the transfer process. This fact demonstrates that counterion parameters are essential in the description of the potential energy hypersurface of the charge-transfer reaction. A deeper insight on the influence of neighboring ions on these reactions has been carried out by examining the changes in charge density topology due to the presence or fluctuations of counterions. This external perturbation modifies the charge density toward the product of the reaction, in the same way that a charge density variation would be obtained by changing the internal reaction coordinate of the isolated system.

A discussion of the limitations and model employed must be carried out before a comparison of our theoretical results with experimental facts is made. First of all, solvent has not been taken into account at all, so that we have used the term "neighboring ions" instead of "ionic atmosphere" throughout the paper, since the latter requires necessarily the presence of solvent. The solvent would be expected to weaken the ionic influence; hence the size of the effects might be over-emphasized. Two reasons can account for this weakening. First, solvent causes a screening between the chemical system and the counterions, which, within a continuum model for the solvent, translates into a dielectric constant larger than 1. Second, solvent participates in the reaction coordinate as well. In particular, we have shown previously,[14-16] for the reactions studied in this paper, that solvent parameters intervene in the reaction coordinate. Therefore, immobility of solvent molecules compensates for the influence of counterion fluctuations on the energetic profile. This fact was shown, with a very simplified model, by Černusák,[20c] who found that hydration partially compensates for the effect of an external cation on proton-transfer potential curves. Another limitation of our model is that a very limited number of neighboring ions have been used. Finally, it is obvious that the quantitative results obtained are dependent on the level of calculation employed. In spite of these three limitations, we think that the results obtained in the present work can be extended qualitatively to processes in solution, so that they can be applied to the ionic atmosphere. As a matter of fact, it seems that neighboring ion motions must be invoked to explain experimental results in several redox processes obtained for concentrated solutions of electrolytes.[41]

From the foregoing considerations, ionic atmosphere movements and motions of the chemical system have been shown to be correlated. This correlation does not mean that the two motions need to be simultaneous. If the two motions are not coupled, one can think of three possibilities. One possibility consists of carrying out the chemical reaction first, followed by a relaxation of the ionic atmosphere. Another possibility consists of a fluctuation of the ionic atmosphere first, followed by the chemical reaction. For a charge-transfer reaction, this means that the charge transfer adjusts itself to the fluctuations of the ionic atmosphere. A third possibility consists of an initial partial fluctuation of the ionic atmosphere, followed by the chemical process, and a final relaxation of the ionic atmosphere that leads to the products. This third mechanism is thought to occur for the solvent[42,43] and for the ionic atmosphere[19] in outer-sphere electron-transfer processes. Besides these points of view, where no coupling between both motions appears, another point of view consists of the simultaneity of the two kinds of motions. In the traditional static contribution of the ionic atmosphere, the latter will always be in equilibrium with the reacting chemical system, so it will just affect the height of the potential energy barrier. Thus, from this point of view, the ionic atmosphere will be adjusted to the chemical system by means of a relaxation. However, in this paper we have shown that the role of the ionic atmosphere is much more active. Not only the height of the barrier will be affected, but also the structure of the transition state will be changed. Since ionic atmosphere parameters do belong to the reaction coordinate, one cannot say that there is an equilibrium between the ionic atmosphere and the chemical system. Thus, fluctuations of the ionic atmosphere may induce the chemical reaction.

To discuss whether neighboring ions movements and the charge-transfer process are coupled or uncoupled, it would be necessary to take the time into account with molecular dynamics calculations. Although this dynamic study on the coupling between movements is still missing, we think that we have demonstrated that neighboring ions parameters, since they belong to the reaction coordinate, have a much more active role in the chemical process that previously thought.

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Registry No. FMe, 593-53-3; F^-, 16984-48-8; H_2O, 7732-18-5; OH^-, 14280-30-9.

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Broken Symmetry Analysis of Spin Coupling in Iron-Sulfur Clusters

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Abstract: We present a method to estimate antiferromagnetic coupling constants for polynuclear transition-metal complexes containing three or more metal sites, starting from broken symmetry molecular orbital calculations. The specific case of three $S = 5/2$ spins that occurs in linear and "cubane" 3Fe-4S clusters is illustrated through scattered wave calculations on $[Fe_3S_4(SH)_4]^{3-}$ and $[Fe_3S_4(SH)_3]^{2-}$. The trends in coupling constants agree with experimental data, but computed values are generally significantly larger than those observed. Prospects for other calculations that use this method are discussed.

The ground states of many polynuclear transition-metal complexes exhibit "antiferromagnetic" coupling, in which the spin vectors associated with the individual metal ions are aligned in opposing directions. Some of the simplest examples of this behavior are found in synthetic and naturally occurring iron-sulfur clusters, in which high-spin Fe(II) or Fe(III) ions are bridged by sulfides.[1] A variety of such structures are known, including those

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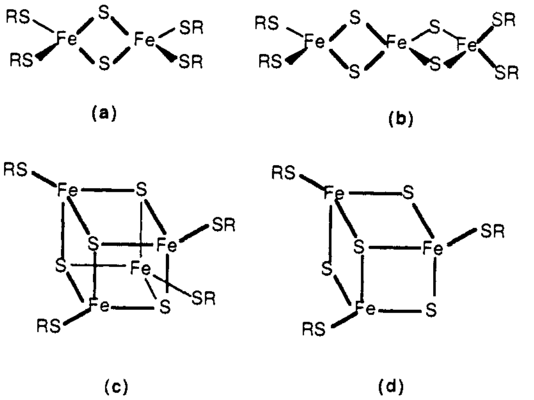

Figure 1. Structures of the iron-sulfur clusters discussed in this paper.

illustrated in Figure 1, which have two, three, and four iron atoms. Although useful qualitative theories of the origins of antiferromagnetic coupling are well known,[2] it remains a difficult task to compute magnitudes of "coupling constants," their dependence upon molecular geometry, or even the ground spin state to be expected for a particular cluster. In earlier work,[3] we have shown how broken symmetry molecular orbital calculations can be used in two-metal systems to estimate the "J" parameter in the conventional Heisenberg spin Hamiltonian

$$\hat{H} = J\hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_2 \qquad (1)$$

where $\mathbf{S}_1$ and $\mathbf{S}_2$ are the spin vectors of the monomers. Here we show how this idea can be extended to clusters of more than two atoms and illustrate the theory with calculations of antiferromagnetic coupling constants for the "linear" and "cubane" three-iron clusters shown in Figure 1.

The two systems we have chosen for illustration are themselves of considerable interest as models for the active sites in certain ferredoxins (from *D. gigas* and *Azobacter vinlandii*) and in aconitase.[4] In their "oxidized" forms, each cluster has three high-spin Fe^{3+} ions with (approximate) tetrahedral coordination to four sulfur atoms, yet the "linear" system has a ground state with $S = 5/2$, whereas the "cubane-like" structure (whose precise geometry is not known) is characterized by $S = 1/2$. The broken symmetry calculations presented here predict such behavior and give useful information about the nature of the low-lying excited states of these systems.

Broken Symmetry Analysis for a Three-Iron Cluster. The crux of our computational approach arises from the recognition that broken symmetry wave functions (in which otherwise equivalent metal sites have different spin populations) are relatively easy to compute and interpret, especially if local density functional methods are used. By contrast, the "correct" wave functions (which are eigenfunctions of $\hat{S}^2$) are generally multiconfiguration states that are considerably more difficult to approximate and understand. Hence, we choose to fit an (assumed) spin Hamiltonian to energies computed from broken symmetry wave functions and use the resulting parameters to estimate the locations of the pure spin states, including the pure-spin ground state. In this section, we outline the way in which this theory works for three $S = 5/2$ spins, as in oxidized three-iron clusters. The basic ideas also apply for more than three centers or when the spins are not all the same; such applications will be described in subsequent publications.

Table I. Coordinates for Linear 3-Fe Cluster[a]

atom	x	y	z	radius
Fe (center)	0.000	0.000	0.000	2.313
Fe (end)	0.000	0.000	5.085	2.313
S*	−2.343	2.343	2.542	2.384
S	2.520	2.520	7.605	2.374
H	3.982	3.982	6.143	1.278

[a] All values are in atomic units.

We assume that the true electrostatic interactions that couple iron spins together can be replaced by an interaction of the Heisenberg type

$$\hat{H} = J_{12}\hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_2 + J_{13}\hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_3 + J_{23}\hat{\mathbf{S}}_2\cdot\hat{\mathbf{S}}_3 \qquad (2)$$

Griffith[5] has worked out the eigenstates of this Hamiltonian, and it may also be used to estimate the energies of broken symmetry states in which each iron atom is either spin-up (with $S = M_S = 5/2$) or spin-down (with $S = 5/2$, $M_S = -5/2$). If for convenience we denote these monomer states as $|\alpha\rangle$ and $|\beta\rangle$, respectively, then broken symmetry kets will have forms such as

$$|\alpha\alpha\beta\rangle \equiv |\alpha_1\rangle\, |\alpha_2\rangle\, |\beta_3\rangle \qquad (3)$$

which represents a state with $M_S = 5/2$ which can be approximately identified with a broken symmetry molecular orbital wave function that places five unpaired spin-up d-electrons on centers 1 and 2 and five spin-down d-electrons on center 3. These broken symmetry kets are not intended to approximate eigenstates of the Hamiltonian; rather, they represent mixed states whose energies can be computed by both molecular orbital and by spin Hamiltonian methods, so that the two may be compared.

The energies of kets like that in eq (3) are relatively straightforward to evaluate since each term in the Hamiltonian couples only two centers at a time. Hence, with $S' \equiv S_1 + S_2$

$$\langle\alpha\alpha\beta|\hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_2|\alpha\alpha\beta\rangle = \langle\beta|\beta\rangle\langle\alpha\alpha|\hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_2|\alpha\alpha\rangle = (\tfrac{1}{2})[S'(S'+1) - S_1(S_1+1) - S_2(S_2+1)] = (25/4) \qquad (4)$$

since $|\alpha\alpha\rangle$ is a pure spin state with $S' = 5$. The mixed-spin states are slightly more complicated but were considered in our earlier work on two-center systems[3a,b,d]

$$\langle\alpha\alpha\beta|\hat{\mathbf{S}}_2\cdot\hat{\mathbf{S}}_3|\alpha\alpha\beta\rangle = \langle\alpha\alpha\beta|\hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_3|\alpha\alpha\beta\rangle = -(25/4) \qquad (5)$$

For a three-iron system we can define a high-spin ket $|\alpha\alpha\alpha\rangle$ (which is a pure spin state with $S = S_{\max} = 15/2$) and three broken symmetry states, $B_1 = |\alpha\alpha\beta\rangle$, $B_2 = |\beta\alpha\alpha\rangle$, and $B_3 = |\alpha\beta\alpha\rangle$, all with $M_S = 5/2$. Their energies are

$$E(S_{\max}) = (25/4)[J_{12} + J_{23} + J_{13}]$$

$$E(B_1) = (25/4)[J_{12} - J_{23} - J_{13}]$$

$$E(B_2) = (25/4)[-J_{12} + J_{23} - J_{13}]$$

$$E(B_3) = (25/4)[-J_{12} - J_{23} + J_{13}]$$

The J's can thus be estimated by comparing the energy differences arising from these formulas with those computed from a broken symmetry molecular orbital approach, and estimates of the pure spin state energies are then made from the resulting parametrized spin Hamiltonian. In the language of our previous papers, we are using the Heisenberg Hamiltonian as a tool to carry out an approximate spin projection on the broken symmetry wave functions.

Scattered Wave Calculations. To illustrate these ideas, we have carried out scattered wave calculations[6] on two models for three-iron clusters, with use of both the Xα and local spin density[7]

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Table II. Antiferromagnetic Coupling Constants[a]

model cluster	theory	exp.
$[Fe_2S_2(SH)_4]^{2-}$	606 (Xα)[c] (geom B)[a] 530 (Xα)[b] (geom A)[a] 620 (Xα-LCAO)[c] (geom B)[a]	366[d] (spinach Fd.) >550[i] (adrenodoxin) 298[e] (synthetic model)
$[Fe_3S_4(SH)_4]^{3-}$ (linear)	544 (Xα)[k] 588 (RXα) 803 (LSD)	300[f] (synthetic model)
$[Fe_3S_4(SH)_3]^{2-}$ (pseudocubane)	369 (Xα) 531 (LSD)	40[j] (*D. gigas* Fd.)
$[Fe_4S_4(SCH_3)_4]^{2-}$	376 (Xα)[h] 574 (LSD)	464[g] (synthetic model)

[a] Values in cm^{-1}, based on eq 1 and 2. All theoretical results are from scattered wave calculations except that marked LCAO, which is used a basis set, RXα = quasirelativistic Xα (ref 6[b]). LSD = local spin density functional (ref 7). In the 2Fe clusters, geometry A has S–H bonds pointing toward the Fe–Fe axis, geometry B has S–H bonds pointing away from Fe–Fe axis, with site symmetry C_{2v} for both (ref 3d,e). [b] Reference 3b. [c] Reference 3d. [d] Reference 21. [e] Reference 22. [f] Reference 8b. [g] Reference 26. [h] Reference 3c. [i] Reference 25. [j] Reference 24. [k] Values for the coupling constant between central and terminal iron atoms. The coupling constant for the two end atoms is computed to be 21 cm^{-1} in the Xα calculation.

approximations for exchange and correlation effects. Our "linear" cluster, $[Fe_3S_4(SH)_4]^{3-}$, is an extended form of that in our previous calculations on 2-Fe clusters and is a idealization of a synthetic cluster prepared by Holm and co-workers.[8] Coordinates and sphere radii for the unique atoms are given in Table I. Structures of "cubane" 3-Fe clusters are not known from high resolution X-ray crystallography. so we prepared a geometry for $[Fe_3S_4(SH)_3]^{2-}$ by removing the $Mo(SH)_3$ "corner" from an $MoFe_3$ cluster recently studied by Cook and Karplus,[9] without changing the remaining geometry or sphere radii. This structure is in accord with EXAFS data on 3-Fe proteins in solution[10] and is also consistent with the 3.0-Å resolution X-ray model of aconitase.[11]

High-spin unrestricted self-consistent wave functions (with 15 unpaired spin-up electrons) were computed in the usual manner from standard programs.[12] Then, the spin-up and spin-down potentials of one iron atom were interchanged, and the solution reconverged to an $M_S = 5/2$ broken symmetry state with a large spin-up population on two irons and a large spin-down population on the third. (As in our previous calculations, significant spin populations are also found on sulfur centers; more complete descriptions of the resulting wave functions will be given elsewhere.) In all cases, the resulting orbital energies were similar to those we have obtained before for two- and four-iron clusters, with the highest occupied orbitals having mainly sulfur character and the lowest unoccupied orbitals being 60–95% iron d-character, of spin opposite to that of the occupied d band.

Results

The formulas above considered the case of three inequivalent $S = 5/2$ centers. The idealized geometries of our calculations have higher symmetry, since all three irons are equivalent in the "cubane" cluster, and the two terminal irons are equivalent in the linear geometry. Hence, in the "cubane" cluster all three J's are equal, and only two calculations are necessary, one with high spin and one where the spin orientation of one iron is opposite to that of the other two. For the linear geometry, there are two independent J's, one connecting the center and terminal iron atoms and one connecting the two terminal iron atoms.

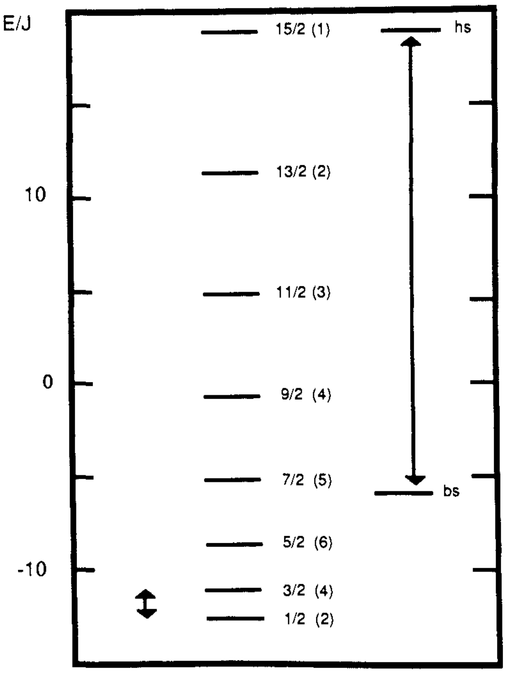

Figure 2. Energy levels for three interacting $S = 5/2$ spins with equal J's. Values in parentheses give the number of states for each value of S. The arrow on the left shows the energy difference involved in a measurement of J with use of magnetic susceptibility, and the arrow on the right shows the energy difference used in the broken symmetry calculation.

As an example, for the pseudocubane 3-Fe cluster, the computed total Xα energy of the high spin state (with 15 unpaired electrons, all spin up) is −13145.354 Ry. Because of the symmetry of our geometric model, all of the J's are equal, so that there is only one unique broken symmetry state, which has five spin-down d electrons most localized on one iron site and 10 spin-up electrons on the other two sites. Its computed total energy is −13145.438 Ry, so that the difference between the two energies is 0.084 Ry or about 9220 cm^{-1}. The spin Hamiltonian energies listed above give an energy difference (for $J_{12} = J_{13} = J_{23} = J$) of 25 J. Equating these two yields the estimate of 369 cm^{-1} cited in Table II. Similar calculations yield the remaining values.

Results are collected in Table II and compared to our previous work on oxidized two-iron clusters. As one would expect from geometric considerations, the coupling between the outer iron atoms in the linear cluster is very small compared to the coupling constants between adjacent irons. This implies[5] that the (pure-spin) ground state of the cluster has $S = 5/2$, in agreement with experiment.[8] Our cubane model has all of the coupling constants equal, which implies (for positive J) that the ground state is characterized by $S = 1/2$, which is also the observed result.[13] The use of the spin Hamiltonian allows us to make such a prediction, even though all of the actual calculations have $M_S > 1/2$ and hence no overlap with the true ground state.

The primary coupling constant in the linear three-iron cluster approximates that in the two-iron cluster (where the local geometries are similar) in agreement with experiment. All of the calculations, however, are significantly higher than the estimated experimental values; possible reasons for this will be discussed below. The "cubane" three- and four-iron clusters, which have similar bridge geometries, are also predicted to have nearly identical J values, suggesting again that these may be determined primarily by the distance between two iron centers and the ge-

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ometry of the bridge that connects them. Further calculations with systematic variations of cluster geometry are planned. (It should be noted that the experimental estimate of J for the four-iron cubane clusters was based on a spin Hamiltonian that did not allow for resonance delocalization, and this result might be altered by a reanalysis of the data.)

The local spin density formulation gives J's about 50% larger than the Xα exchange potential, such that antiferromagnetic coupling is more favored with LSD. The trends on going from one cluster to another are, however, nearly the same in the Xα and LSD models. We have found nearly identical behavior in calculations on $[Fe_4S_4(SCH_3)_4]^{2-,3-}$, and analogous behavior has been seen by others in calculations on transition metal dimers.[14] By contrast, the J values are insensitive to the addition of relativistic corrections or to the use of a basis set expansion rather than the scattered wave model to represent the molecular orbitals.

Discussion

The basic idea of our approach is illustrated in Figure 2, which shows the expected energy level diagram for a three-iron cluster where all of the J's are equal, as in our cubane model. In this case the pure-spin states have energies that are a simple function of the total spin S[5]

$$E(S) = (J/2)[S(S+1) - S_1(S_1+1) - S_2(S_2+1) - S_3(S_3+1)] \tag{6}$$

Experimental estimates of J (e.g., from magnetic susceptibility measurements) essentially use the difference of the $S = 1/2$ and $S = 3/2$ states, as shown on the left. Our computational method, on the other hand, determines J from the difference of energy between the $S = 15/2$ state and a broken symmetry state with $M_S = 5/2$, as shown on the right. In addition to approximations inherent in the calculations (and to uncertainties in the experimental data) a comparison between theory and experiment may fail if the simple Heisenberg Hamiltonian of eq 2 is not adequate to represent the spin ladder in the true system. For example, intrinsic biquadritic terms of the form $j_{12}(\hat{S}_1 \cdot \hat{S}_2)^2$ arise from formal analyses of antiferromagnetic coupling,[3f] but it is not generally known how important these terms should be. Such biquadratic terms (for positive j_{12}) would raise the energies of the higher spin states relative to the lower spin states and would tend to make the computed estimate of J larger than the "experimental" one, as illustrated in Figure 2.

An additional mechanism that can lead to effective biquadratic terms in the spin Hamiltonian are "exchange striction" effects,[15] which are expected to be considerably larger and of a generally similar form. The exchange striction model implies that the geometries and corresponding energies of a system are spin state dependent. Calculations in a fixed geometry such as ours will overestimate J since the geometric relaxation in the excited spin states is not accounted for. The effect will be largest in open and flexible systems, as in [2Fe–2S] and [3Fe–xS] (x = 3,4) clusters. Consider a simple Hamiltonian of the form

$$E(q) = J(q)\hat{S}_1 \cdot \hat{S}_2 + K(\Delta q)^2/2q_0 \tag{7}$$

where Δq is a selected normal mode displacement, $\Delta q = q - q_0$, and K is a force constant. The balance between the exchange term and the harmonic restoring force produces a different geometry (and energy) for each spin state, depending on the slope of $J(q)$. For a simple linear model of $J(q)$ near q_0, the effective Hamiltonian takes the form[15]

$$E = J_0\hat{S}_1 \cdot \hat{S}_2 - j_{12}(\hat{S}_1 \cdot \hat{S}_2)^2 \tag{8}$$

where

$$j_{12} = \left(\frac{q_0}{2K}\right)\left(\frac{\partial J}{\partial q}\right)_0^2 \tag{9}$$

The exchange striction effect is, therefore, largest for those low-frequency normal modes where $J(q)$ varies strongly. More sophisticated models for exchange striction are available in the literature,[15] but the underlying phenomena are similar to the simple linear model. Exchange striction is known to be important in various solid-state systems and may be an important, unrecognized phenomena in [2Fe–2S] and [3Fe–xS] clusters. In [2Fe–2S] proteins, for example, resonance Raman spectroscopy[16] shows numerous low-frequency bending modes below 200 cm^{-1}. (Some are below 100 cm^{-1}.[17]) Folding modes along the S*–S* bridge of the 2Fe–2S* plane should cause substantial changes in J, as should Fe–SR torsion modes. Much more theoretical analysis will be necessary to determine if these modes are likely to have important consequences for observed coupling constants; the theory outlined in this paper provides an approach to such an analysis.

It is also important to point out that all our calculations have used rather high geometric symmetries: the overall point group is D_{2h} for [2Fe–2S], C_{3v} for [3Fe–4S], and D_{2d} for [4Fe–4S]. The magnetic orbital overlaps (particularly for σ type orbitals) and the magnetic couplings are probably higher in these symmetric geometries than in the lower symmetries characteristic of [2Fe–2S] proteins and synthetic analogues. Hence it is clear that there are significant uncertainties in our calculations, as seen also in the difference between the Xα and LSD results.

In spite of these quantitative uncertainties, the method discussed here has considerable potential for understanding spin coupling in transition-metal systems. It can readily be applied to systems with more than three sites or with mixed metals, such as Mo–Fe clusters of potential importance in nitrogenase,[9,18] and has the important advantage of being applicable to systems whose ground state cannot be represented by a single configuration. As others have shown, the resulting eigenfunctions of the spin Hamiltonian can be very useful in interpreting ESR and Mossbauer spectra in terms of tensors appropriate to the individual sites.[4b] These additional comparisons to experiment can often be used to validate a particular choice of spin Hamiltonian. Since the assumed geometry can be systematically varied, it should be possible to obtain reasonable estimates of exchange striction effects and of the overall dependence of coupling constants on cluster geometry. Such calculations are in progress.

The clusters discussed here are in their fully oxidized states, in which the five d-electrons on each iron site are only slightly delocalized among the metal sites (although there is significant delocalization onto the sulfur atoms, as we have discussed elsewhere.[3e]) When these systems are reduced, the "extra" electrons are often found to be extensively delocalized over more than one metal center. In this case, additional "resonance" terms need to be added to the Heisenberg Hamiltonian of eq 2. Recently, Papaefthymiou et al.[19] have proposed a spin Hamiltonian model for reduced three-iron clusters that contains resonance splittings proportional to $(S' + 1/2)$, where S' is the dimer spin, in accord with theoretical expectations,[3d,20] and have shown that it gives a

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good account of spectral observations. We will show elsewhere that enough independent broken symmetry molecular orbital calculations can be computed to determine all of the parameters in this spin Hamiltonian as well. Thus the scheme outlined here should enable connections to be made between spin Hamiltonian models and practical calculations for a wide range of localized and delocalized polynuclear transition-metal complexes.

Note Added in Proof. Magnetic susceptibility measurements on the oxidized 3-Fe cluster in *D. gigas* yield $J > 200$ cm^{-1}, in qualitative agreement with the present results.[26]

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Ultraviolet Resonance Raman Excitation Profiles of Tyrosine: Dependence of Raman Cross Sections on Excited-State Intermediates

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Abstract: Ultraviolet resonance Raman (UVRR) excitation profiles have been measured for tyrosine with excitation between 217 and 240 nm. Resonance excitation enhances Raman scattering from vibrational modes that distort the ground-state configuration toward the configuration of the excited state. The excitation profiles of tyrosine, in conjunction with previously presented excitation profiles of tyrosinate, indicate the sensitivity and selectivity available for excitation of tyrosyl residues in proteins. Parameters are developed for the choice of excitation wavelength for the study of tyrosyl residues in proteins. A model is developed which predicts the effect of increasing the incident laser power on the measured Raman cross sections and excitation profiles. The model specifically includes depletion of ground-state analyte molecules and population of excited-state (spectroscopically silent) intermediates. The effects of optical saturation phenomena on UVRR studies of proteins are discussed.

Ultraviolet resonance Raman spectroscopy (UVRR) is a powerful new technique for physical, biophysical, and analytical studies. This technique offers a means of studying molecular structure and dynamics both in the excited and ground states of molecules.[1-21] In a wide range of biological applications, RR has been used to study proteins and nucleic acids, as well as to probe the mechanism of energy transduction in visual processes,[22,23] and ligand binding to prosthetic groups of heme proteins.[22-26] Recent UVRR studies in this and other laboratories have shown the potential of the technique, but have also demonstrated the experimental difficulties inherent to UVRR.[28,29] While the selective enhancement of individual aromatic amino acids is possible with excitation wavelengths between 220 and 250 nm,[21] a combination of photochemical and saturation effects can make UVRR measurements extremely difficult. The difficulties encountered in the study of monomeric aromatic amino acid solutions can be expected to also arise in studies of proteins.

In this report we examine the UV resonance Raman excitation profiles of aqueous solutions of tyrosine. These excitation profiles, in conjunction with the previously reported excitation profiles of tyrosinate,[21] indicate the selectivity available for UVRR excitation of individual tyrosyl residues in proteins. The excitation profiles also contain information about the excited states of tyrosine, since the degree of enhancement of a given vibrational band is related

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