# Effect of Pressure on the Electronic Structure of Phthalocyanine and Iron Phthalocyanine Derivatives*

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The electronic structures of phthalocyanine, ferrous phthalocyanine, and the adducts with pyridine, 3-picoline, 4-picoline, and piperidine have been studied to 175 kbar pressure using optical absorption and Mössbauer resonance. One observes shifts of the optical absorption peaks to lower energy and changes in relative intensity of peaks which can be explained in terms of changes in the configuration interaction. Fe(II) in ferrous phthalocyanine is in an intermediate spin configuration at all pressures. In the axially coordinated adducts the Fe(II) is low spin at 1 atm. For the pyridine and picoline adducts this is caused by the increased backbonding to the axial ligands in addition to the phthalocyanine and by repulsion due to $\sigma$ bonding. These factors both tend to separate the $d_{z^2}$ orbitals from the $d_\pi$ orbitals. In the piperidine adduct only the latter factor is operative. With increasing pressure the low spin compounds convert partially to a new spin state, believed to be intermediate spin. The picolines show the most conversion, the pyridine adduct less, and the piperidine complex still less. The general explanation lies in the decrease in backbonding at high pressure caused by the tendency for occupation of the ligand $\pi^*$ orbitals by ligand $\pi$ electrons. A similar effect has been observed in ferrocyanides and in phenanthroline complexes. The differences among the various adducts can be explained in terms of differences in the degree of $\pi$ backbonding and $\sigma$ bonding.

The basic structure of phthalocyanine consists of four pyrrole rings interconnected by nitrogen bridges. In the phthalocyanines there is a benzene ring fused to each pyrrole subunit. The giant ring structure is planar and fully conjugated. In $H_2Pc$ the two hydrogens are considered to be attached to opposite nitrogens, but there is evidence that they are hydrogen bonded to adjacent nitrogens.[1] Much information has been published concerning phthalocyanine and its metal derivatives. A book by Moser[2] and a review by Lever[3] offer two general sources of information concerning the chemistry and application of phthalocyanines.

Ferrous phthalocyanine, FePc, can serve as a model compound for the biologically important hemes. It is particularly useful because of the difficulty of stabilizing ferrous hemes in the solid state. FePc is also planar, with the iron coordinated to the four pyrrole nitrogens. Organic bases, such as pyridine, can coordinate to the iron by forming bond perpendicular to the phthalocyanine molecule. The hexacoordinated compounds are analogous to the biologically important hemochromes and can serve as model compounds for the hemoproteins. In both FePc and axially coordinated FePc, the iron is in $D_{4h}$ symmetry.

In this paper we present studies of the electronic structure of $H_2Pc$, FePc, and the hexacoordinated derivatives with pyridine, 3-picoline, 4-picoline, and piperidine to pressures of 175 kbar. The high pressure optical absorption and Mössbauer resonance techniques used have been described elsewhere.[4–6] The phthalocyanine was purchased from Pfaltz and Bauer Inc. The ferrous phchclocyanine was prepared by the method of Moss *et al.*[7] using iron enriched to 90% in $^{57}Fe$. The hexacoordinated derivatives were prepared by dissolving ferrous phthalocyanine in the appropriate solvent, letting it stand for a few days, and then evaporating the solvent. Alternatively Soxhlet extraction was used. The analyses were close to the calculated values. (See the discussion on forms of ferrous phthalocyanine in the final section.)

## OPTICAL DATA

Because of the strong absorption of light in the red region of the visible and near ultraviolet regions of the spectrum, phthalocyanine compounds have long been important blue and blue-green dyes. The transitions involved are ligand $\pi-\pi^*$ transitions. The optical absorption of $H_2Pc$ as a function of pressure is shown in Figs. 1 and 2. The visible transition shift to lower energy by 1.2 kK (1 kK=1000 cm$^{-1}$) in the pressure range 20–140 kbar, and the visible peaks fade relative to the peaks in the near ultraviolet region. Note also that the two bands in the ultraviolet spectra both shift to lower energy. The higher energy band shifts to lower
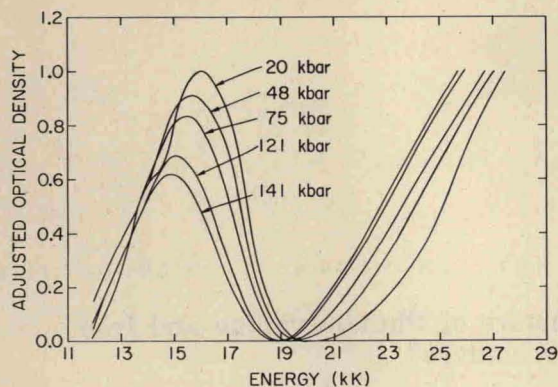
FIG. 1. Visible spectra of phthalocyanine as a function of pressure.



FIG. 3. Visible spectra of FePc(Py)₂ as a function of pressure.

energy by about 1.5 kK in the pressure range 20–140 kbar. Also the lower energy band fades relative to the higher energy band and shifts less. Over the same pressure range, the shift of the low energy tail of the combined ultraviolet peaks is about 1.8 kK at 80% of the maximum intensity of the combined bands. The visible spectrum was normalized to the ultraviolet spectrum by matching the shift of the tail of the ultraviolet peak. The shift was measured at 80% of the peak maximum. This shift was then arbitrarily set at an intensity of 1.0 in the visible spectra. In $H_2Pc$ a modest departure from $D_{4h}$ symmetry causes the low energy peaks to be split into four bands. In the solid state this vibrational structure is not completely resolvable, which accounts for the broadness of the lower energy peaks.

The optical spectra of FePc are not shown because of the sensitivity of its properties to shear, as discussed below. It should also be pointed out that the optical spectra of $H_2Pc$ are probably of the $\alpha$ polymorphic form, as $H_2Pc$ has been shown to transform from the $\beta$ to the $\alpha$ form by shearing in KBr.[8]

The optical absorption of the pyridine adduct of ferrous phthalocyanine, $FePc(Py)_2$, is shown in Figs. 3 and 4. The effects of pressure are similar, i.e., the visible
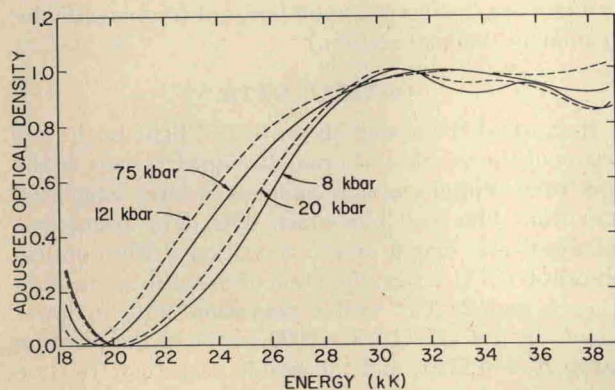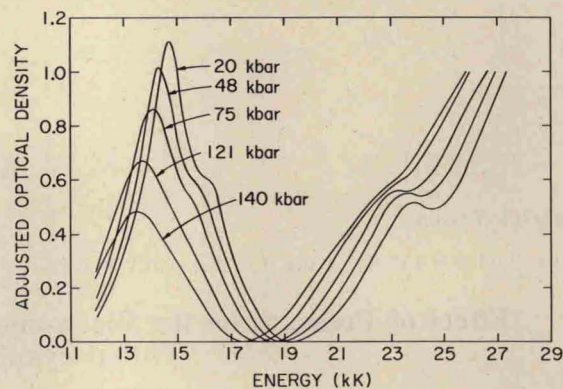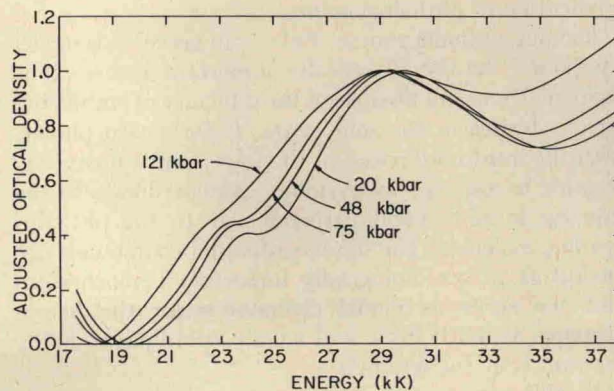
peaks shift to lower energy by 1.2 kK in the pressure range 20–140 kbar, and the low energy peaks fade relative to the higher energy peaks. In this compound the two ultraviolet bands are too close to be resolved. The shift of the tail is about 1.6 kK over the same pressure range. Note that there is an additional peak in $FePc(Py)_2$ at about 24 kK. This transition has been interpreted as a metal to ligand charge transfer.[9] The $FePC(Py)_2$ spectra are similar to the 3-picoline and 4-picoline adduct of FePc, and therefore the latter are not shown. The shifts of the low energy peaks appear in Table I.

## MÖSSBAUER DATA

The Mössbauer spectrum of FePc at 1 atm is shown in Fig. 5. The isomer shift and quadrupole splitting as a function of pressure are shown in Figs. 6 and 7, respectively. The isomer shift shows a small decrease, indicating some increase in the electron density at the nucleus. The quadrupole splitting shows a large increase of nearly 0.7 mm/sec in 170 kbar. At 1 atm the isomer shift is 0.39 mm/sec, and the quadrupole splitting is 2.58 mm/sec. These values compare closely to literature values,[10,11] ranging from 2.60 to 2.67 mm/



FIG. 2. Ultraviolet spectra of phthalocyanine as a function of pressure.



FIG. 4. Ultraviolet spectra of PePc(Pyr)₂ as a function of pressure.