from the reaction with CF_3CH_2OH is that H^+ transfer is exothermic by 15.6 kcal mol^{-1} in the former reaction. This excess energy is deposited in the vibrational manifolds of the components of the complex of H^+ transfer $[(CF_3)_2CDH/^{-}OCH(CF_3)_2]$ which reduces the lifetime of the complex and separation occurs. The increased steric bulk of $(CF_3)_2CHOH$ compared to CF_3CH_2OH may also contribute to the separation of this complex.

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Pressure Effects on the Intervalence Transfer Electronic Absorption Band of the Mixed-Valence Bis(fulvalene)diiron Monocation in Various Media†

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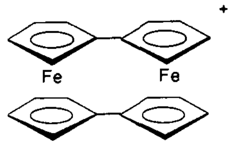
Abstract: The pressure dependence of the two intervalence transfer (IT) electronic absorption bands of the mixed-valence bis(fulvalene)diiron cation is examined in various media. In general, a blue shift with increasing pressure is seen for both IT bands in all media. The blue shifting is attributable to an intramolecular effect, where an increase in pressure leads to an increase in the energy separation between the bonding ground and antibonding excited states of the IT transition. At high pressures and to variable degrees in the different media (crystal lattice, PMMA polymer, intercalated into zeolite 13X) compression leads to intermolecular effects on the energy of the two IT bands. Data obtained for the zeolite-intercalated bis(fulvalene)diiron cation are analyzed in terms of the PKS vibronic model. Values for the electronic and vibronic coupling parameters are obtained from spectra measured in the range of 11–138 kbar. The value of the PKS electronic coupling factor ϵ was shown to increase by a factor of ~1.5 over this pressure range. The degree of valence localization in the bis(fulvalene)diiron cation can be changed appreciably with pressure. From $|\epsilon|$ and the PKS vibronic coupling factor λ evaluated for the low-energy IT band it was calculated that $|\epsilon|/\lambda^2$, a ratio that characterizes the valence localization, increases continuously from 0.59 at 11 kbar to 0.78 at 89 kbar.

Pressure tuning spectroscopy (PTS) has been shown to be effective in studying the energy perturbations on valence orbitals resulting from pressure-induced compression of condensed phases.[3] Compression of crystals consisting of molecular units or large molecular ions leads to a reduction in interatomic and intermolecular distances which increases the overlap of valence orbitals. An electronic absorption band for a molecular moiety will shift to either higher or lower energy dependent on the balance between intramolecular and intermolecular effects of compression. In the case of intramolecular effects, an excitation from a bonding to an antibonding orbital should increase in energy with an increase in pressure. On the other hand, as a result of attractive van der Waals intermolecular interactions, a bonding to antibonding excitation localized on one molecular unit will generally shift to lower energy upon an increase in the pressure. This shift to lower energy as a result of intermolecular effects reflects the greater polarizability of the excited-state molecule with an electron in the antibonding orbital compared to the ground-state molecule.

Very recently we reported[4] the effect of pressure-induced freezing on the energy of the intervalence transfer (IT) electronic absorption band of binuclear mixed-valence complexes in solution. The energy of the IT band was monitored as the pressure was increased until, at pressures less than 10 kbar, the solutions froze. Essentially no shifts of the IT bands were observed, which is in marked contrast to the prediction of the dielectric continuum model[5,6] for the solvent reorientation contribution to the energetics of the IT band.

In view of the interesting results obtained for the IT bands of mixed-valence complexes in solution, PTS was applied to the study of IT bands of mixed-valence complexes in the solid state. The hemihydroquinone picrate salt of bis(fulvalene)diiron monocation (I), compound **1**, was selected for this initial PTS study on solids with pressures up to 163 kbar.



I

Mixed-valence cation I has been the object of considerable investigation.[7–20] The two iron ions in various salts of cation I

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have been indicated to be equivalent on the ^{57}Fe Mössbauer,[8,10,13,15,17] ESCA,[8,10,18] and IR[17] time scales. As a result of an appreciable electronic interaction between the two halves of cation I, this mixed-valence ion has an electronically delocalized structure with no potential-energy barrier for interion electron transfer. It has been argued that the intermolecular interaction in I is either via a direct Fe–Fe orbital overlap[13,14,16,17] or propagated through the fulvalenide ligands.[10-12,15,19] In agreement with the former suggestion, the X-ray structure[20] of the picrate salt of I showed that the Fe–Fe distance (3.636 (1) Å) in cation I is 0.34 (2) Å shorter than the same distance in the unoxidized Fe_2^{II} complex. The shortening of the Fe–Fe distance in I is accommodated by ring tilts of 9.6° in one metallocene unit and 10.4° in the other with the opening of the tilts toward the centroid of cation I.

Experimental Section

Solid-state electronic absorption spectra were recorded with the samples loaded into a inconel gasketed diamond anvil cell, using the ruby fluorescence method of pressure calibration.[21] A 100W Oriel quartz tungsten halogen lamp with a Kratos quartermeter monochromator with 2100 blaze gratings at a slit width of 1 mm was used. Transmitted light was detected by an Opto-Electronics PbS photoconductor. Light pipes were used to connect the diamond anvil cell to the monochromator and the PbS cell. The PbS cell was operated with a 100V DC bias. A light chopper was placed between the light source and the monochromator. The AC component of the PbS cell was measured with a PAR model 8 lock-in amplifier.

Samples of compound **1** were prepared by literature methods.[20] Good microanalytical data were obtained.

Compound **1** was studied dissolved in poly(methyl methacrylate) (PMMA). The PMMA thin film was formed by co-dissolving **1** and PMMA in nitromethane and subsequently evaporating the solution slowly. Compound **1** was also studied as a crystalline solid with mineral oil as a pressure medium. A few initial optical experiments were carried out with the crystallites dispersed in CsCl or CsI.

Samples of cation I intercalated into either the supercage of zeolite 13X (Linde) or the interlamellar region of a synthetic mica-montmorillonite (SSM-100 from Source Clay Minerals Repository) were prepared by sorbing the unoxidized bis(fulvalene)diiron from a benzene solution into the aluminosilicate as reported previously.[22] In these cases cation I is in the pores of the aluminosilicates and the counteranion is afforded by the negatively charged aluminosilicate surface. The samples of I–clay and I–zeolite 13X were loaded into the diamond anvil cell without any additional pressure transmitting medium.

Electronic absorption spectra were least-squares fit to Gaussian peaks by using the computer program SKEW.

Results and Discussion

Pressure Shifting of IT Bands of the Bis(fulvalene)diiron Cation in Different Media. The NIR electronic absorption spectrum of cation I in various media exhibits two peaks. The pressure dependencies of these two peaks were studied. There are differences in detail but, in general, qualitatively similar pressure-dependent behavior is observed for the two peaks of cation I, whether cation I is present in the crystal environment of compound **1** or as compound **1** dissolved in PMMA. In fact, the two NIR peaks show a similar pressure dependence for cation I intercalated into the supercage of 13X zeolite and, to a lesser extent, for cation I intercalated into the interlamellar region of a clay. In all cases, both NIR peaks shift to higher energy with pressure. At higher pressures especially, the low-energy peak tends to shift less rapidly than does the high-energy peak. The intensity of the high-energy peak increases relative to the low-energy peak in all media as the pressure is increased.

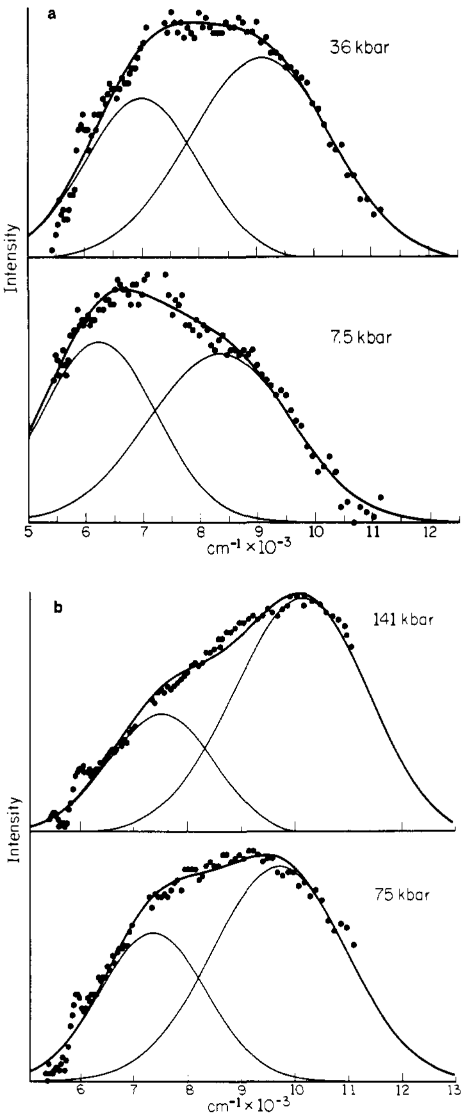

Figure 1. (a) NIR electronic absorption spectrum at 7.5 and 36 kbar of crystalline bis(fulvalene)diiron picrate hemihydroquinone (**1**) with mineral oil as a pressure medium. (b) NIR electronic absorption spectrum at 75 and 141 kbar of crystalline bis(fulvalene)diiron picrate hemihydroquinone (**1**) with mineral oil as a pressure medium.

Table I. Data for NIR IT Absorption Bands of Crystalline Bis(fulvalene)diiron Picrate Hemihydroquinone[a]

	E_{max} (cm^{-1} × 10^{-3})[b]			E_{max} (cm^{-1} × 10^{-3})[b]	
pressure (kbar)	low-energy band	high-energy band	pressure (kbar)	low-energy band	high-energy band
8	6.22	8.30	86	7.29	9.65
12	6.28	8.38	99	7.43	9.87
25	6.80	8.69	108	7.45	9.91
36	6.97	9.02	119	7.52	9.98
48	7.21	9.38	127	7.52	10.04
59	7.26	9.52	141	7.54	10.08
69	7.34	9.59	163	7.60	10.20
75	7.42	9.74			

[a] The IT bands were fit with Gaussian line shapes with fill-width at half-maximum fixed at 2900 and 2300 cm^{-1}, respectively, for the low- and high-energy IT bands and a skew equal to zero. [b] Maximum of the IT band as obtained from the Gaussian fit.

Figure 1 shows typical NIR electronic absorption spectra obtained at four different pressures for microcrystals of **1**. Close

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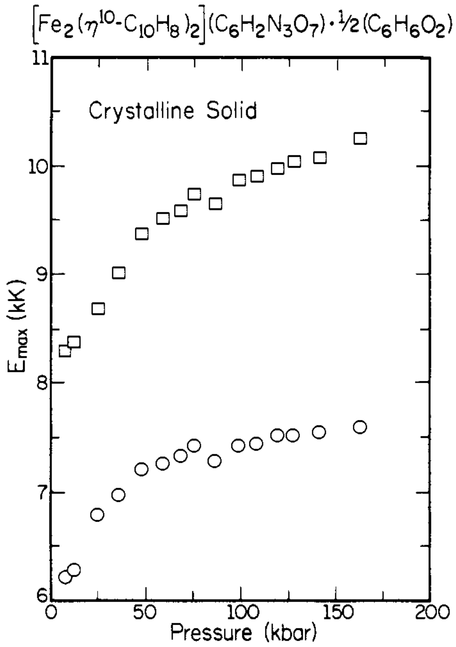

Figure 2. Pressure dependence of the energy corresponding to the band maximum, E_{max}, plotted for the two IT bands observed for bis(fulvalene)diiron picrate hemihydroquinone (**1**) with mineral oil as a pressure medium.

examination of the NIR spectra of **1** obtained at several pressures clearly indicates that there are two IT bands present at all pressures. The presence of two electronic absorption bands in the NIR region for cation I was first deduced[23] from the non-Gaussian appearance of the NIR absorption for a solution of cation I. The 77 K NIR spectrum of the I_3^- salt of cation I in a KBR pellet was reported later.[17] This improved resolution spectrum clearly shows two bands in the NIR spectrum. Very recently Talham and Cowan[24] verified the presence of two electronic transitions. They used the vibronic PKS model[25] to analyze the band contour of the NIR absorption for cation I. It was concluded that two IT band contours are needed to explain theoretically the NIR spectrum of cation I in the context of the PKS theory. The origins of the two IT bands for cation I will be discussed below.

The NIR spectra of the picrate salt **1** measured at a variety of pressures for the microcrystalline sample (see Figure 1 and Table I) were least-squares fit to two Gaussian curves. As can be seen in Figure 1, this fitting procedure works well. Summarized in Table I are the fitting parameters for the two IT bands seen at various pressures up to 163 kbar. The pressure dependence of the energy corresponding to the band maximum, E_{max}, is plotted in Figure 2 for the two IT bands observed for microcrystalline **1**. As can be seen in Figure 2, both of the IT bands of **1** initially exhibit an appreciable pressure shifting to higher energy: 27 cm^{-1}/kbar for the 8.3 × 10^3 cm^{-1} band and 26 cm^{-1}/kbar for the 6.2 × 10^3 cm^{-1} band in the range of 7.5 to 48 kbar. At higher pressures the two peaks are not shifting blue as rapidly per increment of pressure: 5 cm^{-1}/kbar for the higher energy band and only 2.5 cm^{-1}/kbar for the lower energy band in the 108 to 163 kbar region. In all four media there was an increase of area of the higher energy peak relative to the lower energy peak with increasing pressure. In general, the total area under the two peaks increased with pressure up to about 110 kbar. There appeared to be a slight decrease at higher pressures which may or may not have been an artifact. All observations as to peak location and relative areas were totally reversible.

Table II. Data for the NIR IT Absorption Bands of Bis(fulvalene)diiron Picrate Hemihydroquinone Doped into Poly(methyl methacrylate)[a]

	E_{max} (cm^{-1} × 10^{-3})[b]			E_{max} (cm^{-1} × 10^{-3})[b]	
pressure (kbar)	low-energy band	high-energy band	pressure (kbar)	low-energy band	high-energy band
		Run 1			
4	6.23	8.23	74	7.45	9.49
21	6.49	8.43	82	7.45	9.54
35	6.88	8.63	92	7.51	9.71
45	7.10	8.93	105	7.61	9.89
53	7.66	9.14			
		Run 2			
10	6.18	8.21	81	7.37	9.49
21	6.27	8.34	92	7.36	9.59
33	6.53	8.51	101	7.51	9.75
41	6.68	8.62	115	7.43	9.98
51	7.09	9.00	127	7.59	10.09
60	7.10	9.05	141	7.62	10.40
71	7.27	9.33			

[a] The IT bands were fit with Gaussian line shapes with full-width at half-maximum fixed at 2900 and 2300 cm^{-1}, respectively, for the low- and high-energy IT bands and a skew equal to zero. [b] Maximum of the IT band as obtained from the Gaussian fit.

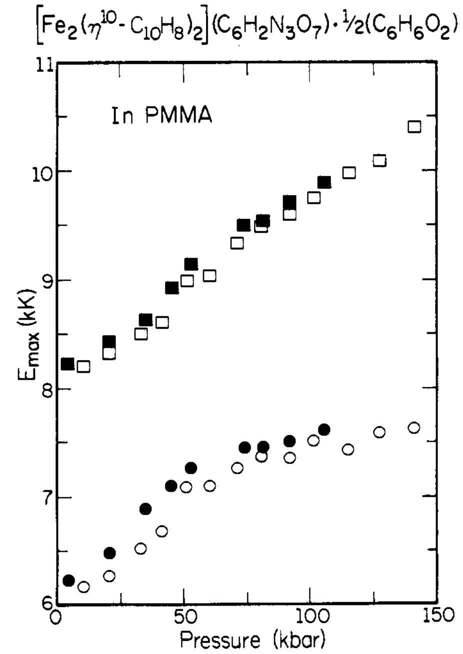

Figure 3. Pressure dependence of the energy corresponding to the band maximum, E_{max}, plotted for the two IT bands observed for bis(fulvalene)diiron picrate hemihydroquinone (**1**) dissolved in poly(methyl methacrylate). Two independent determinations (filled and unfilled symbols) were carried out.

In the case of this microcrystalline sample of **1**, the shifting of the two IT bands as a function of pressure obviously could reflect not only compression effects on individual molecules but interactions between molecules. From the X-ray crystal structure[20] of **1**, it is known that the packing arrangement in the crystal consists of alternating stacks of bis(fulvalene)diiron cations and planar picrate anions. The hydroquinone "solvate" molecules sit next to these alternating stacks. The application of pressure could lead to a compression of cations I and picrate anions in each stack and lead to specific intermolecular pressure effects.

Other environments for cation I were investigated in order to understand the pressure dependencies for the two IT bands of microcrystalline **1**. By dissolving the picrate salt **1** and poly(methyl methacrylate) in nitromethane and evaporating the solution to give a thin film it was possible to dope **1** into a polymer matrix. The complex was apparently dissolved in the polymer. At most there would be combinations of picrate anions and mixed-valence cations I at various sites in the polymer. The pressure dependence of the NIR spectrum of this PMMA-doped sample of **1** was investigated in two separate runs. Parameters resultant from

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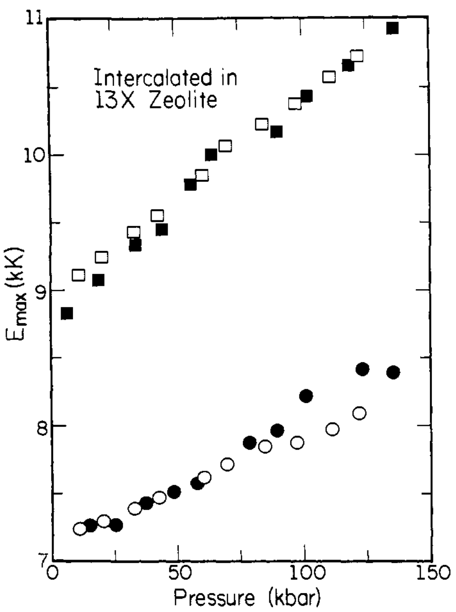

Figure 4. Pressure dependence of the energy corresponding to the band maximum, E_{max}, plotted for the two IT bands observed for mixed-valence bis(fulvalene)diiron cation intercalated into the supercage of zeolite 13X. Two independent determinations (filled and unfilled symbols) were carried out.

least-squares fitting of the spectra are given in Table II. The area of the higher energy band again increases somewhat with increasing pressure; however, the area of the lower energy band decreases. Again the two IT bands are seen to shift blue with increasing pressure. The reproducibility of data is good between separate runs (see Figure 3), as is generally found. Also, the pressure effects are quite reversible: the NIR spectrum measured after the release of the pressure is very close to that obtained at the lowest pressure.

As can be seen in Figure 3 for the PMMA-doped **1**, the higher energy IT band shifts essentially linearly throughout the range of 4.1–141 kbar. The best straight line through all of the points has a slope of 17 cm^{-1}/kbar (correlation coefficient is 0.990). On the other hand, the lower energy band shifts at 20 cm^{-1}/kbar in the 4.1–80-kbar region and at a considerably decreased rate (5 cm^{-1}/kbar) above ~80 kbar.

Perhaps the best medium to isolate the mixed-valence cation I is in the "supercage" of 13X zeolite. Zeolites are three-dimensional aluminosilicates that have pores of varying size. The "supercage" of 13X zeolite is a polyhedron with 26 faces and 48 vertices. The 26 faces consist of 4 with 12 vertices, 4 with 6 vertices, and 18 with 4 vertices. The void inside the "supercage" is lined with oxygen atoms. It has been estimated[26] that a sphere with a 11.8-Å diameter could be inscribed inside the "supercage". The mixed-valence cation I (without picrate anion) sits inside this cage. Negative charge on the aluminosilicate framework serves as the counteranion for cation I.

In Figure 5 and Table III are summarized the data for the pressure dependence of the IT bands for 13X zeolite-imbibed mixed-valence bis(fulvalene)diiron cation. In the range of 11–122 kbar the higher energy IT band more than doubles in area, whereas the area of the lower energy IT band is reduced in area by a factor of ~2. It is interesting that E_{max} for both of the IT bands shifts linearly to the blue with increasing pressure. The best straight lines through the data give slopes of 16 and 9 cm^{-1}/kbar for the higher energy and lower energy IT bands, respectively.

The behavior of the higher energy IT band is similar for the PMMA-doped and 13X zeolite-imbibed samples. The slopes of the two straight lines differ by a small amount, which could reflect differences in the compressibility of the two media. There is one significant difference. The E_{max} versus pressure lines are nearly parallel; however, E_{max} at ambient pressure changes from 8.1 × 10^3 cm^{-1} for PMMA-doped **1** to 9.0 × 10^3 cm^{-1} for 13X zeolite-imbibed cation I. The environment of the "supercage" leads to a 900 cm^{-1} blue shift of the higher energy IT band.

Table III. Data for NIR IT Absorption Bands of the Bis(fulvalene)diiron Cation Intercalated into 13X Zeolite[a]

	E_{max} (cm^{-1} × 10^{-3})[b]			E_{max} (cm^{-1} × 10^{-3})[b]	
pressure (kbar)	low-energy band	high-energy band	pressure (kbar)	low-energy band	high-energy band
			Run 1		
11	7.24	9.12	70	7.73	10.06
20	7.30	9.25	85	7.85	10.23
33	7.39	9.43	97	7.88	10.37
43	7.47	9.55	111	7.98	10.56
60	7.62	9.85	122	8.09	10.72
			Run 2		
11	7.26	8.67	78	7.84	9.93
19	7.25	8.94	89	7.95	10.18
37	7.47	9.25	102	8.27	10.44
45	7.54	9.41	125	8.50	10.67
62	7.65	9.68	138	8.48	10.82

[a] The IT bands were fit with Gaussian line shapes with full-width at half-maximum fixed at 2900 and 2300^{-1}, respectively, for the low- and high-energy IT bands and a skew equal to zero. [b] Maximum of the IT band as obtained from the Gaussian fit.

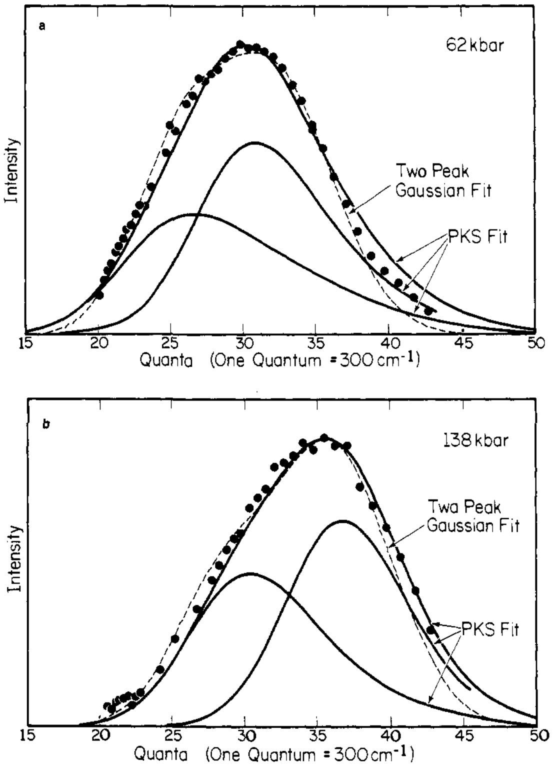

Figure 5. (a) Fit of the NIR spectrum of zeolite 13X intercalated bis(fulvalene)diiron cation at 62 kbar. The solid lines show the two peaks and their sum calculated by using the parameters given in Table V, which were obtained by fitting the data to the PKS theory. The dashed line is the fit of the data when the sum of two Gaussian peaks is used. (b) Fit of the NIR spectrum of zeolite 13X intercalated bis(fulvalene)diiron cation at 138 kbar. The solid lines show the two peaks and their sum calculated by using the parameters given in Table V, which were obtained by fitting the data to the PKS theory. The dashed line is the fit of the data when the sum of two Gaussian peaks is used.

There is also a blue shift of about 900 cm^{-1} seen for the lower energy IT band of the 13X zeolite-imbibed cation I relative to other environments. The high-pressure slope (5 cm^{-1}/kbar) for the lower energy IT band in the PMMA-doped environment is close to the 9-cm^{-1}/kbar change seen throughout the pressure range for the 13X zeolite-imbibed cation I.

The pressure dependence of the NIR spectrum for cation I intercalated into the interlamellar region of the synthetic mica-

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Table IV. Data for NIR IT Absorption Bands of Bis(fulvalene)diiron Cation Intercalated into SSM-100 Synthetic Mica-Montmorillonite Clay[a]

	E_{max} (cm^{-1} × 10^{-3})[b]			E_{max} (cm^{-1} × 10^{-3})[b]	
pressure (kbar)	low-energy band	high-energy band	pressure (kbar)	low-energy band	high-energy band
3	5.97	7.95	70	6.36	8.47
13	5.97	7.98	84	6.47	8.82
25	6.06	8.07	103	6.44	9.06
36	6.09	8.10	111	6.37	9.14
49	6.14	8.26	122	6.34	9.27
60	6.19	8.36			

[a] The IT bands were fit with Gaussian line shapes with full-width at half-maximum values given by the formula (2900 cm^{-1} + 50 cm^{-1}/10 kbar) and (1800 cm^{-1} + 100 cm^{-1}/10 kbar) for the low- and high-energy IT bands, respectively, and with skew fixed at zero. [b] Maximum of the IT band as obtained from the Gaussian fit.

montmorillonite clay SSM-100 was examined in the range of 3.4–122 kbar. Least-squares fitting data are given in Table IV. It is to be noted that at ambient pressures both of the IT bands of the clay-intercalated cation I are shifted by 0.2–0.4 × 10^3 cm^{-1} to lower energy compared to the band positions for either microcrystalline **1** or PMMA-doped **1**. The orientation of the negatively charged aluminosilicate layers relative to the mixed-valence cation I perhaps leads to this small shifting to the red. The higher energy IT band for the clay-intercalated cation I shifts by 10–11 cm^{-1}/kbar to the blue with increasing pressure. Over the whole pressure region, the lower energy IT band blue shifts only ~5 cm^{-1}/kbar.

The initial studies of the IT band of cation I employed the picrate salt intimately mixed with either CsCl or CsI, which are commonly used pressure transmitting media. However, there was an irreversibility in the appearance of the IT band as a function of pressure that is probably due to a chemical reaction occurring between the cesium salt and compound **1**. At pressures above 70 kbar the intensity of the IT band fell off dramatically with increasing pressure, and upon release of the pressure the spectrum did not return to the original spectrum. In the case of the CsI medium a new electronic absorption band appeared in the 9.6–12 × 10^3 cm^{-1} region above 70 kbar. From independent experiments it was shown that this new band seems to be attributable to I_3^- ions, resulting from I^- ions diffusing into the lattice of compound **1**, followed by a redox reaction. The effects of pressure on the IT band of **1** in CsCl (or CsI) at pressures below the onset of irreversibility were similar to those reported above for **1** dispersed in mineral oil.

Origin of Pressure Shifts of IT Bands for Bis(fulvalene)diiron Monocation. Because of the qualitatively similar pressure shift behavior for the two NIR bands of cation I in all media it is reasonable to assume that the first-order effect of pressure is the same in all cases, with second-order perturbations of greater or lesser importance in different media. In the zeolite supercage clearly one is observing individual cations interacting with the anionic charge of the supercage. It seems probable that in PMMA there are ion pairs dissolved in the polymer medium. In the crystal, of course, the environment about each cation I consists of other cations and anions of compound **1**.

There are probably two possible explanations for the two "IT" bands seen in the NIR spectrum of cation I in a variety of media. One explanation was suggested earlier.[23] The theoretical description of the electronic structure of a binuclear mixed-valence complex generally involves the "extra" electron being located in one particular d-orbital on either of the two transition-metal ions.[25] This electronic lability leads to a strong vibronic coupling with the out-of-phase combination of the totally symmetric metal–ligand stretching vibrational mode on the two halves of the complexes. For the case of weak or moderate electronic coupling, two potential-energy surfaces develop. The potential-energy ground state has a double-well appearance. The barrier in this ground-state surface disappears when the electronic coupling between the two metal ions becomes large. One excited state also results regardless of the magnitude of the electronic coupling. In the case of Fe^{II}Fe^{III} metallocenes this description may need to be modified, as briefly suggested before.[23] As has been indicated by both experimental[27] and theoretical (molecular orbital)[28] papers, two one-electron molecular orbitals of the Fe^{III} ferrocenium cation are close in energy, namely the nonbonding e_{2g} and a_{1g} orbitals. The former molecular orbitals are largely the metal $d_{x^2-y^2}$ and d_{xy} orbitals, whereas the main contribution to the a_{1g} MO is from the metal d_{z^2} orbital. Thus, for Fe(η^5-C$_5$H$_5$)$_2^+$ the $^2A_{1g}$ excited state is probably within 2 × 10^3 cm^{-1} of the $^2E_{2g}$ ground state. This near-energy degeneracy of two d-orbitals of the Fe^{III} metallocene site could lead to two excited states, not just one excited state from a vibronic model of the electronic structure of a binuclear mixed-valence cation.

A recent theoretical paper[29] on the Creutz-Taube binuclear ruthenium complex and previous extended Hückel molecular orbital calculations[19] on biferrocene, bis(fulvalene)diiron, and their monocations suggest another possible explanation for the appearance of two IT bands for cation I. It is possible that, in addition to an excited state wherein the "extra" electron resides in a molecular orbital which is comprised dominantly of metal $d_{x^2-y^2}$ (d_{xy}) orbitals, there is also an excited state where the "extra" electron resides in a molecular orbital which is largely fulvalenide in parentage. Thus, two low-lying excited states could be present, leading to two IT bands.

It is suggested that the linear shifting of both IT bands to the blue in the 11–122-kbar range for 13X zeolite-imbibed cation I reflects largely intramolecular effects. Because of the size of the "supercage" and its relative incompressibility when filled,[30] cation I probably suffers little change in *inter*molecular interactions with pressure. The higher energy IT band shifts more rapidly than the lower energy IT band perhaps due to the fact that the d_{z^2} metal orbital is pointed at the fulvalenide ligands, whereas the $d_{x^2-y^2,xy}$ orbitals are directed away from the fulvalenide ligands.

In the case of PMMA-doped compound **1**, the higher energy IT band blue shifts essentially linearly as it does in the zeolite "supercage". However, the lower energy IT band for the PMMA-doped sample shifts initially at 20 cm^{-1}/kbar, then above ~80 kbar the rate of shifting decreases to 4.7 cm^{-1}/kbar. The behavior of this lower energy IT band may reflect the combined effects of intramolecular and intermolecular interaction. There are likely ion pairs of cation I and a picrate anion sitting near to each other in the polymer. Depending on the relative orientation of these two ions in the polymer, compression of the medium could lead to different effects on the two excited states of cation I.

In the case of the microcrystalline sample of **1** the pressure dependencies of both of the IT bands of cation I seem to be affected by two factors. Initially both peaks are shifting rapidly (~25 cm^{-1}/kbar) up to a pressure of ~75 kbar, above which both IT bands shift more gradually with further increase in the pressure. From the X-ray structure[20] of **1** it is known that there are alternating stacks of planar picrate anions and bis(fulvalene)diiron monocations. The plane of the picrate anion is nearly parallel to that of the neighboring fulvalenide ligands. The hydroquinone moieties serve as insulators between the alternating stacks. It is likely that compression of this lattice could affect the two excited states differently via intermolecular van der Waals forces.

The pressure dependencies observed for the two IT bands of clay-intercalated cation I are difficult to analyze in detail, for we do not know the relative orientation of bis(fulvalene)diiron cations in the interlamellar region between the aluminosilicate sheets. Furthermore, it is known[22] that the EPR signal for cation I intercalated in the clay differs appreciably from the EPR signal

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Table V. Electronic (ϵ) and Vibronic (λ) Coupling Parameters Evaluated by Fitting the Two IT Bands of the 13X Zeolite-Intercalated Bis(fulvalene)diiron Cation

pressure (kbar)	low-energy band		high-energy band	
	ϵ^a	λ^a	ϵ^a	λ^a
11	−9.5	4.0	−11.8	4.0
19	−10.0	4.0	−12.8	4.0
37	−10.0	4.0	−12.5	4.0
45	−10.5	4.0	−13.2	4.0
62	−11.5	4.0	−14.2	4.0
78	−12.0	4.0	−15.0	4.0
89	−12.5	4.0	−15.6	4.0
102	−13.0	4.5	−16.2	4.0
125	−13.8	4.5	−16.8	4.2
138	−14.0	4.5	−17.5	4.2

[a] These parameters are given in units of $h\nu = 300$ cm^{-1}.

observed for the I_3^- salt of cation I. Specific cation–cation interactions in the clay interlamellar region have been advanced[22] as the origin of the difference in the EPR signal. In contrast, the EPR signal for the 13X zeolite-imbibed cation I looks similar to those observed for 77 K frozen glasses containing cation I. In other words, the magnetic dilution of cation I in the 13X zeolite supercages is good. The mixed-valence cations are well insulated from one another.

Theoretical Analysis of IT Bands. In view of the fact that Talham and Cowan[24] were able to analyze the IT band observed for cation I in solution by using the PKS vibronic model,[25] a similar analysis of our data was carried out. The NIR band for cation I in zeolite 13X was fit by treating the band as two IT transitions. As in the previous calculation,[24] the value of $h\nu$ for the totally symmetric metal–ring stretch was set at 300 cm^{-1}. One might expect this to increase with pressure: however, even a value of 320 cm^{-1} at the high pressures made the fit considerably poorer. By analyzing the band contour at each pressure, values for the PKS electronic (ϵ) and vibronic (λ) coupling parameters were evaluated. Values of ϵ and λ are given in Table V, and the fits to the spectra obtained at 62 and 138 kbar are illustrated in Figure 5. The electronic coupling parameter was found to increase in magnitude continuously with pressure for both of the IT transitions; ϵ increased by a factor of $\sim$1.5 over the range of the measurements. The ratio of the ϵ value of the higher energy IT band compared to the ϵ value for the lower energy IT band remained remarkedly constant at 1.25. This ratio was not fixed in the analysis; values of ϵ were established separately at each pressure. The fitted magnitudes of the vibronic coupling parameter remained quite constant for both IT transitions, except at the highest pressures. The fit was found to be quite sensitive to the value of λ. A 5% change in λ displaced the peaks significantly. It should be remarked that the PKS vibronic model fit the shape of the two IT peaks observed above 35 kbar much better than those observed at lower pressures, where the data did not display the requisite high-energy "tail".

The changes in $|\epsilon|$ with pressure for the two IT bands of cation I in zeolite 13X, when multiplied by 300 cm^{-1} ($=h\nu$), are remarkably close to the observed changes of $E_{\max}$ for the two IT bands. The data obtained for cation I in the other media did not cover the high-energy "tail" well enough to give suitable PKS fits. However, since $E_{\max}$ changes are essentially parallel from one medium to another, one can infer that changes in ϵ would mirror the peak shifts for all media.

Talham and Cowan[24] reported ϵ values of −10.5 and −3.0 (all quantities in units of $h\nu = 300$ cm^{-1}) and λ values of 3.5 and 3.95 for the low- and high-energy IT bands, respectively. Their λ value of 3.5 for the low-energy IT band differs appreciably from the λ value we obtained for this band at low pressures. This difference is clearly beyond our experimental error in determining the band contour and any error in fitting the band. The ϵ values they gleaned from their analysis are about 10% larger than those we obtained in analyzing the bands observed at low pressures. Perhaps these differences are attributable to the fact that the NIR spectrum which Talham and Cowan[24] were presumably using was that for cation I in solution, whereas in our case cation I was intercalated in zeolite 13X.

In the context of the PKS vibronic model the $|\epsilon|/\lambda^2$ ratio characterizes the level of valence trapping in a mixed-valence complex.[25] The complex with very weak electronic coupling (class I) has $|\epsilon|/\lambda^2 \ll 1$ and has very trapped valences, i.e., it is electronically localized. Strong electronic coupling (class III) leads to $|\epsilon|/\lambda^2 > 1$ and in this limit the complex is electronically delocalized. There is no potential-energy barrier for intramolecular electron transfer in such a class III complex. Class II complexes have intermediate levels of electronic coupling such that $|\epsilon|/\lambda^2 \leq 1$.

Talham and Cowan[24] used their $|\epsilon| = 10.5$ and $\lambda = 3.5$ ($|\epsilon|/\lambda^2 = 0.86$) values for the lower energy IT band of cation I to characterize cation I as being at the class II–III borderline. For comparison they found that analysis of the solution-state IT band for the biferrocenium mixed-valence cation gives $|\epsilon| = 8.7$, $\lambda = 3.8$, and $|\epsilon|/\lambda^2 = 0.6$, which is a little further from the class II–III borderline. It was very recently found[31] that the biferrocenium cation in the I_3^- salt changes from valence-trapped to valence-detrapped on the ^{57}Fe Mössbauer time scale in the 300 to 357 K range. Salts of various dialkyl-substituted mixed-valence biferrocenium cations become valence-detrapped at even lower temperatures.[31,32]

Examination of Table V shows that the level of valence localization of cation (I) changes appreciably with pressure. From the $|\epsilon|$ and λ values evaluated for the low-energy IT band it can be calculated that $|\epsilon|/\lambda^2$ increases continuously from 0.59 at 11 kbar to a value of 0.78 at 89 kbar, where it could be identified as borderline class II–III. It is interesting that further increase in the pressure above 89 kbar leads to a discontinuous change in $|\epsilon|/\lambda^2$ to a value of 0.64 at 102 kbar. Above this pressure $|\epsilon|/\lambda^2$ increases to 0.69 at 135 kbar. The true change in λ at 89–102 kbar for the low-energy peak in particular is very probably less abrupt that was obtained by our fitting procedure. Nevertheless, it appears that there is some tendency for $|\epsilon|/\lambda^2$ to decrease in the range above 100 kilobars.

Conclusions and Comments

The main conclusions of this study of the pressure dependence of the NIR spectrum of the mixed-valence bis(fulvalene)diiron cation (I) are four in number. Cation I does exhibit two IT bands as was suggested previously by examination[24] of the ambient pressure spectrum. The changes in the appearance of the NIR spectrum as the pressure is increased can only be explained by the presence of two IT bands. Both of the IT bands of cation I shift blue with increasing pressure. This blue shift is intramolecular in nature. An increase in pressure leads to an increase in the energy difference between the bonding ground and antibonding excited states that are involved in the IT transition.

Third, in addition to the intramolecular pressure effects, there is evidence of less dominant intermolecular effects. The energy shifts of the IT bands of cation I do change somewhat from one medium such as the crystal lattice of the I_3^- salt to another medium such as the supercage of zeolite 13X.

Finally, as indicated by an analysis of the IT band with the PKS theory, the application of pressure can appreciably change the level of valence localization in cation I. Further study of this observation is needed. IT would be particularly informative if ^{57}Fe Mössbauer or EPR spectroscopy could be used to study the effects of pressure on cation I. The effects of pressure on other mixed-valence complexes should also be studied.

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