TABLE VI. Shift of $\pi \rightarrow \pi^*$ peak ($\Delta\nu$, cm^{-1}). Shift of lower energy edge (0.90 relative absorbance). Pressure (kbar).

Derivative	ν_0	20	40	60	80	100	120	140
				Class A				
ACA(1)	34 610	−200	−425	−670	−925	−1185	−1500	−1970
TFACA(5)	33 680	−70	−150	−285	−450	−665	−950	−1310
MACA(9)	33 770	−150	−250	−370	−400	−630	−760	−890
				Class B				
FTFA(6)	28 475	−270	−545	−815	−1090	(−1370)	(−1645)	
TTFA(7)	28 040	−320	−710	−915	−1220	−1530	(−1835)	
BTFA(8)	30 810	−545	−1100	−1660	−2220	(−2775)	(−3330)	
PACA(10)	33 365	−100	−220	−365	−555	−790	−1080	−1455
				Class C				
DPM(3)	34 685	−165	−345	−515	−685	−860	−1030	(−1205)

Shift of lower energy edge (0.50 relative absorbance). Pressure (kbar).

Derivative	ν_0	20	40	60	80	100	120	140
				Class A				
ACA(1)	33 120	−310	−570	−890	−1270	−1710	−2270	−3230
TFACA(5)	31 940	−240	−440	−710	−1050	−1460	−1950	−2520
MACA(9)	31 610	−220	−400	−640	−900	−1190	−1510	−1860
				Class B				
FTFA(6)	26 985	−350	−700	−1050	−1400	(−1650)		
BTFA(8)	28 425	−670	−1330	−1990	−2650	(−3310)		
PACA(10)	32 000	−360	−650	−1040	−1500	−2000	−2550	−3220
				Class C				
DPM(3)	32 820	−380	−1140	−1560	−1730	−1860	−2130	−2810

Fe(TTFA)₃ and Fe(DBM)₃, and assigned the low energy bands to various crystal field transitions. Intensity considerations would seem to rule out this possibility however.

Neither of the peaks can be directly associated with the $\pi_3 \rightarrow t_{2g}$ transfer presumably involved in the reduction. In any case, however, the areas under the charge transfer peaks should correlate approximately with the fraction of ferric sites present.

The areas of the two charge transfer bands in the high pressure optical spectra have been estimated by assuming Gaussian shapes and subtracting the large tail of the intense intraligand transition. The two charge transfer bands were treated independently; hence the "background" subtracted involves both the $\pi \rightarrow \pi^*$ tail and a portion of the other charge transfer band. Thus the absolute values of the bandwidths and intensities may be incorrect but the trends in the area changes are considered a good first order approximation.

TABLE VII. Shift of CT₁ band center ($\Delta\nu$, cm^{-1}). Pressure (kbar).

Derivative	ν_0	20	40	60	80	100	120	140
				Class A				
ACA(1)	22 190	−656	−865	−1080	−1275	−1505	−1835	−2340
TFACA(5)	22 390	−425	−550	−640	−790	−940	−1130	−1445
MACA(9)	20 550	−180	−365	−555	−740	−925	−1115	−1300
				Class B				
FTFA(6)	19 230	−300	−600	−900	−1205	−1505	−1805	−2100
TTFA(7)	20 010	−365	−700	−1035	−1355	−1700	−2140	−2750
BTFA(8)	20 440	−305	−605	−910	−1215	−1520	−1825	−2130
PACA(10)	21 300	−420	−840	−1260	−1685	−2110	−2535	−2960
				Class C				
DPM(3)	22 975	−215	−430	−635	−830	−1070	−1365	−1775

TABLE VIII. Shift of CT_2 band center ($\Delta\nu$, cm^{-1}). Pressure (kbar).

Derivative	ν_0	20	40	60	80	100	120	140
Class A
ACA(1)	28 405	−140	−270	−410	−550	−690	−830	(−960)
TFACA(5)	27 425	−150	−290	−340	−590	−735	−880	(−1025)
MACA(9)	26 600			−850	−850			
Class B
FTFA(6)	25 320	−130	−260	−385	(−520)	(−650)		
BTFA(8)	25 520	−295	−590	−835	(−1180)	(−1470)		
PACA(10)	26 985	−80	−180	−340	−620	(−1000)		
Class C
DPM(3)	28 170	−230	−460	−695	−925	(−1155)		

Figures 18, 19, and 20 show the normalized area of the lower energy charge transfer band CT_1 as a function of pressure for ACA(1), TFACA(5), and PACA(10). The smoothed area estimates for both charge transfer bands of these and the remaining derivatives for which optical data were obtained are included in Table V. The data points and the solid curve refer to the normalized area; the dashed curve represents the percent of ferric ion as obtained from Mössbauer measurements. As seen in these typical examples, the charge transfer band area estimations generally fall somewhat above the Mössbauer ferric ion concentration curve. This is not unreasonable since previous high pressure optical measurements by Stephens and Drickamer[49] showed a general increase in charge transfer band intensity with pressure in several inorganic and organic complexes. This indicates an increase in transition moment with decreasing interatomic distance and is consistent with Mulliken's[50,51] theoretical work on charge transfer spectra. Thus there is competition between the increase in intensity expected because of the charge transfer character and the decrease accompanying the loss of ferric sites as they are converted to ferrous sites. Nevertheless, the agreement is very good (in some cases it is probably fortuitous). This has important implications in the examination of high pressure changes of oxidation state in other transition metal complexes which cannot be measured with Mössbauer resonance.

In addition to the estimation of the charge transfer band areas, measurements of the positions and shifts of all absorption peaks were made. These latter data are not essential for this study but are included as they may be useful in other work. The positions of the charge transfer band centers (CT_1 and CT_2) may be correlated with the intraligand $\pi \to \pi^*$ transition as shown in Fig. 21. The data were obtained from KBr spectra at atmospheric pressure. Such a correlation may arise from admixing of locally excited ligand functions or from coincidence of ground or excited states. The red shifts of all absorption peaks to lower energy with increasing pressure are given in Tables VI, VII,

and VIII. No general correlation between the shifts of the charge transfer peaks and the intraligand transition peak was observed. The intraligand band shows appreciable broadening with increasing pressure, as has also been observed by Fisher and Drickamer[5] and Grenoble et al.[7] The broadening was less extreme for the charge transfer bands. The high pressure data allow brief comment on the possible assignments, of which only the lower energy charge transfer band is in question. Calculation of the effect of pressure on the crystal field splitting based on Lintvedt's[49] assignments (i.e., CT_1 is $\pi \to e_g$, CT_2 is $t_{2g} \to \pi^*$) does not yield reasonable trends in the $e_g - t_{2g}$ energy difference. Some derivatives show small initial increases; however, in general decreases of the order of 1000 cm^{-1} are observed at 100 kbars. All other high spin systems studied in this laboratory have shown increases of this same order in the ligand field splitting. This, plus the fact that no peak appears in the near infrared corresponding to a $\pi \to t_{2g}$ transition casts considerable doubt on Lintvedt's assignments. It may also be that there is significant $\pi \to \pi^*$ admixture in these peaks as suggested by Hanazaki et al.[46,47] although the intensity changes with pressure assure the predominant charge transfer character.
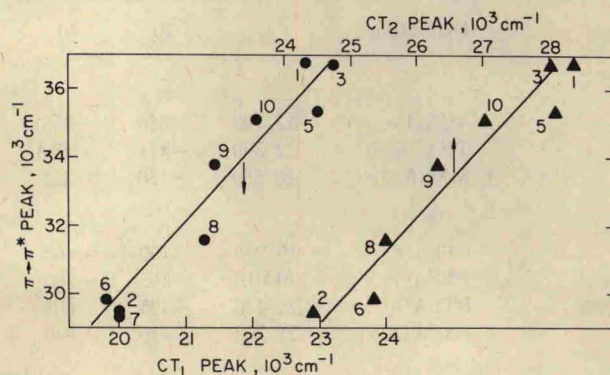

FIG. 21. Location of intraligand vs charge transfer peaks—atmospheric pressure.