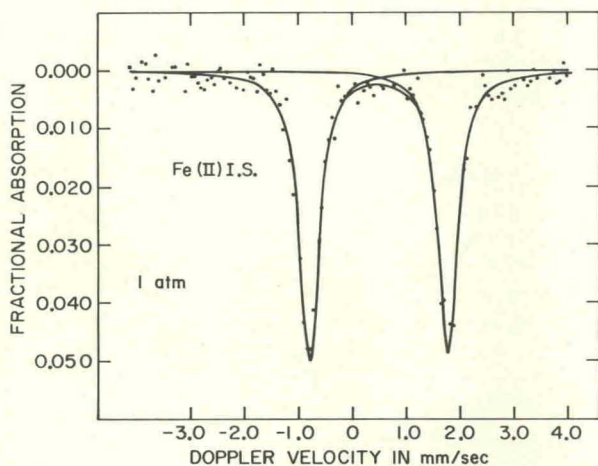
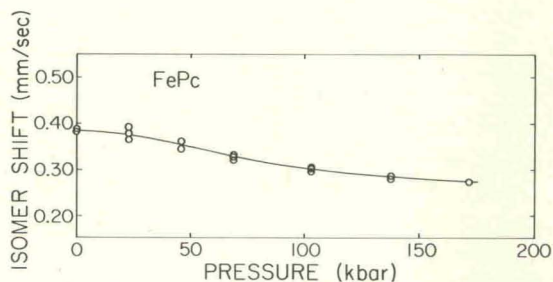
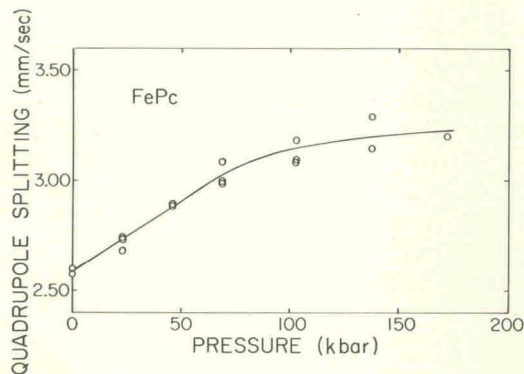
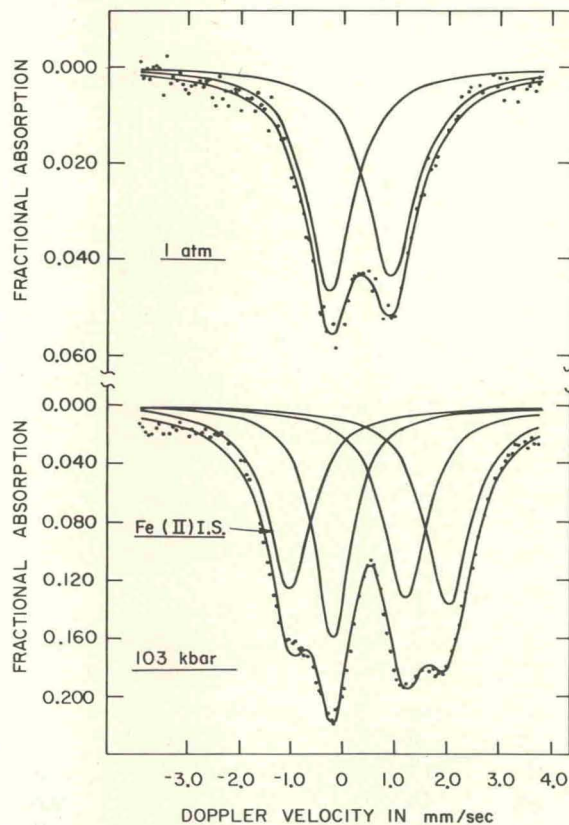


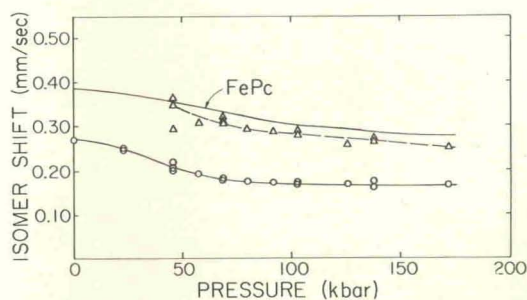
TABLE I. Pressure-induced shifts (kK) of low energy peaks in H_2Pc and $FePc(L)_2$.

| Pressure (kbar) | Shift (kK) | | | | |
|-----------------|------------|-------|-------|-------|-------|
| | 20 | 50 | 80 | 110 | 140 |
| H_2Pc | 0(16.15) | -0.42 | -0.69 | -0.91 | -1.15 |
| $FePc(Py)_2$ | 0(14.73) | -0.37 | -0.68 | -0.91 | -1.16 |
| $FePc(4-Pic)_2$ | 0(14.60) | -0.34 | -0.64 | -0.82 | -1.00 |

FIG. 5. Mössbauer spectra of $FePc$.FIG. 6. Isomer shift vs pressure for $FePc$.FIG. 7. Quadrupole splitting vs pressure for $FePc$.FIG. 8. Mössbauer spectra of $FePc(Py)_2$.

sec for quadrupole splitting, and from 0.40 to 0.46 mm/sec for isomer shift. It has been established that $FePc$ is a true intermediate spin complex, although its magnetic susceptibility of approximately $3.9 \mu_B$ is substantially higher than the spin only value of $2.8 \mu_B$.¹²⁻¹⁵ The large quadrupole splitting is indicative of an unsymmetric distribution of electrons in the iron d orbitals, as well as the lack of cubic symmetry.

The Mössbauer spectra of $FePc(Py)_2$ at 1-atm and at 138 kbar, is shown in Fig. 8. At 1 atm the spectrum consists of two peaks with a quadrupole splitting of

FIG. 9. Isomer shift vs pressure for $FePc(Py)_2$. O, Low spin; Δ , intermediate spin.

2.01 mm/sec and an isomer shift of 0.27 mm/sec. These values compare to literature values^{7,11,16} of 2.02 to 2.07 mm/sec for quadrupole splitting and 0.26 to 0.37 mm/sec for isomer shift. At high pressure, in addition to the original peaks, new peaks appear and grow in area relative to the original peaks. The isomer shifts of the two species of $\text{FePc}(\text{Py})_2$ are shown in Fig. 9; and in Fig. 10 the quadrupole splittings of both pairs are shown. For convenience, the isomer shift and quadrupole splitting of FePc are also shown in both figures. It is immediately apparent that the new high pressure material has Mössbauer parameters close to that of FePc and that they follow the same pressure dependence. Thus, the high pressure material is probably intermediate spin ferrous iron, similar to FePc . $\text{FePc}(\text{Py})_2$ at atmospheric pressure is diamagnetic, and the isomer shift of 0.27 mm/sec is characteristic of low spin ferrous compounds. Thus, with pressure, the ferrous iron in $\text{FePc}(\text{Py})_2$ undergoes a spin flip from low spin to intermediate spin. The percent intermediate spin is shown in Fig. 11.

In addition to the pyridine adduct of FePc , the 3-picoline, the 4-picoline, and the piperidine adducts were studied as a function of pressure. With increasing pressure these compounds showed the same change of spin state. The conversions are compared in Fig. 11. The quadrupole splittings and isomer shifts of both low spin and intermediate spin are compared in Table II. It should be pointed out that this effect was reversible in that the new peaks disappeared upon release of pressure.

DISCUSSION

The optical spectra of phthalocyanines have been widely studied, and recently, molecular orbital calculations have been completed by Försterling and Kuhn¹⁷ using a projected electron density method. The calculations give reasonable agreement with experimental values. The calculations indicate that the highest occupied π orbital has a_{1u} symmetry. The wavefunction associated with this symmetry has maximum electron

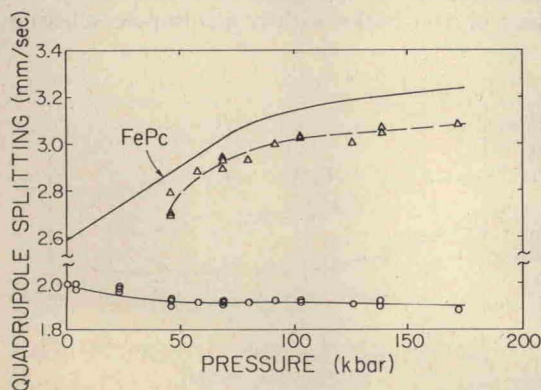


FIG. 10. Quadrupole splitting vs pressure for $\text{FePc}(\text{Py})_2$. \circ , low spin; \triangle intermediate spin.

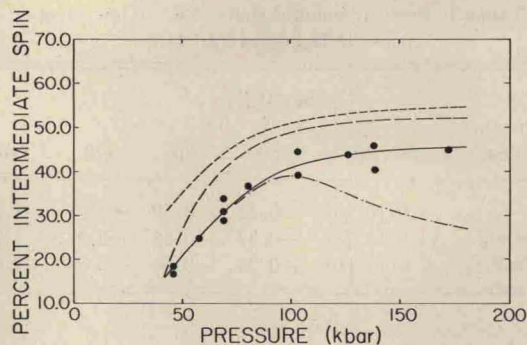


FIG. 11. Percent conversion to intermediate spin vs pressure for hexacoordinated adducts of FePc . \bullet — \bullet $\text{FePc}(\text{Py})_2$ --- $\text{FePc}(3\text{-Pic})_2$; - - - $\text{FePc}(4\text{-Pic})_2$; - · - $\text{FePc}(\text{Pip})_2$.

density on the pyrrole carbons which are adjacent to the pyrrole nitrogens. The lowest $\pi-\pi^*$ transition is then given as $a_{1u} \rightarrow e_g^*$. The antibonding wavefunctions associated with the e_g^* levels have maximum electron density on the outer carbons of the pyrrole rings and on the nitrogen bridge atoms. Thus, the lowest energy transition involves some transfer of charge away from the center of the molecule. The next higher transition is $a_{2u} \rightarrow e_g^*$. However, there is a b_{2u} orbital and an a_{1u} orbital close in energy to the a_{2u} orbital, and the resulting transitions are therefore mixed through configuration interaction. This is essentially the same result obtained by Weiss *et al.*¹⁸ For simplicity, following Weiss, the lowest transition, $a_{1u} \rightarrow e_g^*$, is labeled Q , and with increasing energy the transitions are labeled B , N , and L . The B , N , and L transitions are mixed through configuration interaction, the net effect of which is that the B transition is lowered in intensity and the N transition is raised in intensity.

In phthalocyanine itself, the B and N transitions are split somewhat. In the solid state, the B transition is at approximately 30.3 kK, and the N transition is at approximately 35.4 kK. Because of the smaller degree of mixing, the N transition is somewhat weaker than the B transition. Figure 2 shows the effect of pressure on the B and N transitions. They both shift to lower energy, but the N peak shifts more than the B peak. This increases the configuration interaction, and therefore increases the intensity of the N peak at the expense of the B peak. Since the visible Q peak is normalized relative to the maximum absorption of the combined B and N peaks, as the N peak grows in intensity, the Q peak decreases in relative intensity, as shown in Fig. 1. The same configuration interaction occurs in FePc and $\text{FePc}(\text{Py})_2$, but their B and N transitions at 1 atm are already extensively mixed [see Fig. 5 of Ref. (9)], causing the N transition to be the most intense, with the B transition appearing as a shoulder on the low energy side. With pressure, mixing is increased, the N transition gains intensity, and the Q transition decreases in relative intensity. With the optical apparatus used,