Here the $^4T_2$ level (4680–4980 cm^{-1}) is split into two bands in the infrared region, ^4E and ^4B, with ~250 ± 50 cm^{-1} separation. This splitting is analogous to that which we observe here, although much less in magnitude, indicating perhaps a larger noncubic contribution in the Co^{2+}–CdF$_2$ system than in the garnets.

Transition $^4A_2 \rightarrow {}^4T_2(F)$.—From the position of the lowest absorption band we estimate *Dq* to be ~380 cm^{-1}. This leads to a value of $B' = 972$ cm^{-1}, which is slightly greater than the measured free-ion value of 970 cm^{-1}.[13] This, of course, only reflects the fact that the original values substituted into the Tanabe–Sugano equations were obtained from very broad bands. For example a B' value of ~870 cm^{-1} is obtainable for Co^{2+}–CdF$_2$ if the shoulders at 6450 and 18,000 cm^{-1} are assumed to be the electronic origins of the two broad bands. As one might expect, in a system which contains fluoride ion as the ligand, these values of B' indicate very little covalence.

Comparison of the *Dq* value obtained from measurements on this system, 380 cm^{-1}, and the *Dq* obtained for Co^{2+}–CaF$_2$(2), 340 cm^{-1}, indicates a surprisingly large difference in energy when one takes into account that there is only 0.02-Å difference between the ionic radii of Cd^{2+} (0.97 Å) and Ca^{2+} (0.99 Å).[14] The relatively low *Dq* of both Co^{2+}–CdF$_2$[15] is undoubtedly caused by the difference between the ionic radius of the Co^{2+} ions (0.72 Å)[16] and that of the ion for which it is substituted. Variation in *Dq* between the Ca^{2+} and Cd^{2+} hosts, on the other hand, must be a specific reflection of altered nearest neighbor polarizations, perhaps in an obvious way. In fact, evidence has been obtained recently[8,17] that Cd^{2+} probably participates in a greater degree of covalent bonding than Ba^{2+}, Sr^{2+}, or Ca^{2+} in the alkaline earth fluorides.

Transitions $^4A_2 \rightarrow {}^4T_1(F)$, $^4T_1(P)$.—The assignment of these bands has been given earlier. At 4°K the number of fine components in the $^4T_1$(F and $^4T_1$(P) bands, Figure 3, Table I, is larger than that which can be accounted for by spin–orbit coupling alone and undoubtedly represents a combination of spin–orbit origins, low-symmetry components, and vibrations. More cannot be said owing to a lack of definitive polarization data.

Acknowledgment. This research was supported in part by NSF Grant GP-7920.

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(13) Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 753 (1954).

(14) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p 346.

(15) Based upon: *Dq*(Td Co^{2+} in garnet) ≈ 460 cm^{-1},[12] with the oxygen charge being about twice that of fluorine, or *Dq*(Td for F$^-$ as a ligand) ≈ 300 cm^{-1};[11] from the consideration that *Dq*(cubic) should equal ~2*Dq*(Td), we would expect *Dq*(cubic) to be 460–600 cm^{-1}.

(16) A. F. Wells, "Structural Inorganic Chemistry," 3rd ed, Oxford University Press, London, 1962, p 70.

(17) J. D. Axe and G. D. Pettit, *J. Phys. Chem. Solids*, **27**, 621 (1966).

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The Effect of High Pressure on the Vibrational Spectra of Square-Planar Coordination Compounds

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The effect of high pressures (up to 50 kbars) on the molecular vibrations of square-planar coordination compounds of the type MX$_2$L$_2$ (where M = Pt^{II} or Pd^{II}, X = Cl or Br, and L = (CH$_3$)$_2$S) has been studied over the infrared spectral frequency range, 4000–200 cm^{-1}. Emphasis has been placed on the region containing the molecular vibrations of the ligand and it is shown that certain molecular motions are more sensitive than others to changes in the external pressure, both in terms of frequency shifts and changes in intensity. Conclusions are reached as to the effectiveness of this technique for deducing vibrational assignments.

Introduction

A recent report by Postmus, Nakamoto, and Ferraro[1] has described the effect of high pressure on the symmetric and antisymmetric metal–halogen stretching modes of four types of coordination compounds. Their results show that whereas the peak positions are relatively insensitive to pressure, the intensity of the symmetric metal–halogen stretching mode decreases markedly, compared to that of the antisymmetric mode, with increasing external pressure. It was concluded that this technique may be used in the assignment of metal–halogen and metal–ligand stretching vibrations in coordination compounds of suitable symmetry. From their study it would appear that the technique may prove valuable in the interpretation of absorptions in higher spectral regions. The vibrational assignment of the spectra of coordination compounds containing more than seven atoms is, at the very least, difficult. Thus, it was decided to extend the above study to include molecular vibrations of the ligand in the hope of elucidating the nature of this rather interesting effect.

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(1) C. Postmus, K. Nakamoto, and J. R. Ferraro, *Inorg. Chem.*, **6**, 2194 (1967).

Complexes of the types *cis*- and *trans*-MX_2L_2 (where $M = Pt^{II}$ or Pd^{II}, X = Cl or Br, and $L = (CH_3)_2S$) were chosen since a complete vibrational assignment has been made for both the ligand modes[2] and the metal–ligand modes[3] over the frequency range 4000–100 cm^{-1}.

Experimental Section

Spectra were recorded in the mid-infrared region using a Perkin-Elmer Model 621 spectrophotometer equipped with a 6X double-beam condenser. High-resolution spectra were also obtained in certain regions, including the region 400–200 cm^{-1}, using a Perkin-Elmer Model 225 spectrophotometer equipped with a prototype beam condenser.[4]

The miniaturized high-pressure diamond window cell used in this study was developed by Weir, Van Valkenburg, and Lippincott.[5] Samples in the diamond cell were handled according to a technique described elsewhere.[6] The solid material was placed on the diamond surface and pressure was then applied. The sample was worked by applying and removing pressure until there was no extrusion of sample from between the diamond surfaces. This process also had the effect of reducing any abnormal pressure gradients in the sample. The sample was observed through a microscope during the period of the working cycle to ensure that no changes of phase occurred in the pressure ranges studied.

The highest pressure desired was applied to the sample and the cell was mounted in the appropriate beam condenser. Subsequent spectra of the sample under pressure were recorded as the pressure was removed in increments to minimize the possibility of sample extrusion. The spectra recorded at the final applied pressure of zero were then compared with spectra measured prior to the application of pressure. In all cases, the two spectra obtained at zero applied pressure were found to be in complete agreement.

The pressure on the solid samples has been shown to occur as a gradient, parabolic in nature with the maximum pressure in the center of the diamond surfaces.[7] This pressure gradient can cause a broadening of some of the observed absorption bands, with a resulting loss of resolution. Some apparent intensity loss may be observed due to the gradient, but all intensity changes reported here are greater than that expected from pressure broadening of the bands. Because of this gradient, all pressures mentioned in this work are applied pressures determined by calibrating the spring force constant and measuring the effective pressure surfaces of the diamonds. (Average area size of standard cell diamond surfaces is 10^{-3} in.^{2}.) In certain cases, where more accurate comparisons of band intensities were required, gasketed samples were used to minimize the pressure gradient. Gaskets were made from a 0.002-in. thick brass sheet in which a hole was punched to be smaller than the effective area of the diamonds being used.

The preparation, purification, and characterization of the bis(dimethyl sulfide)dihaloplatinum(II) and -palladium(II) complexes have been described elsewhere[3] and relevant analytical results are contained therein.

Results and Discussion

A. Low-Frequency Region: Metal–Ligand Bond Vibrations.—Square-planar complexes of the type MX_2L_2 exist in either a *cis* or a *trans* configuration. In the *cis* configuration, infrared selection rules dictate that both the symmetric and the antisymmetric stretching vibrations of the metal–ligand bond will be active whereas for the *trans* complex only the antisymmetric mode will be observed. In the low-frequency spectra of the complexes described above two distinct absorption regions are found, namely, that containing bands associated with metal–sulfur stretching modes and that containing stretching vibrations of the metal–halogen bonds. These regions have been well established in the infrared[3] spectra and may be summarized as follows: ν(M–S) 300–320 cm^{-1}, ν(M–Cl) 280–360 cm^{-1}, and ν(M–Br) 200–260 cm^{-1}.

In the infrared spectra of the *trans* compounds only the antisymmetric modes are observed. As expected from the results of Postmus, *et al.*,[1] these modes are found to be almost insensitive to changes in the external pressure in terms of both intensity and frequency shift (the average frequency shift per 20 kbars of applied pressure being of the order of 3 cm^{-1}).

For the *cis* compounds both symmetric and antisymmetric modes are active. In the case of *cis*-$PtCl_2((CH_3)_2S)_2$, however, the two absorption bands associated with ν(Pt–S) occur at very similar frequencies to the two bands associated with ν(Pt–Cl). The over-all appearance of this band is a broad absorption with a maximum at *ca.* 320 cm^{-1}. Assuming that the symmetric modes decrease in intensity with applied pressure, it should be possible to resolve features of the remaining absorptions due to the antisymmetric modes. However, the natural band width was too broad to be resolved. This may be due in part to pressure broadening of those absorptions which do not change in intensity with pressure. In the spectrum of *cis*-$PtBr_2((CH_3)_2S)_2$ two main absorptions are observed in the low-frequency region. One is of medium intensity at 240 cm^{-1}, and the other, of stronger intensity, appears at 225 cm^{-1}. When pressure is applied, the band at 225 cm^{-1} loses intensity relative to that at 240 cm^{-1}, characteristic of a symmetric–antisymmetric relationship as described by Postmus, *et al.*[1] The strong absorption at 225 cm^{-1} is therefore assigned to the symmetric mode of ν(Pt–Br), and that at 240 cm^{-1}, to the antisymmetric mode. The corresponding metal–sulfur vibrations give rise to absorptions that are too weak to be observed under pressure.

One interesting feature which appears in many of the spectra of the *trans* compounds is the pressure sensitivity of a band of medium intensity at 290–300 cm^{-1} (*cf.* Figure 1). This absorption has been assigned to the symmetric bending mode of the C–S–C skeleton of the dimethyl sulfide ligand.[3] (Symmetric in this case implies a symmetric motion of the carbon atoms above and below the plane of the MX_2S_2 framework. The equivalent antisymmetric mode is a bending mode of the M–S–C skeleton.) As the pressure is increased, the absorption becomes weaker indicating a symmetric mode. It appears, therefore, that in the low-frequency spectral region pressure sensitivity may be a criterion for symmetric vibrations other than symmetric stretching vibrations in a molecular system. However, strong

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[2] J. R. Allkins and P. J. Hendra, *Spectrochim. Acta*, **24A**, 1305 (1968).

[3] J. R. Allkins and P. J. Hendra, *J. Chem. Soc.*, *A*, 1325 (1967).

[4] On loan from the Perkin-Elmer Corp., Norwalk, Conn.

[5] C. E. Weir, A. Van Valkenburg, and E. R. Lippincott in "Modern Very High Pressure Techniques," R. A. Wentorf, Ed., Butterworth Inc., Washington, D. C., 1962, p 51.

[6] L. S. Whatley, E. R. Lippincott, A. Van Valkenburg, and C. E. Weir, *Science*, **144**, 968 (1964).

[7] E. R. Lippincott and H. C. Duecker, *ibid.*, **144**, 1119 (1964).

vibrational interactions are known to occur especially in the low-frequency region and this may contribute significantly to the observed pressure effect.

B. Mid-Infrared Region Vibrations of the Ligand.

1. 1600–400 Cm^{-1}.—The spectral region between 1600 and 400 cm^{-1} may be divided by group frequency considerations into three main regions:[2] 650–750 cm^{-1}, stretching vibrations of the C–S–C skeleton; 900–1050 cm^{-1}, rocking vibrations of the methyl groups; 1300–1450 cm^{-1}, methyl deformation modes. Representative spectra of a typical complex at 0, 4, 8, 12, 18, 30, and 40 kbars of applied pressure are shown in Figure 1 and the corresponding frequency values are listed in Table I.

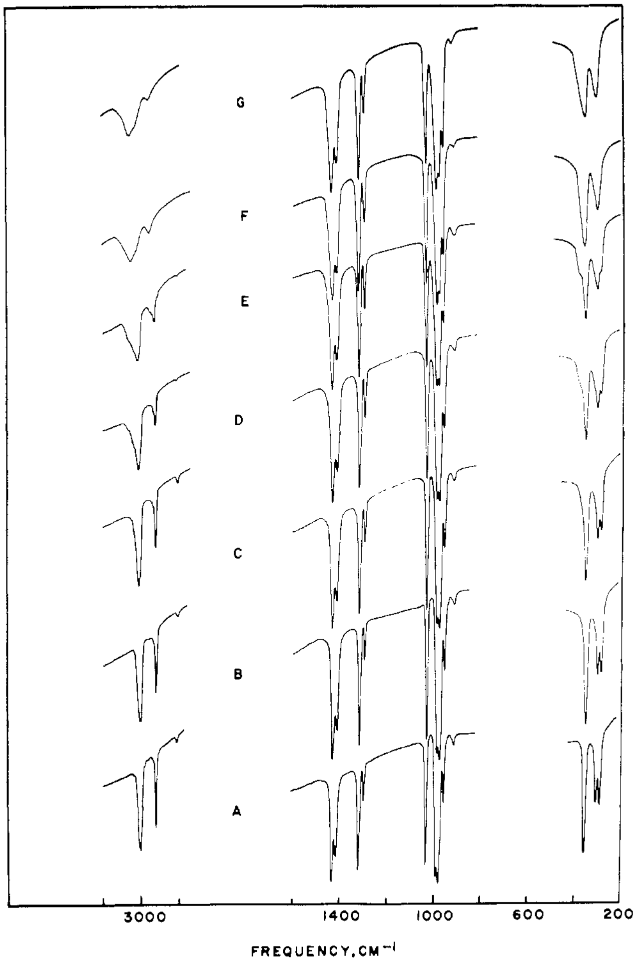

Figure 1.—Pressure-frequency-intensity relationship in the infrared spectrum of *trans*-$PdCl_2((CH_3)_2S)_2$. Applied pressure in kbars: (A) 0; (B) 4; (C) 8; (D) 12; (E) 18; (F) 30; (G) 40.

The carbon–sulfur stretching modes give rise to extremely weak absorptions in the infrared spectra of the complexes, and very little, if any, data could be gathered. It appears that there is a slight increase in frequency of the symmetric stretching mode with increasing pressure but no evaluation of intensity variations could be made.

In the methyl rocking region, qualitative observations are made since no dramatic changes are found with variations in the pressure. As a general rule the rocking modes of the *cis* compounds exhibit slightly more sensitivity to pressure (*ca.* 5-cm^{-1} shift per 20 kbars of pressure) than do the corresponding *trans* compounds (*ca.* 2-cm^{-1} shift per 20 kbars of pressure). In all cases the frequency shift is to higher frequencies. The only rocking mode to show any appreciable change in intensity is that of the A_2 symmetry species (using the vibrational symmetry of the free ligand[8]) which is infrared inactive in the free ligand. The activity in the solid complex has been explained by changes in the selection rules due to complex formation. Since the intensity increases with increasing pressure (in opposition to the normally observed effect) an explanation in terms of increased activity due to greater pressure distortion of the molecular symmetry is preferred in this case. It is of interest to note that the absorption band associated with the A_1 class (fully symmetric) rocking mode, which appears at *ca.* 1030 cm^{-1} in the spectra of the complexes, varies niether in intensity nor in frequency.

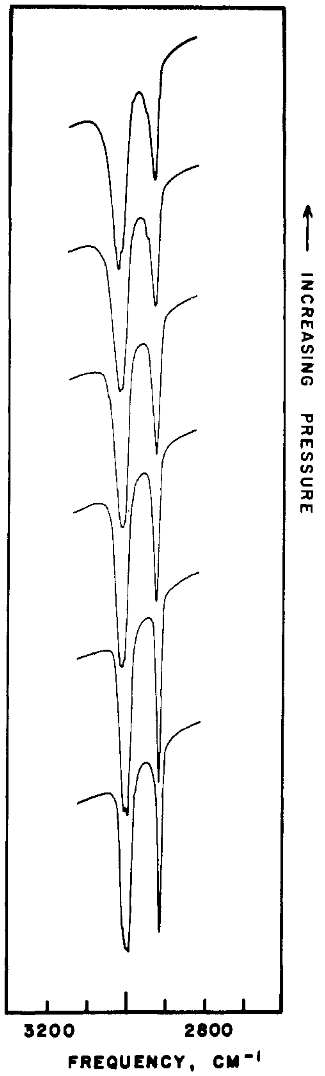

Figure 2.—Pressure–intensity relationship in the C–H stretching region of a gasketed sample: 2900 cm^{-1}, C–H symmetric stretching modes; 3000 cm^{-1}, C–H antisymmetric stretching modes.

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(8) J. R. Allkins and P. J. Hendra, *Spectrochim. Acta*, **22**, 2075 (1966).

TABLE I[a]

FREQUENCY (CM^{-1})–PRESSURE RELATIONSHIP OBSERVED IN THE SPECTRUM OF *trans*-$PdCl_2((CH_3)_2S)_2$

Applied pressure, kbars							
0	4	8	12	18	30	40	Assignment[b]
292 m	293 m	293 w	296 sh	298 sh	N.O.	N.O.	CSC sym bend
309 m	310 m	310 m	311 mw	311 mw	312 mw[c]	314 mw[c]	Pd–S antisym str
359 ms	361 ms	361 ms	361 ms	361 m	362 m[c]	363 m[c]	Pd–Cl antisym str
							CH_3 rock
917 vw	917 vw	918 vw	920 vw	921 vw	922 vw	922 vw	B_1
959 mw	959 mw	959 mw	960 m	961 m	963 m	966 m	A_2
981 s	981 s	981 s	981 s	981 s	983 ms	985 ms	B_2
991 s	990 s	991 s	991 s	991 s	992 s	992 s	
1033 ms	1033 ms	1034 ms	1033 ms	1033 ms	1033 ms	1033 ms	A_1
1296 w	1296 w	1296 w	1296 w	1297 w	1296 w	1297 w	CH_3 sym def
1320 ms	1320 ms	1320 ms	1320 ms	1320 ms	1320 ms	1320 ms	
1413 m	1413 m	1413 m	1413 m	1413 m	1413 m	1413 m	CH_3 antisym def
1432 ms	1432 ms	1432 ms	1432 ms	1432 ms	1432 ms	1432 ms	
2919 m	2920 m	2920 mw	2922 w	2924 w	2950 vw, br	2958 vw, br	C–H sym str
3000 m	3000 m	3002 m, sh					C–H antisym str
3005 m	3007 m	3009 m	3010 m	3012 m, br	3046 mw, br	3055 mw, br	

[a] Abbreviations: s, strong; m, medium; w, weak; v, very; br, broad; sh, shoulder; sym, symmetric; antisym, antisymmetric; str, stretch; def, deformation; n.o., not observed. [b] References 2 and 3. [c] Owing to the small size of the diamonds (*ca.* 4.14 × 10^{-4} in.^{2}) required to produce very high pressures and owing to the inherent decrease in the intensity of incident radiation in the low-frequency region, only estimated values of the pressure-broadened band head frequencies could be made.

The absorptions associated with the methyl deformations of the ligand (1300–1450 cm^{-1}) are completely insensitive to the effect of applied pressures up to 40 kbars. It is again noteworthy that the fully symmetric deformation mode shows no pressure effect, in contrast to that observed for the symmetric stretching mode of the metal–ligand bond.

2. 3200–2800 Cm^{-1}: C–H Stretching Region.—The C–H stretching region of the spectra contains, in general, two main absorptions. One is associated with the symmetric stretching modes and the other with the antisymmetric modes. On the application of pressure to the sample, a marked decrease in the intensity of the absorption band for the symmetric modes is observed. Conversely, the intensity of the absorption associated with the antisymmetric stretching modes remains unaffected. This relationship is found to hold in all of the compounds studied and is similar to that observed by Postmus, *et al.*, for the metal–ligand stretching region. In order to reduce the shear forces exerted on the sample, a series of spectra was obtained using gasketed samples. These are shown in Figure 2 from which it can be seen that a pressure effect does in fact exist. Absolute applied pressures cannot be obtained using gasketed samples since an undeterminable amount of pressure is absorbed by the gasket material.

In addition to the pressure effect on the band intensity described above, a definite increase in frequency is observed for the absorptions in this region. Both symmetric and antisymmetric modes are affected. Pressure studies were therefore extended to 50 kbars and representative spectra showing the behavior of *trans*-bis(dimethyl sulfide)dibromoplatinum(II) over the pressure range 0–50 kbars are shown in Figure 3. The corresponding observed frequencies are listed in Table II. Similar results were obtained for all sample spectra in this region.

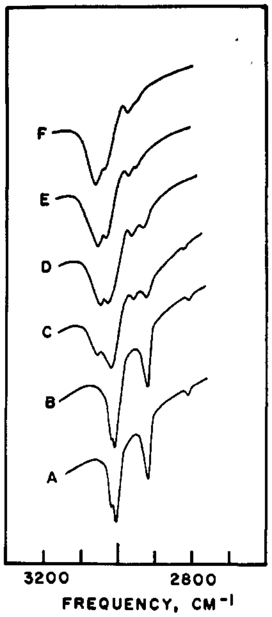

Figure 3.—Pressure–intensity–frequency relationship for absorption bands in the C–H stretching region of *trans*-$PtBr_2((CH_3)_2S)_2$. Applied pressure in kbars: (A) 0; (B) 10; (C) 20; (D) 30; (E) 40; (F) 50.

At 20 kbars of applied pressure new bands appear, initially as shoulders, some 30 cm^{-1} higher than the original absorptions (*i.e.*, the absorptions originally associated with the symmetric and antisymmetric C–H stretching modes at normal pressure). These new bands then increase in intensity as the original absorptions decrease, with increasing applied pressure. It appears, therefore, that there is a transfer of intensity from the lower frequency to a higher frequency absorp-

TABLE II

C–H STRETCHING REGION OF THE INFRARED SPECTRUM (cm^{-1}) OF *trans*-$PtBr_2((CH_3)_2S)_2$

Applied pressure, kbars										
0	5	10	15	20	25	30	35	40	45	50
				Symmetric C–H Stretching Region						
2919 m	2919 m	2920 mw	2920 w	2922 w	2928 w	2928 sh				
				2955 sh	2955 w	2960 w	2963 w, br	2965 w, br	2966 vw, br	2966 vw, br
				Antisymmetric C–H Stretching Region						
3006 m	3006 m	3008 m	3008 m	3008 sh						
3014 sh	3015 sh	3016 m	3018 m	3019 m	3023 mw	3028 mw	3032 mw	3035 mw	3036 sh	3038 sh
				3050 sh	3052 mw	3053 mw	3057 mw	3058 mw	3058 mw	3059 mw, br

tion in both the symmetric and the antisymmetric C–H stretching regions. Thus, the frequency increase with increasing pressure observed in this region is not gradual but is rather of a stepwise nature with a "switchover" of intensity from the original lower to a new higher frequency band occurring at 20 kbars. The initial implication is that a phase change occurs at *ca.* 20 kbars but since (a) no visible change of phase was observed under the microscope over the entire pressure range studied and (b) other methyl group vibrational modes did not show any marked change in frequency at 20 kbars, this explanation is doubtful. One possible interpretation is that some form of intramolecular rearrangement occurs which affects only the frequencies of the C–H stretching vibrations. This could involve some form of rotation of adjacent methyl groups on any one ligand to give a sterically more favorable but energetically less favorable conformation of the molecule at high external pressures. Alternatively, the methyl groups, assumed to lie above and below the plane of the PtS_2X_2 framework, could be forced into the plane by the external pressure. This latter explanation, however, may be discounted from the standpoint that in the *cis* compounds this would be highly unfavorable sterically and the spectra of the *cis* compounds exhibit pressure effects identical with those of the *trans* complexes.

Conclusions

It appears that the application of pressure to square-planar coordination compounds initially affects only those vibrational modes which involve an inherent expansion of the molecular volume. In the compounds studied these modes may be defined as the metal–halogen symmetric stretching mode, the carbon–sulfur–carbon symmetric bending mode, and the carbon–hydrogen symmetric stretching mode. It is assumed from the work of Postmus, *et al.*, that the metal–ligand symmetric stretching mode would behave in a similar manner. The initial result of increasing pressure is to decrease the intensity of the absorptions associated with these "expansion" vibrations. It is thought that this effect is in some way connected with intermolecular interactions since it has been indicated that high pressures result in a shortening of intermolecular distances.[9] A stage may then be reached at which intermolecular repulsions are great enough to prevent further compression of the lattice volume and the effect of increased pressure then causes some form of inter- or intramolecular rearrangement.

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(9) J. W. Brasch, Y. Mikawa, and R. J. Jakobsen, "XIII Colloquium Spectroscopicum Internationale, Ottowa, Adam Hilger Ltd., London, 1967, p 174.