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## Atomistic Simulations of Oleic Imidazolines Bound to Ferric Clusters

Sunder Ramachandran,<sup>†,‡</sup> Bao-Liang Tsai,<sup>†</sup> Mario Blanco,<sup>†</sup> Huey Chen,<sup>§</sup> Yongchun Tang,<sup>§</sup> and William A. Goddard III<sup>\*,†</sup>

Materials and Process Simulation Center, Beckman Institute (139-74), Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, and Chevron Petroleum Technology Company, 1300 Beach Boulevard, La Habra, California 90631

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The oleic imidazoline (OI) class of molecules is used extensively for corrosion inhibitor oil field pipeline applications. However, there is no model for understanding how they work. As a first step in elucidating this mechanism we carried out quantum mechanical calculations on clusters involving  $\text{Fe}^{3+}$ ,  $\text{H}_2\text{O}$ ,  $\text{OH}$ , and OI. These calculations are used to determine the MS force field for molecular dynamics simulations.

## 1.0 Introduction

Corrosion causes enormous industrial expense leading to a large market for corrosion inhibitors. Development of such corrosion inhibitors has been slowed because *the mechanism by which these chemical compounds prevent corrosion is not understood*.<sup>1</sup> Experimental evidence in support of specific mechanisms is difficult because

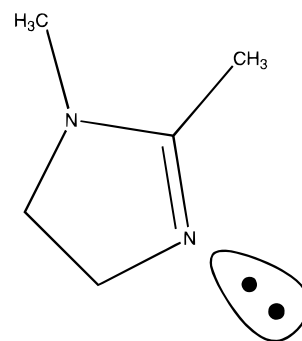
- they are used in low concentrations (a few parts per million),
- the operating environments are quite complex, and
- it is difficult to experimentally observe the atomistic nature of the fluid/metal interface.

In this paper we report quantum chemical (QC) calculations on clusters involving oleic imidazoline (OI) inhibitors and develop the MS force field (FF) to be used in molecular dynamics (MD) simulations. As a model OI, we use the molecule 1,2-dimethylimidazoline (OI-1-C) in Figure 1.

## 2.0 Results

**2.1 The GVB Model of  $\text{Fe}_2\text{O}_3$ .** At pH values in the range of 4–6 (for oil field applications the pH  $\sim$  4.5), the stable oxide<sup>2,3</sup> of Fe is  $\alpha\text{-Fe}_2\text{O}_3$  (hematite). Thus we expect that the Fe surface will be covered by this native oxide. Consequently we studied the interactions of OI with the  $\text{Fe}_2\text{O}_3$  surface. In  $\alpha\text{-Fe}_2\text{O}_3$  crystal the Fe is in a distorted octahedral site with three bonds at 1.946 Å (with OFeO bond angles of 111.8°) and three at 2.116 Å.<sup>4</sup> The GVB model of  $\text{Fe}_2\text{O}_3$  postulates that the bonding in  $\text{Fe}_2\text{O}_3$  can be described as follows:

- There are three covalent partially ionic (CPI) bonds with bond distances of 1.946 Å. These correspond to the formal charge of +3. Each CPI bond involves some 4s and 4p atomic character on the Fe as the electron in each orbital is partially transferred to the oxygen atom.
- The Fe also has five electrons in d orbitals (a  $d^5$  configuration) coupled to high spin ( $S = 5/2$ ).
- The remaining three  $\text{Fe}\cdots\text{O}$  bonds (2.116 Å) are of donor–acceptor (DA) or Lewis base–Lewis acid type. This involves a lone pair on the O (the Lewis base) coordinating to the Fe (the Lewis acid).



**Figure 1.** 1,2-Dimethylimidazoline used as a model for OI corrosion inhibitors. (The ring  $\text{CH}_2$  groups are implicit.) The lone pair that coordinates to the Fe is indicated.

**2.2 Cluster Calculations for  $\text{Fe}_2\text{O}_3$ .** To test the GVB model of  $\text{Fe}_2\text{O}_3$ , we first carried out QC calculations<sup>5–8</sup> (RHF/LAV3P\*) on the  $\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_3$  cluster. We find the structure in Figure 2 with three CPI bonds of 1.916 Å (with OFeO bond angles of 109.3°) and three DA bonds of 2.259 Å. In the GVB model the CPI bond should be approximately trans to a DA bond, and indeed the cluster leads to an average angle of 160.3° while the crystal leads to 162.2°. Also the Fe–O–Fe bond angle in hematite between CPI bonds is 119.7°, while the Fe–O–H bond angle in the cluster is 121.8°. The close correspondence of the geometries for the  $\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_3$  cluster and the  $\text{Fe}_2\text{O}_3$  crystal confirms the GVB model of  $\text{Fe}_2\text{O}_3$ .

To examine the character of the orbitals, we carried out GVB calculations. Here we correlated the three Fe–O CPI bonds, the three Fe–OH<sub>2</sub> DA bonds, and all nine OH bonds [GVB-(15/24)]. Figure 3a shows the two  $\text{Fe}\cdots\text{O}$  GVB orbitals for the Fe–OH CPI bond. One orbital corresponds closely to an  $\text{sp}^3$  hybrid orbital on the O, while the other has some Fe  $\text{sp}$  character in addition to the O character. The GVB overlap is 0.87, indicating a fairly ionic bond. The covalent nature of the bond is shown in the buildup of electron density between the atoms. The ionic nature is clear by the large participation of the oxygen orbitals in the both GVB orbitals. Figure 3b shows the two GVB orbitals of a Fe–OH<sub>2</sub> donor–acceptor bond from a GVB calculation correlating all 24 valence pairs (to make the lone pairs unique). Here the orbitals correspond to the lone pair of the oxygen in the  $\text{H}_2\text{O}$ , with in–out or radial correlation. This pair forms a Lewis base to Lewis acid bond to the Fe.

From the QC calculations (RHF/LAV3P\*) on the cluster, we developed the MS FF in Tables 1 and 2. [Here the MS denotes that the FF is meant to be used for materials simulations.] This

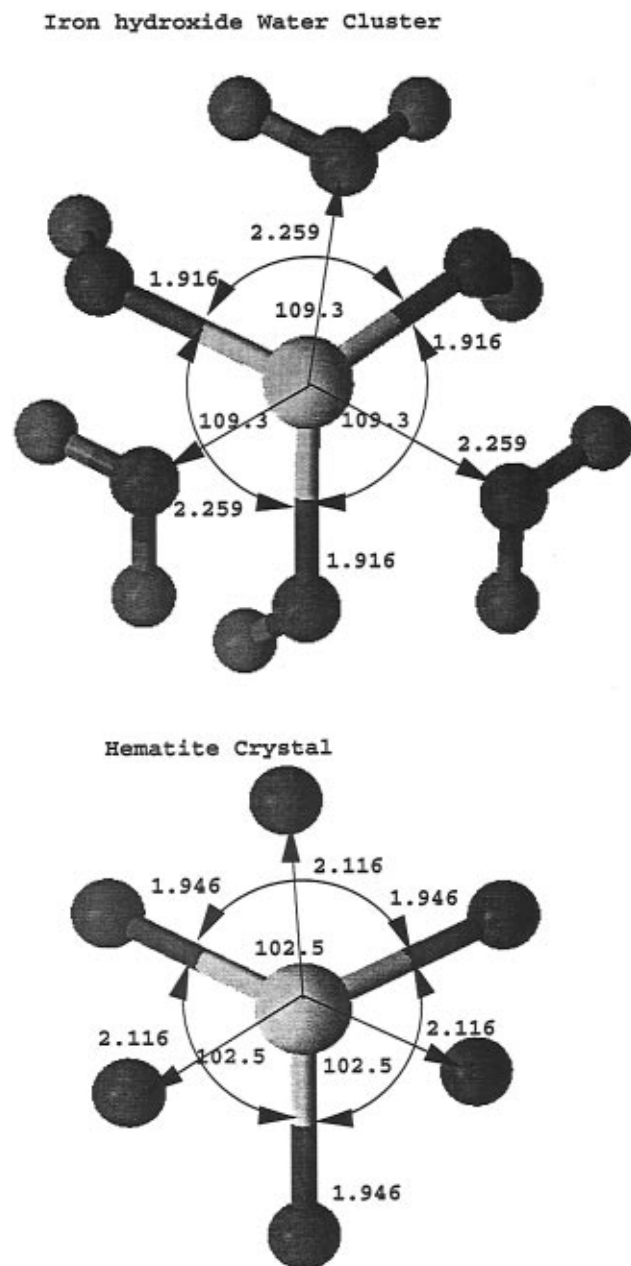
\* To whom correspondence should be addressed.

<sup>†</sup> California Institute of Technology.

<sup>‡</sup> Current Address: Baker Performance Chemicals Incorporated, 3900 Essex Lane, 3rd floor, Houston, Texas 77027.

<sup>§</sup> Chevron Petroleum Technology Company.

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**Figure 2.** (a)  $\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_3$  cluster optimized using QM (HF/LAV3P\*). (b) Geometry from the  $\alpha\text{-Fe}_2\text{O}_3$  crystal.

FF is based on the generalized valence bond (GVB) model of  $\text{Fe}_2\text{O}_3$ . Thus we distinguish an Fe—OH CPI bond (which uses the Fe—O<sub>3</sub> valence parameters in Table 1A) from the Fe $\cdots$ OH<sub>2</sub> DA bond (which uses the Fe $\cdots$ O<sub>3</sub> nonbond parameters in Table 2B). We started with the Dreiding FF and modified only geometric parameters to fit the QC results. As a test of the GVB model for  $\text{Fe}_2\text{O}_3$ , we then used the MS FF to describe the  $\alpha\text{-Fe}_2\text{O}_3$  crystal. This leads to lattice parameters of  $a = b = 5.00$  Å,  $c = 13.76$  Å, which compares well with the experimental lattice parameters  $a = b = 5.038$  Å,  $c = 13.77$  Å.<sup>4</sup>

**2.3 Binding Energies of  $\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_2$  and N-Containing Molecules.** We assume that the binding of OI corrosion inhibitor molecules to the iron oxide surface involves Fe—N interactions. In order to model this interaction, we use the GVB model of  $\text{Fe}_2\text{O}_3$  which suggests that in water the surface Fe can be modeled as  $\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_3$ . Thus we used the  $\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_2(\text{Nm})$  cluster to represent OI bond to oxide surface. In order to understand whether OI is special, we calculated the

bond energies between various small N-containing molecules (Nm) and the iron oxide cluster.

We first investigated the GVB model using three different basis set schemes:

- LANL1DZ—Hay and Wadt's basis (3s2p5d/2s2p2d) and 18-electron effective core potential for Fe,<sup>9</sup> D95V (DZ)<sup>10</sup> basis for the nonmetals.
- LAV3P\*—Hay and Wadt's basis (3s2p5d/3s2p2d) and 18-electron effective core potential for Fe, 6-31G\* basis for the nonmetals.
- LACV3P\*—Hay and Wadt's basis (9s5p5d/3s3p2d) and 10-electron effective core potential for Fe,<sup>9</sup> 6-31G\* basis for the nonmetals.

All calculations with LANL1DZ and LACV3P\* were done at the UHF level using the Gaussian 92 program, while with LAV3P\* the calculations were done at the RHF level using PSGVB program. Table 3 lists the  $\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_2\text{—H}_2\text{O}$  bond energy calculated using the three schemes. The LACV3P\* basis is the most accurate (including an explicit treatment of the 3s, 3p core electrons); however, Table 3 shows that LAV3P\* leads to bond energies within 1 kcal/mol. Thus the simple treatment of only the eight valence electrons on the Fe is adequate. Similarly the smaller LANL1DZ basis gives results comparable to the more extensive LAV3P\* basis. Therefore, we used LANL1DZ for all further calculations.

The bond energies calculated (UHF/LANL1DZ) for various N-containing molecules are also listed in Table 3. The snap bond energy shows the electronic effects. Thus  $\text{NH}_3$  with  $D = 28.8$  kcal/mol is a stronger Lewis base than  $\text{H}_2\text{O}$  with  $D = 24.9$  kcal/mol. However, the adiabatic bond energies for  $\text{NH}_3$  and  $\text{H}_2\text{O}$  are closer, 12.2 and 11.7 kcal/mol, respectively, indicating the importance of steric effects. These calculations show that the  $\text{sp}^2$  ligand  $\text{NH}=\text{CH}_2$  bonds to  $\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_2$  comparably with the  $\text{sp}^3$  ligand  $\text{NH}_2\text{—CH}_3$ , but both are much better than the  $\text{sp}^1$  ligand NCH. We find that the  $\text{sp}^2$  ligand imidazoline makes a much stronger bond (41.8 kcal/mol snap bond energy) to the Fe atom of  $\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_2$  than  $\text{NH}=\text{CH}_2$ , indicating a special role for the imidazoline ring. This extra bonding is consistent with the excellent corrosion inhibition for these OI compounds.

**2.4 Binding of OI.** On the surface of  $\text{Fe}_2\text{O}_3$  we expect the OI to bond strongly as a Lewis base to the  $\text{Fe}^{3+}$ . In aqueous environments we assume that there is an  $\text{H}_2\text{O}$  at this surface site of  $\text{Fe}_2\text{O}_3$  that must be displaced. Thus we optimized the structure of  $\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_2$  (OI-1-C) with the results in Figure 4. The average Fe—OH distance is 1.930 Å (an increase of 0.014 Å) with an OFeO angle of 106.0° (a decrease of 3.3°). The average DA bond is 2.358 Å to  $\text{H}_2\text{O}$  (an increase of 0.10 Å) with an Fe $\cdots$ OI bond of 2.245 Å.

The snap bond energy (no change in other ligands) is 37.0 kcal/mol for OI compared to 22.3 kcal/mol for  $\text{H}_2\text{O}$ . This indicates that the dative bond due to the  $\text{Nsp}^2$  lone pair orbital of OI is considerably stronger than that of the  $\text{Osp}^3$  lone pair orbital of  $\text{H}_2\text{O}$ .

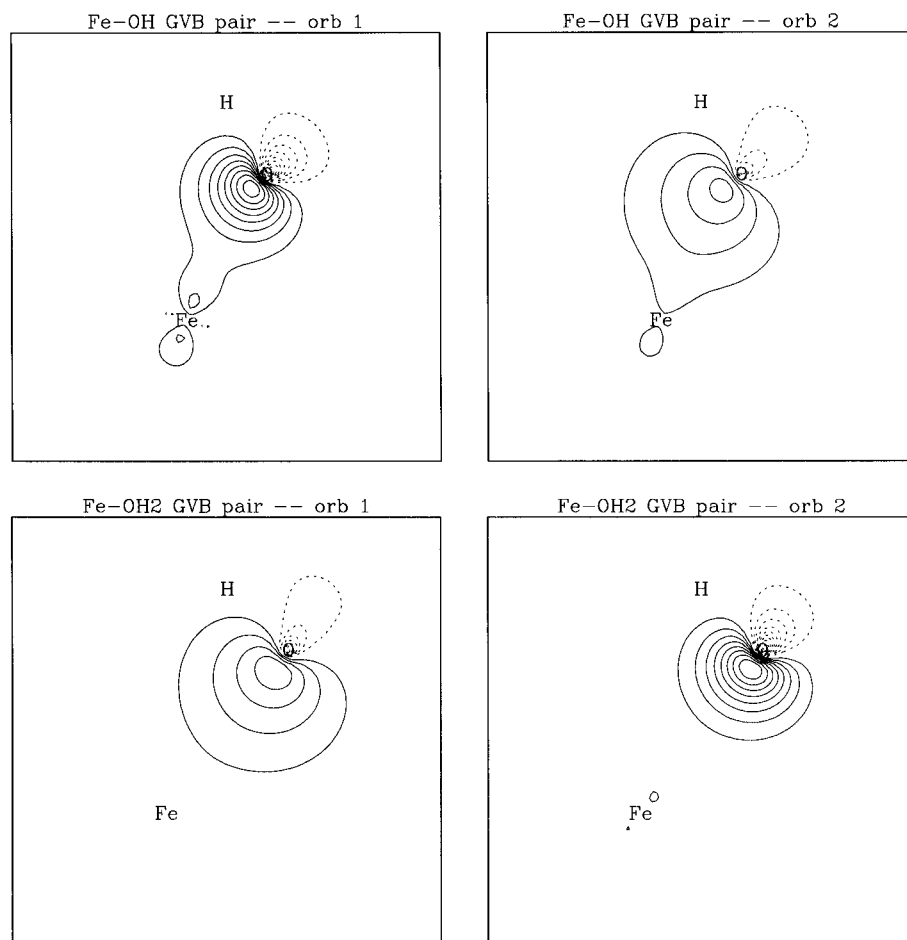
Allowing the ligands to relax after breaking the bond (the adiabatic bond energy), the desorption energy for OI is 16.6 kcal/mol versus 12.9 for  $\text{H}_2\text{O}$ . The decreased adiabatic bond energy versus the snap bond energy reflects crowding in the six-coordinate site.

Combining these quantities, we estimate the energetics in (1)



$$\Delta E_1^{\text{AD}} = -3.7 \text{ kcal/mol (exothermic)} \quad (1b)$$

$$\Delta E_1^{\text{snap}} = -14.7 \text{ kcal/mol} \quad (1c)$$



**Figure 3.** GVB contour diagram of the electron pairs of (a) Fe–OH CPI bond and (b) Fe–OH<sub>2</sub> donor–acceptor bond.

**TABLE 1: Valence Parameters for the MS FF<sup>a</sup>**

(A) Bond Stretch (Harmonic):  $E(R) = \frac{1}{2}K_b(R - R_b)^2$

type	$K_b$ (kcal/mol/Å)	$R_b$ (Å)	type	$K_b$ (kcal/mol/Å)	$R_b$ (Å)
Fe–O <sub>3</sub>	1050.0 <sup>a</sup>	1.925 <sup>a</sup>	N <sub>3</sub> –C <sub>3</sub>	700.0 <sup>b</sup>	1.462 <sup>b</sup>
Fe–O <sub>3z</sub>	1050.0 <sup>a</sup>	1.972 <sup>a</sup>	N <sub>3</sub> –R–C <sub>3</sub>	700.0 <sup>b</sup>	1.460 <sup>b</sup>
O <sub>3</sub> –H	700.0 <sup>b</sup>	0.98 <sup>b</sup>	N <sub>3</sub> –R–C <sub>2</sub>	1050.0 <sup>b</sup>	1.380 <sup>b</sup>
C <sub>2</sub> –C <sub>3</sub>	700.0 <sup>b</sup>	1.430 <sup>b</sup>	N <sub>2</sub> –C <sub>3</sub>	700.0 <sup>b</sup>	1.460 <sup>b</sup>
C <sub>2</sub> –C <sub>2</sub>	1400.0 <sup>b</sup>	1.330 <sup>b</sup>	N <sub>2</sub> –C <sub>2</sub>	1400.0 <sup>b</sup>	1.250 <sup>b</sup>
N <sub>3</sub> –H	700.0 <sup>b</sup>	1.022 <sup>b</sup>	C <sub>2</sub> –H	700.0 <sup>b</sup>	0.9900 <sup>b</sup>

(B) Bond Stretch (Morse):  $E(R) = D_b[e^{\alpha_b(R-R_b)} - 1]^2$  where  $K_b = 2D_b\alpha_b^2$

type	$D_b$ (kcal/mol)	$K_b$ (kcal/mol/Å)	$R_b$ (Å)
C <sub>3</sub> –H	95.1 <sup>c</sup>	741.372 <sup>c</sup>	1.0765 <sup>c</sup>
C <sub>3</sub> –C <sub>3</sub>	85.8 <sup>c</sup>	884.994 <sup>c</sup>	1.4841 <sup>c</sup>

(C) Angle Bend (Harmonic Cosine):  $E(\theta) = \frac{1}{2}K_\theta(\cos \theta - \cos \theta_0)^2$  Where  $K_\theta = C \sin^2 \theta_0$

type	$K_\theta$ (kcal/mol)	$\theta_0$ (deg)	type	$K_\theta$ (kcal/mol)	$\theta_0$ (deg)
Fe–O <sub>3</sub> –X	300.0 <sup>a</sup>	124.50 <sup>a</sup>	X–N <sub>2</sub> –X	100.0 <sup>b</sup>	109.47 <sup>b</sup>
Fe–O <sub>3z</sub> –X	400.0 <sup>a</sup>	126.30 <sup>a</sup>	X–C <sub>3</sub> –X	100.0 <sup>b</sup>	109.47 <sup>b</sup>
O <sub>3</sub> –Fe–O <sub>3</sub>	400.0 <sup>a</sup>	116.80 <sup>a</sup>	X–C <sub>2</sub> –X	100.0 <sup>b</sup>	120.0 <sup>b</sup>
O <sub>3z</sub> –Fe–O <sub>3z</sub>	300.0 <sup>a</sup>	107.60 <sup>a</sup>	H–C <sub>3</sub> –H	55.6076 <sup>c</sup>	119.393 <sup>c</sup>
X <sub>3</sub> –N <sub>3</sub> –X	100.0 <sup>b</sup>	106.70 <sup>b</sup>	C <sub>3</sub> –C <sub>3</sub> –H	65.7301 <sup>c</sup>	117.7291 <sup>c</sup>
X–N <sub>3</sub> –X	100.0 <sup>b</sup>	120.00 <sup>b</sup>	C <sub>3</sub> –C <sub>3</sub> –C <sub>3</sub>	84.1810 <sup>c</sup>	121.24 <sup>c</sup>
C <sub>3</sub> –N <sub>3</sub> –C <sub>2</sub>	100.0 <sup>b</sup>	109.47 <sup>b</sup>			

(D) Torsion:  $E(\phi) = \frac{1}{2}|V_T|(1 - (V_T/|V_T|) \cos P_\phi)$

type	P	$V_T^d$	type	P	$V_T^d$
X–C <sub>2</sub> –C <sub>3</sub> –X	3 <sup>a</sup>	2.0 <sup>a</sup>	C <sub>2</sub> –N <sub>2</sub> –C <sub>3</sub> –X	3 <sup>a</sup>	2.0 <sup>a</sup>
N <sub>2</sub> –C <sub>2</sub> –N <sub>3</sub> –X	6 <sup>a</sup>	–1.0 <sup>a</sup>	X <sub>3</sub> –N <sub>2</sub> –C <sub>2</sub> –X	2 <sup>a</sup>	–10.0 <sup>a</sup>
O <sub>3</sub> –Fe–O <sub>3</sub> –X	6 <sup>a</sup>	0.5 <sup>a</sup>	H–C <sub>3</sub> –C <sub>3</sub> –H	3 <sup>c</sup>	–5.1686 <sup>c</sup>
O <sub>3z</sub> –Fe–O <sub>3z</sub> –X	6 <sup>a</sup>	0.5 <sup>a</sup>	C <sub>3</sub> –C <sub>3</sub> –C <sub>3</sub> –H	3 <sup>c</sup>	–6.1626 <sup>c</sup>
X <sub>3</sub> –N <sub>3</sub> –C <sub>3</sub> –X	3 <sup>b</sup>	2.0 <sup>b</sup>	C <sub>3</sub> –C <sub>3</sub> –C <sub>3</sub> –C <sub>3</sub> <sup>+</sup>	3 <sup>c</sup>	–5.7070 <sup>c</sup>
X–N <sub>3</sub> –R–C <sub>2</sub> –X	2 <sup>a</sup>	–2.0 <sup>a</sup>			

**TABLE 1 (Continued)**

(E) Bond–Angle and Bond–Bond Cross-Terms: $E_{ax} = D_1(\cos \theta - \cos \theta_0)(R_1 - R_{b1}) + D_2(\cos \theta - \cos \theta_0)(R_2 - R_{b2}) + K_{rr}(R_1 - R_{b1})(R_2 - R_{b2})$						
type	$D_1$ (kcal/mol)	$\theta_0$ (deg)	$R_{b1}$ Å	$D_2$ (kcal/mol)	$R_{b2}$ Å	$K_{rr}$ (kcal/mol/Å <sup>2</sup> )
H–C <sub>3</sub> –H	–22.6583 <sup>c</sup>	119.393 <sup>c</sup>	1.0765 <sup>c</sup>	–22.6583 <sup>c</sup>	1.0765 <sup>c</sup>	3.1321 <sup>c</sup>
C <sub>3</sub> –C <sub>3</sub> –H	–34.3195 <sup>c</sup>	117.7291 <sup>c</sup>	1.4841 <sup>c</sup>	–25.9234 <sup>c</sup>	1.0765 <sup>c</sup>	1.3684 <sup>c</sup>
C <sub>3</sub> –C <sub>3</sub> –C <sub>3</sub>	–54.0185 <sup>c</sup>	121.24 <sup>c</sup>	1.4841 <sup>c</sup>	–54.0185 <sup>c</sup>	1.4841 <sup>c</sup>	26.2187 <sup>c</sup>
(F) Inversion (Cosine Harmonic) $E(\psi) = \frac{1}{2}C(\cos \psi - \cos \psi_0)^2$ Where $K_\psi = C \sin^2 \psi_0$						
type	$K_\psi$ (kcal/mol)		$\psi_0$ (deg)			
C <sub>2</sub> –X–X–X	5.00 <sup>a</sup>		0.0 <sup>b</sup>			
N <sub>2</sub> –X–X–X	6.80 <sup>a</sup>		40.0 <sup>a</sup>			

<sup>a</sup> Values optimized in this paper. <sup>b</sup> Values from ref 12. <sup>c</sup> Values from ref 13. <sup>d</sup> Positive implies that the cis configuration is maximum, whereas negative implies that it is a minimum.

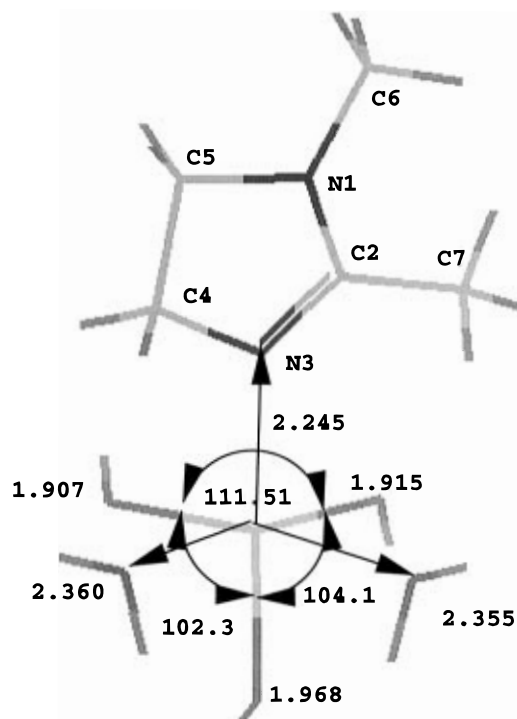
**TABLE 2: van der Waals Parameters for the MS FF<sup>a</sup>**

(A) Diagonal Nonbond Terms (exp-6): $E(R) = D_v\{[6/(\zeta - 6)] \exp[\zeta(1 - r)] - [\zeta/(\zeta - 6)]\rho^{-6}\}$ Where $\rho = R/R_v$			
type	$R_v$ (Å)	$D_v$ (kcal/mol)	$\zeta$
H	3.166 50 <sup>c</sup>	0.020 00 <sup>c</sup>	11.200 0 <sup>c</sup>
O <sub>3</sub>	3.404 60 <sup>b</sup>	0.095 70 <sup>b</sup>	13.483 <sup>b</sup>
O <sub>2</sub>	3.404 60 <sup>b</sup>	0.095 70 <sup>b</sup>	13.483 <sup>b</sup>
Fe	4.540 00 <sup>b</sup>	0.055 00 <sup>b</sup>	12.000 0 <sup>b</sup>
C <sub>3</sub>	3.48 10 <sup>c</sup>	0.079 18 <sup>c</sup>	13.000 0 <sup>c</sup>
C <sub>2</sub>	3.841 00 <sup>c</sup>	0.079 18 <sup>c</sup>	13.000 <sup>c</sup>
N <sub>3</sub>	3.660 00 <sup>b</sup>	0.069 00 <sup>b</sup>	13.843 <sup>b</sup>
N <sub>2</sub> R	3.660 00 <sup>b</sup>	0.069 00 <sup>b</sup>	13.843 <sup>b</sup>
N <sub>2</sub> R	3.660 00 <sup>b</sup>	0.069 00 <sup>b</sup>	13.843 <sup>b</sup>

(B) Off-Diagonal Nonbond Terms (Morse):

$E(R) = D_v[\chi^2 - \chi]$ Where $\chi = \exp[1/2\zeta(1 - \rho)]$ and $\rho = R/R_v$			
type	$R_v$ (Å)	$D_v$ (kcal/mol)	$\zeta$
O <sub>3</sub> –Fe	2.4180 <sup>a</sup>	5.14 <sup>a</sup>	11.0 <sup>a</sup>
O <sub>3z</sub> –Fe	2.4180 <sup>a</sup>	5.14 <sup>a</sup>	11.0 <sup>a</sup>
N <sub>2</sub> –Fe	2.2800 <sup>a</sup>	8.1 <sup>a</sup>	10.0 <sup>a</sup>
N <sub>2</sub> R–Fe	2.2800 <sup>a</sup>	8.1 <sup>a</sup>	10.0 <sup>a</sup>
N <sub>3</sub> –Fe	2.432 <sup>a</sup>	7.0 <sup>a</sup>	11.0 <sup>a</sup>

<sup>a</sup> Values optimized in this paper. <sup>b</sup> Values from ref 12. <sup>c</sup> Values from ref 13.



**Figure 4.** Fe(OH)<sub>3</sub>(H<sub>2</sub>O) (OI-1-C) cluster optimized using QM (HF/LANLIDZ).

**TABLE 3: Bond Energies for Fe(OH)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>–(molecule) from Quantum Chemical Calculations**

	LANL1DZ	LAV3P*	LACV3P*
(a) cluster Fe(OH) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub> –OH <sub>2</sub> bond energy (Fe···OH <sub>2</sub> )			
snap	24.94	22.28	22.46
adiabatic	11.72	12.88	11.75
(b) cluster Fe(OH) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub> –NH <sub>3</sub> bond energy (Fe···NH <sub>3</sub> )			
snap	28.82		
adiabatic	12.24		
(c) cluster Fe(OH) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub> –NH <sub>2</sub> CH <sub>3</sub> bond energy (Fe···NH <sub>2</sub> CH <sub>3</sub> )			
snap	30.14		
adiabatic	12.28		
(d) cluster Fe(OH) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub> –NHCH <sub>2</sub> bond energy (Fe···NHCH <sub>2</sub> )			
snap	29.46		
adiabatic	12.49		
(e) cluster Fe(OH) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub> –NCH bond energy (Fe···NCH)			
snap	11.85		
adiabatic	0.44		
(f) cluster Fe(OH) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub> –OI bond energy (Fe···OI)			
snap	41.77	36.89	
adiabatic	14.76	16.57	

Removing an H<sub>2</sub>O from the OI complex leads to (2)



$$\Delta E^{\text{AD}} = +9.7 \text{ kcal/mol} \quad (2b)$$

$$\Delta E^{\text{snap}} = +20.6 \text{ kcal/mol} \quad (2c)$$

These calculations indicate that OI adsorbs to the iron cluster more strongly than water. On the Fe<sub>2</sub>O<sub>3</sub> surface, constraints due to the Fe<sub>2</sub>O<sub>3</sub> framework should lead to energetics intermediate between snap (which allows no ligand rearrangement) and adiabatic (allowing full rearrangement). In addition, we expect that the Fe for the Fe<sub>2</sub>O<sub>3</sub> surface will be more positive than in the cluster (since neighboring Fe are more electron-positive than H), leading to larger bond energies. This agrees with the experimental observation that OI molecules absorb rapidly.<sup>11</sup>

**2.5 The MS FF.** **2.5.1 Valence Parameters.** We developed the MS FF to describe the geometries and energetics based on these cluster results. This is based on the GVB model of bonding. Thus we consider that there are three CPI Fe–O bonds using the valence parameter of Table 1 and three DA Fe···O bonds using the nonbond parameters of Table 2.

We started with the Dreiding<sup>12</sup> FF (using the exponential-six vdW parameters) and the MSXX FF for hydrocarbons<sup>13</sup> and modified them based on QC calculations on clusters.

The standard Dreiding atom types are used. Thus O<sub>3</sub> is an sp<sup>3</sup> O used in H<sub>2</sub>O. The iron atom in the ferric clusters is

denoted as Fe. The oxygen atom in the hydroxyl groups of the ferric clusters is also denoted as O<sub>3</sub>. The QC studies show that the O–Fe–O angle is 109.3° in the ferric cluster but 102.3° in hematite. Thus we define an O<sub>3z</sub> atom type to be used in hematite. We use N<sub>R</sub> to denote the nitrogen atom in the 1 position in the ring (involved in a  $\pi$  bond), while N<sub>2</sub> denotes the sp<sup>2</sup> nitrogen atom in the 3 position of the imidazoline ring (the atom coordinated to the Fe). The sp<sup>3</sup> nitrogen atom in amino ethyl side groups is denoted as N<sub>3</sub>. The sp<sup>3</sup> and sp<sup>2</sup> carbon atoms are denoted as C<sub>3</sub>, and C<sub>2</sub> atom types.

Table 1 describes the valence interaction terms of the MS FF. The terms are obtained from the Dreiding FF<sup>12</sup> and MSXX FF for hydrocarbons<sup>13</sup> with adjustments made to reproduce the ferric cluster and imidazoline ring QM results. The bond stretch force constants for iron–oxygen interactions use the Dreiding FF values for bond order of 1<sup>1/2</sup>. The following valence interactions are used where where

i. harmonic bond stretch terms

$$E(R) = \frac{1}{2}K_R(R - R_e)^2 \quad (3)$$

ii. Morse bond stretch terms

$$E(R) = D_b[e^{\alpha_b(R-R_b)} - 1]^2 \quad (4)$$

$$k_b = 2D_b\alpha_b^2 \quad (5)$$

iii. harmonic cosine angle stretch terms

$$E(\theta) = \frac{1}{2}C(\cos \theta - \cos \theta_0)^2 \quad (6)$$

$$K_\theta = C \sin^2 \theta_0 \quad (7)$$

iv. torsional  $n$ -fold potentials

$$E(\phi) = \frac{1}{2}|V_T| \left( 1 - \frac{V_T}{|V_T|} \cos P\phi \right) \quad (8)$$

v. bond–angle and bond–bond cross-terms of the form

$$E_{ax} = D_1(\cos \theta - \cos \theta_0)(R_1 - R_{b1}) + D_2(\cos \theta - \cos \theta_0)(R_2 - R_{b2}) + k_r(R_1 - R_{b1})(R_2 - R_{b2}) \quad (9)$$

vi. inversion terms of the form

$$E(\psi) = \frac{1}{2}C(\cos \psi - \cos \psi_0)^2 \quad (10)$$

where

$$K_\psi = C \sin^2 \psi_0 \quad (11)$$

It also has one-center angle–angle cross-terms and two-center angle–angle terms identical to the type given by Karasawa, Dasgupta, and Goddard<sup>13</sup> for the hydrocarbon interactions (pertaining to atom types C<sub>3</sub> and H).

Nonbond interactions are characterized by electrostatic and van der Waals interactions. The van der Waals interactions have exponential-six and off-diagonal Morse potentials. These are given in Table 2.

**TABLE 4: Charges (electron units) for Fe(OH)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>, Imidazoline, and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>**

	MS FF	QM
(a) Fe(OH) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub>		
Fe	1.56	1.56
O (OH)	−0.98	−1.04
H (OH)	0.46	0.41
H (H <sub>2</sub> O)	0.41	0.43
O (H <sub>2</sub> O)	−0.82	−0.75
(b) 1,2-Dimethylimidazoline (See Figure 4)		
N1 (1 position on ring)	−0.240	−0.344
C2 (2 position on ring)	0.800	0.826
N3 (3 position on ring)	−0.560	−0.783
C4 (4 position on ring)	−0.288 <sup>a</sup>	0.393
C5 (5 position on ring)	−0.288 <sup>a</sup>	−0.261
C6 (1-methyl)	−0.432 <sup>a</sup>	−0.311
C7 (2-methyl)	−0.432 <sup>a</sup>	−0.604
H8 (C4 Hydrogen)	0.144 <sup>a</sup>	−0.016
H9 (C4 Hydrogen)	0.144 <sup>a</sup>	−0.009
H10 (C5 Hydrogen)	0.144 <sup>a</sup>	0.108
H11 (C5 Hydrogen)	0.144 <sup>a</sup>	0.119
H12 (C6 Hydrogen)	0.144 <sup>a</sup>	0.161
H13 (C6 Hydrogen)	0.144 <sup>a</sup>	0.113
H14 (C6 Hydrogen)	0.144 <sup>a</sup>	0.113
H15 (C7 Hydrogen)	0.144 <sup>a</sup>	0.159
H16 (C7 Hydrogen)	0.144 <sup>a</sup>	0.174
H17 (C7 Hydrogen)	0.144 <sup>a</sup>	0.160
(c) $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> Crystal		
Fe	1.317	
O	−0.878	

<sup>a</sup> Charges fixed to values from ref 13.

**2.5.2 Charges.** Potential-derived charges (PDQ) were obtained from QC calculations on Fe clusters and the imidazoline head group. These are shown in Table 4. Adjustments were made to eliminate effects of charge transfer as shown in Table 4. In order to be able to predict charges for various substitutions of the OI and for the Fe<sub>2</sub>O<sub>3</sub> surface, we modified the QEq parameters<sup>14</sup> to reproduce the QC charges. These new QEq\* parameters are  $X_{Fe} = 3.100$  eV,  $\frac{1}{2}J_{Fe} = 3.400$  eV, and  $R_{Fe} = 1.30$  Å. These values were then used in the extension of the QEq method<sup>14</sup> for periodic systems<sup>15</sup> to determine charges in hematite (see Table 4). Charges on the hydrocarbon tail are determined identically as for MSXX FF<sup>13</sup> (making each methylene unit electrically neutral, see Table 4). The charges on water were taken from Stillinger and Rahman<sup>16</sup> (see Table 4). The charges for hydroxyl and amine compounds used in a later papers<sup>17</sup> follow the MSXX FF convention (keeping each functional group electrically neutral) with the hydrogen atoms of hydroxyl and amine groups at 0.45 and 0.36, respectively.

**2.5.3 Validation.** The results from MSX FF calculations on the cluster are compared with QC results in Table 5. The structures and energetics of the adiabatic (minimum energy) structures for the MS FF are in excellent agreement with the QC. The snap bond energy for QC is larger than for the FF. This probably arises from the assumption of constant charges assumed in the FF. We consider it more important that the adiabatic energies be well described.

**2.6 The Pendant Group.** Most OI CI have a short pendent group, e.g.  $-\text{CH}_2-\text{CH}_2-\text{X}$ , where X is polar (X = NH<sub>2</sub> or OH). These polar groups can form a DA bond to a second Fe at the surface. Although this would appear to be beneficial, replacement with an alkyl group<sup>1</sup> seems to work nearly as well. Thus OI-17(8=9)-CCN (1-aminoethyl-2-oleicimidazoline) and OI-17(8=9)-C (1-methyl-2-oleicimidazoline) lead to CIE (corrosion inhibition efficiency) of 92% and 90%, respectively. However, replacement of the pendent group with H [OI-17(8=9)-H](2-oleicimidazoline) leads to a dramatic decrease to CIE = 77%. In order to determine the origin of this effect, we

**TABLE 5: Comparison between Quantum Mechanical and FF Results for Fe(OH)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub> and Fe(OH)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> (OI-1-C)**

	MS FF	QM (LAV3P*)
(a) Cluster Fe(OH) <sub>3</sub> (H <sub>2</sub> O) <sub>3</sub>		
Fe...OH <sub>2</sub>	2.259 Å	2.259 Å
Fe—OH	1.916 Å	1.916 Å
HO—Fe—OH	109.3°	109.3°
Fe—O—H	121.8°	121.8°
bond energy (Fe...OH <sub>2</sub> )		
snap	16.43	22.30
adiabatic	12.87	12.86
(b) Cluster Fe(OH) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub> (OI)		
Fe...N	2.245 Å	2.245 Å
Fe...OH <sub>2</sub>	2.317 Å	2.358 Å
Fe—OH	1.913 Å	1.930 Å
HO—Fe—OH	109.27°	105.97°
bond energy (Fe...OI)		
snap	23.67	36.96
adiabatic	16.56	16.57
(c) Fe <sub>2</sub> O <sub>3</sub> Crystal		
	MS FF	exptl
Fe—O	1.946 Å	1.946 Å
Fe...O	2.087 Å	2.116 Å
O—Fe—O	102.1°	102.3°
Fe—O—Fe	119.2°	119.7°
O...Fe—O	162.2°	162.2°
lattice parameters		
a = b	5.00 Å	5.038 Å
c	13.76 Å	13.77 Å

**TABLE 6: Snap Bond Energies (kcal/mol) for Fe(OH)<sub>3</sub>(OI) from *ab Initio* Quantum Mechanical Calculations**

method	basis set	snap bond energy	
		OI-1-C	OI-1-H
UHF	LANL1DZ	69.7	68.5
UMP2	LANL1DZ	61.4	59.9
UHF	LAV3P**	64.0	63.3
UMP2	LAV3P**	58.4	57.6

carried out QM and MD studies. Three possible explanations come to mind:

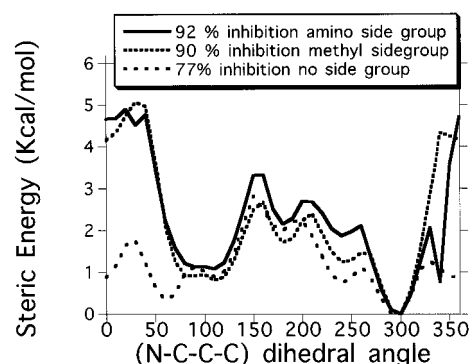
1. modification in the binding of the OI to the iron oxide surface;
2. effect on the configuration of the hydrocarbon tail;
3. effect on the packing of H<sub>2</sub>O molecules in the cavity at the surface formed by the OI monolayer.

To consider the role of bond energy, we examined the snap binding energies of OI-1-C and OI-1-H (1-methylimidazoline) to Fe(OH)<sub>3</sub> using unrestricted Hartree–Fock (UHF) and second-order Møller–Plesset perturbative methods (UMP2) with the LANL1DZ<sup>6,8</sup> and LAV3P\*\*<sup>7,8</sup> basis sets. These results (Table 6)<sup>6,7</sup> indicate that the deletion of a methyl group decreases the snap binding of the inhibitor by 1–2 kcal/mol out of 36 kcal/mol. This indicates that the large decrease in inhibition efficiency does not result from changes in the binding of the inhibitor to the surface.

A second function of the pendant group might be to restrict conformation of the hydrocarbon chain. Figure 5 shows the conformational energy (using the MS FF) as a function of N–C–C–C dihedral angle for three molecules:

- a. OI-17(8=9)-CCN,
- b. OI-17(8=9)-C, and
- c. OI-17(8=9)-H. The energies were determined by keeping the hydrocarbon tail all-trans with the double bond in the cis position.

The results indicate that a pendant group dramatically increases the steric energy of the molecule at 0° (overlap of carbon atoms) by 3 kcal/mol. This restriction of rotation about the C–C bond could be important in restricting the configuration involved in the monolayer. Free motion of the tail makes it

**Figure 5.** Steric energy vs N–C–C–C dihedral angle for 1-aminoethyl-2-oleicimidazoline (solid line, 92% CIE), 1-methyl-2-oleicimidazoline (dashed line, 90% CIE), and 2-oleicimidazoline (dotted line, 77% CIE).

easier for water to diffuse into a position on the surface between two different adsorbed tails. Attachment of the pendant group to an inhibitor molecule drastically restricts rotation of the hydrocarbon chain, leading to a barrier of 5.0 kcal for the methyl and aminoethyl side chains. Thus with the pendent group, an inhibitor molecule bound to a surface has its tail locked into position. This may lead to a rigid film, reducing free motion of water to the surface. This could be important for corrosion inhibition.

Since the N–H bond is polar, such pendent groups may make DA bonds to additional Fe on the surface, dislodging additional H<sub>2</sub>O. This may enhance stability. However, this may also encourage additional H<sub>2</sub>O to remain in the cavity formed at the surface. This may be expelled at higher temperature, disordering the film.

### 3.0 Summary

We used quantum mechanical calculations on ferric clusters to i. develop the GVB model of crystalline  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, ii. determine the relative binding of OI and other nitrogen-containing molecules to Fe(OH)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>, iii. determine the relative binding of OI and H<sub>2</sub>O to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, iv. construct the MS FF for OI and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, and v. assess the effect of the pendant group on configurational changes of the hydrocarbon tail. These results show that representative ferric clusters can be used to model the crystalline environment and to create an appropriate FF. This MS FF has now been used to study the mechanism of the corrosion inhibition of OI inhibitors.<sup>17</sup>

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