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# Vibrational and Raman intensity analysis of a ferredoxin model, dithiodiiron hexacarbonyl

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served for ruthenocene; it is assignable to either Ru-X stretching or ring-metal-ring bending. The ring-metal-ring bending motion,  $\omega_{22}$ , of ruthenocene was calculated<sup>15</sup> to be  $\sim 185\text{ cm}^{-1}$  by using the  $\omega_4/\omega_{22}$  ratio of ferrocene. Here  $\omega_4$  is the symmetrical ring-metal-ring stretch. A low-energy band appears at  $225\text{ cm}^{-1}$  in  $[\text{Ru}(\text{cp})_2\text{Br}]\text{Br}_3$ . If this band is the ring-metal-ring bending vibration in ruthenocene shifted to higher energy by ring crowding caused by the halogen substitution, it would be reasonable to expect the iodo-substituted molecule to exhibit the higher energy vibration. Thus the observed shift in this low-energy band in going from the iodo to the bromo complex is in better agreement with the Ru-X stretching mode assignment. It may be pointed out that the antisymmetrical ring-metal-ring stretching frequency at  $446\text{ cm}^{-1}$  in ruthenocene is lowered to  $419\text{ cm}^{-1}$  in  $[\text{Ru}(\text{cp})_2\text{I}]\text{I}_3$ , which indicates that the bonding between the metal and the rings is weakened. This is further support for assigning the  $211\text{-cm}^{-1}$  band of  $[\text{Ru}(\text{cp})_2\text{I}]\text{I}_3$  as the Ru-I

(15) E. R. Lippincott and R. D. Nelson, *Spectrochim. Acta*, **10**, 307 (1958).

stretch instead of the ring-metal-ring bending vibration. The higher energy bands at  $578, 920, 976$ , and  $1436\text{ cm}^{-1}$  observed for  $\text{Ru}(\text{cp})_2\text{I}^+$  ( $579, 920, 975$ , and  $1440\text{ cm}^{-1}$  for  $\text{Ru}(\text{cp})_2\text{Br}^+$ ) are all assignable to ring vibrations which do not give rise to observable bands in the more symmetrical ruthenocene molecule.

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**Registry No.**  $[\text{Ru}(\text{cp})_2\text{I}]\text{I}_3$ , 39427-31-1;  $[\text{Ru}(\text{cp})_2\text{Br}]\text{Br}_3$ , 39427-30-0.

**Supplementary Material Available.** Calculated and observed structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche ( $105 \times 148\text{ mm}$ ,  $24\times$  reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-301.

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## Vibrational and Raman Intensity Analysis of a Ferredoxin Model: $\text{S}_2\text{Fe}_2(\text{CO})_6^1$

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Raman and infrared spectra are reported for  $\text{S}_2\text{Fe}_2(\text{CO})_6$ , and for the syn and anti isomers of  $(\text{CH}_3\text{S})_2\text{Fe}_2(\text{CO})_6$ . The  $\text{S}_2\text{Fe}_2$  cluster in the former compound is similar to proposed structures for iron-sulfur proteins of the 2Fe-2S\* class. Symmetric stretching modes are identified for  $\text{S}_2\text{Fe}_2(\text{CO})_6$ , and their frequencies are satisfactorily calculated by a simple force field, all of whose elements have reasonable values. In particular the Fe-Fe stretching force constant,  $1.3 \pm 0.2\text{ mdyne/\AA}$  appears satisfactory for a Fe-Fe single bond. The Raman intensities can be accounted for with a reasonable set of internal coordinate polarizability derivatives. The modes primarily associated with vibrations of the  $\text{S}_2\text{Fe}_2$  cluster display preresonance Raman enhancement, which is probably associated with cluster electronic transitions in the visible and near-ultraviolet regions.

### Introduction

The successful acquisition of Raman spectra for rubredoxin<sup>2</sup> and adrenodoxin<sup>3</sup> suggests that Raman spectroscopy will be useful in exploring structural features of iron-sulfur proteins.<sup>4</sup> Studies in this area are under way in this laboratory, and we report here a vibrational and Raman intensity analysis for a model compound  $\text{S}_2\text{Fe}_2(\text{CO})_6$  whose structure<sup>5</sup> is shown in Figure 1. Supporting data are provided by the analogous compound  $(\text{CH}_3\text{S})_2\text{Fe}_2(\text{CO})_6$ ,<sup>6</sup> which lacks a sulfur-sulfur bond. The analysis is also of interest in connection with Raman studies of compounds containing metal-metal bonds.<sup>7</sup>

(1) This investigation was supported by Public Health Service Grant GM 13498 and by National Science Foundation Grant GP 10122.

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### Experimental Section

$\text{S}_2\text{Fe}_2(\text{CO})_6$  was prepared by the method of Hieber and Beck.<sup>8</sup> Reddish crystals were obtained from the crude product by sublimation at  $40^\circ$  under vacuum.  $(\text{CH}_3\text{S})_2\text{Fe}_2(\text{CO})_6$  (Pressure Chemical Co.) was separated into its syn and anti isomers by King's chromatographic procedure.<sup>9</sup> Spectral quality methylcyclohexane and carbon tetrachloride were deaerated for use as solvents for solution spectra.

Raman spectra were obtained on solutions and crystalline powders sealed in X-ray capillary tubes, using transverse excitation by 6471- and 6764-Å lines of an  $\text{Ar}^+-\text{Kr}^+$  mixed-gas laser (Coherent Radiation Model 52 MG). The Raman spectrometer and its calibration have been previously described.<sup>10</sup> Depolarization ratios,  $\rho_i$ , were obtained by analyzing the scattered light with a polaroid disk. Raman intensities were measured using 6764-Å excitation. Band areas were determined with reference to the  $847\text{-cm}^{-1}$  band of the methylcyclohexane solvent, which was in turn calibrated against the  $459\text{-cm}^{-1}$  ( $\nu_1$ ) band of  $\text{CCl}_4$  in a mixture of the two liquids. Over-

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**Table I.** Vibrational Frequencies<sup>a</sup> (cm<sup>-1</sup>) for S<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub> and *syn*- and *anti*-(CH<sub>3</sub>S)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>

S <sub>2</sub> Fe <sub>2</sub> (CO) <sub>6</sub>		(CH <sub>3</sub> S) <sub>2</sub> Fe <sub>2</sub> (CO) <sub>6</sub>	
Raman		Raman	
	Ir	Syn	Anti
88 m		78 w	80 m, b
106 s, b		96 s	
127 sh		107 s, b	107 s, b
			124 sh
191 s (p)		160 w, b	168 m
267 m		209 s	205 s
		268 m	258 w-m
			288 w-m
314 m		320 m-w, b	320 m
329 s (p)		352 m	350 m-s
447 w	447 m	450 w, b	450 w
463 w	462 sh		
475 m (p)	475 m-s	477 w, b	480 w, b
495 w (p)	493 m-s	503 w, b	
			520 vw
554 m (p)	561 vs		
	591 s		
	614 vs		
	625 sh		
1981			
2014			
2089			

<sup>a</sup> All (CH<sub>3</sub>S)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub> data are for crystalline powders, as are the Raman frequencies above 1900 cm<sup>-1</sup> for S<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>. Methylcyclohexane solution values are given for the S<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub> Raman bands below 600 cm<sup>-1</sup> (used in the intensity analysis). Ir data are for Nujol mulls. Symbols: p, polarized; s, strong; m, medium; w, weak; sh, shoulder; v, very; b, broad.

lapping bands were resolved with the aid of a Du Pont 310 curve resolver.

Infrared spectra of S<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub> in Nujol mulls were recorded between 400 and 800 cm<sup>-1</sup> on a Beckman IR-12 spectrometer.

### Spectra and Assignments

Vibrational frequencies are listed in Table I for S<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub> and the *syn* and *anti* isomers of (CH<sub>3</sub>S)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>. Figure 1 displays a set of internal coordinates for S<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub> which has effective C<sub>2v</sub> symmetry. Contributions of the internal coordinates to the vibrational symmetry classes are given in Table II.

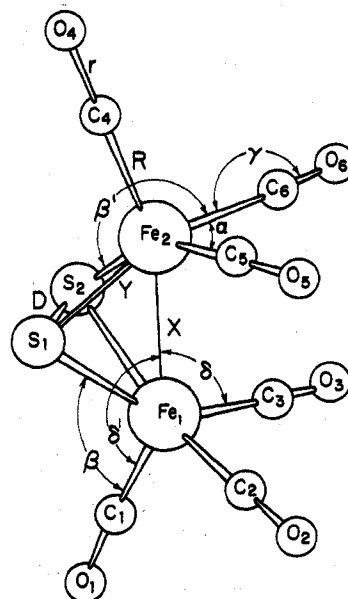
The molecule has 42 normal modes, which classify as 13 A<sub>1</sub> + 9 A<sub>2</sub> + 11 B<sub>1</sub> + 9 B<sub>2</sub>. All are Raman active, while all but the A<sub>2</sub> modes are infrared active as well. Interior angles (FeFeS, FeSFe, FeSS, SFES) of the central Fe<sub>2</sub>S<sub>2</sub> tetrahedron are omitted from the list of internal coordinates in Table II; they are completely redundant with the Fe-Fe, Fe-S and S-S bonds which form the sides of the tetrahedron.

The C-O stretching modes are expected near 2000 cm<sup>-1</sup>. Three Raman bands are seen in this region (Figure 2) at 2089, 2014, and 1981 cm<sup>-1</sup> in the solid. The remaining three expected C-O modes can be assigned to infrared bands, reported by Hieber and Beck,<sup>8</sup> at 2081, 2038 and 1996 cm<sup>-1</sup>, none of which appear to be coincident with the Raman bands. The absence of the infrared frequencies in the Raman spectrum, and *vice versa* must be attributed to accidental intensity cancellations. The highest two Raman bands are polarized, with the 2089 cm<sup>-1</sup> band having about half the intensity of the 2014-cm<sup>-1</sup> band. Since the intensity for symmetric stretching modes is expected to be roughly proportional to the number of bonds being stretched, these bands can be associated with the two axial C-O bonds and the four equatorial C-O bonds, respectively. The modes involving the CFEC, CFeS, and FeFeC bending are expected at frequencies near or below 100 cm<sup>-1</sup>. Undoubtedly they contribute to the

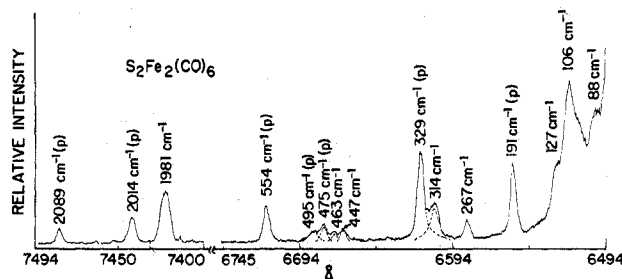
**Table II.** Contributions of Internal Coordinate Types to the Vibrations of S<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>

Internal coordinate	No. of contributions to each symmetry class			
	A <sub>1</sub>	A <sub>2</sub>	B <sub>1</sub>	B <sub>2</sub>
X, Fe-Fe bond	1			
D, S-S bond	1			
Y, Fe-S bond	1	1	1	1
R, Fe-C bond <sup>a</sup>	2	1	2	1
r, C-O bond <sup>a</sup>	2	1	2	1
γ, FeCO angle <sup>a</sup>	2	1	2	1
α, CFeC angle <sup>a</sup>	2	1	2	1
β, CFeS angle <sup>b</sup>	3	3	3	3
δ, FeFeC angle <sup>a</sup>	2	1	2	1
Total	16	9	14	9
Redundancies <sup>c</sup>	3		3	

<sup>a</sup> These coordinates fall into two types: sets (1), transforming as A<sub>1</sub> + B<sub>1</sub>, contain *axial* Fe-C and C-O bonds, *axial* FeCO and FeFeC angles, and CFeC angles which connect the equatorial Fe-C bonds; sets (2), transforming as A<sub>1</sub> + A<sub>2</sub> + B<sub>1</sub> + B<sub>2</sub>, contain *equatorial* Fe-C and C-O bonds, *equatorial* FeCO and FeFeC angles, and CFeC angles which connect *axial* with *equatorial* Fe-C bonds. <sup>b</sup> The CFeS angles are of two types, one (A<sub>1</sub> + A<sub>2</sub> + B<sub>1</sub> + B<sub>2</sub>) involving axial carbon atoms and the other (2 A<sub>1</sub> + 2 A<sub>2</sub> + 2 B<sub>1</sub> + 2 B<sub>2</sub>) involving equatorial carbon atoms. <sup>c</sup> The redundancies involve the various angles around the iron atoms.



**Figure 1.** Structure of S<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub> (taken from ref 5) with internal coordinates defined. Molecular parameters: distances FeFe = 2.550 Å, SS = 2.010 Å, FeS = 2.228 Å, FeC = 1.776 Å, CO = 1.142 Å; angles CFEC = 96° 30', SFES = 53° 32', FeSFe = 69° 54', C<sub>1</sub>Fe<sub>1</sub>S<sub>1</sub> = C<sub>4</sub>Fe<sub>2</sub>S<sub>2</sub> = 103° 24'.



**Figure 2.** Raman spectrum of polycrystalline S<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>, with 6471-Å Kr<sup>+</sup> laser excitation. Polarized bands are marked (p); the state of polarization was determined in methylcyclohexane solution. Instrument conditions: slit width 7 cm<sup>-1</sup>; sensitivity 10<sup>-9</sup> A, scan rate 8 Å/min; time constant 3 sec.

complex and unresolved feature in the Raman spectrum (Figure 2) which peaks at 106 and 88  $\text{cm}^{-1}$ . Detailed assignments in this region are impractical.

The remaining modes, involving Fe-Fe, Fe-S, S-S, and Fe-C stretching and FeCO bending are expected to lie between 150 and 600  $\text{cm}^{-1}$ . The strong polarized Raman band at 191  $\text{cm}^{-1}$  undoubtedly corresponds to Fe-Fe stretching. Stretching modes of bonds between first transition row metals have been identified<sup>7a</sup> near 200  $\text{cm}^{-1}$ , including the Co-Co stretch<sup>11</sup> (207  $\text{cm}^{-1}$ ) in the structurally similar  $(\text{C}_2\text{H}_5)_2\text{Co}_2(\text{CO})_6$ . The syn and anti isomers of  $(\text{CH}_3\text{S})_2\text{Fe}_2(\text{CO})_6$  also show this band, at 209 and 205  $\text{cm}^{-1}$ , respectively (Table I). Whether the  $\sim 15\text{-cm}^{-1}$  increase from the  $\text{S}_2\text{Fe}_2(\text{CO})_6$  value represents an increase in the Fe-Fe bond strength or simply reflects a change in vibrational coupling is unclear.

The strong polarized band at 329  $\text{cm}^{-1}$  (350  $\text{cm}^{-1}$  for the  $(\text{SCH}_3)_2\text{Fe}_2(\text{CO})_6$  isomers) can be associated with the symmetric Fe-S stretching mode. Similar modes have been assigned at 345  $\text{cm}^{-1}$  in bis(dithioacetylacetonato)iron(II),<sup>12</sup> at 314  $\text{cm}^{-1}$  in rubredoxin,<sup>2</sup> and at 350  $\text{cm}^{-1}$  in adrenodoxin.<sup>3</sup> The depolarized bands at 314 and 267  $\text{cm}^{-1}$  can also be assigned to two of the three expected nontotally symmetric Fe-S modes. Similar features are seen at 320 and  $\sim 260$   $\text{cm}^{-1}$  in  $(\text{CH}_3\text{S})_2\text{Fe}_2(\text{CO})_6$ . The remaining strong polarized band at 554  $\text{cm}^{-1}$  is assignable to S-S stretching, since it is not observed in  $(\text{CH}_3\text{S})_2\text{Fe}_2(\text{CO})_6$ . Sulfur-sulfur stretching modes have been identified<sup>13</sup> over a range of frequencies from 430 to 600  $\text{cm}^{-1}$ . The quartet of Raman bands between 440 and 500  $\text{cm}^{-1}$ , two of which are polarized, are then left for the Fe-C stretching and FeCO bending modes,<sup>14</sup> as are three additional frequencies, 591, 614, and 625  $\text{cm}^{-1}$ , observed only in the infrared spectrum.

### Normal-Coordinate Analysis

An approximate normal-coordinate analysis was carried out to clarify the nature of the observed normal modes. Schachtschneider's programs<sup>15</sup> GMAT and FPERT were used to construct the  $G$  matrix and to solve the secular equations, with least-squares adjustment of the force constants.<sup>16</sup> All atoms in the structure were included; the molecular parameters are given in Figure 1. Only the  $A_1$  block was calculated, since only  $A_1$  vibrations can be identified with confidence in the spectra. The CFeS and FeFeC angle bending coordinates were left out of account; they were expected to contribute mainly to modes at unobservably low frequencies. Of the two expected CFeC modes, one was assigned to the 106- $\text{cm}^{-1}$  Raman peak, even though it is not observably polarized, since CMC modes have been assigned close to this frequency in other polynuclear carbonyls.<sup>17,18</sup> The exact frequency is of little importance since the purpose of including the CMC coordinates was mainly to allow for their interaction with the Fe-Fe stretching coordinate. Of the remaining nine  $A_1$  modes, Fe-Fe, Fe-S, S-S, 2 Fe-C, 2 C-O, and 2 FeCO, only

the last two are unaccounted for in the Raman spectrum. On the basis of trial calculations, they were assigned to two strong infrared bands, at 591 and 641  $\text{cm}^{-1}$ .

Valence force constants were used to construct the  $F$  matrix.<sup>16</sup> The main interest in this calculation was to define vibrational modes of the  $\text{S}_2\text{Fe}_2$  cluster. Consequently, a single C-O stretching force constant was used. It was adjusted to calculate frequencies intermediate between the two observed bands at 2014 and 2089  $\text{cm}^{-1}$  and subsequently held fixed. Also the force constants for the two independent sets of Fe-C and FeCO coordinates were constrained to single values, even though slight differences might be anticipated between the two sets. The principal force constants were estimated from literature values for analogous systems and were then refined to fit the observed frequencies. It was found that a small Fe-S, S-S interaction constant was required to calculate the 554- and 329- $\text{cm}^{-1}$  frequencies with accuracy. In the final calculation, all force constants were allowed to vary independently. The results are given in Tables III and IV.

The frequencies which primarily involve motions of the  $\text{S}_2\text{Fe}_2$  cluster are fit to within experimental accuracy. The frequencies which primarily involve motions of the Fe-C-O units are reproduced satisfactorily for our purposes. The fit could easily be made exact with inclusion of more degrees of freedom. We are not primarily concerned with the accuracy of the force constants for the Fe-C-O units, but we note that they are reasonable when compared with corresponding force constants for related transition metal carbonyls.<sup>14,17,18</sup> The S-S stretching constant, 2.50  $\text{mdyn}/\text{\AA}$ , is in accord with the value, 2.55  $\text{mdyn}/\text{\AA}$ , reported for 2,3-dithiobutane<sup>19</sup> and with the approximate value, 2.5  $\text{mdyn}/\text{\AA}$ , given by Wilson, *et al.*,<sup>16</sup> for  $\text{S}_2\text{H}_2$ . The Fe-S stretching constant 1.62  $\text{mdyn}/\text{\AA}$  is slightly higher than that reported for bis(dithioacetylacetonato)iron(II),<sup>12</sup> 1.45  $\text{mdyn}/\text{\AA}$ . Strictly speaking force constants within the  $\text{S}_2\text{Fe}_2$  cluster are not comparable with molecules having open frameworks. The force constants are only defined with respect to a given geometry,<sup>16</sup> and there are redundancies in the  $\text{S}_2\text{Fe}_2$  cluster involving the interior angles, which do not arise in open frameworks. The fact that the bond stretching force constants are nevertheless quite similar to those found for open-framework analogs suggests that these differences may be taken up in the Fe-S, S-S interaction constant.

This impression is strengthened by a comparison of the Fe-Fe force constant with the Mn-Mn force constant,<sup>17c</sup> 0.59  $\text{mdyn}/\text{\AA}$ , in the open-framework molecule  $\text{Mn}_2(\text{CO})_{10}$ . Iron(I) is isoelectronic with manganese(0), but the Fe-Fe distance in  $\text{S}_2\text{Fe}_2(\text{CO})_{10}$  (and many other molecules with Fe-Fe bonds<sup>20</sup>) is nearly 0.4  $\text{\AA}$  shorter than the Mn-Mn distance<sup>21</sup> in  $\text{Mn}_2(\text{CO})_{10}$  (2.55 vs. 2.92  $\text{\AA}$ ). Applying Badger's rule,<sup>22</sup> as modified by Herschbach and Laurie,<sup>23</sup> one predicts a force constant ratio,  $f_{\text{Fe-Fe}}/f_{\text{Mn-Mn}}$ , of 2.32, which is gratifyingly close to the observed ratio of 2.19. We conclude that 1.3  $\text{mdyn}/\text{\AA}$  is a satisfactory force constant for an Fe-Fe single bond. [From the Herschbach and Laurie modification,<sup>23</sup>  $f(\text{mdyn}/\text{\AA}) = [(a_{ij} - d_{ij})/(r_e - d_{ij})]^3$ ;  $r_e$  is the internuclear distance, while  $a_{ij}$  and  $d_{ij}$  are empirical constants. For bonds joining third-row atoms,  $a_{ij} = 2.58$ ,  $d_{ij} = 1.41$ .]

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Table III. Adjusted Valence Force Constants (mdyn/Å) for S<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>

Stretching		Bending		Stretch-Stretch interaction	
Fe-Fe	1.29	FeCO	0.87	Fe-S, S-S	-0.09
Fe-S	1.62	CFeC	0.11		
Fe-C	2.59				
S-S	2.50				
C-O	16.20				

Table IV. Normal-Coordinate Analysis for S<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>, A<sub>1</sub> Symmetry Block

Frequencies, cm <sup>-1</sup>		Potential energy distribution: percentage from each major contributor <sup>a</sup>
Obsd	Calcd	
2089	2057	C-O 95
2014	2057	C-O 95
614	624	FeCO 65, Fe-C 11, Fe-S 13
591	584	FeCO 87, Fe-C 7
554	552	S-S 54, Fe-S 23, FeCO 23
495	486	Fe-C 70, FeCO 14, Fe-Fe 9
475	480	Fe-C 59, S-S 25, Fe-C 6
329	326	Fe-S 48, Fe-C 31, S-S 11
191	191	Fe-Fe 78, Fe-S 10, Fe-C 8
106	105	CFeC 99
	49	CFeC 96

Av discrepancy 1.2%

<sup>a</sup> The numbers are percentage contributors to the potential energy of each normal mode from the *F* matrix elements *F*<sub>ij</sub>, identified by the internal coordinate *i*.

We examined the effects of several interaction constants on the calculation of the Fe-Fe force constant and found that an Fe-Fe, CFeC interaction constant (the CFeC angles involving the *axial* Fe-C bonds) does have an appreciable effect. A value of +0.1 mdyn for this interaction constant forced *f*<sub>FeFe</sub> down to 1.02 mdyn/Å, while a value of -0.1 mdyn forced *f*<sub>FeFe</sub> up to 1.44 mdyn/Å. No other interaction constant (e.g., Fe-Fe, Fe-C or Fe-Fe, Fe-S) had a comparable effect. We conclude that the uncertainty in the present *f*<sub>FeFe</sub> value is on the order of ±0.2 mdyn/Å.

Table IV lists the main contributions of the various force field elements to the potential energies of the normal modes. These figures largely confirm the assignments made above, but they also reveal substantial coordinate mixing in the middle frequency region. The S-S (554 cm<sup>-1</sup>) and Fe-S (329 cm<sup>-1</sup>) stretching modes show considerable mutual mixing and have appreciable contributions also from Fe-C-O bending and Fe-C stretching, respectively. On the other hand the 191-cm<sup>-1</sup> mode is shown to be fairly pure Fe-Fe stretching.

### Raman Intensities

While a rigorous analysis of the Raman intensities is precluded because of the approximate nature of the normal-coordinate analysis, and also (as discussed below) because of preresonance enhancement, we are nevertheless able to provide a satisfactory account of the Raman intensity pattern, thereby lending confidence to the approximate force field.<sup>24</sup> The measured intensities and depolarization ratios were converted to mean molecular polarizability derivatives,  $\bar{\alpha}'_Q$ , with the usual intensity equation.<sup>24,25</sup> The values are given in Table VI. The sign ambiguities arise because the Raman intensity is proportional to  $(\bar{\alpha}'_Q)^2$ . Bond polarizability theory<sup>7,25</sup> allows a connection between molecular

Table V. A<sub>1</sub> Eigenvector Elements<sup>a</sup> for S<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>

<i>ν</i> (calcd), cm <sup>-1</sup>	FeFe	SS	FeS	FeC	FeCO
624	-0.097	-0.059	-0.269	+0.234	-1.015
584	+0.018	-0.042	-0.123	+0.045	+0.034
552	+0.021	+0.197	+0.323	-0.104	-0.484
486	+0.097	-0.042	+0.029	-0.219	-0.302
480	-0.033	+0.117	-0.105	+0.324	+0.191
326	+0.046	-0.052	+0.271	+0.210	-0.041
191	-0.114	-0.010	+0.036	-0.035	+0.025

<sup>a</sup> The elements are given as  $\sqrt{N_j}l_{ij}$ , where *N<sub>j</sub>* = 1, 1, and 4 for *j* = FeFe, SS, and FeS, respectively. The elements for FeC and FeCO are sums of  $\sqrt{N_j}l_{ij}$  for the two independent sets (axial *N<sub>j</sub>* = 2 and equatorial *N<sub>j</sub>* = 4) of FeC and FeCO coordinates.

Table VI. Depolarization Ratios and Molecular Polarizability Derivatives for Intermediate Frequency A<sub>1</sub> Bands of S<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>

<i>ν</i> , cm <sup>-1</sup>	<i>ρ<sub>i</sub></i> <sup>a</sup>	$\bar{\alpha}'_Q$ , <sup>b</sup> Å <sup>2</sup>	$\bar{\alpha}'_Q$ (calcd) <sup>c</sup>
614		<i>d</i>	-0.03
591			-0.08
554	0.05	±0.90	+0.60
495	0.1	±0.2 <sup>e</sup>	-0.25
475	0.1	±0.6 <sup>e</sup>	+0.69
329	0.08	±1.26	+0.69
191	0.08	±0.65	-0.27

<sup>a</sup> Depolarization ratio for polarized incident light and analyzed scattered light. <sup>b</sup> Mean molecular polarizability derivative, obtained<sup>25</sup> from the molar Raman intensity, relative to the internal standard (the 847-cm<sup>-1</sup> band of the methylcyclohexane solvent). <sup>c</sup> Values calculated *via* eq 1, using the following internal coordinate polarizability derivatives:  $\bar{\alpha}'_{\text{FeFe}} = 2.2$ ,  $\bar{\alpha}'_{\text{FeS}} = 1.0$ ,  $\bar{\alpha}'_{\text{SS}} = 2.0$ ,  $\bar{\alpha}'_{\text{FeC}} = 2.0$ ,  $\bar{\alpha}'_{\text{FeCO}} = 0.1$ ,  $\bar{\alpha}'_{\text{CFeC}} = 0$  (see text). <sup>d</sup> Not observed in the Raman spectrum. <sup>e</sup> Because of overlap of the individual bands, *ρ<sub>i</sub>*'s and  $\bar{\alpha}'_Q$ 's for these two modes could not be determined with accuracy. The total value of the two  $\bar{\alpha}'_Q$ 's, 0.80, is considered to be reliable.

and internal coordinate polarizability derivatives,  $\bar{\alpha}'_u$ , *via* the equation

$$\bar{\alpha}'_Q = \sum_j \sqrt{N_j} l_{ij} \bar{\alpha}'_{u_j} \quad (1)$$

where *l<sub>ij</sub>* is the eigenvector element connecting the normal-coordinate *Q<sub>j</sub>* with the symmetry coordinate *S<sub>j</sub>*, which is made up of *N<sub>j</sub>* internal coordinates of the set *u<sub>j</sub>*. The eigenvectors are obtained in the normal-coordinate analysis, and the relevant elements are listed in Table V.

Table VI compares the measured  $\bar{\alpha}'_Q$ 's with a set calculated *via* eq 1 using a reasonable set of  $\bar{\alpha}'_u$ 's estimated from studies of related molecules.<sup>10,25-28</sup>

This calculation establishes that the Raman intensities of the two predominantly Fe-C stretching bands and the vanishingly low intensities of the predominantly Fe-C-O bending modes can be accounted for with a reasonable set of internal coordinate polarizability derivatives, together with the eigenvectors obtained from the normal-coordinate analysis. On the other hand, Table VI shows that the predominantly Fe-Fe, Fe-S, and S-S stretching bands are all more intense than expected, by factors of 2.4, 1.8, and 1.5, respectively. These discrepancies are reasonably attributed to preresonance enhancement of the Raman intensity. While S<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub> has negligible absorption at the excitation wavelength, 676.4 nm, the compound is deep red and its electronic absorption spectrum<sup>29</sup> is dominated by a strong peak

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at 335 nm ( $\epsilon 1.19 \times 10^4 M^{-1} \text{ cm}^{-1}$ ) and a broad shoulder at  $\sim 470$  nm ( $\epsilon \sim 10^3 M^{-1} \text{ cm}^{-1}$ ). These are undoubtedly the transitions mainly responsible for preresonance enhancement. Inasmuch as in  $\text{Fe}(\text{CO})_5$  the electronic transitions are at and above 244 nm,<sup>30</sup> the lower energy transitions of  $\text{S}_2\text{Fe}_2(\text{CO})_6$  are ascribable largely to the  $\text{S}_2\text{Fe}_2$  cluster. It is entirely reasonable that the cluster vibrational modes are the ones to experience enhancement of the Raman intensity. It would be interesting to explore this resonance effect further, using excitation within the absorption bands. Our attempts to do this have so far been frustrated by decomposition of the sample.

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## Conclusions

Both the frequencies and Raman intensities of the  $A_1$  modes of  $\text{S}_2\text{Fe}_2(\text{CO})_6$  are satisfactorily accounted for with a simple valence force field and one (Fe-S, S-S) interaction constant. The magnitudes of the force constants are all reasonable and in particular  $f_{\text{Fe-Fe}} = 1.3 \pm 0.2 \text{ mdyn/\AA}$  is satisfactory for an iron-iron single bond. The modes primarily associated with vibrations of the  $\text{S}_2\text{Fe}_2$  cluster display preresonance Raman enhancement, which is probably associated with cluster electronic transitions in the visible and near-ultraviolet regions.

**Registry No.**  $\text{S}_2\text{Fe}_2(\text{CO})_6$ , 14243-23-3; *syn*-( $\text{CH}_3\text{S}$ ) $_2\text{Fe}_2(\text{CO})_6$ , 19976-88-6; *anti*-( $\text{CH}_3\text{S}$ ) $_2\text{Fe}_2(\text{CO})_6$ , 19976-87-5.

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## Photoelectron Spectra of Substituted Benzenes. III. Bonding with Group V Substituents

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The electronic structure of the group V phenyl compounds  $\text{C}_6\text{H}_5\text{XH}_2$  where X = N or P,  $(\text{C}_6\text{H}_5)_2\text{XH}$  where X = N, P, or As, and  $(\text{C}_6\text{H}_5)_3\text{X}$  where X = N, P, As, or Sb has been investigated through the use of He(I) photoelectron spectroscopy and CNDO/2 MO calculations. The spectra of benzylamine and dichloro- and dimethylphenylphosphine and the He(II) spectra of phenylphosphine have also been obtained in order to assist in identification and assignment of the above series. The results show that the nitrogen nonbonding orbital in the phenylamines is more tightly bound than the phenyl  $\pi$  orbitals while in the phenylphosphines, -arsines, and -stibine the nonbonding orbital is at lowest binding energy. The destabilization of the n orbital and stabilization of the  $\pi$  orbitals in the P, As, and Sb molecules relative to the N molecules are taken as evidence for a shift of electron density from the phenyl groups toward the P, As, and Sb atoms. These shifts suggest that the heavier central atoms are capable of using expanded basis sets which include nd orbitals in the molecular bonding.

## Introduction

Sharp contrasts exist in the chemical properties of nitrogen compounds as compared to those of other group V compounds. The most common explanation for these differences is the capability of expansion of the valence shells in the third-, fourth-, and fifth-row elements in order to accommodate extra electron density. The nitrogen atom has only the 2s and 2p atomic orbitals available for bonding while the heavier atoms have ns, np, and nd orbitals available. The question of if and when these nd orbitals partake in bonding has been a subject of much debate.

Evidence for and against d-orbital participation in aromatic compounds containing group V atoms has been presented. Much of this evidence has come from studies of ultraviolet absorption spectra. The absorption spectra of the phenylamines, -phosphines, and -arsines have been studied by several workers.<sup>1-9</sup> These spectra exhibit band structure in the

near-ultraviolet region (200–300 m $\mu$ ), the identity of which remains unsolved. Some of the most convincing interpretations<sup>1,9</sup> have proposed intense  $n \rightarrow \pi^*$  and weak  $\pi \rightarrow \pi^*$  benzene-like transitions in this region. The participation of d orbitals in the transitions has been suggested by several of these authors. Bissey and Goldwhite<sup>2</sup> claimed that their application of the "substitution interference method" of Goodman, *et al.*,<sup>10,11</sup> provides positive evidence for d-orbital participation in the bonding of phenylphosphine.

The implication of d-orbital participation in bonding through shifts observed in absorption spectra can be misleading, for it is difficult to determine whether the shifts are caused by a stabilization of the initial or final state involved in the transition. Since photoelectron spectroscopy is based on an absolute energy scale, it is possible to estimate the degree of d-orbital participation through shifts in the binding energies of occupied molecular orbitals in the ground state. Shifts in the binding energies of certain orbitals have been used as evidence for d-orbital participation in the bonding of some group IV<sup>12-15</sup> and organometallic phosphorus<sup>16</sup> compounds.

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