

# GC-10 Highlight



System	Dimer E, kcal/mol		Dimer R, Å		$\Delta H_{\text{vap}}$ , kcal/mol		Molecular Volume, Å <sup>3</sup>		Density, g/cm <sup>3</sup>	
	pff	QM	pff	QM	pff	exptl	pff	exptl	pff	exptl
CH <sub>4</sub> <sup>a</sup>	-0.44	-0.50	3.86	4.06	1.89	1.96	62.2	62.8	0.428	0.424
C <sub>2</sub> H <sub>6</sub> <sup>a</sup>					3.32	3.62	94.4	91.5	0.529	0.546
C <sub>3</sub> H <sub>8</sub> <sup>a</sup>					4.79	4.49	123.9	126.0	0.591	0.581
C <sub>4</sub> H <sub>10</sub> <sup>a</sup>					5.62	5.35	157.2	160.3	0.614	0.602
CH <sub>3</sub> OH <sup>b</sup>	-5.63	-5.59	2.81	2.80	8.84	8.95	67.0	67.7	0.794	0.786
Acetone <sup>b</sup>	-5.74	-5.76	3.38	3.28	7.91	7.48	127.4	123.0	0.757	0.784
Acetamide <sup>b</sup>	-12.9	-12.8	3.01	2.94	13.5	13.4	109.0	109.3	0.899	0.897
DME <sup>b</sup>	-1.45	-1.46	3.46	3.09	5.68	5.14	105.8	104.1	0.723	0.735
CH <sub>3</sub> SH <sup>b</sup>	-2.77	- <sup>c</sup>	3.77	- <sup>c</sup>	5.96	5.87	92.5	90.0	0.864	0.888
C <sub>2</sub> H <sub>5</sub> SH <sup>b</sup>					6.73	6.58	121.9	123.8	0.846	0.833
Benzene <sup>d</sup>	-3.14	-2.34	3.57	3.64	8.20	8.09	153.7	148.4	0.844	0.874
Phenol <sup>d</sup>	-5.87	-5.68	3.10	2.98	13.9	13.8	146.5	147.8	1.067	1.058

<sup>a</sup>Experimental data from *J. Phys. Chem.*, 98, 1994, 13077. Liquid simulations done at boiling temperatures: -161.49°C for methane, -88.63°C for ethane, -42.1°C for propane, -0.5°C for butane. <sup>b</sup>Experimental data from *J. Am. Chem. Soc.*, 118, 1996, 11225. Liquid simulations done at 25°C for methanol, 25°C for acetone, 221.15°C for acetamide, -24.60°C for DME, 5.96°C for CH<sub>3</sub>SH, 25°C for C<sub>2</sub>H<sub>5</sub>SH. Acetamide liquid state density compared with the OPLS-AA result from the same reference. <sup>c</sup>*Ab initio* gas-phase calculations in progress. <sup>d</sup>Experimental data from *J. Comp. Chem.*, 14, 1993, 206.

## Simulating Pure Liquids with a Polarizable Force Field

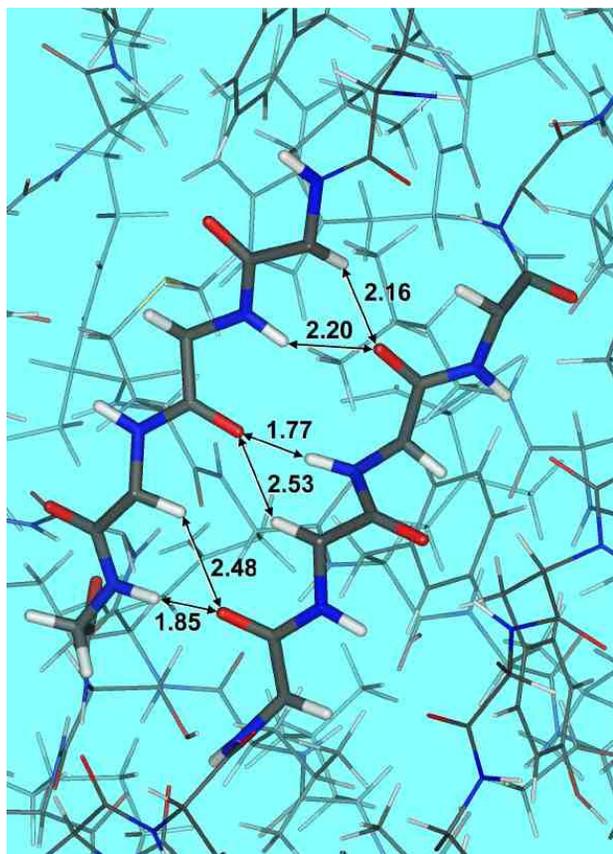
**Electrostatics consists of permanent charges on all sites and inducible dipoles on heavy atoms and polar hydrogens. It is fitted directly to *ab initio* data. VdW parameters include a 12-6 Lennard-Jones and an exponential parts and are chosen to reproduce *ab initio* gas-phase dimerization energies and distances. The coefficients before the  $1/r^{12}$  and  $1/r^6$  terms depend only on the element (same for all oxygens, same for all carbons, etc.). All liquid phase results obtained with NPT molecular dynamics simulations of 216 molecules.**

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## The Potential Role of C<sup>α</sup>-H...O=C Hydrogen Bonds in Establishing Protein Structure



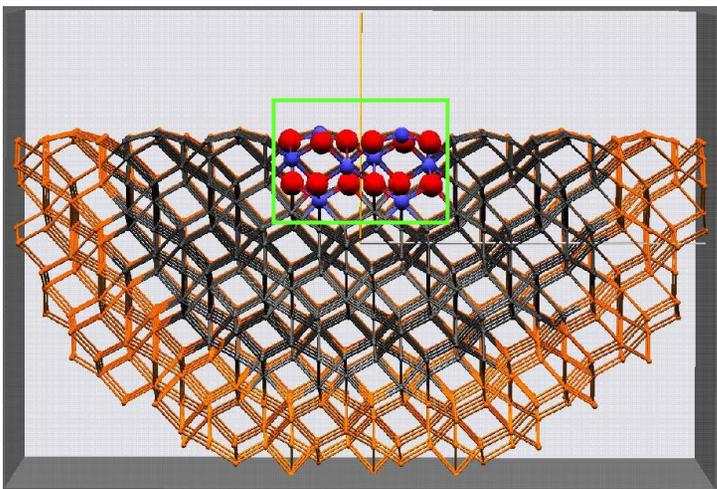
Although the existence of C<sup>α</sup>-H...O=C hydrogen bonds in protein structures recently has been established, little is known about their strength, and therefore, the relative importance of these interactions. We have discovered that similar interactions occur in N,N-dimethylformamide dimers. High level ab initio calculations (MP2/aug-cc-TZVP) yield electronic association energies ( $D_e$ ) and association enthalpies ( $\Delta H^{298}$ ) for three dimer geometries. These data provide a lower limit of  $D_e = -2.1$  kcal/mol for the C<sup>α</sup>-H...O=C hydrogen bond. A linear correlation between C-H...O bond energies and gas phase proton acidity was then established. The gas phase proton acidity of a peptide C<sup>α</sup>-H hydrogen was calculated to be 355 kcal/mol and used to estimate values of  $D_e = -4.0 \pm 0.5$  kcal/mol and  $\Delta H^{298} = -3.0 \pm 0.5$  kcal/mol for the C<sup>α</sup>-H...O=C hydrogen bond in a protein. The magnitude of this interaction, roughly 1/2 the strength of the N-H...O=C hydrogen bond, suggests that C<sup>α</sup>-H...O=C hydrogen bonding interactions represent a hitherto unrecognized, significant contribution in the determination of protein conformation. This work was highlighted in *Chemical and Engineering News*, May 8, 2000, p. 15. "How Strong is the C<sup>α</sup>-H...O=C Hydrogen Bond?". D.A. Dixon, J. Garza, B.P. Hay, and R. Vargas, *J. Am. Chem. Soc.*, **2000**, 122, 4750.

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## Point Charge Arrays to Produce Ionic Crystal Fields for Surface Ab-Initio Simulations: Application to Hematite ( $\alpha\text{-Fe}_2\text{O}_3$ )



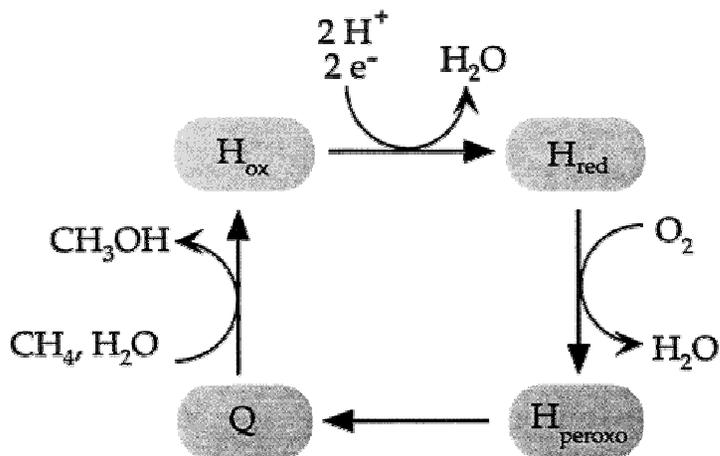
The understanding of the surface chemistry of iron oxides is one of the key issues in the study of environmental problems such as the transport of organic material and heavy metals as they move through soil. In performing ab-initio simulations of ionic crystals, the crystal is modeled using a cluster of ions embedded in an array of point charges. These point charges must be chosen to reproduce the crystal field at the surface of the crystal. A method for determining the right charges was developed. The point charges are obtained by a self consistent loop of fitting the charges to reproduce the field obtained by ab-initio calculations, using gradient corrected DFT, in the region of the cluster and its surroundings. This method was applied to the study of the basal plane of hematite. It was found that for a point charges approach, the electrostatic properties converge to crystal values, as function of the size of the cluster, for clusters of the order of 60 atoms. The work function of this surface was calculated in 5.6 eV, in reasonable agreement with experimental measurements.



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## Ab Initio Quantum Chemical Study of the Methane Monooxygenase (MMO) Catalytic Cycle

### Simplified Reaction Cycle for MMOH



Within the hydroxylase component (MMOH) of the multicomponent soluble MMO system, the oxidation of methane to methanol by dioxygen is catalyzed at non-heme dinuclear iron active sites. A large-scale theoretical model ( $\sim 100$  atoms) of the MMOH active site has been constructed. The model has been shown to energetically and structurally reproduce the species in the catalytic cycle. In the present work, *ab initio* quantum chemical density functional (DFT) methods employing the B3LYP functional are being used to study the following reactions in the catalytic cycle: 1) the conversion of methane to methanol by intermediate Q, a high-valent Fe(IV)Fe(IV) species; 2) the isomerization of intermediate P ( $H_{peroxo}$ ), a diferric species, into Q; and 3) the oxidation of the resting diferrous state ( $H_{red}$ ) by dioxygen to form intermediate P.

Dunietz, et al. J. Am. Chem. Soc. 2000, 122, 2828-2839.  
Gherman, et al. J. Am. Chem. Soc. 2001, 123, 3836-3837.  
Guallar, et al. J. Am. Chem. Soc. submitted.  
Jaguar 4.1, Schrodinger, Inc., Portland, Oregon, 2000.

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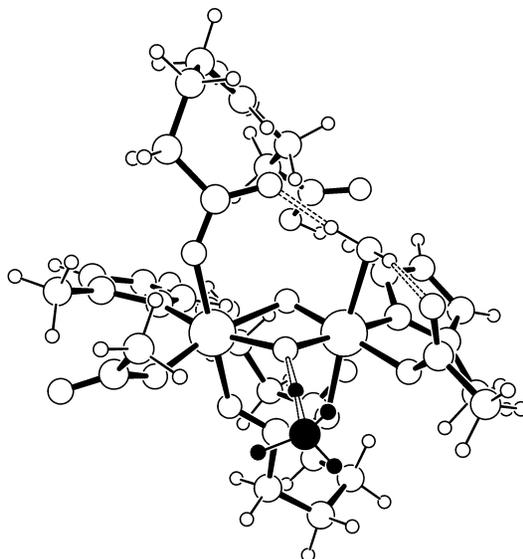
## *Ab Initio* Quantum Chemical Study of the Methane Monooxygenase (MMO) Catalytic Cycle

For each reaction, energy maps of the reaction coordinates are obtained, transition states and transient intermediates are identified, and reaction mechanisms are concluded. The dynamics of the reaction of methane and ethane with Q have also been studied. The results complement experimental data and serve as an integral part in understanding the enzymatic function of MMOH.

*(a) Minimized transition state for first step of methane activation by Q*

*(b) Core structure of this state.*

*(a)*



*(b)*

