

Optical Versus Thermal Transitions in Solids at High Pressure

(electrons/excitations/theoretical)

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ABSTRACT Pressure-induced electronic transitions have been observed in a wide variety of materials. In particular, Mössbauer resonance studies under high pressure have revealed changes of oxidation state and spin state of iron as a function of pressure. These processes involve the thermal transfer of an electron to a new ground state of the system. The difference in energy between states is frequently measured by optical absorption. In this paper, we relate the energy of the optical absorption peak and its half-width to the difference in thermal energy between the two states as a function of pressure. We show that the optical peak will broaden with pressure only if there is a difference between the force constants of the ground and excited states. These relationships permit the prediction from optical absorption data of the pressure at which a new ground state will be obtained. We demonstrate that the predictions are qualitatively correct for the reduction of Fe(III) in a series of ferric hydroxamates, and for the low-spin to high-spin transition of Fe(II) in ferrous phenanthroline complexes.

Pressure tends to shift the energy of one set of orbitals with respect to another. This can frequently lead to a new ground state for the system, or a ground state greatly modified by configuration interaction. This new ground state may have very different physical and chemical properties.

A common technique for determining the difference in energy between the ground state and an excited electronic state is by optical absorption, which, of course, gives a measure of this difference subject to definite restrictions. On the other hand, the process of electron transfer to establish a new ground state at high pressure is a thermal one. Since it is sometimes useful to relate these processes, it is important to understand their differences. In many cases, the thermal energy is apparently much smaller than the energy observed optically. We shall show that this is reasonable, present an approximate relationship between them, and present experimental results that verify the equations.

First we note that a large difference in energy between optical and thermal transitions has been observed for several processes at one atmosphere. The color centers induced in alkali halides by x-irradiation or by excess alkali or halide characteristically absorb in the visible or ultraviolet regions of the spectrum (2-4 eV) (1). Yet, these color centers can be bleached thermally at moderate temperatures—in some cases as low as 100°K.

In redox reactions in aqueous solutions (2), one measures electron transfer between a given metallic ion in two oxidation states (e.g., $\text{Ti}^{+3} \rightleftharpoons \text{Ti}^{+4}$, $\text{Cr}^{+3} \rightleftharpoons \text{Cr}^{+2}$, etc.). The thermal energy associated with the electron transfer is, of course, zero, since the ground states are the same, but these solutions typically absorb in the region 2-3 eV.

There are a number of reasons for the difference in energy associated with the two types of transitions; two of these can be observed in the schematic configuration coordinate diagram of Fig. 1. Here the potential energies of the ground and excited states are plotted against some characteristic displacement of the system.

In the first place, optical transitions are subject to the Franck-Condon principle, while thermal transitions are not. Optical transitions occur rapidly compared with nuclear motions, so that they are represented vertically (or nearly so, subject to the uncertainty principle) on configuration coordinate diagrams. Thermal transitions are much slower and can take advantage of nuclear rearrangement.

In the second place, the mixing of states by configuration interaction is a common phenomenon. This results from partial relaxation of the Born-Oppenheimer condition due to spin-orbital or electron-lattice coupling. In a solid of the complexity of those considered here, there will always be an appropriate vibration to mix two states of almost any symmetry. As can be seen from Fig. 1, configuration interaction can increase significantly the difference between the energies associated with optical and thermal transitions.

There are two other important factors not illustrated in Fig. 1. Optical processes are subject to selection rules ($g \rightarrow u$ or $u \rightarrow g$). In the time scale associated with these thermal transitions, any selection rules formally associated with them are relaxed. Since there can be energy differences of the order of 1 eV or more between the highest occupied levels of g and u parity, this factor can make a significant contribution to the difference under consideration.

Finally, one must recognize that the diagram in Fig. 1 is grossly oversimplified in two ways. In the first place, it indicates only a single configuration coordinate. In a pressure-induced thermal process, the pressure selects the volume of the system as the appropriate configuration coordinate. Optical processes in general involve more configuration coordinates, which can serve also to increase the difference in energy in-

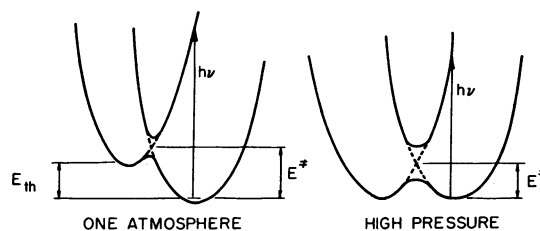


Fig. 1. Schematic configuration coordinate diagram.

volved in the two processes. In the second place, the electronic states are shown as nondegenerate, whereas for many systems (e.g., the excited states of the F-center in crystals of alkali halides) electronic degeneracy exists that puts into question the whole Born–Oppenheimer approximation on which such configuration coordinate pictures are based. This problem has been discussed by Henry, Schnatterly, and Slichter (3). These, in fact, are limiting factors in the analysis presented below. The radiationless transition of the optically excited electron to the bottom of the excited-state potential well must be a multiphonon process. Between the molecular vibrations and the lattice vibrations, there would appear always to be ample modes available to dissipate the energy.

There have been several theoretical treatments of one aspect or another of electron transfer processes at zero pressure by Marcus (4, 5) and Hush (6, 7). Henry, Schnatterly, and Slichter (3), and Henry and Slichter (8) considered the effect of pressure and other stresses on optical spectra, and included the effects of electronic degeneracy. They, however, treat only the case for which the spring constants of the various normal modes are the same for the ground and excited electronic states. We give below a simplified analysis that extends the work of these authors to include the effect of pressure for differing spring constants, but we do not include electronic degeneracy.

A schematic diagram is presented in Fig. 2. We assume initially a single configuration coordinate, Q , and harmonic potential wells with different force constants, ω and ω' , for the ground and excited states, respectively. At zero pressure, the value of Q corresponding to the minimum of the potential well of the excited state is displaced from that of the ground state by Δ . The energy difference between the bottoms of the two wells is E_{th} , which at zero pressure, we label E_0 . The quantities E^+ and E^- are discussed later. Addition of an external pressure displaces the equilibrium values of Q for both ground and excited states. Its effect is like adding a gravitational force to the problem of a mass on a spring. We, therefore, take the ground state potential energy, V_g , to be

$$V_g = \frac{1}{2}\omega^2 Q^2 + pQ. \quad [1]$$

In the second term on the right, one assumes that the pressure works against an area A that is independent of pressure, so that it can be incorporated into p or Q . Similarly, for the excited state one can write

$$V_e = \frac{1}{2}(\omega')^2(Q - \Delta)^2 + pQ + E_0. \quad [2]$$

At the potential minimum

$$\frac{\partial V_g}{\partial Q} = 0 = \omega^2 Q + p \quad [3]$$

so

$$Q = \frac{-p}{\omega^2} \quad [4]$$

and

$$\frac{\partial V_e}{\partial Q} = 0 = \omega'^2(Q - \Delta) + p \quad [5]$$

so

$$Q - \Delta = \frac{-p}{\omega'^2}. \quad [6]$$

We assume throughout this part of the analysis that ω and ω' are independent of pressure. Then,

$$(V_g)_{\text{min}} = -\frac{1}{2} \frac{p^2}{\omega^2} \quad [7]$$

and

$$(V_e)_{\text{min}} = p\Delta - \frac{p^2}{2\omega'^2} + E_0. \quad [8]$$

If we let $Q' = Q + (p/\omega^2)$, $Q' = 0$ is then the bottom of the new ground state. Substituting in [1] and [2], we get

$$V_g = (V_g)_{\text{min}} + \frac{1}{2}\omega^2 Q'^2 \quad [9a]$$

and

$$V_e = (V_e)_{\text{min}} + \frac{1}{2}\omega'^2(Q' - \Delta')^2, \quad [9b]$$

where

$$\Delta' \equiv \Delta + p \left[\frac{1}{\omega^2} - \frac{1}{\omega'^2} \right]. \quad [10]$$

Eq. [9] shows that we can eliminate the explicit pressure dependence by going to a new coordinate Q' and considering harmonic wells of altered energies and relative displacements in coordinate, but of unaltered spring constants, a result familiar to many.

Then E_{th} , the difference between the potential wells, is

$$E_{\text{th}} = E_0 + p\Delta + \frac{p^2}{2} \left[\frac{1}{\omega^2} - \frac{1}{\omega'^2} \right]. \quad [11]$$

At zero pressure

$$h\nu_{\text{max}} = E_0 + \frac{1}{2}\omega'^2\Delta^2 \quad [12]$$

so, at pressure p

$$h\nu_{\text{max}} = E_{\text{th}} + \frac{1}{2}\omega'^2\Delta'^2 \quad [13]$$

$$= E_0 + p\Delta + \frac{p^2}{2} \left[\frac{1}{\omega^2} - \frac{1}{\omega'^2} \right] + \frac{\omega'^2}{2} \left[\Delta + p \left[\frac{1}{\omega^2} - \frac{1}{\omega'^2} \right] \right]^2. \quad [14]$$

From Eqs. [13] and [14], we see that there are two components that affect the shift of the optical absorption peak maximum with pressure. In addition to the vertical displacement of the potential wells (the change in E_{th}), there is also the possibility of a horizontal displacement along the configuration coordinate (a change from Δ to Δ'), that is to say, different spring constants for the ground and excited states along that coordinate. Since these may have opposing effects on ν_{max} , a relatively small change in location of the optical absorption peak maximum may be consistent with a significant change in E_{th} .

We shall now develop a formula for the peak width. We shall first define a width δE , which is proportional to but not equal to the Gaussian half-width $\delta E_{1/2}$, and then transfer to the latter value.

For a harmonic oscillator, one can express the energy at the terminal points of the oscillation Q^\pm , (for simplicity we neglect zero-point effects since they are unimportant at the temperatures that the experiments were performed):

$$\frac{1}{2}\omega^2 Q^2 = \frac{1}{2}kT \quad [15]$$

$$Q^\pm = \pm \left[\frac{kT}{\omega^2} \right]^{1/2}. \quad [16]$$

Note $|Q^+| = |Q^-|$. Then, referring to Fig. 2

$$E^+ = E_0 + \frac{1}{2}\omega'^2(Q^+ - \Delta)^2 - \frac{1}{2}\omega^2(Q^+)^2 \quad [17]$$

$$E^- = E_0 + \frac{1}{2}\omega'^2(Q^- - \Delta)^2 - \frac{1}{2}\omega^2(Q^-)^2. \quad [18]$$

Then, for zero pressure

$$(\delta E)_{p=0} \equiv |E_+ - E_-| = \left| \frac{-2\omega'^2\Delta}{\omega} (kT)^{1/2} \right| \quad [19]$$

At $p \neq 0$, we simply replace Δ by Δ' , so

$$(\delta E)_p = \left| \frac{-2\omega'^2}{\omega} \left[\Delta + p \left[\frac{1}{\omega^2} - \frac{1}{\omega'^2} \right] \right] (kT)^{1/2} \right| \quad [20]$$

This equation contains the important implication that the peak width changes with pressure only if $\omega' \neq \omega$, i.e., if the spring constants of the two states are different.

This result agrees with the "rigid shift" theorem of Henry, Schnatterly, and Slichter. They showed that when $\omega = \omega'$, the changes in the first three moments of the optical absorption line produced by pressure are consistent with the rigid displacement of the line in energy without change in shape. At $p = 0$,

$$h\nu_{\max} = E_0 + \frac{1}{8} \frac{(\delta E)^2 \omega^2}{kT \omega'^2}. \quad [21]$$

This equation will, however, hold at any pressure, since Δ , and thus Δ' , has been eliminated. Following Hush (7), one can transform from the width δE to the half width of a Gaussian peak $\delta E_{1/2}$, then:

$$h\nu_{\max} = E_{\text{th}} + \frac{1}{16 \ln 2} \frac{(\delta E_{1/2})^2 \omega^2}{kT \omega'^2}. \quad [22]$$

At 25°, if one expresses $\delta E_{1/2}$ in eV, one obtains

$$h\nu_{\max} = E_{\text{th}} + 3.6(\delta E_{1/2})^2 \frac{\omega^2}{\omega'^2}. \quad [23]$$

This constitutes a relationship between observed maxima for optical absorption, the thermal energy, and the half width of the peak observed. Several limitations are discussed below. Nevertheless, some interesting comparisons between systems can be made. Unfortunately, most of the optical absorption measurements made so far at high pressure are not sufficiently accurate to use these equations in their full strength. When Eq. [23] relating $h\nu_{\max}$, E_{th} , and $\delta E_{1/2}$ is used, it is usually necessary to make a rough estimate of the ratio $(\omega/\omega')^2$. For several systems where calculations can be made, the factor is in the range 0.9–0.98, even when the half-width changes by 50% in 100 kbars. Thus, for rough calculations of the pressure where $E_{\text{th}} = 0$, even the assumption $(\omega'/\omega)^2 = 1$, which is not strictly consistent with a pressure-dependent peak half-width (see Eq. [19]) gives a reasonable approximation.

From the above equations one can derive several expressions that should be subject to evaluation from sufficiently precise data:

$$\left(\frac{\partial h\nu_{\max}}{\partial p} \right) = \frac{\omega'^2}{\omega^2} \left[\Delta + p \left(\frac{1}{\omega^2} - \frac{1}{\omega'^2} \right) \right] \quad [24]$$

$$\left(\frac{\partial h\nu_{\max}}{\partial p} \right)_{(p=0)} = \frac{\omega'^2}{\omega^2} \Delta \quad [25]$$

$$\left(\frac{1}{\delta E_{1/2,0}} \right) \frac{\partial \delta E_{1/2}}{\partial p} = \frac{(1/\omega^2) - (1/\omega'^2)}{\Delta} \quad [26]$$

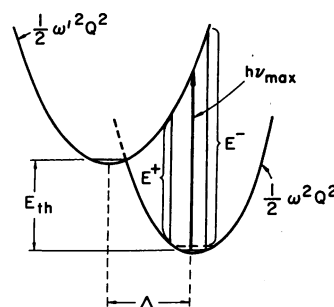


FIG. 2. Schematic diagram defining transition variable.

There are several limitations on the above results, some of which can be rather easily removed. It is probable that ω and ω' are dependent on pressure. As a first assumption, it is possible that terms like (ω'^2/ω^2) vary slowly with pressure compared with $\tau = [1/\omega^2 - 1/\omega'^2]$. Then

$$\frac{\partial h\nu_{\max}}{\partial p} = \frac{\omega'^2}{\omega^2} (\Delta + p\tau) + p \frac{\partial \tau}{\partial p} \left[\frac{p}{2} + \omega'^2(\Delta + p\tau) \right] \quad [27]$$

$$\frac{1}{(\delta E_{0(1/2)})_0} \frac{\partial \delta E_{1/2}}{\partial p} = \frac{\tau + p(\partial \tau / \partial p)}{\Delta} \quad [28]$$

It requires, of course, very accurate data to distinguish these equations from Eq. [24] and [26].

A serious approximation involved in this calculation is the assumption of a single configuration coordinate. As indicated earlier, optical transitions generally involve coordinates other than the volume. More generally, one must recognize that the pressure couples to several modes, so that the extra potential energy arising from pressure, V_p , becomes

$$V_p = p \sum_i c_i Q_i \quad [29]$$

We find that

$$\Delta_i' = \Delta_i + p c_i \left[\frac{1}{\omega_i^2} - \frac{1}{\omega_i'^2} \right] \quad [30a]$$

$$(V_p)_{\min} = -\frac{1}{2} p^2 \sum_i \frac{c_i}{\omega_i^2} \quad [30b]$$

and so forth (i.e., p is replaced by $p c_i$, and the quantities Δ , Δ' , ω , ω' acquire subscripts i)

$$h\nu_{\max} = E_{\text{th}} + \frac{1}{2} \sum_i \omega_i'^2 \Delta_i'^2 = E_{\text{th}} + \frac{1}{16kT \ln 2} \sum_i (\delta E_{i,1/2})^2 \frac{\omega_i'^2}{\omega_i'^2} \quad [31]$$

If we define an average ratio of the squares of the spring constants

$$\left\langle \frac{\omega_i'^2}{\omega_i^2} \right\rangle \equiv \frac{\sum_i (\omega_i'^2/\omega_i^2) (\delta E_{i,1/2})^2}{(\delta E_{1/2})^2}, \quad [32]$$

where $(\delta E_{1/2})^2$ is the total Gaussian half-width of the optical line, we get the relation

$$h\nu_{\max} = E_{\text{th}} - \frac{(\delta E_{1/2})^2}{16kT \ln 2} \left\langle \frac{\omega_i^2}{\omega_i'^2} \right\rangle \quad [33]$$

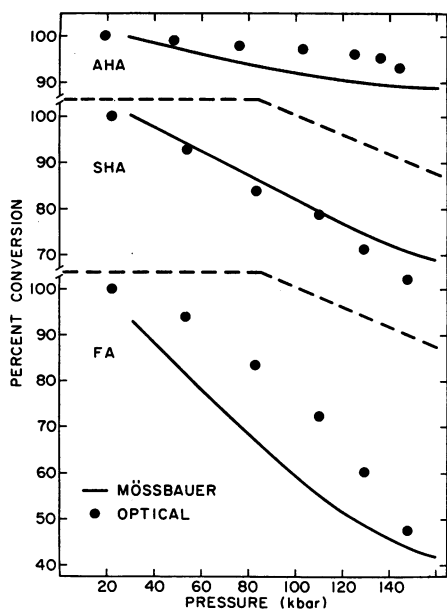


FIG. 3. Comparison of conversion of Fe(III) to Fe(II) with pressure, as measured by optical absorption and Mössbauer resonance for three ferric hydroxamates. *AHA*, tris-(acetohydroxamato)iron; *SHA*, tris-(salicylhydroxamato)iron; *FA*, ferrichrome A.

If we represent the physical system by only a few normal modes, and assume pressure couples to only one, Eq. [24] and [25] remain the same except that subscripts 1 are added to ω , ω' , Δ , and Eq. [26] is replaced by

$$\left| \frac{\partial(\delta E_{1/2})}{\partial p} \right| = \left| \frac{2\omega_1'^2}{\omega_1^2} \left(\frac{1}{\omega_1^2} - \frac{1}{\omega_1'^2} \right) \right| (kT)^{1/2}. \quad [34]$$

Again we note that the difference between ω_1^2 and $\omega_1'^2$ is responsible for the pressure dependence of the width.

If we assume a value for $\langle \omega_1/\omega_1'^2 \rangle$ we can apply Eq. [33] to compute E_{th} from measured $h\nu_{max}$ and $(\delta E_{1/2})^2$.

The effect of applied shear is sometimes of interest since it gives information about coupling to displacements other than volume changes, as is shown in the work of Henry, Schnatterly, and Slichter (3). In the context of the analysis presented here, shear could affect the magnitude of the variables Δ , ω , ω' , and E_{th} , defined in Fig. 2. Large shear distortions could remove degeneracies among normal modes and increase the importance of some configuration coordinates that are not significant for thermal processes under purely hydrostatic conditions. It could also intensify or otherwise modify configuration interaction. The magnitude of the energy barrier between the two ground states, discussed below, could be affected by strong shear forces. In principle, shear effects, as well as hydrostatic effects, are scientifically interesting, but the presence of a large and unresolved component of shear associated with a quasi-hydrostatic experiment could complicate the analysis.

It is at times of use to calculate the energy E^\ddagger , exhibited in Fig. 1 at the intersection between the potential wells, as an approximation to the energy barrier between the two ground states. For the case $\omega = \omega'$, analyses by Marcus (4, 5) and

Hush (6, 7) give for this energy:

$$E^\ddagger = \frac{(h\nu_{max})^2}{4(h\nu_{max} - E_{th})}, \quad [35]$$

which also holds for the case of multiple configuration coordinates.

The analysis for $\omega \neq \omega'$ gives a much more complex relationship, which is not of quantitative use in view of the limitations discussed below. In the first place, configuration interaction, as illustrated qualitatively in Fig. 1, insures that the energy barrier will be less than E^\ddagger . Hush (7) has presented an analysis for the system $Cr^{+3}-Cr^{+2}$ with H_2O ligands. He showed that the difference between E^\ddagger and the top of the barrier increases rapidly with decreasing distance between oxygens, and should therefore increase with pressure.

In the second place, tunnelling through the barrier could reduce the effective barrier height, although for the relatively heavy atoms typically involved in the high-pressure studies discussed here, the probability of tunnelling is not high. Nevertheless, Eq. [35] may be useful as a first approximation for comparison of the relative change in the barrier with pressure for a series of related compounds.

So far there is only a limited amount of data that relates the location and half width of an optical absorption peak in a semiquantitative way to a thermal electron transfer process at high pressure. We discuss briefly two such sets of results.

The reduction of ferric iron to the ferrous state has been observed at high pressure in a wide variety of solids. The experimental observations and the pressure dependence of the conversion have been discussed in detail elsewhere (9-11). The mechanism involves the transfer of a ligand electron from a nonbonding π orbital to a metal d_π orbital, which is nonbonding or slightly antibonding. The reduction is identified by the change in the Mössbauer resonance spectrum, since high-spin ferrous and ferric ions have quite distinct spectra. It typically takes place over a considerable range of pressure. A study of reduction has recently been published (12) involving three ferric hydroxamate derivatives that are models for biologically active compounds, and one biological hydroxamate, ferrichrome A. The model compounds studied include tris-(acetohydroxamato)iron(III), tris-(benzohydroxamato)iron(III), and tris-(salicylhydroxamato)iron(III). The conversions are typically obtained by measurement of the relative areas under the ferrous and ferric Mössbauer resonance peaks. The area under the optical ligand to metal charge-transfer peak should also reflect the reduction (the fraction of ferric sites available), modified, however, by the increase in transition probability with increased overlap. Results for two of the model compounds and ferrichrome A are presented in Fig. 3.

TABLE 1. Optical versus thermal transitions: ferric hydroxamates and ferrichrome A for 10% reduction of Fe(III)

Compound	Pressure	$h\nu_{max}$	$\Delta E_{1/2}$	E_{th}
Tris-(acetohydroxamato)iron	125	2.80	0.90	-0.11
Tris-(benzohydroxamato)iron	105	2.70	0.875	-0.06
Tris-(salicylhydroxamato)iron	70	2.54	0.84	-0.02
Ferrichrome A	37	2.65	0.835	+0.11

Energies in eV, pressures in kilobars.

TABLE 2. Thermal versus optical transitions $\pi-\pi^*$ for phenanthroline

Pressure	$h\nu_{\max}$	$\Delta\nu_{1/2}$	E_{th}
0	4.6	0.95	+1.35
50	4.45	1.05	+0.45
100	4.30	1.14	-0.40
150	4.20	1.20	-0.98

Energies in eV, pressures in kilobars.

The correspondence between optical and Mössbauer results is quite satisfactory. The discrepancy is larger for ferrichrome A than for the model compounds. The peaks in the atmospheric Mössbauer spectrum of ferrichrome A are considerably broadened by magnetic hyperfine splitting (13), so that the estimation of areas is quite difficult, especially at lower pressures.

It is possible also to apply Eq. [33] to the optical data if we assume a value for $\langle\omega_i^2/\omega_i'^2\rangle$. In Table 1 we see the value for E_{th} , the ground state energy of the reduced state, relative to the oxidized state, from the values of ν_{\max} and $\Delta E_{1/2}$, corresponding to the pressure where there is 10% reduction if we assume $\langle\omega_i^2/\omega_i'^2\rangle = 1$. For the three model compounds, E_{th} is slightly negative. For ferrichrome A, E_{th} is slightly positive. Thus, E_{th} has been reduced to a value where one would expect significant conversion.

A second type of electronic transition involves a change in spin state of ferrous iron. Ferrous complexes with molecules that have available π^* orbitals tend to have relatively large ligand fields, because the backdonation of metal d_π electrons into these empty ligand π^* orbitals stabilizes the d_π orbitals. If the ligand field is sufficiently large, the iron may be in the diamagnetic low-spin state instead of the state of maximum multiplicity (high spin) predicted by Hund's rule. The spin state at high pressure can be identified from the Mössbauer spectrum. The ferrous phenanthroline complexes provide an example of this phenomenon. There are two types of complexes with quasioctahedral symmetry. The bis-(phenanthroline) complexes involve two phenanthrolines occupying four coordination sites, with anions on the other sites. In the Tris complexes, phenanthrolines occupy all coordination sites. At 1 atm, the Bis complexes are generally high spin, but with a crystal field near the crossover point. The Tris complexes are low spin. The effect of pressure on the spin state has been rather extensively studied (14, 15). At modest pressures in

most Bis complexes, the iron begins to transform from high to low spin. By 40 kbars the transformation stops, and at higher pressures in many Bis complexes there is a net low-spin to high-spin transformation. The Tris complexes of low spin initiate transformation to the high-spin state near 30 kbars, and may transform 25–30% by 150 kbars.

It has been shown that the $\pi-\pi^*$ transition lying near 4–4.5 eV shifts to lower energy and broadens with increased pressure. It is postulated that partial thermal occupation of the ligand π^* orbitals by ligand electrons reduces the backdonation and, therefore, the ligand field. It is possible to make an approximate calculation of the relative thermal stability of the π^* and π orbitals (again assuming $\omega \cong \omega'$) by the use of high-pressure optical absorption data (14). The results are shown in Table 2. At atmospheric pressure, the π orbital is stable by over an electron volt. Somewhere above 50 kbars the π^* orbital becomes lower in energy. The transformation actually initiates at about 30–40 kbars, but in view of the approximations involved the agreement is reasonable.

The availability of accurate high-pressure optical absorption data on condensed systems should make possible the prediction of electronic transitions by thermal processes in transition metal and rare earth compounds, as well as in various organic compounds involving conjugated π systems.

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