

Pressure Tuning Spectroscopy

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A fundamental effect of compression for condensed phases is to decrease interatomic and intermolecular distances and to increase overlap of the outer electronic orbitals. Since the spacial characteristics of various types of orbitals are different, their energies are perturbed in different degrees by compression. The study of these energy perturbations is well characterized as "pressure tuning spectroscopy" (PTS). Since the optical, electrical, magnetic, and chemical properties of condensed phases depend on the characteristics and spacing of the energy levels, the applications and implications of PTS are very broad. They include such various topics as insulator-conductor transitions, the band structure and impurity levels of semiconductors, the electronic structure of alkali, alkaline earth, and rare earth metals, the magnetic characteristics and spin state of metals and magnetic insulators, energies, efficiencies, and rate processes in inorganic and organic phosphors, protein conformation in solution, and chemical reactivity in molecular crystals and solutions. A number of these phenomena are discussed in recent reviews.¹⁻⁴ (The wide variety of high-pressure optical techniques used for PTS are described in the papers cited here as well as in references contained in those papers.)

In this paper we confine ourselves to some recent investigations of high-pressure optical absorption which illustrate how pressure tuning experiments can increase our understanding of electronic interactions and electronic excitations in molecular crystals and solutions, and crystals containing large molecular ions.

As two molecular fragments are brought together to react, a bonding orbital and an antibonding orbital (or a series of each), are formed. The first-order effect of compression is to stabilize the bonding orbital relative to the antibonding orbital. In this simple picture an excitation from a bonding to an antibonding orbital should increase in energy (blue shift) with increasing pressure. We are, however, dealing not with an isolated molecule, but with a molecule in a crystal lattice or solution where it interacts with other molecules of the same or different type. For molecular crystals and so-

lutions of crystals of large molecular ions the primary intermolecular interaction is an attractive one of the van der Waals type. The attraction can be expressed by the following proportion:

$$E \sim -\frac{\alpha_1\alpha_2}{R^6}$$

where R is the distance between interacting species, α_1 is the polarizability of the molecule or bond, and α_2 is the polarizability of the medium as seen by the electron cloud of the molecule. In general, although not always, the molecule is more polarizable when the electron is in the antibonding orbital since it is less tightly bound when in the excited state. The intermolecular interaction should then contribute a red-shift component to the effect of compression. The basic effect of polarizability is discussed in detail elsewhere.^{1,5} A major aspect of our discussion will be to present cases where there are different degrees of balance between intramolecular and intermolecular effects of compression.

TCNQ and Its Complexes

A recent study of the $\pi-\pi^*$ excitation in tetracyanoquinodimethane (TCNQ), its ion and three of its complexes illustrates a number of the above factors.⁶ In Figure 1 we show the shift of this excitation with pressure in the crystalline solid and with (TCNQ)⁰ dissolved in PMMA (poly(methyl methacrylate)) and PC (polycarbonate). The initial slopes are -41 and -28 $\text{cm}^{-1}/\text{kbar}$. The smaller rate of shift for the polymeric media is consistent with the lower polarizabilities of the polymers relative to the crystal.

A second set of observations involves $\text{K}^+(\text{TCNQ})^-$, $\text{TEA}(\text{TCNQ})_2$, and $\text{Qn}(\text{TCNQ})_2$ where K^+ is the potassium ion, TEA is the tetraethylammonium ion, and Qn is the quinolium ion. Figure 2 shows the shifts of (TCNQ)⁻ in PMMA and PC. Here it is possible to separate two vibrational levels. The shifts are the same for the three salts. The slopes are -3 and -5 $\text{cm}^{-1}/\text{kbar}$

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 (2) Drickamer, H. G. *Int. Rev. Phys. Chem.* 1982, 2, 171.
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 (4) Drickamer, H. G.; Schuster, G. B.; Mitchell, D. J. In *Radiationless Transitions* Lin, S. H., Ed.; 1980; p 289.
 (5) Brey, L.; Schuster, G. B.; Drickamer, H. G. *J. Am. Chem. Soc.* 1979, 101, 129.
 (6) Tkacz, M.; Jurgensen, C. W.; Drickamer, H. G. *J. Chem. Phys.* 1986, 84, 649.

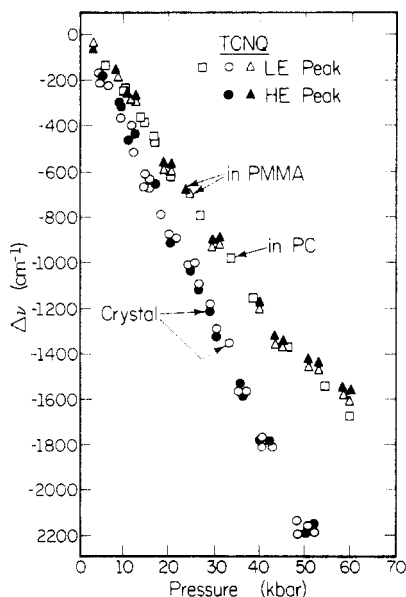


Figure 1. Peak shift vs. pressure $\pi \rightarrow \pi^*$ excitation for $(\text{TCNQ})^0$ in the crystalline solid and dissolved in PMMA.

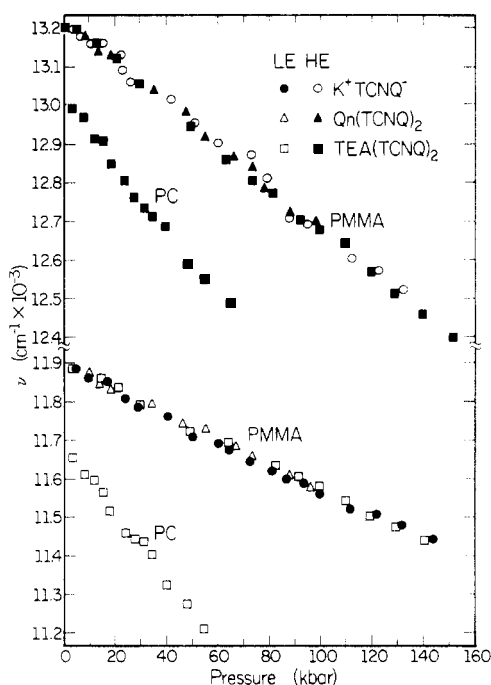


Figure 2. Shift of $\pi \rightarrow \pi^*$ excitation with pressure for $(\text{TCNQ})^-$ in PMMA and PC.

in PMMA and -8 and $-9 \text{ cm}^{-1}/\text{kbar}$ in PC. These are markedly smaller than the shifts for $(\text{TCNQ})^0$ in the same media. The extra electron occupies an antibonding orbital so that the excitation is between antibonding orbitals which offer only a little in polarizability. With these small shifts it is possible to observe the effect of the slightly larger polarizability of the PC versus PMMA (aromatic versus vinyl groups). The fact that the two vibrational modes show different shifts indicates an unusually large and environmentally sensitive shift of the excited state vibrational mode responsible for the splitting. Tanner's data (ref 7) also indicate that the vibronic splitting is sensitive to the environment.

(7) Tanner, D. B.; Miller, J. S.; Rice, M. J.; Ritsko, J. J. *Phys. Rev. Lett.* 1980, 13, 5835.

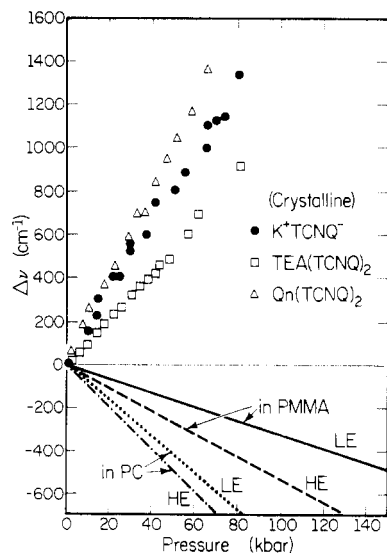


Figure 3. Shift of $\pi \rightarrow \pi^*$ excitation with pressure for three crystalline salts of $(\text{TCNQ})_2^{2-}$.

In Figure 3 we show the shifts attributed to this excitation for three crystalline complexes. In this case we observe shift attributed to this excitation for three crystalline complexes. In this case we observe shifts to *higher* energy of $+11$, $+17$, and $+19 \text{ cm}^{-1}/\text{kbar}$. In the crystalline state $(\text{TCNQ})^-$ exists as the dimer (2 TCNQ^{2-}). Here the effect of compression on the intradimer interactions dominates over the van der Waals intermolecular interactions. In order to accommodate to the different sizes of the cations the dimers assume somewhat different geometries in the three crystals which accounts for the different degrees of blue shift observed. This study illustrates how pressure tuning can separate the effects of differing environment and different occupation of electronic orbitals.

Metal Cluster Compounds

Metal cluster compounds provide a fruitful subject for the application of pressure tuning techniques. These compounds may involve anywhere from two to twenty metal atoms connected by metal-metal bonds stabilized by appropriate ligands. While there is much to be learned from high-pressure investigations of large clusters, in this review one shall restrict ourselves to two classes of relatively simple materials: (1) Binuclear clusters where, in first order, the orbitals involved in bonding between the metals can be classified as σ , π , or δ according to their angular momentum around the bond axis. (2) A trinuclear cluster where the spectrum allows one to extract the relative shifts of two bonding orbitals with respect to one another and of two antibonding orbitals with respect to one another.

For the binuclear clusters we emphasize here compounds of rhenium (Re) or manganese (Mn) with carbonyl or halide ligands. Molecular orbital calculations⁸⁻¹⁰ indicate that, in general, the highest energy bonding orbital is of δ symmetry, with a π orbital below that and a σ orbital at still lower energy. The antibonding orbitals lie in inverse order so that the $\delta-\delta^*$

(8) Levenson, R. A.; Gray, H. G. *J. Am. Chem. Soc.* 1975, 97, 6042.

(9) Bursten, B. E.; Cotton, F. A.; Fenwick, P. E.; Stanley, G. G. *J. Am. Chem. Soc.* 1983, 105, 3082.

(10) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms* 1982; pp 356-446.

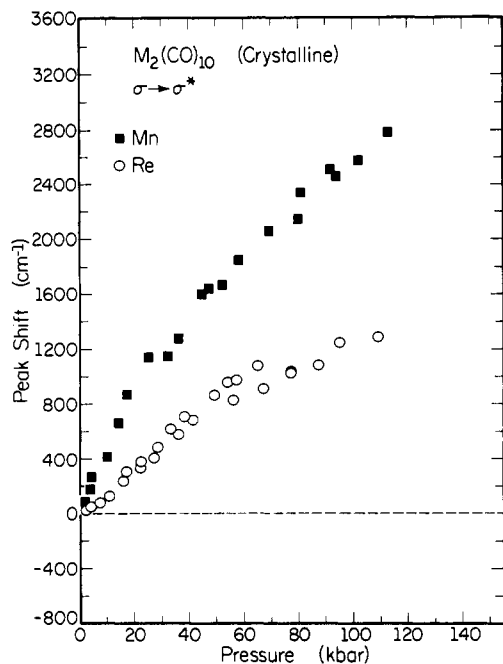


Figure 4. Shift of $\sigma \rightarrow \sigma^*$ excitation with pressure: crystalline $\text{Mn}_2(\text{CO})_{12}$ and $\text{Re}_2(\text{CO})_{12}$.

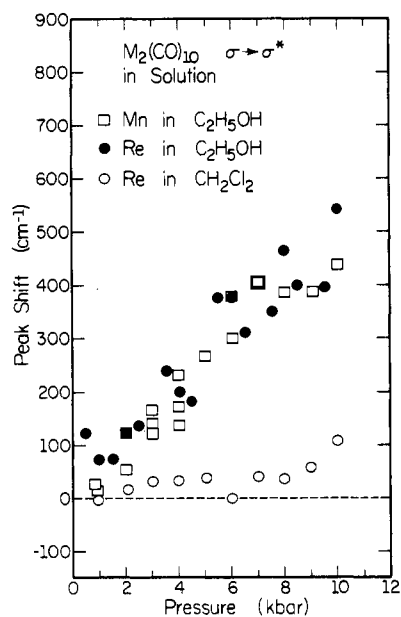


Figure 5. Shift of $\sigma \rightarrow \sigma^*$ excitation with pressure: $\text{Mn}_2(\text{CO})_{12}$ and $\text{Re}(\text{CO})_{12}$ in ethanol and $\text{Re}(\text{CO})_{12}$ in CH_2Cl_2 .

excitation is usually in the red part of the spectrum, the $\pi \rightarrow \pi^*$ lies in the blue or green, and the $\sigma \rightarrow \sigma^*$ in the near UV. For a variety of reasons including the presence of intense charge-transfer peaks, it is usually not possible to observe all three excitations in a single molecule.

The σ orbitals usually have their maximum density very close to the bond, the δ orbitals are most delocalized, and the π orbitals are intermediate.¹¹ Each type of excitation should then represent a different balance between intramolecular and intermolecular interaction.

In Figure 4 we exhibit the shift with pressure of the $\sigma \rightarrow \sigma^*$ excitation in $\text{Mn}_2(\text{CO})_{10}$ [$\nu_0 = 31900 \text{ cm}^{-1}$] and $\text{Re}_2(\text{CO})_{10}$ [$\nu_0 = 29500 \text{ cm}^{-1}$]¹² in the solid state. The

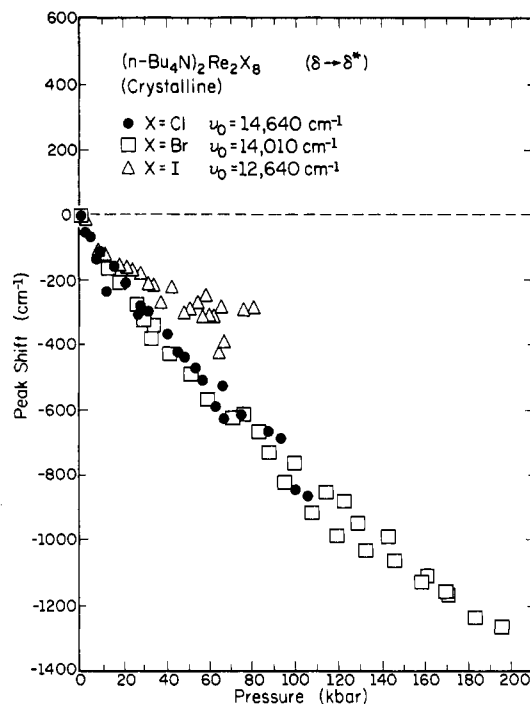


Figure 6. Shift of $\delta \rightarrow \delta^*$ excitation with pressure for crystalline tetrabutylammonium halides of rhenium.

Table I
Peak Locations and Assignments for $\text{Cs}_3\text{Re}_3\text{Cl}_{12}$

peak location, cm^{-1}	assignment
(1) 8300	$7e'' \rightarrow 2a_1''$
(2) 12700	$7e'' \rightarrow 8e''$
(3) 19000	$5a_2'' \rightarrow 8e''$

blue shifts indicate, as we might expect, that the intramolecular stabilization effect discussed at the beginning of the article is dominant. The initial shifts are 50 and $17 \text{ cm}^{-1}/\text{kbar}$, respectively. Intermolecular interactions are not negligible, however, as illustrated in Figure 5. Although the initial shifts with pressure in the solid state differ by a factor of almost three, in ethanol the shifts are substantially identical ($45 \text{ cm}^{-1}/\text{kbar}$). In the highly polarizable dichloromethane the blue shift for $\text{Re}_2(\text{CO})_{10}$ is only about $7.5 \text{ cm}^{-1}/\text{kbar}$, less than half that obtained for the solid.

To investigate the $\delta \rightarrow \delta^*$ and $\pi \rightarrow \pi^*$ excitations we turn to the tetrabutylammonium halides of rhenium. In Figure 6 we exhibit the shifts for the $\delta \rightarrow \delta^*$ excitations for the three halides in the solid state.¹³ The large red shifts obtained indicate that the van der Waals' interactions are dominant. It should be pointed out that an isomerization process taking place in the iodide affects the accuracy of the data.¹⁴ In Figure 7 we show the shift of the $\pi \rightarrow \pi^*$ excitation. Here the balance between intra- and intermolecular effects is more nearly equal, with a modest dominance for the former.

In general, pressure tuning studies measure the difference in energy between a bonding and an antibonding state. $\text{Cs}_3\text{Re}_3\text{Cl}_{12}$ is a trinuclear rhenium complex which provides the opportunity to measure the effect of pressure on the energy differences between a pair of bonding orbitals and between a pair of antibonding

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(14) Carroll, T. L.; Shapley, J. R.; Drickamer, H. G. *J. Am. Chem. Soc.* 1985, 107, 5802.

(11) Reference 10, p 439.

(12) Carroll, T. L.; Shapley, J. R.; Drickamer, H. G. *Chem. Phys. Lett.* 1985, 119, 340.

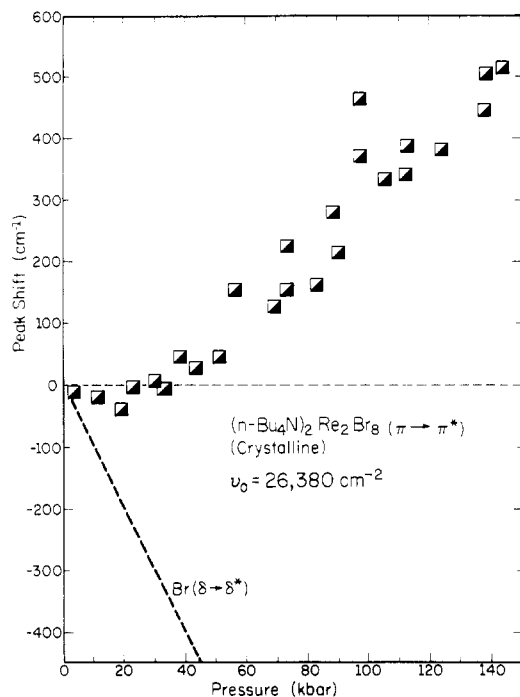


Figure 7. Shift of $\pi\text{-}\pi^*$ excitation with pressure for crystalline tetrabutylammonium bromide.

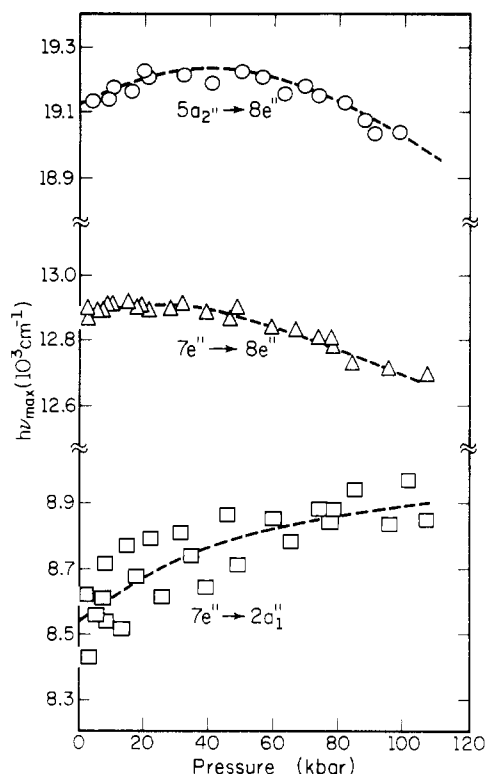


Figure 8. Peak shifts with pressure for three $\pi\text{-}\pi^*$ excitations in $\text{Cs}_3\text{Re}_3\text{Cl}_{12}$.

orbitals. The spectrum contains three peaks: one a very weak peak ($\epsilon \cong 40 \text{ M}^{-1} \text{ cm}^{-1}$) at 8300 cm^{-1} , a second with $\sigma \cong 450 \text{ M}^{-1} \text{ cm}^{-1}$ at 12700 cm^{-1} , and a third with ($\epsilon \cong 1600 \text{ M}^{-1} \text{ cm}^{-1}$) at 19000 cm^{-1} . These have all been assigned¹⁵ to metal $\pi\text{-}\pi^*$ excitations. The assignments are shown in Table I. The difference in shift between (1) and (2) gives the energy difference between two antibonding orbitals, while the difference in shift be-

(15) Bursten, B. E.; Cotton, F. A.; Greene, J. C.; Seddon, E. A.; Stanley, G. G. *J. Am. Chem. Soc.* **1980**, *102*, 955.

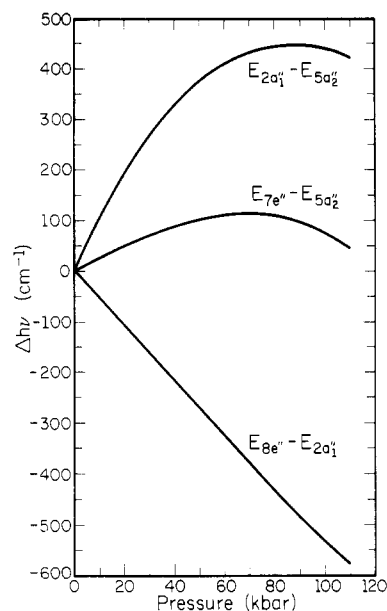


Figure 9. Energy differences (normalized at 0 at one atmosphere) vs. pressure for: (a) a pair of bonding orbitals ($E_{7e''} - E_{5a_2''}$), (b) a pair of antibonding orbitals ($E_{8e''} - E_{2a_1''}$), (c) a metal bonding and antibonding orbital ($E_{2a_1''} - E_{5a_2''}$).

tween (2) and (3) similarly compares to bonding orbitals.

Figure 8 exhibits the shifts of the three peaks with pressure to 110 kbar.¹⁶ These are the results of three separate loads. The scatter of the data from the low-energy peak location is due to its very weak intensity. The peaks were fit to least-squares polynomials as indicated by the dashed lines. The lower two curves of Figure 9 show the pressure shifts for the energy difference between two unoccupied metal-metal antibonding levels ($2a_1''$ and $8e''$) and between two occupied metal-metal bonding levels ($7e''$ and $5a_2''$). To establish the atomic parentage the z axis on each rhenium atom was chosen to lie in the plane of the triangle. The metal d orbitals capable of contributing to the $7e''$ and $8e''$ orbitals are the d_{xy} and the d_{yz} atomic orbitals; the symmetry adapted combination has one nodal plane between the metal atoms. The $5a_2''$ level should consist of rhenium d_{yz} orbitals in a totally metal-metal bonding combination (no nodes), while the $2a_1''$ level should consist of rhenium d_{xy} orbitals in a totally Re-Re antibonding combination with three nodes. We may, in first order, make the somewhat oversimplifying assumption that the differences among these levels are primarily the differences in the symmetry of the parent atomic d orbitals.

This assumption is not unreasonable for the two antibonding levels $8e''$ and $2a_1''$ since they both have $\sim 75\%$ metal character (almost entirely from atomic d orbitals)¹⁵ and the distribution of ligand character among terminal, bridging, and in-plane chlorines is nearly identical. Thus it appears that the atomic d_{yz} orbitals are stabilized in energy with increasing pressure relative to the d_{xy} orbitals.

The situation with respect to the bonding orbitals $7e''$ and $5a_2''$ is more complex. According to Bursten et al.¹⁵ they have only 59% and 42% Re character respectively and in the case of $5a_2''$ there are measurable contribu-

(16) Roginski, R. T.; Shapley, J. R.; Drickamer, H. G. *Chem. Phys. Lett.* **1986**, *127*, 185.

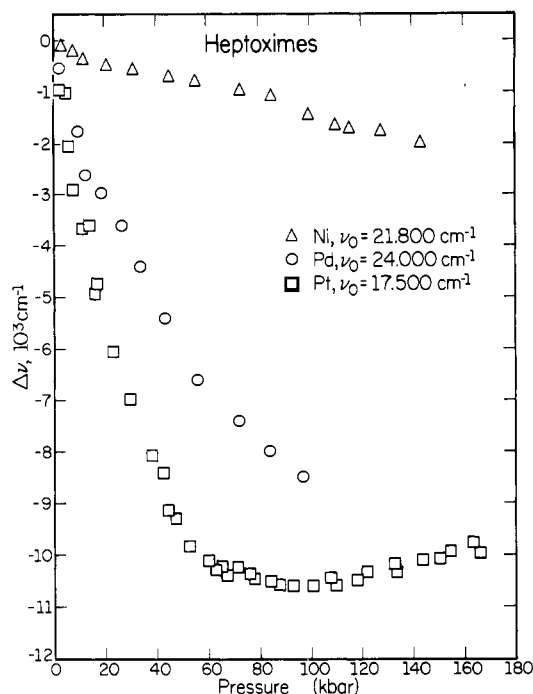


Figure 10. Shift of metal $d \rightarrow p$ excitation in nickel, palladium, and platinum heptoxime.

tions from metal p and f orbitals. Also, the distribution of ligand contributions among the three types of chlorines is markedly different for the two molecular orbitals. The shallow maximum shown in Figure 9 may represent a balance between a change in energy of the atomic d_{xy} orbitals with pressure and a redistribution of the various ligand contributions to the two energy states.

Further information can be extracted from the top curve in Figure 9, which shows the energy difference change between the $2a_1''$ and the $5a_2''$ levels. This difference initially shows a fairly large blue shift (initial slope $\sim 11 \text{ cm}^{-1}/\text{kbar}$) with a maximum energy difference of 450 cm^{-1} occurring near of 90 kbar. Since the $5a_2''$ level is metal-metal bonding with d_{yz} orbitals, and the $2a_1''$ level is metal-metal antibonding with d_{xy} orbitals, this trend directly shows the dramatic stabilization of the rhenium d_{yz} orbitals relative to the d_{xy} orbitals at low to intermediate pressures. However, as the pressure is further increased, there is some tendency towards stabilization of the $2a_1''$ level relative to the $5a_2''$ level, probably as a result of the significantly different (and possibly changing) ligand character in these levels.

Metal Chain Crystals—Intensity Borrowing

A subject of considerable interest in spectroscopy is intensity borrowing between electronic or vibrational states. A special case is Fermi resonance which involves intensity transfer between coupled vibrational levels. This has recently been shifted as a function of pressure and the effect of pressure tuning of vibrational levels has been demonstrated quantitatively in terms of agreement between theory and experiment.¹⁷⁻¹⁹ Intensity borrowing between two different electronic excitations is more complex and less susceptible to simple

(17) Schindler, W.; Zerda, T. W.; Jonas, J. *J. Chem. Phys.* **1984**, *81*, 4306.

(18) Zerda, T. W.; Bradley, M.; Jonas, J. *Chem. Phys. Lett.* **1985**, *117*, 566.

(19) Bradley, M.; Zerda, T. W.; Jonas, J. *J. Chem. Phys.* **1985**, *82*, 4007.

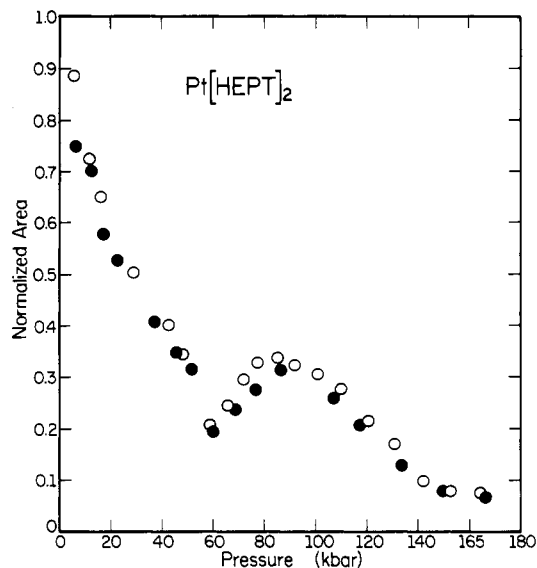


Figure 11. Normalized integrated intensity of $d \rightarrow p$ excitation peak in platinum heptoxime vs. pressure. The two sets of symbols indicate different loads.

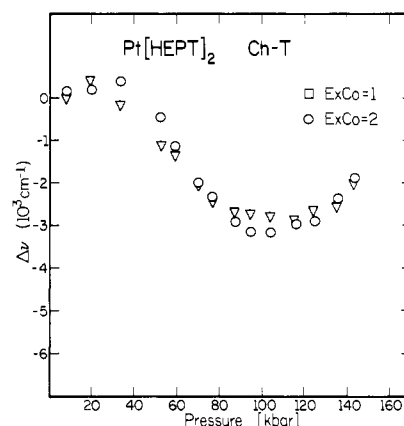


Figure 12. Shift of tail of charge-transfer peak vs. pressure at extinction coefficients of one and two for platinum heptoxime.

quantitative analysis. Nevertheless it can be well illustrated from high-pressure studies.

A variety of glyoxime ligands form complexes with d^8 metals. Many of these crystallize in layers with the complexes stacked with alternate molecules rotated 90° and, for symmetrical ligands, the metals form a chain.²⁰⁻²¹ In general, the distance between layered molecules is the same for the Ni, Pd, and Pt metal complexes so that it is established by the organic ligand. A rather intense absorption peak occurs in the visible region of the spectrum which is not present for the molecules in solution. It has been assigned to an interband nd to $(n+1)p$ excitation so that the excited states of predominantly $(n+1)p$ character are stabilized in the crystal with respect to the occupied levels. Figure 10 shows the change in peak location with pressure for nickel, palladium, and platinum heptoxime.²² The initial effect of compression is to increase this stabilization. This effect intensifies in the order $\text{Pt} > \text{Pd} > \text{Ni}$ because of the greater spacial extent of the orbitals with larger n value. At sufficiently high pressure the overlap repulsion of the platinum p orbitals with the molecules above and below causes a reversal of this

(20) Godycki, L. E.; Rundle, R. E. *Acta Crystallogr.* **1953**, *6*, 487.

(21) Ganks, G. V.; Barnum, D. J. *Am. Chem. Soc.* **1958**, *80*, 3579.

(22) Tkacz, M.; Drickamer, H. G. *J. Am. Phys.* **1986**, *85*, 1184.

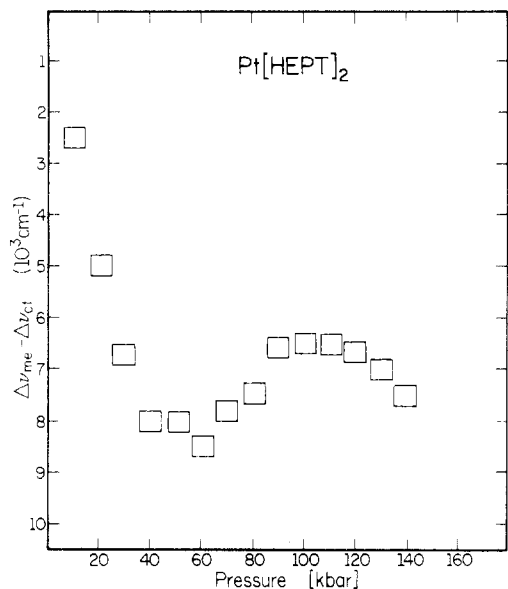


Figure 13. Difference in shift of the metal d to p excitation peak and shift of tail of charge transfer peak vs. pressure for platinum heptoxime. Note agreement with Figure 12.

process and a resultant blue shift. Similar shift behavior is observed for a variety of other metal glyoxime systems.²²

The intensity of the d \rightarrow p excitation has been the subject of some consideration. Ohashi et al.²³ ascribe a significant part of the intensity to intensity borrowing from the intraatomic metal to ligand charge-transfer peak which lies at higher energies. In Figure 11 we show the change in integrated intensity (area under the peak) with pressure for Pt(HEPT)₂. There is a large initial drop in intensity, followed by a rise from \sim 60 to 90 kilobars and a subsequent decrease. In Figure 12 we show the shift of the low-energy tail of the charge-transfer peak taken at extinction coefficients of one and two. Figure 13 exhibits the difference between the shift of d-p peak and the charge-transfer excitation. An increase in this difference should correspond to a decrease in intensity borrowing and a consequent decrease in integrated areas, and vice versa. As can be seen from Figures 11 and 13, the intensity changes and differences in energy mirror each other extremely closely. This is, then, a rather elegant demonstration of intensity-borrowing effects. Other glyoxime systems exhibit similar behavior although in a less dramatic fashion.

Summary of Further Possibilities for PTS

The above examples constitute only a sampling of the variety of possible pressure tuning studies of interest to chemists. We mention here a few experiments currently under way:

(23) Ohashi, Y.; Hanazaki, I.; Nagaura, S. *Inorg. Chem.* 1970, 9, 2551.

Electron donor acceptor complexes normally have a neutral ground state while the excited state is largely ionic. Pressure tends to stabilize the ionic state so that it is possible in some cases to establish this ionic state as the stable form at high pressure.

There exist "photochromic" materials which, when irradiated in an absorption peak in the ultraviolet develop a new absorption peak in the visible spectrum. Other, labeled "thermochromic" develop an absorption in the visible when heated. Normally these states are mutually exclusive, but with pressure it appears possible to change from photochromic to thermochromic behavior.

A variety of materials have been synthesized which contain metal ions in two different valence states. In some classes of these materials intervalence transfer can be observed via optical absorption, molecular spectroscopy of Mossbauer resonance. The study of pressure effects on intervalence transfer is in its initial stages, but it is clear that pressure can change the rate of intervalence transfer significantly.

Preliminary investigations indicate that a number of metal-cluster compounds isomerized under pressure with change in the types of electronic excitations discussed earlier in the text as well as in the infrared spectrum. These isomerizations may be either continuous over a large pressure range or discontinuous (first order).

High pressure is proving to be a powerful tool for studying solvent effects on such phenomena as radiative and nonradiative rates of luminescent decay, electron-transfer processes, and reactivity. With pressure one can vary such macroscopic properties as viscosity, dielectric constant, etc. at constant temperature which can provide definitive tests of theories of these phenomena.

The theme of this paper is the pressure tuning spectroscopy of electronic excitations, but pressure tuning of molecular spectra (vibrational and rotation) can also be studied by means of infrared or Raman spectra. A variety of information can be extracted concerning attractive and repulsive molecular interactions, vibrational force constants, vibrational dephasing, and relaxation phenomena. It is also possible to follow the rates of chemical processes such as isomerization from such spectra.

One can expect to see this powerful tool more and more widely used in modern chemistry.

I would like to acknowledge the central role of my students and co-workers and, in particular, the contributions of Professor John Shapley to the metal-cluster work have been essential. Support from the Materials Science Division of the Department of Energy under contract DE-AC02-76ER01198 is gratefully acknowledged.

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