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Effects of high external pressures on the electronic spectra of coordination compounds

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Dedicated to Professor Barry Lever on his 65th birthday

Contents

Abstract

The use of pressure to perturb the electronic and physical structure of coordination compounds provides an important insight into the nature of the interaction between a transition-metal center and the surrounding ligands as well as intermolecular interactions. This perturbation of the electronic structure has become known as 'pressure-tuning' — a

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technique which has found many applications in science. These types of measurements can reveal interesting phenomena such as changes in electronic spectra due to structural distortions (piezochromism), spin-crossovers (changing the ground electronic state of the coordination compound), changes in the ligand-field causing shifts in electronic transitions, and changes in radiative processes and emitting states. When the conventional theoretical parameters for analyzing electronic spectra are adapted to accommodate pressure as a variable, changes to the electronic spectra of coordination compounds can be rationalized and explained. The diamond-anvil cell, DAC, is the most widely used device to apply pressure to a sample. For applications in electronic spectroscopy, there are several types of DACs that are used to study perturbations of electronic energy levels. In this review, some examples of the effects of pressure-tuning on the electronic energy levels of coordination compounds will be described. These examples will be grouped according to the particular electronic phenomenon exhibited upon application of pressure or the class of coordination compounds studied. Also, the most common DACs currently available for high-pressure research will be illustrated and the techniques for their use will be discussed.

Keywords: Pressure-tuning; Electronic spectroscopy; Coordination compounds; Diamond-anvil cell; Transition-metal complexes

1. Introduction

The application of pressure to a coordination compound, either as a solid or in solution, brings about changes to the electronic spectra and reveals useful information about the structural and electronic features of such compounds. Changes to the electronic spectra upon compression, will provide insight into the environment of the transition-metal center and enable the experimentalist to design a coordination system to fit a specific application or to test a theory.

There are a number of excellent general and specific review articles [1–9], books [10–12], and other contributions [13–16] that have already dealt with many aspects of pressure-tuning electronic and vibrational spectroscopy. For a recent review covering many important contributions in the last 15 years of pressure-tuning applications in mainly vibrational spectroscopy, see Ref. [17]. This present review will, however, focus on the pressure behavior of some selected coordination compounds and the important theoretical considerations behind the observed phenomena.

When studying pressure effects on the electronic spectra of coordination compounds, we are primarily concerned with ligand-field, or d–d, electronic transitions. Depending on the nature of the ligands, other electronic transitions can exist such as intraligand π–π^* and metal $\rightarrow$ ligand and ligand $\rightarrow$ metal charge-transfer transitions (MLCT and LMCT, respectively). It is these observable electronic features of particular ligands that are interesting when applying pressure to study possible effects on metal–ligand interactions. Typically, one considers pressure effects on the ligand-field splitting, Δ, together with the Racah parameters, B and C, as a means of quantifying the interactions between the metal(s) and ligands as a function of

pressure. By and large, authors use plots that relate these parameters as the ordinate, to pressure, as the abscissa, to understand the behavior of the electronic spectra under pressure.

The net effect of pressure is to decrease the sample volume, which generally results in an increase of the frontier MO overlap and affects the metal–ligand bond distances. This perturbation will then alter the parameters describing the electronic environment of the transition-metal center and bring about observable changes in the electronic spectra of the coordination compound. These changes are, in general, a result of the bonding character and topology of specific MOs being altered. As the molecular geometry and, subsequently, electronic structure become altered, shifts in electronic transition bands and changes in band shape tend to occur. The degree to which these changes will be noticeable in the spectra will depend on the transition-metal center, symmetry of the complex, and the electron population of the d-orbitals. The effects of structural rearrangements on the electronic spectra of coordination compounds under pressure are usually explained by the changes to ligand-field energy levels although this is more accurately described by configuration coordinate diagrams with states that move vertically and horizontally as well as changing the shape of the potential energy surfaces. Since pressure shifts electronic energy levels, there is a possibility of excited-state electronic energy levels, in close proximity, interacting significantly and causing drastic changes in the electronic and magnetic properties of the system. According to Drickamer and Frank, pressure can bring about these sorts of changes to a coordination compound system, especially where gaps between allowed and forbidden energy levels are decreased to allow a noticeable interaction [11]. In addition, there have been several theoretical models for pressure effects on molecular electronic spectra that take this situation into account [18–22]. Much of this work has stemmed from the original Drickamer, Frank, and Slichter model [18] for the effects of pressure on molecular electronic spectra and provides a physical basis for understanding these effects in a quantitative manner.

Because the ligand-field and geometry of a complex influence its electronic properties and spectra, it is important to consider how changes in molecular geometry under pressure occur and the mechanistic pathways by which these changes proceed. To assist in understanding these phenomena, Ferraro and Long have suggested applying orbital symmetry rules to high-pressure work to explain solid-state structural interconversions [12,37]. These orbital symmetry rules suggest that a molecular rearrangement will take place along a particular normal coordinate as pressure is applied to a solid coordination system and lead to a more energetically favorable configuration for that pressure. In general, for pressure-tuning applications, it is well known that pressure couples most favorably with the totally symmetric normal vibrations [11]. The rules then predict that the most energetically favored distortion of the original molecular geometry, which leads to a new point group symmetry of the molecule, will be the result of the displacement of a normal coordinate representation possessing the same symmetry as the product of the HOMO and LUMO wavefunctions of the molecule. However, because of the various competing effects of solid-state interactions, this may not always be

observed in pressure-tuning applications in spectroscopy since these forces exert a strong influence on molecular geometry and also change significantly upon compression. The orbital symmetry rules do not take into consideration how these intermolecular forces will be affected by the application of pressure to the system and the consequent effects on intramolecular properties. To understand the role of intermolecular effects in solid-state changes to molecular geometry under pressure, the occurrence of phase transitions and careful monitoring of vibrational spectra will be important in correlating these effects to changes in the pressure-tuned electronic spectra. Although the potential utility of the orbital symmetry rules is most appealing to applications in pressure spectroscopy, there have been no detailed studies into the possibility of using this theory. However, such a knowledge of allowed molecular geometries, i.e. a structural pathway, as a function of pressure would be most beneficial when interpreting pressure-tuned electronic spectra.

To better appreciate how pressure can alter the electronic structure of coordination compounds, it is first necessary to give a brief overview into how pressure is actually applied to the sample and what can be expected to take place. Pressure spectroscopists, mainly Drickamer and Frank [11] and Ferraro [12], have classified, somewhat qualitatively, four possible changes that can occur when pressure is applied to a typical coordination compound.

It must be emphasized that any variation of pressure, no matter how small, will bring about some changes in both the physical and electronic structure of a coordination compound, and so Table 1 simply gives the reader an idea of how pressure could possibly affect the sample. In many real cases, these four classes can be further divided into subclasses depending on the intrinsic electronic and physical properties of the coordination compounds concerned.

Modern pressure devices allow this experimental parameter to be varied with relative ease and it is now possible to examine a number of interesting pressure-induced phenomena associated with coordination compounds. For example, studying the coupling of vibrational modes with electronic transitions of molecular coordination systems has yet to receive much attention due to the fact that not very many transition-metal compounds exhibit vibronic structure. One likely reason for the dearth of these studies is the fact that it is often difficult to resolve vibronic structure using conventional pressure devices. Experimental difficulties in this branch of pressure-tuning spectroscopy are often encountered when cryogenic temperatures (~ 5 K) are required to resolve long vibronic progressions in coordination compound systems. Also, it may become difficult to control the temperature of the cell and to effectively irradiate the sample because of condensation on the optical windows. However, special DACs and other techniques will be illustrated and discussed later in this review that have the ability to not only reach low temperatures but which can be regulated effectively at low temperature as pressure is applied. If a resolved structure can be obtained, one can expect that the pressure-induced displacement of the ground- and excited-state potential surfaces with respect to one another will have effects on the vibronic structure as well as shifting the transitions higher or lower in energy. In a related review of this area, Curie et al. [15] have discussed the effects of hydrostatic pressure on the vibronic

Table 1
Possible effects of compressing coordination compounds

Class 1	Class 2	Class 3	Class 4
No significant structural or electronic changes. Mostly rearrangement of atoms or molecules with no noticeable change in electronic spectra.	Physical structure change with small or negligible changes in electronic structure.	Electronic structure change with small or negligible changes in physical structure.	Significant change in both electronic and physical structure.
→change in space group and shifts in band energy	→piezochromism	→spin-crossovers	→spin-crossovers and drastic changes in spectra

transitions of impurity doped crystals by using a harmonic configuration coordinate model to treat systems with vibrational modes capable of coupling with electronic transitions.

2. Diamond-anvil cell

The DAC has been, by far, the most common piece of laboratory equipment used to vary pressure for spectroscopic studies. Its requirement of only a small amount of sample, solid or solution, and the generally non-destructive nature of the technique make it an ideal tool for studying the electronic spectra of coordination compounds.

The concept of the DAC operation is a simple one — the opposing faces of two gem quality diamonds, usually type IIa with a modified brilliant-cut, are pressed against each other by either mechanical or hydraulic forces. The faces of the diamonds must be parallel to each other and the size of these faces determines the pressures that can be reached. To avoid possible pressure gradients across the sample, a gasket made of either stainless steel or indium is used to act as both a sample chamber and to negate the likelihood of pressure gradients. The gasket hole ranges in size depending on the operating pressure range of a particular DAC. Normally, this hole is around 100–300 μm in diameter. For solids, it is necessary to use a pressure-transmitting medium, such as Nujol or methanol–water, to guarantee a hydrostatic or, at least, a quasi-hydrostatic environment for the sample. Of course, the addition of pressure-transmitting media, especially protic solvents, may likely quench the electronic spectra, depending on the sample used, to the point where any interesting features of the spectra are unobservable. The use of a pressure-transmitting medium is mostly up to the experimentalist. For example, if the sample is a crystalline powder, then it may not be entirely necessary if modest pressures (< 50 kbar) are used. For larger single crystals, however, it is important to use such a medium to ensure that pressure is applied uniformly.

Over the years, a number of different types of DACs have been invented to study pressure-tuning effects on a variety of different systems. The most used and well known will be presented here. Perhaps the most common DAC in use today is the Weir–Van Valkenburg cell [16,23], which is used mostly in studying pressure effects on vibrational spectra but is also useful for room-temperature studies of electronic spectra. Fig. 1 shows the layout of the Weir–Van Valkenburg DAC and its components.

Applying pressure to the sample is achieved by simply turning the screw on the cell and this action will then force the two diamond anvils together, generating pressures up to 70 kbar. Also, the compact nature of this cell and its light weight make it a good choice for spectrometers interfaced with a microscope since it can be fixed in place quite easily. Refs. [12,16,23] give both a historical perspective and background of the technical development of the Weir–Van Valkenburg DAC.

There exist more specialized DACs that are capable of reaching low and high temperatures together with high pressures. The hydrothermal DAC [24] has an

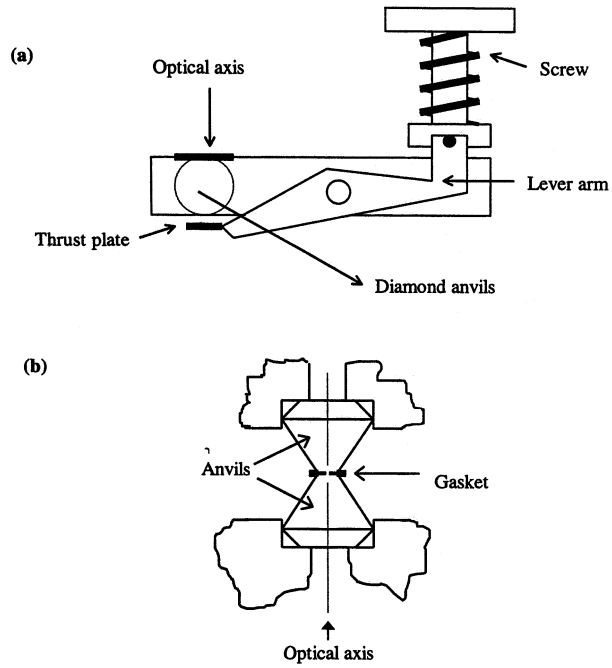

Fig. 1. The Weir–Van Valkenburg DAC: (a) side view and (b) view of the gasketed diamond-anvils.

operating temperature range from −190 to 1200°C and can achieve pressures up to 250 kbar. Pressure is applied by tightening three screws uniformly using a hex wrench. This DAC has molybdenum wires wrapped around the diamond supports that act as heaters and as a means of controlling temperature for the low-temperature experiments. Liquid nitrogen can be added directly into this DAC or it can be boiled in an external reservoir and passed through the cell, using a carrier gas, to achieve low temperatures. However, the latter procedure does not permit temperatures as low as the former method because of the low heat capacity of the nitrogen gas. Thermocouples, together with a thermometer, can be used to regulate and vary temperature or a voltmeter can be employed in conjunction for calibrating temperature as a function of change in voltage across the thermocouples. One major drawback with this method is the condensation on the optical windows that occurs upon cooling. However, this usually does not present a problem for many pressure-tuning applications in electronic spectroscopy. Fig. 2 shows a pictorial layout of the hydrothermal DAC.

In order to achieve cryogenic temperatures, the Bell and Mao DAC [25] and the Webb et al. DAC [26] provide the experimentalist with the ability to operate at very low temperatures (e.g. 0.3 K for the Webb DAC) and pressures up to 150 kbar. These types of cryogenic DACs [25,26] have been used to study solidification of molecular hydrogen as well as studying the metallization of xenon [12]. The Webb DAC incorporates both a cryogenic ^{3}He–^{4}He dilution refrigerator and the diamond

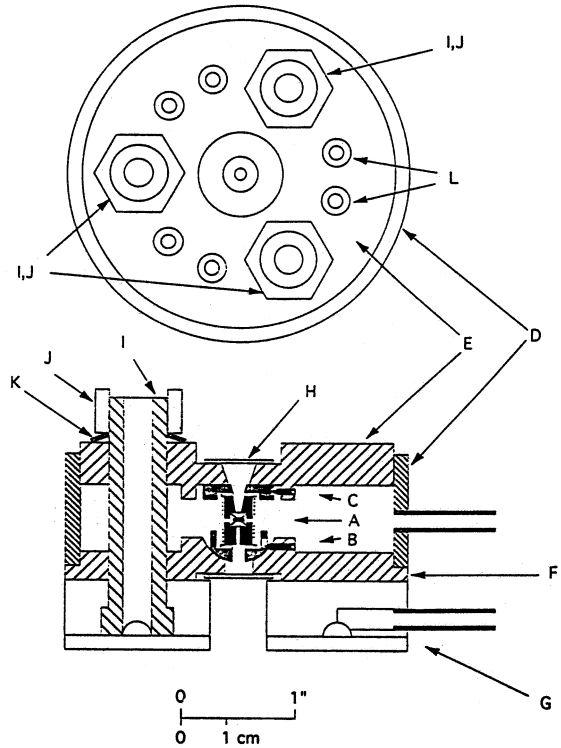

Fig. 2. Schematic of the hydrothermal DAC. The individual parts are as follows: (A) diamond-anvils, heaters, heat barriers; (B) ball joint for orienting lower anvil; (C) sliding disk for positioning the upper anvil; (D) cylinder for enclosing inert gas chamber; (E) upper platen; (F) lower platen; (G) base with cooling chamber; (H) upper and lower windows; (I), (J) posts and threaded nuts for applying force; (K) belleville springs; (L) electric feedthroughs. Reprinted with permission from Bassett et al. [24]. © 1993 American Institute of Physics.

anvils thereby allowing a continuous variation of pressure while keeping the temperature constant. In addition, a SQUID magnetometer is used inside the cell to permit monitoring of small changes in the magnetic moment of the sample.

High-pressure applications in electronic spectroscopy require that a calibrant with well-known behavior under pressure be used to identify the pressures at which the experiment is being performed. For many high-pressure, electronic spectroscopy experiments, ruby is often the calibrant of first choice. This calibration method was pioneered by Forman and co-workers in 1972 [27] and was later taken to higher pressures by Piermarini in 1973 by using the Decker equation-of-state for NaCl compressed with ruby [28]. Ruby exhibits a strong $^4A_{2g} \leftarrow {}^2E_g$ doublet emission that red shifts with pressure. The doublet arises from a spin–orbit coupling, induced distortion of the ^2E_g state in the O_h-coordinated Cr(III), located on an Al(III) site of the α-Al_2O_3 host lattice. The strong phosphorescence emissions have been termed R_1 (694.2 nm) and R_2 (692.8 nm) and can be excited by either He/Ne- or Ar-ion lasers. To calibrate the pressure on the sample, the following equation is used [29].

$$P(\text{Mbar}) = 3.808[((\Delta\lambda/R_1) + 1)^5 - 1) \quad \text{where } \lambda \text{ and } R_1 \text{ in Å} \tag{1}$$

This method of calibration is only useful up to ~ 160 kbar with $\pm 10\%$ error, after which the pressure response from ruby is non-linear and the actual pressure is underestimated at higher pressures.

Sometimes the ruby emissions interfere with the sample spectra to the point where they are indistinguishable or else the ruby emissions are too intense compared to that of the sample. In these cases, another calibrant must be used, such as octahedrally coordinated V(II) in an MgO host lattice, which exhibits a $^2E \rightarrow {}^4A_2$ phosphorescence (R line) band at ~ 870 nm that shifts linearly with pressure up to 100 kbar [30].

In order to get a reproducible ruby emission for all sample runs, it is important that the sample area is irradiated uniformly. This is more important for systems interfaced with microscopes equipped with high power objectives. The experimentalist will likely have to leave the excitation source unfocused to ensure that the ruby emission does not swamp the sample spectra and to guarantee reproducible and well resolved R_1 and R_2 lines. Fig. 3 shows the calibration curve obtained for the R_1 line as a function of pressure.

3. Theoretical treatment of pressure-induced changes in electronic spectra

Because of the relatively high symmetry of the transition-metal center of most coordination compounds, group theory and ligand-field theory (LFT) provide a

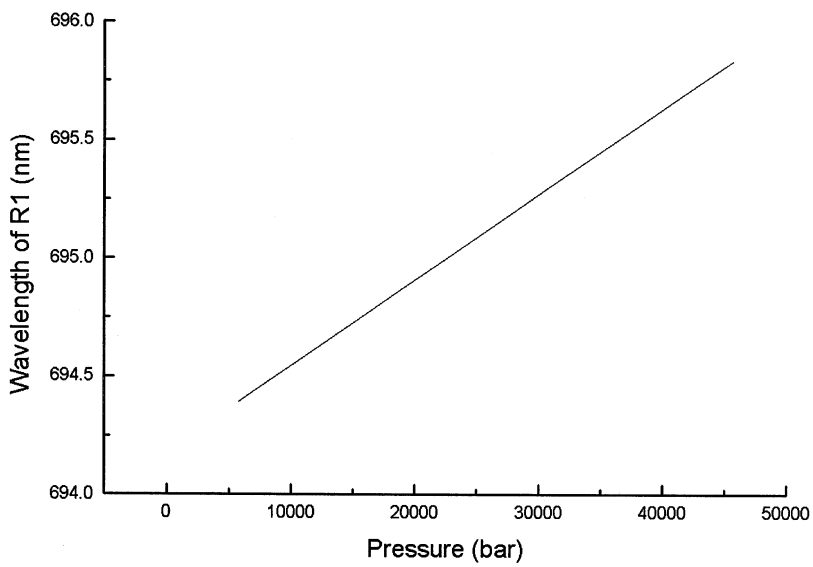

Fig. 3. The shift of the R_1 ruby emission line as a function of pressure. The ambient position of the R_1 line is at 694.18 nm.

strong basis for evaluating the electronic spectra as a function of pressure-induced changes. There are a number of books that cover the theory of inorganic electronic spectroscopy and provide the reader with a firm understanding of the electronic structure of coordination compounds [31–36]. These texts explain the essential groundwork for understanding how the variation of pressure can assist in probing further into the nature of the electronic structure of coordination compounds. To assist in augmenting pressure-tuning methods to the theory of electronic spectroscopy, Ferraro [12], together with Drickamer and Frank [11], have laid the foundation for understanding pressure effects on both electronic and vibrational spectra.

There are a number of ways that pressure can effect intramolecular and intermolecular interactions. The degree to which pressure influences these properties depends largely on the nature of the molecule. Therefore, it is of great importance when conducting a pressure experiment that one has a general idea of the strength of interaction of these forces relative to one another and that the molecular geometry is understood. This is especially so in electronic spectroscopy because of the interrelation between molecular geometry and electronic properties.

In this review, we will be mostly concerned with pressure effects on solid coordination compounds but some solution examples will also be considered. The solids will generally be molecular in nature. This condition of a molecular solid or a solid dissolved in a solvent implies that the main force of intermolecular interaction is the attractive van der Waals force expressed as

$$E \sim -\alpha_1\alpha_2/R^6 \tag{2}$$

where R is the distance between the interacting molecules and the polarizabilities, α_1 and α_2 the molecular polarizability and the polarizability of the medium or other molecules, respectively. The effects of this interaction with the onset of pressure and its consequences will be discussed after some basic thermodynamic and structural distortion effects on the electronic spectra have been reviewed. It will also be important to remember that, in solids, the intermolecular forces will have an influence on how the intramolecular parameters change with pressure.

Since we are interested in changes of the electronic and physical structures of molecular coordination compounds as pressure is varied, some thermodynamic considerations must be addressed. The amount of energy going into the system is found from the work integral

$$W = -\int P \, \mathrm{d}V \tag{3}$$

However, because DAC pressure experiments involve such a small sample volume, one can make a rather crude approximation of the work integral to get a feel for how much energy is perturbing the system. This approximation involves simply treating the changes to pressure and volume, in a P–V diagram, as averages, resulting in an area under a triangle

$$W = -1/2(\Delta P \Delta V) \tag{4}$$

It must be stressed that this is only presented as a rough approximation to the actual work integral. A more thorough solution requires that the path-dependent work integral be specified by an equation of state. Or, a better estimate comes from considering the fact that the isothermal compressibility varies strongly with pressure when using this parameter in lieu of an equation of state to solve the work integral. However, such calculations are beyond the scope of this review. For a complete background of this problem in pressure studies of solids, see Refs. [12–14].

Another pressure phenomenon of interest is the occurrence of phase transitions. These events may be of great importance should interesting features appear coincidentally in the pressure-tuned electronic spectra. Ref. [17] gives a brief overview of phase transitions and their implications on molecular structure.

To determine how lattice packing forces or intermolecular van der Waals forces are responsible for such changes in the electronic and accompanying vibrational spectra, studies can be done varying both the ligands and/or counter-ions to determine which effects dominate, more or less, at certain pressures. Such studies are helpful in understanding the structural pathways open to a solid coordination compound and their implications on the electronic structure when probed by spectroscopy.

3.1. Pressure-induced structural deformations: the orbital symmetry rule

To help understand how pressure-induced structural transformations are brought about and how they influence electronic spectra, Ferraro and Long [37] have suggested applying orbital symmetry rules, originally formulated by Bader [38,39] and furthered by Pearson [40–43]. Pearson's orbital symmetry rules were first used for predicting the course of a chemical reaction by considering the effect of frontier orbital symmetries on possible mechanistic routes leading to rearrangement of electron distribution and molecular geometry, somewhat similar to the classic Woodward–Hoffmann rules. These orbital symmetry considerations may have relevance in studying pressure-induced effects on the electronic spectra of coordination compounds due to changes in molecular geometry and bond lengths which then affect the energy separation of d-orbital splittings of the transition-metal center. One of the difficulties in applying these rules to pressure-induced changes in molecular geometry is the fact that intermolecular interactions have a strong influence on how the molecule can distort. However, distortions of the totally symmetric vibrational modes are almost always the predominant first response to pressure. So it follows that one can safely assume that it is these modes that lead to the maximum relaxation of the electron distribution energy of a molecular solid under pressure to a point where the displacement of non-totally symmetric modes become more favorable. This is where the orbital symmetry rules would supposedly take over and provide a possible route to the new overall molecular geometry.

The orbital symmetry rules are based on second-order perturbation theory and group theory. Group theory plays an important role in this process because it simplifies calculations for the perturbation expressions to give a picture into whether a distortion will lead to a more stable molecular structure.

The first step in applying this treatment is attributing a point group to the nuclear configuration of the molecule, along with assignment of the normal coordinates for a specific configuration [40]. Since this particular application of Pearson's symmetry rules pertains to solid coordination compounds, the crystals are assumed to be molecular so that there are only van der Waals forces between molecules. When a molecule is distorted along a particular normal coordinate, the potential energy surface of the ground state in a certain molecular geometry, neglecting the first-order contribution, is given by the following equations [37,40]:

$$E = E_0 + 1/2Q^2 \int \psi_0 \left| \frac{\partial^2 V}{\partial Q^2} \right| \psi_0 \, d\tau + \sum_k \frac{\left[Q \int \psi_0 \left| \frac{\partial V}{\partial Q} \right| \psi_k \, d\tau \right]^2}{\Delta E} \tag{5}$$

$$E = E_0 + f_{00}Q^2 + f_{0k}Q^2 \tag{6}$$

where Q is the normal coordinate displacement, V the nuclear–nuclear and nuclear-electronic potential energy, E_0 the energy corresponding to Q_0 (the original nuclear positions), and ΔE the difference in energy, $E_0 - E_k$, between two coupled states, ground and higher electronic states. In addition, the first-order correction to the molecular configuration energy does not appear in Eq. (5) because all first-order structural deformations are assumed to have already occurred [40]. This is attributed to displacements occurring along totally symmetric normal coordinates, such as bond lengthening and bending, until the energy is minimized. Another consideration to be taken into account is that the energy difference, ΔE, between two states must be around 4 eV or less [40]. Also, the ground-state must be non-degenerate and it is assumed that for degenerate states, molecular distortions, in the first-order, will take place and split the degeneracy.

Eq. (6) shows the relations of the minimized energy of the undistorted molecule, E_0, and the second-order perturbation terms, $f_{00}\ Q^2$ and $f_{0k}\ Q^2$, representing the distortion-induced change in energy and the changes in the initial wavefunction ψ_0, respectively [37,40]. The $f_{0k}\ Q^2$ term is always negative because of the need to fit the original nuclear coordinates to the distorted molecular configuration and the $f_{00}\ Q^2$ term is always positive because the initial energy is assumed to be minimized for the undistorted molecular geometry [37,40]. Also, the f_{00} term is like a spring constant since it supplies a restoring force for displaced nuclei and the sum of the two constants, f_{00} and f_{0k}, is the experimental force constant for the normal coordinate described by Q [40]. Now, there are parameters available that may allow application of this theory in pressure-tuned electronic and vibrational spectra by fitting experimental results.

Depending on the magnitudes of f_{00} and f_{0k}, the stability of a possible change in molecular configuration can be predicted. Using Pearson's nomenclature, there are three possible cases presented by Ferraro and Long that relate the magnitudes of f_{00} and f_{0k} to the likelihood of a structural rearrangement taking place upon compression of a solid sample. If $f_{00} \gg f_{0k}$, then the initial molecular configuration is stable and no change in geometry is expected. If $f_{00} \cong f_{0k}$, then a distortion along the normal coordinate, Q, is possible although the initial geometry is somewhat stable.

If $f_{00} \ll f_{0k}$, then a structural change may occur spontaneously along the normal coordinate to a more stable configuration [37,40]. As Pearson explained, approximations must be made to find the probable magnitude of f_{0k}, which gives insight into the stability of the possible new molecular geometry. These approximations include limiting the sum over all k electronic excited states to one or two as well as replacing the total ground-state many-electron wavefunction, ψ_0, with the HOMO irreducible representation and the first excited-state wavefunction, ψ_k ($k = 1$), with the corresponding LUMO irreducible representation [40]. In this situation, the transition probability charge density (to be elaborated later), $\psi_0\psi_k$, can be written in terms of MO wavefunctions as the product of the HOMO and LUMO wavefunctions, $\Phi_{\mathrm{HOMO}}\Phi_{\mathrm{LUMO}}$. Furthermore, the ΔE term in Eq. (5) implies that the lowering in energy of the configuration will be greatest for the normal coordinate displacement that allows interaction with the lowest electronic excited states of that specific configuration [39]. For molecular solids under pressure, a rearrangement of molecular geometry will then be assumed to be a cooperative process that allows maximum relaxation of the energy of electron distribution of that particular configuration at a certain pressure.

It is now important to consider the effects of the operators, $\partial V/\partial Q$ and $\partial^2 V/\partial Q^2$ (Eq. (5)), when they operate on the excited- and ground-state wavefunctions, as well as on the ΔE term representing the relaxation of electron distribution energy. Then, the magnitudes of f_{00} and f_{0k} can be compared in the manner discussed previously to predict which molecular geometry will be most favored at high pressure. It turns out that the symmetry conditions of the operators in the integrals of the f_{00} and f_{0k} terms dictate that to be non-zero, the direct product of two representations of the ground and excited states must contain the representation of the third [40]. This third representation is the normal-coordinate displacement, Q, which the ground and excited states are offset from each other and by using the above substitutions for the wavefunctions with the irreducible representations of the HOMO and LUMO, the direct symmetry product

$$\Gamma_{\Phi\mathrm{HOMO}} \otimes \Gamma_Q \otimes \Gamma_{\Phi\mathrm{LUMO}} \tag{7}$$

contains the irreducible representation of the normal-coordinate displacement [37,40]. This means that for an allowed molecular distortion, i.e. a non-zero representation for the above direct product, that the normal coordinate displacement must have the same symmetry as $\Phi_{\mathrm{HOMO}}\Phi_{\mathrm{LUMO}}$. This transition probability is now explicitly defined as the amount of charge transferred within the molecule resulting from the nuclear displacements. This term, labeled ρ_{0k}, when integrated over all space is equal to zero [39]. The substitution of the ground and excited states many-electron wavefunctions by the irreducible representations of the HOMO and LUMO wavefunctions will now be equal to the probability density. With this in mind, the transition density, in terms of Φ_{HOMO} and Φ_{LUMO}, is non-zero provided that the symmetry representation of the transition density is the same as Q. The direct product is then

$$\Gamma_{\rho_{0k}} = \Gamma_{\Phi_{\mathrm{HOMO}}} \otimes \Gamma_{\Phi_{\mathrm{LOMO}}} = \Gamma_Q \tag{8}$$

which reiterates that in order to have a non-zero representation for $\Gamma_{\rho_{0k}}$, the normal coordinate displacement must have the same symmetry as the probability density. However, for possible pressure applications, the influence of intermolecular properties will become more prominent with increasing pressure and may cause some deviations from what is predicted by this theory.

Ferraro and Long have stressed that molecular packing, lattice forces, ligand flexibilities, metal–ligand bond distances, d–d electron transition energies, MO overlap and orientation, and hydrogen bonding must also be considered for solid-state structural interconversions [37]. Also, in pressure applications to solids, some researchers have suggested that distortion along only one mode does not explain some of the behavior seen experimentally [22], thus requiring potential surfaces of higher dimensions. In addition, these authors have mentioned in the proposed application of Pearson's symmetry rules that there exists the possibility of normally forbidden modes becoming allowed, in a lower site symmetry of the transition metal center and intermolecular effects becoming dominant. This can be understood by consulting correlation tables for modes of high symmetry that split when molecular distortions and bond breaking occur giving rise to a different point group of lower symmetry. Nevertheless, because pressure tends to couple most strongly with the totally symmetric vibrational modes, then it may be safely assumed that displacement of these modes is the first response to pressure. Ferraro and Long have also provided examples of coordination compounds, with coordination numbers 4–6, that exhibit a change in molecular geometry with pressure to support the applicability of the orbital symmetry rules to pressure-induced solid-state structural interconversions [37]. These results do not, however, apply the orbital symmetry rules as they were just laid out. Interestingly, there have been no detailed, critical tests into the applicability of this theory to pressure-induced conversions of molecular geometry reported in the literature. Therefore, the validity of using such rules is still not certain based on the experimental data available.

Even though the orbital symmetry rules were originally formulated to describe symmetry effects on the relaxation of the energy of electron distribution, they have some relevance in pressure-induced structural interconversions. The possibility of describing interrelations of metal–ligand bond lengths and angles as a function of pressure by using a model based on the orbital symmetry rules would be of great interest to all chemists. Now with increasingly better spectral resolution available from modern instruments and the well-characterized electronic structures of many coordination compounds, there is already a good basis in place for studies to further justify the use of orbital symmetry rules in pressure applications.

3.2. Pressure effects on the molecular orbitals of coordination compounds and shifts of electronic energy bands

Having recognized the potential applicability of Pearson's work to pressure-induced changes in molecular geometry, as suggested by Ferraro and Long, it is necessary to look at the coordination system under pressure with a broader perspective and address how intermolecular effects play a role in determining the

appearance of the electronic spectra. In conjunction with intramolecular pressure-induced structural distortions, the intermolecular interactions in either solid molecular crystals or solution coordination compounds will have to be taken into consideration when explaining pressure effects on electronic spectra. As inferred from the previous section, structural distortions are the result of an imbalance between the intramolecular and intermolecular interactions and the consequent change in the electronic spectra can be explained by understanding which force dominates at high pressures. Here we will explain how a particular shift in energy of an electronic energy band will provide insight into which effect, intramolecular or intermolecular, is stabilizing or destabilizing the electronic transition.

It is not completely certain how intermolecular effects will influence molecular geometry. The orbital symmetry rules provide a possible explanation for intramolecular distortions but do not explain how competing effects, such as the van der Waals forces in molecular crystals or molecules dissolved in solvents, will have influence on the preferred molecular geometry and the routes leading to them. These competing effects can, however, provide an idea of how the MOs will be perturbed and explain the shifts in energy bands commonly seen in electronic spectra. To describe these pressure-induced shifts to either lower or higher energy, it is necessary to consider, for example, an MO representing a metal–ligand bond for a simple ML_6 octahedral complex. As pressure is applied, the volume becomes smaller which corresponds to a decrease in metal–ligand bond length, which will in turn cause an increase in the energy in both the bonding and anti-bonding components of the MO. Because of the overlap topology of the anti-bonding component, this will typically result in an increase of energy much faster than does the bonding component or, in LFT terminology, an increase in the ligand-field energy, Δ. Now, assuming that the anti-bonding component is the LUMO of the system, an electronic transition from the non-bonding component, t_{2g}, to that of the anti-bonding component, e_g^* will lead to an increase in absorption or emission energy. This blue-shift is essentially an intramolecular effect because the increase in energy separation was a result of the metal–ligand bond shortening upon compression. This result is more of a generality of the behavior of a simple system where the bonding and anti-bonding components of the MO correspond to the HOMO and LUMO of the system. However, in actual cases involving coordination compounds, the electronic transitions do not always arise from a simple configuration; therefore, a more in-depth look at how the transition metal centers d-orbitals are split by the Jahn–Teller and spin–orbit coupling effects will be necessary.

In the other case where intermolecular forces influence the electronic transition, the dominant force is the attractive van der Waals interaction between molecules in a crystal or solvents. Since many electronic transitions in coordination compounds result from transitions from bonding or non-bonding components to anti-bonding ones, this situation will be used to illustrate the effect of pressure on intermolecular interactions. An electronic transition to an orbital of anti-bonding character will result in the excited-state becoming more polarizable because the electron is not bound as tightly as in the ground state. Because of this increased polariziblity and the fact that pressure decreases the volume, thus decreasing R in Eq. (2), the van

der Waals attractive force is increased. In this scenario, pressure will stabilize the anti-bonding state and lead to a decrease in the emission energy. This red-shift is predicted for such a case as long as the competing intramolecular effects are less perturbed by the application of pressure.

In cases of lower symmetry due to Jahn–Teller effects, spin–orbit splitting, or non-equivalent ligands, there will be more combinations of different types of electronic transitions depending on the overall d electron distribution. For example, if the HOMO is bonding and the LUMO is anti-bonding in character, then an electronic transition will be strongly blue-shifted upon the application of pressure. Conversely, a strong red-shift will occur in the opposite case. When the HOMO and LUMO have the same character, the relative strength of this interaction will determine which will be stabilized or destabilized more readily with pressure. Such an effect can be understood better by spectroscopic results and understanding how the competing forces will influence the electronic transition between two such components. Additionally, when electron-pairing energies, Π, are relatively close to the energy separation between ground and excited states, pressure may stabilize or destabilize these states depending on the electronic configuration and population of these levels. For example, a molecule with a ground state singlet may likely be stabilized in the excited state if the energy separation between ground and excited states is close to the electron-pairing energy. Such a case would result in a red-shift of the electronic transition band with pressure due to the reduced repulsion energy experienced by electrons in the same level.

By presenting such scenarios with the onset of pressure, we only qualitatively explain how the intermolecular effects may influence electronic transitions by first influencing intramolecular effects. Any anomalies in the pressure-tuned electronic spectra can be better understood by consulting an MO diagram and consideration of competing effects from intermolecular or solvent interactions. Though the shifts in electronic transitions were explained in terms of metal–ligand bond length changes and subsequent MO energy changes, activation of bending modes under pressure will also be a factor. This is important since changes to bond angles will often occur more readily with the onset of pressure than changes to bond lengths.

Another interesting possibility involving a luminescence pressure experiment may also be the shifting of allowed and forbidden excited states, represented by potential surfaces along a configuration coordinate, and causing a change in the radiative processes. Internal conversions are one of the likely consequences of such a pressure-induced interaction of close-lying, spin-allowed and forbidden excited levels. The other, less dramatic, consequence being a change in the luminescence efficiency by either enhancing or retarding radiative processes to non-radiative processes.

The crossing over to a spin-forbidden level and consequent emission, with or without release of vibrational energy, corresponds to a change from fluorescence to phosphorescence. Kenney et al. have provided an excellent example of this when they studied the pressure effects on the emissive properties of a Cr(III) system [44]. When excited state distortions become more noticeable, non-radiative processes tend to become more efficient with increased pressure. This can be readily seen in

the luminescence spectra when, together with an energy shift of the band, the intensity also decreases significantly.

3.3. Pressure effects on molecular electronic spectra

Now that pressure effects on molecular geometry and energy levels have been covered, the following changes to the molecular electronic spectra will now be discussed in terms of potential surfaces along normal coordinates using several model systems. Details from the derivations of the high-pressure models will not be discussed here. However, some of the results obtained will be summarized briefly.

There have been several theoretical studies of the effects of pressure on molecular electronic spectra that have stemmed from work by Drickamer and co-workers. The original model was formulated by Drickamer, Frank and Slichter (DFS) [18] and this was concerned with band shifts of absorption spectra along with pressure-induced changes to electronic structures. The DFS model specified a relation between energy band maxima and full-width at half maximum (FWHM) of peak height to the difference in energy between the minima of the ground and excited potentials. The harmonic potentials, for the ground-and excited-states, respectively, used in this model are as follows

$$V = 1/2Q^2 + Qp \tag{9}$$

$$V' = 1/2\omega'^2(Q - q)^2 + Qp + E_0 \tag{10}$$

where ω is the force constant, p the pressure, Q the configuration coordinate, and E_0 and q the energy of the electronic origin and coordinate offset between the potential minima, respectively [11,18].

The DFS model assumes that pressure couples with the displacement of a single normal coordinate of the molecule. As pressure is applied to the system, the consequent shifts of these levels can be explained by operating on the potential functions accordingly, i.e. shifting them along the normal coordinate as well varying the electronic origin, E_0.

Lin has developed a more mathematically rigorous theoretical model based on the initial DFS model [19]. This model has expanded on the DFS model in that it treats pressure-induced changes in absorption and emission spectra as well as non-radiative processes. Harmonic potentials are used in Lin's derivation to explain pressure-induced changes to the molecular electronic spectra. Essentially, Lin's results have reproduced the simple DFS model via a quantum mechanical approach.

It is important to note that some authors have considered anharmonicity in their theoretical treatments when pressure is applied to a molecular system. Tompkins was the first to account for this when he showed some inconsistencies in Lin's results [20,21]. Tompkins used Morse potentials in his analyses rather than the harmonic model used by Lin. These are shown for the ground and first excited electronic states, respectively

$$V = D(1 - e^{-\beta Q})^2 + cpQ \tag{11}$$

$$V^* = D^*(1 - e^{-\beta^*(Q-q)})^2 + rcpQ + E_0 \quad (12)$$

where D, β, D^*, β^*, and c are constants, p the pressure, Q the normal coordinate displacement, r the ratio coupling constant in the excited state to that of the ground-state, and E_0 and q represent the energy and normal separation between the potential minima. In his treatment, Tompkins makes the following assumptions based on the DFS model. First, the pressure dependence of peak height and bandwidth is second order and first order, respectively. Also, the constants of the Morse potential, β and D, are independent of pressure and the parameters describing the potential as a function of pressure are averaged over all the normal modes and configuration coordinates [21].

Differentiation of the two Morse potentials with respect to the normal coordinate displacement, setting these equal to zero and then solving the exponentials corresponds to the lowest vibrational levels of the ground and excited states. Tompkins obtained expressions for pressure-induced changes by differentiating the resulting equations for the potential minima for the ground and first excited states with respect to pressure [21]. Also, to better account for the experimentally observed quadratic dependence of absorption and emission energies as a function of pressure, Tompkins expanded the energy terms in a Maclaurin series to second-order in pressure [20,21]. Electronic transitions, according to the Franck–Condon principle, can now be evaluated by further manipulation of this model system.

One of the more up-to-date formulations of pressure effects on molecular electronic spectroscopy comes from Kesarwani and Varshni [22]. This work builds on the DFS model using Kratzer–Fues potentials to account for anharmonicity. The respective potential functions for the ground and excited states are

$$V = D\left(\frac{Q}{Q+\rho}\right)^2 + cpQ \quad (13)$$

$$V^* = D^*\left(\frac{Q-q}{Q-q+\rho^*}\right)^2 + rcpQ + E_0 \quad (14)$$

where D, ρ, D^*, ρ^*, and c are constants, p the pressure, Q the configuration coordinate, r the ratio of the coupling constant in the excited-state to that of the ground-state, and E_0 and q represent the energy and normal separation between the potential minima. As the authors point out, the Kratzer–Fues potential is much simpler than is the Morse potential because it has much simpler expressions in that some steps do not require Maclaurin expansions meaning that the final results have a better degree of approximation [22]. The mathematical treatment of this model using Kratzer–Fues potentials is analogous to the previous models and will not be discussed further.

This latest model was tested for six fused aromatic organic molecules and the results were compared to the other existing models as well as to experimental data. The authors noted some discrepancies between experiment and theory, such as the unlikelihood of only a single configuration coordinate displacement, constants in the Kratzer–Fues potential may be pressure dependent, and the assumption that all parameters can be regarded as averages over all the normal modes may not be accurate.

Depending on the type of coordination compound system under study, these various formulations may provide useful information on how the electronic spectra change under pressure. The choice of a particular model is also dependent of the coordination compound system. Some cases will fit the basic harmonic model whereas others will need to account for anharmonicity, depending on the shape of the electronic band observed. Also, when modeling pressure-tuned electronic spectra multiple normal coordinate displacements might have explained some discrepancies encountered when comparing the calculations to actual molecular electronic spectra.

Another possible adaptation of conventional models to pressure applications is the angular overlap model (AOM). The fundamental assumption of the AOM is that the stabilization and destabilization energies of the bonding and anti-bonding MOs, respectively, are proportional to the square of the overlap integral. The overlap integral is split into separate radial and angular parts, the radial part being dependent on the metal–ligand bond length and the angular part is dependent on the overall molecular geometry. So, the destabilization of atomic states of the transition metal center is proportional to the angular part of the overlap integral. As it turns out, this method can be very useful in pressure studies because, when the molecular geometry changes with increasing pressure, the corresponding changes to the electronic structure can be found quite easily. This is done using a minimal number of parameters to describe the possible types of overlap such as, σ overlap and both symmetric and anti-symmetric π overlap.

It must be pointed out that, in spite of the existence of these various models for treating pressure-tuned molecular electronic spectra, there are not many well-known studies done with coordination compounds using these models or variations of them. As it has been inferred from the models presented, one would ultimately require resolved vibronic structure in order to effectively determine the actual normal coordinate offset and electronic origin. In the case of pressure-tuned electronic spectra of coordination compounds, resolution of long vibronic progressions are rarely reported thus severely limiting the ability to extract much useful information from the spectra other than that gained from using ligand-field levels.

4. Pressure effects on some coordination compound systems

To illustrate some applications of pressure-tuning effects on electronic spectra of coordination compounds, examples will be presented here that demonstrate interesting changes in their electronic spectra upon compression. First, examples showing the effects of pressure-induced molecular distortions on electronic spectra, i.e. piezochromism, will be discussed. In these studies done by Drickamer and co-workers, the mechanism and possible effects of competing forces on the rearrangement are considered for a series of Cu(II) complexes. It is pointed out, in a general manner, that differences in possible geometries that a molecule can assume are a result of a delicate balance between all possible types of interaction in the crystal lattice. The result of compression is then to throw off this balance and bring about

a new molecular geometry [46]. This can either occur continuously over all pressures, indicating a stochastic process, or else abruptly, which is often interpreted as a first- or second-order phase transition. Also of interest when studying this phenomenon is that the differences between the different molecular geometries for a particular system become less distinct at higher pressures [46]. Electronic absorption spectroscopy, together with IR spectroscopy, is used to characterize and indicate how pressure-induced molecular distortions will alter the electronic structure and the electronic transitions. Of most importance in these studies is that they provide evidence for the existence of a structural pathway between different molecular geometries. Such studies may also serve as a means of furthering the application of the orbital symmetry rules discussed in Section 3.1 in pressure spectroscopy. However, the work reported here was not done with the orbital symmetry rules in mind.

Another interesting branch of pressure-tuning electronic spectroscopy involves changing the ligand-field parameters of coordination compounds and causing a drastic change in their electronic and magnetic properties. This spin-crossover effect is a phenomenon which has been thoroughly studied using mostly octahedral Fe(II) and Fe(III) coordination compounds as well as other $3d^{4-7}$ complexes. Essentially, as the sample is compressed, the ligand-field around the transition metal center is altered to the point where the ligand-field splitting energy becomes less than the spin-pairing energy and a spin-crossover will occur. This entropy-driven phenomenon is best understood with potential surfaces, each representing a possible spin state, along a configuration coordinate. Because the ligand-field splitting energy is proportional to the inverse fifth or sixth power of the metal–ligand distance, r, the pressure-induced shortening of metal–ligand bond lengths has the same effect as ligand substitution on the metal center. Now, as pressure is applied to the system, solid or solution state, these potentials can shift both vertically and horizontally thus causing a change in ground state. Also, following such behavior using a Tanabe–Sugano diagram may further explain these spin-state changes. Fig. 4 shows a d^5 Tanabe–Sugano diagram, the crossover point (for a particular value of Δ) is at the center [45]. Later, this will be discussed in detail using some examples from the literature and covering some of the basic theory for this particular pressure-induced phenomenon.

Of all the observations made when pressure is applied to a sample, the most commonly reported are the shifts of absorption, emission, and/or charge transfer bands and the change in band shapes. The shifts are attributed to both changes in the electronic and physical structure of the coordination compound when pressure is applied as discussed in Section 3.3. Also, as pressure shifts electronic energy bands, it may also markedly effect the type of radiative and non-radiative processes. This is best seen in luminescence experiments where the area under the emission band changes with the application of pressure. This area is also a measure of the efficiency of the emission. So, when the area under an emission band decreases with pressure, this indicates that non-radiative transitions become more efficient with higher pressure. Examples will be presented which illustrate pressure-induced shifts of energy bands as well as changes in luminescence efficiency.

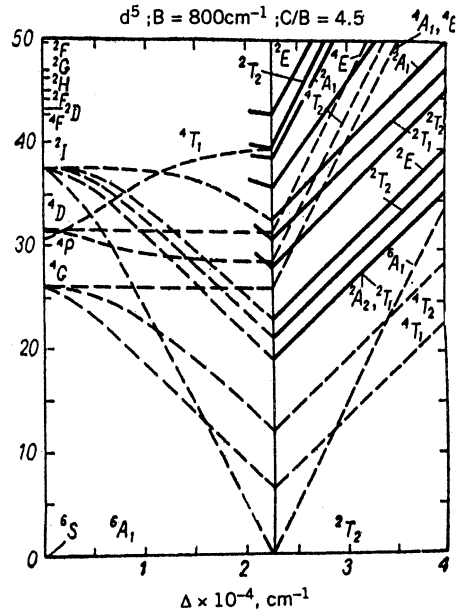

Fig. 4. Tanabe–Sugano diagram for a d^5 transition metal showing the crossover point.

To give a brief overview of trends in some coordination compounds, typical pressure ranges, and observations in the pressure-induced changes to their electronic spectra, Table 2 shows a selection of examples in which shifts in electronic energy levels upon compression have been reported in the literature. Many of these studies demonstrate and sometimes quantify how the fundamental parameters describing electronic transitions change with applied pressure.

The selection of compounds in Table 2 is meant to provide examples of how either absorption or emission peaks shift with pressure and is not meant to be an exhaustive catalog of all studies of coordination compounds under pressure. Some of the compounds listed are actually emissive transition-metal ions doped into a lattice whose electronic spectra were monitored as a function of pressure. These are not considered to be true molecular coordination compounds.

4.1. Piezochromism

Piezochromism has been defined as an intramolecular effect of pressure on the electronic spectrum of a compound. When pressure is applied to a coordination compound, structural deformations can lead to a new overall symmetry of the molecule and have profound effects on its electronic spectrum. Some possible explanations and mechanisms for such changes in molecular geometry with pressure were discussed in detail in Section 3.1. Drickamer and Bray have pointed out in their studies of piezochromism that compression of a solid will result in an imbalance of the forces that relate to the overall molecular geometry and how the

Table 2
Some examples of shifts reported in literature studies [a]

Compound	Author(s)	Pressure range	Peak shift/(type)	Ref.
$Cr(NH_3)_4F_2{\cdot}AsF_6$	Schaffer et al.	→100 kbar	Blue shift (absorption)	[79]
MX_6^{2-} M = Ir,Os,Pb,Pt X = Cl^-, Br^-, I^-	Balchan and Drickamer	Depends on compd. (up to 120 kbar)	Red shift (charge transfer)	[85]
Cl–Re^I $(CO)_3X$ X = 1, 10 phenanthroline	Salman and Drickamer	→10 kbar	Blue shift (luminescence)	[70]
Ni(II)compounds: $Ni(o\text{-}phen)_3(NO_3)_2$, $Ni(\alpha\text{-}\alpha'dip)_3Br_2$, $Ni(en)_2(SCN)_2$	Stephens and Drickamer	→150 kbar	Shifts not reported	[84]
Ni(II) and Cr(II) complexes: also with $K_3Fe(CN)$ and $CoSO_4{\cdot}7H_2O_6$	Parsons and Drickamer	→100 kbar	Blue shift (absorption)	[82]
$[(CN)_5FeCN\text{-}Pt\text{-}(NH_3)NCFe(CN)_5]^{4-}$	Lewis et al.	→1.5 kbar	Blue shift (charge transfer)	[86]
tris-Ru(II) and Os(II) w/2,2′-bipyridyl and 1,10-phenanthroline	Fetterolf and Offen	→300 kbar	Red shift (luminescence)	[74]
K_2NaGaF_6:Cr(III) (CrF_6^{3-})	Dolan et al.	→61 kbar	Blue shift (luminescence)	[87]
$Na_3In_2Li_3F_{12}$: Cr(III)	de Viry et al.	→40 kbar	Blue shift (luminescence)	[88]
fac-SRe(I) $(CO)_3L$ S = pyridine and quaternized poly(4-vinylpyridyl) L = α-diimine w/$CF_3SO_3^-$	Lang et al.	→70 kbar	Red shift (luminescence)	[71]
$Re_2(piv)_4Cl_2$ and $Re_2(piv)_4Br_2$ piv = pivalato with $(n\text{-}Bu_4N)_2$	Roginski et al.	→75 kbar	Red shift (absorption)	[89]
$[Cr(III)F_6](NH_4)_3$	Kenney et al.	→71 kbar	Blue shift, red shift (fluorescence, phosphorescence)	[44]
$[Re_2Cl_8]^{2-}$ and $[Mo_2Cl_8]^{2-}$ w/$(n\text{-}Bu_4N)_2$	Shapley and Drickamer	→200 kbar	Red shift (absorption)	[90]
Ru(II)$(bpy)_3$ and Ru(II)$(py)_2(bpy)_2$	Drickamer et al.	→70 kbar red shift	Red shift (luminescence)	[77]

[a] Most of the compounds examined possess either O_h or approximately D_{4h} symmetry or occupy lattice sites of these symmetries. The spectroscopic measurements were performed for either the solid state, in solution, or in a polymer matrix.

molecules order themselves in the crystal [46]. The varying degrees by which these forces are altered will determine by how much the molecular geometry will change from the original configuration.

Drickamer and co-workers, as well as Ferraro and his group, have studied the effects of pressure-induced rearrangements on the electronic spectra for a series of 4- and 5-coordinate Cu(II) complexes [46–51]. In their piezochromic studies, Drickamer and co-workers have discussed these rearrangements in terms of structural parameters. It was noted that differences in molecular geometry among the different classes of compounds studied became less distinct at higher pressures and that changes to the molecular configurations follow specific structural pathways [46]. The latter, according to Drickamer, represent allowed configurations of a solid-state species. The structural parameters that describe these geometrical changes are the stretching or bending vibrational modes of the molecule. Also, one of the most important observations in this work was how the molecular rearrangements occurred at higher pressures. The authors pointed out that some rearrangements take place continuously over all the range of pressures, while others involved a discontinuous process. The former represents a stochastic process while the latter is a first-order phase transition. Also, for the most part, rearrangements within the Cu(II) coordination sphere can be related to the dihedral angle of the complexes. This observation showed that the most susceptible mode of displacement, for these particular systems, was a bending mode of the molecule. As mentioned previously, the intermolecular forces and their varying contributions to the stability of the molecular geometry at high-pressure play an important role in determining which normal mode is displaced.

In a paper by Bray et al. a series of crystalline and polymer-dispersed, square-planar $[CuL_2]X_2$ complexes, where L = *N*,*N*-diethylethylenediamine(dieten) and X = BF_4^-, ClO_4^-, Cl^-; L = *N*,*N*-dimethylethylenediamine(dimeen) and X = BF_4^-; L = ethylenediamine(en) and X = BF_4^-, were studied as a function of pressure. This work illustrated that increasing pressure led to an increase in the interaction between the anion and the CuN_4 molecular plane [47]. Both electronic and IR spectroscopy were used to characterize these structural deformations. With the onset of higher pressures, the symmetry of the d^9 Cu(II) cation was reported to change from an idealized D_{4h} to D_{2h}. The authors stated that the presence of a tetragonal distortion of the D_{4h} energy splitting, verified by electron spin resonance (ESR) and polarized absorption spectroscopy, overrides the actual C_i symmetry and thus permits the use of the higher symmetry point group. Also, this approximation was assumed valid by the authors because the doubly degenerate d_{xz} and d_{yz} orbitals are not split significantly upon compression, which is what is predicted when the symmetry is altered slightly to a D_{2h} point group.

One of the most notable observations made in this study was the dramatic red-shift of the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition over a small pressure range for the dieten compound [47]. Also, significant blue-shifts were reported for the d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{x^2-y^2}$ transitions. The authors claimed that the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition is a measure of the tetragonal distortion present in these complexes. The dramatic red-shift of this particular transition, upon compression, in the dieten complexes

was attributed to a molecular rearrangement in which a marked decrease in anion-molecular plane distance as well as an increased out-of-plane covalent interaction between the anion and the d_{z^2} orbital of the Cu(II) ion took place [47]. These changes resulted in an increase in energy of the d_{z^2} orbital relative to that of the $d_{x^2-y^2}$ orbital, thereby accounting for the observed red shifts. These molecular rearrangements, in the polymer matrices, were considered to be the result of a stochastic process in which the rearrangement depends only on the free energy difference between the two molecular geometries. As the authors pointed out, in the case of the crystalline solids, this means that all the molecules must rearrange simultaneously, i.e. a totally cooperative process — a first-order phase transition [47]. The extent of cooperativity was used in this work to describe the relation between the stochastic and first-order phase transition extremes. So, changes in molecular configuration can be explained in terms of differences between intermolecular forces and packing forces in the molecular crystal that allow the molecular geometry to distort along a particular structural pathway. Also, as the authors noted, rearrangements of the molecular geometry that would be unfavorable in terms of free energy for a 'free molecule' would become allowed if this configuration would serve to lower the overall free energy of the entire molecular crystal [47].

In a related study, Bray and Drickamer investigated pressure effects on various tetrachlorocuprate(II) salts [48]. The complexes investigated were $Cs_2[CuCl_4]$, bis(trimethylbenzylammonium) tetrachlorocuprate, (*N*-phenylpiperazinium) tetrachlorocuprate, bis(*N*-phenylpiperazinium) tetrachlorocuprate bis(hydrochloride), and bis(*N*-methylphenylthylammonium) tetrachlorocuprate. The changes in molecular geometry, upon the application of pressure, and the effects on the electronic spectra were reported. According to the authors, the dihedral angles of the complexes were most affected by pressure [48]. The symmetry of all the compounds in the solid state was determined by the 'balance of two opposing effects', such as the lattice packing forces and anion–cation hydrogen bonding. The geometries of the complexes ranged between tetrahedral and square-planar. The authors also suggested that causing an imbalance of the competing interactions will lead to structural distortions along a stereochemical pathway and the different configurations encountered represent intermediate points on this pathway. The electronic spectra of the $[CuCl_4]^{2-}$ anions were studied up to ~ 80 kbar and changes to the spectra were evaluated in terms of the variation of the dihedral angle of each compound. Fig. 5 shows the crystal field splittings of the two extremes and intermediate geometries achieved by compressing the $[CuCl_4]^{2-}$ anion as a function of changing dihedral angle.

The electronic transitions were most affected in systems where the dihedral angle was large, i.e. $(tmba)_2CuCl_4$ and $(NphpipzH_2)CuCl_4$ [48]. Upon compression of these two complexes, the spectra changed quite drastically indicating significant changes in the $[CuCl_4]^{2-}$ configuration. Fig. 6 shows the pressure dependence of the electronic spectra as energy (kK) (1000 cm^{-1}) versus pressure (kbar).

In addition to the ligand-field transitions of the five complexes, there were very intense high-energy charge-transfer transitions that red shifted with increasing

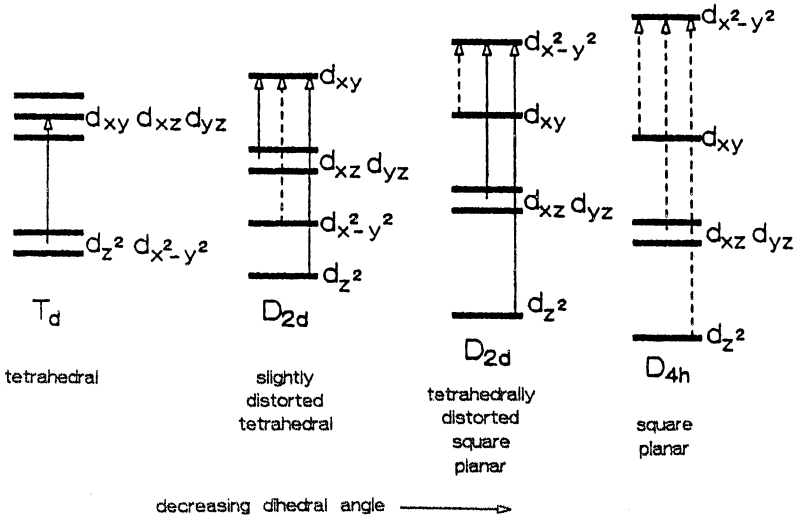

Fig. 5. One-electron energy levels of the tetrachlorocuprate ion in various geometries. Reprinted with permission from Bray and Drickamer [48]. © 1990 American Chemical Society.

pressure. This became a problem at the higher pressures (~ 80 kbar) when these charge-transfer transitions interfered significantly with the ligand field bands, which could no longer be resolved unambiguously [48].

Finally, pressure effects on a series of 5-coordinate Cu(II) complexes were also studied by Bray and Drickamer [49]. $[Cu(phen)_2(OH)_2]$ $(BF_4)_2$ (phen = 1,10 phenanthroline), $[Cu(bipy)_2(OH)_2]$ (S_2O_6) (bipy = 2,2′-bipyridyl), and $[Cu(bipy)_2]Cl$ X (X = ClO_4^-, $NO_3 \cdot 3H_2O$, $PF_6 \cdot H_2O$, and $Cl \cdot 6H_2O$) were examined. The aim of this particular study was to verify if, in fact, trigonal-bipyramidal complexes are more readily perturbed structurally than are square-pyramidal complexes. The latter has been shown to be the case in several 5-coordinate Ni^{2+} and Co^{2+} compounds studied earlier by Ferraro et al. [50,51].

The pressure-induced isomerizations in these studies were reported to follow certain structural pathways. These pathways are based on solid-state structural parameters relating to the overall coordination number and symmetry of the complex. Furthermore, for higher symmetry complexes, there are fewer structural pathways available for the molecular geometry. To illustrate the notion of a structural pathway for a particular coordination number, Fig. 5 shows the energy of a configuration, for one of the $[CuN_4]X$ complexes versus the dihedral bond angle, which was shown to vary significantly with pressure [49]. This pathway illustrates the routes of distortion from the configurations mentioned earlier and gives insight into the possible phase transitions that may accompany the structural distortions, depending on the profile of the potential energy diagram.

One of the chief results from the above study was that long, apical bonds are destabilized significantly under pressure. This apical distance was then used as a

parameter to describe the pronounced sensitivity of the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition (trigonal bi-pyramidal configuration). It was reported that complexes with smaller apical distances resulted in lower energy $d_{z^2} \rightarrow d_{x^2-y^2}$ transitions and low-energy shoulders as well. All the d–d electronic transitions were blue-shifted with higher

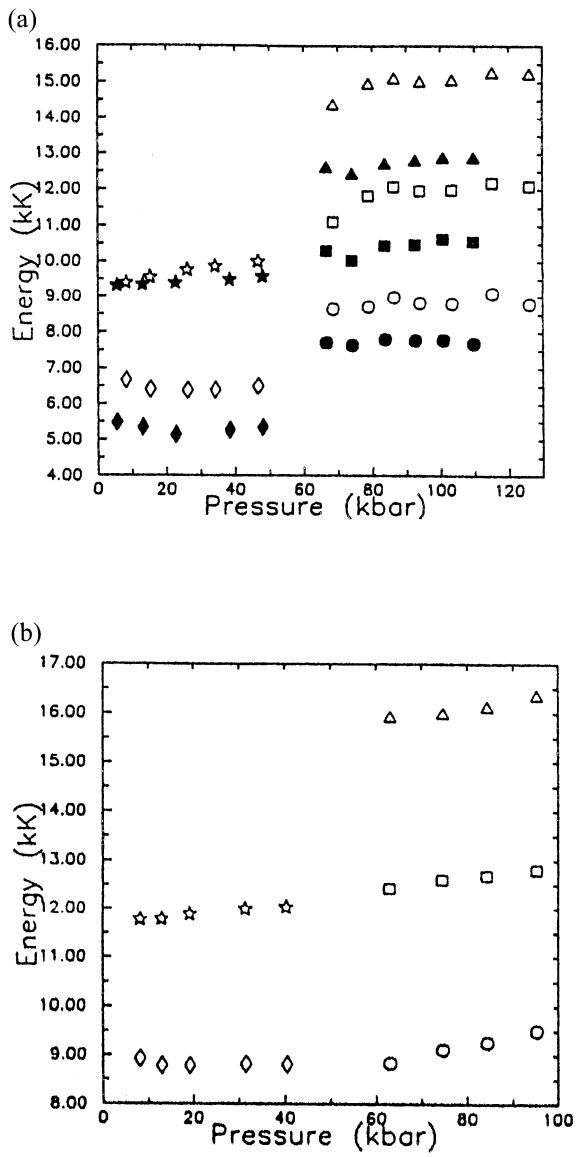

Fig. 6. Pressure dependences of the energies of the electronic transitions in: (a) $(tmba)_2CuCl_4$ and Cs_2CuCl_4; (b) $(NphpipzH_2)CuCl_4$. Reprinted with permission from Bray and Drickamer [48]. © 1990 American Chemical Society.

pressure. Depending on the complex studied and its original symmetry, the degree of separation (in terms of cm^{-1}) between the high- and low-energy d–d, transitions are related. For example, referring to Fig. 7, complexes on route B showed an energy separation of ~ 7000 cm^{-1} between the high- and low-energy bands, whereas those on the trigonal bipyramidal point showed separations of 4000–5000 cm^{-1} and have distorted bands in their electronic absorption spectra [49].

4.2. Pressure-induced spin crossover effects on electronic spectra

The spin-crossover phenomenon has proved to be a very interesting area in modern pressure studies on coordination compounds. Because our focus is on the effects of pressure on the electronic spectra, we will limit ourselves to studies which focus only on this approach to alter electronic structures or discuss results obtained by the application of pressure. The spin-crossover phenomenon was originally discovered by Cambi and co-workers in 1931 and, recently, there has been considerable interest in the possibility of using thermal- or light-induced crossovers for switching device applications [52]. Pressure has also been used to complement these other means of inducing crossovers, resulting in greater insight into the electronic and magnetic properties of many coordination systems. For a complete and recent review of spin-crossover phenomena, including extensive theory, brought about photochemically or by changes in temperature or pressure, see Ref. [52].

LFT can be used to treat spin-crossover systems. Using the Tanabe–Sugano diagram for the particular d^n complex e.g. see Fig. 4 in Section 4, as well as a configuration coordinate diagram for either a high-spin (HS) or low-spin (LS) system, the possible changes in spin-state can be understood. The configuration coordinate can either be the metal–ligand distance, r, or, especially when the ligands are not all the same type, the totally symmetric normal coordinate, Q. Fig. 8 shows two potentials corresponding to different states.

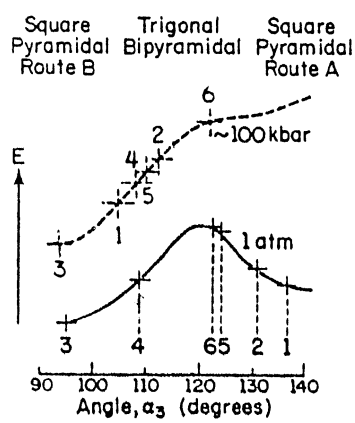

Fig. 7. Energy of the CuN_4X complex as a function of the bond angle, at ambient pressure (solid curve) and ~ 100 kbar (dashed curve). Reprinted with permission from Bray and Drickamer [49]. © 1991 American Chemical Society.

The strength of the ligand-field splitting of the transition-metal d-orbitals, according to basic LFT, is inversely proportional to the fifth or sixth power of the metal–ligand distance. Together with the intrinsic properties of the ligand, these inverse proportionalities determine the magnitude of the splitting energy, Δ. Under ambient conditions, ground states will exist as HS when Δ is less than the electron pairing energy, Π and as LS when the opposite is true. There is also coexistence between the HS and LS in systems due to variations in the vibrational and electronic state population from the effects of temperature on the Boltzmann distribution. This region of coexistence contains Δ values for which the difference between the two spin states is approximately $kT + \hbar\omega$. Outside of this region, excited states can be populated depending on the temperature. In solid coordination compounds, the cooperative effects discussed earlier are very important because application of an external pressure will have a great influence on these effects. Now, as pressure is applied to the system, the metal–ligand bond distance will decrease thus increasing Δ. Also, the Racah parameters, B and C, describing electron–electron interactions decrease with pressure, opposite of what Δ does. The spin-crossover occurs when $\Delta = \Pi$, as a result of a significant perturbation of the local environment of the central transition-metal atom (ion) which may 'feel' the cooperative solid-state interactions throughout the crystal. It is these interactions that support an ordered system but, because the spin-crossover is driven by entropy, these effects are negated when either temperature or pressure is increased. Additionally, there are two types of spin-crossovers that may occur. Spin transitions can be either continuous or discontinuous. For the solution-state case, the spin-crossover is always gradual and may be attributable to the non-rigid environment of the coordination compound. A solid will likely show a discontinuous spin change when structural rearrangements take place. This discontinuous spin-crossover in a solid represents a phase transition and thus occurs at a particular pressure and temperature. Alternatively, a continuous change in spin-state would

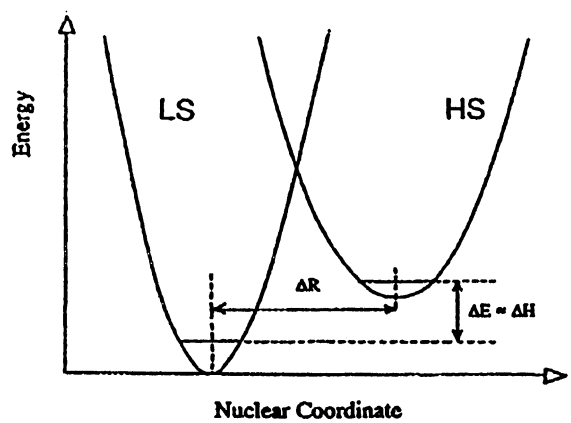

Fig. 8. Configuration coordinate diagram showing potentials for HS and LS states. E is the energy and Q is the normal coordinate which is displaced by pressure.

show no dramatic changes in molecular geometry and likely represents a displacement along a totally symmetric mode, which might also correspond to a steady shift of vibrational and electronic bands. Typically, a rearrangement in molecular geometry will stabilize the new spin configuration but this does not mean that spin-crossovers arising from distortions within the same point group will be less likely to occur. For both types of transition in a molecular solid, the extent of cooperativity of solid-state interactions plays an important role in determining the type of spin-crossover which may occur as the crystal is compressed. In pressure-induced spin-crossover applications with solids, it is preferable that crystals are not crushed thus preserving long-range order. Everett has considered this possibility in his theory of discontinuous spin transitions and that the domains mentioned earlier are important in determining the mechanism of the phase transition accompanying the spin-crossover [53]. There is also the possibility that the central atoms, being of the same molecular system, but on different lattice sites in crystalline solid will be in different spin states which are temperature dependent [54]. Also, for solid spin-crossover systems, there may be a statistical distribution of both HS and LS states within the solid [55], implying that certain structural phenomena are stabilizing the two states. In any case, when selecting a candidate coordination system, it is important to consider the ligand-field energy separation near a crossing point of two states to make the likelihood of a spin-crossover occurring much more probable over a reasonable pressure range.

The transition-metal centers that are usually studied in spin-crossover systems happen to be mostly 6-coordinate octahedral d^{4-7} Fe(II and III), Co(II), and sometimes Cr(III), Mn(II), and Ni(II) complexes, as well as some d^{5-8} complexes of lower symmetry [56]. All of these complexes naturally have a ligand-field splitting energy, Δ and electron-pairing energy, Π relatively close to one another in magnitude so that such a change is more likely to occur upon perturbation by pressure. High- to low-spin conversions are the most commonly studied spin-crossover transitions in the literature. However, the nature of spin-crossover ($HS \rightarrow LS$ or $LS \rightarrow HS$) depends on the temperature and the actual quantum mechanical ground state of the system. Aside from using absorption and emission spectroscopy for studying spin-crossovers, Mössbauer spectroscopy and magnetic susceptibility measurements can sometimes be undertaken to verify that the spin-state has changed upon compression. Raman spectroscopy is also useful in verifying that a phase transition has occurred (Fig. 9).

For a start, let us consider the equilibrium of two electronic states as a function of temperature [56], followed by a high-pressure study on the same and related complexes [57]. One initial study involved the effect of temperature on the equilibria between the $^5T_2$–$^1A_1$ states for Fe(1,10-phenanthroline)$_2$(NCS)$_2$ and Fe(1,10-phenanthroline)$_2$-(NCSe)$_2$ HS compounds. This was then followed by a pressure-tuning study on some of the same compounds by Fisher and Drickamer, who examined the effect of pressure on several Fe(II) 1,10-phenanthroline and 2,2′-bipyridyl complexes.

König and Madeja [56] have monitored the magnetic moments of both of the iron compounds above and compared their results with those obtained from a

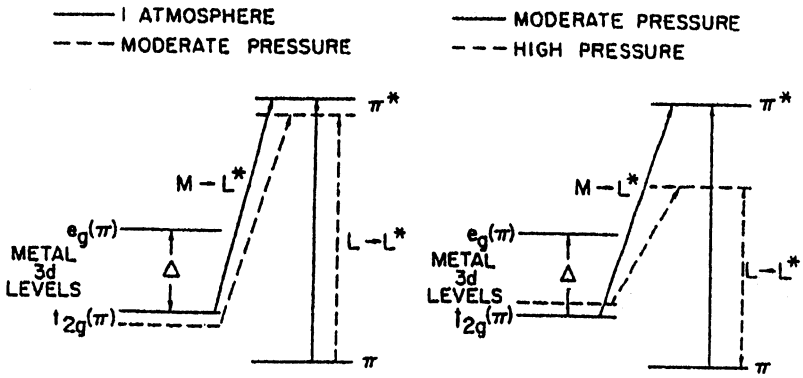

Fig. 9. Simplified MO diagram illustrating effects of pressure. Reprinted with permission from Fisher and Drickamer [57]. © 1961 American Institute of Physics.

Mössbauer investigation. Based on the predictions of the Van Vleck equation for magnetic susceptibility, the results agreed qualitatively for the $^1A_1$ state being close to the higher energy $^5T_2$ state [56]. The quadrupole splittings obtained from the Mössbauer spectra confirmed the presence of these two states. The two compounds were claimed to exist above the critical temperature in a $^5T_2$ state and below this temperature in a $^1A_1$ state. This was also rationalized by the temperature dependence of the electronic and vibrational spectra of these two compounds. From the electronic spectra, the Racah parameter, *B*, showed changes corresponding to the different ground states. It was also inferred from the vibrational spectra that a significant change in molecular geometry had occurred in the spin-crossover. The pressure behavior will now be compared for these two compounds at room temperature.

For the sake of distinguishing between the results obtained in the previous study, only the compounds studied in the temperature-dependent Mössbauer spectra will be considered. Fisher and Drickamer [57] found that the quadrupole splittings in the pressure-tuned Mössbauer spectra, for the two iron compounds, increased as pressure was applied. This change indicated a change from LS to HS in both of these complexes. At ambient pressure, the $Fe(phen)_2(NCS)_2$ complex was completely in the HS state. At 15 kbar, this complex was between 60–70% converted to the LS state [57]. However, as pressure was increased, the amount of the LS state was decreased. This type of behavior was not observed with the diisoselenocyanate complex which was converted entirely to the LS isomer. The strange behavior of the diisocyanate complex was attributed to significant back-bonding interactions that might have made complete conversion unattainable. Optical absorption showed red shifts of the $\pi-\pi^*$ and charge-transfer bands with the former shifting faster than do the latter. The following ligand-field diagram illustrates the pressure effects observed in the absorption spectra for the compounds studied.

Ferraro and Takemoto have investigated the pressure effects on the far-IR spectra of the same Fe(II) HS complexes studied by Drickamer and Fisher, i.e.

Fe(1,10-phenanthroline)$_2$ X_2 and Fe(2,2′-bipyridine)$_2$ X_2, where $X = NCS^-$ or $NCSe^-$ [58]. The purpose for this study was to shed light on the disagreement in interpreting the Mössbauer spectra that are assumed to be in spin-state equilibrium for Fe(II) and (III) complexes. A previous study of these compounds had showed a temperature dependence of the far-IR spectra. The effects of increasing pressure, as stated in the Drickamer and Fisher article, are not enough to convert completely the HS state to the LS one. As it turns out, Ferraro and Takemoto's work had confirmed Drickamer's Mössbauer results that complete conversion to the LS state was not possible, at low energy. However, cooling Fe(bpy)$_2$(NCS)$_2$ to 100 K allowed a complete conversion and subsequent heating to 353 K caused the system to revert back to the HS state. In this particular investigation, it was claimed that pressure had paralleled the temperature effects. In addition, a combination of temperature and pressure could bring about complete conversion of the HS to the LS state in Fe(phen)$_2$ X_2, based on the results from Fe(phen)$_2$(NCS)$_2$ and Fe(phen)$_2$(NCSe)$_2$. The reason suggested for complete conversion at low temperature and high pressure was the strengthening of the Fe–N bonds due to back-bonding effects from the metal t_2 orbitals to the ligand π^* orbitals. The onset of pressure was said to drive the back-bonding mechanism and to reduce the probability of an intraligand $\pi \rightarrow \pi^*$ transition by occupying the π^* orbitals [58].

Konno and Mikami-Kido have also investigated temperature and pressure effects on the spin state of Fe(bpy)$_2$(NCS)$_2$ by using electronic absorption spectroscopy and single-crystal X-ray crystallography [59]. For the latter method, the temperature was varied from 298–110 K and the changes in crystal structure were monitored. There were significant structural distortions accompanying the change from the HS to the LS state. This distortion was observed when the sample was cooled from 298 to 175 K and, upon further cooling, no additional structural changes were reported. Heat capacity measurements have also provided evidence of a thermal anomaly at 213 K associated with the spin-crossover. This result is also indicative of a phase transition occurring that involves a spin-state change. As discussed earlier, the significant shortening of the Fe–N bonds in the Fe(N)$_6$ coordination sphere are attributed to back-bonding effects. The pressure-tuned absorption spectra showed a MLCT maximum around 540 nm for the HS state. Upon compression and cooling to 77 K, the crystal showed a darkening of color and a large red shift of the absorption edge. At 40 kbar, the spectra exhibited two maxima with a supposed vibronic progression which was in agreement with the LS state absorption spectra that had two peaks at 538 and 595 nm [60]. At 330 kbar, the authors reported the appearance of 'net-like' boundaries that were said to be due to a domain structure. At this point, the spectrum showed a slight blue shift which could be attributed to a reconversion of the LS state back to the HS state. As the pressure was lowered back down to ambient, the position of the absorption band shifted 10 nm from its original position, presumably due to the molecules undergoing a small cooperative rotation in the LS form. The authors reiterated that in order to understand fully the mechanism of the spin-crossover phenomenon, changes to molecular geometry and cooperative effects leading to the transition such as Jahn–Teller distortions and vibronic coupling should be investigated further.

In a study using Fe(III)dithiocarbamate complexes, which happen to be the same which Cambi and co-workers used when they originally discovered the spin-crossover phenomenon, Butcher et al. [61] have investigated the nature and mechanism of the HS–LS spin-crossover and the possible existence of intermediate states. Temperature and pressure effects on spectroscopic, magnetic, and crystallographic data were undertaken for the $Fe(S_2CNR^1\text{-}R^2)_3$ complexes in different solvents. The important energy states of these complexes lie near a crossover point for HS ($^6A_1$) and LS ($^2T_2$), so it is quite easy to perturb the system with changes in pressure and temperature and achieve a spin-crossover. In addition to overall molecular geometry or environment of the transition-metal center, changes in ligand structure, especially those in which back-bonding can participate, exert influence the electronic properties of the central ion. The authors proposed two models for spin-crossovers: (1) a fast thermal equilibrium between separate HS and LS states to produce a weighted average of the HS and LS Mössbauer peaks at any given temperature and (2), a single 'mixed' spin state which would invalidate *S* as being a good quantum number [61]. It was said that Mössbauer spectroscopy could not be used to distinguish between the two models — however, a weak band was reported to grow slightly as pressure was increased to 6 kbar. This band was assigned to the $^2T_2 \rightarrow {}^2T_1$, ^2A transition and, at increased pressures, was found to favor the ground state ($^2T_2$). Vibrational spectroscopy also confirmed the presence of two states, one favored by pressure at the other's expense; this confirmation involved comparing the intensities of the two peaks corresponding to the Fe–S vibrations at different pressures [61]. Butcher et al. claimed that their results were further supported by other physical methods such as ESR and that, for the Fe(III) dithiocarbamates, there appeared to be only an equilibrium mixture of HS and LS states and not a mixed state.

The visible and far-IR spectra of several 5-coordinate, solid Co(II) complexes were examined by Ferraro and co-workers as a function of pressure. Co(2-diphenylphosphinoethyl)$_3$ amines ($=np_3$) of the type $[Co(np_3)X]\ B\Phi_4$, where X = Cl^-, Br^-, or I^-, are all normally HS, except for $[Co(np_3)I]I$, which is LS at ambient conditions [62]. X-ray crystallography has shown that the HS state is trigonal bipyramidal [63] and the LS state is tetragonal pyramidal [64]. Changes in the electronic absorption spectra were used to characterize the different spin states. Fig. 10 shows the absorption spectra for some Co(II) complexes at various pressures.

From Fig. 10, it can be seen that the HS state has two distinguishable bands, one intense and one weak band at high and low energy, respectively; the LS state has a broad band at low energy with only a small shoulder of the previously intense band remaining. These bands were not assigned by the authors but it was concluded that pressure favors the LS state and tetragonal-pyramidal molecular geometry [62].

Another study of solid Co(II) systems by Sacconi and Ferraro employed pressure and low temperature to study spin-crossover effects [65]. Tridentate amines with thiocyanates are used as ligands in the 5-coordinate cobalt complexes of the general formula, $Co(nnp)(NCS)_2$. These complexes were examined by far-IR and electronic

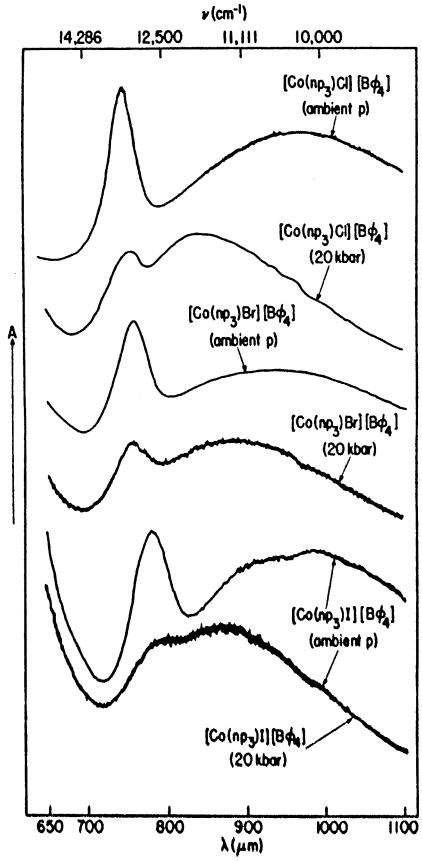

Fig. 10. Absorption spectra of $[Co(np_3)Cl]B\Phi_4$, $[Co(np_3)Br]B\Phi_4$ and $[Co(np_3)I]B\Phi_4$ at ambient and 20 kbar pressure. Reprinted from Ferraro et al. [62]. © (1979), with permission from Elsevier Science.

absorption spectroscopy at pressures up to 20 kbar and at temperatures of 300 and 100 K. At 10 kbar (300 K), there was a reported change in the spectrum that was probably due to partial conversion from a HS to a LS state. However, at 20 kbar (300 K), the spectrum 'washes out'. When the temperature was lowered to 100 K, complete conversion to the LS state was detected. From this observation, temperature effects clearly dominated. In any event, both high pressure and low temperature were shown to favor the LS state. The electronic spectra recorded were inconclusive in establishing whether or not a spin-crossover had occurred [65]. However, the significant blue-shifts observed were indicative of an increase in ligand-field energy. Two mechanisms were suggested to be responsible for the spin-state transition under pressure. It was also proposed that some spin pairing (LS state) initially occurred because of an increase in Δ which was aided by back-donation of Co(II) electrons to the π^* orbitals of the ligands, predominantly NCS^-. At higher pressures, this back-bonding effect was apparently hindered by intraligand $\pi \rightarrow \pi^*$ electron transfer thereby stopping the conversion to the LS state.

Ferraro and co-workers have also looked into pressure and temperature variations to achieve spin-crossovers in a series of Cu(II) and Ni(II) systems. The Cu(*N*-diethylethylenediamine)X_2 and Ni(*N*-diethylethylenediamine)X_2 complexes, where X = inorganic anion, were examined using electronic and IR spectroscopy [66]. These complexes showed a strong red shift for the d–d absorption band as the temperature was increased. The mechanisms for this behavior were designated as continuous and discontinuous thermochromism. These mechanisms are associated with a distortion of the tetragonal metal environment and the axial interaction between the MN_4 plane and anions, as concluded by Lever [67]. A strong anion dependency was shown in the pressure-tuned absorption spectra with small red-shifts observed in the Cu(dieten)$_2X_2$ complexes, whereas a blue-shift occurred in the Ni(dieten)$_2X_2$ complexes. For the latter species, as the anions became larger and thus more polarizable, the degree of blue-shift became smaller. Also with I^- as the anion, a red-shift occurred for the Ni(dieten)$_2X_2$ complex. The differences between the pressure and temperature effects on the electronic spectra were attributed to the geometry of the complexes. As the temperature was increased, the electronic spectra were typical of 6-coordinate Cu(II) and Ni(II) complexes, whereas with increasing pressure, the electronic spectra were characteristic of 4-coordinate complexes on the basis of color changes. In addition, because of the anomalous blue-shifts for the nickel complexes, it was suggested that there was less anion interaction with the complex in the axial direction. Higher temperatures were needed for activation of thermochromism mechanism for the nickel complexes.

As a comparison to the pressure-tuned electronic spectra of the Fe(II) 1,10-phenanthroline complexes discussed earlier, Zarembowitch et al. have examined these compounds with XANES [68]. The conversion of the HS state to a LS one was monitored as a function of pressure and reported as a ratio of the two states which was in agreement with the previous pressure and temperature studies performed on these complexes.

A study by Jeftic and Hauser revealed how the application of pressure accelerates the relaxation from HS → LS in Fe(II) systems. The HS → LS relaxation of $[Zn_{1-x}Fe_x(ptz)_6](BF_4)$; where ptz = 1-propyltetrazole and $x = 0.1$, was found to increase by one order of magnitude at low temperature and an external pressure of 1 kbar [69]. A thermal spin transition occurs from the LS ($^1A_1$) state at low temperature to the HS state ($^5T_2$) at high temperature, the same being true for the neat $[Fe(ptz)_6]^{2+}$ complex [69]. In the pressure-tuned, single-crystal absorption spectrum, at 44 K, the band maximum ($\sim$560 nm) shows a blue-shift with increasing pressure, indicating a decrease in the metal–ligand bond lengths. At the temperature that the spectra were recorded, the system is in the LS state and the authors claimed that the application of the external pressure accelerates the HS → LS relaxation significantly.

All of the studies thus far have shown that pressure, along with temperature on some occasions, can be used to convert the spin-state of certain coordination compounds. As suggested from these studies, the spin-crossovers are the result of rearrangement of the molecular geometries which, in turn, alters the electronic structures and favors changes in spin-state. Also, most of these studies used

complementary techniques to study the spin-crossover phenomena. Such use of multiple techniques is extremely important to characterize properly spin-crossovers and the changes they bring about to the molecules and overall systems. To determine if a phase transition has occurred with spin-crossover, the accompanying vibrational spectra may be very helpful. Also, monitoring the magnetic moments of the samples is, of course, crucial in such studies. Though we chose to limit our coverage of spin-crossover and related phenomena to some relatively simple systems in which the effect of pressure on the electronic and magnetic properties, there is some current interest in exchange interactions and spin-state relaxation processes which are covered quite well in Ref. [52]. Overall, the spin-crossover phenomenon is an area with vast possibilities for future research and the use of external pressures has a great significance and relevance within this area.

4.3. Pressure effects on excited-state decay

In Section 3.2, we discussed how pressure shifts electronic energy bands and affects band intensities. The latter are considered indicative of the type of relaxation from the excited-state. The normal coordinate displacement, along a single or multiple vibrational modes, which the molecules distort, will play a role in the relaxation from the excited-state. It is known that the molecule will relax, radiatively, from the excited-state when the excited-state potential energy surface has a minimum along the normal coordinate which was displaced. Essentially, non-radiative relaxations are the result of a marked distortion of the excited-state and are seen as a decrease in emission intensity.

To explain non-radiative excited-state decay becoming more efficient with higher pressures, the energy gap law may been applied to pressure applications of luminescence spectroscopy [70–72]. A series of pressure studies has been undertaken for selected Re(I) and Ru(II) complexes in different solvent media, as well as low-temperature measurements to determine the effect on the radiative and non-radiative decay rates from excited states. These decay rates are represented by the following equations:

$$k_{\mathrm{r}} = \phi/\tau \tag{15}$$

$$k_{\mathrm{nr}} = (1-\phi)/\tau \tag{16}$$

where k_{r} and k_{nr} corresponding to the radiative and non-radiative decay rates, respectively, ϕ the radiative quantum yield, which is the ratio of the number of molecules undergoing an electronic transition versus the number of photons absorbed by the sample, and τ the lifetime of the excited state. As mentioned in Section 3.2, radiative quantum yields are measured by numerical integration of the emission peak. To relate the latter quantity to the intensities of the electronic transitions, the ratio of the quantum yields at high pressure to that at ambient pressure, ϕ/ϕ_0 is proportional to the intensities at high pressure to those at ambient pressure, I/I_0, [74–76]. The quantum yield is usually corrected for changes in refractive index, such as solvent media, and is proportional to the square of the ratio between the refractive index of the solvent to that of a standard. Since these

experiments were carried out with solvents of different polarity, k_r will depend on the dielectric constant of the solvent, ε.

Salman and Drickamer [70] have investigated the effects of pressure and freezing on the luminescence for complexes of the general formula, $ClRe(CO)_3X$, where X = 1,10-phenanthroline and 4,7-diphenyl-1,10-phenanthroline. In addition, five different solvents were employed in studying these effects, viz. *m*-xylene, chloroform, acetonitrile, heptanol, and dimethyl formamide (DMF). At the phase transition of the solvent, there was a dependence of the radiative rate of the luminescence on the polarity of the solvent. On the other hand, the solid forms of the complexes showed no changes in radiative rate with pressure. The polarity of the solvent is clearly crucial for this effect. The authors concluded that there was a good correlation between k_r and ε for both compounds in all the solvents for which the phosphorescence emission of the two complexes was investigated. The change in ε for *m*-xylene was described by the Clausius–Mossotti equation because this solvent changes density with increased pressure. For polar solvents, such as heptanol and DMF, it was noted that ε increased much faster with pressure and this was attributed to increasing anisotropy of the dipoles [70]. Also, for polar solvents, a large and discontinuous drop was reported for k_r and ε. This drop was explained by the large decrease in the orientational polarizability of the solvent molecules as temperature was decreased and the samples underwent a phase transition and solidified.

For non-radiative rates in the liquid and solid state, the energy-gap law states that k_{nr} depends exponentially on the energy gap between the ground and excited states [72]. The authors have reported a decrease in k_{nr} with increasing pressure in the solid-state, which resulted in a blue-shift of the emission band. They explained this decrease by the energy-gap law, which also exhibits an exponential dependence on the probability of a non-radiative transition. The dependence was demonstrated by plotting $\ln(k_r)$ versus emission energy. According to the energy-gap law, this relationship should be linear and any deviations from linearity could most likely be explained by a change in shape of the ground-state potential surface as evidenced by a decrease in the emission peak half-width.

In a related study, the effect of pressure on the luminescence energy and efficiency of $SRe(I)(CO)_3L$ complexes, where L = 1,10-phenanthroline and 2,2′-bipyridine and X = simple anions such as Cl^-, Br^-, CN^- and organic ligands, were investigated in polymeric media and in the crystalline form [71]. The polymeric media chosen were quaternized poly(4-vinylpyridine) (QPVP), poly(4-vinylpyridine), and poly(acrylic acid). From previous studies, it was concluded that the emitting state is a spin-forbidden triplet that arises from a metal–ligand charge-transfer (MLCT) at room temperature. The authors aimed to tune the photophysical and photochemical properties by varying the solvent, the ligands, the temperature, and the pressure to change excited-state properties of the complexes. The complexes in this study were reported to have multiple emission characteristics. As the temperature was lowered to 77 K, two emissions were observed, the MLCT [$Re \rightarrow \pi^*$(phen)] and an intraligand π–π^* transition, the former occurring at lower energy [71]. The intense MLCT band dominated the spectra at low temperature and

even more so at room temperature. For almost all of the compounds, pressure-induced red shifts were observed in the emission spectra and this was attributed to the electrons in the excited-states becoming more polarizable. The degrees of red-shift were also determined by the interactions with the solvent media, such as dipole-induced dipole interactions. Because the excited state is triplet in character, this was said to be less 'tunable' due to the necessity to keep parallel spins apart thereby reducing the polarizability of the excited state. As pressure was increased, intensities changed to a varying degree depending on the solvent medium. These intensity changes were rationalized by using the energy-gap law. In an analogous study involving the MLCT transitions in similar Re(I) compounds, the plot of $\ln(k_{nr})$ versus the emission energy was shown to be linear [72]. It was claimed that the energy gap law in pressure-tuning luminescence studies can be used to interpret the relation between luminescence intensity and energy. In general, if a pressure increase leads to a decrease in luminescence intensity and energy, then k_{nr} will increase.

In some extensive work on the luminescence spectra and luminescence efficiency of Ru(II) tris-bipyridyls, the effects of high-pressure have been thoroughly investigated [73–75]. The interesting photophysical and photochemical properties of these compounds can be pressure-tuned and allow a critical test of the theory for the relaxation from excited states. Yersin and Gallhuber have examined the spectroscopic properties of single crystals of $[Ru(bpy)_3]^{2+}[PF_6]$ (bpy = 2,2′-bipyridyl) under pressure. This was the first pressure study of single crystals of this compound, which previously had been investigated while incorporated into glassy matrices, mixed crystals, or in solution [73]. A red-shift, sharpening of the luminescence spectra and a decrease in the intensities were among the features observed as the pressure was increased. Fig. 11 shows the unpolarized luminescence spectra collected at 1, 25 and 52 kbar (295 K).

The observed electronic transitions were assigned to a MLCT ($t_{2g} \rightarrow \pi^*$) and an intraligand ($\pi \rightarrow \pi^*$) transition. These transitions were classified in the D_3' double group to account for spin–orbit coupling effects [73]. Also, the intensities were reported to decrease tenfold by the time that 35 kbar was reached. The explanation for this observation was that the emission process was coupled to an energy barrier corresponding to a non-radiative relaxation of the excited state that was lowered by pressure. The non-radiative relaxation was studied for $[Ru(bpy)_3]^{2+}$ in solution and was shown to be an activated process that was dependent on the type of solvent [73]. A correlation between solution and solid-state effects on non-radiative relaxations to the ground state may be inferred from this example.

Further studies by Fetterolf and Offen have attempted to clarify the effect of solvents by studying the effects of pressure on the luminescence spectra, quantum yields, and lifetimes of excited states using Ru(II) and some Os(II) polypyridyl complexes [74–76]. The authors first investigated the pressure effects on the MLCT transition and how the excited state loses its energy through non-radiative mechanisms back to the ground state. Ru(II) and Os(II) tris-2,2′-pyridyl and tris-1,10-phenanthroline complexes were used to investigate these effects. Luminescence experiments were performed for the complexes dissolved in acetonitrile for pres-

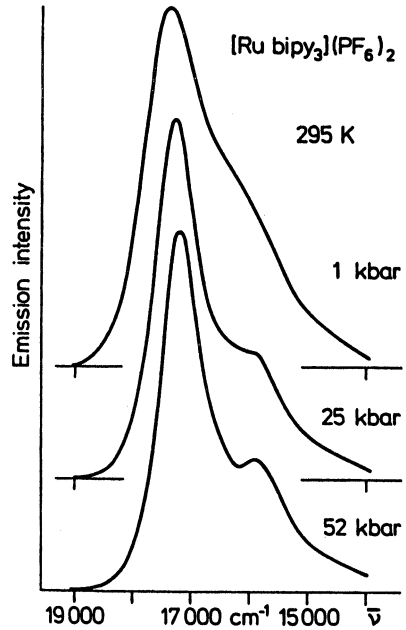

Fig. 11. Unpolarized emission spectra of single-crystal $[Ru(bpy)_3](PF_6)$. Reprinted with permission from Yersin and Gallhuber [73]. © (1984) American Chemical Society.

sures up to 30 kbar and at a temperature range of 2–70°C. The radiative and non-radiative rates for the MLCT emission increased up to the highest operating pressure [74]. For the Ru(II) complexes, the pressure effects decreased the lifetimes of the excited states, τ, quite significantly because a third channel from the MLCT → ligand-field state was thermally accessible but not by pressure [74]. The reciprocal of the lifetime of the excited state is proportional to the exponential of the energy barrier for crossing over from the MLCT state to those of the ligand-field states. Thus, as the energy barrier increases with pressure, the lifetime becomes smaller, as was observed by the authors in this case. Also, red-shifts were observed in the emission and absorption bands with the latter being ~ 2–3 times greater than that of the former [74], and the pressure dependences of the quantum yield, ϕ, were determined from the corrected intensities, I. Finally, measurement of the activation volumes for τ leading to the various decay channels were found from Eq. (17)

$$\Delta V_\tau = -RT\left[\frac{\partial \ln \tau^{-1}}{\partial P}\right]_T \tag{17}$$

to be $\Delta V_\tau = 11.5$ ml/mol for the MLCT → ligand-field deactivation of $[Ru(bpy)_3]^{2+}$ in acetonitrile [74].

In a follow-up study by the same authors, the pressure dependences of the luminescence lifetimes for $[Ru(bpy)_3]Cl_2$ and $[Ru(phen)_3]Cl_2$ in H_2O and D_2O were

studied. As in the previous work, the pressure effects on the lifetime of the excited state, τ, were dependent on the temperature of the solution. The authors proceeded in a similar fashion to find the activation volumes for the three possible decay channels as a function of pressure, solvent, and temperature and determined whether or not such a treatment can be generalized with protic solvents [75].

Fetterolf and Offen next used the loss of luminescence intensity to monitor the photosubstitution reactions of $[Ru(bpy)_3]Cl_2$ and $[Ru(phen)_3]Cl_2$ in acetonitrile for pressures up to 30 kbar and temperatures ranging from 15–60°C. The reaction appears as follows [76]:

$$[*Ru(bpy)3]2^{+} + Cl^{-} + [*Ru(bpy)_2bpyoCl]^{+} + CH_3CN \rightarrow [Ru(bpy)_2(CH_3CN)(Cl)]^{+} + bpy \quad (18)$$

Overall, pressure decreased the rate of photoreaction at all temperatures, which were reported in terms of apparent activation volumes. Time dependences of the luminescence intensities were compared with those determined from the spectra taken at moderate and high pressures. It was found that higher pressures caused much smaller decreases in intensity as time increased [76]. This situation was represented by plots of I/I_0 versus time and reflected the rate of photolysis. Also, the photochemical quantum yields showed decreases for both complexes as the temperature and pressure were increased. Furthermore, it was noted that the quantum yield was more sensitive to pressure at higher temperatures for both complexes. It is thought that the MLCT → ligand-field state is an intermediate in the photosubstitution reaction and that the energy barrier for the ligand-field state is dominant along the reaction coordinate, while being responsible for the strong temperature dependence in the activation volumes reported previously [76]. The presence of ion-pairing was suggested as a reason behind the temperature dependence of the activation volume as well as solvent type and polarity.

Recently, a comprehensive review was published by Yersin and Strasser that covers, exclusively, relaxation dynamics in some coordination systems. This includes a section on $[Ru(bpy)_3]^{2+}$ which looks at, among other physical effects, pressure dependence on the excited-state decay [78]. We have included this section on pressure-dependent relaxation dynamics to augment the other pressure studies on electronic spectra of coordination compounds to give a broader background into all of the relevant points of interest. This is most vital when considering pressure-induced changes in luminescence efficiency and the vibrational modes responsible for the changes in efficiency. By explaining the pressure-induced changes in terms of activation volumes and the energy-gap law, the possible excited-state decay channels can be better understood. Also, it is equally important to select a molecule that exhibits interesting electronic features that have been characterized properly. Such is the case with the popular $[Ru(bpy)_3]^{2+}$ complex, which is known for its well-studied electron-transfer properties in the ground and excited state. Now, a firm understanding exists for studying excited-state phenomena and the changes which take place with application of an external pressure.

4.4. Pressure effects on the fundamental parameters of electronic spectra

When applying pressure-tuning methods to electronic spectroscopy, it is of utmost importance to define the effects of pressure on the ligand-field parameters describing a coordination system. Earlier, it was mentioned that Tanabe–Sugano diagrams can be adapted to pressure studies. For example, the ligand-field energy, Δ, changes linearly with pressure so that pressure can replace the ligand-field energy as the abscissa in these diagrams. In addition, as pressure alters Δ, the effects on the electronic states can be understood by considering the slope of these states on a particular d^n Tanabe–Sugano diagram. For example, the steeper the slope of a state, the more it will be influenced by pressure. In addition, pressure may lead to the further repulsion of states of like symmetry which can be explained by perturbation theory. Also, to describe the change of the environment of the transition metal center, modern ligand-field models can be used to help explain pressure-induced changes to electronic spectra, such as the AOM previously discussed. The AOM has the advantage that it can be used for any complex provided the geometry is known. While there are other quantitative and semi-quantitative methods for calculating the MO energies for the formation of a coordinate system, e.g. density functional methods, based on either empirical information or ab initio calculations, few of these methods have been used in pressure applications (Fig. 12).

Several studies will now be presented in which the pressure dependences of the fundamental ligand-field parameters have been examined. Schäffer and co-workers have reported an important study in which the pressure-tuning of partial quenching of parametrical tetragonality of a Cr(III) complex has been investigated [79]. Electronic absorption spectra of $[Cr(NH_3)_4F_2]$ $[AsF_6]$ were pressure-tuned up to 100 kbar. It was shown through parametric analysis that the Cr–N single bonds were more compressible than are the Cr–F bonds due to a partial multiple bond character of the ammonia ligands [79]. This situation was attributed to the fact that, for octahedral complexes, the e_g orbitals, by symmetry, can only form σ bonds and not π bonds, whereas the t_{2g} orbitals are capable of such π interactions. By the previous argument, the ligand-field energy, Δ, can be written as a difference between the σ and π antibonding energy [79]

$$\Delta = \Delta_\sigma - \Delta_\pi \tag{19}$$

The spectrochemical series for ligating atoms were described in terms of the above condition. Yamatera and McClure have used these components to redefine a spectrochemical series based on Δ_σ and Δ_π [80,81]. The spectrochemical series can be written as:

$$\begin{aligned} &Br^- < Cl^- < H_2O < NH_3 < F < OH^- \quad \Delta_\sigma \\ &NH_3 < Br^- < Cl^- < H_2O < F^- < OH \quad \Delta_\pi \end{aligned} \tag{20}$$

The pressure dependence on these spectrochemical parameters can now be understood and compared to the effects of pressure on the traditional nephelauxetic series. In this case, because of the tetragonal nature of the CrN_4F_2 complex, D_{4h}

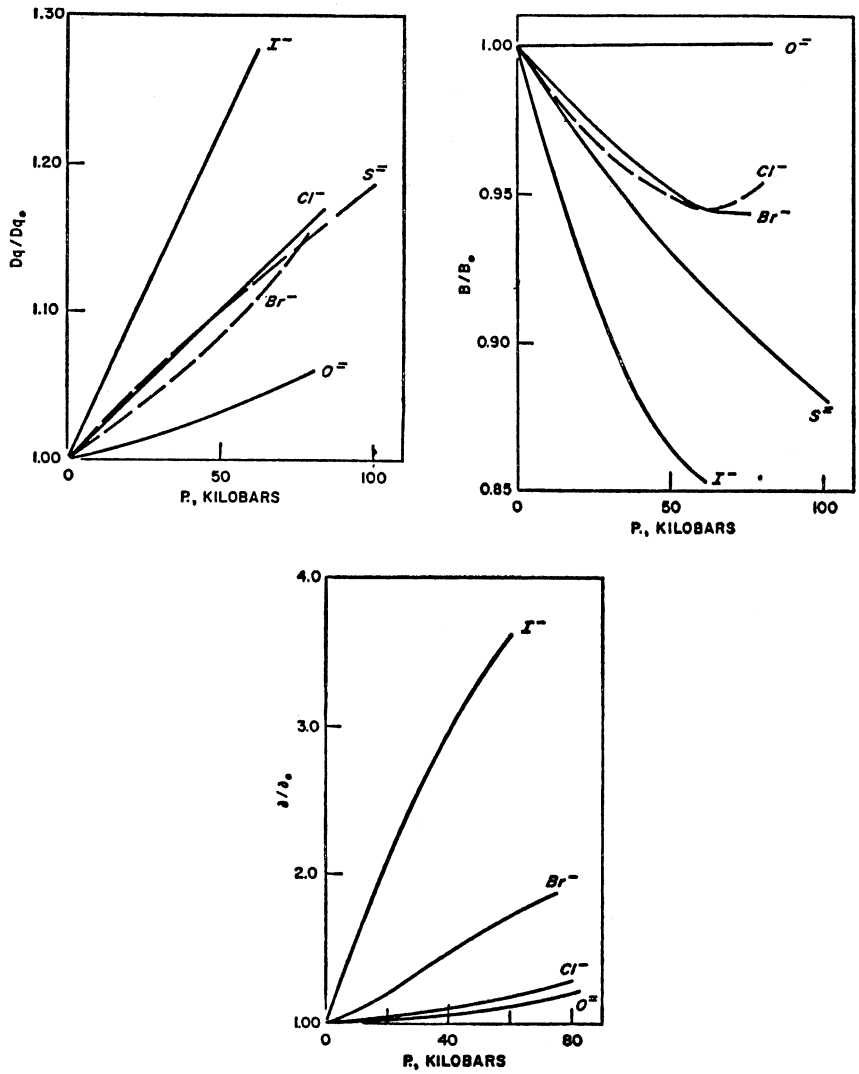

Fig. 12. Pressure dependence of: (a) Δ; (b) B; and (c) δ with varying ligands around a Co(II) center. Reprinted with permission from Stephens and Drickamer [84]. © American Institute of Physics.

symmetry best describes the molecular geometry. The tetragonal ligand-field was now written as mutually orthogonal parametric operators which are described in terms of the average octahedral field, Δ(d), and for the parametrically independent tetragonal fields, Δ_σ and Δ_π [79].

By employing the AOM method, the overall ligand-field was partitioned into separate components and the overall ligand-field is a sum of all these separate contributions. Empirical parameters, i.e. transition energies, are now compared to

the expressions obtained from the AOM. The changes observed for the separate ligand parameters are rationalized from the pressure-tuned ligand-field spectra. According to the Tanabe–Sugano diagram, the ground-state for this octahedral d^3 system, is $^4A_{2g}$ with transitions to spin-allowed excited states, $^4T_2$, a^4T_1, and b^4T_1, being observed. The separate ligand-field parameters, Δ_N and Δ_F, both increased with pressure, Δ_N more than Δ_F. Also, the Racah parameter, B, increased smoothly with increasing pressure [79]. All of the transitions to the triply degenerate quartet excited states split and blue-shift with increasing pressure. In short, this quantitative treatment of the pressure dependence of separate contributions to the ligand-field energy provides an excellent first approach in establishing the chemical significance of these methods.

Drickamer and co-workers have applied pressure-tuning techniques to many coordination systems in effort to study the behavior of electronic spectra under pressure [82–85]. The first examples investigated by these researchers involved Fe(III), Co(II), Cr(III), and Ni(II) octahedral complexes [82]. Electronic absorption and, sometimes charge-transfer, spectra were pressure-tuned up to ~ 130 kbar for $CoSO_4 \cdot 7H_2O$, $K_3[Fe(CN)_6]$, $[Ni(NH_3)_6]SO_4$, $[Ni(H_2O)_6]SO_4$, $[Cr(NH_3)_6]Cl_3$, and $KCr(SO_4)_2 \cdot 12H_2O$. The pressure dependences on the ligand-field energies were determined for these complexes and, in all cases, the absorption maxima exhibited blue-shifts with increasing pressure and increases in the ligand-field energy Δ. Also, the approximate changes in metal–ligand bond lengths were described in terms of the changes to Δ. Intensity changes were rationalized as changes in the oscillator strength related to the energy maxima of the absorption peaks. These changes in oscillator strength, which are proportional to the natural logarithm of (I/I_0), were estimated from the changes in Δ and ν_{max} [82].

In some related work, Stephens and Drickamer investigated the effect of pressure on some Ni(II) and Co(II) complexes [83]. The first paper involved an examination of five tetrahedral Co(II) and two tetrahedral Ni(II) complexes. Changes to Δ, the Racah parameters, and the spin–orbit splittings were noted from the pressure-tuned electronic absorption spectra [83]. It was shown through changes in the spectra that Δ increased while the interelectronic repulsion Racah parameter, B, decreased with pressure. The rationale for these observations was attributed to the large polarizabilities of the ligands. In addition, spin–orbit coupling effects were studied for the five Co(II) complexes. Some spin–orbit splitting, δ, was noted for the $^4T_1$ excited-state, which appeared to have split into at least three components.

In a closely similar study, the same authors examined five Ni(II) complexes: $Ni(o\text{-phen})_3(NO_3)_2$, $Ni(\alpha\text{-}\alpha'\text{dip})_3Br_2$, $Ni(en)_2(SCN)_2$, $KNi(Gly)_3$, and NiO, where o-phen = o-phenanthroline, α-α'-dip = α-α'dipyridyl, and en = ethylenediamine [84]. The electronic absorption spectra of these complexes were pressure-tuned up to 150 kbar and the effects on Δ and B were determined. In general, Δ increased with pressure thus causing a blue-shift in the absorption bands while B decreased with increasing pressure. The latter was attributed to an increase in covalency between the Ni(II) center and the ligands when pressure was applied [84]. Increasing polarizability was also considered to be a factor. The authors further stated that calculation of B as a function of pressure provides a convenient means of explaining deviations from LFT.

Since most of the coordination systems discussed so far have been 3d transition metals, it is worthwhile considering some complexes of heavy transition metals. Balchan and Drickamer have studied the effect of pressure on the charge-transfer transitions of some 4d and 5d transition metal complexes of the general formula, MX_6 where M = Ir(IV), Pt(IV), Pd(IV), Os(IV), and Pb(IV) and X = Cl^-, Br^-, and I^-. In the eight complexes studied, red shifts occurred for the LMCT, $\pi \rightarrow t_{2g}$ transitions for the iridium and osmium complexes and $\pi \rightarrow e_g$ transitions for the platinum and palladium complexes, and all the bands displayed pressure broadening [85]. For $[IrCl_6]^{2-}$, however, a reversal in the direction of the shift was noted. The effects of spin–orbit coupling were also thought to have increased with pressure.

These studies illustrate effectively how pressure can cause changes to the electronic properties of coordination compounds and thus help to define more explicitly the parameters that describe these properties. It would therefore be most beneficial to employ modern theory and quantitative methods in understanding how pressure affects electronic transitions in coordination compounds.

5. Conclusions

Since the pioneering high-pressure work of Bridgman (see Ref. [10] for a detailed background), pressure-tuning applications in spectroscopy have become much more practical and versatile. Aside from the applications to electronic spectroscopy, there are a multitude of potential uses for this technique in such diverse fields as materials science and geology. With the advances in the modern theory of electronic structures of coordination compounds, the variation of pressure will provide further insight into the limits of the application of such theoretical principles. Since the basic effects of pressure are well known for both solid- and solution-state coordination compounds, it is now important to augment pressure studies by treating the spectra using more up-to-date theoretical models.

Pressure-induced perturbations of a solution or solid coordination system can be quite significant and an imbalance of the disparate forces governing molecular geometry and intermolecular interactions can lead to dramatic changes in the electronic structure of these coordination systems. Most often, it is very difficult to determine whether the intramolecular or intermolecular properties will be influenced more under pressure and how they interact and influence one another. This competing nature of the intramolecular and intermolecular forces presents a large hurdle to overcome when studying pressure effects on electronic spectra. Then, further probing into the nature of electronic structure by studying pressure effects will ultimately be useful for finding many more potential chemical applications of the conventional theory. Furthermore, critical tests into the validity of formulations and models, such as the orbital symmetry rules, for use in pressure-induced molecular distortions should prove beneficial in expanding conventional electronic spectroscopy. We include the discussion on orbital symmetry rules to point out that it would be highly desirable to have a theory which may suggest possible distortion

routes of molecular geometry under pressure and better describe the relationship between structural and electronic parameters. It can be inferred from the section on piezochromism that there exists a potential basis for applying the orbital symmetry rules discussed in Section 3.1. Careful studies involving multiple spectroscopic methods will likely be needed to properly carry out such experiments. However, the prospective benefits of the utility of such a theory would be most valuable for further work in this field.

In addition to the pressure-induced changes in molecular geometry, the use of pressure to cause drastic changes in the ground state of a coordination complex is an active area of interest. The spin-crossover phenomenon can be studied not only with external pressure application but with other methods as well. Some of the most current work involves the use of pressure, as well as temperature and light variation, to study exchange interactions and spin-state relaxation in some interesting inorganic systems. Some of the most recent work in this area has been covered quite well in Ref. [52]. We have, however, chosen to cover some of the more classical studies which focus almost exclusively on the pressure-tuned electronic spectra of coordination systems to illustrate how pressure is a factor in this phenomenon. Even so, future work in this area will most probably involve studies on similar systems due to the many interesting features of coordination systems with transition-metal centers.

In addition, the distortions that occur when excited-state energy levels are populated have an effect on the radiative efficiency of luminescence, thus making these processes interesting to study under pressure. This is most obvious in that one of the common effects of external pressures is to decrease luminescence intensity. The excited-state distortions will most likely occur along the totally symmetric normal coordinates. However, there may also be distortions along non-totally symmetric coordinates, depending on the symmetry of the excited-state MO. The structural rearrangements arising from the application of pressure will then have an effect on excited-state distortions as well, especially if pressure can further split a degenerate low-lying excited state. Pressure-tuning the resonance Raman spectra of coordination systems may provide additional insight into excited-state molecular distortions and complement the electronic spectra. This would also complement studies done on luminescence lifetimes and how they change with pressure. Additionally, almost all pressure studies of the electronic spectra of molecular coordination systems yield broad unresolved bands, resonance Raman would then be most helpful in understanding molecular distortions in the excited state.

Over the next few years, it is anticipated that there will be many more experimental studies undertaken and that quantitative theoretical treatments of the resulting pressure-tuning data will become common. Despite the wealth of information yielded in pressure-tuning applications in electronic spectroscopy, the amount of this information actually extracted from the experiment is usually very limited quantitatively speaking. Therefore, obtaining resolved vibronic structure, by lowering the temperature as well as careful selection of coordination system, would be most beneficial in advancing the current theory by better defining the changes in physical structure that are responsible for the features of the electronic bands under

pressure. We hope this review has shown that the application of external pressures in spectroscopic methods has many promising applications in not only coordination systems but in other fields as well.

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