CALCULATION OF PHYSIORSPTION ENERGIES OF DIPOLAR MOLECULES ON α-Fe₂O₃ (III) SURFACE USING A CRYSTAL FIELD CLUSTER MODEL

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ABSTRACT

A complete electrostatic intermolecular potential

\[
U(R, \beta, \iota, \theta, \phi) = \sum_{k=0}^{\infty} \sum_{j} \left( \frac{\mu C_k(R, \iota_j, \theta_j, \phi_j)}{R^2} \cos \beta_j + \frac{\mu \psi_k(R, \iota_j, \theta_j, \phi_j)}{R^3} \sin^2 \beta_j \right) + \sum_{k=0}^{\infty} \sum_{j} \frac{\mu Q_k(R, \iota_j, \theta_j, \phi_j)}{R^4} f_k(R, \iota_j, \theta_j, \phi_j) \cos \beta_j
\]

has been developed from a single zero-overlap physical theory, without recourse to ad hoc 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 H₂O, H₂O, H₂O and NH₃ physisorption energies at an oxygen vacant site on the (III) surface of α-Fe₂O₃. 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. However, inspite of its industrial importance α-Fe₂O₃ 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

\[
\Delta U(R) = \Delta E_{LZ, pair}(R) + \phi(R) \ldots (1)
\]

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

\[
\Delta E_{LZ, pair}(R) = \Delta E_{el}(R) + \Delta E_{ind}(R) + \Delta E_{disp}(R) \ldots (2)
\]

The long-range attractive components in (2) have firm theoretical basis. 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 of van der Waals potential, a united 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. Quantum mechanically, it has been shown 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-Fe₂O₃ are now generally recognized as localized. 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 adsorbate 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

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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$_5^{2-}$ cluster site. This choice of cluster naturally assures 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$_5^{2-}$ 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$_5^{2-}$ cluster giving a FeO$_5^{2-}$ 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$_5^{2-}$ adsorbate cluster Hamiltonian

It is convenient to choose an effective Hamiltonian for the 3d$^7$ valence electrons of the Fe$^{3+}$ ion of the FeO$_5^{2-}$ adsorbate cluster. All the O$^{2-}$ as well as Fe$^{3+}$ ions other than those at the site of physisorption provide a 'external' electrostatic field so that the only core electrons are those of the Fe$^{3+}$ at the site of physisorption, i.e. the FeO$_5^{2-}$ 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$_5^{2-}$ adsorbate cluster is

$$H_{\text{eff}} = H_{\text{eff}}^{(0)} + H_{\text{cf}}^{(0)} + H_{\text{so}} + H_{\text{ad}} \ldots (3)$$

where $H_{\text{eff}}^{(0)}$ is the effective Hamiltonian for the 3d-elections; $H_{\text{cf}}^{(0)}$ is the crystal field approximated to that due to the five O$^{2-}$ ligaeds taken as point charges; $H_{\text{so}}$ is the spin-orbit coupling energy for the 3d$^7$ electrons and $H_{\text{ad}}$ is the potential energy due to the adsorbate dipole. For the physisorption energy calculations, only $H_{\text{so}}$ and $H_{\text{ad}}$ are considered as perturbations so that $H_{\text{eff}}$ may be expanded as

$$H_{\text{eff}} = H_{\text{eff}}^{(1)} + H_{\text{ad}} + H_{\text{so}} + H_{\text{ad}} \ldots \ldots \ldots \ldots (4)$$

where $H_{\text{eff}}^{(1)}$ is equal to the sum of $H_{\text{eff}}^{(0)}$ and $H_{\text{cf}}^{(0)}$ and $H_{\text{so}} + H_{\text{ad}}$ is usually much smaller than $H_{\text{so}}$ 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.

$H_{\text{ad}}$ 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$_5^{2-}$ cluster (site) on the (111) surface and the admolecule dipole. Figure 2 shows the interaction between the admolecule dipole and the FeO$_5^{2-}$ 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

$$U(TP, \beta) = \sum \frac{(j) \theta_j q}{TP} \cdot \left( \frac{1}{1 + K_1 1/2} \right) \cdot \left( \frac{1}{1 + K_2 1/2} \right) \ldots \ldots \ldots (5)$$

where

$$K_1 = \frac{J^2}{4 TP^2} \left( \frac{1}{TP} \right) \cos (\beta - \alpha) \ldots \ldots \ldots (6)$$

$$K_2 = \frac{J^2}{4 TP^2} + \left( \frac{1}{TP} \right) \cos (\beta - \alpha) \ldots \ldots \ldots (7)$$

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

Figure 1(b). Adsorption at an oxygen vacancy on $\alpha$-$Fe_2O_3$ (111) face.
and the summation \( \Sigma(j) \) is over all 3d-electrons of the Fe\(^{3+} \) ion. Assuming that \( K_i, K_j < \angle 1 \), equation (5) becomes

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

where \( \mu, \eta, \xi \) etc. are the ad molecule permanent dipole, octopole, and odd higher multipole moments defined as

\[
\mu = q_1; \eta = q_2; i = q_3; \text{etc.} \] .......................... (8)

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

\[
U_\mu(TP, \beta) = -\frac{\mu}{TP} \sum (j) e_j \cos(\beta - \alpha) \] .......................... (9)

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

\[
\cos(\beta - \alpha) = \left( 1 - \frac{r_j^2 \sin^2 \theta_j}{TP^2} \right) f(TP, r_j, \theta_j), \] .......................... (10)

\[
\cos \beta = \frac{\sin \beta \cdot r_j \sin \theta_j}{TP} \] .......................... (11)

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

\[
f(TP, r_j, \theta_j) = \sum_{n=0}^{\infty} C_n \left( -\frac{r_j^2 \sin^2 \theta_j}{TP^2} \right)^n \] .......................... (12)

with the coefficients \( C_n \) in (11) given by

\[
C_n = \left( \frac{1}{2} - \theta \right) \cdot \left( \frac{1}{2} - \theta - 1 \right) \cdots \left( \frac{1}{2} - \theta - n \right) \] .......................... (13)

\[
\left( \frac{1}{2} - \theta - (n+1) \right)! \] .......................... (14)

Using the value of \( \cos(\beta - \alpha) \) from equation (10), we have

\[
U_\mu(TP, \beta, r, \theta) = \left[ \frac{\mu}{TP^2} \sum (j) e_j \right] f(TP, r_j, \theta_j) \cos \beta \] .......................... (15)

\[
\sum (j) e_j \sin \theta_j \cdot r_j \sin \beta \] .......................... (16)

From \( \Delta T \) in Figure 2, it is easy to see that, using cosine rule,

\[
\cos(\beta - \alpha) = \left( 1 - \frac{r_j^2 \sin^2 \theta_j}{TP^2} \right) f(TP, r_j, \theta_j) \] .......................... (17)

\[
\cos \beta = \frac{\sin \beta \cdot r_j \sin \theta_j}{TP} \] .......................... (18)

\[
\mu \sum (j) e_j \sin \theta_j \cdot r_j \sin \beta \] .......................... (19)

\[
\left( \frac{1}{2} - \theta - (n+1) \right)! \] .......................... (20)

\[
\mu \sum (j) e_j \sin \theta_j \cdot r_j \sin \beta \] .......................... (21)

\[
\sum (j) e_j \sin \theta_j \cdot r_j \sin \beta \] .......................... (22)

\[
\cos \beta = \frac{\sin \beta \cdot r_j \sin \theta_j}{TP} \] .......................... (23)
\[
\frac{1}{TP} = \frac{1}{R} \sum_{k=0}^{\infty} C_k \left( \frac{R_j}{R} \right)^k Y_j^m(\theta_j, \phi_j) \\
\text{...............(14)}
\]

where \( C_k = \{4\Pi/(2k+1)\} \) \( Y_j^m(\theta_j, \phi_j) \). Substituting for the value of \( 1/TP \) in (13) we obtain for the admolecule dipole the potential energy

\[
U_\mu(R, \beta, x, \Theta, \phi) = \sum_{k=0}^{\infty} \sum_{j} \left[ -\frac{\mu C_k(R, x_j, \Theta_j, \phi_j)}{R^2} + \frac{\mu Q_k(R, x_j, \Theta_j, \phi_j)}{R^4} \right] \cos \beta \\
- \sum_{k=0}^{\infty} \frac{\mu \mu_k(R, x_j, \Theta_j, \phi_j)}{R^3} \sin \beta \\
\text{...............(15)}
\]

where \( C_k, \mu_k \) 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

\[
C_k(R, x_j, \Theta_j, \phi_j) = e_j [g_k(R, x_j, \Theta_j, \phi_j) \\
\text{...............(16)}
\]

\[
u_k(R, x_j, \Theta_j, \phi_j) = e_j [g_k(R, x_j, \Theta_j, \phi_j) \\
\text{...............(17)}
\]

\[
Q_k(R, x_j, \Theta_j, \phi_j) = e_j [g_k(R, x_j, \Theta_j, \phi_j) \\
\text{...............(18)}
\]

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

\[
f_k(R, x_j, \Theta_j, \phi_j) = \sum_{n=0}^{\infty} \left( \frac{R_j}{R} \right)^n g_k(R, x_j, \Theta_j, \phi_j) \\
\text{...............(19)}
\]

where the \( g_k \) function is defined as

\[
g_k(R, x_j, \Theta_j, \phi_j) = [C_k \cos^2(\Theta_j, \phi_j)]^3 \\
\text{...............(20)}
\]

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

\[
U_{\mu \nu}(R, x, \Theta, \phi) = \\
\text{...............(21)}
\]

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

\[
U_{\mu \nu}(R, x, \Theta, \phi) = \sum_{k=0}^{\infty} \sum_{j} \left[ -\frac{\mu C_k(R, x_j, \Theta_j, \phi_j)}{R^2} + \frac{\mu Q_k(R, x_j, \Theta_j, \phi_j)}{R^4} \right] \\
\text{...............(22)}
\]

Thus, the total interaction potential \( U \) can be written in terms of the \( U_{\mu \nu} \) and \( U_{\mu \nu} \) potential energy terms

\[
U(R, \beta, x, \Theta, \phi) = U_{\mu \nu}(R, x, \Theta, \phi) \\
\text{...............(23)}
\]

Dipolar ligands such as \( H_2O^+ \), \( H_2O \), \( HO^+ \) and \( NH_3 \) always bind to metal ions with their negative end to the metal\(^{3+} \), that is \( Fe^{3+} \text{............} O^+ \text{............} (H_2O)^+ \), \( Fe^{3+} \text{............} N^+ \text{............} (H_2O)^+ \text{etc.}.\) 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

\[
U(R, x, \Theta, \phi) = U_{\mu \nu}(R, O^+, x, \Theta, \phi) \\
\text{...............(24)}
\]

and the dipole-dipole interaction term simply vanishes.

**Physicosorption energy of the admolescence**

In order to study the stability of the admolecule dipole-surface entity, we shall consider the potential energy \( U(R, r, \theta, \phi) \) in equation (24). For now, \( U(R, r, \theta, \phi) \) is the perturbation operator \( H_0 \) of (3) whose matrix elements over the appropriate electronic state of the \( Fe^{3+} \) in the admolecule dipole - \( FeO_2^- \) surface complex are required. Because tetragonal distortion causes low spin configuration in the octahedral \( FeO_6^{3-} \) complex\(^7\), we have assumed a low spin configuration for the \( Fe^{3+} \) ion in the \( FeO_2^- \) 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, \( U(R, r, \theta, \phi) \) must transform as the total symmetric representation of \( C_{4v} \) point group of \( FeO_2^- \).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.

---

\[ C_{q} Y_{k}^{p}(\Theta, \Phi) = Y_{k}^{p}(\Theta, \Phi) \]

\[ \text{all } k \text{ values} \ldots \ldots (25) \]

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

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

\[ \Delta U_{\mu}(R) = \left( \frac{\psi(2E)}{U_{\mu}(R, z)} \right) / \psi(2E) \left( R^{2} \right) \]

\[ \Delta U_{\mu}(R) = \sum_{k=0}^{\infty} \left( -\frac{\mu < \psi(2E) > \sum_{j} C_{k}(R, \tau_{j}, \theta_{j}, \phi_{j})}{R^{2}} \right) \]

\[ + \mu < \psi(2E) > \sum_{j} Q_{k}(R, \tau_{j}, \theta_{j}, \phi_{j}) \cdot \frac{\psi(2E)}{ \left( R^{4} \right) } \]

\[ \Delta U_{\mu}(R) = \sum_{k=0}^{\infty} \Delta U_{\mu,k}(R) \ldots \ldots (27) \]

\( \Delta U_{\mu}(R) \) 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 \( \Delta U_{\mu}(R) \) 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:

\[ \Delta U_{\mu}^{2}(R) = \sum_{k=0}^{4} \Delta U_{\mu,k}(R), \quad \Delta U_{\mu}^{4}(R) = \sum_{k=1}^{4} \Delta U_{\mu,k}(R) \quad \text{and} \quad \Delta U_{\mu}^{2}(R) = \Delta U_{\mu,5}(R) \ldots \ldots (28) \]

The physiosorption energy \( \Delta H_{e} \), as shown in Figure 1b, is calculated as the equilibrium binding energy obtained from the P.E. curves of the potential functions (28),

\[ \Delta H_{e} = \Delta U_{\mu}^{2}(R_{e}) \quad \text{and} \quad \Delta H_{e} = \Delta U_{\mu}^{2}(R_{e}) \ldots \ldots (29) \]

\[ \text{RESULTS AND DISCUSSION} \]

The binding energies and equilibrium distances of \( \text{H}_{2}\text{O}^{+}, \text{H}_{2}\text{O}, \text{HO}^{-} \) and \( \text{NH}_{3} \) dipoles, as obtained from equation (29), in the surface complex \( \text{FeO}_{2}^{2-} \) dipole \( \beta=\text{O}^{2-} \) model are presented in Table 1. The binding energies generally fall in the range of physisorption energies. Looking at the values of \( \Delta H_{e} \) and \( \Delta H_{e} \) and the corresponding equilibrium distances of the dipoles from the ferric ion, one immediately sees that \( \Delta U_{\mu}(R) \) has little effect on the properties of the \( \text{FeO}_{2}^{2-} \) dipole \( \beta=\text{O}^{2-} \) surface complex; its inclusion in the energy calculation does not shift the position of the van der Waals minimum.

\[ R_{e} + \delta \text{ of } \Delta H_{e} = R_{e} \text{ of } \Delta H_{e} \ldots \ldots \ldots (31) \]

appreciably, \( \delta \) being 0.212Å only. However, the depth of the well considerably increased by a constant amount of -33.8126\( \mu \) kcal/mol, \( \mu \) being the dipole moment of an adsorbate in atomic units. Apparently, \( \Delta U_{\mu}(R) \) is very large but only important when considering intermolecular lattice energy because 33.8126\( \mu \) 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 \( \Delta H_{e} \). On the other hand, \( \Delta H_{e} \) is in the normal range of physisorption energy; admolecules will be held and ordered at the surface at room temperature.

\[ \text{/\( \Delta H_{e} \text{/}} (kT_{\text{room}}=0.597 \text{kcal/mol} \text{; } T_{\text{room}}=27^\circ \text{C}) \ldots \ldots (32) \]
As for $\Delta H^\text{ad}$, admolecules will be held at the surface only below about $T = -270^\circ$C. For this, one may conclude that the higher potential energy functions in (27) with $k = 5, 6, 7, \ldots$, $\infty$ 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 $\text{H}_2\text{O}^+$, $\text{H}_3\text{O}^+$, $\text{H}_2\text{O}$, $\text{HO}^-$ and $\text{NH}_3$ dipoles on $\alpha$-$\text{FeO}_x$ is very difficult to come by. This is rather scarce even on other transition metal oxides of the iron group with the general formula $\text{M}_2\text{O}_3$. Notwithstanding, the values we obtained, i.e. $\Delta H^\text{ad}$ for the dipoles under study, are in the range of normal physisorption energies.

From equations (16), (18), (27) and (30) the intermolecular potential function $\Delta U^\text{ad} [R]$ can be rewritten in the simple form of a function of potentials for each $k$ index

$$\Delta U^\text{ad}_{k} [R] = \sum_{k=0}^{\infty} \left( -\frac{\mu C_k}{R^{2k+2}} + \frac{\mu B_k}{R^{4k+4}} \right)$$

$$= \sum_{k=0}^{\infty} \Delta U^\text{ad}_{\mu,k} [R] \ldots (33)$$

where the $C_k$ and $B_k$ are quantum averages given as

$$C_k = \langle \sum \langle j \rangle \phi_j [C_k Y_k^0 (\Theta_j, \Phi_j)]^2 \rangle \ldots (34)$$

and

$$B_k = \langle \sum \langle j \rangle \phi_j \mu [C_k Y_k^0 (\Theta_j, \Phi_j)]^4 \sin^2 \theta_j \rangle \ldots (35)$$

From (33) we see that $\Delta U^\text{ad} [R]$ 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

$$\Delta U^\text{ad}_{LJ} [R] = -\frac{C}{R^2} + \frac{B}{R^6} \ldots (36)$$

that was proposed by Lennard-Jones long time ago.

The third member of this series, $2k+2, 4k+4$ family of potentials, i.e. $\Delta U^\text{ad}_{\mu,2} [R]$ with $k=2$, is a 12-6 potential function

$$\Delta U^\text{ad}_{\mu,2} [R] = -\frac{\mu C_2}{R^6} + \frac{\mu B_2}{R^{12}} \ldots (37)$$

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

$$\Delta U^\text{ad}_{LJ} (R) = 4\varepsilon \left( \frac{\sigma^{12}}{R^{12}} - \frac{\sigma^6}{R^6} \right) \ldots \ldots (38)$$

$\varepsilon$ 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 $\Delta U^\text{ad}_{\mu,2} [R]$ 12-6 potential has been calculated for the $\text{FeO}_x^2^+$ dipole; dipole = $\text{H}_2\text{O}^+$, $\text{H}_3\text{O}^+$, $\text{HO}^-$ and $\text{NH}_3$ surface complex. The minimum for all the dipoles occurred at about $R = 1.272\text{Å}$. 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 $\Delta U^\text{ad}_{\mu,2} [R]$ 12-6 potential agrees well with $\Delta H^\text{ad}$ for all the dipoles. This reveals that the $\Delta U^\text{ad}_{\mu,2} [R]$ 12-6 potential can reasonably well predict the energetics of intermolecular interactions as much as

$$\Delta U^\text{ad}_{\mu} [R] = \sum_{k=0}^{\infty} \Delta U^\text{ad}_{\mu,k} [R]$$

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 than any other form of semi-empirical intermolecular potential.

**CONCLUSION**

The energetics of the adsorption of $\text{H}_2\text{O}^+$, $\text{H}_3\text{O}^+$, $\text{HO}^-$ and $\text{NH}_3$ dipoles at an oxygen vacant site on the (111) face of $\alpha$-$\text{FeO}_x$ have been calculated as a first order intermolecular electrostatic interaction energies between a dipole and the ferric ion of an $\text{FeO}_x^2^+$ 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 $\text{Fe}^{3+}$.

The intermolecular electrostatic potential that is used in the physisorption enthalpy calculations 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 $\text{Fe}^{3+}$ ion in the intermolecular potential $\Delta U^\text{ad}_{\mu,2} [R]$ 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 $U^\text{ad} (R, \beta, r, \theta, \phi)$ of (15) as well as...
ΔU_{el}(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_{1}(R,β,R,θ̂,φ̂) and ΔU_{el}(R) decreases exponentially with R in agreement with the semi-empirical theories. These exponential functions e_{k}(R,β,R,θ̂,φ̂) and their average, which may be defined as

$$\Delta \phi_{k}(R) = \left< \sum (j) Q_{k}(R,\theta_{j},\phi_{j}) \right> \left/ \sum (j) Q_{k}(R,\theta_{j},\phi_{j}) \right> \tag{39}$$

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

REFERENCES


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

$$U_{ej} = \theta_{ej} \left( \frac{1}{r} - \frac{1}{AP} \right) \tag{A-1}$$

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

$$\frac{1}{r} - \frac{1}{AP} = \frac{\sin \alpha - \sin \beta'}{TP \sin (\beta - \alpha)} \tag{A-2}$$

using sine rule, so that

$$U_{ej} = \frac{\theta_{ej} TP \sin (\beta - \alpha)}{TP \sin (\beta - \alpha)} (\sin \alpha - \sin \beta') \tag{A-3}$$

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

$$\sin \alpha = \left[ TP^{2} \sin^{2} (\beta - \alpha) \right]^{\frac{1}{2}} \tag{A-4}$$

and

$$\sin \beta = \left[ TP^{2} \sin^{2} (\beta - \alpha) + \frac{1}{2 TP \cos (\beta - \alpha)} \right]^{\frac{1}{2}} \tag{A-4}$$

\[ \sin\beta' = \frac{TP^2 \sin^2 (\beta - a)}{[TP^2 \sin^2 (\beta - a) + \left( \frac{1}{2} + TP\cos (\beta - a) \right)^2]^{\frac{1}{2}}} \]  \hspace{1cm} (A-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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