

TABLE VII. Shift of  $\pi-\pi^*$  band ( $\Delta\nu$ ,  $\text{cm}^{-1}$ ).

Compound	Pressure (kilobars)					
	20 (position)	50	75	100	120	140
<b>Fe(phen)<sub>2</sub>X<sub>2</sub></b>						
Cl	(35 900)	-780	-1430	-1990	-2300	-2420
NCS <sub>e</sub>	(35 470)	-1000	-1440	-1650	-1730	-1770
N <sub>3</sub>	(36 630)	-610	-1250	-1940	-2500	-3040
NCO	(36 800)	-1130	-1940	-2640	-3050	-3320
CN(1H <sub>2</sub> O) <sup>a</sup>	(36 000)	-900	-1380	-1780	-2160	-2380
<b>Fe(phen)<sub>3</sub>X<sub>2</sub></b>						
N <sub>2</sub> (6H <sub>2</sub> O)	(37 110)	-730	-1340	-1750	-2000	-2150
SCN(1H <sub>2</sub> O)	(35 870)	-1050	-1800	-2350	-2600	-2670
1,10-phenanthroline	(35 820)	-970	-1520	-2000	-2350	-2710

<sup>a</sup> Waters of hydration are indicated in parentheses.

### OPTICAL ABSORPTION RESULTS

Studies of optical spectra as a function of pressure are of assistance in understanding these effects. In Fig. 13 we show spectra at various pressures for the visible region of the spectrum for a typical bisphenanthroline complex, Fe(phen)<sub>2</sub>(NCO)<sub>2</sub>. Because of the *cis* configuration for bisphenanthroline complexes there is sufficient distortion on the approximately octahedral ligand field to cause splitting of the  $t_{2g}(\pi)$  levels into a higher energy nondegenerate and a lower energy doubly degenerate level. Therefore, two metal-ligand charge transfer bands are expected and are indeed observed in the optical spectrum (at 4 kbar located about 19 200  $\text{cm}^{-1}$  and 16 200  $\text{cm}^{-1}$ , respectively). First, consider the lower pressure to about 40 kbar where rapid high- to low-spin state change occurs (Fig. 8). This region is characterized by a small red shift of both charge transfer peaks and a smaller shift of the low energy tail of the phenanthroline  $\pi-\pi^*$  band. This behavior is also reflected in the ultraviolet spectrum of Fe(phen)<sub>2</sub>(NCO)<sub>2</sub> as a function of pressure which affords one an observation of the phenanthroline  $\pi-\pi^*$  transitions (Fig. 14). One observes a steady red

shift of the  $\pi-\pi^*$  band with pressure above 20 kbar. In the higher pressure region (above 40 kbar for the NCO compounds) where the low-spin state reverses toward high spin with increasing pressure (or as in the halides, low-spin state increases at a much slower rate) several changes occur in the visible spectrum. One observes a sudden relative intensity increase and accompanying red shift of the lower energy metal-ligand charge transfer peak. The higher energy charge transfer peak shows a steady shift to lower energy with pressure. Especially, there is a rapid shift of the low energy tail of the ligand  $\pi-\pi^*$  band (Fig. 13) and a large red shift of the peak (Fig. 14). As is shown in Figs. 15 and 16, the charge transfer and ligand  $\pi\rightarrow\pi^*$  transitions for the tris complexes also exhibited a large shift to lower energy with increasing pressure.

It is of interest to compare the shifts of the various charge transfer peaks and the ligand  $\pi-\pi^*$  band as a function of pressure for bis- and trisphenanthroline ferrous compounds. The shift of the  $\pi-\pi^*$  band with pressure for many of the compounds is presented in Table VII, where the shifts are given relative to the location at 20 kbar. The bis compounds shift 1800-

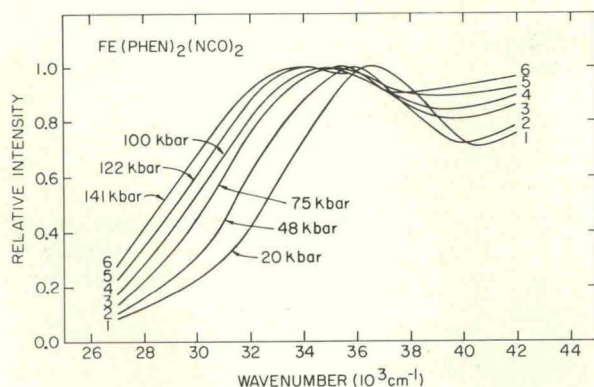


FIG. 14. Ultraviolet absorption spectra vs pressure, Fe(phen)<sub>2</sub>(NCO)<sub>2</sub>.

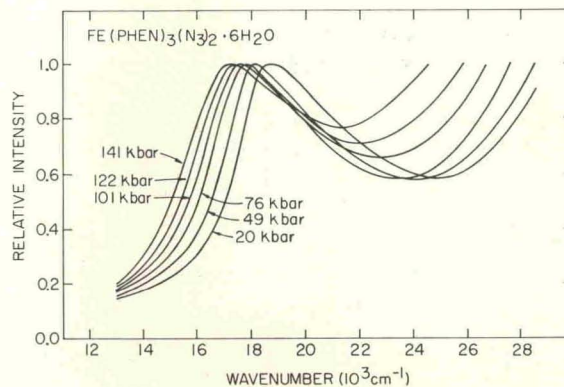


FIG. 15. Visible absorption spectra vs pressure, Fe(phen)<sub>3</sub>(N<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O.



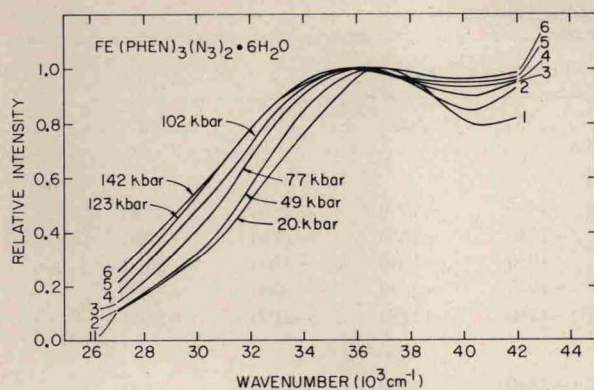


FIG. 16. Ultraviolet absorption spectrum vs pressure,  $\text{Fe}(\text{phen})_3(\text{N}_3)_2 \cdot \text{H}_2\text{O}$ .

$3300 \text{ cm}^{-1}$  and the tris compounds shift  $2100\text{--}2700 \text{ cm}^{-1}$  to lower energy from 20 to 140 kbar. It is noted that the  $\pi\text{--}\pi^*$  band in pure phenanthroline shifts by  $2700 \text{ cm}^{-1}$  to lower energy from 20 to 140 kbar. The shifts of the higher and lower energy metal-to-ligand charge transfer peaks with pressure are tabulated in Tables VIII and IX relative to the location at 20 kbar. Both charge transfer bands shift to lower energy with pressure, and the shift is of the same order. (Two charge transfer bands are resolved for some bispheanthroline compounds only.) The shifts of the single charge transfer band for the tris compounds are also comparable ( $1400\text{--}1850 \text{ cm}^{-1}$  to lower energy). The shifts of the metal-ligand charge transfer bands and the ligand  $\pi\text{--}\pi^*$  bands correlate with each other. That is, a smaller shift of the  $\pi\text{--}\pi^*$  band corresponds to a smaller shift of the charge transfer band for the same compound as compared to others. It is important to note that the  $\pi\text{--}\pi^*$  band is shifting red faster than the charge transfer bands. This means that the ligand  $\pi^*$  level is shifting to lower energy more rapidly than the metal  $3d(\pi)$  levels are with pressure. The red shift of the  $\pi\text{--}\pi^*$  transition has been observed in a variety of aromatic systems<sup>4</sup> and is associated with a dipole

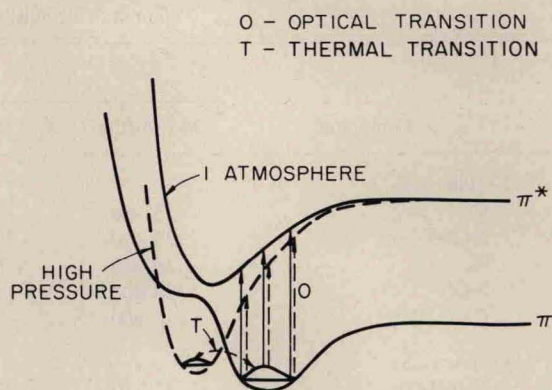


FIG. 18. Schematic configuration coordinate diagram illustrating thermal mixing of  $\pi\text{--}\pi^*$  levels at high pressure.

moment in the excited state larger than that for the ground state. While there are observed differences in the shifts and the locations of the peaks at 20 kbar, these differences do not correlate particularly with the relative amount of conversion from one spin state to another. However, all systems show similar behavior and are consistent with the explanation of the spin state behavior as a function of pressure.

In the low pressure region the behavior of the complexes is characterized by conversion of the ferrous ion to low spin for the high-spin bis compounds, no change in spin state of the low-spin compounds, and modest red shifts of the peaks representing the charge transfer and  $\pi\text{--}\pi^*$  transitions. These conditions are represented by the schematic molecular orbital diagram of Fig. 17(a). The dominant effect is the increase in ligand field with pressure due to the increased back bonding which results from increased overlap of the metal  $\pi$  orbitals with the empty ligand  $\pi^*$  orbitals. The increase in the ligand field overcomes the spin pairing energy and thus brings about the high spin to low spin transition.

At higher pressures there is a tendency for low-spin to high-spin transformation in both the bis and tris

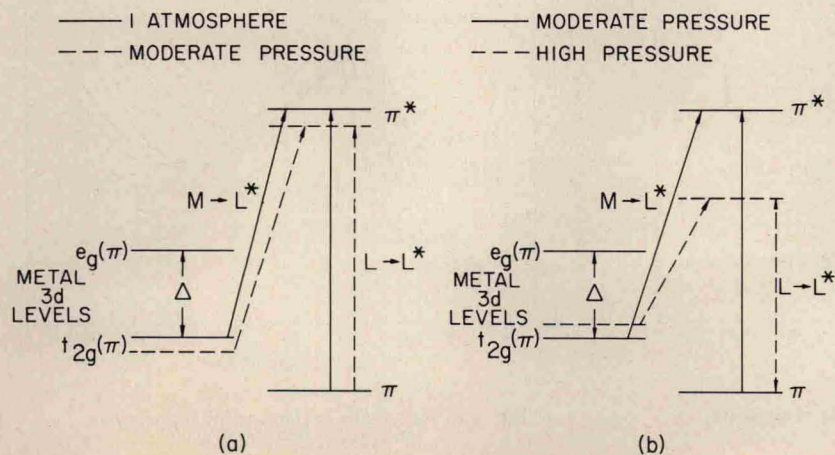


FIG. 17. Simplified MO diagram illustrating effects of pressure.