Structure and Relative Spin-State Energetics of $[Fe(H_2O)_6]^{3+}$: A Comparison of UHF, Møller−Plesset, Nonlocal DFT, and Semiempircal INDO/S Calculations

Dan Harris* and Gilda H. Loew

Molecular Research Institute, 845 Page Mill Road, Palo Alto, California 94304

Andrew Komornicki

Polyatomics Research Institute, 1101 San Antonio Road, Suite 420, Mountain View, California 94043

Received: October 22, 1996; In Final Form: January 8, 1997[⊗]

The optimized structure and spin-state energetics of the iron(ferric)−hexaaquo complex, $[Fe(H_2O)_6]^{3+}$, in high (S = 5/2), intermediate (S = 3/2), and low (S = 1/2) spin states were determined from a common starting structure using unrestricted Hartree−Fock (UHF), Møller−Plesset (MP2), and nonlocal density functional theoretical (DFT) methods. All three methods indicate a high−spin ground state for the iron−water complex, consistent with experimental results. The optimized ground-state geometries were similar to each other and in quantitative agreement with known model-system crystal structures and experimental solution phase scattering data. The energy ordering of the spin states of the cluster was also found to be the same at all levels of calculation: $E(5/2) < E(3/2) < E(1/2)$, in agreement with experiment. This same order of spin-state energies was found using the semiempirical INDO/S method. Optimized geometries for both the quartet and doublet excited states led to similar $Fe-O(H_2)$ bond distances from the UHF, MP2, and DFT methods, with additional distortions present in the DFT excited-state structures. The most significant difference in these results was in the calculated vertical transition energies between the sextet ground state and the low lying quartet state: specifically UHF (30 253 cm^{-1}), MP2 (20 040 cm^{-1}), DFT (9895 cm^{-1} (BPW91); 9302 cm^{-1} (BLYP)), and semiempirical INDO/S (10 875 cm^{-1}) with the DFT and INDO/S result in good agreement with the experimental determined vertical transition energy of 12 300 cm^{-1}. Comparison of the lowest computed DFT sextet−quartet transition energies for the iron−water cluster (9895 cm^{-1}) and the Fe^{3+} ion (30 890 cm^{-1}) indicates the coordination of Fe^{3+} by water ligands to be a significant perturbation on the excited-state energies relative to the ground state.

Introduction

Reliable computation of optimized geometries, energies, and electronic structure of transition metal containing systems is known to require extensive electron correlation effects. DFT methods based on the seminal work of Hohenberg, Kohn, and Sham[1,2] are promising alternatives to the traditional *ab initio* methods for characterizing these systems because they include electron correlation in the exchange−correlation functional and are not as computationally intensive as traditional SCF *ab initio* methods. The use of nonlocal corrections has been demonstrated to improve the accuracy of transition metal−ligand and metal−metal bond distances,[3] as well as the structure and thermochemistry of iron chlorides and their positive and negative ions.[4]

Nonlocal DFT has also been applied to a range of systems of biochemical interest including optimized geometries of a five coordinate model of the ferrylheme complex[5] and iron sulfur clusters relevant to these centers in proteins.[6] While these studies indicate reasonable structural results may be obtained for these complex iron-containing species using the DFT method, its ability to uniformly predict correct spin-state descriptions and relative spin-state energetics of open shell systems is less clear. Some successful DFT exploration of the relative energetics of excited states of transition metal complexes has been reported, e.g. vanadium and molybdenum oxide cations[7,8] and Ni/C_2H_4.[9] Yet, it is clear that additional test cases are required to determine the adequacy of these calculations to describe electron correlation in transition metal containing systems.

To further assess this capability of DFT relative to other *ab initio* methods, we have chosen the hexaaquo ferric ion, $[Fe(H_2O)_6]^{3+}$, open shell system with ample experimental structural and spectroscopic information for comparison with calculated results. While reasonable structural descriptions of alkali[10] and transition metal aquo complexes may be obtained at the SCF level, the accurate description of the electronic structure and spectroscopy of even simple transition metal complexes requires the inclusion of correlation effects. Moreover, since the relative energies of the three possible spin states (S = 5/2 a sextet; S = 3/2 a quartet; S = 1/2 a doublet) in complexes formed by the ferric ion with ligands are very sensitive to small changes in coordination and bonding, the determination of the ability of these methods to obtain the correct ordering of spin states and energy separations for this system should provide a useful assessment.

There are a number of X-ray structures for iron−water complexes including the $[Fe(H_2O)_6]^{3+}$ species, with various counterions in the second coordination sphere of iron, with an observed range of Fe−O distances of 1.97−2.1 Å.[11−14] In one of these crystal structures, the positions of the water hydrogen atoms have been resolved as well, so the position of all atoms in the ferric−hexaaquo complex are known.[11] EXAFS studies of the ferric ion in solution indicate similar distances.[15,16] These structural studies also indicate that the water coordination number of the ferric ion in solution is 6.

---

* Author to whom correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1997.

S1089-5639(96)03296-3 CCC: $14.00

Spectroscopic studies indicate that the ground state of the $[Fe(H_2O)_6]^{3+}$ is a ^6A state. The lowest lying electronic state transitions in this high-spin violet iron complex $[Fe(H_2O)_6]^{3+}$[17-21] have been assigned as transitions between the ^6A state and a manifold of low lying quartet states, first by comparison of observed spectra with calculations based on crystal field models and later by more detailed semiempirical INDO/S calculation of the spectra of hydrated first transition metal series.[22] The range of excited-state energies of this manifold of quartet states in the hexacoordinate Fe^{3+} complex, $[Fe(H_2O)_6]^{3+}$, is 12 000−26 000 cm^{-1}, similar to the range found in beryl (beryllium aluminum silicate), where Fe^{3+} is coordinated to six oxygens.[23] The lowest energy quartet in both iron−hexaaquo complex and the beryl model system has been determined to be 12 300 cm^{-1} and assigned to be of $^6A_g \rightarrow {}^4T_g(t_{2g})^4(e_g)^1$ transition character.[17] The quartet configurations associated with the higher energy spectral features around 26 000 cm^{-1} have unpaired spin density in the iron e_g d orbitals.

Numerous *ab initio* studies of the ferric−iron water system have appeared. An early *ab initio* study of $[Fe(H_2O)_6]^{3+}$ reported a Fe−O distance of 2.04 Å by constrained optimization of just the Fe−O distances starting with an octahedral geometry.[24] More recently, Sahoo and Das have examined the hexaaquo UHF optimized structures of Mn^{2+}, Cr^{3+}, and Fe^{3+} and, by parametrically varying the Fe-O distances, determined a minimum at 1.99 Å for the $S = 5/2$ state.[25] None of these previous studies of $[Fe(H_2O)_6]^{3+}$ involved complete optimization of the complexes. A study by Bauschlicher of $[Fe(H_2O)_6]^{+}$ and other iron complexes,[26-29] however, did employ full optimization. These studies employed two high-level and computationally demanding methods: modified coupled pair functional (MCPF) as well as a complete active space SCF (CASSCF) multireference configuration interaction (MRCI) approach. The results confirmed the importance of electron correlation in structure determination of such systems.

In the work reported here, we have extended the scope of the previous work by considering whether two less computationally intensive methods of incorporating electron correlation can yield not only reasonable ground-state structures of $[Fe(H_2O)_6]^{3+}$ but also excited-state properties as well. Specifically, we have calculated and assessed the quality of the optimized structures, relative spin-state energetics, and vertical transition energies for the iron(III)−hexaaquo system, $[Fe(H_2O)_6]^{3+}$, by comparisons with experimental results. These calculations were performed using the least computationally intensive quantum chemical methods that incorporate electron correlation based on a single determinental wave function: (i) Møller−Plesset perturbation theory truncated at second order (MP2) based on a UHF determinant and (ii) nonlocal density functional theoretical calculations. To further verify the importance of correlation for the system chosen, we have also included uncorrelated UHF results for comparison. Finally, we have compared the above *ab initio* results with the relative spin-state energetics using the semiempirical INDO[30] method. This method has been extensively used and proven reliable for calculations of electronic structure and spectra and relative spin-state energetics of transition metal containing systems[22] given reasonable input geometries from experimental sources.

Methods

Figure 1 shows the initial geometry for the ferric−hexaaquo complex used for all calculations. It is an idealization of the crystal structure of hexaaquairon(III) nitrate trihydrate.[11] Specifically, all the Fe−O distances have been regularized to the same initial value of 2.0 Å and the oxygen atoms placed along the octahedral axes. Although slight deviations from octahedral symmetry are present in the X-ray structure, they appear to be the result of intermolecular hydrogen-bonding interactions between water molecules or between water and the counterions present in the crystal. The dispositions of the hydrogens of the waters closest to one another in this structure are of a “staggered” nature with the hydrogens of waters “anti” to one another in the same plane. The mean deviation of the hydrogen positions from this regularized pattern in the X-ray structure is 13° except for the cases of those waters involved in intermolecular hydrogen-bonding interactions where the deviations are up to 37°. The point group characterizing the complete structure of the initial complex is D_{2h}.

Basis Sets. The Fe basis employed was a triple-ζ-valence (TZV) contracted Gaussian type orbital basis initially developed by Schäfer, Huber, and Ahlrichs.[31] This basis employs a single contraction to describe inner shells and three uncontracted functions for valence shells. The Gaussian basis employed on iron was (17s/10p/6d) contracted to [6s/5p/3d]. The basis set used for water was a split-valence 6-31G* Gaussian set. Where indicated in the discussion and tables, a single set of f functions was added as a contraction of two primitives with exponents 2.600 and 0.889, with coefficients determined by a least squares fit to a Slater 4f function.

Computational Methodology. All calculations were performed using either Gaussian 92 or Gaussian 94/DFT. We have calculated and compared results from density functional calculations with Møller−Plesset[32] calculations, as candidate procedures that could be applicable to larger open shell transition metal containing systems than considered in this study. Many previous studies have demonstrated that much of the electron correlation effects are recovered at the MP2 level,[33-35] i.e. from determination of the first correction to the Hartree−Fock energy, if a large basis set is used. For this reason, we have used a triple-ζ-valence description on iron and employed MP2-corrected gradients in the geometry optimizations.

In the MP2 calculations on the iron−water cluster two sets of calculations were performed to explore the effect of including 2s and 2p electrons in the correlation treatment. In both sets of Møller−Plesset calculations the 1s orbitals on oxygen were frozen and in the first set of calculations an Ar frozen core was retained on the iron (resulting in 15 frozen orbitals), while in the second set a Ne frozen core was used on iron.

All DFT calculations were performed using the Becke's 1988 functional, which includes the Slater exchange along with corrections including the gradient in the density (nonlocal corrections)[36] in combination with either the Perdew−Wang-'91 (BPW91)[37] or the Lee−Yang−Parr (BLYP) gradient-corrected correlation functionals.[38] In all DFT calculations a “fine” integration grid was employed that uses 75 radial points and 302 angular points for each shell. The stability of the wavefunctions obtained from DFT calculations was tested and verified. As with the SCF calculations, all integrations were performed using a G94 tight criteria of 1.0×10^{-8} rms changes in the density matrix.

The DFT calculations were performed using G94/DFT[39] on Silicon Graphics Indigo2 XZ(R4400) and on a C90 at the NSF Supercomputer Center. Optimizations took 1−2 CPU weeks on the SGI platform and ca. 5 h on the NSF center C90. All MP2 calculations for the ferric−hexaaquo complex were performed on the C90 at the Pittsburgh Computer Center using Gaussian 92.[40]

Frequency calculations were performed for those cases where it was computationally feasible, i.e. for the UHF and DFT levels of calculation, in order to determine both the nature of the

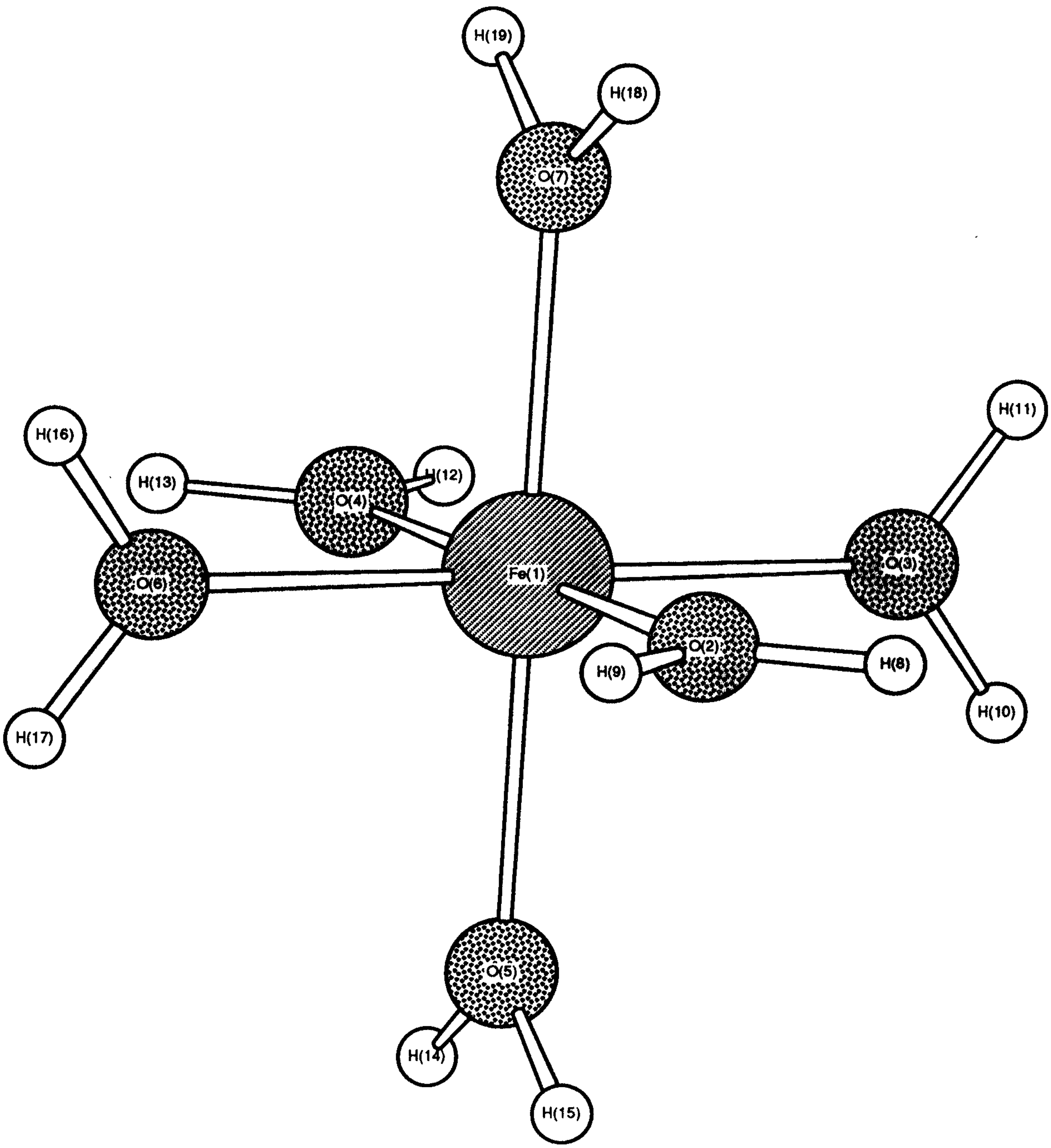

Figure 1. Starting geometry for optimizations for the $S = 5/2$, 3/2, and 1/2 spin states of $[Fe(H_2O)_6]^{3+}$.

stationary point obtained from the optimization as well as to obtain zero-point vibrational energy corrections to the spin-state total energies. It was not possible to compute frequencies at the MP2 level given computational resources.

Semiempirical INDO calculations were performed using a 1988 version of Zerner's INDO program.[30] This formalism excludes multicenter two-electron integral terms. One-center terms are retained. Core integrals are parametrized from atomic spectroscopy and thus include effects of the one-center core effective potential. In this program there are two options for evaluating the two-center–two-electron integrals. In INDO/S they are evaluated from the Mataga–Nishimoto formula as a function of empirical ionization and electron affinities. This procedure is only valid if the same geometry is used to calculate and compare different states of the system and is used in calculating both excited-state energies and spectra. Given their semiempirical nature, some correlation effects are implicit in the empirical parametrization, even without the inclusion of configuration interaction. In the other INDO option, which in this work we will designate as INDO/T, the two-center, two-electron integrals are directly evaluated. This option has been used in these studies in order to determine the energy difference between the spin states with different optimized geometries, using both the structures from MP2 and the DFT calculations.

Results and Discussion

Table 1 lists the six Fe–O distances for the optimized $[Fe(H_2O)_6]^{3+}$ structures in the three spin states[41] from the UHF, MP2, and DFT calculations. All three methods lead to high-spin complexes with six equal Fe–O bond lengths. The Fe–O distances obtained for each type of calculation (UHF, 2.07 Å; MP2, 2.06 Å; DFT, 2.08 Å (BPW91), 2.09 Å (BLYP)) are in good agreement with one another and with the known structures of the high-spin ferric–aquo complex.[11]

The quartet and doublet states depart from the octahedral symmetry of the sextet state, with three unique sets of Fe–O

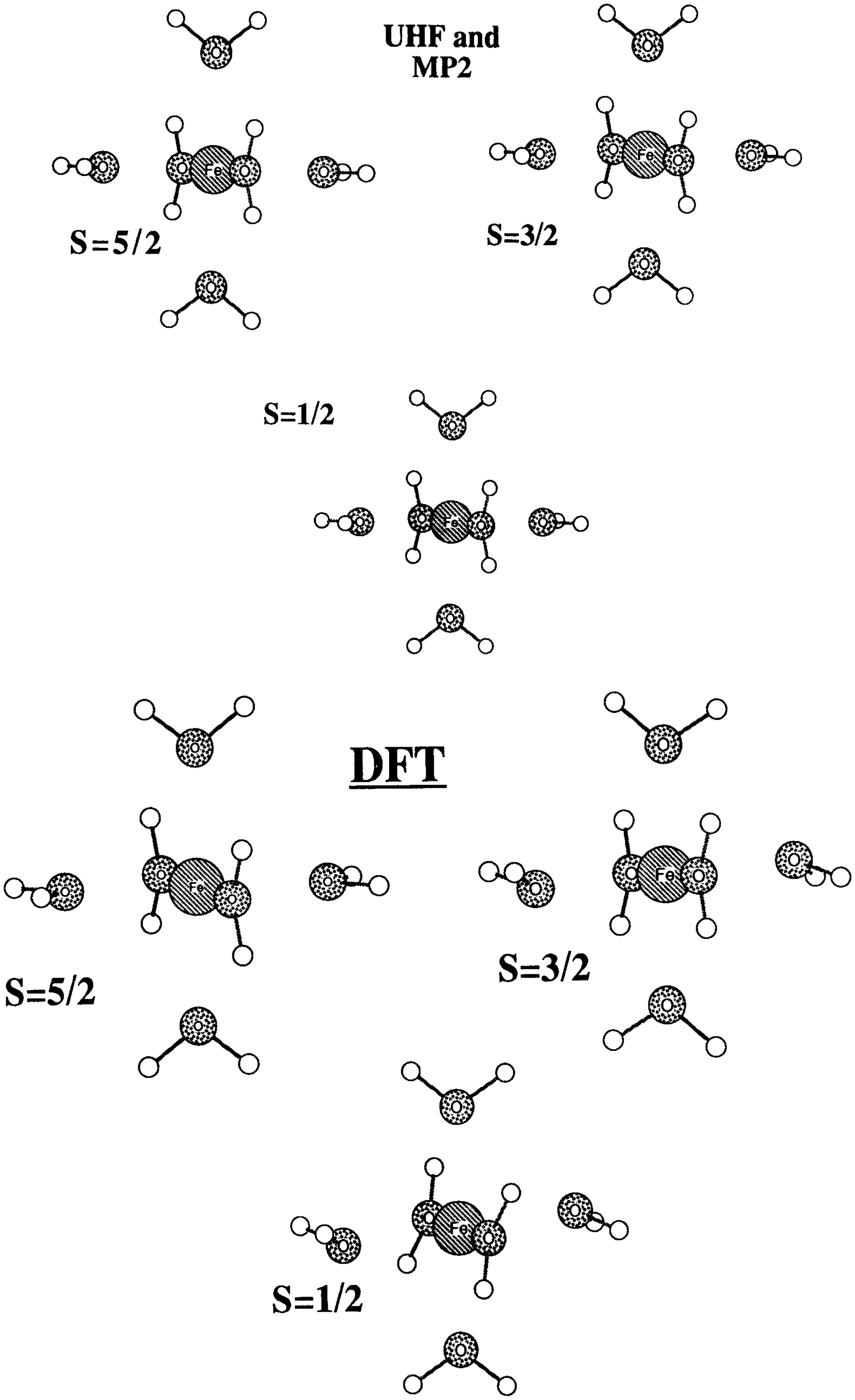

Figure 2. (a, top) Structures obtained from optimizations at the UHF and MP2 level. (b, bottom) Structures obtained from the DFT optimizations.

distances. Fe−O distances opposite one another (c.f. Figure 1) are comparable, resulting in D_{2h} symmetry with respect to the Fe−O distances. The average value of the Fe−O distance for the quartet (UHF, 2.02 Å; MP2, 2.01 Å; DFT, 2.04 Å (BPW91 and BLYP)) and for the doublet states (UHF, 1.97 Å; MP2, 2.01 Å; DFT, 1.97 Å (BPW91), −1.98 Å (BLYP)) are very similar for all three methods. This average value of the Fe−O distance decreases with decreasing spin multiplicity: $R_{\mathrm{Fe-O}}(S = 5/2)_{\mathrm{avg}} > R_{\mathrm{Fe-O}}(S = 3/2)_{\mathrm{avg}} > R_{\mathrm{Fe-O}}(S = 1/2)_{\mathrm{avg}}$ for all methods used.

Figure 2a shows the UHF and MP2 optimized geometries of the entire complex including the position of the hydrogens in the three spin states of $[\mathrm{Fe(H_2O)_6}]^{3+}$. Figure 2b shows the comparable figures for the DFT results. These figures show

TABLE 1: Summary of Fe−O Distances[a] in Optimized $Fe(H_2O)_6^{3+}$ as a Function of Spin State and Method

spin state/ H_2O no.	UHF	UMP2	DFT-(BPW91)	DFT-(BLYP)
$S = 5/2$				
1	2.07	2.06	2.08	2.09
2	2.07	2.06	2.08	2.09
3	2.07	2.06	2.08	2.09
4	2.07	2.06	2.08	2.09
5	2.07	2.06	2.08	2.09
6	2.07	2.06	2.08	2.09
$S = 3/2$				
1	1.95	1.93	1.95	1.95
2	1.95	1.93	1.95	1.95
3	2.00	2.00	2.04	2.05
4	2.00	2.00	2.04	2.05
5	2.10	2.10	2.12	2.13
6	2.10	2.10	2.12	2.13
$S = 1/2$				
1	1.94	1.91	1.95	1.96
2	1.94	1.91	1.95	1.96
3	1.98	1.96	1.95	1.96
4	1.98	1.96	1.95	1.96
5	1.99	1.97	2.00	2.01
6	1.99	1.97	2.00	2.01

[a] All distances in angstroms.

that even with the hydrogens included similar geometries for the sextet complexes are found from all three methods. In contrast, the structures of the DFT quartet and doublet states differ from the corresponding UHF and MP2 excited-state geometries by the differing extent of displacement from the octahedral axis of pairs of waters anti to one another. In the case of the doublet, these methods also lead to a different amount of rotation of pairs of opposite waters about their O1−Fe−O2 bond, further lowering the symmetry of the complex.[42]

Relative Spin-State Energetics of High-, Intermediate-, and Low-Spin $[Fe(H_2O)_6]^{3+}$. Table 2 shows the absolute and relative spin-state energetics of the ferric-ion hexaaquo complex obtained for the geometry-optimized spin states from the UHF, MP2, and DFT calculations, as well as an MP2 calculation at the UHF optimized geometry (MP2//UHF). As seen in this table, all the calculations lead to a high-spin ($S = 5/2$) ground state, in agreement with experiment. Furthermore, all calculations give the same ordering of spin-state energies: $E(5/2) < E(3/2) < E(1/2)$.

The results in Table 2 indicate that the most dramatic difference between the nonlocal DFT calculations and the UHF and MP2 calculations is the magnitude of the spin-state energy splittings. The DFT results, using the BPW91 and BLYP functionals, are seen to be similar as regards the spin-state relative energetics. The energy differences are shown again graphically in Figure 3a together with the additional spin-state energy differences calculated using the INDO/T method with the MP2 and DFT(BPW91) spin-state optimized geometries. The results illustrate that (1) significantly lower spin-state energy splittings are obtained with DFT compared to the UHF, MP2//UHF, or MP2 results, (2) the MP2 results obtained at UHF optimized geometries (MP2//UHF) are similar to the results obtained from MP2 optimizations, and (3) the DFT and INDO/T methods give comparable results for the spin-state energy splittings.

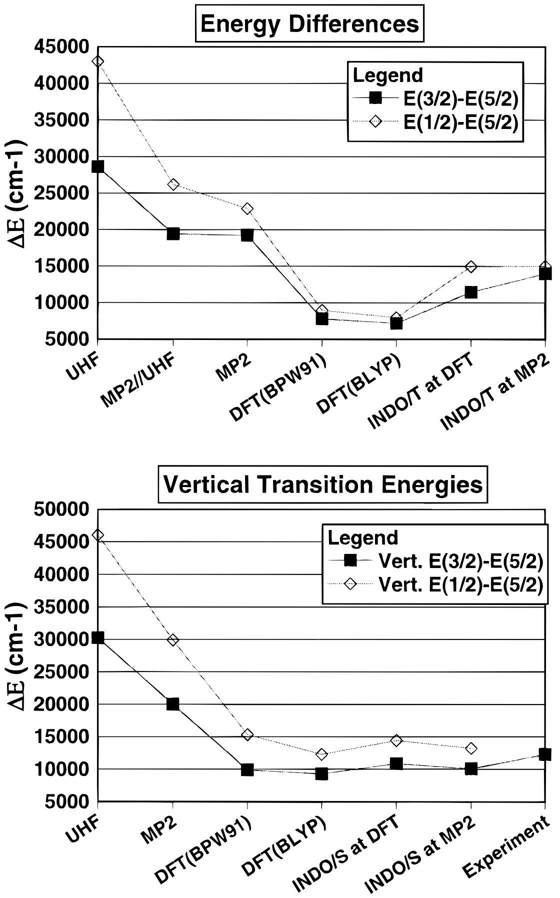

Figure 3. (a, top) Spin-state energy differences for $[Fe(H2O)_6]^{3+}$ complexes as determined from UHF, MP2//UHF, MP2, DFT, and INDO/T (INDO with theoretical gammas at MP2 and DFT geometries) calculations. (MP2 values plotted are for MP2 with Ne frozen core on iron.) (b, bottom) Vertical transition energies for UHF, MP2, DFT, and INDO/S (INDO with spectroscopic/empirical gammas at MP2 and DFT geometries) compared with experiment. (MP2 values plotted are for MP2 with Ne frozen core on iron.)

As shown in Table 2, several factors that could be contributing to the much higher spin-state energy splittings obtained from the MP2 than the DFT calculations were examined. Reducing the frozen core on the iron from argon to neon in the MP2

TABLE 2: Energies[a] of High, Intermediate, and Low Spin State Complexes of $Fe(OH_2)_6^{3+}$ at UHF and MP2//UHF, and DFT Optimized Geometries

state	UHF	MP2//UHF	MP2	DFT
$S = 5/2$	−1717.6432	−1718.8373[c]	−1718.8426[c]	−1721.2692(BPW91)
		−1719.0024[d]	−1719.0086[d]	−1721.1504(BLYP)
$S = 3/2$	−1717.5127	−1718.7359[c]	−1718.7417[c]	−1721.2336(BPW91)
		−1718.9139[d]	−1718.9203[d]	−1721.1176(BLYP)
$S = 1/2$	−1717.4504	−1718.6977[c]	−1718.7040[c]	−1721.2284(BPW91)
		−1718.8830[d]	−1718.8909[d]	−1721.1142(BLYP)
$E(3/2) - E(5/2)$[b]	28 632	22 247[c]	22 137[c]	7811(BPW91)
		19 416[d]	19 373[d]	7196(BLYP)
$E(1/2) - E(5/2)$[b]	42 320	30 628[c]	30 409[c]	8952(BPW91)
		26 196[d]	25 823[d]	7942(BLYP)

[a] All energies are given in hartrees. [b] Energy differences given in cm^{-1}. [c] MP2 with Ar frozen core on iron. [d] MP2 with Ne frozen core on iron.

TABLE 3: Zero-Point Corrected Energies for Spin States and Vertical Transition Energies

spin state	E(5/2)	ZPE(5/2)	E(3/2)^c	ZPE(3/2)	E(1/2)^c	ZPE(1/2)	vertical transition energy (5/2→3/2)	vertical transition energy (5/2→1/2)
UHF	−1717.6431	0.1625	−1717.5056	0.1629	−1717.4352	0.1646	30 253	46 074
							30 168^d	45 613^d
MP2	−1718.8426^a		−1718.7320^a		−1718.6929^a		24 266^{a,d}	32 844^{a,d}
	−1719.0086^b		−1718.9106^b		−1718.8721^b		20 040^{b,d}	29 948^{b,d}
DFT-BPW91	−1721.2692	0.1466	−1721.2244	0.1469	−1721.2000	0.1474	9895	15 358
							9829^d	15 182^d
DFT-BLYP	−1721.1504	0.1449	−1721.1084	0.1453	−1721.0952	0.1457	9302	12 286
							9214^d	12 110^d

[a] Ar frozen core on iron for MP2. [b] Ne frozen core on iron for MP2. [c] Energy of excited state computed at the sextet geometry. [d] Vertical transition energies (in cm^{-1}) estimated without inclusion of zero-point energy.

calculations resulted in some reduction in spin-state energy differences, indicating that the contributions to electron correlation due to the Fe^{3+} 3s and 3p electrons are significant. However, energy differences obtained using the MP2 method with a Ne or Ar frozen core on the iron remained significantly higher than the results from DFT. The effect on the sextet and quartet energies and energy differences from the MP2 calculations by addition of f functions was also examined by performing single-point calculations at the MP2 optimized geometries summarized in Table 1. While the energy of each structure is significantly altered, the sextet−quartet energy difference is lowered by only 10%, e.g. from 19 373 to 18 297 cm^{-1} for the calculations employing a Ne frozen core on iron. Thus, the much larger energy separations obtained in the SCF-based methods compared to the DFT results are not greatly reduced by addition of basis functions of higher orbital angular momentum or by core correlation at the MP2 level.

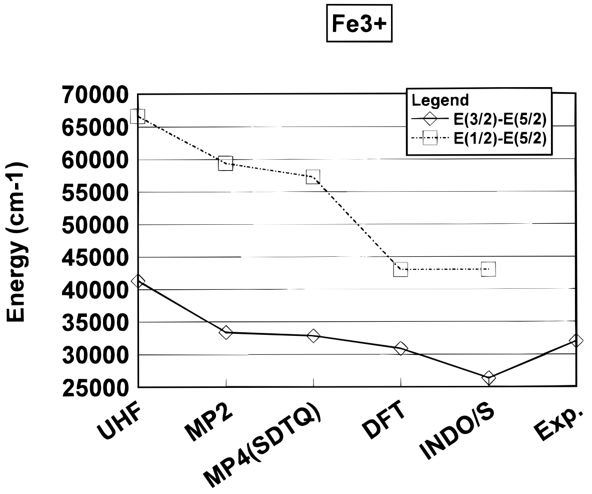

Figure 4. Plots illustrating the relative spin-state energetics of Fe^{3+} as calculated at the UHF, and MP2, MP4 Hartree−Fock level as compared with INDO/S(ZINDO) DFT(BPW91) and experimental values.

Vertical Transition Energies and Comparison with Experiment. While the calculated energy differences between the optimized spin states give a first-order estimate of experimentally observed transitions, the energy difference between the ground state and the excited state computed at the ground-state geometry should provide a better estimate of the vertical transition energy.

Table 3 presents the vertical transition energies of the $[Fe(H_2O)_6]^{3+}$ for the sextet to the quartet and from the sextet to the doublet state. The vertical transition energies without the zero-point corrections shown in the table were obtained directly from the energies of the optimized sextet state and the quartet and doublet states calculated at the optimized sextet ground-state geometry. Comparing Tables 2 and 3, it is seen that the energy differences computed from the minima are indicators of the ordering of the estimated vertical transition energies. Differences in the values of the spin-state energies evaluated at their minima are, as required, a lower bound to the vertical transition energies. The vertical transition energies calculated without the zero-point corrections will only be a good approximation to the observed vertical transition energy if the zero-point corrections in the ground and excited state are the same for a given method. This condition was verified from the zero-point corrections for the UHF and DFT levels of theory given in Table 3. The transition energies calculated at the UHF and DFT cases, before and after zero-point vibrational contributions are introduced, are nearly identical. Given this substantiation, Figure 3b shows the vertical transition energies without zero-point vibrational contributions for the UHF, MP2, and DFT calculations. In addition, the vertical transition energies calculated by the INDO/S method using the MP2 and DFT(BPW91) ground-state geometries are also given. Finally, the known experimental transition energy for the previously assigned sextet−quartet spectroscopic transition in this complex is also plotted. While there is an improvement using MP2 relative to UHF, both the UHF and MP2 results significantly overestimate these energy differences. The nonlocal DFT results using the Perdew−Wang exchange−correlation functional[37] and the INDO/S results are in much better agreement with the experimental value of the lowest sextet−quartet transition of 12 300 cm^{-1}. While the results using the BPW91 and BLYP functionals indicate they both underestimate the transition energies, perhaps an indication of an overestimation of the correlation energy, the BPW91 results are in better agreement with experiment.

Calculation of the Transition Energies of Fe^{3+}. Figure 4 presents the calculated relative energies of the lowest energy spin states of the Fe^{3+} ion using all the methods discussed above and using the same iron basis set as in the iron−water cluster calculations augmented with the auxiliary f shell. In addition, experimental results are presented in this figure obtained from the extensive compilation in C. E Moore's *Atomic Energy Levels* of the detailed electronic-state transitions for states of iron.[43] The results from all calculations shown in this figure indicate that (1) all methods and approximations correctly predict the state of highest spin-state multiplicity that maximizes the exchange interaction to be the ground state of the Fe^{3+} species; (2) for these simple systems (using a triple-ζ basis on iron), most of the effects of correlation are recovered with Møller−Plesset corrections to second order; (3) DFT results are comparable to those from MP4(SDTQ); (4) the results obtained from DFT and INDO/S calculations are in best agreement with the experimental results.

Comparing the isolated ferric ion results with those of the hexahydrated species, a significant perturbative/environmental effect of the ligands is found. The DFT sextet−quartet vertical transition energy of Fe^{3+} is reduced to a third of its value by the addition of the six water ligands, from 30 890 to 9895 cm^{-1}. It may also be seen that the DFT method gives more accurate values of calculated vertical transition energies and relative spin-state energetics than MP2 even at the ionic level where bonding is absent.

Conclusions

The study of the optimized structures and relative spin-state energetics of $[Fe(H_2O)_6]^{3+}$ illustrates that while reasonable agreement is obtained between geometric results for both density functional and Møller−Plesset calculations for a open shell iron system with little configurational mixing, a significant difference exists in the correlation recovered in these two methods, as reflected in relative spin-state energetics.

While the known ground-state geometries are well reproduced at all levels of calculations explored, the advantage of treating correlation through use of functionals clearly manifests itself in the more accurate calculation of known spectroscopic transitions using DFT compared to the results obtained from Møller−Plesset treatment both in the case of the $[Fe(H_2O)_6]^{3+}$ complex and for the unligated Fe^{3+} ion. The results of this study for both the $[Fe(H_2O)_6]^{3+}$ and Fe^{3+} ion also further illustrate the reliability of Zerner's INDO/S semiempirical method for the accurate characterization of transition metal complexes given reliable known structures of the species to be studied.

The reasonableness of the excited-state geometries obtained for the $[Fe(H_2O)_6]^{3+}$ complex cannot be assessed in the absence of experimental information. Clearly, the minimum energy geometries, as confirmed by frequency calculation for the UHF and DFT optimized excited states, differ in a significant manner. Bauschlicher has indicated that the off-axis deformation of the water hydrogens has small energetic consequences in MCPF calculations.[29] Our calculations indicate the oxygen distortions reported for the excited-state quartet and doublet DFT geometries, compared to their positions in the MP2 geometries, correspond to an energy difference of 0.003 hartrees (ca. 2 kcal $\approx$ 500 cm^{-1}) and are thus significant. Studies at twice the integration grid densities (150 radial grid densities) appear to result in similar distortions, and thus the grid densities used in this study do not appear to be the origin of the symmetry lowering observed for these DFT excited states.

The results of this study, overall, indicate the promise of density functional methods for computational examination of systems of biochemical/biomedical interest containing iron for which proper inclusion of correlation effects is vital.

Acknowledgment. Two of the authors (D.L.H. and G.L.) gratefully acknowledge the support of NSF Grant MCB-9305619 and for C90 time at the Pittsburgh Supercomputer Center. We also wish to thank David Woon for his helpful comments and criticism during the course of this work.

References and Notes

(1) Hohenberg, P.; Kohn, L. J. *Phys. Rev. B* **1964,** *136,* 864.

(2) Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140,* 1133.

(3) Fan, L.; Ziegler, T. *J. Chem. Phys.* **1991**, *95,* 7401.

(4) Bach, R. D.; Schobe, D. S.; Schlegel, H. B. *J. Phys. Chem.***1996**, *100,* 8770.

(5) Ghosh, A.; Almlof, J.; Que, L., Jr. *J. Am. Chem. Soc.* **1993,** *98,* 5576.

(6) Mouesca, J.-M.; Chen, J. L.; Noodleman, L.; Bashford, D.; Case, D. A. *J. Am. Chem. Soc.* **1994**, *116,* 11898.

(7) Broclawik, E. *Int. J. Quantum Chem.* **1995**, *56,* 779.

(8) Broclawik, E. *Int. J. Quantum Chem.* **1994,** *52,* 1017.

(9) Papai, I.; Mink, J.; Fournier, R.; Salahub, D. R. *J. Phys. Chem.* **1993**, *97,* 9986.

(10) Feller, D.; Glendening, E. D.; Kendall, R. A.; Peterson, K. *J. Chem. Phys.* **1994**, *100,* 498.

(11) Hair, N. J.; Beattie, J. K. *Inorg. Chem.* **1977**, *16,* 245.

(12) Beattie, J. K., Best, S. P., Skelton, B. W., White, A. H. *J. Chem. Soc., Dalton. Trans.* **1981**, 2105.

(13) Lind, M. D *J. Chem. Phys.* **1967**, *47,* 990.

(14) Palmer, K. J.; Wong, R. Y.; Lee, K. S. *Acta Crystallogr.* **1972,** *B28,* 236.

(15) Brunschwig, B. S.; Creutz, C.; Macartney, D. H.; Sham, T. K.; Sutin, N. *Faraday Discuss. Chem. Soc.* **1982,** *74,* 113.

(16) Magini, M. In *Ions and Molecules in Solution*, VI International Symposium on Solute-Solute-Solvent Interactions, Minoo, Japan, July 4, 1982; Tanaka, N., Ohtaki, H., Tamamushi, R., Eds.; Studies in Physical and Theoretical Chemistry; 1982; Vol. 27, pp 97−108.

(17) Ballhausen, C. J. *Introduction to Ligand Field Theory*; McGraw-Hill Book Co.: 1962; p 253.

(18) Jørgensen, C. K. *Acta Chem. Scand.* **1964**, *8,* 1502.

(19) Schläfer, H. L. Z. *Phys. Chem. (Frankfurt)* **1955**, *4,* 116.

(20) Pappalardo, R. *Nuovo Cimento* **1958**, *8,* 954.

(21) Jorgensen, C. K. *Absorption Spectra and Chemical Bonding in Complexes*; Pergamon: Oxford, England.

(22) Anderson, W. P.; Edwards, W. D.; Zerner, M. C. *Inorg. Chem.* **1986**, *25,* 2758.

(23) Dvir, M.; Loew, W. *Phys. Rev.* **1960**, *119,* 1587.

(24) Sano, M. and Yamatera, H. In *Ab Initio MO Study of* $[M(H_2O)_6]^{3+}$ *Ions. Ions and Molecules in Solution,* A Collection of Invited Papers Presented at the Section Lectures and Microsymposia during the VI International Symposium on Solute-Solute-Solvent Interactions, Minoo, Japan July 4−10, 1982; Tanaka, N., Ohtaki, H., Tamamushi, R. Eds.; Elsevier Science Publishers B. V.: Amsterdam, the Netherlands, Studies in Physical and Theoretical Chemistry; 1982, Vol. 27, p 109.

(25) Sahoo, N.; Das, T. P. *J. Chem. Phys.* **1989**, *91,* 7740.

(26) Langhoff, S. R.; Bauschlicher, C. W. Jr., *Annu. Rev. Phys. Chem.* **1988**, *39,* 181.

(27) Chong, D. P.; Langhoff, S. R.; Bauschlicher, C. W., Jr.; Walch, S. P.; Partrige, H. *J. Chem. Phys.* **1986**, *85,* 2850.

(28) Bauschlicher, C. W., Jr.; Walch, S. P.; Langhoff, S. R. In *Quantum Chemistry: The Challenge of Transition Metals and Coordination Chemistry;* Veillard, A., Ed.; D. Reidel Publishing Co.: Dordrecht, 1986; pp 15−35.

(29) Bauschlicher, C. W., Jr.; Langhoff, S. R. *Int. Rev. Phys. Chem.* **1990,** *9,* 149.

(30) Edwards, W. D. and Zerner, M. C. *Theor. Chim. Acta* **1987**, *72,* 347.

(31) Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994** *100***,** 5829.

(32) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46,* 618.

(33) Taylor, P. R. *Int. J. Quantum Chem.* **1987**, *31,* 521.

(34) Head-Gordon, M.; Pople, J. A.; Frish, M. J. *Chem. Phys. Lett.* **1988**, *153,* 503.

(35) Saebo, S.; Almlof, J. *Chem. Phys. Lett.* **1989**, *144,* 83.

(36) Becke, A. D. *Phys. Rev. A* **1988,** *38,* 3098.

(37) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992,** *45,* 13244.

(38) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37,* 785.

(39) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94,* Revision B.1; Gaussian, Inc.: Pittsburgh, PA, 1995.

(40) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S. et al. *Gaussian 92,* Revision A; Gaussian Inc.: Pittsburgh, PA, 1993.

(41) In all cases, population analyses were performed to (1) confirm the lack of spin contamination, (2) assure the spin states compared were comparable as regards d orbital occupancies. Addition checks were performed by initial occupancy reassignment to verify the excited states converged upon were, in fact, the lowest energy states of the particular spin-state multiplicity and symmetry. Supporting Information is available upon request from the authors.

(42) In the quartet these displacements were +/−0.015 Å with a consequent deviation by 5° from the starting orthogonal O−Fe−O' axes involving this pair of waters; the deviations for the doublet structure oxygen positions were as large as 0.1 Å from their octahdral axes and O−Fe−O deviations as much as 9°.

(43) Moore, C. E. *Atomic Energy Levels*; U.S. National Bureau of Standards Circular No. 467, 1949.