_j) / \psi(^2E) \rangle}{R^2} + \mu \langle \psi(^2E) / \sum (j) Q_k(R, r_j, \Theta_j, \phi_j) \cdot \frac{f_k(R, r_j, \theta_j \phi_j) / \psi(^2E) \rangle}{R^4} \right)$$
$$= \sum_{k=o}^{\infty} \Delta U_{\mu,k}(R) \ldots\ldots (27)$$

$\Delta U_\mu(R)$ is calculated using d STO single zeta basis set and naturally gives rise to potential energy curves yielding binding energy and equilibrium bond distance. The potential energy curves will not be presented here but the binding energy $\Delta U_\mu(R_e)$ and equilibrium bond distance R_e will be quoted.

For the purpose of the calculations, some potential functions have been defined by truncating the expansion (27) as follows:

$$\Delta U_\mu^o(R) = \sum_{k=o}^{4} \Delta U_{\mu,k}(R), \quad \Delta U_\mu^1(R) = \sum_{k=1}^{4} \Delta U_{\mu,k}(R), \text{ and } \Delta U_\mu^2(R) = \Delta U_{\mu,5}(R) \ldots\ldots (28)$$

The physisorption energy ΔH, as shown in Figure 1b, is calculated as the equilibrium binding energy obtained from the P.E. curves of the potential functions (28),

$$\Delta H_o = \Delta U_\mu^o(R_e), \quad \Delta H_1 = \Delta U_\mu^1(R_e), \text{ and } \Delta H_2 = \Delta U_\mu^2(R_e) \ldots (29)$$

However, these have been calculated for the special value of the exponential functions $f_k(R, r_j, \theta_j, \phi_j)$ only, that is

$$2 f_k(R, r_j, \Theta_j, \phi_j) = 1$$

for all k values .....(30)

That is, taking only the term with n = 0 in the expansion (19).

Table 1: Binding energies of H_3O^+, H_2O, HO^- and NH_3 dipoles on the (111) face of α-Fe_2O_3

Binding energy (kcal/mol)	H_2O	H_2O^+	HO^-	NH_3	R_e (Å)
ΔH_o	-27.6746	-24.2534	-24.8578	-22.0029	2.014
ΔH_1	-3.0591	-2.6809	-2.7476	-2.4322	2.226
$\Delta H_2(x10^{-3})$	-6.981	-6.117	-6.270	-5.550	4.330
$\Delta U_{\mu,2}(R_e)$	-2.8621	-2.6278	-2.6936	-2.2167	1.272

RESULTS AND DISCUSSION

The binding energies and equilibrium distances of H_2O^+, H_2O, HO^- and NH_3 dipoles, as obtained from equation (29), in the surface complex (FeO_5^{7-}.dipole β=O°) model are presented in Table 1. The binding energies generally fall in the range of physisorption energies. Looking at the values of ΔH_o and ΔH_1 and the corresponding equilibrium distances of the dipoles from the ferric ion, one immediately sees that $\Delta U_{\mu,o}(R)$ has little effect on the properties of the (FeO_5^{7-}.dipole β=O°) surface complex; its inclusion in the energy calculation does not shift the position of the van der Waals minimum

$R_e + \delta$ of $\Delta H_o \equiv R_e$ of ΔH_1 .....(31)

appreciably, δ being 0.212Å only. However, the depth of the well considerably increased by a constant amount of -33.8126μ kcal/mol, μ being the dipole moment of an adsorbate in atomic units. Apparently, $\Delta U_{\mu,o}(R)$ is very large but only important when considering intermolecular lattice energy because 33.8126μ kcal/mol >> kT, T being in the range of ordinary temperatures.

Though the heat of physisorption could be as high as about 28 kcal/mol in some cases, this is normally an upper limit and so is ΔH_O. On the other hand, ΔH_1 is in the normal range of physisorption energy; admolecules will be held and ordered at the surface at room temperature.

$$/\Delta H_1/ > (kT_{room} \approx 0.597 \text{ kcal/mol}; T_{room} = 27^{oC}) \ldots\ldots (32)$$

As for ΔH_2, admolecules will be held at the surface only below about T = -270°C. For this, one may conclude that the higher potential energy functions in (27) with k = 5, 6,7,....., ∞ are not important; they are responsible for the non-vanishing small attractions that exist between the surface and admolecules. They become important only at very low temperatures.

For the purpose of comparison, experimental data on heats of adsorption is required. Such data for H_2O^+, H_2O, H_2O, HO^- and NH_3 dipoles on α-Fe_2O_3 is very difficult to come by. This is rather scarce even on other transition metal oxides of the iron group with the general formula M_2O_3. Notwithstanding, the values we obtained, i.e. ΔH_1 for the dipoles under study, are in the range of normal physisorption energies.

From equations (16), (18), (27) and (30) the intermolecular potential function $\Delta U_\mu(R)$ can be rewritten in the simple form of a function of potentials for each k index

$$\Delta U_\mu(R) = \sum_{k=o}^{\infty}\left(-\frac{\mu C_k}{R^{2k+2}} + \frac{\mu B_k}{R^{4k+4}}\right)$$

$$= \sum_{k=o}^{\infty} \Delta U_{\mu,k}(R) \quad .. (33)$$

where the C_k and B_k are quantum averages given as

$$C_k = \langle \sum (j)\, e_j [C_k^o Y_k^o(\Theta_j, \phi_j)]^2 . \; r_j^{2k} \rangle \quad ..... (34)$$

and

$$B_k = \langle \sum (j)\, e_j [C_k^o Y_k^o(\Theta_j, \phi_j)]^4 \sin^2 \theta_j . r_j^{4k+2} \rangle \quad ..... (35).$$

From (33) we see that $\Delta U_\mu(R)$ is a simple function of 2k+2, 4k+4 family of potentials which are similar in form to the well-known semi-empirical intermolecular n, m potentials

$$\Delta U_{LJ}(R) = -\frac{C}{R^n} + \frac{B}{R^m} \quad ..... (36)$$

that was proposed by Lennard-Jones[8] long time ago.

The third member of this series, 2k+2, 4k+4 family of potentials, i.e. $\Delta U_{\mu,2}(R)$ with k=2, is a 12-6 potential function

$$\Delta U_{\mu,2}(R) = -\frac{\mu C_2}{R^6} + \frac{\mu B_2}{R^{12}} \quad .... (37)$$

which is similar in form to the most commonly used Lennard-Jones semi-empirical potential[18]

$$\Delta U_{LJ}(R) = 4\epsilon\left(\frac{\sigma^6}{R^6} - \frac{\sigma^{12}}{R^{12}}\right) \quad ..... (38)$$

ε being a negative quantity, that is being used to describe physical adsorption and the behaviour of gases and liquids.

The potential energy curves due to the $\Delta U_{\mu,2}(R)$ 12-6 potential has been calculated for the (FeO_5^{7-}.dipole; dipole = H_2O^+, H_2O, HO^- and NH_3) surface complex. The minimum for all the dipoles occurred at about R = 1.272Å. The binding energies of the dipoles are given in Table 1 in the last row.

It is interesting to note that the binding energy due to the $\Delta U_{\mu,2}(R)$ 12-6 potential agrees well with ΔH_1 for all the dipoles. This reveals that the $\Delta U_{\mu,2}(R)$ 12-6 potential can reasonably well predict the energetics of intermolecular interactions as much as

$$\Delta U_\mu^1(R) = \sum_{k=1}^{4} \Delta U_{\mu,k}(R)$$

of which it is a member. Perhaps this explains the reason why the Lennard-Jones 12-6 potential gives a much better approximation to actual intermolecular potentials thatn any other form of semi-empirical intermolecular potential.

CONCLUSION

The energetics of the adsorption of H_2O^+, H_2O, HO^- and NH_3 dipoles at an oxygen vacant site on the (111) face of α-Fe_2O_3 have been calculated as a first order intermolecular electrostatic interaction energies between a dipole and the ferric ion of an FeO_5^{7-} cluster on the surface. They are in the range of -2.4 to -3 kcal/mol, 2.226Å as equilibrium distance between the centre of the dipole and Fe^{3+}.

The intermolecular electrostatic potential that is used in the physisorption enthalpy calulations has been derived from a single zero-overlap physical theory and the potential contains, in addition to the well known attractive terms, repulsive energy terms as well for the first time. The potential has provided a sound physical and theoretical basis for the Lennard-Jones n,m family of intermolecular potentials - most especially the 12-6 potential, and the long awaited theoretical justification for intermolecular zero-overlap repulsion energy term.

It is to be noted that the valence electrons of Fe^{3+} ion in the intermolecular potential $\Delta U_{\mu,2}(R)$ could be replaced by the electrons of a molecule etc. The wave function for the calculations of C_k and B_k in (34) and (35) could be atomic or molecular in general, so that $U_{\vec{\mu}}(R,\beta,r,\theta,\phi)$ of (15) as well as

$\Delta U_{\mu,2}(R)$ of (33) are, in general, intermolecular potentials applicable to all two body systems provided none of them has a permanent dipole moment. Furthermore, the repulsive part of the potential $U_\mu(R,\beta,r,\theta,\varphi)$ and $\Delta U_\mu(R)$ decreases exponentially with R in agreement with the semi-empirical theories. These exponential functions $f_k(R,r_j,\theta_j,\phi_j)$ and their average, which may be defined as

$$\Delta f_k(R) = \frac{\langle \sum (j) Q_k(R, r_j, \Theta_j, \phi_j) \cdot f_k(R, r_j, \theta_j, \phi_j) \rangle}{\langle \sum (j) Q_k(R, r_j, \theta_j, \phi_j) \rangle} \quad \ldots (39)$$

are simple analytical functions of R. Lastly, the treatment can easily and systematically be extended to multi-body intermolecular electrostatic interactions.

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APPENDIX

From Figure 2, the potential energy provided by the dipole to a 3d electron j of the Fe^{3+} ion situated at some general point P in space is given by

$$U_{e_j} = e_j q \left(\frac{1}{r'} - \frac{1}{AP} \right) \ldots\ldots\ldots (A\text{-}1)$$

From ΔATP and ΔBTP of the same figure, it easy to see that

$$\frac{1}{r'} - \frac{1}{AP} = \frac{\sin\alpha - \sin\beta'}{TP\sin(\beta - a)}, \ldots\ldots (A\text{-}2)$$

using sine rule, so that

$$U_{e_j} = \frac{e_j q}{TP\sin(\beta - a)} (\sin\alpha - \sin\beta') \quad \ldots\ldots\ldots\ldots\ldots\ldots (A\text{-}3)$$

similarly from ΔATP and ΔBTP, using sine rule and some algebra, we obtain

$$\sin\alpha = \frac{[TP^2\sin^2(\beta - a)]^{\frac{1}{2}}}{[TP^2\sin^2(\beta - a) + (/2 - TP\cos(\beta - a))^2]^{\frac{1}{2}}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (A\text{-}4)$$

and

$$\sin\beta' = \frac{[TP^2\sin^2(\beta - a)]^{\frac{1}{2}}}{[TP^2\sin^2(\beta - a) + (/2 + TP\cos(\beta - a))^2]^{\frac{1}{2}}} \quad \ldots (A\text{-}5)$$

Using the values of $\sin\alpha$ and $\sin\beta$ in **(A-3)** we obtained equation (4) summing up over all the valence electrons of Fe^{3+}.

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