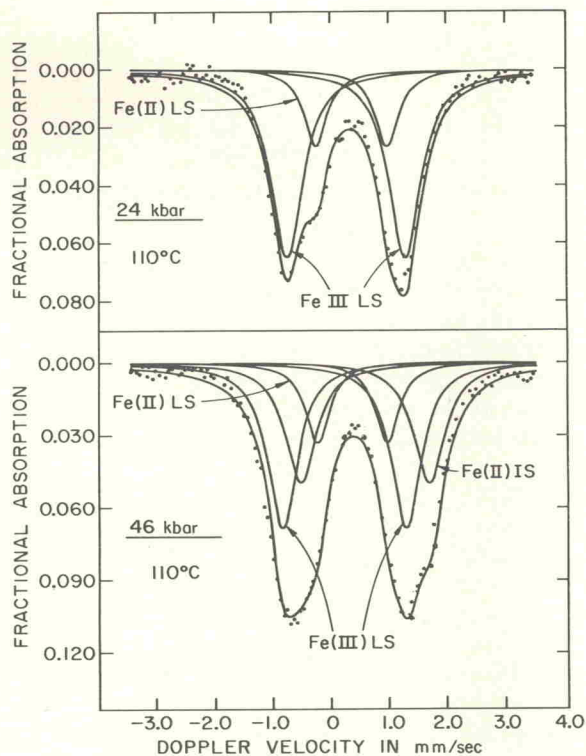
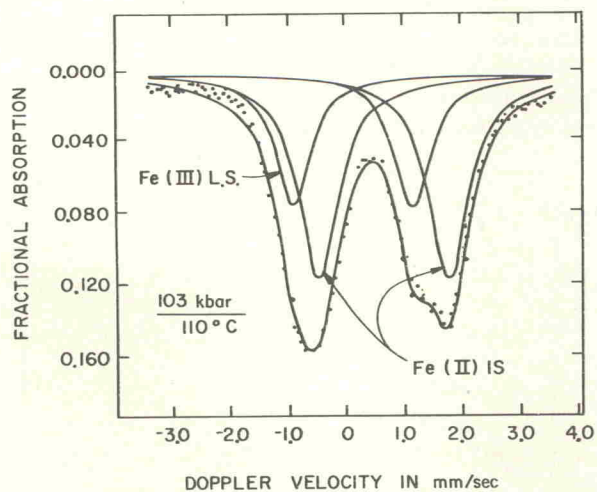


justify the assignment of the peaks induced at moderate pressure and 110° as low spin ferrous iron.

The low spin ferrous phthalocyanine compounds discussed in the previous paper¹⁶ had as typical values of

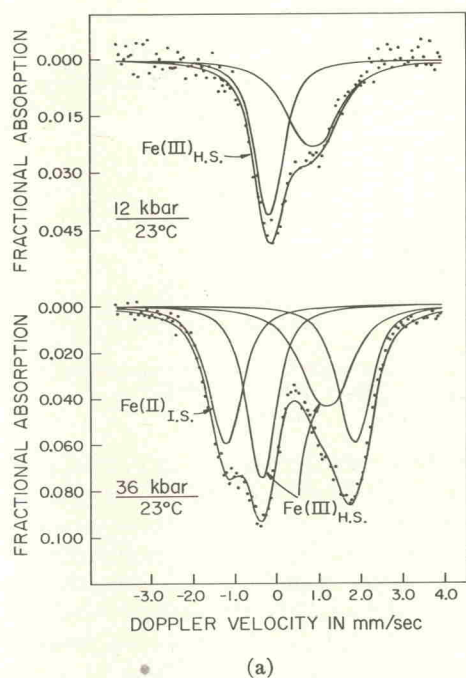


(a)

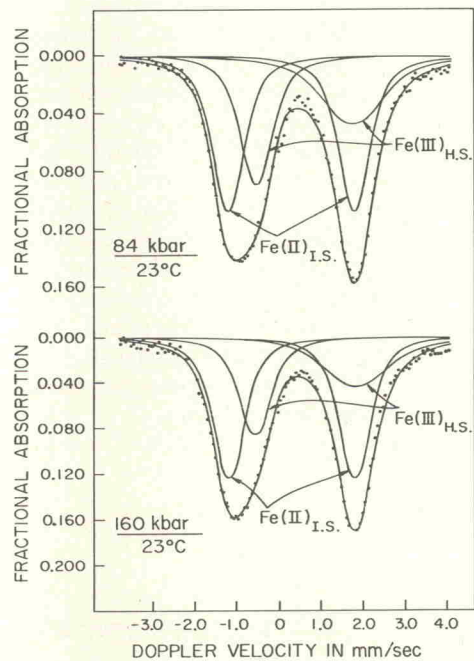


(b)

FIG. 7(a). Mössbauer spectra of imidazole protohemichrome at 110°C for 23 and 46 kbar; (b) Mössbauer spectra of imidazole protohemichrome at 110°C and 103 kbar.



(a)



(b)

FIG. 8. (a) Mössbauer spectra of hemin for 4 and 23 kbar; (b) Mössbauer spectra of hemin for 43 and 140 kbar.

isomer shift and quadrupole splitting at 50 kbar, 0.21 and 1.94 mm/sec, respectively. It was shown there that at high pressure, low spin ferrous iron changed to the intermediate spin state. Typical values at 50 kbar for

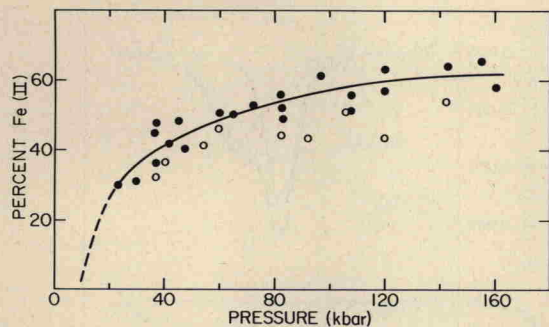


Fig. 9. Yields of high pressure products vs pressure for hemin. ●, -23°C ; ○, -90°C .

the intermediate spin ferrous iron in FePc derivatives are 0.33 mm/sec isomer shift and 2.77 mm/sec quadrupole splitting. Thus, the difference in isomer shift and quadrupole splitting between intermediate spin and low spin states at 50 kbar are, respectively, 0.12 and 0.83 mm/sec for FePc derivatives. Adding these values to the expected values for the room temperature isomer shift and quadrupole splitting of imidazole protoheme stated above, give a range for the intermediate spin isomer shift of 0.47–0.55 mm/sec and for the intermediate spin quadrupole splitting a range of 1.78–1.83 mm/sec. These values compare favorably to the measured values for the hemochrome of 0.51 mm/sec isomer shift and 2.10 mm/sec quadrupole splitting. Thus, imidazole protoheme apparently exhibits with pressure the expected reduction from ferric iron to ferrous iron; at elevated temperatures where the conversion occurs at low pressures, one obtains low spin ferrous material, while at high pressure the ferrous iron apparently has changed to intermediate spin. This reduction and spin flip is best illustrated by referring to the 46 kbar Mössbauer spectrum at 110°C , shown in Fig. 7(a), where all three iron states are present. The percent conversion to ferrous iron shown in Fig. 6 clearly shows the disappearance of the low spin ferrous iron with increasing pressure.

Mössbauer spectra of hemin appear in Figs. 8(a)

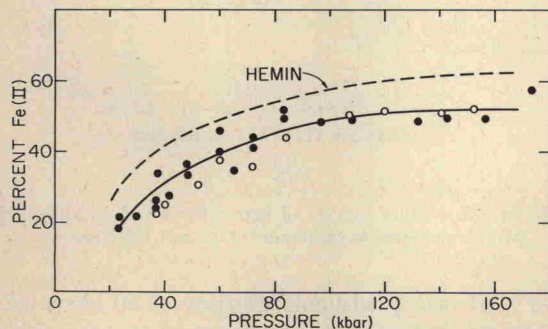


Fig. 10. Yield of high pressure products vs pressure for hematin. ●, -23°C ; ○, -90°C .

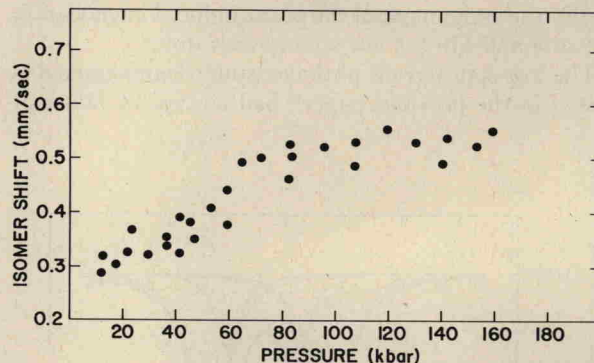


Fig. 11. Isomer shift of Fe(III) in hemin vs pressure at 23°C .

and 8(b). At low pressure the high spin ferric iron exhibits a pair of asymmetric peaks. With increasing pressure the ferric iron reduces to a state labeled intermediate spin ferrous, as discussed below. The quantitative fitting of such spectra to establish both locations and areas of the peaks offers some difficulties. In this work the ferric peaks were fit as an asymmetric pair of pseudo-Lorentzian peaks with equal area, but unequal width. This is consistent with the analysis of Blume¹⁷ who assigned the asymmetry to spin-spin splitting. The ferrous peaks were assumed to be a symmetric pair (equal in area and width). An alternative assumption that they were an asymmetric pair like the ferric peaks was also tried. This mode of fitting made only very modest differences in the areas and locations of peaks, and gave no improvement in χ^2 , which was less than 2.0 for all fits. The differences would in no way affect the discussion below.

At low pressure the ratio of peak widths for the ferric peaks was ~ 1.8 . By about 30 kbar this ratio reduced to 1.4–1.5. This reduction is consistent with the arguments of Blume. At higher pressures, and low concentrations of ferric ion the ratio tended to increase again and reached 1.6–1.9 at 170 kbar. No attempt is made to interpret this increase, as one cannot eliminate the possibility that it is an artifact of the fitting. For molec-

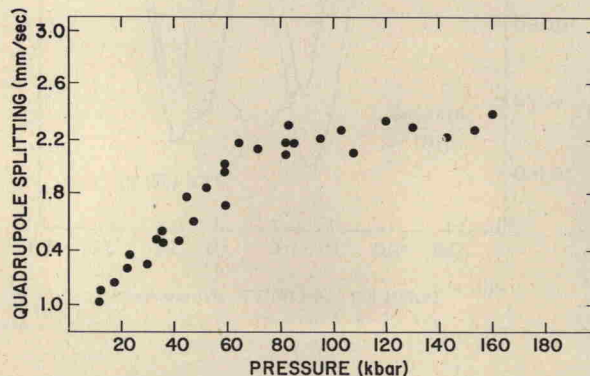


Fig. 12. Quadrupole splitting of Fe(III) in hemin vs pressure at 23°C .