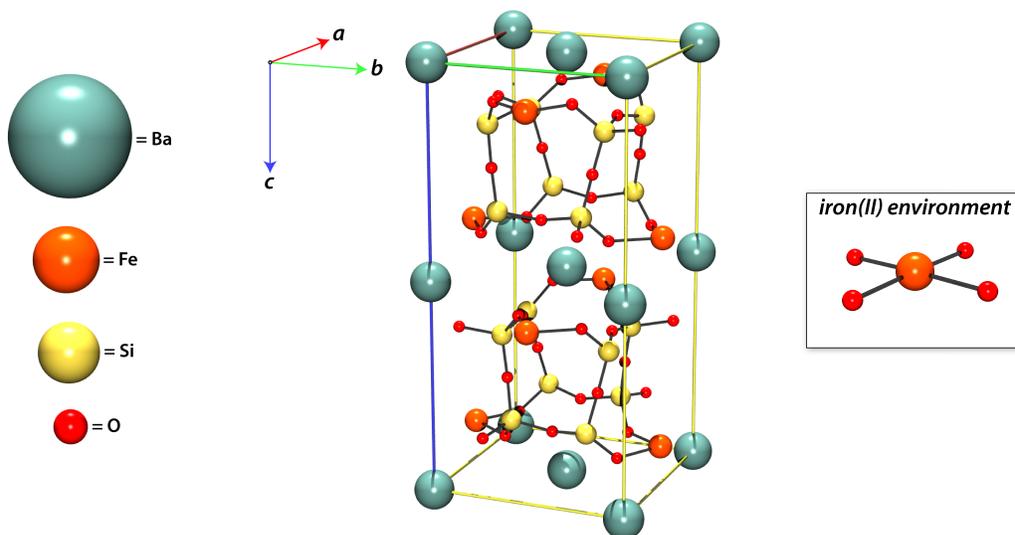


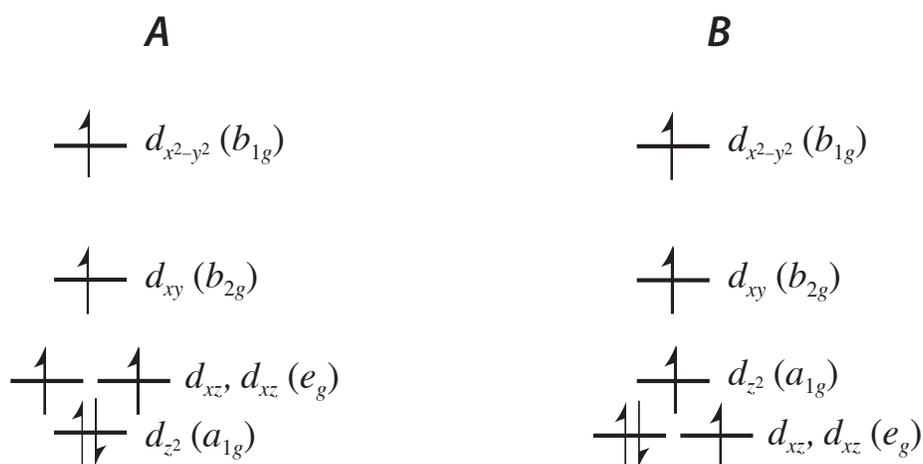
Crystal Field Theory: Analysis of the Iron Sites in Gillespite

One of the first applications of crystal field theory was the description of transition metal sites in minerals (hence *crystal* field!!). An important example in this respect is the mineral gillespite. Gillespite is an iron-containing silicate of formula $\text{BaFeSi}_4\text{O}_{10}$. The unit cell of gillespite is shown below along with the environment around each iron site:



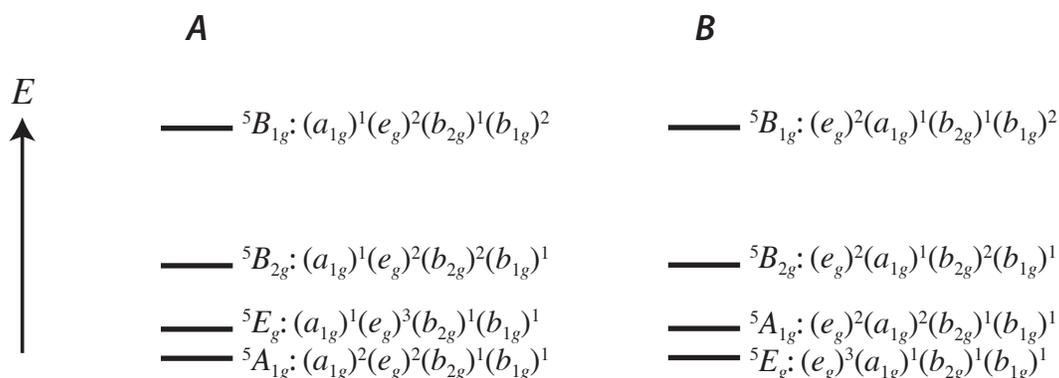
As can be seen from the figure, the geometry about iron is perfectly square-planar. Each Fe-O distances measures approximately 2.0 Å. Magnetic susceptibility measurements of the mineral are consistent with high spin iron(II) centers displaying a magnetic moment of $5.12(5) \mu_B$, which does not change significantly upon lowering the temperature to 77 K. In this example, we will use crystal field theory to understand the electronic structure of the rare square planar iron(II) sites in gillespite. From this analysis we will explain the mineral's electronic absorption spectrum and its magnetism.

Question 1: Construct possible d orbital splitting diagrams for a square planar iron(II) complex using CFT.



Assuming, the interactions between iron and the crystal field are electrostatic in origin, the greatest repulsion will be experienced by the electrons in the $d_{x^2-y^2}$ orbital followed by the d_{xy} orbital (both are in the xy plane). In D_{4h} symmetry, these orbitals have symmetries b_{1g} and b_{2g} , respectively. The remaining d orbitals are effectively non-bonding. Thus, we might envision two possible scenarios for high spin Fe(II) corresponding to placement of the e_g orbitals above (**A**) or below (**B**) the a_{1g} orbital.

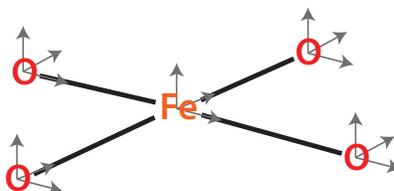
*Question 2: From the d orbital splitting diagrams, determine the ground state terms and all spin-allowed ligand field excited states for case **A** and **B**. [HINT: use a symmetry descent to D_{2h} .]*



The electronic ground state for each of the d orbital configurations will be different. In case **A** the ground state is non-degenerate, whereas in case **B** we have a two-fold degeneracy (unequal population of an e_g set). To determine the appropriate term symbols, we must take direct products of the irreducible representations for each one-electron orbital and correlate the resulting terms with the given configuration (see appendix).

From the state diagram, we see that there are three possible spin-allowed transitions for each case (e.g. ${}^5E_g \leftarrow {}^5A_{1g}$, ${}^5B_{2g} \leftarrow {}^5A_{1g}$, and ${}^5B_{1g} \leftarrow {}^5A_{1g}$ for case **A**). Each transition will be LaPorte forbidden and therefore must gain intensity through vibronic coupling. We will now determine the possible vibronic polarizations for each transition for both case **A** and **B**. To do so, we must first determine the symmetry of the normal vibrational modes for the FeO_4 core in D_{4h} symmetry.

Question 3: Using a square-planar FeO_4 core, determine the $3n - 6$ normal modes of vibration.



D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ_{3n}	15	1	-1	-3	-1	-3	-1	5	3	1

$$\Gamma_{3n} = A_{1g} + A_{2g} + B_{1g} + B_{2g} + E_g + 2A_{2u} + B_{2u} + 3E_u$$

$$\Gamma_{3n-6} = A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u$$

Next we can determine the electric dipole integrals for polarization parallel to (z polarized) and perpendicular to (x,y polarized) the crystallographic c axis (see unit cell diagram above). This axis is normal to the FeO_4 plane.

Question 4: Determine the electric dipole integrals for each transition parallel and normal to the x,y plane. Note that the components of the electric dipole moment operator transform as $a_{2u} + e_u$ in D_{4h} symmetry.

	A			B		
	${}^5E_g \leftarrow {}^5A_{1g}$	${}^5B_{2g} \leftarrow {}^5A_{1g}$	${}^5B_{1g} \leftarrow {}^5A_{1g}$	${}^5A_{1g} \leftarrow {}^5E_g$	${}^5B_{2g} \leftarrow {}^5E_g$	${}^5B_{1g} \leftarrow {}^5E_g$
$\int \psi'_e \mu_z \psi_e d\tau$	E_u	B_{1u}	B_{2u}	E_u	$A_{1u} + A_{2u} + B_{1u} + B_{2u}$	$A_{1u} + A_{2u} + B_{1u} + B_{2u}$
$\int \psi'_e \mu_{x,y} \psi_e d\tau$	$A_{1u} + A_{2u} + B_{1u} + B_{2u}$	E_u	E_u	$A_{1u} + A_{2u} + B_{1u} + B_{2u}$	$A_{1u} + A_{2u} + B_{1u} + B_{2u}$	$A_{1u} + A_{2u} + B_{1u} + B_{2u}$

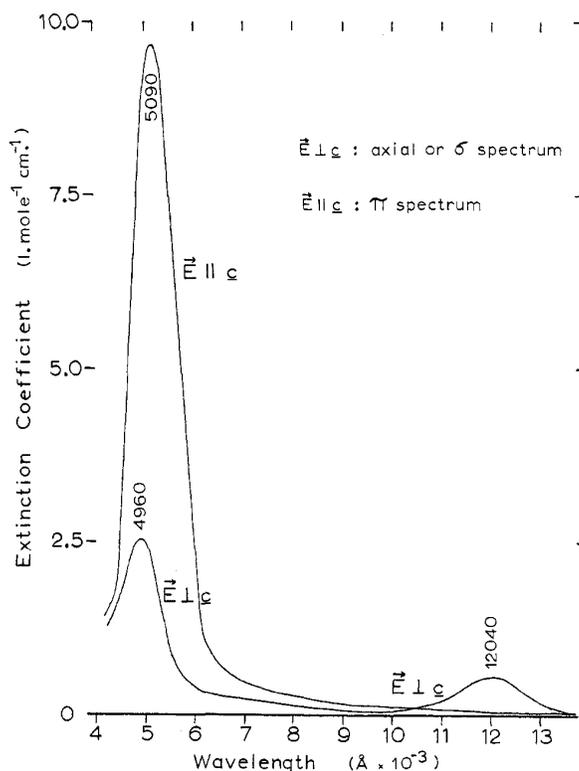
Now by comparing the symmetries of the electric dipole integrals with those of the normal modes we can determine the vibronic polarizations for each transition. For case **B**, it is clear that all transitions will be vibronically allowed with either \parallel or \perp polarization since each of the electric dipole integrals has the same symmetry as at least one normal mode. For case **A**, however, we might expect to see significant effects due to polarization in the electronic absorption spectrum.

*Question 5: Determine which transitions in case **A** will be electric dipole allowed with vibronic coupling and consider how each transition will be affected by polarization.*

Transition	Vibronic Polarization	
	\parallel to c (z)	\perp to c (x, y)
${}^5E_g \leftarrow {}^5A_{1g}$	Allowed	Allowed
${}^5B_{2g} \leftarrow {}^5A_{1g}$	Forbidden	Allowed
${}^5B_{1g} \leftarrow {}^5A_{1g}$	Allowed	Allowed

Therefore, for case **A** we would expect to see little to no dependence on light polarization for two of the possible ligand field transitions (involving 5E_g and ${}^5B_{1g}$ excited states), but a substantial \perp polarization for the ${}^5B_{2g} \leftarrow {}^5A_{1g}$ transition. Also, as is clear from the d orbital diagrams, the energetic separation between the a_{1g} and e_g orbitals is very small (in either case **A** or **B**). So much so, that any transition between the corresponding 5E_g and ${}^5A_{1g}$ states should be so low in energy as to not be observable by routine electronic absorption spectroscopy. Thus, we expect to see two ligand field transitions in the UV-vis-NIR range. If the d orbital splitting is best described by case **A**, we would predict to see a polarization dependence for the band corresponding to the lower energy of the two transitions (${}^5B_{2g} \leftarrow {}^5A_{1g}$). If, however, the d orbital arrangement is best described by case **B**, then we expect to see no significant polarization dependence for either band.

Let us look at the data:



Adapted with permission from Burns, R. G.; Clark, M. G.; Stone, A. J. *Inorg. Chem.* **1966**, *5*, 1268-1272. Copyright 1966 American Chemical Society.

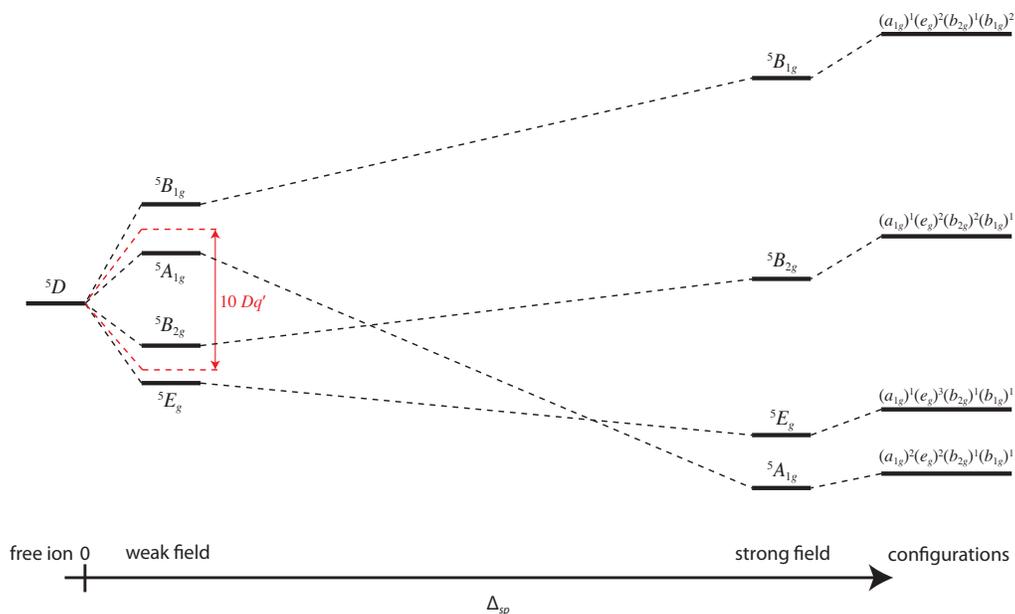
Question 6: Based on the experimental data, which d orbital splitting diagram best describes the electronic structure of the iron(II) sites in gillespite?

As is clear from the spectra, the ligand field transitions do show a polarization dependence. The lower energy transition at 12,040 \AA (8300 cm^{-1}) only appears during \perp polarization. Thus, it appears that the electronic structure of the iron ions in gillespite is best described by the d orbital splitting diagram shown for case **A**. The small energy disparity observed for the $\sim 5000 \text{ \AA}$ ($20,000 \text{ cm}^{-1}$) band under different polarizations arises from differences in energy for the vibrational modes of E_u and B_{2u} symmetry.

What about the magnetic moment of the iron centers? Here too case **A** provides a better theoretical underpinning to the observed experimental data. For a $^5A_{1g}$ ground state we expect no orbital contribution to the magnetic moment (within the Russell-Saunders approximation). The spin only magnetic moment for a high spin d^6 ion ($S = 2$) is $4.90 \mu_B$. The measured moment for gillespite of $5.12(5) \mu_B$ agrees well with the spin only value assuming that small spin-orbit effects account for the slight increase. Note that thermal population of magnetic excited states is unlikely given the temperature independence of the moment down to 77 K.

As a final exercise, let us try and construct a correlation diagram for square planar iron(II). We will only consider quintet states, which simplifies our work since we need only concern ourselves with the splitting of one free ion term, 5D . The weak field splitting of the 5D term can be determined using a correlation table ($R_3 \rightarrow O_h \rightarrow D_{4h}$), and we have already established the strong field states arising from the d electron configurations.

Question 7: Generate a simplified correlation diagram for the 5D free ion term in a square planar crystal field.



The approximate crystal field splitting parameter, Δ_{sp} will be equal to the difference in the energies of the $^5B_{1g} \leftarrow ^5A_{1g}$ and $^5B_{2g} \leftarrow ^5A_{1g}$ transitions, which corresponds to the energy difference between the $d_{x^2-y^2}$ and d_{xy} orbitals. Note that the observed value of $\sim 11,700 \text{ cm}^{-1}$ corresponds very well with the Δ_o value of $\sim 10,000 \text{ cm}^{-1}$ for high spin iron(II) in the octahedral complex, $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$. This result is to be expected since water ligands are a reasonable approximation of the silicate (OSiO_3) ligands in gillespite and $\Delta_{sp} \sim \Delta_o$. Very recently, the first molecular examples of high spin iron(II) in square planar environments have been reported (see Further Reading). Sophisticated electronic structure calculations generally agree with our CFT analysis!

Further Reading

1. Burns, R. G.; Clark, M. G.; Stone A. J. Vibronic polarization in the electronic spectra of gillespite, a mineral containing iron(II) in square-planar coordination. *Inorg. Chem.* **1966**, *5*, 1268-1272.
2. Hazen, R. M.; Burnham, C. W. The crystal structures of gillespite I and gillespite II: a structure determination at high pressure. *Amer. Mineral.* **1974**, *59*, 1166-1176.
3. Wurzenberger, X.; Piotrowski, H.; Klüfers, P. A stable molecular entity derived from rare iron(II) minerals: The square-planar high-spin- d^6 $\text{Fe}^{\text{II}}\text{O}_4$ chromophore. *Angew. Chem. Int. Ed.* **2011**, *50*, 4974-4978.
4. Doerrer, L. H., et. al. High-spin square-planar Co^{II} and Fe^{II} complexes and reasons for their electronic structure. *Angew. Chem.* **2012**, *124*, 1024-1029.

Appendix

This appendix briefly describes the method for determining the term symbols in Question 2 using a symmetry descent from D_{4h} to D_{2h} .

To begin, we first recognize that each term we will arrive at must have a spin multiplicity of 5 so that we only need to consider the orbital terms. To determine the orbital terms, we take the direct product of the representations corresponding to each singly occupied orbital. I will only consider the orbital arrangement from case **A**, but the same method can be used to arrive at the terms for case **B**.

Ground state

For the ground state term in D_{4h} symmetry we have the following direct product:

$$\begin{aligned} \text{Configuration: } & (a_{1g})^2(e_g)^2(b_{2g})^1(b_{1g})^1 \\ e_g \otimes e_g \otimes b_{2g} \otimes b_{1g} &= A_{1g} + A_{2g} + B_{1g} + B_{2g} \end{aligned}$$

In D_{2h} symmetry (descent using C_2' axis) we have the following direct product:

$$\begin{aligned} \text{Configuration: } & (a_g)^2(b_{2g})^1(b_{3g})^1(b_{1g})^1(a_g)^1 \\ b_{2g} \otimes b_{3g} \otimes b_{1g} \otimes a_g &= A_g \end{aligned}$$

In D_{2h} symmetry (descent using C_2'' axis) we have the following direct product:

$$\begin{aligned} \text{Configuration: } & (a_g)^2(b_{2g})^1(b_{3g})^1(a_g)^1(b_{1g})^1 \\ b_{2g} \otimes b_{3g} \otimes a_g \otimes b_{1g} &= A_g \end{aligned}$$

Now correlating from D_{2h} back to D_{4h} we see that we have two possibilities for each of the descents we employed:

$$\begin{array}{ll} D_{2h}(C_2') \rightarrow D_{4h} & D_{2h}(C_2'') \rightarrow D_{4h} \\ A_g \rightarrow A_{1g} \text{ or } B_{1g} & A_g \rightarrow A_{1g} \text{ or } B_{2g} \end{array}$$

Since the terms must be correlated no matter what subgroup we choose, the ground state orbital term must be A_{1g} as this is the only representation common to both descents. Thus the term symbol for the ground state configuration $(a_{1g})^2(e_g)^2(b_{2g})^1(b_{1g})^1$ is ${}^5A_{1g}$.

First excited state

For the spin-allowed excited states, we use the same logic. The first excited state configuration is $(a_{1g})^1(e_g)^3(b_{2g})^1(b_{1g})^1$. This direct product only yields one possibility:

$$a_{1g} \otimes e_g \otimes b_{2g} \otimes b_{1g} = E_g$$

Thus, the term symbol for the excited state configuration $(a_{1g})^1(e_g)^3(b_{2g})^1(b_{1g})^1$ is 5E_g .

Other excited states

The terms for the two higher-energy excited states are determined in like fashion as the ground state.

$$\text{Configuration: } (a_{1g})^1(e_g)^2(b_{2g})^2(b_{1g})^1$$

$$a_{1g} \otimes e_g \otimes e_g \otimes b_{1g} = A_{1g} + A_{2g} + B_{1g} + B_{2g}$$

Performing the symmetry descent to D_{2h} using both possible axes give the following terms:

$$\text{Configuration } (C_2'): (a_g)^1(b_{2g})^1(b_{3g})^1(b_{1g})^2(a_g)^1 \quad \text{Configuration } (C_2''): (a_g)^1(b_{2g})^1(b_{3g})^1(a_g)^2(b_{1g})^1$$

$$a_g \otimes b_{2g} \otimes b_{3g} \otimes a_g = B_{1g} \quad a_g \otimes b_{2g} \otimes b_{3g} \otimes b_{1g} = A_g$$

$$D_{2h}(C_2') \rightarrow D_{4h} \quad D_{2h}(C_2'') \rightarrow D_{4h}$$

$$B_{1g} \rightarrow A_{2g} \text{ or } B_{2g} \quad A_g \rightarrow A_g \text{ or } B_{2g}$$

The only common representation is B_{2g} . Thus, term symbol for the excited state configuration $(a_{1g})^1(e_g)^2(b_{2g})^2(b_{1g})^1$ is ${}^5B_{2g}$.

For the final excited state:

$$\text{Configuration: } (a_{1g})^1(e_g)^2(b_{2g})^1(b_{1g})^2$$

$$a_{1g} \otimes e_g \otimes e_g \otimes b_{2g} = A_{1g} + A_{2g} + B_{1g} + B_{2g}$$

Performing the symmetry descent to D_{2h} using both possible axes give the following terms:

$$\text{Configuration } (C_2'): (a_g)^1(b_{2g})^1(b_{3g})^1(b_{1g})^1(a_g)^2 \quad \text{Configuration } (C_2''): (a_g)^1(b_{2g})^1(b_{3g})^1(a_g)^1(b_{1g})^2$$

$$a_g \otimes b_{2g} \otimes b_{3g} \otimes b_{1g} = A_g \quad a_g \otimes b_{2g} \otimes b_{3g} \otimes a_g = B_{1g}$$

$$D_{2h}(C_2') \rightarrow D_{4h} \quad D_{2h}(C_2'') \rightarrow D_{4h}$$

$$A_g \rightarrow A_{1g} \text{ or } B_{1g} \quad B_{1g} \rightarrow A_{2g} \text{ or } B_{1g}$$

The only common representation is B_{1g} . Thus, term symbol for the excited state configuration $(a_{1g})^1(e_g)^2(b_{2g})^1(b_{1g})^2$ is ${}^5B_{1g}$.