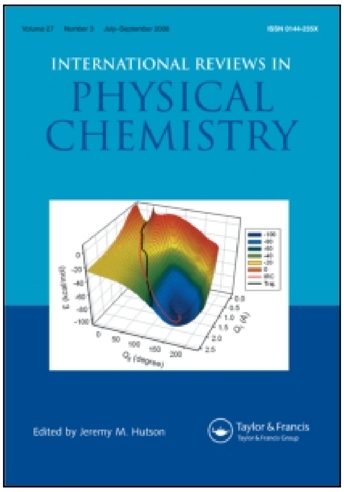

International Reviews in Physical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713724383

Pressure-induced molecular rearrangements in the solid state

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To cite this Article Drickamer, H. G. and Bray, K. L.(1989) 'Pressure-induced molecular rearrangements in the solid state', International Reviews in Physical Chemistry, 8: 1, 41 — 64
To link to this Article: DOI: 10.1080/01442358909353222
URL: http://dx.doi.org/10.1080/01442358909353222

INTERNATIONAL REVIEWS IN PHYSICAL CHEMISTRY, 1989, VOL. 8, NO. 1, 41–64

Pressure-induced molecular rearrangements in the solid state

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In gases molecular rearrangements are stochastic processes, that is, the relative amount of each configuration is determined by the difference in free energy between the molecular configurations. In normal liquids the same relationships apply, although ΔG is perturbed by differences in nearest-neighbour interactions with each configuration. In a strongly bound solid it may be that no molecule can transform until they all do, in this case the process involves a first-order phase transition. In weakly bound molecular crystals, polymers and similar media, the range of interaction may lie between the nearest-neighbour and the macroscopic limit, that is, the process may be neither first order nor stochastic.

We present a series of pressure-induced molecular rearrangements, some of which are stochastic in the crystalline solid, some are first order, and a number are intermediate. Transformations which are first order in the crystalline solid may be higher order to stochastic in a polymeric environment. It is hoped that sufficient systematic study may lead to some degree of predictability as to the effects of the degree of change of molecular geometry involved and the type, and intensity, of bonding forces in the medium on the type of transformation observed.

1. Introduction

Over the past 35–40 years it has been amply demonstrated that pressure is a powerful and versatile tool for examining and understanding the molecular and electronic properties of condensed phases. Basically, compression perturbs the various electronic (or vibrational) energy levels of molecules to different degrees. From this differential perturbation, which we call 'pressure tuning', one can extract a wide variety of information. In this review we show how pressure tuning can be used to understand the nature and mechanism of molecular rearrangements in crystalline solids and other relatively rigid media.

It is useful to present first a few general remarks about molecular rearrangements, especially in rigid media. Molecular rearrangements in the gas phase or in (dilute) solution are stochastic processes, that is, the probability of a given molecule rearranging at some temperature and pressure depends only on the free-energy difference between the two molecular geometries. As a limiting case, in a perfect crystal where the molecules are strongly interacting, all molecules must rearrange simultaneously. This is a totally cooperative process—a first-order phase transition. If the molecules interact only weakly in the crystal, the probability of a given molecule rearranging if its neighbour rearranges may be less than one but greater than that predicted by the free-energy difference between structures. Grain boundaries, surfaces and other crystal defects may contribute to this situation. We use the phrase 'extent of cooperativity' to describe the situation lying between the stochastic and first-order extremes. We regard this aspect as one of the more interesting possibilities of solid state chemistry.

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A related description is that in the gas phase there is no cooperativity, in ordinary liquids there is highly localized (nearest-neighbour) cooperativity, while in a crystal of strongly interacting molecules the cooperativity is macroscopic. In very viscous liquids, polymers, glasses, or weakly bound molecular crystals the extent of cooperativity may be anywhere between the nearest-neighbour limit and the macroscopic limit.

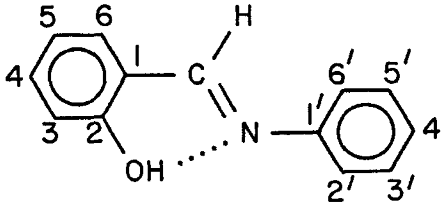
It should be noted that in the situation where there is significant molecular interaction in the crystal, a molecule may rearrange to a structure which would not correspond to the lowest free energy of the 'free molecule', nor of the molecule in a different environment at a given temperature and pressure, provided that this rearrangement allows the assembly of molecules to assume a configuration which sufficiently lowers the free energy of the crystal. A further aspect is that the driving force for pressure-induced molecular rearrangements in solids is as likely to be differences between the configurations with respect to intermolecular forces and packing as it is to be associated with changes of bond length within the molecule.

Since, in these transformations, there is a change in the relative order of the energy levels which accompanies the rearrangement, and frequently there is a new ground state, the electronic spectrum is a very effective probe of the nature of the rearrangement and the pressure dependence of the conversion.

Where a new ground state is formed, one can describe the transformation in physical terms as an electronic transition, or in chemical terms as an isomerization. We present here a series of examples of such pressure-induced rearrangements in crystals and for molecules dissolved in polymers. We shall see that the degree of cooperativity observed depends on the closeness of packing, the rigidity of the medium and the amount of geometrical change involved.

2. Salicylidine anils

The first example involves a rearrangement of a salycilidine anil (Hockert and Drickamer 1977). The structure below is of salicylideneaniline (SA).



The normal state at one atmosphere pressure is the enol form for all of these compounds. This form is characterized by an absorption peak in the ultraviolet at $30\text{–}33 \times 10^3\,\mathrm{cm}^{-1}$. The 5-bromo derivative has the characteristic that, when heated to 120°C, it develops a small absorption peak in the visible near $22\,000\,\mathrm{cm}^{-1}$ (i.e. it is thermochromic). Nuclear magnetic resonance (NMR) measurements indicate that the high-temperature form has the *cis*-keto configuration. This form has a characteristic fluorescence not present in the enol or the *trans*-keto structure.

With increasing pressure at 25°C, a peak grows in the spectrum with the location and fluorescence characteristic of the *cis*-keto form. By 80 kbar it is the dominant peak, and by 120 kbar the ultraviolet peak has disappeared. If one assumes, in first order, equal oscillator strengths for the two peaks one can extract equilibrium constants K_{eq} as a function of pressure. These are plotted in figure 1. From this plot one can calculate a ΔV for the reaction equal to 0·7% of the molar volume. It is possible to measure K_{eq} as

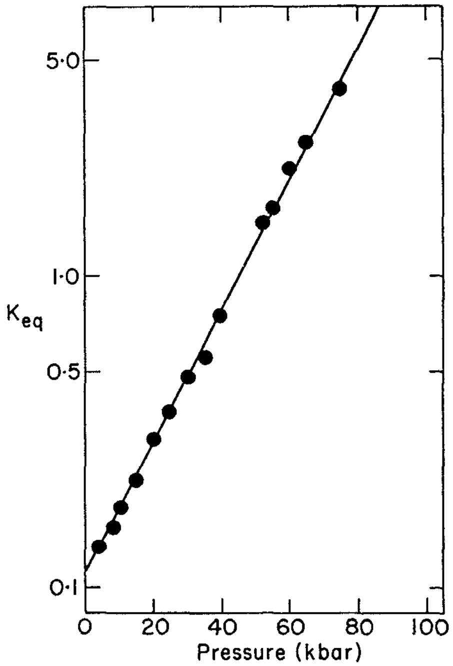


Figure 1. Equilibrium constant for formation of piezochromic product (*cis*-keto form) against pressure for 5-bromasalycilidine anil.

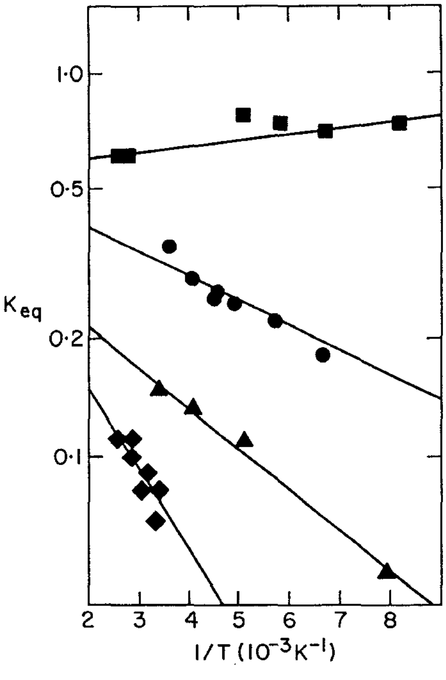


Figure 2. K_{eq} against $1/T$ at various pressures for 5-bromasalycilidine anil: ■, 40 kbar; ●, 20 kbar; ▲, 10 kbar; and ◆, 0 kbar.

a function of temperature at different pressures (figure 2) and calculate ΔH as a function of pressure. The change in ΔH with pressure can be shown to be essentially equal to $P\,\Delta V$, where P is the pressure. The process then has all the characteristics of a stochastic chemical reaction, and is completely reversible. The difference in molecular volumes for the enol and *cis*-keto forms must be very small, but differences in intermolecular forces and in packing could account for the ΔV.

This study illustrates a point which is not always well understood. Temperature and pressure are *not* in general conjugate variables. With increasing temperature one increases the probability of a molecule surmounting an energy barrier of a given height which may separate the two configurations. With pressure one displaces one potential well with respect to the other in energy (and possibly also in relative position along the configuration coordinate). Pressure can act either to augment or to oppose the effect of temperature.

3. $Re_2X_8^{2-}$

Metal cluster compounds are a subject of considerable interest in modern chemistry. In addition to other features they exhibit a metal–metal bond having an orbital angular momentum of two around the bond (a δ bond). δ→δ* excitations exhibit a relatively weak peak, usually in the red or near-infrared part of the spectrum.

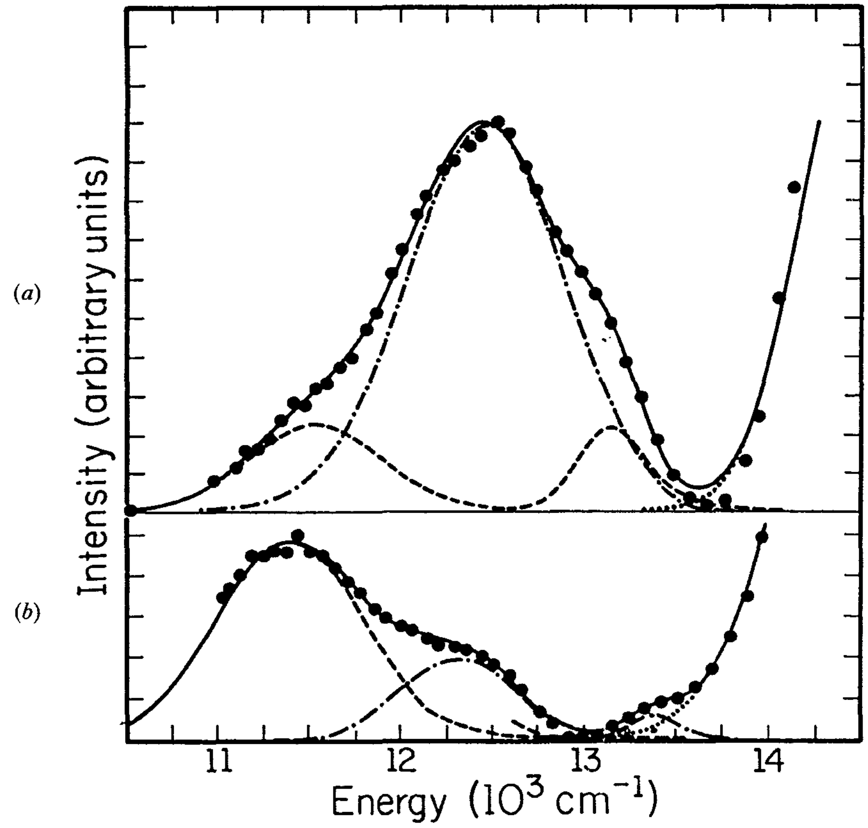


Figure 3. Spectrum of $Re_2I_8^{2-}$ in $(n\text{-}Bu_4N)_2Re_2I_8$ at two pressures: (*a*), 10·1 kbar and (*b*), 54·8 kbar.

A rather simple case with interesting features involves the anion $Re_2X_8^{2-}$ where ($X = Cl$, Br or I). The metal–metal bond lengths in the chloride and bromide are nearly identical. The bond lengths are only slightly longer in the iodide. The halides are eclipsed (i.e. facing each other). Thus the chlorides are well separated relative to either their van der Waals or ionic diameters, the bromides are separated by about their ionic diameter, and the iodide–iodide distance is between the ionic and van der Waals diameters.

In all cases the $\delta \rightarrow \delta^*$ excitation shifts to lower energy with increasing pressure, as is common for bonding–antibonding excitations. For the iodide, a new peak grows in the spectrum with increasing pressure (Carroll *et al.* 1985), figure 3. By 50 kbar it is dominant, and by 70 kbar the original $\delta \rightarrow \delta^*$ peak has disappeared. The area under the new peak at 70 kbar is about one third the area under the $\delta \rightarrow \delta^*$ peak at ambient pressure, so the oscillator strength of the new excitation is clearly lower than that of the original peak. Evidently there has been a rotation of one end of the ion with respect to the other to a secondary minimum along the (rotational) configuration coordinate with a new and smaller overlap of the metal d orbitals. This relieves the strain involved in iodide–iodide overlap at the expense of a somewhat weaker metal–metal bond. Figure 4 shows the area ratios as a function of pressure. The conversion is continuous as it would be for any ordinary chemical reaction. It is of interest to note that significant conversion is noted for the bromide above 180 kbar. Unfortunately by 200 kbar a higher energy peak of considerably greater intensity has moved sufficiently red to obscure the transitions of interest.

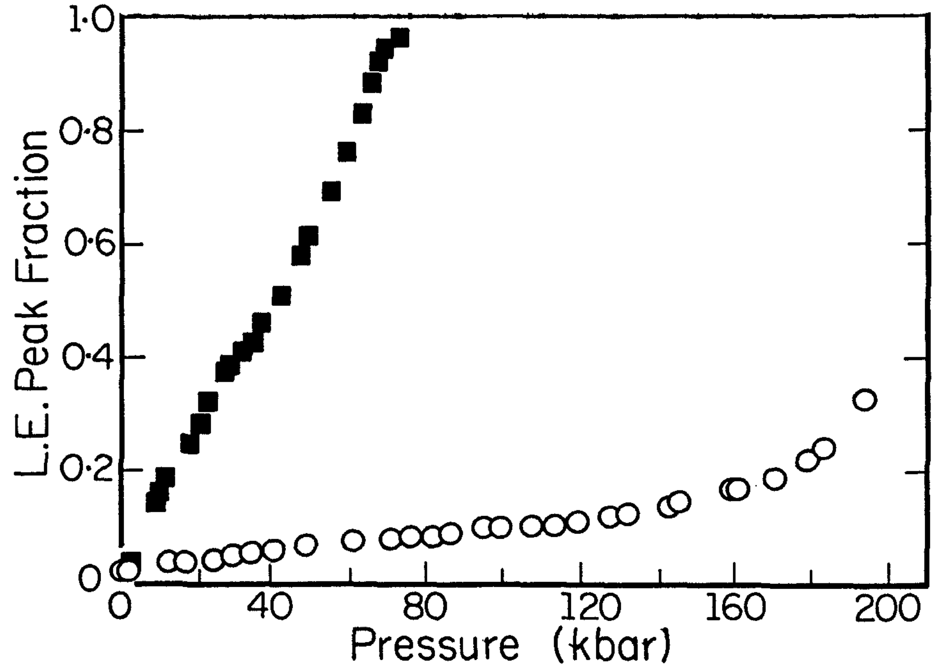
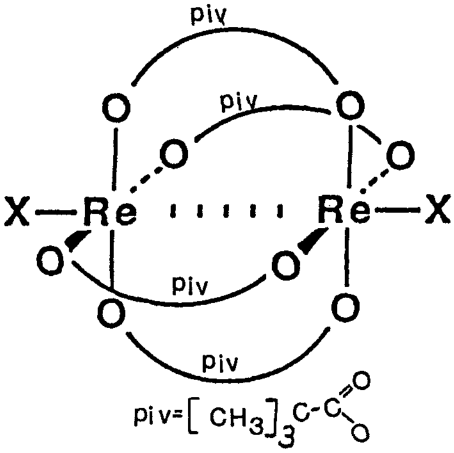


Figure 4. Area fraction of low-pressure peak against pressure for $Re_2I_8^{2-}$ and $Re_2Br_8^{2-}$ in $(n\text{-}Bu_4N)_2Re_2X_8$; ○, X = Br and ■, X = I.

4. $[Re_2(piv)_4X_2]$

A quite different pressure behaviour is exhibited by molecular ions of the type shown below.



Here X may be chloride or bromide (Roginski *et al.* 1988). Both have the same crystal structure and only slightly different lattice parameters, so that the bromide is somewhat more closely packed than the chloride. These materials also exhibit a δ→δ* excitation. Again, a new peak grows in with pressure, this time, however, with a distinctly higher oscillator strength than the original δ→δ* peak. In figure 5 we show the area under the new peak, as well as under the δ→δ* peak, as a function of pressure for the bromide. While there is a little transformation at low pressure, probably at

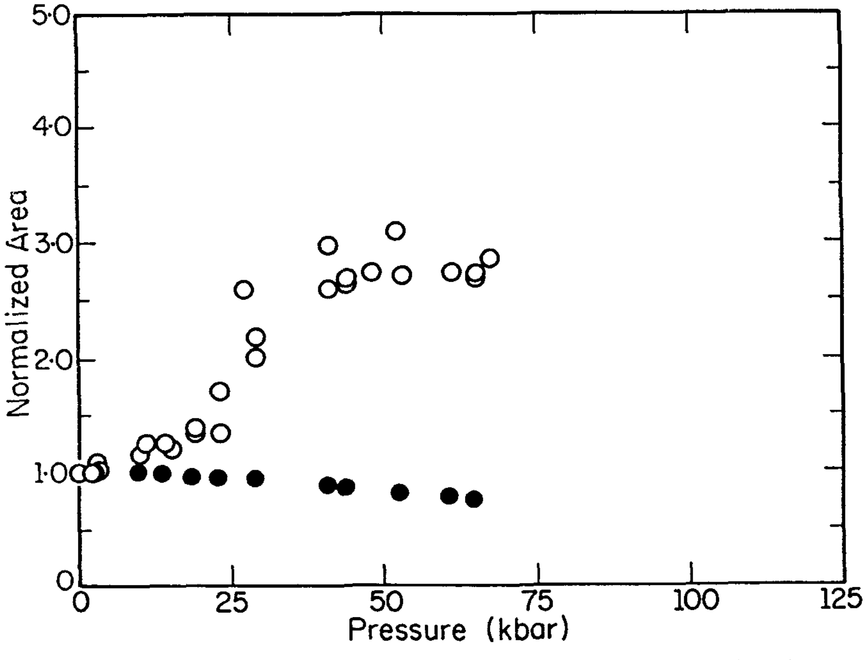


Figure 5. Normalized area under low-energy peak (○) and δ→δ* peak (●) against pressure for polycrystalline $Re_2(piv)_4Br_2$.

crystal defects, the bulk of the conversion takes place in the range 25–30 kbar. These are powdered samples. It seems certain that in a single crystal the process would be truly discontinuous.

Figure 6 shows the corresponding data for the chloride. Here the conversion occurs between 20 and 50 kbar, which is somewhere between the stochastic and first-order limits. This is possibly due to the less crowded nature of the chloride in the lattice. Figures 7 and 8 show the conversion for the bromide and chloride dissolved in PMMA (polymethylmethacrylate). In both cases it occurs continuously over the entire pressure range, as for an ordinary stochastic reaction.

The main thrust of this paper is the pressure dependence of the various rearrangements. The nature of this configuration change is analysed in detail in the original paper. We discuss it only briefly here. Two features for which we must account are the relatively large oscillator strength of the new peak, as is evident from the large increase in its intensity while the δ→δ* peak shrinks only modestly, and two new infrared peaks which grow in at 1700 cm^{-1} and 1300 cm^{-1} in the pressure region where conversion takes place. These two features are not consistent with the rotation discussed for the octaiodide in the previous section.

For other systems Hopkins *et al.* (1987) have indicated that in a transformation from bidentate to monodentate ligands one may expect a δ→δ* excitation at lower energy with greater oscillator strength. In this new configuration one would expect a C=O stretching vibration near 1700 cm^{-1} and a C–O stretch near 1300 cm^{-1}. The process is reversible, although with some hysteresis. This is a little surprising for so drastic a rearrangement, but not impossible. The bulk of the evidence makes this the most likely probability. This is, then, a process which varies from first order to higher order to stochastic, depending on the axial ligand and the medium.

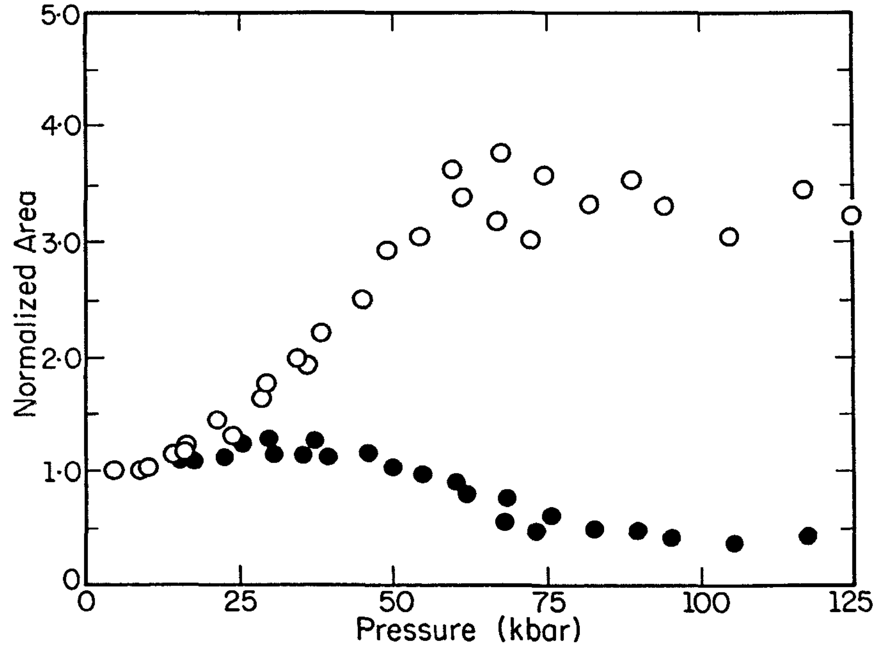


Figure 6. Normalized area under the low-energy peak (○) and δ→δ* peak (●) against pressure for polycrystalline $Re_2(piv)_4Cl_2$.

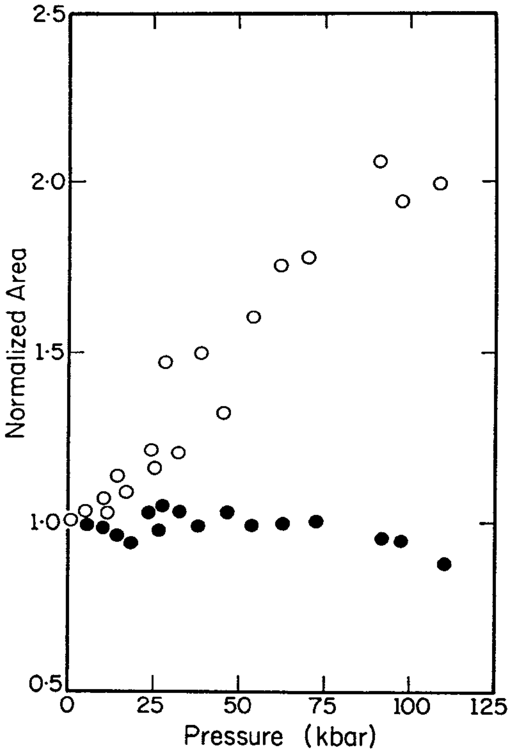


Figure 7. Normalized area under the low-energy peak (○) and the δ→δ* peak (●) against pressure for polymeric $Re_2(piv)_4Br_2$ in PMMA.

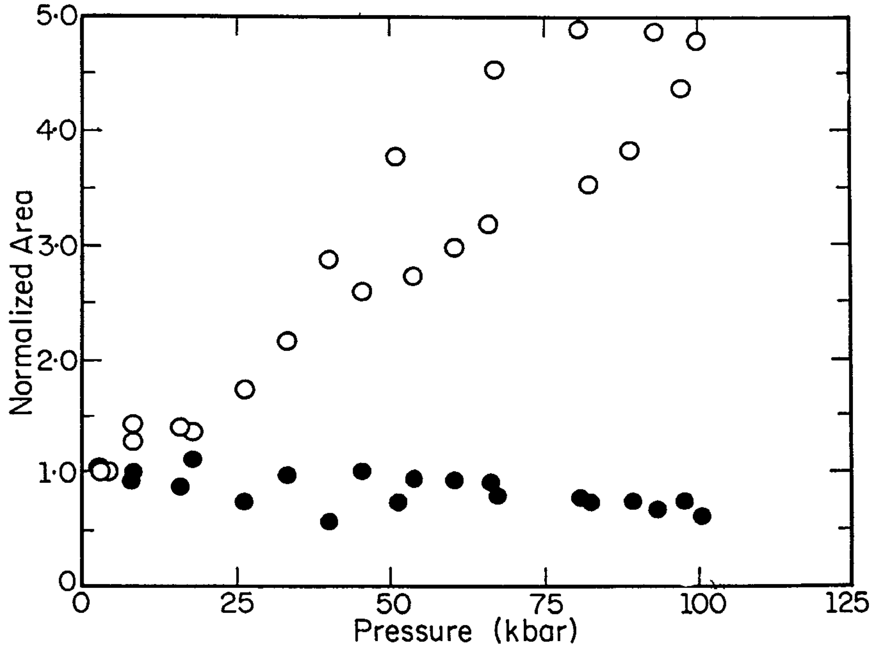


Figure 8. Normalized area under the low-energy peak (○) and the δ→δ* peak (●) against pressure for polymeric $Re(piv)_4Cl_2$ in PMMA.

5. Cu^{2+} complexes

Complexes of Cu^{2+} offer a very fertile field for investigating pressure-induced molecular rearrangements, as the d^9 electronic configuration is very susceptible to Jahn–Teller and related distortions. We discuss here three such cases. In the first, a cation complex of Cu^{2+} rearranges from approximately trigonal bipyramidal (TBP) symmetry to a more nearly square pyramidal (SQP) configuration. In the second the anion $CuCl_4^{2-}$ rearranges from nearly tetrahedral to something approximating a square planar arrangement. In the final case a rearrangement of cation–anion geometry changes the symmetry near the Cu^{2+} from approximately square planar to more nearly octahedral. In some cases the rearrangements are first order (or would be in a perfect crystal), in others they are of higher order, although not stochastic. A given rearrangement may differ in this regard in different media. Structural pathways for rearrangements of the metal containing cations or anions have been well described by Hathaway (1984) and by Muetterties and Guggenberger (1974). All transformations are reversible, although usually with some hysteresis.

In discussing the nature of the observed transitions, we use one-electron d orbital designations as a shorthand indicating the major or root component of a molecular orbital which may involve mixing of various d and ligand contributions. As the symmetry changes, the degree and type of mixing and the molecular orbital designation will, in general, change.

5.1. *Trigonal bipyramidal to square pyramidal transformation*

Hathaway and his collaborators (Ray *et al.* 1978, 1981) have demonstrated that complexes of the form $Cu(dien)(bipyam)X_2.nH_2O$ (dien = diethylenetriamine, bipyam = 2,2-dipyridylamine, X = Cl, ClO_4^-, NO_3^-) can assume conformations which vary from nearly trigonal bipyramidal (TBP) to nearly square pyramidal (SQP). The table lists five Cu(II) complexes which vary from the TBP to the SQP limit. The middle three have the composition noted above. The angle α_3 which characterizes the conformation is shown schematically in figure 9. In figure 10 we note the order of the energy levels associated with the limiting cases, with the allowed transitions indicated by a full arrow and the forbidden ones with a dashed arrow. Since the ground states in the two configurations are different, at some value of α_3, apparently near 140°, there must occur a transformation between these electronic configurations. In figure 11 we show spectra for the Cl^- complex at 4 and 106 kbar (Bray and Drickamer 1989). The relative intensities are consistent with a conformation approaching SQP and change only modestly with pressure. In figure 12 we present spectra for the NO_3^- complex at 5 and 78 kbar. At low pressure it is consistent with the TBP energy diagram while at 78 kbar it has transformed to a more nearly SQP structure. The ClO_4^- spectra differ only in modest degree from the Cl^-, as discussed below.

Five Cu^{2+} complexes varying from trigonal bipyramidal to nearly square pyramidal. The angle α is shown in figure 9.

Complex	α_3	Comment
$[Cu(tren)(NH_3)](ClO_4)_2$	119·2°	model trigonal bipyramid
$[Cu(dien)(bipyam)](NO_3)_2$ (3)	137·2°	distorted trigonal bipyramid
$[Cu(dien)(bipyam)](ClO_4)_2.H_2O$ (2)	151·9°	distorted square pyramid
$[Cu(dien)(bipyam)]Cl_2.2H_2O$ (1)	159·0°	distorted square pyramid
$K[Cu(NH_3)_5](PF_6)_3$	163·8°	model square pyramid

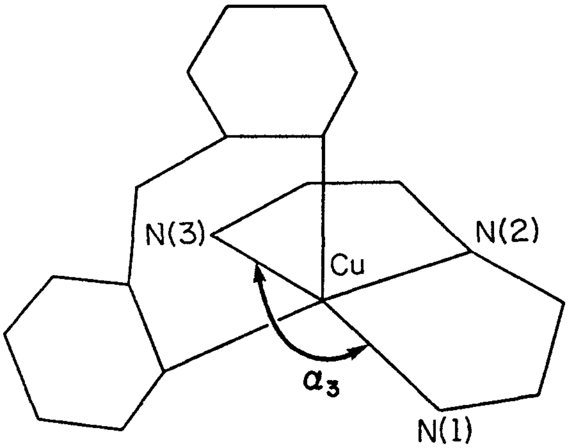


Figure 9. Schematic structure of [Cu(dien)(bipyam)]$^{+2}$ defining the angle α_3 which characterizes the symmetry of the complex.

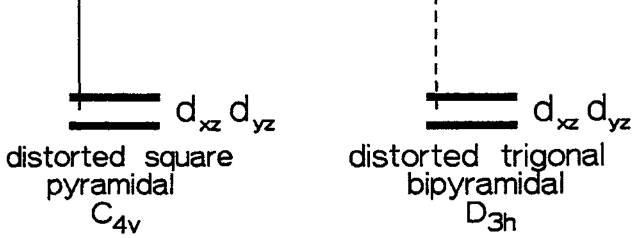


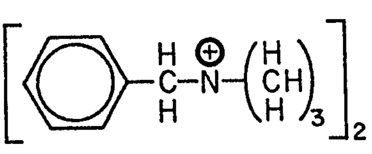
Figure 10. Energy levels characterizing the limiting symmetries (TBP and SQP). The solid lines represent allowed transitions, the dashed lines forbidden transitions.

In figures 13–15 we present the fractional intensities of the peaks as a function of pressure for the Cl^-, ClO_4^- and NO_3^- complexes. For the Cl^- complex there is apparently a modest continuous change with pressure toward the SQP limit. The ClO_4^- complex, which starts farther from this limit, changes more with pressure. The behaviour of the complex above 70 kbar is quite similar to the initial behaviour of the Cl^- complex, so it too exhibits a continuous increase in the dihedral angle α_3. The effect for the NO_3^- complex is more dramatic. The change in the nature of the ground state occurs between 45 kbar and just under 80 kbar, so that it is neither first order nor stochastic. At 78 kbar the relative intensities of the three peaks resemble the Cl^- case at about 30 kbar or the ClO_4^- case at about 70 kbar. Evidently α_3 changes from less than 140° to 150° or more over this pressure range. For all three complexes the peak locations change only modestly with pressure and convey no new information about the transformation. When dissolved in poly(4-vinylpyridine) (4VYPY) all three complexes display spectra consistent with a distorted SQP structure much like that of the ClO_4^- complex, and there are only modest changes in relative intensity with pressure.

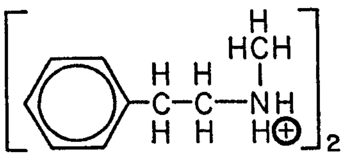
5.2. *The tetrachlorocuprate anion*

The tetrachlorocuprate ion ($CuCl_4^{2-}$) is known to assume a variety of different configurations in the solid state, from nearly tetrahedral to square planar (Smith 1976, and references therein). These configurations represent a compromise between crystal field forces which favour square-planar geometry and chloride–chloride repulsions which are minimized in tetrahedral geometry. Solid state interactions, such as lattice packing and hydrogen bonding which differ with different cations, establish the geometry in each particular case. This geometry is characterized by a dihedral angle which is 90° in tetrahedral symmetry and 0° in square-planar geometry. Several papers (Harlow *et al.* 1975, Battaglia *et al.* 1979) have shown a simple relationship between the electronic spectra and the geometry of the $CuCl_4^{2-}$ ion so that the electronic spectrum is a quite reasonable qualitative indication the dihedral angle. Figure 16 exhibits the splittings expected for the one-electron levels for various distortions from tetrahedral to square planar. The solid lines represent allowed transitions.

In this paper we present a pressure study (Bray and Drickamer 1990) of three complexes Cs_2CuCl_4 (dihedral angle $\delta = 67{\cdot}9°$), $(tmba)_2CuCl_4$ ($\delta = 66{\cdot}6°$) and $(nmpH)_2CuCl_4$ ($\delta = 0$). The latter two cations have the structure shown below.



(tmba)

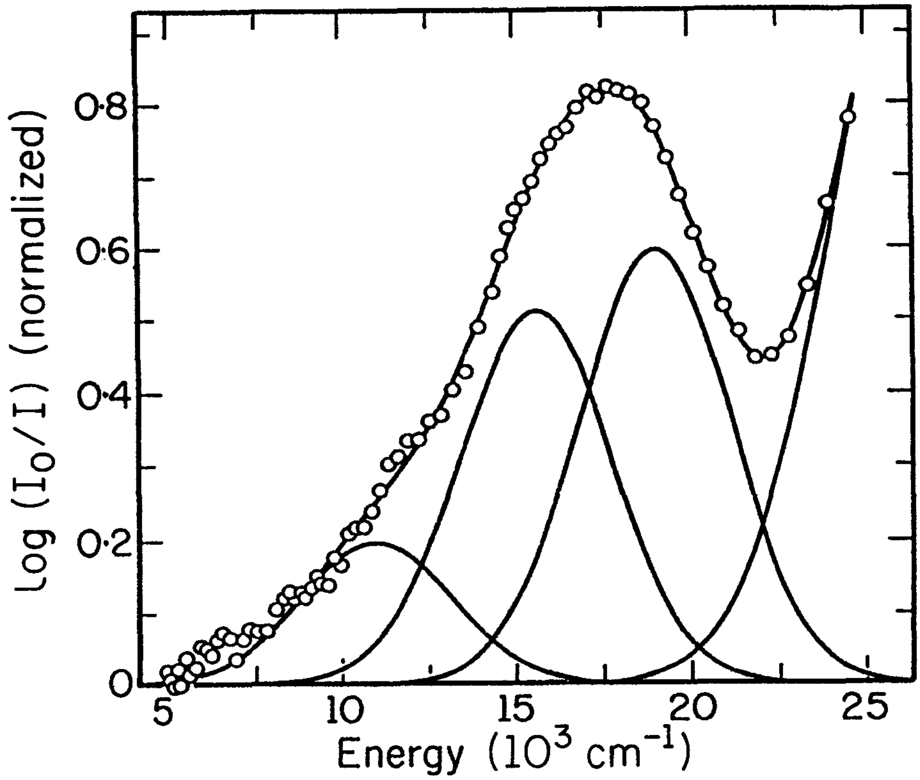


(nmpH)

The first two have the electronic configuration shown in figure 16(*b*), the last is represented by (*d*). Figure 17 shows typical spectra of $(tmba)_2CuCl_4$ at two pressures. The Cs_2CuCl_4 spectra are qualitatively similar. Furlani *et al.* (1967) were unable to locate the forbidden excitation, so the data are fitted with only two peaks. The higher pressure spectra are dramatically different and it was necessary to involve three peaks to get a satisfactory fit.

In figure 18 we show the peak locations as a function of pressure. The change between 50 and 70 kbar is striking. It occurs over a 20 kbar range and thus falls between the extremes of a stochastic process and a first-order transition. The dramatically higher energies above 70 kbar indicates a very significant decrease in the dihedral angle; larger for the $(tmba)_2CuCl_4$ than for Cs_2CuCl_4. The presence of three peaks of comparable intensity indicates sufficient distortion to provide increased d–p or metal–ligand orbital mixing. Also there is a change in ground state between figure 16 (*b*) and (*c*) and it is not clear whether for this complex the ground state at high pressure is d_{xy^2} or $d_{x^2-y^2}$ or a mixture of the two. Comparison with the spectra of complexes known to have dihedral angles between 20° and 50° at ambient pressure would indicate that at high pressure both complexes have values of δ between these limits and not near either extreme.

We turn now to a consideration of the $(nmpH)_2CuCl_4$ compound, which has a square planar symmetry at ambient pressure (Harlow *et al.* 1974). The polarized absorption results of Hitchman and Cassidy (1979) show three reasonably intense peaks. Although none of the excitations is dipole allowed in D_{4h} symmetry, they are each vibronically allowed.



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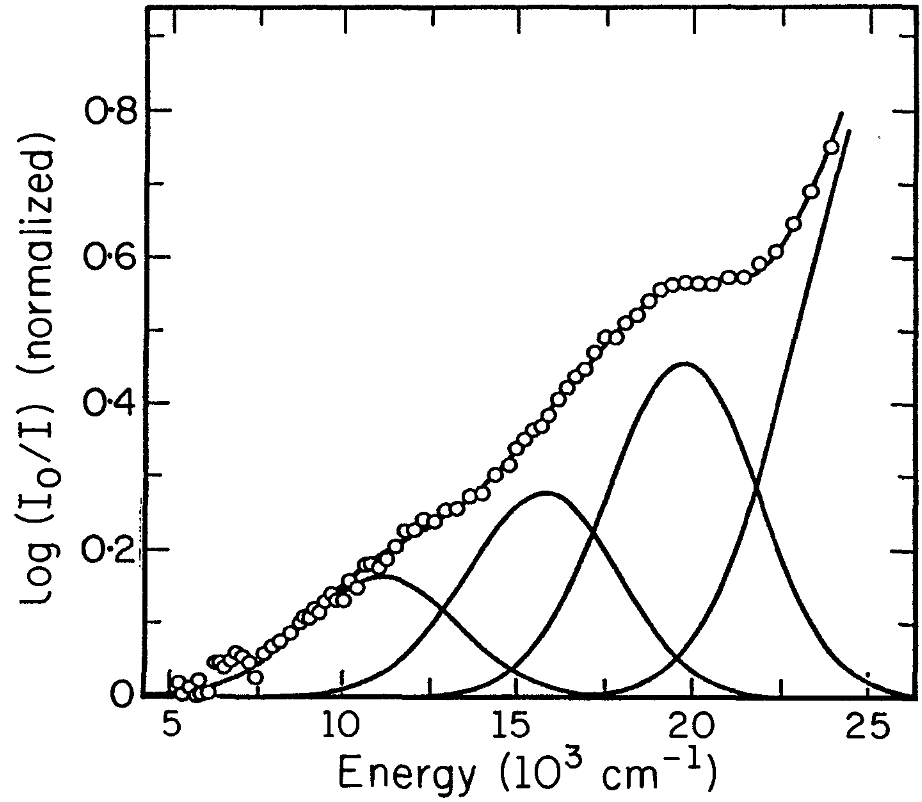


(*b*)

Figure 11. Resolved spectra of polycrystalline [Cu(dien)(bipyam)]$Cl_2.2H_2O$ at (*a*), 4 kbar and (*b*), 106 kbar.

The resolved electronic spectra are shown in figure 19. The two peaks shown at high pressure represent mixtures of d–d excitations. The peak locations appear in figure 20.

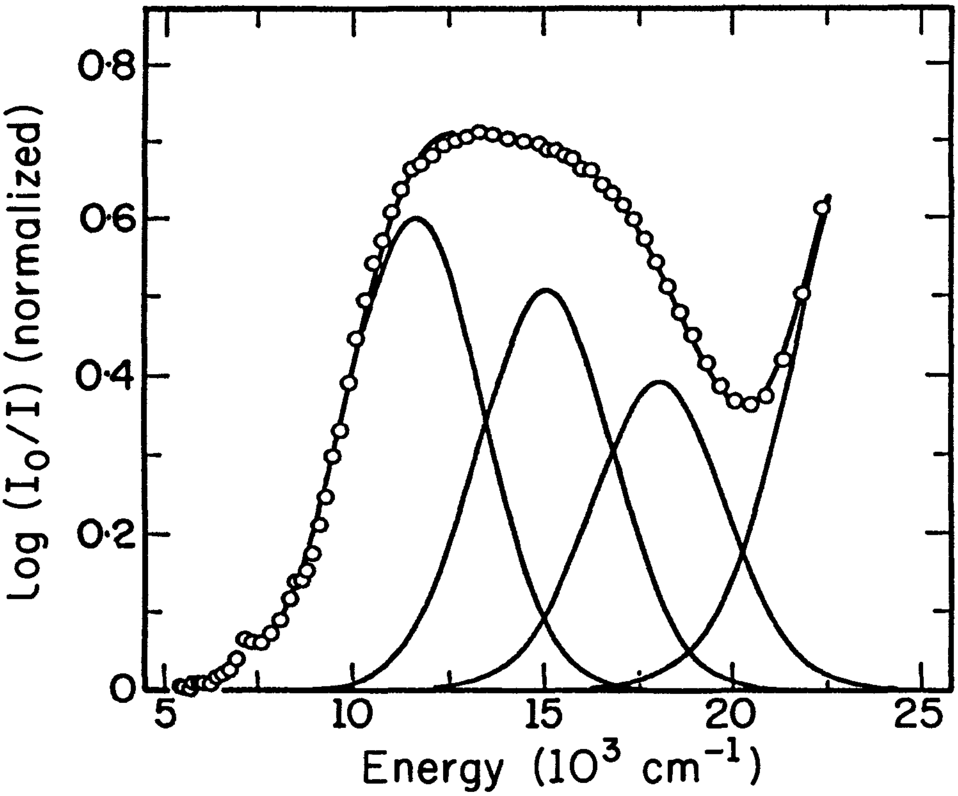
The decrease in excitation energy between 50 and 70 kbar indicates a distinct increase in dihedral angle over this pressure range. Comparison with ambient-pressure spectra of other complexes would indicate a value of δ greater than 20°. For this complex also the rearrangement lies between the limits of a stochastic process and a first-order phase transition. Apparently the effect of compression is to decrease differences in cation–anion interactions so that there is a much smaller spread of dihedral angles among these compounds at high pressure than there is at one atmosphere.

5.3. *Cation–anion rearrangement*

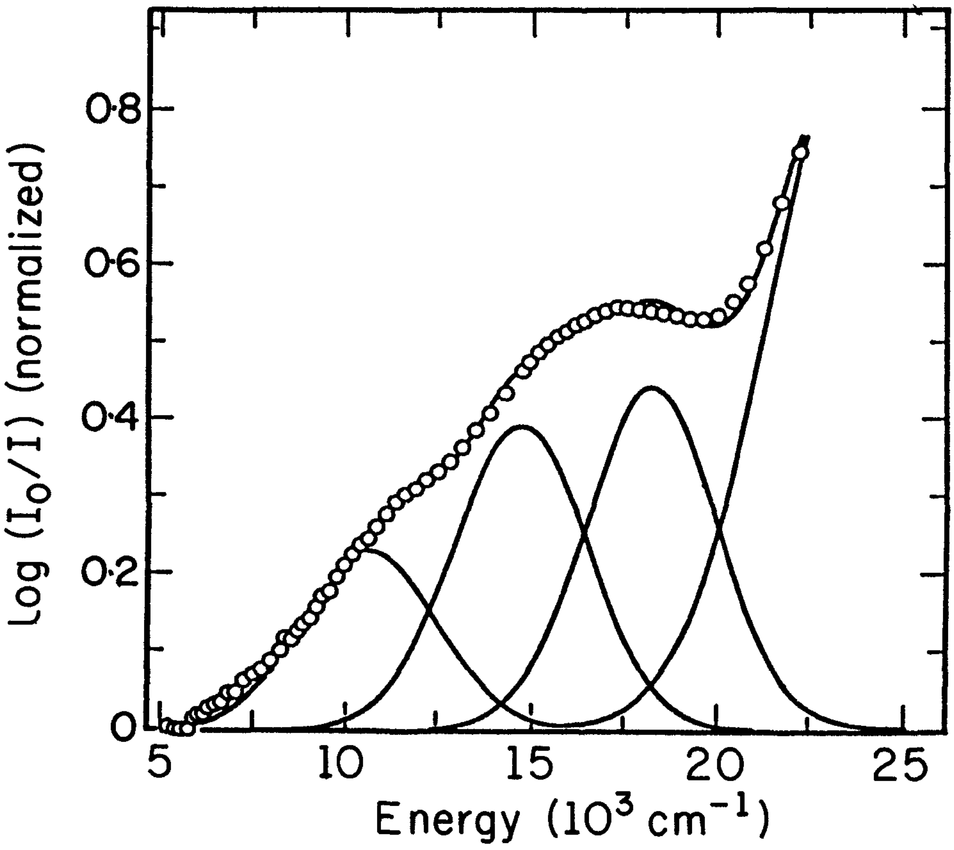
Complexes of Cu^{2+} with ethylenediamine (en) and derivatives such as dimethylethylenediamine (dieten) with a variety of anions have been widely studied at ambient pressure (Fabbrizzi *et al.* 1974, Lever *et al.* 1971), Walsh and Hathaway 1984). The (en) cation is strictly square planar with Cu^{2+} coordinated to four nitrogens. The (dieten) cation is similar but with the ethyl groups in a symmetrical *gauche* orientation.

In particular there are numerous X-ray crystallographic investigations which show the location of the anion *vis à vis* the Cu^{2+} ion. As discussed below, the anion location affects significantly the symmetry near the Cu^{2+} ion, and therefore the electronic spectrum. We have investigated three (dieten) compounds (BF_4^-, ClO_4^- and Cl^-) as well as the (en) complex with BF_4^- anions. We discuss here primarily the behaviour of the BF_4^- complexes, with a brief mention of similarities and differences of the other two.

In the (en) complex there is one fluorine of BF_4^- located directly above and one below the Cu^{2+} at a distance of 2·5–2·6 Å, so that the symmetry around the Cu^{2+} approaches octahedral (the Cu–N distances are about 2·0 Å). The infrared spectrum indicates that the BF_4^- has lost its strictly tetrahedral symmetry. For the (dieten) complex the symmetry is established in part by analogy to other AB_4^- complexes. The BF_4^- is considerably off-centre and the shortest Cu^{2+}–F^- distance is 3·5–3·6 Å. The symmetry at the Cu^{2+} is clearly square planar and the BF_4^- exhibits tetrahedral symmetry in its infrared spectrum. The order of the d levels is symmetry dependent, as is shown in figure 21. The major difference is that for square planar symmetry the d_{z^2} level is the lowest filled level, while for octahedral symmetry it is the highest filled level. Symmetry arguments and experiment both indicate that the $d_{z^2} \rightarrow d_{x^2-y^2}$ excitation should be significantly less intense than the other two excitations shown. Thus, for more nearly octahedral symmetry, one would expect a low-intensity shoulder on the *low*-energy side of the d–d absorption spectrum and such is observed for the (en)



(*a*)



(*b*)

Figure 12. Resolved spectra of polycrystalline [Cu(dien)(bipyam)]$(NO_3)_2$ at (*a*), 5 kbar and (*b*), 78 kbar.

complex. In square-planar symmetry one would expect that the low-intensity peak would be on the *high*-energy side, and indeed it is necessary to introduce such a peak at high energy to fit the ambient-pressure spectrum of the (dieten) complex.

The most significant effect of pressure on the dieten complex is to move the low-intensity shoulder from high to low energy, as is shown in figure 22 (Bray *et al.* 1989). In the crystal this occurs between 74 and 83 kbar. These are powdered materials and in a single crystal we believe the transition would be first order. Above 83 kbar the electronic and vibrational spectra are very much like those of the (en) complex at low pressure and their pressure shifts at pressure above 83 kbar are very much like those of the (en) complex throughout the pressure range.

When the (dieten) complex is dissolved in poly(2-vinylpyridine)(2VYPY) (figure 23) the conversion initiates near 15 kbar and is not complete until 55 kbar. In the intermediate region it is not possible to make a definitive fit since six peaks are present.

Since the polymer is polar but not a polyelectrolyte it is reasonable that there is initially a closer association between cation and anions in the polymer than in the crystal, so that one observes the transformation at lower pressure. In both media the process is reversible but with some hysteresis.

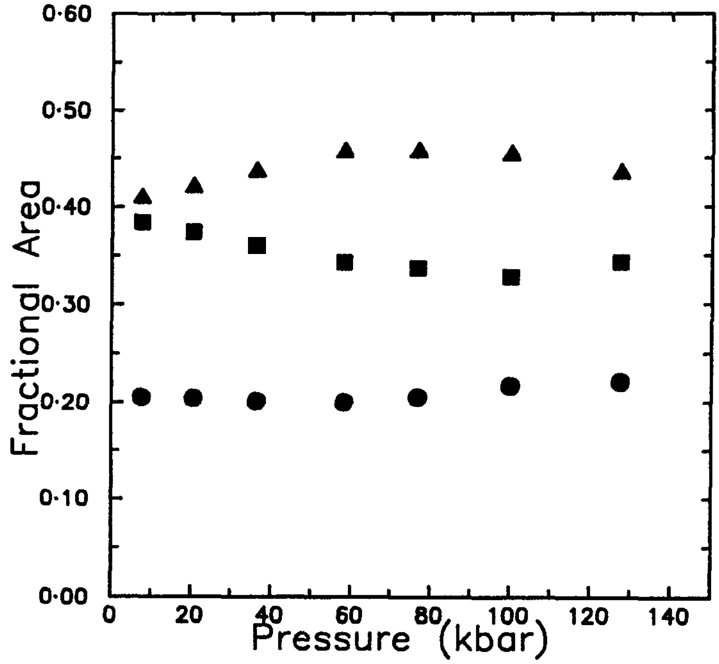


Figure 13. Pressure dependence of the fractional areas of the electronic excitations for polycrystalline [Cu(dien)(bipyam)]$Cl_2.2H_2O$: ▲, d_{xz}, $d_{yz}{\rightarrow}d_{x^2-y^2}$; ■, $d_{z^2}{\rightarrow}d_{x^2-y^2}$; and ●, $d_{xy}{\rightarrow}d_{x^2-y^2}$.

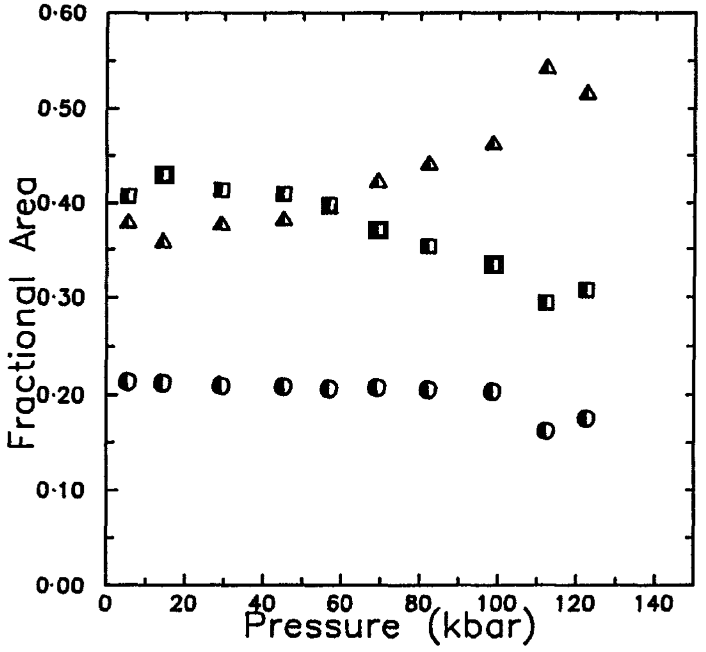


Figure 14. Pressure dependence of the fractional areas of the electronic excitations for polycrystalline [Cu(dien)(bipyam)]$(ClO_4)_2.H_2O$: ▲, d_{xz}, $d_{yz}{\rightarrow}d_{x^2-y^2}$; ■, $d_{z^2}{\rightarrow}d_{x^2-y^2}$; ●, $d_{xy}{\rightarrow}d_{x^2-y^2}$.

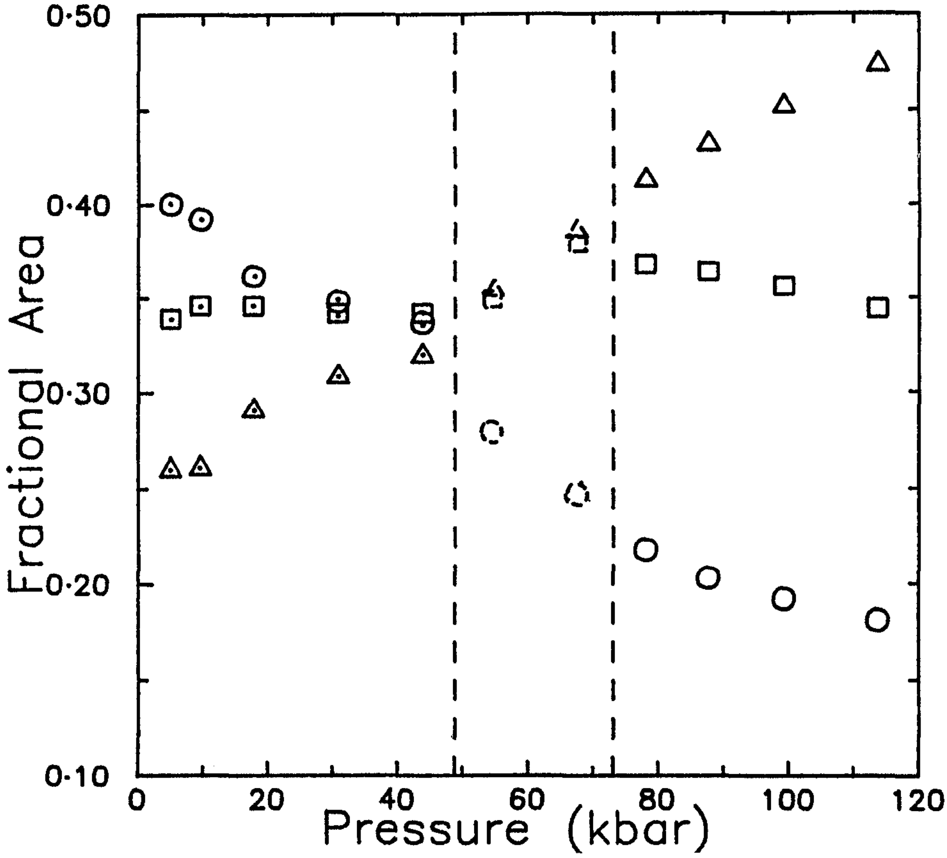


Figure 15. Pressure dependence of the fractional areas of the electronic excitations for polycrystalline [Cu(dien)(bipyam)]NO_3: ⊙, $d_{xy} \rightarrow d_{z^2}$; ⊡, $d_{x^2-y^2} \rightarrow d_{z^2}$; ◬, d_{xz}, $d_{y^2} \rightarrow d_{z^2}$; △, d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$; □, $d_{z^2} \rightarrow \delta_{x^2-y^2}$; and ○, $d_{xy} \rightarrow d_{x^2-y^2}$.

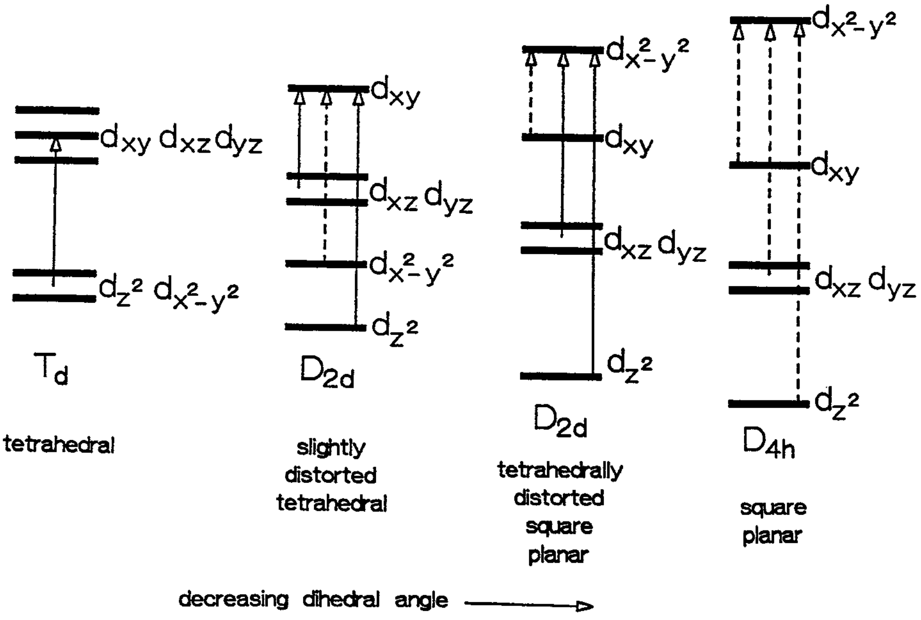
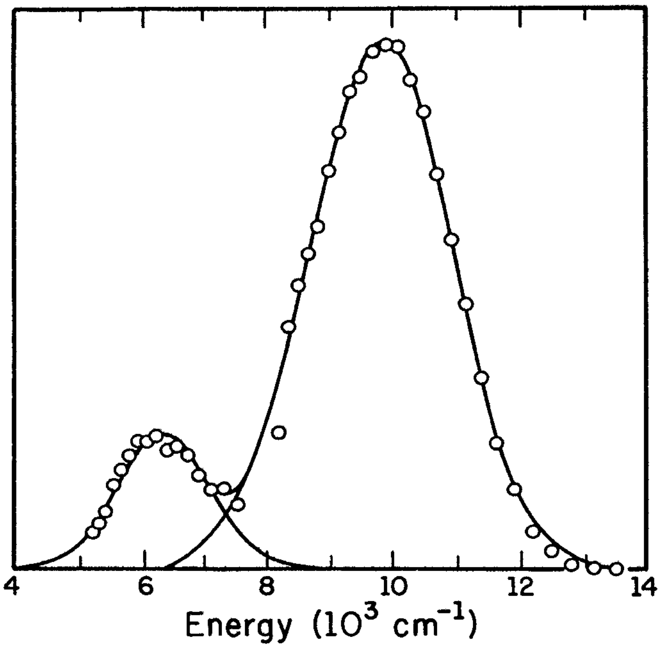
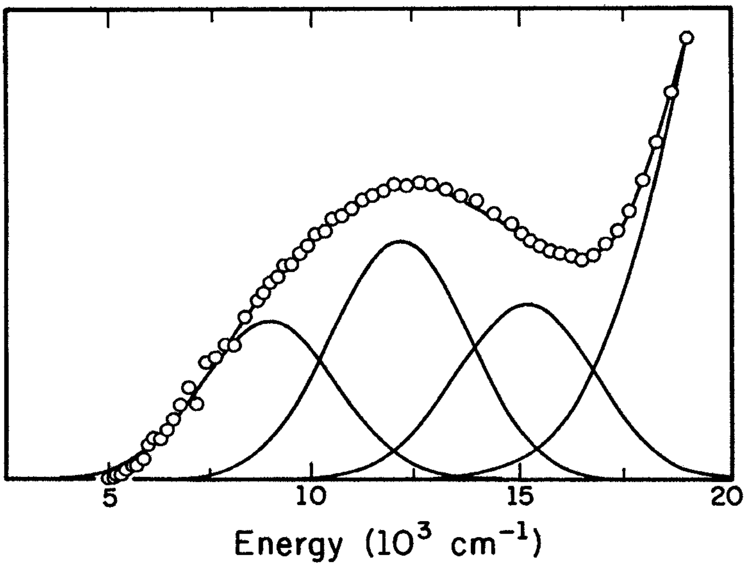


Figure 16. Energy-level diagram associated with various possible symmetries of $CuCl_4^{2-}$ complexes.



(*a*)



(*b*)

Figure 17. Resolved spectra for $(tmba)_2CuCl_4$ at (*a*), 26 kbar and (*b*), 86 kbar.

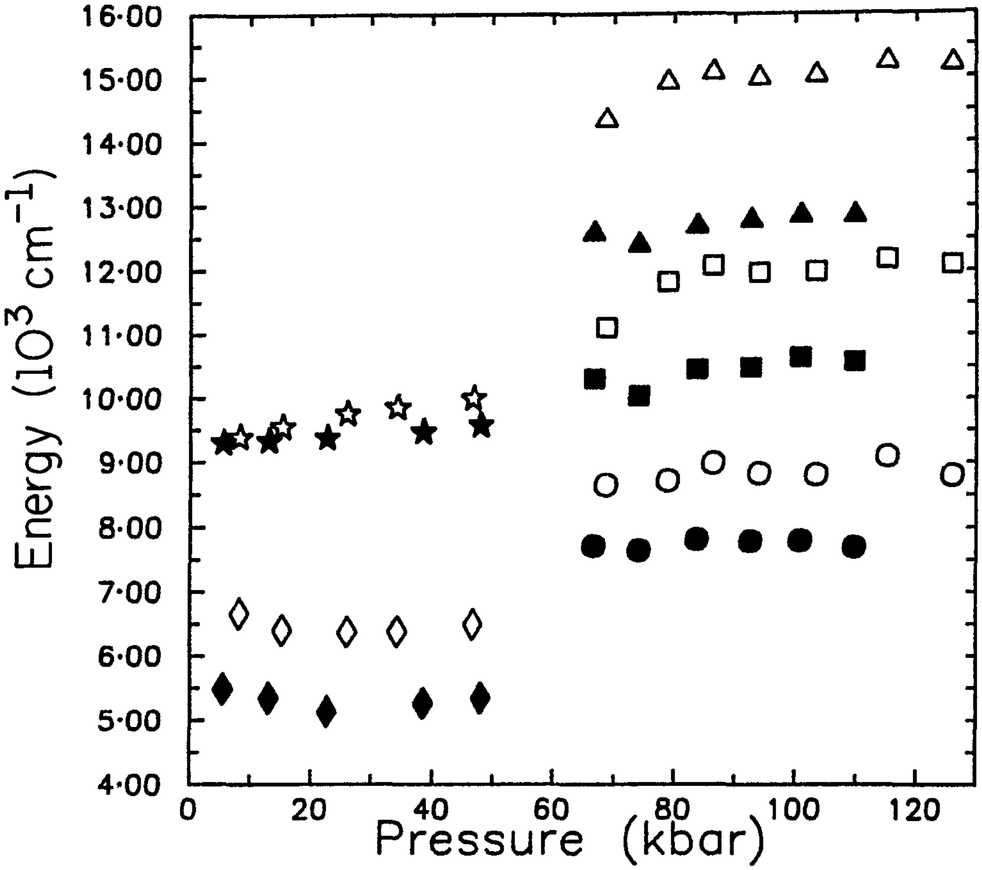
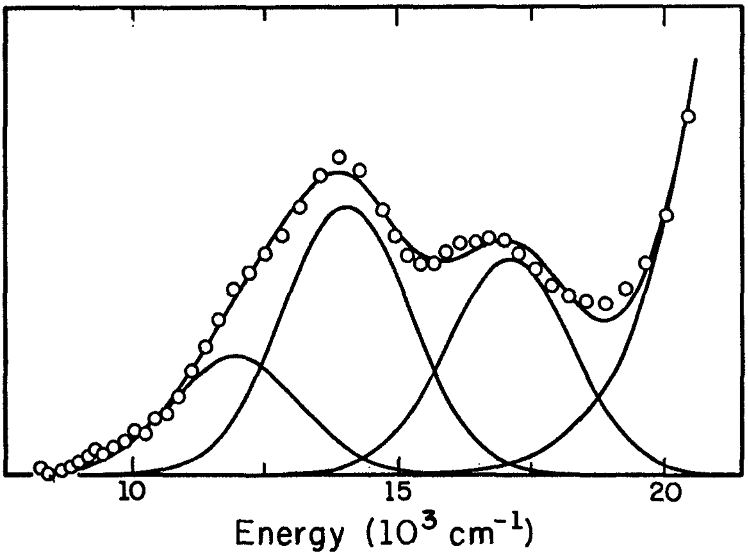
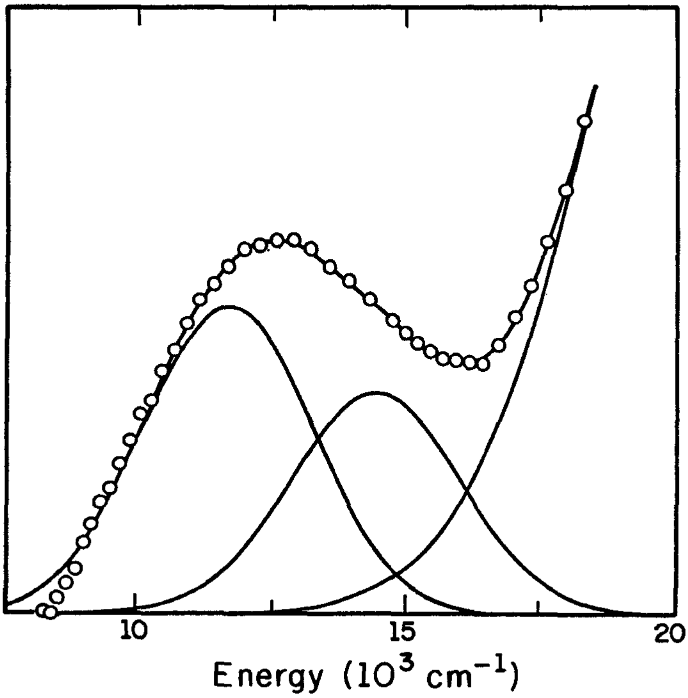


Figure 18. Peak energies against pressure for $(tmba)_2CuCl_4$ (open symbols) and Cs_2CuCl_4 (filled symbols). The stars and diamonds represent the high- and low-energy peaks for the low-pressure configuration. The triangles, circles and squares represent the high-, intermediate- and low-energy peaks for the high-pressure configuration.



(*a*)



(*b*)

Figure 19. Resolved spectra for $(nmpH)_2CuCl_4$ at (*a*), 9 kbar and (*b*), 82 kbar.

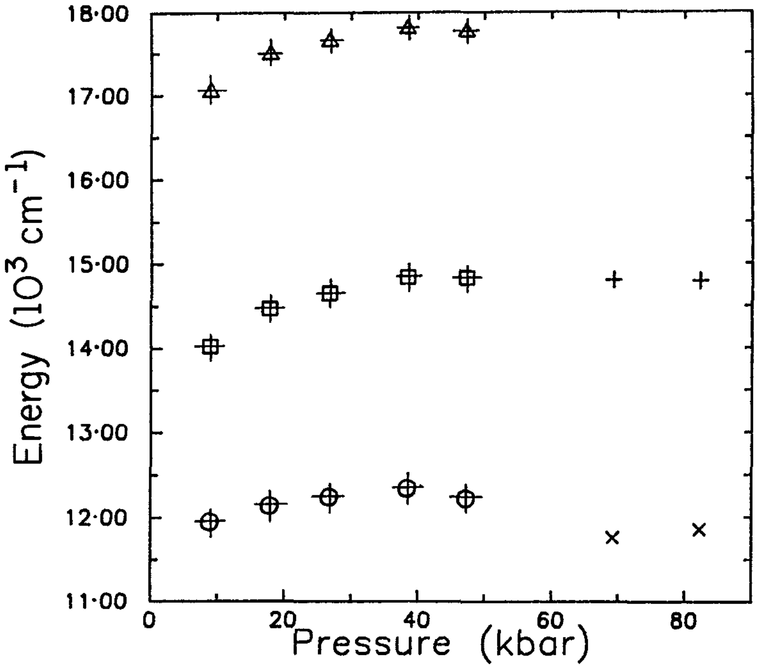


Figure 20. Peak energies against pressure for $(nmpH)_2CuCl_4$ for the low (△, ⊞, ⊕) and high (+, ×) pressure configurations.

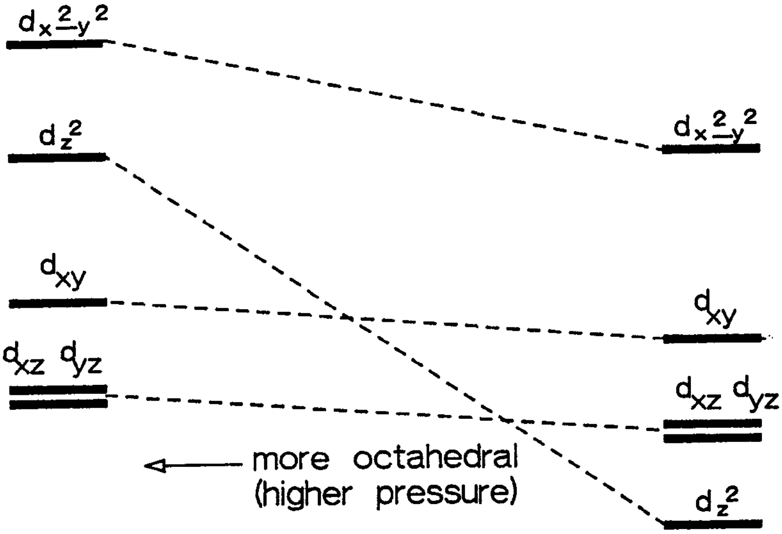


Figure 21. Energy-level diagram for symmetries from square planar to octahedral.

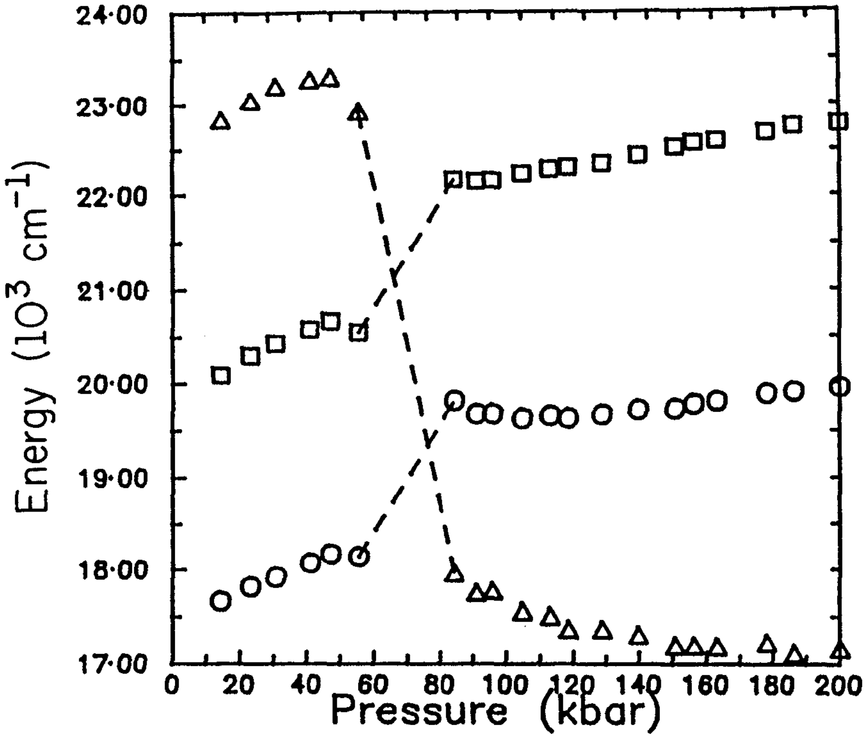


Figure 22. Peak energies against pressure for polycrystalline Cu(dieten)$_2$BF$_4$.

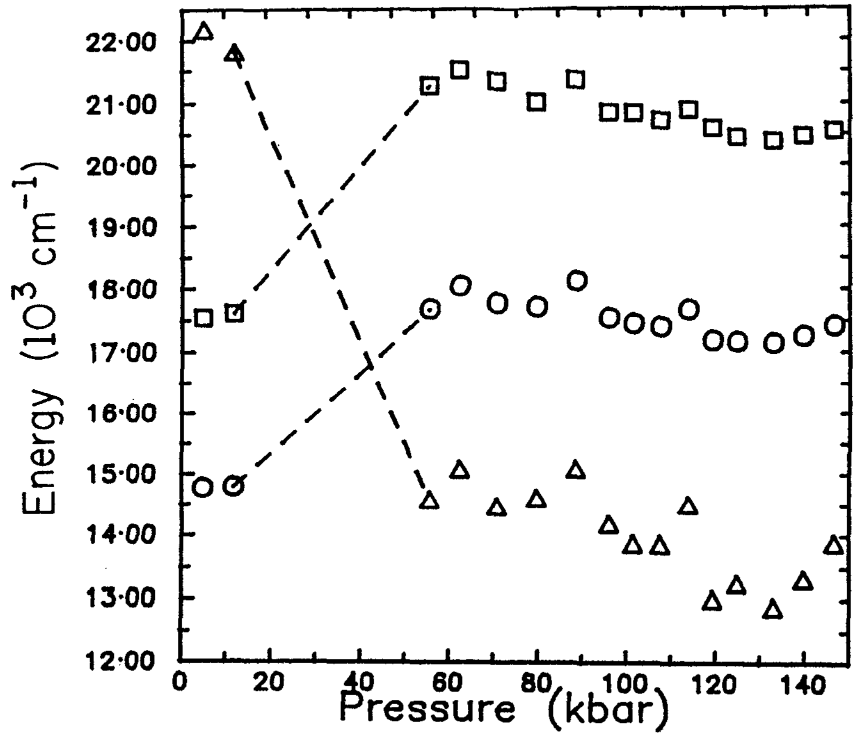


Figure 23. Peak energies against pressure for Cu(dieten)BF$_4$ in poly(2-vinylpyridine).

The complexes with ClO_4^- and Cl^- both exhibited essentially discontinuous conversions in the crystal, but near 40 and 20 kbar respectively. The Cl^- complex, when dissolved in 2VYPY, already exhibited nearly octahedral symmetry at ambient pressure.

6. Summary

In this paper we illustrate the variety of possible ways in which molecular rearrangement can take place in the solid state from stochastic processes, as in a liquid solution, to first-order phase transitions. Intermediate extents of cooperativity also occur. An understanding of these possibilities can lead to broad applications of symmetry-controlled reactivity in rigid media.

Acknowledgments

The authors would like to thank their co-workers and colleagues who have contributed so substantially to the research.

It is a pleasure to acknowledge the support of the Materials Science Division of the Department of Energy under contract DE-AC02-76ER01198.

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