FUNDAMENTAL ORGANOMETALLIC REACTIONS:
APPLICATIONS ON THE CYBER 205

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Abstract

Two of the most challenging problems of Organometallic chemistry (loosely defined) are pollution control with the large space velocities needed and nitrogen fixation, a process so capably done by nature and so relatively poorly done by man (industry). For a computational chemist these problems are on the fringe of what is possible with conventional computers (large models needed and accurate energetics required). A summary of the algorithmic modification needed to address these problems on a vector processor such as the Cyber 205 and a sketch of our findings to date on deNOx catalysis and nitrogen fixation are presented.

Introduction

Two of the most challenging problems in Organometallic chemistry (loosely defined) are pollution control with the large space velocities needed and nitrogen fixation, a process so capably done by nature and so relatively poorly done by man (industry). For a computational chemist these problems (and other similar problems) are on the fringe of what is possible with conventional computers (large models needed and accurate energetics required). The advent of vector processors such as the Cyber 205 is making such studies feasible. A summary of the algorithmic modification needed to address these problems on a vector processor is presented in section I, a sketch of the findings to date for deNOx catalysis is presented in section II,and finally a sketch of the nitrogen fixation results is presented in section III.

I. Algorithmic Modification.

The advent of vector processors is leading to a reexamination of fundamental computational algorithms of general use to computational chemists and the redesign of large scale codes. The present work illustrates both processes for the Cyber 205 computer. Reexamination of fundamental algorithms is illustrated with an examination of the similarity transform, a matrix operation of use to computational chemists. Large scale code redesign is examined through the implementation of a highly vectorized MC-SCF code.

A. Similarity Transform. A common sequence of matrix operations is the similarity transform

$$C = A^T B A \qquad (1).$$

For computational chemistry applications the matrices B and C are usually symmetric and generally stored in lower diagonal form. If the initial B matrix is expanded from upper diagonal form to full matrix representation vector operations are possible for both matrix multiplications. The linked triad instruction on the Cyber 205 is utilized for the first matrix multiplication and a vector dot product operation is used for the second matrix multiplication. In principle one could transpose matrix A and to use the linked triad instruction for both matrix multiplications; however, in this case since we only want slightly more than half of the final results the vector dot product is preferable as it permits selective manipulation of the column indices I and J. As is apparent from Table I the vectorized matrix transformation represents a substantial improvement over scalar mode with enhancements ranging from a factor of 10 to a factor of 40. Note for the 300x300 matrix case we are still approximately a factor of 2 off the maximum rate for the Cyber 205. The consideration of an algorithm where several matrices are transformed at once is in order. In addition it should be noted from Table I that the expansion from lower diagonal form does not add a significant cost (less than 10 percent). Finally, it should be apparent that the MFLOPS rate will be independent of the number of orbitals involved (indices I and J); the vectorized loops run over number of functions not orbitals (indices K and L).

B. SCF Coding Considerations. The fundamental kernel of self consistent field (SCF) codes in general[1,2] is the energy expression

$$E^{el} = \sum_{i,j}^{n} D_j^i h_{ij} + \sum_{\substack{i,j \\ k,l}}^{n} D_{kl}^{ij} (ik|jl) \tag{5},$$

where

$$h_{ij} = \sum_{\mu,\nu}^{m} c_\mu^i c_\nu^j \langle X_\nu | h | X_\nu \rangle \tag{6}$$

$$(ik|jl) = \sum_{\mu,\nu,\sigma,n}^{m} c_\mu^i c_\nu^k c_\sigma^j c_n^l \langle X_\mu(1) X\sigma(2) | r_{12}^{\frac{1}{2}} | X_\nu(1) X_n(2) \rangle \tag{7}$$

The integrals $\langle X_\mu | h | X_\nu \rangle$ and $\langle X_n X_\sigma | r_{12}^{\frac{1}{2}} | X_\nu X_n \rangle$ need only be evaluated once (for a given geometric point), stored conveniently, and repeatively accessed during the orbital coefficient (C_μ^i) and density matrix element $(D_j^i; D_{kl}^{ij})$ optimization stages. For the Restricted Hartree Fock (RHF) wavefunction $D_i^i = 2$, $D_{ij}^{ij} = 2$, $D_{ji}^{ij} = -1$, and the remaining terms are zero.[1] For wavefunctions beyond RHF the wavefunction optimization step represents a vast majority of the time needed to variationally determine E, that is, the calculation of the X_μ integrals is usually relatively insignificant.[2] For this reason initial vectorization efforts have concentrated on enhancing the time intensive stages of an MCSCF (multiconfiguration SCF) program. It is generally accepted[2] that one of the most time intensive steps of a general MCSCF code is the 4 index transformation needed to convert the X_μ integrals to $\emptyset_i$ integrals where

$$\emptyset_i = \sum_\mu C_\mu^i X_\mu \tag{5}.$$

On scalar processors only the unique integrals are stored (the Canonical list) and the loops are structured so as to minimize the number of multiplications performed. On a vector processor

such as the Cyber 205 this step simply amounts to two sequential applications of the matrix transformation described in (1). This transformation will proceed at vector speed provided that for a given ij pair all kl integrals are available for k>l (this corresponds to an effective doubling of the integral file from its canonical length). This expansion of the canonical integral tape is accomplished through a straightforward two level bin sort written to take advantage of the 2 million 64 bit words available on the Cyber 205[3]. Since the vectorizable portions of this integral transform are contained in the matrix transform discussed above, the timing information in Table I applies here. Four index transformations for 50 basis functions will proceed at 28 MFLOPS and 300 basis function transformations in general will achieve 82 MFLOPS. Enhancements over scalar computation on the Cyber 205 will range from a factor of 9 to a factor of 34 for 50 to 300 basis functions. For example, a full integral transformation for 50 basis functions will maximumly take 28 seconds and for 100 basis functions 10 minutes on the Cyber 205.

For a wide class of useful wavefunctions (open-shell HF and perfect pairing-generalized valence bond [GVB-PP] are two such examples) the one- and two- electron density matrices D_j^i and D_{kl}^{ij} are expressible in diagonal form;[1] that is, the only nonzero elements are

$$D_i^i = 2f_i, \quad D_{ij}^{ij} = a_{ij}, \quad \text{and} \quad D_{ji}^{ij} = b_{ij} \qquad (6).$$

The energy expresion (2) simplifies to

$$E = 2\sum_i^n f_i h_{ii} + \sum_{i,j}^n (a_{ij} J_{ij} + b_{ij} K_{ij}) \qquad (7).$$

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where

$$J_{ij} = (ii/jj) \text{ and } K_{ij} = (ij/ij) \tag{8}$$

are the usual Coulomb and exchange integrals. Restricting our attention to this class of wavefunction leads to particularly simple variational equations[1] partitionable into a step where occupied and virtual orbitals are mixed variationally (OCBSE)[4] and a step where independent occupied orbitals are mixed through pairwise rotations.[5] The OCBSE step utilizes terms representable as a vectorizable summation of J_i and K_i operators

$$\langle X_\mu | J_i | X_\nu \rangle \text{ and } \langle X_\mu | K_i | X_\nu \rangle \tag{9}$$

where

$$\langle X_\mu | J_i | X_\nu \rangle = \sum_{\sigma,n} c^i_\sigma \cdot c^i_n (\mu\nu/\sigma n)$$

$$\tag{10}.$$

$$\langle X_\mu | K_i | X_\nu \rangle = \sum_{\sigma,n} c^i_\sigma \cdot c^i_n (\mu\sigma/\nu n)$$

That is

$$\langle X_\mu | H_i | X_\nu \rangle = \sum_j a_{ij} \langle X_\mu | J_j | X_\nu \rangle + b_{ij} \langle X_\mu | K_j | X_\nu \rangle \tag{11},$$

where a set of loops can be written (which are in linked triad form and will run at >170 MFLOPS for more than 50 basis functions) to evaluate the Ith hamiltonian (K runs from 1 to $n(n+1)/2$).

```
              DO 300 J=1,NHAM
              A = A(I,J)
              B = B(I,J)
              DO 100 K = 1, MXS                        (12)
          100 H(K)=H(K)+A*AJ(K,J)
              DO 200 K=1,MXS
          200 H(K)=H(K)+B*AK(K,J)
```

As the rotations step utilizes a subset of the above integrals, the needed vectorization effort is narrowed down to rapidly

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generating the terms in (10). If all σ,n terms $\sigma>n$ are stored for a given $\mu\nu$ the double sums in (10) can be reduced to a single dot product over a combined index γ of length $n(n+1)/2$

$$\langle X_\mu | J_i | X_\nu \rangle = \sum_\gamma D_\gamma^i J_\gamma^{\mu\nu}$$

$$\langle X_\mu | K_i | X_\nu \rangle = \sum_\gamma D_\gamma^i J_\gamma^{\mu\nu} \tag{13}$$

where

$$D_\gamma^i = C_\sigma^i C_n^i$$

$$J_\gamma^{\mu\nu} = (\mu\nu/\sigma n) \tag{14}.$$

$$K_\gamma^{\mu\nu} = ((\mu\sigma/\nu n) + (\mu n/\nu\sigma))/2$$

Currently the D_γ^i are precalculated, stored, and used for an entire SCF iteration. Formulating the problem as in (13) permits vectors ranging from 1275 for 50 basis functions to 45150 for 300 basis functions. This step will function at between 80 and 100 MFLOPS representing enhancements of between 40 and 50 over scalar computation on the Cyber 205. Table II summarizes the timing for calculations ranging up to a 79 basis function calculation consisting of 4096 spatial configurations; that is, a GVB-PP(12/24) wavefunction.[1] If the calculation were stopped after the RHF step the SCF would represent less than 1% of the computational effort. Overall the GVB(12/24) wavefunction optimization represents 14% of the total effort. This is in sharp contrast to computations on scalar computers where this step would account for greater than 95% of the effort. The timing for an SCF iterative cycle for three cases is broken down in Table III. Note that the time needed to generate the terms in (13) is comparable to that needed to diagonalize the variational hamiltonians (OCBSE).

II. DeNOx Catalysis.

The catalytic reduction of nitrogen oxides has become increasingly important in recent years due to legislation aimed at reducing emission levels from non-biological sources[6]. As Nitric Oxide is the major NO_x component of exhaust streams[7] research has focused on the reduction of nitric oxide. Both homogeneous and heterogenous $deNO_x$ studies have been performed[8-11]. The use of base-metal catalysts is of particular interest due to their ready availability and low cost. A transition metal ion of singular importance in pollution control is Fe(II) either as the bulk oxide or ion exchanged into zeolites. These Iron systems have been demonstrated to catalyze the conversion of nitric oxide to nitrogen with a co-reactant such as CO or H_2[8,9]. The mechanism originally proposed by Shelef and Kummer[12] consists of a two stage oxidation reduction sequence. The initial step involves the coupling of two nitric oxides to form nitrous oxide plus an Iron oxide.

$$2NO \longrightarrow N_2O + 'O' \tag{15}$$

The thus formed nitrous oxide is rapidly reduced by the catalyst[8b,8d,10].

$$N_2O \longrightarrow N_2 + 'O' \tag{16}$$

Completing the cycle the Iron oxide is reduced by reaction with carbon monoxide forming carbon dioxide plus the regenerated catalytic site.

$$'O' + CO \longrightarrow CO_2 \tag{17}$$

Efforts have primarily been directed at characterizing reaction (15) as this is likely to be the kinetically most difficult

step[8d]. For homogeneous systems (15) has been suggested to involve an intramolecular coupling of nitrosyl to form a dinitrogen dioxide ligand[11a] which rearranges to a bound cis hyponitrite.

$$1 \qquad\qquad 2 \qquad\qquad 3 \qquad\qquad (18)$$
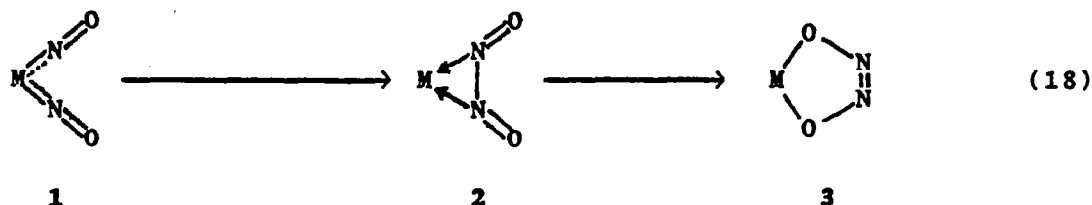
Metal hyponitrites have been established to either decompose to nitrous oxide and the metal oxide[13a] or react with carbon monoxide to from carbon dioxide and nitrous oxide[13b-c].

It should be stressed that transition metal dinitrogen dioxide complexes have never been isolated nor unambiguously detected. Further, only a single mononuclear transition metal hyponitrite complex has been identified[13b].

In this section we report energetic support for the reaction sequence (18) for a model Fe(II) system: the dinitrosyl complex of Iron dichloride $FeCl_2(NO)_2$[14]. The relative energetics[15] and geometries[16] for the chosen complex 1, its coupled cognate dinitrogen dioxide complex 2, and the cis hyponitrite product 3, are discussed below. We find that the coupled products are potentially accessible; 2 is only 29 kcal/mol higher in energy than 1 and 3 only another 19 kcal/mol higher. These species, though unobserved, should be viable given an appropriate ligand backbone. Addition of waters of hydration profoundly affects the relative energies of the hdyrated forms of 1, 2, and 3 (4, 5, and 6 respectively). We find that intermediates 5 and 6 are thermally accessible. Intermediate 5 is 24 kcal/mol more stable

than 4 and 6 is only 4 kcal/mol above 4. This is not suprising as 1 is a 16 electron system, 2 is a 14 electron system, and 3 is a 12 electron system (unusual participation by the pi lone pairs was not observed in the wavefunction of 3 or 6).

A correlation of the bonding orbitals demonstrates that the coupling reaction 1 to 2 or 4 to 5 will be thermally allowed (occupied reactant orbitals correlate with occupied product orbitals[17]). Further, the LUMO is a non-bonding d orbital of B_2 symmetry indicating that this correlation diagram will be valid for systems with up to 2 more electrons. Finally, one of the high lying occupied orbitals is a non-bonding A_1 d orbital suggesting that the correlation diagram will be valid for systems with up to two fewer electrons. Thus group VI through group VIII metal dications are potential active catalysts.

Because Fe(II) dinitrosyls are structurally uncharacterized, because only a single transition metal hyponitrite complex has been structurally characterized, and because dinitrogen dioxide complexes are unprecedented a detailed discussion of the bond distances and bond angles that were optimized is in order. We find the N-Fe-N angle for the dinitrosyl is 94.9 degrees, as expected for a {M(NO)2}^{8} system[16b]. The Fe-N distance of 1.69 A is in agreement with experimental structures for linear Iron dinitrosyls (1.66 A[18a] to 1.71 A[18b]). For the dinitrogen dioxide complex 2 we find a N-N distance of 1.53 A, longer than normal N-N single bonds (ranging from 1.402 A to 1.492 A[19]) but still significantly shorter than that for free dinitrogen dioxide (2.24 A[20]). This is consistent with substantial nitrogen-nitrogen sigma

bonding. The Fe-N distance found for the dinitrogen dioxide complex (2.23 A) is in accord with the Fe(II) nitrogen bond distance of 2.26 A[21] in $[Fe(C_4H_8NH)_6][Fe_4(CO)_{13}]$. Finally, for the cis hyponitrite complex 3 our Fe-O distance of 1.74 A compares favorably with 1.69 A (the sum of the ionic radii for OH^- (1.18 A) and an estimate for the ionic radius for four coordinate Fe(IV) (0.51 A)[22]). Our N-N distance of 1.21 A is the same as the N-N distance determined by X-ray crystallography for $[(Ph_3P)_2Pt(N_2O_2)]$[13b], the only structurally characterized hyponitrite.

Summarizing, we have demonstrated that (17) is a probable reaction sequence for group VI through group VIII transition metal deNO$_x$ catalysts. Specifically our energetics and correlation diagram suggest that dinitrogen dioxides are thermodynamically and kinetically accessible cognates of dinitrosyl complexes. We believe that these results can be extended to heterogeneous Fe(II) catalyzed deNO$_x$ processes as well. In fact we speculate that the stretching frequencies observed by Hall[8c] at 1917 cm^{-1} and 1815 cm^{-1} are due to bound dinitrogen dioxide which is blue shifted relative to the free compound (which has frequencies[23] at 1870 cm^{-1} and 1776 cm^{-1}. Because the coordination sphere of Fe(II) ion exchanged into zeolites is thought[24] to contain three oxygen ligands our energetics suggest the frequencies assigned to a dinitrosyl are instead due to the kinetically accessible and thermodynamically favored dinitrogen dioxide moiety. Further, it should be noted that dinitrosyl stretching frequencies as high as 1900 cm^{-1} are rare. In conclusion we suggest that the kinetically (and thermodynamical-

ly) most difficult step in (17) is the isomerization of the dinitrogen dioxide complex 2 (or 5) to the cis hyponitrite complex 3 (or 6).

III. Nitrogen fixation.

The fixation of dinitrogen is a reductive process of both biological and large scale industrial interest. Thermodynamically the conversion of dinitrogen to ammonia is straightforward and the conversion to hydrazine is feasible under high pressures (ΔG_{298} for these processes are -7.9 kcal/mol and +22.0 kcal/mol respectively; if the pressure is increased to 100 atm then the ΔG_{298} for hydrazine formation is +16.7 kcal/mol).

In the known nitrogen-fixing organisms the catalytic reduction of dinitrogen is carried out by molybdoenzymes known as nitrogenases[25]. These nitrogen-fixing enzymes consist of two protein components, a Fe-Mo protein and a Fe protein. Further, an iron-molybdenum cofactor has been isolated from the Fe-Mo component protein of nitrogenase. In fact extracts of the Mo-Fe component from inactive mutant strains of microorganisms are activated by addition of this cofactor. Two models of the active site have been proposed that are consistent with Mossbauer and EPR spectroscopic data[26] and EXAFS analysis[27] of the Fe-Mo cofactor. Unfortunately the models of such active sites synthesized to date do not reduce dinitrogen[28-30].

Industrially, dinitrogen reduction occurs over an Iron catalyst at high temperatures and pressures. The rate determining step is either the dissociative chemisorbtion of dinitrogen[31]

$$2* + N_2 \longrightarrow 2N-* \qquad (19)$$

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or the simple chemisorbtion of an activated form of dinitrogen

$$* + N_2 \longrightarrow N_2\text{-}* \qquad (20)$$

Both of these processes are likely followed by rapid reaction with hydrogen (either molecular hydrogen of chemisorbed atomic hydrogen).

Thus, for both biological and industrial nitrification the activation of dinitrogen is a prerequisite for reaction with reductants such as hydrogen. Until very recently the observed forms of dinitrogen were bound to the metal with the nitrogen-nitrogen multiple bond largely intact (non-activated).
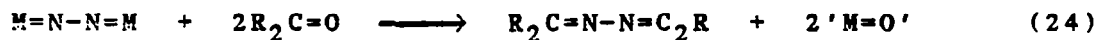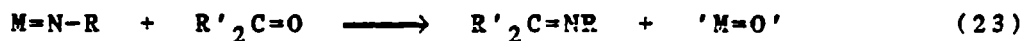
$$M \equiv N \equiv N \qquad\qquad M \equiv N \equiv N \equiv M \qquad\qquad M \overset{N}{\underset{N}{\big|\big|}} \qquad (21)$$

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Thus these model compounds will only reduce dinitrogen under rather harsh conditions[32].

An understanding of a recently observed dinitrogen binding mode (analogous to organic azines)

$$M \equiv N - N \equiv M \qquad (22)$$

8

will provide additional insight into biological and industrial nitrification. The reactivity and structural characteristics of a new class of Tantalum complexes[33] suggest the bonding pattern 8 in (22). The Ta-N bond distances of 1.796 A and 1.840 A are quite similar to those observed in normal Tantalum imido complexes[33] (1.765 A to 1.77 A). In addition, reactions (23) and (24) are both observed[33] (reactions characteristic of metal-ligand multiple bonding).

$$M=N-R \ + \ R'_2C=O \ \longrightarrow \ R'_2C=NR \ + \ 'M=O' \quad (23)$$

$$M=N-N=M \ + \ 2R_2C=O \ \longrightarrow \ R_2C=N-N=C_2R \ + \ 2'M=O' \quad (24)$$

Finally, there is an observable 'activation' of the nitrogen-nitrogen bond (N-N bond distances of 1.282 A and 1.298 A compared to free dinitrogen which has a N-N bond distance of 1.0976 A).

In this section we report energetic support for the kinetic and thermodynamic accessibility of **8** for molybdenum complexes. Our model consists of a bimetallic complex consisting of two Molybdenumtetrachloride units bridged by a dinitrogen molecule. For this complex we have characterized the 'reaction path' connecting the two likely resonance structures **7** and **8**

$$Cl_4Mo-N=N-MoCl_4 \quad \longleftrightarrow \quad Cl_4Mo=N-N=MoCl_4 \quad (25)$$

$$\textbf{9} \qquad\qquad\qquad\qquad\qquad \textbf{10}$$
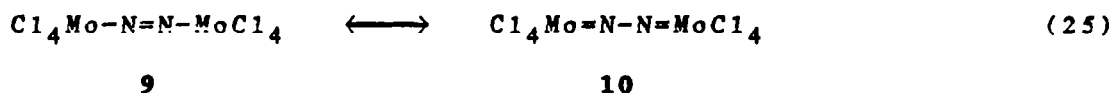
We find local minima characteristic of each resonance structure indicating the 'resonance' interaction between these two forms is not enough to result in a single averaged structure[34]. However, the resonance interaction is sufficient to provide a very low barrier interconnecting them (less than 1 kcal/mol). Thermodynamically we find **9** to be 20 kcal/mol more stable than **10** for the tetrachloride ligand backbone. This thermodynamic difference could easily be overcome by an alteration of the ligand backbone and future studies will concentrate on this. Geometrically, for **9** the Mo-N distance is 2.28 A and the N-N distance is 1.10 A and for **10** the Mo-N distance is 1.82 A and the N-N distance 1.23 A. This is in accord with a suggestion that the tetrachloride backbone does not fully activate the dinitrogen (a fully activated N-N distance should be on the order of 1.30 A).

Table I. Comparison of Scalar and Vector Matrix Transformations.
(for various sized matrices, times in sec.)

Matrix size NxN)	Scalar (with Opt.)			Vector (times x 100)				Ratio (S/V)	MFLOPS (vec.)
	First Mult.	Second Mult.	Total Time	Expand Array	First Mult.	Second Mult.	Total Time		
50	0.041	0.083	0.124	0.063	0.78	0.51	1.36	9.1	27.8
100	0.32	0.65	0.96	0.23	3.65	2.59	6.48	14.8	46.5
150	1.07	2.58	3.64	0.51	9.34	6.91	16.76	21.7	60.5
200	2.52	6.74	9.25	1.01	19.34	14.32	34.67	26.7	69.3
250	5.39	14.35	19.74	1.83	33.43	25.64	60.90	32.4	77.1
300	9.90	27.14	37.03	2.92	53.22	42.23	109.84	33.7	82.4

Table II. Timing Breakdown for MC-SCF Energy Generation.
(times in seconds)

Step	Molecule/No. of basis functions			
	H_2O/7	$FeCl_2 \cdot (H_2O)_2$/43	$FeCl_2(NO)_2$/65	$FeCl_2(NO)_2(H_2O)_2$/79
Calculate One electron Integrals	0.13	36.4	48.5	81.0
Calculate Two electron Integrals	1.06	86.6	191.7	535.5
Sort Two Electron Integrals	0.05	14.7	94.3	247.7
Generate Extended Huckel Starting Guess	----	0.8	1.1	----
Obtain Hartree Fock Energy (10 it.)	0.11	1.8	3.1	----
Obtain MC-SCF Energy (10 it.)	----	----	72.5	137.5
Total Time	1.35	140.3	411.2	1001.7
% of Time HF	8.1	1.3	0.8	----
MC-SCF	----	----	17.5	13.7

Table III. SCF Timing Breakdown for an Individual Cycle.
(Times in seconds, rates in MFLOPS)

Wavefunction Description	Generate J_i and K_i Matrices		Transform J_i and K_i Matrices	OCBSE	Orbital Rotations	Optimize a_{ij} and b_{ij}	Total
	Time	Rate	Time	Time	Time	Time	Time
H_2O MBS HF	0.0001	4.6	0.006	0.004	----	----	0.011
$FeCl_2 \cdot (H_2O)_2$ HF	0.0082	49.0	0.017	0.078	----	----	0.177
$FeCl_2(NO)_2$ HF	0.0310	60.6	0.034	0.241	----	----	0.306
GVB(12/24)	2.012	81.4	2.832	1.990	0.328	0.091	7.253
$FeCl_2(NO)_2(H_2O)_2$ GVB(12/24)	4.302	88.2	5.322	3.515	0.516	0.090	13.745

Acknowlegement

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the five gaussian basis described previously (15j). The N and O basis sets were valence double zeta as discussed previously (15h). The basis sets on the waters of hydration were minimum basis sets where the linear parameters were optimized for $FeCl_2(H_2O)_2$, the O exponents as above, and the H exponents were Huzinaga's four quassian set (15k) (scaled by 1.2). b) Davis, J. H.; Goddard III, W. A.; Harding, L. B. J. Am. Chem. Soc., 1977, 99, 2919-2925. c) Bobrowicz, F. W.; Goddard III, W. A. In "Modern Theoretical Chemistry: Methods of Electronic Structure Theory", H. F. Schaefer III, Ed., Plenum Press: New York, 1977 Vol. 3 Chapter 4, pp 79-127. d) Harding, L. B.; Goddard III, W. A. J. Am. Chem. Soc., 1976, 98, 6093-6099. e) Casewit, C. J.; Goddard III, W. A. ibid., 1982, 104, 3280-3287. f) Melius, C. F.; Olafson, B. D.; Goddard III, W. A. Chem. Phys. Lett., 1974, 28, 457-462. g) Rappe', A. K.; Smedley, T. A.; Goddard III, W. A. J. Phys. Chem., 1981, 85, 1662-1666. h) Rappe', A. K.; Goddard III, W. A. In "Potential Energy Surfaces and Dynamics Calculations", D. G. Truhlar, Ed., Plenum Press, New York, 1981 pp. 661-684. i) Wachters, A. J. H. J. Chem. Phys., 1970, 52, 1033-1036. j) Rappe', A. K.; Smedley, T. A.; Goddard III, W. A. J. Phys. Chem., 1981, 85, 2607-2611. k) Huzinaga, S. J. Chem. Phys., 1965, 42, 1293-1302.

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