THE FAR INFRARED SPECTRA OF SEVERAL PYRAMIDAL TRIHALIDES

DISSERTATION

Fresented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

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Approved by: . . . Adv

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INTRODUCTION

The trihalides of the fifth group of elements of the periodic table are of the XY, pyramidal type, the base of the pyramid being formed of the three halogen atoms arranged as an equilateral triangle and the apex of the pyramid being an atom of nitrogen", phosphorus, arsenic, antimony or bismuth. For this type of molecule there are four distinct vibrational fundamental frequencies, and for the halogens having mass greater than that of fluorine and with the peak atom of the mass of phosphorus or greater, all of these frequencies will lie at wavelengths longer than 20 microns.

The five molecules treated in this investigation are phosphorus trichloride, phosphorus tribromide, antimony trichloride, antimony tribromide and arsenic trichloride. Of these five molecules, four have been previously studied by means of Raman spectroscopy, the exception being SbBr3. The only infrared investigation was the examination of the 189 cm $^{-1}$ vibration of PCl₃ by O'Loane (1) who used reststrahlen techniques. Several of the lighter molecules of this family have been studied in recent years (z) (5), their fundamental frequencies falling into the wave length region shorter than 25 microns. Some of the analytic methods used

^{*} The nitrogen compounds tend to be explosive.

J. O'Loane, J. Chem. Phys., 21, 669 (1953) M. K. Wilson, J. Chem. Phys., 20, 1716 (1952) H. Gutowsky, J. Chem. Phys. 20, 1652 (1952) (1)

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in interpreting these spectra are also employed in this study.

The recent acquisition of a reflection grating ruled with 550 lines per inch made possible the extension of the range of The Ohio State University far infrared spectrometer so that it can be used between 20 and 140 microns; this fact, coupled with some modifications of the instrument which permitted liquid and solid samples to be rather easily introduced into the light path made it possible to measure the far infrared spectra of these substances.

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HISTORY

The trihalides of the nitrogen column of the periodic table are pyramidal in shape (point group C_{3y}) and are thus similar to ammonia, phosphine and arsine in their gross spectral features. The pyramidal XY3 type of molecule is the simplest nonlinear, nonplanar molecule and has thus been well investigated both experimentally and theoretically during the past three decades. In addition to the literature which deals with the pure rotational spectra of XY3 symmetric top molecules there exists a large body of papers dealing with their vibrational frequencies. Dennison (4) and Lechner (5) did early theoretical work on the XY_K normal mode problem and attempted a comparison with the then known ammonia vibration bands. Howard and Wilson (6) approached the problem using a rather more accurate potential function while Rosenthal (7) worked it out using the most general harmonic potential function consistent with the symmetry of the molecule; namely a six constant function, but one wherein the six constants were not easily visualized in terms of directly apparent physical forces in the molecule such as those associated with bending and stretching.

D. M. Dennison, philosophical Magazine, <u>1</u>, 195 (1926) F. Lechner, Wiener Ber. <u>141</u>, 663 (1932) J. Howard and E. Wilson, J. Chem. Phys. <u>2</u>, 630 (1934) J. Rosenthal, Fhys. Rev. <u>47</u>, 235 (1935) (4)

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The question of interaction between the rotation and internal angular momentum was attacked piecemeal by several investigators and has been treated comprehensively by Shaffer (8) who applied the quantum mechanical perturbation theory to account for anharmonicities and vibration-rotation interaction. Recently there has been another flurry of theoretical activity, mainly concerned with analysis of the pyramidal hydrides of the nitrogen group of the periodic table. In the present report the treatment will follow that of Howard and Wilson for the most part.

It can be shown quite simply from group theory that molecules of this structure have all of their vibrational fundamentals both infrared and Raman active (10); consequently there was a considerable number of Raman spectra obtained from these molecules, especially during the early years of that branch of spectroscopy. Reports of these Raman investigations are listed by Kohlrausch (11) and Herzberg (12) and were liberally used in this undertaking, both as guides to approximate line locations and as aids in assignment.

Brockway (13) made an electron diffraction study of

(8)	W. H. Shaffer, J. Chem. Phys. 9, 607 (1941)
(9)	L. Burnelle, J. Chem. Phys. 18, 1300 (1950)
(10)	J. Walter, H. Eyring, and G. Kimball, Quantum Chemistry
	New York, 1944
(11)	K. W. F. Kohlrausch, Der Smekal-Raman-Effekt, Ergan-
	zungsband, 1931-1937, Berlin, 1938.
(12)	G. Herzberg, Molecular Spectra and Molecular Structure
	II Infrared and Raman Spectru of Polyatomic Molecules,
	New Ylrk, 1945.
(13)	L. O. Brockway, Rev. Mod. Phys. 8, 231 (1936)

several of these molecules, obtaining bond distances and angles. Recently very accurate values of the bond angles have been obtained from microwave measurements reported by Gordy and coworkers (14). The angles used in the treatment of the data obtained in the present investigation are taken from these microwave results except for SbBr₃ for which Brockway's electron diffraction data are the best available.

⁽¹⁴⁾ W. Gordy, W. Smith, and R. Trambarulo, <u>Microwave Spec-</u> troscopy, New York, 1953.

EXPERIMENTAL PROCEDURE

Instrumentation

The spectrograph used for obtaining the data is that constructed at The Ohio State University (15). In the two years since it was previously described, however, some changes in design have been made which bear reporting in some detail.

It was suggested by Professor Ely E. Bell of this laboratory that the cause of a plague of instability troubles in the signal output might lie in the fact that the Golay detector was supported in such a fashion as to be within the evacuated portion of the spectrograph when data were being taken. As a result, if the gas chamber of the detector leaked at all the pressure of the working gas in the detector (usually xenon) might eventually drop sufficiently to change the sensitivity. To correct this, the arrangement shown in Figure 1 was designed and constructed.

This scheme leaves the detector in the atmosphere with, however, only a centimeter path length for the radiation in the open air. The one or two of the strongest water vapor lines remaining in the spectrum (as a result of

⁽¹⁵⁾ R. A. Oetjen, W. H. Haynie, W. M. Ward, R. L. Hansler, H. E. Schauwecher and E. E. Bell, J.O.S.A. <u>42</u>, 559 (1952)



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DETECTOR MOUNT FIGURE 1 7

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the few millimeters pressure of atmospheric water) are completely removed by sending a stream of commercial dry nitrogen through a small tube.

Figure 1 shows the arrangement; the radiation from the exit slit of the spectrometer enters from the left and is reflected from the plane mirror to the ellipsoidal mirror at the bottom from whence it is focused on the sensitive element of the Golay detector slightly above the small polyethylene window.

Two other rather important improvements were made with a view towards greater stability. It was observed that the rotatable table upon which the reststrahlen filtering crystals were mounted had a rather large amount of mechanical play. This table can be rotated to any of four positions by a motor controlled from the outside and there is a considerable gear train necessary to link the motor and the table. Although the arc of free play was no more than a degree or so it was sufficient to throw the image of the source far enough from its proper position on the entrance slit to make several percent difference in the energy falling on the detector.

The fault was remedied by installing a detent mechanism on the reststrahlen table. A spring loaded ball bearing is forced into one of four shallow conical holes on the under side of the reststrahlen table and so holds the table in one precisely reproducible position for each of the four reststrahlen positions. The original electrical arresting

apparatus was necessarily also retained. This is a microswitch, the lever of which rides against a cam mounted on the shaft which supports the table; thus when the table reaches approximately the correct position the driving motor stops, and the detent mechanism brings the table into position.

It was thought probable that another source of instability might lie in brightness fluctuations of the Golay exciter lamp. This lamp is fed from an automobile storage battery so that one would expect any rapid voltage variations to be slight, but on the other hand the signal output is extremely sensitive to the intensity of the exciter lamp, a one percent change in lamp potential producing a ten percent change in signal. In order to maintain a more accurate control over the lamp voltage the circuit shown in Figure 2 was arranged.

At the start of a spectrometer run, a meter reading is made and then further readings -- and adjustments if needed -- are made at regular intervals during the course of the run. The scheme presupposes stability on the part of the dry cells (B), but this is not unreasonable inasmuch as they are actually used only during the very brief interval when the testing switch (S) is closed.

All of these modifications have worked quite well in practice and the instrument is now stable to within 2 percent.

A combination of two factors has extended the wavelength range of the spectrometer. A Golay detector with a diamond window has been received, on loan from the Naval

Research Laboratories. Heretofore a quartz-windowed detector was used which put an upper limit on the frequency range of the spectrometer of about 220 cm -1 as a consequence of the opacity of quartz to higher frequency radiation. The diamond-windowed detector, however, seems to have no marked absorptions down to 13 microns wavelength (670 cm⁻¹).

Also we have received from the University of Michigan a diffraction grating, ruled with 553 lines per inch and blazed at about 30 microns. This grating was installed in the instrument and calibrated using the theoretical water vapor lines of Randall, Dennison, Ginsburg and Weber (16) and Benedict (17). Table I below gives an indication of the accuracy at present obtainable with the instrument. The column headed frequency gives the spectral location. The Reproducibility indicates the magnitude of the frequency difference which occurs between two measures of the same absorption line. This error arises from improper synchronization between the strip chart and the grating drive Veeder counter and from the two percent or so of noise which is present during spectral runs made with the instrument parameters commonly used. There is also a gradual and rather small (0.1 cm $^{-1}$ in most regions) shift in the central image position. By

⁽¹⁶⁾ H. M. Randall, D. M. Dennison, Nathan Ginsburg and Louis R. Weber, Phys. Rev. <u>52</u>, 160 (1937)
(17) W. S. Benedict, private communication, 1950.



EXCITER LAMP CONTROL FIGURE 2

checking the central image position periodically this can, however, be eliminated as a source of error. The Calibration Accuracy gives the magnitude of the difference between the frequencies of the theoretically predicted water vapor lines and the calibration curve plotted from a mean grating constant. The method of calibration was to measure the angle through which the grating turned (on the assumption that counter readings were linear with angle) in going from the central image to various well defined water vapor lines. From these an effective grating constant was calculated from the equation

$\mathcal{T}(cm^{-1}) = K csc \Theta$

and on the basis of 15 theoretically predicted lines scattered throughout the spectral range a mean grating constant was calculated. This constant was then used to construct the calibration table for the instrument.

TABLE I

Frequency	Reproduci bility	Calibration Accuracy
100 cm ⁻¹	0.02 cm ⁻¹	0.01 cm ⁻¹
200	0.08	0.02
300	0.05	0.09
400	0.10	0.12
500	0.16	0.15

The sharp change between 200 cm $^{-1}$ and 300 cm $^{-1}$ is caused by the change in grating used for obtaining spectra in the

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region, below 220 cm⁻¹ the 180 line per inch grating being used and above this frequency the 550 line per inch grating.

Finally there was constructed a sodium chloride chopper which can be used interchangeably with the previously existing potassium bromide chopper. Sodium chloride is transparent from the visible spectral region out as far as about 18 microns in the thicknesses used for chopper blades. At wavelengths longer than 18 microns it becomes quite opaque and consequently it is now possible to obtain a workable signal for radiation from this wave length on out to longer wavelengths.

Thus the instrument is now capable of delivering reliable data over the spectral region between 60 and 500 cm -1 with the accuracies indicated in Table J above.

A further change was made in the instrument in preparation for running several materials including those which form the substance of this report. A hole was cut through the boiler plate tanks surrounding the spectrometer; the hole being placed so that its center was directly above a line joining the entrance slit and the center of the spherical mirror immediately preceding the entrance slit. Through this hole it is possible to lower a cylindrical brass pot in the fashion shown in Figure 3. The cylinder has polyethylene windows on either side of it and a flat plate silver soldered to the top. Thus, when the pot is lowered into position an O-ring under the top plate assures an air



EVACUABLE CHAMBER

FIGURE 3

tight seal against the spectrometer tank and the windows are aligned with the radiation path.

The disadvantage of this is that it necessitates two additional windows as well as ribbing across the windows (since there is an area of six square inches of 0.010 inch polyethylene window across the window). Thus there is a light loss of thirty percent or thereabouts. Weighed against this, however, is the tremendous temporal advantage to having a small chamber, separate from the rest of the spectrometer, which can be evacuated in two minutes and through which a convenient portion of the radiation path is accessible from the outside.

Besides its convenience for introducing solid samples and the liquid cell (presently to be described) into the radiation path, the pot itself has a diameter of six inches and so can be used as a gas cell.

Samples

The materials covered in this report are five: the trichlorides of phosphorus, antimony and arsenic and the tribromides of phosphorus and of antimony. The pertinent physical constants are given in Table II below (18) (19):

 ^{(18) &}lt;u>Handbook of Chemistry and Physics</u>, Cleveland, Ohio, 1949.
 (19) <u>International Critical Tables</u>, New York, 1943.

TABLE II

	Melting Point	Boiling Point	Vapor Pressure (room temp.)				
PCl ₃	-91°C	75.5°C	25. 0 cm Hg				
AsCl ₃	-18	130.2	2.6				
PBr ₃	-40	172.9	6.4				
SbCl ₃	73.4	223					
SbBr ₃	96.6	280					

All of these samples were obtained commercially (Mallinckrodt C.P.) and the liquids were used without further purification while the solids were purified by dissolving them in CS_2 . Both antimony trichloride and antimony tribromide are very soluble in carbon disulfide while the impurities (mainly SbOCl from reaction with water) are much less so.

Cells

A fairly simple technique was devised for obtaining the spectra of the solids SbCl₃ and SbBr₃. A good grade of commercial paraffin was first melted in a beaker, the volume used being perhaps 20 cm³. Such paraffin has no sharp melting point, but at the temperature at which it is reduced to a watery consistency it is something above 100°C and thus well above the melting points of the two solids considered. To the molten paraffin was added a small sample of purified SbBr₃ or SbCl₃, which would thereupon melt and dissolve. It is important that these solid trihalides be purified in the manner indicated above, otherwise when this mixing is carried out a considerable residue will be left and the entire melt will become tinged with red, causing general spectral absorptions.

The melt is next poured onto a confined surface of mercury which has been previously heated so that solidification will not take place upon contact. After cooling, the paraffin-plus-sample disc is removed and can then be placed in the light path and the spectrum run.

The paraffin technique was used out of necessity. The trihalides are very nearly insoluble in all the common nonpolar solvents (polar solvents are opaque at these frequencies) and with present window materials it is not possible to run the cell at a high enough temperature to melt the SbCl₃ or SbBr₃. Powders simply scatter all of the radiation.

The problem of designing a liquid cell for use in this spectral region was solved reasonably well although there is need for improvement. The general requirements for such a cell are no different from those for a near infrared liquid cell. Here it is absolutely necessary that the cell can be relied upon to remain tightly sealed for considerable periods in a vacuum. This necessity arises from the difficulty in completely removing water vapor from the light path. Commercially dry gases (such as dry nitrogen) show water vapor

absorptions for path lengths of more than a few inches and, while dessicants such as P_2O_5 will eventually dry a chamber of no more than a few cubic feet in volume, the time required is usually several hours. Thus it seemed most expedient to devise a cell which could be placed in the evacuable pot, the drying process being reduced in this fashion to a matter of a few minutes.

The main difficulty in the construction of the liquid cell is that there are so few satisfactory window materials in the far infrared. The most transparent substances are long chain hydrocarbons such as paraffin, mineral oil and the classic window material, polyethylene. We use the latter throughout and it is quite satisfadory in the way of transparency and strength and (for the most part) inertness: gualities which make it admirable for gas cells; but it has the drawback of being flexible. The area of the beam at the point where the samples were introduced is about 25" by 1" and the vapor pressures of the liquids ranged up to 1/6 atmosphere at room temperature (Table II). This large a pressure, even with polyethylene 0.035" thick, would cause bulging of the polyethylene window so that the liquid level would be lowered and part of the radiation beam would pass through the empty cell when the cell was placed in a vacuum.

It would have been possible to arrange a cell with a sufficiently large reservoir capacity to prevent such an extreme drop in liquid level; indeed something of this sort

was actually tried but the bulging caused defocusing to an extent that made the method impracticable.

Another difficulty was that of getting a suitable spacer between the windows. It had to seal tightly enough to the polyethylene to prevent any leaking at the vapor pressures of the liquids and in addition it had to be at least as inert as (and preferably more so than) polyethylene. Polyethylene itself was used as a spacer for the AsCl₅ cell; however, it is necessary to use a wax to form a seal between the polyethylene surfaces, since the substance will not seal tightly to itself. The arrangement finally settled upon is shown in Figure 4 in the exploded drawing of the cell components. The outside sections are coarse wire screen with a wire diameter of 1/32" and a screen spacing of 1/4". The spacer was cut from 0.048" Koroseal and presented a crosssectional window area of 1" x 2" which is slightly smaller than the beam size at this point. However, the Golay detector as presently arranged has a sensitive area which encompasses only about a third of the total radiation incident on the detector nose. Hence the cell is large enough to include all of the usable beam. The wire screen has a geometric opacity of 30% and the actual opacity is very close to this. By carefully aligning the screens whenever the cell was assembled the light loss with two windows was very little more than with a single window.

The windows themselves were of 0.035" polyethylene and



LIQUID CELL COMPONENTS

FIGURE 4

were sufficiently rigid that when used with the grating reinforcers neither severe defocusing nor troublesome drop in the liquid level occurred when the cell was introduced into the pot and the pot evacuated. It should be remarked that polyethylene, while chemically inert with respect to these liquids, did show a tendency to absorb them and the cell would, over a period of several hours, lose a good fraction of its contents from the liquid soaking through the polyethylene window and evaporating to the outside. Almost all of the data runs were of an hour's duration or less so that in this investigation the effect was not overly bothersome. It does mean that one is constantly pumping a little of the trihalide vapor through the vacuum pumps, a process which causes very rapid disintegration of the pump oil.

To actually form the cell the components shown in Figure 4 were clamped together in the arrangement shown in Figure 5. At the time of assembly a hypodermic needle is left inserted between the components as shown in the sketch. The liquid is introduced into the cell through this needle after which the needle is withdrawn and the front clamping plate drawn up tight. It is of considerable importance that the needles be thoroughly rinsed afterwards with ethyl alcohol, otherwise chemical action will destroy the needles after two or three usings.

The cell assembly shown in Figure 5 has the purpose of not only holding the cell components tightly together and



FIGURE 5

placing them properly in the beam, but also allowing the samples to be run at different temperatures. The rods holding the lower copper cell clamping assembly to the upper brass fitting are hollow stainless steel tubes, silver soldered both to the copper block and to the brass cylinders above. A cross sectional view of the construction is shown in Figure The cylindrical brass extensions at the top are made 6. with a view to having the thermal path between the copper block and the spectrometer tanks as long as can be conveniently arranged. By circulating liquid of the desired temperature through the tubing the copper block, and hence the sample. can very quickly be brought to the same temperature. The principal restricting factors in all this are the properties of polyethylene at extreme temperatures. Above 100°C it becomes soft and loses strength rapidly with increasing temperature: for low temperatures, however, the situation is a good deal more satisfactory. Even when immersed in liquid nitrogen (-196°C), polyethylene remains somewhat pliable and is not seriously weakened.

A small hole was drilled into the clamping plate as indicated in the figure, and into this was inserted a copperconstanan junction. The thermocouple leads were taken out through the electrical leadthrough also shown in Figure 6, and the other junction placed in melting ice. A fairly rough calibration made with iso-octane, liquid nitrogen, and a salt-ice-water mixture gave enough points to be able to



CROSS SECTION OF CELL ASSEMBLY

FIGURE 6

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establish a curve sufficiently good to determine the cell temperature to within 10°C. This could be much improved with a more carefully measured calibration.

No spectral measurements of substances at low temperatures have as yet been made with the system except for a spectrum made between 50 and 70 microns with the empty cell at the temperature of liquid nitrogen. This was done to determine whether the polyethylene would undergo any phase transitions which would affect its transparency for far infrared radiation at low temperatures. No changes in transparency were observed.

• • • •

THEORY

Group Theory

This family of molecules, like ammonia, belongs to the point group C_{3v} , which is to say it has a threefold (vertical) axis of rotational symmetry and three vertical reflection planes. Figure 7 shows the covering operations possible with this type of molecule.

The group elements are

 $\begin{aligned} \xi &= \text{ identity} \\ C_3 &= \text{ rotation by } 120^\circ \text{ about z axis} \\ C_3^2 &= \text{ rotation by } 240^\circ \text{ about z axis} \\ \mathbf{V} &= \text{ reflection in xz plane} \\ \mathbf{V} &= \text{ reflection in a plane containing the symmetry axis and making an angle of } \\ 60^\circ \text{ with the x-axis.} \end{aligned}$

T = reflection in a plane containing the symmetry axis and making an angle of 120° with the x-axis.

If we now define the product of two of the group elements to be the single operation which has the same result as that produced by one of the group operations followed by another of the operators, then we can arrange a multiplication table in which the column headings are those operations carried out first and the row headings those carried out second. The operator at the intersection of the row and column is the operator which is equivalent to the



SYMMETRY ELEMENTS OF THE $c_{\overline{\mathbf{3v}}}$ group

FIGURE 7

two operations carried out in succession. This is shown in Table III:

3	C3	C_3^2	J.	J,	σ ,"
3	C3	C ₃ ²	۳	۵۳,	יע"
C3	C ² 3	3	σv	T "	$\sigma_{\mathbf{v}}$
C3	3	C3	σ _Y "	σv	σ,'
Jy	σ,"	σ_{v}	З	C ² ₃	C3
σ,'	ፍ	ር "	C3	3	C ² 3
σ."	۳ ۰ ,	T _v	C_3^2	C3	3
	E C 3 C 3 C 3 C 3 C 3 C 3 C 3 C 4 C 4 C 4 C 4 C 4 C 4 C 4 C 4 C 4 C 4	$\begin{array}{ccc} & & C_3 \\ \hline & & C_3 \\ \hline & & C_3 \\ \hline & & C_3^2 \\ \hline & & C_3^2 \\ \hline & & & C_3^2 \\ \hline & & & & C_3^* \\ \hline & & & & & \\ \hline & & & & & \\ \hline & & & &$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

TABLE III

The "classes" of elements composing a group are defined as those elements X_i which are transformed among themselves by the transformation $X_i = Y^{-1}X_jY$ where Y is any element of the group, the group multiplication operation was defined above and the element standing to the right represents the first operation to be carried out. For this group we find that the elements are formed into the classes

 $\left\{ \mathcal{E} \right\}, \left\{ \mathcal{C}_{3}, \mathcal{C}_{3}^{2} \right\}, \left\{ \sigma_{v}, \sigma_{v}', \sigma_{v}'' \right\}$

It can be shown that to every group there is a simply isomorphic group of matrices and since the $C_{\odot V}$ is a group

formed by geometric operations we can construct the elements of its isomorphic matrix group simply by writing out the transformation matrices for the covering operations. For example from the planar rotation matrix

$$C\varphi = \begin{bmatrix} \cos\varphi & -\sin\varphi & 0 \\ \sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

we obtain the C_3 and C_3^2 matrices. The three reflection matrices can either be obtained by considering what happens to each of the coordinates under the reflection operations or more formally by using the rotation matrices and the multiplication table. The matrices isomorphic to the C_{3v} group are then

$$E_{n}^{*} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$C_{3}^{*} \begin{pmatrix} -\frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{3}} & 0 \\ -\frac{1}{\sqrt{3}} & 0 \\ -\frac{1}{\sqrt{3}} & 0$$

which will then give the C_{3V} multiplication table under the operation of matrix multiplication.

Now it may happen that the matrices isomorphic to a group can be "reduced", which is to say they can be put into a form wherein each matrix is composed of a number of submatrices arranged along its diagonal. Thus

 $D[X_j] = \begin{bmatrix} D_{(n)}[X_j] & O \\ D_{(n)}[X_j] & O \end{bmatrix}$

where X_j is the jth element of the group and each submatrix $D^{i}(X_j)$ is also isomorphic to the group element X_j .

This reduction, if possible, is performed by means of a similarity transformation, that is G^{-1} D G, where G is an orthogonal matrix. It is a property of such a similarity transformation that it leaves the sum of the diagonal elements invariant, for

Trace $(G^{-1}DG) = \sum_{i} \sum_{m} \sum_{i} G_{ii}^{-1} D_{im} G_{mi}$, and since G is orthogonal $\sum_{i}^{I} G_{mi} G_{ii}^{-1} = \delta_{mi}$ where $\delta_{mi} = \frac{O}{I}$ is equal to Trace D.

Moreover, since elements of the same class are obtained from each other by similarity transformations, it follows that all matrices isomorphic to elements constituting a class are characterized by having the same trace.

If, then, we take a matrix group simply isomorphic to

our geometric group and reduce it completely -- that is, until the submatrices on the diagonals of our resulting matrices cannot all be further reduced by a similarity transformation -- we shall have obtained some (but not necessarily all) of the irreducible representations of the group. The following orthogonality relation can be shown (20) to hold between the irreducible representations

 $\sum_{\alpha,\beta} D_{\alpha\beta}^{(i)} [X_i] D_{\mu\nu}^{(m)} [X_i] = \frac{g}{\sqrt{d_1 d_m}} \delta_{\alpha\mu} \delta_{\beta\nu} \delta_{im}$

where X_i is the corresponding group element, the superscript indicates which of the irreducible representations is meant, and the subscripts indicate row and column of the irreducible representation. The d_m is the dimension, i.e., the number of rows or columns of the square matrices which are the mth irreducible representation, and the symbol g is the number of elements in the group.

Also, if there are s classes in the group, there will be s different irreducible representations and the sum of the squares of the dimensions will equal the order of the group, that is

 $d_1^2 + d_2^2 + d_3^2 + \dots + d_s^2 = g$

It is a happy fact that the results available from group theory for spectroscopy can be obtained without a (20) Walter, Eyring, and Kimball, op. cit.

knowledge of the irreducible representations themselves but from their traces, or characters, to use the more usual terminology in group theory. Putting the quantities with which we are dealing in the form of an array we have



where the $\chi_m^{(i)}$ is the character of matrix isomorphic to the elements of the mth class (denoted by ζ_m) and belonging to the ith irreducible representation (denoted by row heading $D^{(i)}$).

One can, by using a method outlined in (21), derive the group characters from a knowledge only of the multiplication table of the group. For the C_{3v} group this results in the table below which is just a special case of the array above:

TABLE IV

	3	2 C 3	3 G V
Al	1	l	1
A2	l	l	-1
Е	ะ	-1	0

⁽²¹⁾ H. Margenau and G. Murphy, The Mathematics of Physics and Chemistry, New York, 1943

The column headings give a typical member of the class and the number of elements in the class. The row headings give all of the irreducible representations for the C_{3v} group where we have replaced the $D^{(m)}$ of the previous general array with the usual spectroscopic notation; nondegenerate (i.e., $l \ge l$) representations are denoted by A and doubly degenerate ($2 \ge 2$) ones by E. The subscripts on the A's indicate their symmetry with respect to reflections in the vertical planes.

The thorough treatment of the application of group theory to the quantum mechanical prediction of spectra is somewhat lengthy but quite straightforward. In its barest essentials the theory rests on the fact that a coordinate transformation operator, such as the group elements we have been considering, act upon the Schrödinger eigenfunctions in such a fashion as to produce irreducible representations of the group. The meaning of this will be seen a little more clearly in the following; let us express some one of our covering operations by R and allow it to operate on the Schrödinger equation for the ith energy level, thus $R(H\Psi_{i} - E_{i}\Psi_{i})$ = 0. For a conservative system the Hamiltonian is a functional expression of the total energy and so cannot be dependent on the coordinate description of the system, whence R and H must commute. Since E is a constant we have then $HR\Psi - E; R\Psi = 0$, that is, the functions obtained by operating on the eigenfunctions of the Hamiltonian with a covering
operator are also eigenfunctions of the Hamiltonian and beyond that also correspond to the same energy levels. For the nondegenerate case, since our eigenfunctions must be normalized we have that $R \not{}_{i} = \pm \not{}_{i}$, and indeed, this operation does produce all of the irreducible representations contained in Table IV for the two 1 x 1 irreducible representations, A_1 and A_2 .

If we are dealing with a degenerate eigenvalue the situation is more involved. Here we have that the operator X_n produces a linear combination of the degenerate eigenfunctions

$$X_{n} \Psi_{i}^{j} = \sum_{k=1}^{f} D_{jk}^{(m)} [X_{n}] \Psi_{i}^{k} g_{=1,2,\cdots,f}$$

wherein Ψ is the jth function of the ith eigenvalue and the $D_{jk}(X_n)$ are the expansion coefficients which also, when collected into a matrix, form one of the irreducible representations of the group. In this case we have assumed it to form the mth one.

The eigenfunctions are said to form a <u>basis</u> for the group and for the case of a molecule with only harmonic forces the eigenfunctions have the form (22):

(22) Walter, Eyring, and Kimball, op. cit.

$$\begin{split} & \bigvee_{v_{i}v_{z}v_{3}\cdots v_{n}} = e^{\frac{1}{2}\left\{\sum_{i}c_{i}Q_{i}^{2} + \sum_{j}\sum_{\alpha}^{f_{i}}c_{j}Q_{j\alpha}^{2}\right\}} \\ & \times \left\{\prod_{i}H_{v_{i}}(c_{i}Q_{i})\right\}\left\{\prod_{j}\prod_{\alpha}^{f_{j}}H_{v_{\alpha}}(c_{j}Q_{j\alpha})\right\} \end{split}$$

where f_{i} is the degeneracy of the jth energy level and $c_{i} = \begin{pmatrix} y_{i} \\ h \end{pmatrix}^{1/2}$. The Q's are the normal coordinates going with each classical normal mode of vibration of frequency (in the case of degeneracy there will be more than one normal coordinate for each frequency; this is indicated by the second subscript on the Q's for the degenerate vibrations). The $H_{v}(cQ)$ are the hermite polynomials as functions of the various coordinates $c_{i}Q_{i}$ and $c_{j}Q_{j}\propto$.

We next need a result proved in (23) (page 187) that a product of characters can be written as a sum of the characters of the irreducible representations. Thus, from Table IV above we see that if we write out the characters of the irreducible representations for all the group operations we have, for example:

(23) Walter, Eyring, and Kimball, op. cit.

	3	C3	C ₃	σ.,	σ'n	<u>م</u> *'
E	2	-1	-1	0	0	0
Е	2	-1	-1	0	0	0
ΕE	4	l	1	0	0	0

or EE = A + A + E and other products may be worked out in a similar fashion.

In order to find the forms of the vibrations permitted by the symmetry of the molecule it is necessary to find the character of the vibrational representation. This is (24) the trace of that matrix which transforms the vibrational coordinates under one of the group operators. To find this character we must first consider the matrix which transforms arbitrary displacements of the atoms in the molecule under This the various covering operations which form the group. matrix we term the displacement matrix and its trace the displacement character. In our XY3 case we would have, for example, a column vector of the form $(5x_1, 5y_1, 5z_1, 5x_2,$ δy_2 , δz_2 , δx_3 , δy_3 , δz_3 , δx_4 , δy_4 , δz_4) wherein a δx_1 describes an instantaneous displacement of the ith particle in the x (space fixed) direction during the motion of the molecule. The only atoms in the molecule which will contribute to this trace are those which the covering operation will not interchange with other atoms in the molecule. In a C_{3}

⁽²⁴⁾ Mimeographed notes of Professor W. H. Shaffer, The Ohio State University, 1948.

rotation about the symmetry axis, for example, the motion of the three base atoms, which all move on to equivalent positions, will be represented by only off diagonal elements in the transformation matrix. The peak atom, on the other hand, will have its displacement vector transformed by a 3 x 3 matrix lying on the diagonal of the complete displacement transformation matrix. Quantitatively the identity operator will have the trace 12 and the rotation operators $1 + 2 \cos 120^{\circ}$. To obtain the trace of the reflection operator we can consider the simple case in which the vertical reflection plane contains one of the horizontal axes, say the x axis. Then, if we label the atoms #1 for the peak X atom and #2, #3, and #4 for the three Y atoms we shall have: $\delta z_1 + \delta z_1$, $\delta x_1 \rightarrow \delta x_1$, $\delta z_2 + \delta z_2$, $\delta x_2 \rightarrow \delta x_2$; but $\delta y_1 \rightarrow -\delta y_1$ and $\delta y_2 \rightarrow -\delta y_2$ and the trace is 2. Thus, using Γ_D as the displacement character (we reserve the D symbol for irreducible representations):



and this can be reduced to a sum of irreducible representations either by an inspired inspection or by an orthogonality relation derivable from the one between the components of the irreducible representations given on Page 31 above. The relation between the characters is:

$$\sum_{m=1}^{S} \mathcal{X}_{m}^{(i)} \mathcal{X}_{m}^{(j)} g_{m} = g \delta_{ij} \qquad g_{m \text{ in mth class}}^{n \text{ number of elements}} g_{m \text{ order of group}}$$

and since any character can be expanded from the irreducible characters (25) in the form

 $\chi_m = \sum_{i=1}^{s} a_i \chi_m^{(i)}$

we can obtain the coefficients a, by the usual method for expansion in orthogonal functions. In any event the displacement character when expanded is

$$\int_{O} = 3A_1 + A_2 + 4E$$

which is not, at yet, the vibrational character in that we still have included the translations and rotations of the whole molecule. The procedure for eliminating these characters is indicated in the following paragraphs (26).

From the coordinate transformation matrices we obtained on Page 29 above we see that (since the column vectors upon which the matrices act are in the usual form (x, y, z)z transforms as A_1 and that the coordinate pair (x, y) transforms together as E. This suffices to dispose of the characters for pure translation which is merely a vector displacement (x, y, z).

For the rotational characters, we must consider how an axial vector such as the angular momentum transforms under

⁽²⁵⁾

Walter, Eyring, and Kimball, op. cit. cf. Walter, Eyring, Kimball, op. cit., and Shaffer, mimeographed notes. (26)

the group operations. This can be done by finding the transformation coefficients for each of the components of the infinitesimal rotation vector $R_x = y \ \delta z - z \ \delta y$ and forming these coefficients into the transformation matrices going with each of the covering operations. When this is done we find that the vector (R_x, R_y, R_z) transforms under our

grou	ip op	erac	lous as	C_3		(Γv	_
ſi	õ	0	Cos IZOº	-sin 120	o o]	[-cos 2×60°	-sin 2 × 60'	, 0
0	١	0	sin Iza	Cosizo	° 0	-sin 2x60°	cos 2 x 60°	0
0	Q	IJ	0	0	ر ا	0	O	IJ

66 being the angle that the intersection of the vertical reflection plane and the xy plane makes with the x-axis.

We are now equipped to give the character table showing the characters of the rotations and coordinates and products of coordinates (the latter from the matrices which transform "vectors" of the type ($x^2 - y^2$, xy) etc. according to the group operations) going with each of the irreducible representations:

TABLE V

	٢	2(3	300	
z^2 , $x^2 - y^2$ z A_1	1	. 1	l	
R _z A ₂	1	1	-1	
$x^2 - y^2 xy$ (x,y) E	2	-1	0	
	12	0	2	

From this we see that the character for pure translation and rotation is $f_{yr} = A_1 + A_2 + 2E$; and since $f_0 = 3A_1 + A_2 + 4E$, we have remaining for the pure vibration character $f_{vig} + 2A_1 + 2E$. That is, we shall have six fundamental vibrations (as expected for a four atom non-linear molecule), but of these two are doubly degenerate, thus only four distinct vibrations appear.

To find the optically active transitions we must remember that they only occur in direct absorption and emission when the transition value of the dipole moment is different from zero, or from the conservation of charge, if we have $\int \Psi_{x} \Psi_{d} z = 0$ where the x is one of the body fixed coordinates x, y, or z. The Raman spectrum appears when integrals of the form $\int \psi, xy \psi d\tau$ differ from zero. Now, if the integrals do have non-zero values, then the integrands must be invariant under all of the group operations, that is they must have characters which include the totally symmetric A1 representation. Since we are mainly concerned with the vibrational fundamentals we first consider integrals of the type $\int \Psi_{o,0,1,0,0,0} \mathcal{X} \Psi_{o,0,0,0,0,0,0,0,0,0} d\tau$. From Fage 35 we see that the ground state harmonic eigenfunctions are completely symmetric. For the first vibrationally excited state the exponential factor, having the transformation properties of a number, will be completely symmetric while the first Hermite polynomial has the symmetry of the normal coordinate which it contains, a fact which is obvious

when one considers that $H_1(x) = 2x$. To check on the possibility or impossibility of a particular transition being optically active one has to multiply together the characters of the three functions forming the integrand of the expectation value integral. If the resulting character can be expressed as some sum of the characters of the irreducible representations which includes the totally symmetric representation A_1 , then the transition is possible. This, of course, says nothing about the intensity nor does the fact that an absorption is allowed by group theoretical predictions assure that it will actually occur. However, if we ignore rotation-vibration interaction, the reverse situation is a certainty; a line forbidden by group theory will not appear.

To calculate the allowed transitions for overtones and combination bands the same procedure is used only now it is necessary to know the characters of the excited vibrational levels. We know already the characters of the wave functions for v = 0 and v = 1, and so those for larger v's can be found from the following (27):

 $\chi_{v}(R) = \left[\chi(R)\right]^{v} \text{ for } f = 1 \text{ (no degeneracy)}$ $\chi_{v}(R) = \frac{1}{2} \left[\chi_{v-1}(R)\chi(R) + \chi(R^{v})\right] \text{ for } f^{=2}$

(27) L. Tisza, Z. Physik, 82, 48 (1933)

$$\chi_{v}(R) = \frac{1}{3} \left[2\chi(R)\chi_{v-1}(R) - \frac{1}{2}\chi_{v-2}(R)[\chi(R)]^{242} + \frac{1}{2}\chi(R^{2})\chi_{v-2}(R) + \chi(R^{v}) \right] \quad \text{for } f = 3$$

where $\chi_{\vee}(\mathbf{R})$ is the character of the vth simple harmonic oscillator wave function under the operation R -- or rather, under the class of operations of which the group element R is a member. A lso $\chi_{0}(\mathbf{R})$. I and for degenerate levels the value of v is the sum of the v's going with each eigenfunction of the energy level, that is, $\mathbf{v} = \sum_{\mathbf{r} \in \mathbf{V}} \mathbf{v}_{\mathbf{R}}$.

From the formulae above, the theorem on the expansion of any characters in terms of the characters of the irreducible representations and the fact that we know the characters for the two lowest v values we can construct the table following for the XY, eigenfunctions.

TABLE VI

Quantum Number						
Coordinate to which eigen- function belongs.	0	l	2	ა	4	5
Q1 or Q2	Al	Al	Al	Al	Al	Al
$\left. \begin{array}{c} Q_{3a} \\ Q_{3b} \end{array} \right\}_{or} \left. \begin{array}{c} Q_{4a} \\ Q_{4b} \end{array} \right\}$	Al	E	A ₁ +E	A ₁ +A ₂ +E	a <mark>1+</mark> 5E	a _l +a ₂ +2e

The XY₃ molecule exhibits the rather peculiar property of allowing (insofar as can be predicted by group theory) every conceivable transition in both the Raman and the infrared. It was this circumstance, coupled with the relative simplicity of the molecule, which prompted the early Raman investigations on these substances.

Normal Vibrations

From the foregoing it can be seen that a fundamental difficulty arises immediately in any attempt to interpret the observed spectrum of the XY, in that two of the vibrational fundamentals are doubly degenerate. This means that four of the six generalized force constants degenerate into two pairs of equal constants. What one usually wants, however, is some rather more easily visualized valence force constants. If the molecule is described in terms of bond lengths or bond angles, the transformation to normal coordinates will be by some linear transformation as $\xi_{i} = \sum_{ik} a_{ik} x_{k}$, where the x; are displacements of straightforward nature, such as an increase in bond length or a change in a bond angle. It is generally with respect to displacements such as this that force constants are given. Since the normal coordinates are linearly related to the displacements the potential and kinetic energies are quadratic functions (to the harmonic approximation) of these non-degenerate coordinates (that is, normal coordinates going with non-degenerate vibrations) are only transformed into themselves or into

their negatives by any of the covering operations which form The degenerate normal coordinates will be the group. transformed among themselves by the same matrices which transformed the degenerate vibrational eigenfunctions (28). When the potential energy is expressed in terms of these normal coordinates, it will be found that no cross terms exist between coordinates of different symmetry species for if there were cross products it would mean that they would change sign under some of the covering operations and this would make the potential energy of the molecule dependent on how the system is viewed. Thus the harmonic potential function for the $\mathtt{XY}_{\mathbf{x}}$ molecule will be, when expressed in normal coordinates (29):

 $2V = C_{11}\xi_{1}^{2} + 2C_{12}\xi_{1}\xi_{2} + A_{22}\xi_{2}^{2} + C_{33}[\xi_{3a}^{2} + \xi_{3b}^{2}]$ $+2c_{34}\left[\xi_{3a}\xi_{4a}+\xi_{3b}\xi_{4h}\right]+c_{44}\left[\xi_{4a}^{2}+\xi_{4h}\right]$

and so contain six independent force constants. Since we have but four distinct fundamental frequencies we are forced either to use more equations by measuring isotopic shifts or else to ignore certain of the potential constants.

The latter procedure was that used by Dennison (30) who assumed that the restoring forces were only those directed along the interatomic bonds and thus used a potential

⁽²⁸⁾

Walter, Eyring, and Kimball, op. cit. T. Y. Wu, Vibration Spectra and Structure of Polyatomic Molecules, Peking, China, 1939. Dennison, op. cit. (29)

⁽³⁰⁾

constant of the form

 $2V = \alpha_{1}\left[Q_{12}^{2} + Q_{13}^{2} + Q_{14}^{2}\right] + \alpha_{2}\left[Q_{23}^{2} + Q_{24}^{2} + Q_{34}^{2}\right]$

where in the Q_{ij} is the change in the length of the i-j bond, the X atom being #1 and the three Y atoms #2, #3, and #4.

Lechner also assumed a two constant potential of the

 $2V = \alpha_{1}\left[Q_{12}^{2} + Q_{13}^{2} + Q_{14}^{2}\right] + \alpha_{1}Y_{0}^{2}\left[\delta_{23}^{2} + \delta_{24}^{2} + \delta_{34}^{2}\right]$

with the Q_{ij} as above and the δ_{ij} the change in the angle $Y_i - X - Y_j$. r_0 is the equilibrium X-Y distance.

Each of these potential functions gives, when the appropriate secular equation is solved, a quadratic in the square of the frequency. Since there are but two force constants, the four fundamental frequencies are sufficient to determine them twice. Each of these two constant treatments gives the same expression for the angle between the X-Y bond and the symmetry axis of the pyramid (the angle β). It is (31):

$$\cos^{2}\beta = \frac{1}{\left(\frac{2\sigma_{3}\sigma_{4}}{\sigma_{1}\sigma_{2}}\right)^{2} + \frac{3m - M}{3m + M}}$$

(31) Herzberg, op. cit.

where \mathbf{v}_{i} is the ith fundamental frequency and the masses in the XY₃ molecule are Mm₃. Figure 8 shows the form of the classical normal vibrations for the XY₃ molecule and the notations used here for the various frequencies.

Another, more involved, treatment of the XY₃ vibration problem was that of Howard and Wilson (32), who considered a four constant potential function. In this they took account of cross terms between coordinate and angle changes as well as simply changes themselves, thus: $2V = \alpha_1 \left[Q_{12}^2 + Q_{13}^2 + Q_{14}^2 \right] + 2\alpha_1 \left[Q_{12}Q_{13} + Q_{13}Q_{14} + Q_{14}Q_{12} \right] + \alpha_1 r_0^2 \left[\delta_{23}^2 + \delta_{24}^2 + \delta_{34}^2 \right] + \alpha_1 r_0^2 \left[\delta_{23} \delta_{24} + \delta_{24} \delta_{34} + \delta_{23} \delta_{34} \right]$

where the Q_{ij} and the δ_{ij} are as indicated above in the potential function of Lechner. This potential gives (33) the following two quadratics for the four separate frequencies

$$m^{2}\lambda^{2} - \left\{ (a_{i}+2a_{i}')N+(\alpha_{i}+2\alpha_{i}')LC \right\} m\lambda + (a_{i}+2a_{i}')(\alpha_{i}+2\alpha_{i}')b\delta = 0$$

$$\left[m^{2}\lambda^{2}-\left\{\frac{1}{2}(a,-a;)(c+1)+(\alpha,-\alpha')QW\right\}m\lambda+(a,-a;)(\alpha,-\alpha')QD\right]^{2}=0$$

- (32) J. Howard and E. Wilson, op. cit.
- (33) cf. Herzberg, op. cit.





C₄

NORMAL VIBRATIONS OF THE XY3 MOLECULE FIGURE 8

where
$$\lambda_i = 4\pi^2 c^2 \sigma_i^2$$
 $(\sigma_i \ln cm^{-1})$
 $N = \frac{3m}{M} cos^2 \beta + i$ $\Im = \frac{3m}{M} + i$ $b = 4 cos^2 \beta \cdot Q$
 $C = \frac{3m}{M} sin^2 \beta + i$ $W = \left[\left[\frac{3m}{2M} \right] sin^2 \beta - i \right] sin^2 \beta + 2$
 $Q = \frac{3}{4 - 3 sin^2 \beta}$ $D = \left[\frac{3m}{M} - i \right] sin^2 \beta + 2$

In order to obtain the potential constants from the frequencies the above quadratics must be turned inside out and this yields two quadratics in two linear combinations of two of the force constants and these may then be solved to give the constants themselves. Thus

$$\left[\left< + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 < + 2 <+ 2 < + 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2 <+ 2$$

$$\alpha_{1} + 2\alpha_{1}' = \frac{m^{2}\lambda_{1}\lambda_{2}}{(\alpha_{1}+2\alpha_{1}')\omega_{1}} \qquad \alpha_{1} - \alpha_{1}' = \frac{m^{2}\lambda_{3}\lambda_{4}}{(\alpha_{1}-\alpha_{1}')QD}$$

Howard and Wilson applied this to some early Raman data. The method gives certainly very reasonable results when used with the present infrared measurements -- although it was necessary to change some of the earlier assignments in SbCl₃ and some of the derived force constants (especially the cross terms) are greatly different from the ones obtained from Raman data.

Rosenthal, in a series of parers, treated the molecules

on the basis of the most general six constant potential functions (34). If we again assume the peak atom to be #1 and the three Y atoms to be #2, #3, and #4, the potential function considers changes in bond lengths and is $2V = \alpha_1 \left(Q_{12}^2 + Q_{13}^2 + Q_{14}^2\right) + 2\alpha_2 \left(Q_{12}Q_{13} + Q_{13}Q_{14} + Q_{14}Q_{12}\right) + \alpha_2 \left(Q_{23}^2 + Q_{24}^2 + Q_{34}^2\right) + 2\alpha_2 \left(Q_{23}Q_{24} + Q_{24}Q_{34} + Q_{23}Q_{34}\right) + 2\alpha_3 \left(Q_{12}Q_{34} + Q_{13}Q_{14}^2 + Q_{14}Q_{13}^2\right) + \alpha_4 \left(Q_{34}Q_{13} + Q_{14}Q_{14}Q_{12}^2\right) + \alpha_4 \left(Q_{34}Q_{13} + Q_{14}Q_{14}Q_{12}^2\right) + 2\alpha_3 \left(Q_{12}Q_{34} + Q_{13}Q_{14}^2 + Q_{14}Q_{13}^2\right) + \alpha_4 \left(Q_{34}Q_{13} + Q_{14}Q_{14}Q_{14}^2\right) + Q_{14}Q_{14}Q_{14}^2\right)$ This again yields a quadratic in the frequencies but one containing all the six possible constants geometrically permitted for a harmonic potential function and thus is of no use unless we have isotopic molecules to work with; in which case a number of very interesting relationships can be derived.

It happens that of the five atoms with which we are dealing three are doubly isotopic. The relative abundance of the chlorine isotopes are 3:1, and the two isotopes of bromine and antimony appear in nearly equal amounts. That this will lead to a considerable number of isotopic molecular hybrids is apparent from the following. Consider the atomic masses as M, M', m and m', the molecule being Mm_3 . If we denote by P(M), P(M'), P(m) and P(m'), the fraction of each isotope appearing, we shall have these abundances for

(34) J. Rosenthal, op. cit.

the molecules:

TABLE VII

Mm ₃ ;	$P(M)(P(m))^{3}$	M'm ₃ ;	$P(M')(P(m))^{3}$
Mm2 ^m ';	3P(M)P(m')(P(m)) ²	M'm2m';	$3P(M')P(m')(P(m))^2$
Mmmż;	$3P(M)(P(m!))^{2}P(m)$	M [†] mm [†] ;	3P(M')(P(m')) ² P(m)
Mm g ;	P(M)(P(m')) ³	M'm';	P(M')(P(m')) ³

Whence, as will be seen for SbBr_3 especially, we can have a large number of various kinds of hybrid molecules. These hybrids are not of the XY₃ type at all except insofar as the potential energies are concerned -- since we assume that the force constants do not change when an isotopic substitution is made. This situation too was considered by Rosenthal and Salant (35) on the basis of the most general six-constant potential function. If one considers $\mathbf{T}_1, \mathbf{T}_2, \mathbf{T}_3$ and \mathbf{T}_4 to be the four fundamental frequencies for the Mm₃ molecule and if we take M and m to be the changes in mass upon going to another isotope (where $\frac{\delta M}{M}$ and $\frac{\delta m}{M} <<1$) we shall have the following relations amongst the frequency shifts:

For Mm₃ to Mm₂ (m + 8 m)

parallel frequencies; $\frac{\delta \sigma_1}{\sigma_1} + \frac{\delta \sigma_2}{\sigma_2} = -\frac{\left[\frac{M}{m} + i\right] \delta m}{2(3m + \delta m)}$ (35) J. Rosenthal and E. Salant, <u>op. cit</u>. perpendicular frequencies;

$$\frac{\delta\sigma_3}{\sigma_3} + \frac{\delta\sigma_4}{\sigma_4} = -\frac{\delta m}{\delta m} \left[\frac{m}{m} - \frac{2}{b} + 3 \right], \frac{\delta\sigma_5}{\sigma_5} + \frac{\delta\sigma_6}{\sigma_6} = -\frac{\delta m}{\delta m} \left[\frac{m}{mb} + 1 \right]$$

where $b=1+\frac{2\mu}{m}\cot^2\beta$ and $\mu=\frac{mM}{M+3m}$

It should be noted that the symmetry which is lost in hybridizing the molecule removes the degeneracy in the two perpendicular frequencies so that, while $T_3 = T_5$ and $T_4 = T_6$, $\delta T_3 \neq \delta T_5$ and $\delta T_4 \neq \delta T_6$.

For the case that the X atom is replaced, we have

$$\frac{\delta\sigma_1}{\sigma_1} + \frac{\delta\sigma_2}{\sigma_2} = \frac{\left(\frac{\mu}{m} - 1\right)\delta M}{2(m+\delta M)} \text{ and } \frac{\delta\sigma_3}{\sigma_3} + \frac{\delta\sigma_4}{\sigma_4} = \frac{\left(\frac{\mu}{m} - 1\right)\delta M}{2b(m+\delta M)}$$

this substitution leaving the symmetry as before.

For the case of the isotopic molecule $Mm_3^{!}$ there is an exact (i.e., not dependent on $Sm \ll m$) relationship between the original and displaced frequencies, it is:

$$\left[\frac{\sigma_{i}'\sigma_{z}'}{\sigma_{i}'\sigma_{z}'}\right]^{2} = \frac{m\mu}{m'\mu'}, \\ \left[\frac{\sigma_{3}'\sigma_{4}'}{\sigma_{3}\sigma_{4}}\right]^{2} = \frac{b'm\mu}{b'm'\mu'} \text{ where } \sigma_{i}' = \sigma_{i} + \delta\sigma_{i}$$

Note that this latter expression can also be used to calculate the shift for a replacement M to $M + \delta M$ and indeed these two last expressions are equivalent if one assumes $\frac{\delta M}{M}$ to be very small and $\Im m + M \approx \Im m + M'$. The four constant Howard and Wilson potential function gives the same expression for the frequency product ratios as does Rosenthal's. The actual magnitude of the frequency shifts for isotopic substitutions which leave the C_{3v} symmetry cannot be obtained without knowing the potential constants involved. We can calculate these shifts on the basis of the Howard-Wilson potential function frequency expressions in the following manner;

If we put

 $A = \alpha_1 + 2\alpha_1' \qquad Q = \alpha_1 - \alpha_1'$ $B = \alpha_1 + 2\alpha_1' \qquad B = \alpha_1 - \alpha_1'$

then we have for the roots of the secular equations (see Page 46):

$$\lambda_1 + \lambda_2 = \frac{AN + BLC}{m} \qquad \lambda_3 + \lambda_4 = \frac{\frac{1}{2} \alpha [(c+i] + BQW}{m}$$
$$\lambda_1 \lambda_2 = \frac{ABLY}{m^2} \qquad \lambda_3 \lambda_4 = \frac{\alpha \otimes QD}{m^2}$$

If now we take the variation of the expressions and solve them simultaneously between the two expressions for the same type of frequency, we shall obtain expressions for the absolute magnitude of the isotopic frequency shifts, thus:

$$\delta \lambda_1 = -\lambda_1 \frac{\delta m}{m} + \frac{\lambda_1 [A \delta N + B \omega \delta c]}{m(\lambda_1 - \lambda_2)} - \frac{A B \omega \delta \delta}{m^2 (\lambda_1 - \lambda_2)}$$

or returning to the original notation and writing the frequencies in reciprocal centimeters.

$$\delta\sigma_{1} = -\frac{\delta m}{2m}\sigma_{1} + \frac{[A\delta N + BL\delta C]\sigma_{1}}{8\pi^{2}c^{2}m[\sigma_{1}^{2} - \sigma_{2}^{2}]} \frac{2ABL\delta \delta}{[8\pi^{2}c^{2}m]^{2}[\sigma_{1}^{2} - \sigma_{2}^{2}]\sigma_{1}}$$

$$\delta \sigma_{3}^{2} = -\frac{\delta m}{2m} \sigma_{3}^{2} + \frac{\left[\frac{1}{2} Q \delta C + B Q \delta W\right] \sigma_{3}^{2}}{8\pi^{2} c^{2} m \left[\sigma_{3}^{2} - \sigma_{4}^{2}\right]} - \frac{2 Q B Q \delta D}{\left[8\pi^{2} c^{2} m\right]^{2} \left[\sigma_{3}^{2} - \sigma_{4}^{2}\right] \sigma_{3}^{2}}$$

The value of the displacement of the other fundamental frequency in each of the pairs being given by the same expression with the subscripts reversed -- thus replace 1 by 2 and 2 by 1, and 3 by 4 and 4 by 3. These are valid only for isotopic replacements which do not disturb the symmetry as $\mathbb{M} \rightarrow \mathbb{M} \rightarrow \mathbb{K}$ or for all three Y atoms of mass m being replaced by three atoms of m $+ 5 \mathbb{M}$.

If we form sums of these expressions similar to those on Page 51, we again obtain those given there (to the approximation $M \neq M + \delta M$) while for the isotopic displacement of the frequencies with the substitution $Mm_{3} \rightarrow M(m + \delta m)_{3}$, we get

$$\frac{\delta\sigma_1}{\sigma_1} + \frac{\delta\sigma_2}{\sigma_2} = -\frac{\delta m}{2m} \left[\frac{\mu}{m} + 1\right], \quad \frac{\delta\sigma_3}{\sigma_3} + \frac{\delta\sigma_4}{\sigma_4} = -\frac{\delta m}{2m} \left[\frac{\mu}{m} - 1\right]$$

Finally, making use of the first of these expressions and the Rosenthal formula for the Mm_3 to $M(m + \delta m)m_2$ replacement we can get an expression for the substitution $Mm_3 \rightarrow M(m + \delta m)_2 m$.

It is

,

$$\frac{\delta \sigma_{i}}{\sigma_{i}} + \frac{\delta \sigma_{z}}{\sigma_{z}} = -\frac{\delta m}{3m} \left[\frac{\mu}{m} + 1 \right]$$

The same procedure gives for the perpendicular bands,

$$\frac{\delta \sigma_3}{\sigma_3} + \frac{\delta \sigma_4}{\sigma_4} = -\frac{\delta m}{6m} \left(\frac{\frac{2\mu}{m} - 1}{b} + 3 \right)$$
$$\frac{\delta \sigma_5}{\sigma_5} + \frac{\delta \sigma_6}{\sigma_6} = -\frac{\delta m}{6m} \left(\frac{\frac{2\mu}{m} - 3}{b} + 5 \right)$$

EXPERIMENTAL RESULTS

(1) Phosphorus Trichloride

The PCl3 used was Mallinckrodt C.P. obtained commercially and no attempt was made to purify it further. It is a clear liquid with an extremely pungent odor. It is also a violent poison, largely because it will react with water to produce HCl and $H_{2}PO_{3}$, the latter especially, like most phosphorus compounds, being extremely dangerous.

Kohlrausch (36) gives the Raman determined frequencies as:

> TABLE VIII **J** 510 cm⁻¹ $G_2 = 257 \text{ cm}^{-1}$ $\sigma_{3} = 480 \text{ cm}^{-1}$ **√**₄ = 190 cm⁻¹

with no estimate of probable accuracy.

Brockway (37), on the basis of electron diffraction measurements, gives an X-Y distance of 2.00 A and an X-Y-X angle of 101° ($\beta = 64^{\circ}$). The best microwave measurements (38) yield $\beta = 62^{\circ}15^{\circ}$, however, and this smaller value will

⁽³⁶⁾ (37)

Kohlrausch, <u>op</u>. <u>cit</u>., p. 144. Brockway, <u>op</u>. <u>cit</u>. Gordy, Smith, and Trambarulo, <u>op</u>. <u>cit</u>. (38)

be used in the calculations contained in this report.

The cell was filled as previously described, all of the manipulations being carried out under a hood. This precaution, as well as such others as the wearing of gloves and goggles, is absolutely necessary. The vapor pressure of the liquid is 15 cm of Hg and the air in a closed room will become impossible to breathe a few minutes after a bottle of it is opened to the air. After the cell was filled, it was immediately taken to the spectrometer, the windows of the cell were sluiced off with methyl alcohol, and the cell was placed in the evacuable chamber which was then exhausted. It is necessary to exercise extreme caution in filling the cell since any of the PCl, which happens to slop onto the outside of the cell windows will soon spread out and produce a precipitate which scatters the radiation rather badly. The alcohol removes this, but after the cleaning the cell should be put into a vacuum as quickly as possible. If the cell is left in the air for any more than a few minutes, enough of the PCl will soak through the polyethylene window to react with the water vapor in the air to produce the same precipitate. The PCL, will eventually attack the Koroseal spacer and cause it to harden and crack and so leak. This Koroseal reaction usually requires several hours. however, and so is not of much consequence.

The procedure used in measuring the spectra of this and of the other liquids was to run the spectrometer through

the wavelength region under investigation, first with the cell empty and then with the cell filled with the liquid. This comparison with the empty cell was made partly to form an estimate of the relative intensities of the different frequencies and partly to assure accuracy in locating the line position, since the intensity of the radiation background changes quite rapidly with frequency in some of the regions.

In making assignments it was assumed initially that the Raman investigators were correct. Moreover, by comparison with the other XY_3 molecules having fundamentals in the near infrared, it can be seen that the following rules will be generally applicable((39):

- 1) Frequencywise (in the notation of Figure 8): $\sigma_4 < \sigma_2 < \sigma_3$ 2) The intensity of σ_5 is greater than that of σ_1 .
- 3) Also, σ_1 is usually larger than σ_3 .
- 4) σ_2 and σ_4 are both bending modes and it is quite reasonable to expect them to have the lowest frequencies.

The spectrum obtained is shown in Figure 9, the path lengths being, neglecting a probable residual ten-percent bulging of the cell windows, 1.2 millimeters for all of the runs except the supplementary measurement on the \mathbf{T}_1 absorption. This was obtained using a thicker spacer composed of

(39) M. K. Wilson, op. cit.

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Koroseal and 0.010" polyethylene clamped together and thus represents a path length of approximately 1.5 mm. millimeters.

The assignments are immediately obtained from the rules of thumb indicated above and agree with the Raman assignments as well as giving quite acceptable force constants.

The principal factor limiting the accuracy of locations of the line centers was the fact that the absorptions when measured with the substance in this phase are quite broad, none of them having half-widths of under five or six cm⁻¹. The errors inherent in the instrument itself have already been discussed in the section of this report dealing with experimental techniques, and these introduce much less uncertainty than that caused by the broad width of the line.

The measured vibrational fundamentals, then, to the accuracy possible, are

 $\mathbf{J}_{1} = 507.4 \stackrel{+}{=} 0.5 \text{ cm}^{-1} \\
 \mathbf{J}_{2} = 260.1 \stackrel{+}{=} 0.2 \text{ cm}^{-1} \\
 \mathbf{J}_{3} = 493.5 \stackrel{+}{=} 0.5 \text{ cm}^{-1} \\
 \mathbf{J}_{4} = 189.0 \stackrel{+}{=} 0.3 \text{ cm}^{-1}$

The constants used in the reduction of the data are given in the following table along with the force constants of the four constant potential function given in the Theoretical Section. The angle β is that indicated above and the distance r_0 is the X-Y distance in the molecule, obtained from the microwave determination of the B value of

TABLE IX

 $\beta = 62^{\circ}15'$ $a_{1} = 21.72 \times 10^{4} \text{ dynes/cm}$ $M_{p} = 30.98 \text{ amu}$ $a_{1} = 0.933 \times 10^{4} \text{ dynes/cm}$ $M_{c1} = 34.98 \text{ amu} (75\%)$ $a_{1} = 3.195 \times 10^{4} \text{ dynes/cm}$ $M_{c1} = 36.98 \text{ amu} (25\%)$ $a_{1} = 0.672 \times 10^{4} \text{ dynes/cm}$ $a_{1} = 2.998 \times 10^{10} \text{ cm/sec}$ $C = 2.998 \times 10^{10} \text{ cm/sec}$ $V_{o} - 2.043 \times 10^{-8} \text{ cm}$

No difficulty was experienced in calculating the constants and, as an arithmetical check, the frequencies were recalculated from the force constants. The frequencies were all with 0.1% of their observed values.

From the percentages of the naturally occurring isotopes of phosphorus and chlorine given in the above table, the percentages of the various hybrids of FCl_3 which will be present in a random mixture are:

$$\begin{array}{ccccccc} P^{31}C1_{3}^{35} & 42.1\% \\ P^{31}C1_{3}^{35}C1_{3}^{37} & 42.1\% \\ P^{1}C1_{5}^{35}C1_{2}^{37} & 14.0\% \\ P^{31}C1_{3}^{37} & 1.6\% \end{array}$$

(40) Gordy, op. cit.

From this it is evident that the two molecules which will contribute most significantly to the absorptions are the purebred $P^{31}Cl_{3}^{35}$ and the hybrid $P^{31}Cl_{2}^{35}Cl_{2}^{37}$.

Using the atomic masses given above in Table IX, we obtain the sum relationships of the isotopic frequency shifts as discussed in the Theoretical Section.

For the parallel bands

$$\frac{\delta \sigma_1}{507.4} + \frac{\delta \sigma_2}{260.1} = -0.01148$$

and for the perpendicular bands

$$\frac{\delta \sigma_3}{493.5} + \frac{\delta \sigma_4}{189.0} = -0.0136$$

$$\frac{\delta \sigma_5}{493.5} + \frac{\delta \sigma_6}{189.0} = -0.0115$$

Values which can be satisfied by the shifts

$$\delta \sigma_{1} = -2.3 \text{ cm}^{-1}$$

 $\delta \sigma_{2} = -1.5 \text{ cm}^{-1}$
 $\delta \sigma_{3} = -2.0 \text{ cm}^{-1}$
 $\delta \sigma_{4} = -1.5 \text{ cm}^{-1}$

and these are well within the displacements compatible with the line shapes in Figure 9.

(2) Arsenic Trichloride

AsCl₃ is quite similar to PCl₃ chemically and the methods used in obtaining its spectrum are also much like those employed with the phosphorus halide. Commercially obtained Mallinckrodt C.P. AsCl₃ was used in the liquid cell described above. The only major difference was that it was necessary to use a thinner liquid sample so that in place of the Koroseal spacer a 0.010" spacer of polyethylene was used. This was smeared with Silicone Vacuum Wax in order to make a liquid-tight seal. The precautions about cleaning the outside of the cell are also to be observed here as well as the safety measures, although the lower vapor pressure of this liquid (2.6 mm Hg) makes it a good deal easier to work with.

Kohlrausch gives the Raman frequencies as

with no estimate of probable accuracy.

Brockway's electron diffraction measurements are 2.16 A for the X-Y distance and 103° for the X-Y-X angle (β =64°). The microwave data give 61°01' for β and this value will be used in the calculations. Figure 10 shows the experimental results obtained for AsCl_3 . The absorptions for the $\mathbf{\sigma_2}$ and $\mathbf{\sigma_4}$ vibrations were obtained with the 0.010" (0.4 mm) spacer and also with the Koroseal spacer. The $\mathbf{\sigma_4}$ and $\mathbf{\sigma_3}$ vibrations were measured using the cell with the Koroseal spacer and the supplementary $\mathbf{\sigma_3}$ run was made by soaking polyethylene overnight in AsCl₃ and then measuring the spectrum of the soaked sheet. This latter method was followed for the $\mathbf{\sigma_3}$ absorption because its strength was such as to make difficult good frequency determinations in any liquid thickness possible with this cell.

The measured vibrational fundamentals are

 $\mathbf{G}_{1} = 411.8 \stackrel{\pm}{=} 1.0 \text{ cm}^{-1}$ $\mathbf{G}_{2} = 193.6 \stackrel{\pm}{=} 0.5 \text{ cm}^{-1}$ $\mathbf{G}_{3} = 386.7 \stackrel{\pm}{=} 0.5 \text{ cm}^{-1}$ $\mathbf{G}_{4} = 155.3 \stackrel{\pm}{=} 0.7 \text{ cm}^{-1}$

and the following table gives the constants used in the calculations as well as the calculated force constants. There were no difficulties encountered in the calculation of the force constants and an arithmetical recheck showed them to fit the data to within the probable error. The value of r_0 is taken from the microwave data reported in Gordy (41).

(41) Gordy, Smith, and Trambarulo, op. cit.





FAR INFRARED SPECTRUM OF As Cl₃

TABIE XI

$$\beta = 61^{\circ}01' \qquad a_{1} = 21.44 \times 10^{4} \text{ dynes/cm}$$

$$M_{As} = 74.93 \text{ amu} \qquad a'_{1} = 1.87 \times 10^{4} \text{ dynes/cm}$$

$$M_{C1} = 34.98 \text{ amu} (75\%) \qquad \alpha_{1} = 2.18 \times 10^{4} \text{ dynes/cm}$$

$$M'_{C1} = 36.98 \text{ amu} (25\%) \qquad \alpha'_{1} = 0.26 \times 10^{4} \text{ dynes/cm}$$

$$r_{o} = 2.161 \times 10^{-8} \text{cm}$$

The percentages of the various molecular hybrids will be just as for PCl₃, that is

$$As^{75}Cl_3^{35}$$
 42.1% $As^{75}Cl_2^{35}Cl_3^{37}$ 42.1% $As^{75}Cl_3^{35}Cl_2^{37}$ 14.0% $As^{75}Cl_3^{37}$ 1.6%

and only the two most abundant molecules will be considered here. Using the atomic masses given above, we find, for the parallel bands $\delta\sigma_{1}$ $\delta\sigma_{2}$

$$\frac{\delta \sigma_1}{\sigma_1} + \frac{\delta \sigma_2}{\sigma_2} = -0.013$$

and for the perpendicular bands

$$\frac{\delta \sigma_3}{\sigma_3} + \frac{\delta \sigma_4}{\sigma_4} = -0.017$$
$$\frac{\delta \sigma_5}{\sigma_5} + \frac{\delta \sigma_6}{\sigma_6} = -0.013$$

Values which can be satisfied by the shifts

$$\delta \sigma_1 = -2.0 \text{ cm}^{-1}$$
 $\delta \sigma_2 = -1.5 \text{ cm}^{-1}$
 $\delta \sigma_3 = -2.0 \text{ cm}^{-1}$ $\delta \sigma_4 = -1.3 \text{ cm}^{-1}$

which, again, are in agreement with the line shapes (Figure 10).

(3) Phosphorus Tribromide

This is the most difficult to handle of the substances investigated. It fumes violently when exposed to air, and attacks all of the common waxes so that it is impossible to store it for any length of time after once opening the glass sealed bottle in which it is obtained commercially. Its vapor pressure is 6.4 cm Hg, and it was handled in exactly the same fashion as the PCl₃ treated above.

The Raman frequencies from Kohlrausch are

and the only value for the angle discovered in the literature was that of Pauling (42), who gives 100° for the Br-P-Br angle, or $\beta = 62^{\circ}12^{\circ}$. This value, however, leads to immediate difficulties in that we obtain imaginary force constants.

(42) L. Pauling, op. cit.

As may be seen from the theoretical section above, it must be that, using the Howard and Wilson potential function, in order to have real force constants

$$\frac{[\lambda_1 + \lambda_2]^2}{\lambda_1 \lambda_2} \geq \frac{4NC}{7}$$

or upon substitution and reduction

$$\frac{\lambda_1 - \lambda_2}{6m} \sqrt{\frac{\gamma}{\lambda_1 \lambda_2}} \ge \sin\beta\cos\beta$$

It is assumed that in Figure 11, $\mathbf{\sigma}_1$ and $\mathbf{\sigma}_3$ must lie so close together that they cannot be resolved as separate lines. The spectra in Figure 11 are from runs made with the 1.2 millimeter cell except for the supplementary run from 380 cm⁻¹ to 400 cm⁻¹, which was made using the above-mentioned method of soaking the polyethylene in the liquid PBr₃. Also a search was made from 340 cm⁻¹ to 460 cm⁻¹ to attempt to locate $\mathbf{\sigma}_1$ separate from $\mathbf{\sigma}_3$. As a consequence of the fact that $\mathbf{\sigma}_1$ is overlain by $\mathbf{\sigma}_3$, the position of $\mathbf{\sigma}_1$ is in doubt by some 10 cm⁻¹; this presumes that the intensity of $\mathbf{\sigma}_3$ is much larger than that of $\mathbf{\sigma}_1$, which is the case for the other molecules studied. The measured vibrational frequencies are, therefore

$$\mathbf{J}_{1} = 392 \pm 5 \text{ cm}^{-1} \\
 \mathbf{J}_{2} = 161.3 \pm 0.5 \text{ cm}^{-1} \\
 \mathbf{J}_{3} = 392.2 \pm 0.5 \text{ cm}^{-1} \\
 \mathbf{J}_{4} = 115.7 \pm 0.7 \text{ cm}^{-1}$$

Using the relationships given above we can derive the restrictions on the bond angle corresponding to the extreme





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values assumed for σ_1 . These turn out to be

$$387 \text{ cm}^{-1}$$
 $24^{\circ}51 \times \beta \times 65^{\circ}9 \times 397 \text{ cm}^{-1}$ $26^{\circ}09 \times \beta \times 63^{\circ}51 \times 397 \text{ cm}^{-1}$

The angle picked to use was 64° , both because it corresponds to $\sigma_1 = 392 \text{ cm}^{-1}$ and because it bears the same ratio to the electron diffraction data as do the microwave to electron diffraction determinations for SbCl₃ and AsCl₃. The constants and results for this molecule are summarized below.

TABLE XIII

 $\beta = 64^{\circ} \qquad a_{1} = 18.27 \times 10^{4} \text{ dynes/cm}$ $M_{P} = 30.98 \text{ amu} \qquad a_{1}' = 0.342 \times 10^{4} \text{ dynes/cm}$ $M_{Br} = 78.93 \text{ amu} (50\%) \qquad \alpha_{1}' = 2.398 \times 10^{4} \text{ dynes/cm}$ $M_{Br}' = 80.93 \text{ amu} (50\%) \qquad \alpha_{1}' = 0.693 \times 10^{4} \text{ dynes/cm}$ $r_{0} = 2.24 \times 10^{-8} \text{ cm}$

From the isotope abundance we see that the molecular hybrids will be present in the following percentages

p3lBr ⁷ 9	12.5%
$P^{31}Br_{2}^{79}Br^{81}$	37.5%
$P^{31}Br^{79}Br_{\varkappa}^{81}$	37.5%
P ³¹ Br ⁸¹	12.5%

The largest shifts will probably be produced by the complete
bromine substitution and these displacements in frequency can be calculated from the formulae given above; they are

$$\delta \sigma_{1} = -0.90 \text{ cm}^{-1}$$

 $\delta \sigma_{2} = -1.88 \text{ cm}^{-1}$
 $\delta \sigma_{3} = --0.40 \text{ cm}^{-1}$
 $\delta \sigma_{4} = -1.57 \text{ cm}^{-1}$

which a re quite in accordance with Figure 11.

(4) Antimony Trichloride

This is a solid melting at 73.4°C and was prepared for observation by the method described in the experimental section above. The molten SbCl₃ was always dissolved to saturation in the paraffin and the solid sheets of paraffinplus-SbCl₃ whose spectrawere measured had thicknesses of about 1 mm or slightly more.

The previously obtained Raman frequencies are

and the infrared spectrum obtained is shown in Figure BAll of these runs were made with paraffin-sample sheets of about 1 mm except for the extra σ_1 measurement which was





FIGURE 12 FAR INFRARED SPECTRUM OF SbCl3

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with a sample of 2.5 mm thickness. The infrared frequencies and assignments assumed are

$$\mathbf{J}_{1} = 376.5 \stackrel{\pm}{=} 0.7 \text{ cm}^{-1} \\
 \mathbf{J}_{2} = 164.0 \stackrel{\pm}{=} 0.5 \text{ cm}^{-1} \\
 \mathbf{J}_{3} = 356.1 \stackrel{\pm}{=} 0.5 \text{ cm}^{-1} \\
 \mathbf{J}_{4} = 128.1 \stackrel{\pm}{=} 0.5 \text{ cm}^{-1}$$

The microwave data give a Cl-Sb-Cl angle of 99.5⁰ and the constants assumed and calculated for this molecule are given in the following table.

TABLE XV

β =	610481		a _l =	20.96 x	104	dynes/cm
M _{Sb} =	120.88 amu	(56%)	a <u>1</u> =	1.551 x	104	dynes/cm
M _{Cl} =	34.98 amu	(44%)	م 1 =	1.64 x	10 4	dynes/cm
^M i =	36.98 amu	(75%)	≪1 =	0.303 x	104	dynes/cm
r _o =	2.325 x 10	- ⁸ cm				

These atomic masses will give quite a large number of hybrid molecules although not all of them will be present to any appreciable extent.

Sb ¹²¹ C135	23.5%	Sb ¹²³ Cl ³⁵	18.5%
sb ¹²¹ c1 ³⁵ c1 ³⁷	23.5%	sb ¹²³ c12 ⁵ c1 ³⁷	18.5%
sb ^{lzl} C1 ³⁵ C12 ⁷	7.8%	sb ¹²³ Cl ³⁵ Cl ³⁷	6.2%
Sb ^{1×1} C1 ³⁷	0.9%	Sb ¹²³ C137	0.7%

From this it can be seen that the only symmetric substitution of any consequence will be the $Sb^{1\times 1} \rightarrow Sb^{1\times 3}$ change. This produces the relatively negligible frequency shifts

$$\delta \sigma_{1} = -0.595 \text{ cm}^{-1}$$

$$\delta \sigma_{2} = -0.370 \text{ cm}^{-1}$$

$$\delta \sigma_{3} = -0.772 \text{ cm}^{-1}$$

$$\delta \sigma_{4} = -0.098 \text{ cm}^{-1}$$

However, the substitution of the chlorines produces considerably larger displacements. The principal hybrids are the Sb^{1×1}Cl³⁵₂Cl³⁷ and Sb^{1×3}Cl³⁵₂Cl³⁷, and for these we obtain $\frac{\delta\sigma_1}{\sigma_1} + \frac{\delta\sigma_2}{\sigma_2} = -0.014$ $\frac{\delta\sigma_3}{\sigma_3} + \frac{\delta\sigma_4}{\sigma_4} = -0.018$ $\frac{\delta\sigma_5}{\sigma_5} + \frac{\delta\sigma_6}{\sigma_6} = -0.013$ values which are satisfied by

$$\delta \sigma_{1} = -1.5 \text{ cm}^{-1}$$

 $\delta \sigma_{2} = -1.9 \text{ cm}^{-1}$
 $\delta \sigma_{3} = -5.0 \text{ cm}^{-1}$
 $\delta \sigma_{4} = -0.5 \text{ cm}^{-1}$

and which are, to a certain extent, compatible with the appearance of the \P_3 absorption in Figure 12. It will be noticed that at about 350 cm⁻¹ there is evidence of a secondary absorption. This is displaced from the main absorption by about 5.0 cm⁻¹ and so could well be explained on the basis of the indicated frequency shifts. The long sloping absorption on the low frequency side of the \P_3 minimum is similar in form to the \P_3 absorption of SbBr₃ to be described in the next section. Neither of these seem to be explainable

in terms of properties of the isolated molecule.

It is interesting to note the size of the shifts for the complete substitution of the chlorines even though the concentration of these is too small to be observable.

> $\delta \sigma_1 = -8.64 \text{ cm}^{-1}$ $\delta \sigma_2 = -3.44 \text{ cm}^{-1}$ $\delta \sigma_3 = -7.52 \text{ cm}^{-1}$ $\delta \sigma_4 = -3.52 \text{ cm}^{-1}$

(5) Antimony Tribromide

This substance has not heretofore been observed either by Raman or Infrared methods. The best value for the bond angle is the value 96° for the Br-Sb-Br angle which is quoted by Pauling on the basis of electron diffraction measurements. The material was prepared for observation in the same fashion as SbCl₃, except that the extra precaution of two dissolutions and recoveries from CS_2 was followed in this case; this represented an attempt to get as pure a sample as possible because the spectrum shows some puzzling features which were first attributed to possible impurities.

The spectrum obtained is shown in Figure 13. The two lwwest frequencies are unequivocal enough but the question of how to assign the absorption between 220 cm⁻¹ and 250 cm⁻¹ has not been satisfactorily answered. The broad absorption has a number of separate minima and these



FIGURE 13 FAR INFRARED SPECTRUM OF SbBr3

persist, both in relative intensity and in position as the concentration of the ${\rm SbBr}_{5}$ in the paraffin is changed.

All observed absorption minima are given in the following table.

As can be seen from Figure 13, the 248.4 cm⁻¹ absorption is the most prominent in the broad absorption region.

The initial attempt at an explanation of the very wide absorption band was on the assumption of isotopic frequency shifts, and, indeed, this molecule shows a greater number of hybrids than any of the others examined. The percentages of isotopes naturally present and the bond angle and Sb-Br distance are

β = 6	52 ⁰			Y ₀ =	2.55	x 10	-8 cm
$^{ m M}$ Sb	7	120.88	(56%)	^m Br	=	78.9	(50%)
M'Sb	2	122.88	(44%)	$^{m}\!\mathrm{Br}$	2	80.9	(50%)

which yield the percentages of molecules shown below:

Sb ¹²¹ Br ₃ 79	7.0%	$\mathrm{Sb}^{123}\mathrm{Br}_3^{79}$	5.5%
sb ¹²¹ Br ⁷⁹ Br ⁸¹	21.0%	${ m Sb}^{123}{ m Br}_2^{79}{ m Br}^{81}$	16.5%
sb ¹²¹ Br ⁷⁹ Br ⁸¹	21.0%	Sb ¹²³ Br ⁷⁹ Br ⁸¹ 2	16.5%
sb ¹²¹ Br 3	7.0%	Sb ¹²³ Br ₃ ⁸¹	5.5%

and the calculated sums of frequency shifts are, from the formulae above

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$$Sb^{121}Br_{3}^{79} \rightarrow Sb^{121}Br_{3}^{81}$$

$$\frac{\delta\sigma_{1}}{\sigma_{1}} + \frac{\delta\sigma_{2}}{\sigma_{2}} = -0.017$$

$$\frac{\delta\sigma_{3}}{\sigma_{3}} + \frac{\delta\sigma_{4}}{\sigma_{4}} = -0.019$$

$$Sb^{121}Br_{3}^{79} \rightarrow Sb^{121}Br_{2}^{79}Br^{81}$$

$$\frac{\delta\sigma_{1}}{\sigma_{4}} + \frac{\delta\sigma_{2}}{\sigma_{2}} = -0.006$$

$$\frac{\delta\sigma_{3}}{\sigma_{3}} + \frac{\delta\sigma_{4}}{\sigma_{4}} = -0.007, \quad \frac{\delta\sigma_{5}}{\sigma_{5}} + \frac{\delta\sigma_{6}}{\sigma_{6}} = -0.005$$

$$Sb^{121}Br_{3}^{79} \rightarrow Sb^{121}Br^{79}Br_{2}^{81}$$

$$\frac{\delta\sigma_{1}}{\sigma_{1}} + \frac{\delta\sigma_{2}}{\sigma_{2}} = -0.011$$

$$\frac{\delta\sigma_{3}}{\sigma_{3}} + \frac{\delta\sigma_{4}}{\sigma_{4}} = -0.012, \quad \frac{\delta\sigma_{5}}{\sigma_{5}} + \frac{\delta\sigma_{6}}{\sigma_{6}} = -0.013$$

$$Sb^{121}Br_{3}^{79} \rightarrow Sb^{123}Br_{3}^{79}$$

$$\frac{\delta\sigma_{1}}{\sigma_{1}} + \frac{\delta\sigma_{2}}{\sigma_{2}} = -0.006$$

$$\frac{\delta\sigma_{3}}{\sigma_{3}} + \frac{\delta\sigma_{4}}{\sigma_{4}} = -0.005$$

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using the Pauling value of 61° for the angle . The difference between the sum for two substitutions such as $sb^{121}Br_3^{79} \rightarrow sb^{121}Br_2^{79}Br^{81}$ and $sb^{123}Br_3^{79} \rightarrow sb^{123}Br_2^{79}Er^{81}$ is small and need not be considered. The assumption which would seem to come the nearest to explaining the absorption in the 250 cm⁻¹ region would be that it represents the total spread of frequencies between the lowest possible frequency three-quarters of the frequency shift for any one species is assumed to occur in the ${f \sigma_l}$ and ${f \sigma_c}$ vibrations, this allows a frequency range of only 14 cm⁻¹, which would be strongly ab-It is true of course that when prepared in this sorbed. fashion, the substances show bands that are quite broad, but even with this it is hard to see how the necessary range of 30 cm⁻¹ can be produced.

Table XVIII gives the constants calculated on the basis of extreme assumptions regarding the assignments.

TABLE XVII

Assignme (frequen	nts Assu cies in	cmed)			Force co (dyn	onstants nes/cm)	s x 10 ⁻⁴
(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm^{-1})	а,	Q.1	¢,	م ر *
248.4 222.3 248.4 222.3 237.0 248.4	108.5 108.3 108.5 108.5 108.5 108.5	243.4 222.3 222.3 248.4 248.4 237.0	90.8 90.8 90.8 90.8 90.8 90.8	16.86 13.38 14.73 15.51 16.25 15.87	0.83 0.54 1.89 -0.52 0.22	1.53 1.55 1.54 1.54 1.53 1.53	0.10 0.11 0.10 0.11 0.11

The last two make use of a 237 cm⁻¹ minimum which appears in Figure 13 as the smaller absorption, just to the lower frequency side of the main 248 cm⁻¹ absorption.

SUMMARY AND CONCLUSIONS

The spectra of five pyramidal trihalides were obtained and, except for SbBr₃, the four fundamental frequencies were located with reasonable accuracy. Using a four constant harmonic potential function devised by Howard and Wilson force constants were calculated on the basis of the observed frequencies. In Table XVIII the force constants thus calculated are given, along with the bond angles ass umed in making the calculations. The extreme values possible for SbBr₃ are given.

Substance	Bond Angle	Force	Constar	nts (dyr	ns/cm)
	β	<u>a_x10</u> -4	$\frac{a_1 x10}{a_1 x10}$	4 <u>x1</u> 0-	4 <u>4 x1</u> 0-4
PCl ₃	62 ⁰ 17'	21.72	0.93	3.19	0.67
\texttt{AsCl}_3	61 ⁰	21.44	1.87	2.18	0.26
SbCl	610501	20.96	1.55	1.64	0.30
PBr ₃	65 ⁰	18.27	0.34	2.40	0.69
SbBr ₃	62 0	$\{ 13.4 \\ 16.8 \}$	0.22 1.89	1.53 1.55	0.10 0.11

TABLE XVIII

The questions of anharmonicities and vibration-rotation interactions cannot be answered on the basis of data obtained from molecules in a condensed state. The frequency shifts resulting from anharmonicity would be very small. For a molecule such as water these shifts are all le ss than

five percent and in PCl₃ we deal with atoms of much greater mass and force constants of a third of the magnitude. This means that the oscillations will be of rather small amplitude and hence, that the effect of the anharmonic constants will not be important.

Rotation-vibration interactions could not, in our present stage of instrumentation, be studied even if the spectra were obtained with the substances in the gaseous phase. The most favorable of the molecules, PCl_3 , has a B value of 0.088 cm⁻¹ (44), which means that the spacing of the rotational lines would be 0.716 cm⁻¹, which is too small for resolution with the spectrograph. The band envelopes could be measured and for PCl_5 , since the P and R Branch maxima would be separated by 12 cm⁻¹.

The most valuable result of getting the far infrared spectrum of these substances in the gaseous phase would be the determination of the effect of condensation on the vibrational frequencies. Mielsen and Ward (43) attempted a study of the frequency shifts accompanying change of aggregation for several molecules including FCl₃. They used Raman techniques to make this investigation, however, and it should be possible to improve considerably on their accuracy with the infrared instrument now at our disposal. However,

(43) J. Nielsen and Ward, J. Chem. Phys. <u>10</u>, 81 (1942)
(44) Gordy, Smith, and Trambarulo, <u>op. cit.</u>

in order to carry out this measurement some improvements in cell design will have to be worked out. During the course of the present investigation, two attempts were made at measuring gaseous PCl₃, it being the only one of these substances having a high enough vapor pressure to be used with the cell lengths now available to us. In the first case the cell window was polyethylene and in the second case Teflon. In both instances it was found that the plastics absorbed the trihalide to such an extent that, after exhausting the cell of the PCl₃ vapor, the "empty cell" gave the same spectrum as it had with 20 cm pressure of the vapor present.

The solution to this is to have a multiple path cell (so that low pressure vapors could be run) with windows of crystal quartz. In order to keep the window size as small as possible, the windows would have to be placed near the entrance slit of the spectrometer.

Finally, the question of the SbBr₃ absorption should be further investigated. The author attempted to find a non-polar solvent for SbCl₃, SbBr₃, and BiCl₃, with no success w hatever. However, a possible approach would be to evaporate a thin layer of SbBr₃ onto a sheet of polyethylene and obtain the spectrum of the solid. This would indicate immediately whether the appearance of the band is due to the SbBr₃ actually being in the solid state when the paraffin solution technique is used.

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AUTOBIOGRAPHY

I, Philip W. Davis, was born in St. Louis, Missouri on June 19, 1925. Very shortly thereafter the family moved to Columbus, Ohio, where I have lived (with minor interruptions) ever since. My secondary education was received from The Ohio State University High School and upon graduation I entered the Army of the United States. I was discharged in 1946. I then enrolled in The Ohio State University and was graduated with a Bachelor of Science degree with majors in physics and mathematics in December, 1948. The following September I entered the Graduate School of The Ohio State University. In the fall of 1950 I was appointed a Research Associate, a position which I have held since then with the exception of the year 1952-53, when I was a University Fellow.