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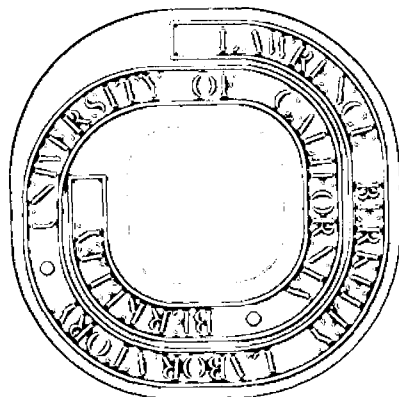
Robert W. Hand, William J. Hunt, and Henry F. Schaefer III

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ELECTRONIC STRUCTURE OF IRON TRIFLUORIDE¹

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Abstract

Ab initio quantum mechanical electronic structure calculations have been carried out on the neutral molecule FeF_3 . An essentially "double zeta" basis set of contracted gaussian functions was used. Calculations were carried out for three different F Fe F angles, 120° , 109.471° , and 90° . The high-spin ${}^6A_1'$ state is predicted to be the ground state and have a planar or nearly planar equilibrium geometry. For planar geometry, the low spin ${}^2A_1'$ state is predicted to lie 7.66 eV above the high-spin state. A Walsh-like analysis is used to discuss the possible geometries of other transition metal trifluorides. The electronic structure is further discussed on the basis of Mulliken populations, and a variety of molecular properties are reported.

Introduction

Ab initio electronic structure calculations are now becoming feasible for a variety of transition metal complexes.⁴⁻¹⁴ These calculations have already considerably furthered our fundamental understanding of the electronic structure of these interesting molecules, and the future appears very bright for this area of research. The most serious criticism which can be raised of these calculations⁴⁻¹⁴ concerns the choice of basis set. In most of the calculations, either a minimum basis set (one function per occupied atomic orbital of the separated atoms) or a slightly better than minimum basis was used. The deficiencies of such small basis sets are well known.⁴ Only in the work of Wachters and Nieuwpoort¹¹ on NiF_6^{4-} and $NiFNi^{+3}$ was a true double zeta⁴ quality basis used. A double zeta basis is twice the size of a minimum basis and thus includes, for example, for the F atom, two 1s functions, two 2s functions, two $2p_x$ functions, two $2p_y$ functions, and two $2p_z$ functions.

In earlier papers,^{15,16} we have employed larger basis sets (double zeta or slightly more extended) to study the electronic structures of two relatively simple molecules, ZnF_2 and CaF_2 . In the present work, we extend the same methods to the somewhat larger FeF_3 molecule. Our motivation in carrying out such computations is the belief that the resulting wave functions will yield properties qualitatively closer to the Hartree-Fock values than would be possible using smaller minimum or near-minimum sets. This in turn will, hopefully, lead us to an understanding of the usefulness of the Hartree-Fock approximation, when applied to transition metal complexes.

Of the transition metal trifluorides, from TiF_3 to CuF_3 , all but NiF_3 and CuF_3 have been prepared in the laboratory.¹⁷ However, relatively little is

known about the gaseous molecules in terms of their geometries, electronic structures, and other molecular properties, e.g., dipole and quadrupole moments.¹⁷ The geometry of the neighboring molecule ScF_3 has been the subject of two studies. Hauge, Hastie, and Margrave¹⁸ have suggested that ScF_3 is planar, due to the absence of the ν_1 frequency in the IR spectrum of the matrix-isolated species. On the other hand, Kaiser, Falconer, and Klemperer¹⁹ have suggested that ScF_3 is a polar molecule (possibly T-shaped) based on their molecular beam electric deflection experiments. Hastie, Hauge, and Margrave²⁰ have also studied TiF_3 in neon and argon matrices, and their work suggests a pyramidal C_{3v} equilibrium geometry.

Rather than carrying out self-consistent-field calculations on each of the transition metal trifluorides, a less costly and more qualitative approach was adopted. We decided to choose a single molecule, FeF_3 , and construct an ab initio Walsh diagram,²¹ from which it might be possible to predict the geometries of the entire series of transition metal trifluorides.

FeF_3 is a good choice for the present study since it lies about halfway through the series and is the first molecule for which each of the transition metal d-like orbitals becomes occupied. Figure 1 shows the traditional crystal field picture²² of the d-orbital energies of Fe^{+3} in the field of three F^- ions. In this simple picture, the energy separation between the high and low spin states is given by

$$\Delta E = 2\Delta - 2P \quad (1)$$

In equation 1, Δ is presumably the difference between the e'' and e' orbital energies, while P is a somewhat nebulous quantity called the "average pairing

energy". Of course, if we know ΔE from experiment and obtain Δ from a Hartree-Fock calculation, we can deduce a semi-empirical value of P.

Finally, we point out that a good deal is known about the thermochemistry of the free FeF_3 molecule. Specifically, Zmbov and Margrave²³ have determined the $\text{F}_2\text{Fe-F}$ bond dissociation energy to be 100 kcal/molecule from mass spectrometry. Combined with the F Fe-F dissociation energy (112 kcal/mole) and that of diatomic Fe F (108 kcal), they²³ conclude that the atomization energy of FeF_3 is 320 kcal/mole = 13.9 eV.

Details of the Calculations

The chosen basis set of contracted gaussian functions was completely analogous to that used previously¹⁵ for ZnF_2 . For Fe, Wachters²⁴ (14s 9p 5d) primitive gaussian basis was contracted to (9s 5p 2d). To allow a description of the Fe 4p orbital, not occupied in the SCF wave function for the electronic ground state of the atom, an additional set of p functions with exponent $\alpha = 0.23$ was included. For the Fe atom, then, this basis is of slightly better than double zeta⁴ quality. For the F atom, we chose the standard (4s 2p) Dunning contraction²⁵ of the Huzinaga²⁶ primitive (9s 5p) gaussian basis. The complete basis thus includes 69 contracted functions, obtained from 146 primitive gaussians. The most serious weakness of this basis is probably the lack of an additional set of diffuse p functions on fluorine to describe the F^- negative ion.

The calculations were performed on the Lawrence Berkeley Laboratory CDC 7600 using a version of POLYATOM²⁷ modified to carry out open-shell SCF and multiconfiguration SCF calculations using the methods developed by Hunt, Hay, and Goddard.²⁸ Obtaining the first properly converged SCF solution was quite difficult, several different extrapolation and averaging schemes being required. However, for the remaining geometries the SCF calculations converged smoothly using the first solution as a set of starting orbitals.

All calculations reported here were carried out for a single Fe-F bond distance, namely $1.9 \text{ \AA} = 3.59048$ bohrs. This distance was chosen on the basis of the experimental bond distances²⁹ for TiF_3 and CoF_3 .

Energy Results

The high-spin state of planar FeF_3 is of ${}^6A_1'$ symmetry, while the low-spin state is of ${}^2A_1'$ symmetry.³⁰ For pyramidal FeF_3 these two symmetries become 6A_1 and 2A_1 . Table I gives the calculated total energies and Mulliken population analyses. There it is seen that the planar high-spin state is predicted to lie 0.2814 hartrees = 7.66 eV = 177 kcal/mole below the low-spin state. This result is consistent with the experimental observation that iron(III) nearly always²² forms high-spin complexes. However, it is clear³¹ that the Hartree-Fock approximation will be better for the sextet state than for the doublet. Alternatively, there will be more correlation energy^{31,32} associated with the 2A state than with the 6A state. Nevertheless, we doubt that this correlation energy correction will make the sextet-doublet splitting much less than 5 eV.

For the high-spin state, calculations were also carried out for tetrahedral ($\theta(\text{F-Fe-F}) = 109.47^\circ$) and octahedral ($\theta = 90^\circ$) bond angles. In each case, the equivalence of all F-Fe-F bond angles implies a C_{3v} geometry. At 109.47° , the calculated total energy is 0.0237 hartrees = 14.9 kcal/mole higher than for the planar geometry. This energy difference is large enough to strongly suggest that FeF_3 is either planar or nearly planar. Positive confirmation of the planarity of FeF_3 would require at least one more calculation, perhaps at $\theta = 118^\circ$. At $\theta = 90^\circ$, the total energy lies 0.0912 hartrees = 57.2 kcal above the planar result.

The Mulliken populations of Table I suggest that the sextet state is somewhat more ionic than the doublet. The iron atom has a "charge" of $+1.72$ for the ${}^2A_1'$ state and $+1.96$ for the ${}^6A_1'$ state. The fact that in both cases the

Table I. Energies (in hartrees) and Mulliken atomic populations for iron trifluoride. θ is the F-Fe-F bond angle.

| | $\theta = 120^\circ$ ${}^2A'_1$ | $\theta = 120^\circ$ ${}^6A'_1$ | $\theta = 109.47^\circ$ 6A_1 | $\theta = 90^\circ$ 6A_1 |
|---------------------|------------------------------------|------------------------------------|--------------------------------------|----------------------------------|
| Total Energy | -1560.5897 | -1560.8711 | -1560.8474 | -1560.7799 |
| Potential Energy | -3120.7653 | -3121.7208 | -3121.6825 | -3121.6259 |
| Kinetic Energy | +1560.1756 | +1560.8497 | +1560.8351 | +1560.8460 |
| Virial Ratio $-V/T$ | 2.000265 | 2.000014 | 2.000008 | 1.999958 |
| Electronic Energy | -1795.1812 | -1795.4626 | -1797.8093 | -1804.1533 |
| Nuclear Repulsion | +234.5915 | +234.5915 | +236.9619 | +243.3735 |
| Fe Population | 24.277 | 24.041 | 24.053 | 24.104 |
| F Population | 9.574 | 9.653 | 9.649 | 9.632 |

charge is less than the formal value +3 is typical of ab initio calculations with similar basis sets.^{15,16} However, the relative inability of our basis to describe F^- may be another factor leading to the relatively small positive charge on iron. In addition, Table I indicates that FeF_3 becomes slightly less ionic as it is bent. The charge on Fe goes from +1.96 at $\theta = 120^\circ$ to +1.90 at $\theta = 90^\circ$.

In a simple picture, the changes in electronic structure in going from TiF_3 to CuF_3 are due to the filling of the d-orbitals of the metal ion M^{+3} . For FeF_3 , a Walsh-like diagram for these d-like orbitals is shown in figure 2. The numerical values of the calculated orbital energies are given in Table II. Figure 1 indicates that the calculated $1e''$, $6a_1'$, and $5e'$ orbital energies all increase as the molecule becomes pyramidal. This fact, taken with our earlier prediction that FeF_3 itself is planar, allows us to predict that CoF_3 , NiF_3 , and CuF_3 will also be planar. Further, if the Walsh argument²¹ is correct, the bending force constants of FeF_3 , CoF_3 , NiF_3 , and CuF_3 should be progressively larger.

It should also be noted that the $8a_1$ and $5e$ orbital energies cross somewhere between the planar and tetrahedral F-Fe-F bond angles. This means that the simple picture given in figure 1 becomes erroneous for non-planar FeF_3 . The calculated orbital energies imply that for tetrahedral and octahedral bond angles, the energetically lowest low-spin state will have orbital occupancy $8a_1^2 5e^3$ and thus be of 2E symmetry.

Figure 3 shows the remaining valence orbital energies of FeF_3 . These orbitals, roughly speaking correspond to the 2p atomic orbitals of the three F^- ions. We see that these ϵ 's also increase as the molecule is bent. Therefore,

Table II. Orbital energies for FeF_3 . The occupation numbers in parentheses refer to the 2A_1 state.

| Orbital | | Occupation Number | $\theta = 120^\circ$ | $\theta = 120^\circ$ | $\theta = 109.47^\circ$ | $\theta = 90^\circ$ |
|----------|----------|----------------------|----------------------|----------------------|-------------------------|---------------------|
| C_{3V} | D_{3h} | | ${}^2A_1'$ | ${}^6A_1'$ | 6A_1 | 6A_1 |
| $1a_1$ | $1a_1'$ | 2 | -261.6750 | -261.7158 | -261.7118 | -261.7007 |
| $2a_1$ | $2a_1'$ | 2 | -32.2669 | -32.3122 | -32.3076 | -32.2950 |
| $3a_1$ | $1a_2''$ | 2 | -27.7132 | -27.7941 | -27.7889 | -27.7754 |
| $1e$ | $1e'$ | 4 | -27.7641 | -27.7904 | -27.7861 | -27.7742 |
| $2e$ | $2e'$ | 4 | -26.2955 | -26.2671 | -26.2530 | -26.2164 |
| $4a_1$ | $3a_1'$ | 2 | -26.2955 | -26.2671 | -26.2530 | -26.2164 |
| $5a_1$ | $4a_1'$ | 2 | -4.4454 | -4.5118 | -4.5071 | -4.4947 |
| $6a_1$ | $2a_2''$ | 2 | -2.9877 | -3.0831 | -3.0764 | -3.0606 |
| $3e$ | $3e'$ | 4 | -3.0232 | -3.0733 | -3.0693 | -3.0585 |
| $7a_1$ | $5a_1'$ | 2 | -1.5478 | -1.5337 | -1.5190 | -1.4860 |
| $4e$ | $4e'$ | 4 | -1.5440 | -1.5293 | -1.5147 | -1.4756 |
| $5e$ | $1e''$ | 2(4) | -0.8270 | -1.0403 | -1.0284 | -1.0110 |
| $8a_1$ | $6a_1'$ | 1 | -0.8180 | -1.0363 | -1.0322 | -1.0154 |
| $6e$ | $5e'$ | 2(0) | - | -0.9780 | -0.9703 | -0.9423 |
| $9a_1$ | $7a_1'$ | 2 | -0.6616 | -0.6745 | -0.6547 | -0.6247 |
| $7e$ | $6e'$ | 4 | -0.6600 | -0.6593 | -0.6471 | -0.6204 |
| $8e$ | $7e'$ | 4 | -0.6365 | -0.6304 | -0.6256 | -0.5932 |
| $9e$ | $2e''$ | 4 | -0.6298 | -0.6286 | -0.6054 | -0.5561 |
| $10a_1$ | $3a_2''$ | 2 | -0.6468 | -0.6251 | -0.6191 | -0.5938 |
| $1a_2$ | $1a_2'$ | 2 | -0.6202 | -0.6105 | -0.5938 | -0.5486 |

even if the Fe^{3+} d-orbital energies were constant as a function of bond angle, the transition metal trifluorides would still be expected to be increasingly planar in going from TiF_3 to CuF_3 .

One of the more surprising results to be gleaned from Table II is the fact that the half-occupied $1e''$, $6a'_1$, and $5e'$ orbital energies all lie below the fully occupied $7a'_1$, $6e'$, $7e'$, $2e''$, $3a''_2$, $1a'_2$. This is clearly contrary to intuition, which suggests that the partially occupied orbitals should have the highest orbital energies. To be certain the behavior found did not correspond to an energetically higher solution of the SCF equations, on several occasions we reoccupied the orbitals by orbital energy and began the SCF procedure again. In each case a much higher total energy resulted at first, and additional SCF iterations eventually brought us back to the original surprising SCF wave function. However, this unusual pattern of orbital energies was not without precedent; Schaefer and Bagus³³ recently found a similar situation for the MnH molecule. Furthermore, this phenomena is not simply due to the fact that open- and closed-shell orbitals are treated differently in SCF procedures.³⁴ That is, we expect the calculated Koopmans' theorem ionization potentials to agree qualitatively with experiment. The moral of this story is that the minimization of the total SCF energy of an open-shell system need not correspond to the minimization of a sum of occupation numbers times orbital energies. More chemically, the sextet $3d^5$ structure of the Fe^{3+} ion is clearly apparent in the FeF_3 molecule, even though there are higher-lying fully occupied molecular orbitals.

One of the basic assumptions of simple molecular orbital theory is that a single orbital energy level diagram will suffice to describe the electronic

structure of all the excited states, as well as the ground state, of a particular molecule. Therefore, one purpose of an ab initio study, such as that presented here, is to investigate the limitations of such approximations. A comparison of the orbital energies of the ${}^2A'_1$ and ${}^6A'_1$ states of FeF_3 is given in Table II. There we see that most of the corresponding orbital energies agree to within 1 or 2 eV. The serious exceptions to this pattern are the $1e''$ and $6a'_1$ orbital energies, which lie more than $0.2 \text{ hartrees} = 5.4 \text{ eV}$ higher for the low-spin state than for the high-spin case. Unfortunately, these are just the orbitals one would like to use in a simple discussion of the electronic structure of FeF_3 . On the brighter side, the order of the $1e''$ and $6a'_1$ orbitals is the same in both the high-spin and low-spin calculations. Viewed in perspective, it is probably not fruitful for the theoretician to try to convince the practicing inorganic chemist to abandon his orbital energy level diagram. In fact, we must admit that such a diagram, despite its inherent inconsistencies, can be a useful tool for the classification of otherwise confusing experimental data.

Molecular Properties

As we mentioned in the introduction, almost nothing is known concerning the molecular properties of the transition metal trifluorides. Therefore, the calculated properties of FeF_3 , seen in Table III, are true predictions.

Fortunately, there have been enough comparisons⁴ between ab initio properties (computed at roughly the present level of accuracy) and experiment to give us some confidence in the predictions made herein.

As is invariably the case, the calculated dissociation energy is less than experiment. This is a result of the correlation energy being greater for the molecule than for the separated atoms.⁴ The calculated FeF_3 ionization potential (16.6 eV) may be compared to those of the Fe atom (7.9 eV), Fe^+ (16.2 eV), and Fe^{++} (30.6 eV).

Only the non-zero moments of the electronic charge distribution are shown in Table III. For example, it is clear from symmetry that $\langle x \rangle = \langle y \rangle = \langle z \rangle = 0$, and thus the molecule has no dipole moment. The first nonvanishing multipole moment, the quadrupole moment, should be independent of origin. As a test of the program, we computed θ with respect to both the Fe and F atoms. The results differed by 0.00002×10^{-24} esu \cdot cm². The octupole moment tensor of Table III was calculated with respect to the Fe atom point charge nucleus.

The calculated potentials at the nuclei and diamagnetic shielding should be within a few percent of experiment. The electric field $E_x(\text{Fe})$ is zero by symmetry and $E_x(\text{F})$ would be zero for an exact Hartree-Fock calculation at equilibrium geometry. Perhaps the least reliable of the predicted properties are the electric field gradient tensors. Experience has shown⁴ that using comparable basis sets, calculated field gradients may differ by as much as 50% from experiment.

Table III. Molecular properties of planar FeF_3 in the ${}^6A_1'$ state. Unless indicated, all quantities are given in atomic units^b.

| | | | |
|--|-----------------------------------|----------------------------------|--------------------------------|
| Dissociation energy (eV) relative to Fe + 3F | 8.5 (13.9 ^a) | | |
| Ionization potential (eV) | 16.6 | | |
| Second moments of the electronic charge distribution | $\langle xx \rangle$ -205.64 | $\langle yy \rangle$ -205.64 | $\langle zz \rangle$ -18.26 |
| Third moments of the electronic charge distribution | $\langle xxx \rangle$ -334.48 | $\langle xyy \rangle$ 334.48 | |
| Quadrupole moment tensor (10^{-24} esu · cm ²) | θ_{xx} | θ_{yy} | θ_{zz} |
| Nuclear contribution | 117.03 | 117.03 | -234.06 |
| Electronic contribution | -126.00 | -126.00 | 252.00 |
| Total | -8.97 | -8.97 | 17.94 |
| Octupole moment tensor (10^{-34} esu · cm ³) | Ω_{xxx} | Ω_{xyy} | |
| Nuclear contribution | 555.89 | -555.89 | |
| Electronic contribution | -595.12 | 595.12 | |
| Total | -39.23 | 39.23 | |
| Potential at nucleus | $\Phi(\text{Fe})$ | $\Phi(\text{F})$ | |
| | -115.324 | -26.611 | |
| Electric field at nucleus | $E_x(\text{Fe})$ | $E_x(\text{F})$ | |
| | 0.00 | 0.16 | |
| Diamagnetic shielding | $\langle 1/r_{\text{Fe}} \rangle$ | $\langle 1/r_{\text{F}} \rangle$ | |
| | -122.844 | -36.748 | |
| Electric field gradient at iron | $q_{xx}(\text{Fe})$ | $q_{yy}(\text{Fe})$ | $q_{zz}(\text{Fe})$ |
| Nuclear contribution | -0.29 | -0.29 | 0.58 |
| Electronic contribution | 1.39 | 1.39 | -2.79 |
| Total | 1.10 | 1.10 | -2.21 |
| Electric field gradient at fluorine | $q_{xx}(\text{F})$ | $q_{yy}(\text{F})$ | $q_{zz}(\text{F})$ |
| Nuclear contribution | -1.22 | 0.58 | 0.64 |
| Electronic contribution | 0.04 | 0.08 | -0.13 |
| Total | -1.17 | 0.66 | 0.51 |

(continued)

Table III (continued)

^aRef. 23.

^bS. Rothenberg and H. F. Schaefer, J. Chem. Phys., 53, 3014 (1970).

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Footnotes and References

- (1) Work performed under the auspices of the U. S. Atomic Energy Commission.
- (2) Miller Fellow
- (3) Alfred P. Sloan Fellow
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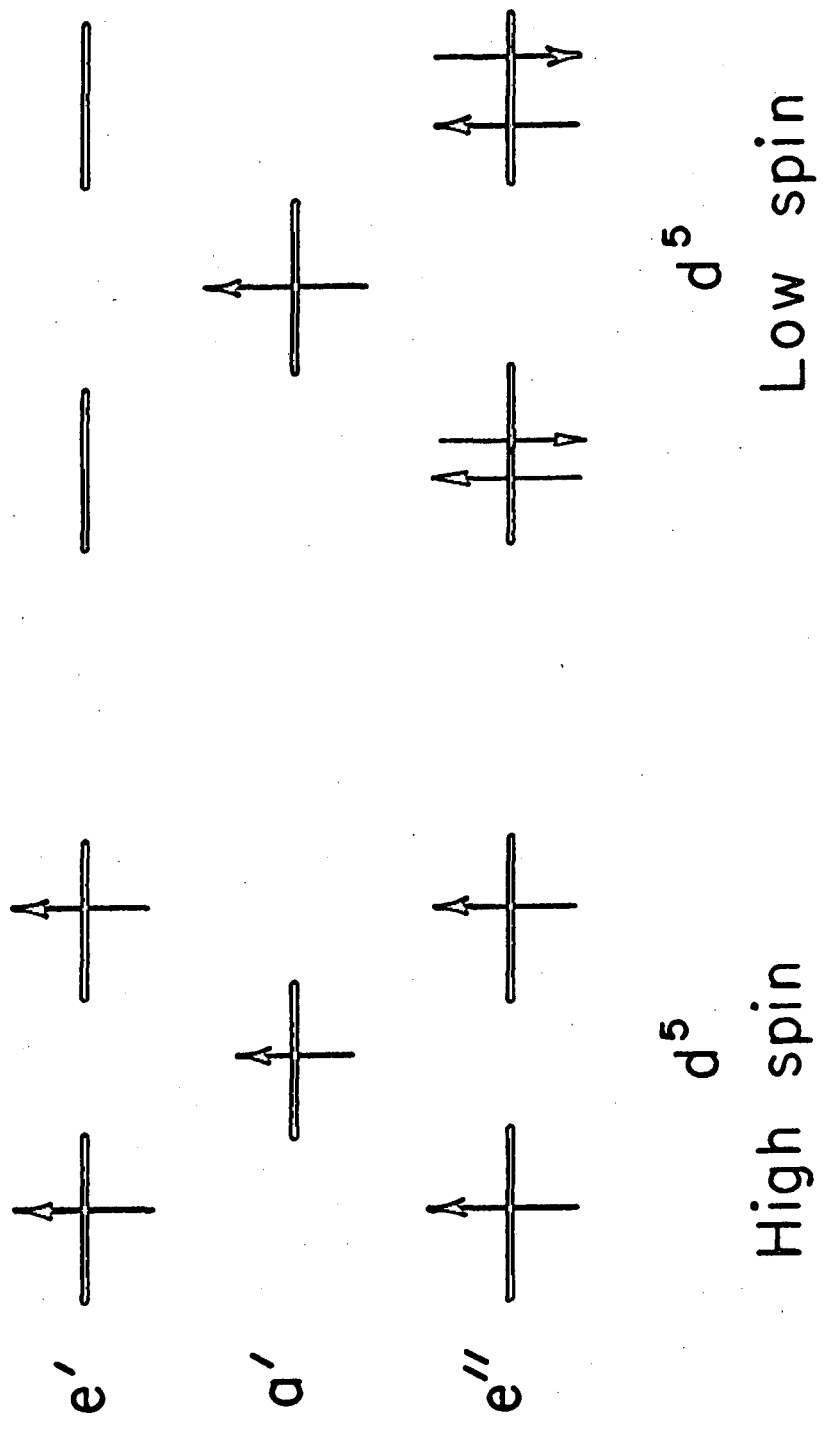
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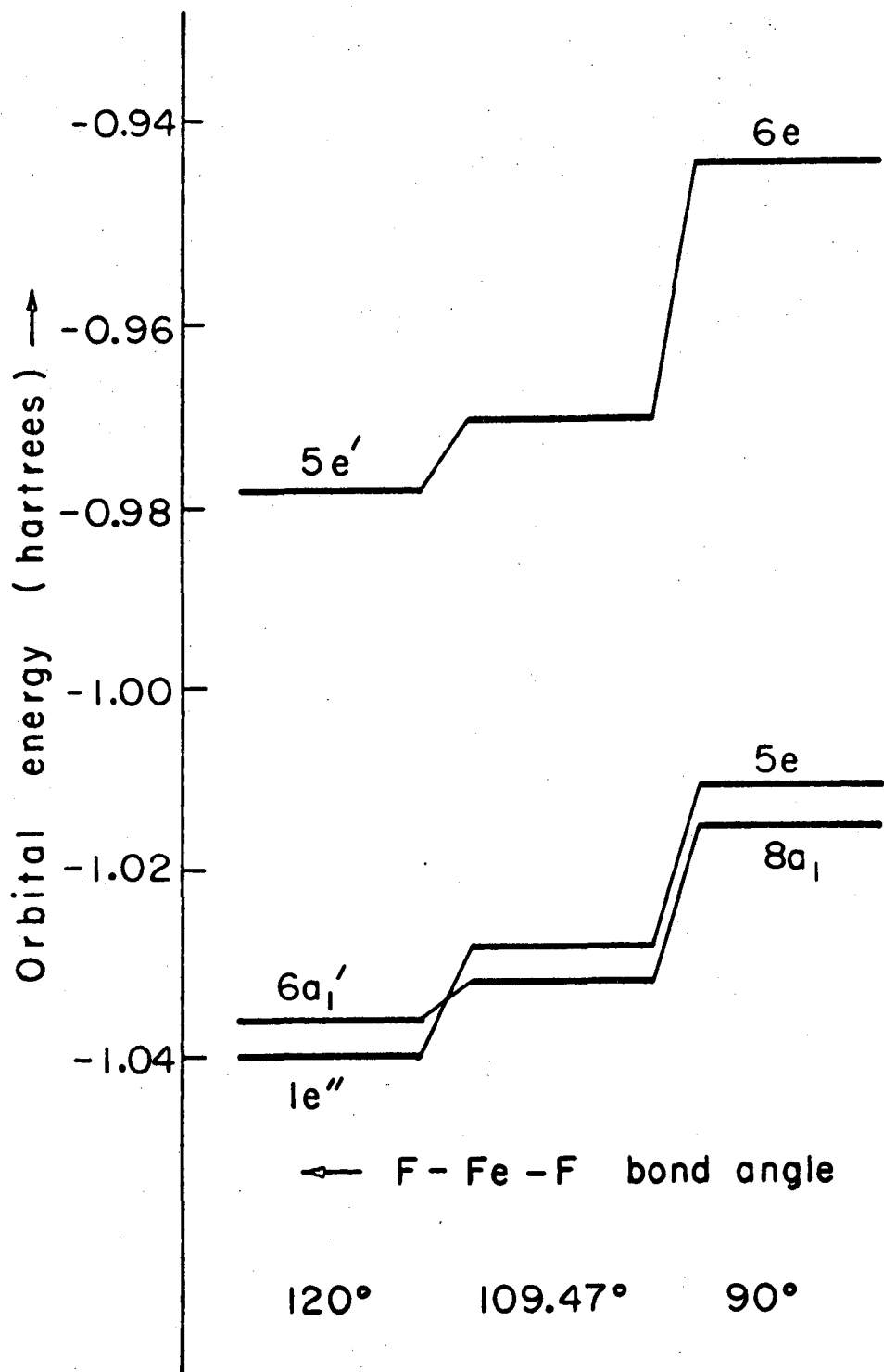
Figure Captions

- Fig. 1. Schematic representation of the electronic structure of the high- and low-spin states of planar FeF_3 .
- Fig. 2. Diagram of FeF_3 orbital energies for those orbitals corresponding to the d-orbitals of Fe^{+3} in a crystal field picture.
- Fig. 3. The six highest-lying orbital energies of FeF_3 as a function of geometry. In a rough picture these orbitals correspond to the 2p orbitals of the three F^- ions.



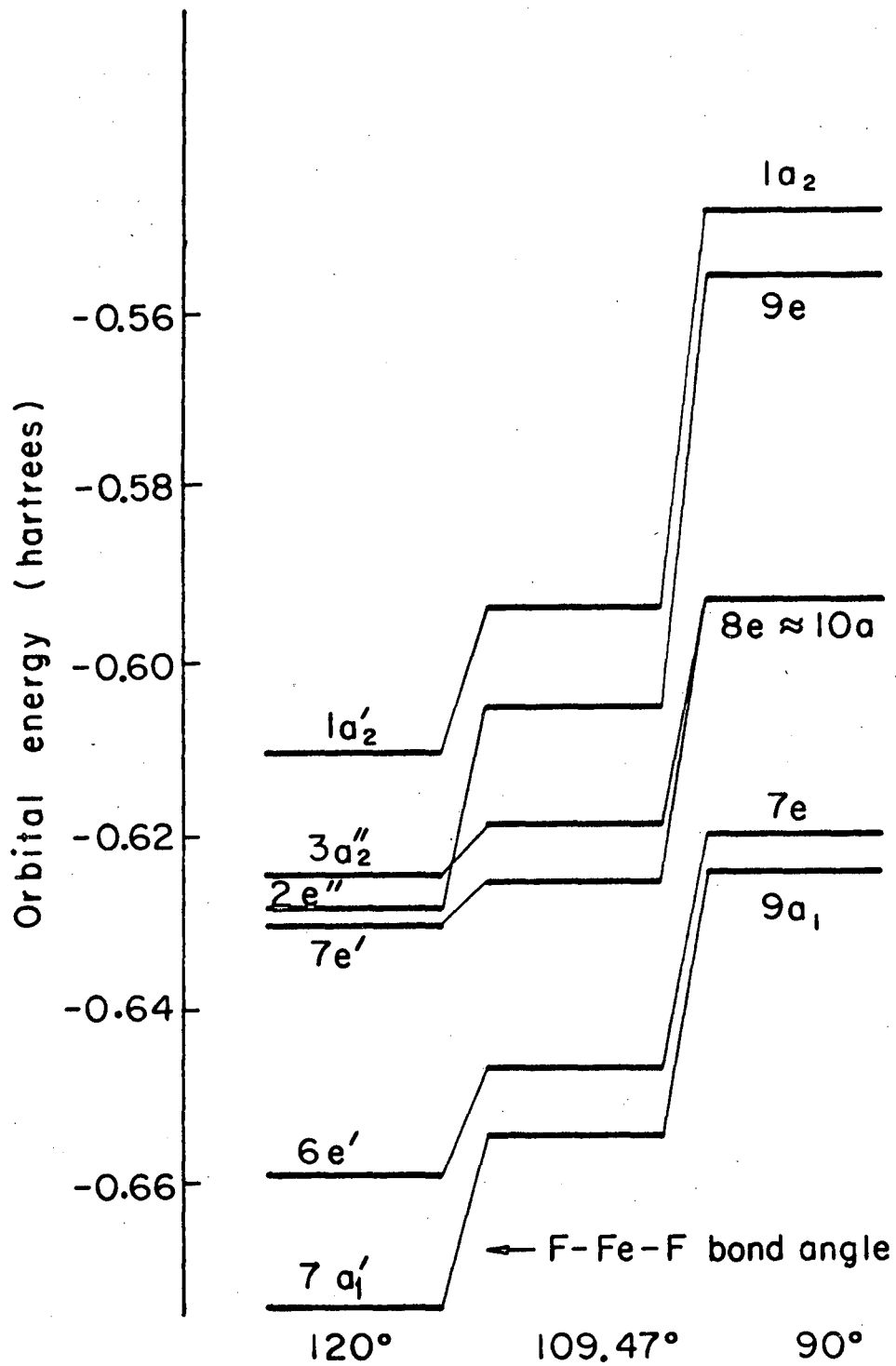
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Fig. 1



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Fig. 2



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Fig. 3

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