



Fig. 4.—Quadrupole splitting vs. pressure for Fe(III) ion in hemin and hematin.

Let us consider first the low-pressure region. From equation (2), we see that a transfer of charge to the ring from the bonding metal orbitals would result in an increase in quadrupole splitting and quite possibly an increase in isomer shift by changing the shielding or the s -character of the bonding orbitals. As conversion increases, the probability that an unconverted molecule would have one or more converted neighbors increases. The reduced ions have a deficiency of electrons on the chlorine and possibly on the ring. These charge deficiencies can interact with the electronic wave functions on an unconverted molecule, making metal-to-ring transfer in the bonding orbitals more difficult and the reverse transfer easier. This could be one factor in the change of direction of the isomer shift and quadrupole splitting. In addition, one would expect a decrease in isomer shift due to the spreading of the $3d$ -orbitals, as occurs in most compounds. Interaction of the Cl^- ion with charge-deficient neighbors could spread out its charge, changing z_1 and further affecting the quadrupole splitting. There is not sufficient information for a definitive calculation, but the above factors could reasonably account for the observed results.

The ferrous ion formed from both hemin and hematin has an isomer shift in the neighborhood of 0.45–0.50 relative to metallic iron, which varies little with pressure. This is significantly lower than the isomer shift for normal high-spin Fe(II). Pullman's¹² suggestion that back donation from the metal d -orbitals to the delocalized π -orbitals of the ring is important in metalloporphyrins is probably the explanation. The quadrupole splitting of the Fe(II) hemin spectrum varies from 2.9 mm/second at 20 kb to 2.8 mm/second at 100 kb; that from hematin was about 0.1 mm/second greater. These are typical values for high-spin ferrous ion.

There has been considerable discussion of the effect of spin-spin relaxation on

the peak shapes in hemin,^{2, 13} which we will not take up here, but it might be mentioned that the ratio of ferric peak widths was about 2:1 at atmospheric pressure, and less than 1.2:1 just before the quadrupole splitting disappeared.

Summary.—The effect of pressure and temperature has been studied on the Mössbauer spectra of hemin and hematin. Both reduce reversibly to the ferrous state with pressure, with an equilibrium constant given by the relationship $K = AP^B$. The hemin reduces at measurably lower pressures than the hematin. The reaction is exothermic in these compounds, which is in contrast to all previous systems studied. This observation is related to deformation of the potential wells with temperature. Both the isomer shift and quadrupole splitting for the ferric ion increase with pressure in the low-pressure region, go through a maximum at the pressure where the conversion first becomes significant, and then decrease rapidly at higher pressures. The effects of electron transfer between the porphyrin ring and the iron, and the interaction with neighboring molecules containing reduced iron are considered.

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