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**T**O elucidate the structure of molecules and the changes that occur as they react often takes a toolbox full of analytical instruments. Until recently, electron diffraction, x-ray diffraction and mass spectroscopy have been the best such tools. Now Raman spectroscopy of the sample in gaseous form is turning out to be an equally powerful wrench.

Introduction of intense ion lasers and highly efficient spectroscopic systems has brought analytical time down from an unpopularly long weekend to under an hour in some instances. Specific applications of this growing technique will illustrate its unique ability to unravel molecular mysteries.

—ED.

## HIGH TEMPERATURE GAS PHASE RAMAN SPECTROSCOPY

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Gas phase Raman spectroscopy is attractive because the separation of molecules is so great that interactions are essentially absent; spectra thus pertain to the molecules themselves not to interactions which frequently complicate the spectra of solids and liquids.

The importance of Raman spectroscopy as a technique for examining gases and vapors at high temperatures is very evident in vibrational spectroscopy of inorganic species. The Raman spectrum of a gas ideally contains information on rotational, vibrational and occasionally, electronic transitions. Pure rotation bands are relatively intense in the Raman effect, but the species for which rotational bands can be resolved are restricted to molecules with relatively low moments of inertia. Further, for molecules with a permanent dipole such great accuracy is obtainable from microwave studies that there may be little justification for examining their Raman spectra. Even where the molecule has no dipole it must be remembered that molecules with tetrahedral and octahedral symmetry do not yield a pure rotational Raman spectrum (1).

Investigating vibration-rotation spectra in the Raman effect is complicated by the fact that totally symmetric (polarized) fundamentals tend to have relatively strong Q branches ( $\Delta v = \pm 1$ ,  $\Delta J = 0$ ) leading to line-like spectra. Depolarized bands are frequently weak. It is thus safe to say that as a general technique for molecular structure investigation high resolution gas phase Raman spectroscopy is of restricted applicability and interest, although band contours may be of value in making assignments.

We have recently developed simple techniques for studying the vibrational Raman spectra of vapors at temperatures up to 1000°C, opening a new field of exploration for the chemist. The furnace (2) and cooling shields shown in Figure 1, are operated in conjunction with a Spectra Physics Model 140

argon ion laser and a Spex 1401 double spectrometer. Two holes in the tubular furnace allow passage of the laser beam through the sample compartment. At right angles to the line of these small holes are two larger holes, one for collecting Raman light and the other for observing the specimen during an experiment. The furnace is so designed that the spectrometer does not "see" the cell walls at the point of entrance of the laser to the cell and similarly for the exit. Collected Raman light arises principally from the scattering material at a point on the axis of the sample tube where the laser is focussed. The sample cell for our experiments is normally

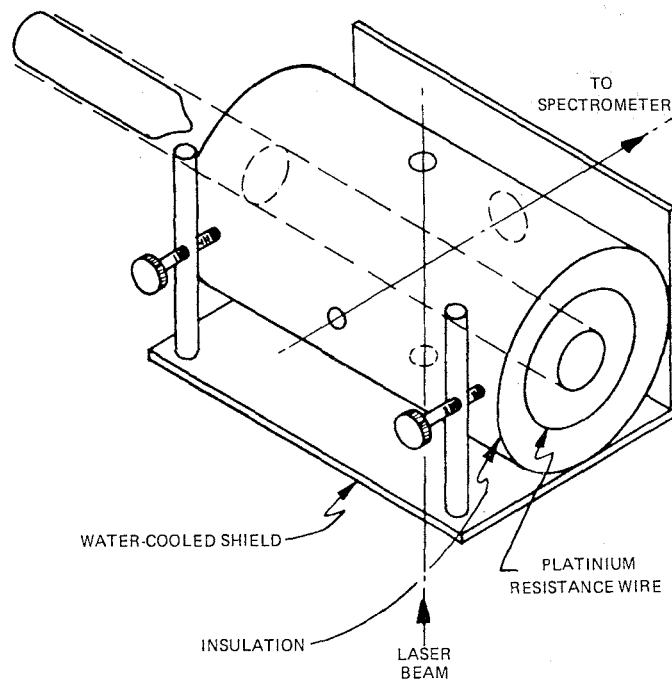


Figure 1. Resistance-wound furnace assembly showing cooling shields through which water is circulated.

borosilicate or silica glass, rounded at one end and (after appropriate filling) sealed via a constriction at the other. The diameter is of the order of 10 mm (approximately the same as that of the furnace to facilitate accurate centering) and the capacity about 3 ml. When carrying out gas phase studies it is essential to "peak up" the instrument before each series of runs. This is conveniently carried out by taking advantage of the intense resonance fluorescence spectrum of iodine which is readily excited by radiation at 4880Å. The tube containing the (trace of) iodine is of the same diameter as that in subsequent experiments. To date, we have not made any modifications to the spectrometer, detector assembly or laser.

It is difficult to overemphasize the importance of the technique to chemists. With gas phase Raman spectroscopy it is possible to study constituents of inorganic vapors at various pressures and temperatures and gain the advantages of:

1. a closed isothermal system at a known temperature and pressure;
2. no interfering solvent bands;
3. glass and silica being excellent materials for general resistance to chemical attack;
4. few problems due to fragility of optical materials or gaskets, and no need to vary the window materials to suit different wavelength ranges;
5. cells being in essence sealed ampoules which can be taken directly from a vacuum line or preparation train straight to the spectrometer.

Also, it is usually possible by ancillary PVT measurements to characterize unambiguously the species present.

The superiority of this type of gas phase Raman spectroscopy over similar infrared studies lies in the characterization of known discrete species making it possible to note:

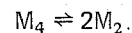
1. structural changes between different phases (this requires a combination of gas-phase, melt and single crystal Raman spectroscopy);
2. dissociation, polymerization and redistribution phenomena in the gas phase;
3. depolarization ratio of Raman bands of molecular species which cannot be obtained in melts or in solution;
4. the structure of gas phase species (in favorable cases).

As far as we are aware the only gas phase Raman spectroscopy at temperatures above 200°C prior to our work at Southampton University is that on P<sub>4</sub>, (3), HgCl<sub>2</sub>, HgBr<sub>2</sub> and HgI<sub>2</sub>, (4). In this account we shall concentrate on high temperature species and select appropriate examples to illustrate the power of this technique.\*

\*At Southampton we have studied, to date: P<sub>4</sub>; P<sub>2</sub>; As<sub>4</sub>; As<sub>2</sub>; MCl<sub>5</sub> (M = P, Sb, Nb, Ta, Mo); MBr<sub>5</sub> (M = Nb, Ta); MX<sub>3</sub> (M = Al, Ga, In; X = Cl, Br, I); HgXY (X, Y = Br, Cl, I); WOCl<sub>4</sub>; TeCl<sub>4</sub>; Re<sub>2</sub>O<sub>7</sub>; MoF<sub>6</sub>; WCl<sub>6</sub>; Fe<sub>2</sub>Cl<sub>6</sub>; Re<sub>3</sub>Cl<sub>9</sub>; P<sub>4</sub>O<sub>6</sub>; P<sub>4</sub>O<sub>10</sub>; As<sub>4</sub>O<sub>6</sub>; Be<sub>2</sub>Cl<sub>4</sub>; ZnX<sub>2</sub> (X = Cl, Br, I); GaBr<sub>2</sub>Cl; GaBrCl<sub>2</sub>; SeO<sub>2</sub>; MoO<sub>2</sub>Cl<sub>2</sub>; SnCl<sub>2</sub>; SnClBr; PbCl<sub>2</sub>; Ga<sub>2</sub>Cl<sub>6</sub>; Al<sub>2</sub>Cl<sub>6</sub>; "GaCl<sub>2</sub>"; NbOCl<sub>3</sub>.

## ELEMENTAL VAPORS

**Phosphorus and Arsenic:** These elements give virtually colorless vapors which have been shown from electron diffraction studies (5,6) to contain P<sub>4</sub> and As<sub>4</sub> tetrahedral molecules. At higher temperatures, dissociation occurs to the diatomic and monatomic species (7). Using gas phase Raman spectroscopy it is possible (8,9) to study the equilibrium



In Figure 2 we show spectra for arsenic and phosphorus while in Table 1 the assignments follow those previously suggested (3).

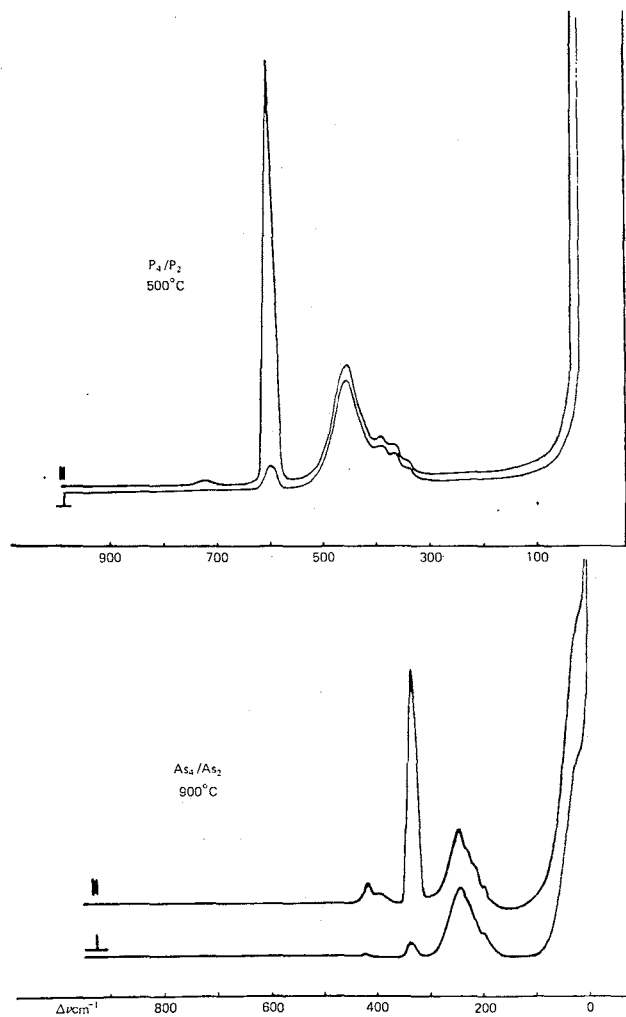


Figure 2. The Raman spectra of gaseous phosphorus at 500°C and gaseous arsenic at 900°C.

At first sight the results on P<sub>2</sub> and As<sub>2</sub> may appear novel, but it must be remembered that the vibrational and rotational constants of many diatomics have been known for a long while from detailed analysis of the electronic spectra of these molecules. The values of 775 and 421 cm<sup>-1</sup> for the vibrational frequencies obtained from gas phase Raman studies compare reasonably with those reported previously (10) (from  $\omega_e - 2\omega_e x_e$ ) of 775 and 427 cm<sup>-1</sup> respectively.

TABLE 1  
RAMAN SPECTRA \*\*\*

Phosphorus (500°C)			Arsenic (900°C)		
807vw	$\nu_2 + \nu_3$	P <sub>4</sub>			
775vw*†		P <sub>2</sub>			
720vw(p)	$2\nu_3$	P <sub>4</sub>	421vw(p)*†		As <sub>2</sub>
			400vwsh(p)	$2\nu_3$	As <sub>4</sub>
600s(p)	$\nu_1$	P <sub>4</sub>	340s(p)	$\nu_1$	As <sub>4</sub>
450m	$\nu_2$	P <sub>4</sub>	250m	$\nu_2$	As <sub>4</sub>
360wsh**	$\nu_3$	P <sub>4</sub>	200wsh**	$\nu_3$	As <sub>4</sub>
240vw	$\nu_1 - \nu_3$	P <sub>4</sub>	40vw	$\nu_2 - \nu_3$	As <sub>4</sub>

\*These bands became more intense with increasing temperature

\*\*Position of central branch quoted

\*\*\*Reference 8, 9

†Observed only at higher temperatures (~1000°C) and low pressures

**Sulphur and Selenium:** Both of these elements are of interest owing to the occurrence of rings and chains in the gas phase. Previous work on sulphur suggests that the only species present to an appreciable extent at lower temperatures (200-300°) in the saturated vapors are S<sub>6</sub>, S<sub>7</sub> and S<sub>8</sub>, (11, 12). As the spectra of S<sub>6</sub> and S<sub>8</sub> are well documented (13, 14) it was possible (apart from difficulties associated with band overlap) to pick out these species in the Raman spectrum of gaseous sulphur (8).

In Table 2 and Figure 3(a) and (b) the Raman spectra of saturated sulphur vapor at 180° and 250° are shown, together with plausible assignments. It seems reasonable to assign the polarized band at 237 cm<sup>-1</sup> (lying between the polarized band at 218 cm<sup>-1</sup> (S<sub>8</sub>) and the polarized band at 269 cm<sup>-1</sup> (S<sub>6</sub>)) to S<sub>7</sub>.

At higher temperatures the spectra become dominated by resonance fluorescence effects. In our experience resonance fluorescence phenomena are the greatest interfering factor in studies of the Raman spectra of gases. A very small

TABLE 2

THE RAMAN SPECTRUM OF SULPHUR

Assign.	Saturated† Vapor (180°C)	S <sub>8</sub> (in CS <sub>2</sub> † solution)	Melt† (120°C)	S <sub>6</sub> (solid or solution*)
S <sub>8</sub> +S <sub>6</sub>	483(2.2p)	474(3.9p)	474(5.1p)	476s(p)
S <sub>6</sub>	451(0.1)			451w
S <sub>8</sub>	445(0.1)	438(0.3)	439(0.5)	
S <sub>6</sub>	269(0.5p)			266m(p)
S <sub>8</sub> +S <sub>7</sub>	237(1.2p)	242(0.3)	239(0.4)	
S <sub>8</sub>	218(5.5p)	216(6.8p)	219(8.4p)	
S <sub>6</sub>	201(0.3)			204mw
S <sub>8</sub>	151(4.8)	151(3.7)	153(5.3)	
S <sub>8</sub>	76(0.7)		80(1.0)	

† Reference 8

\* Reference 14

NOTE: To facilitate presentation most of the data are tabulated rather than plotted. Numerical values are in cm<sup>-1</sup>; the designations mean: s-strong, v-very, m-moderate, w-weak, br-broad, sh-shoulder, (p)-polarized, (dp)-depolarized.

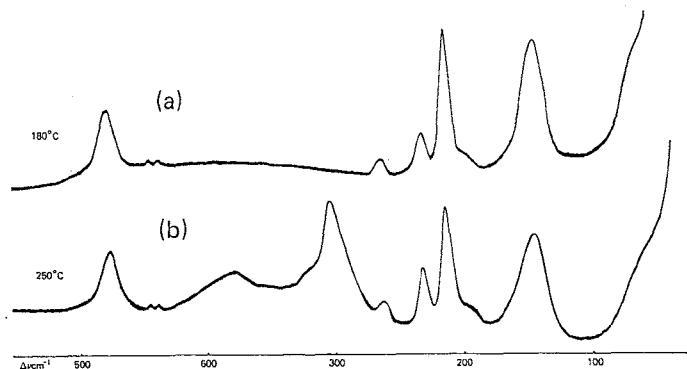


Figure 3. The Raman spectra of gaseous sulphur at 180°C and 250°C.

quantity of a species which can undergo the highly efficient resonance fluorescence process can effectively dominate the whole spectrum because of the weakness of the Raman effect. In our hands studies of selenium vapor under 4880A excitation yielded only resonance fluorescence spectra. Figure 4 indicates results of attempting to obtain the Raman spectrum of natural selenium in the gas phase. A more extensive spectrum showed many such complex patterns, repeating on both the Stokes and the anti-Stokes side of the exciting line. The complexity of this spectrum is due to the presence of several isotopes in naturally occurring selenium. On switching to isotopically pure <sup>80</sup>Se the rather beautiful spectrum of Figure 5 was produced revealing the presence of a repeat

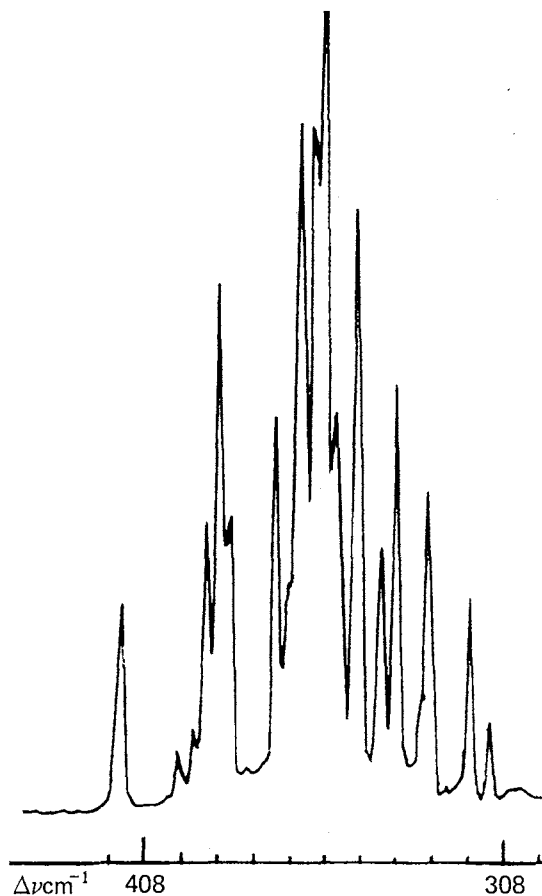


Figure 4. Part of the resonance fluorescence spectrum of natural selenium.

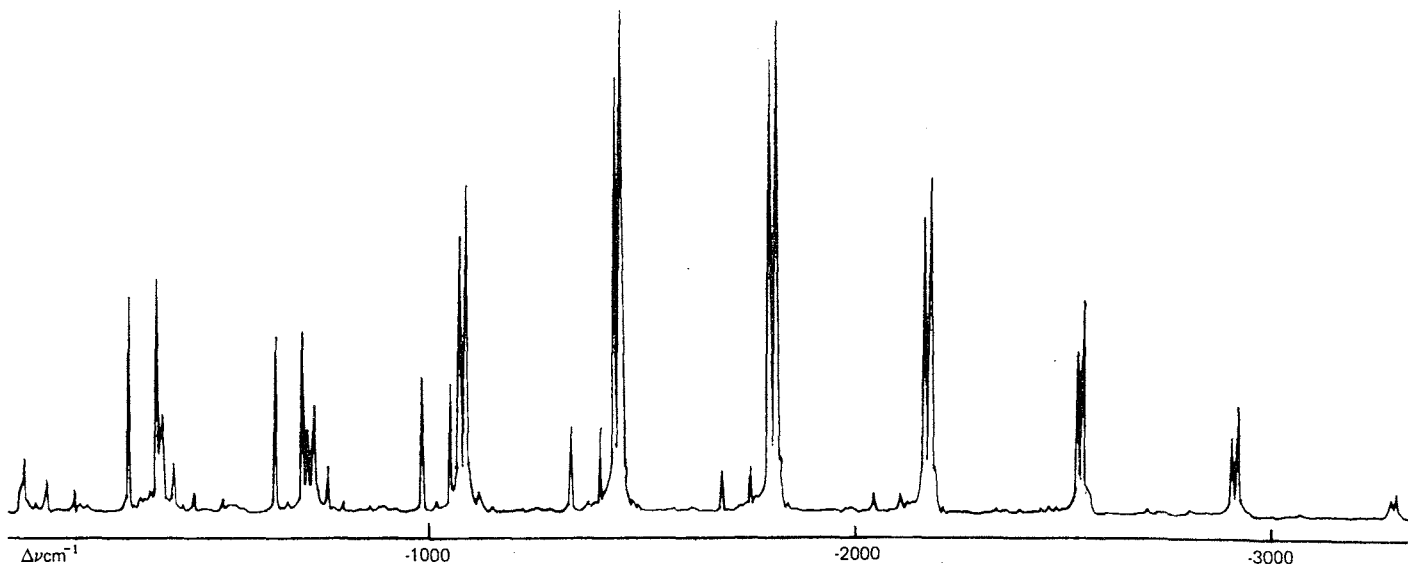


Figure 5. Part of the resonance fluorescence spectrum of  $^{80}\text{Se}_2$ .

pattern of a principal band split in to P and R branches. Such phenomena have been known since the classical work of Wood (15) in 1906. The spectrum observed can be completely interpreted from the electronic data of Barrow, Chandler and Meyer (16) on  $^{80}\text{Se}_2$ . Selective excitation occurs from approximately  $v'' = 14$   $J'' = 40$ . For the 4880A line there is insufficient energy for excitation in  $\text{BO}_u^+ - \text{XO}_g^+$  so we assume that excitation occurs in  $\text{B1}_u - \text{X1}_g$ . The wing pattern arises from Franck-Condon factors and the P/R splitting from the selection rule  $\Delta J \pm 1$  for a  $^3\Sigma_u - ^3\Sigma_g$  transition.

The spectrum obtained does not derive from the Raman effect because:

1. the pattern repeats roughly every  $350 \text{ cm}^{-1}$  (in this case with an extensive series of anti-Stokes bands);
2. the spectrum can readily be obtained when the vapor pressure of the selenium is well below a fraction of a millimeter of mercury;
3. the lines are not strongly polarized;
4. the isotopic splittings due to several isotopes of selenium in the naturally occurring element could not be observed in a normal low resolution Raman experiment. (The difference in the resonance fluorescence is that essentially two transitions ( $\Delta J \pm 1$ ) only are being observed at a high  $J''$  value).

For Raman scattering of a diatomic molecule if we put  $\alpha'_{xx} = \alpha'_{yy} = \alpha'_{ij} = 0$  while  $\alpha'_{zz} \neq 0$  then  $\rho_n = 1/2$  and  $\rho_p = 1/3$  ( $\rho_n$  and  $\rho_p$  refer to depolarization ratios using natural and polarized incident light respectively). The experimental  $\rho_p$  value is about 0.8. It must be remembered that the life time of the excited state for the resonance fluorescence process is long compared with the rotation of a molecule, whereas for Raman spectroscopy the reverse is true. Further, if collisions occur during the life time of the excited state, without quenching the fluorescence process, then the relationship within a laboratory frame of reference is completely lost and hence  $\rho = 1$ .

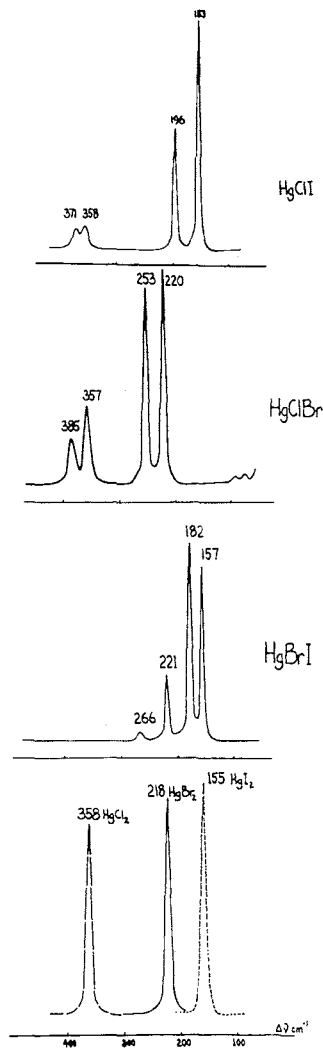


Figure 6. The gas-phase Raman spectrum of equimolar mixtures of  $\text{HgX}_2$  and  $\text{HgY}_2$  (X, Y = Cl, Br, I).

## TRIATOMIC MOLECULES

**Linear:** The mixed halides of mercury (Hg XY, where X, Y = Cl, Br, I) represent a simple series for Raman gas-phase studies. (The pre-laser work (4) on HgX<sub>2</sub> species should be noted here). In Figure 6 we show spectra obtained from equimolar quantities of the dihalides of mercury. The spectra are almost self-explanatory and clearly show the presence of HgClBr, HgClI and HgBrI (17). Resonance fluorescence effects from traces of molecular I<sub>2</sub> were observed in the species containing iodine.

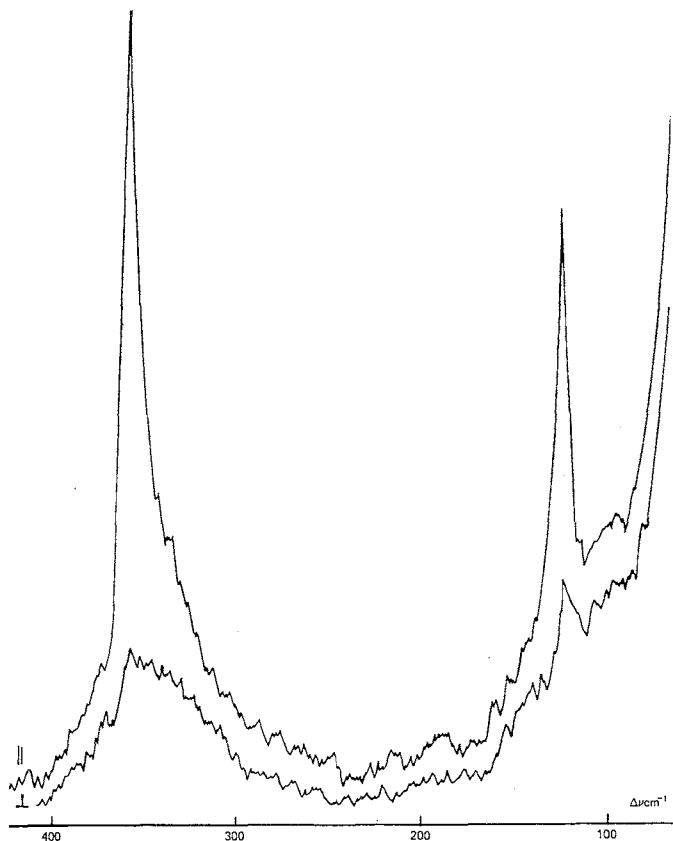


Figure 7. The gas phase Raman spectrum of SnCl<sub>2</sub> at 650°C.

**Bent:** The results obtained above with the linear triatomics may be contrasted with those from SnCl<sub>2</sub> (18) which clearly show the presence of discrete bent symmetrical species, (Figure 7).

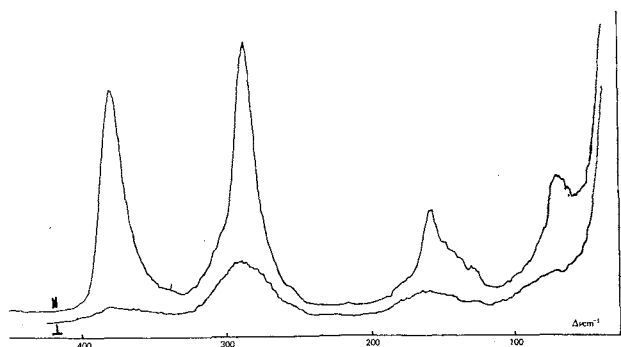


Figure 8. The gas phase Raman spectrum of tellurium tetrachloride at 350°C.

## PENTATOMICS

**Tellurium Tetrachloride:** Monomeric in the gas-phase (19,20), TeCl<sub>4</sub>, according to early electron diffraction work, has a C<sub>2v</sub>\* structure (21) which may be considered to be based on a trigonal bipyramid with a vacant equatorial position. Its nature in the solid state and in solution in benzene and acetonitrile has been the subject of several investigations, and some conflicting experimental results (22, 23).

Gas phase Raman spectroscopy has to some extent resolved this problem. Spectra of TeCl<sub>4</sub> (Table 3 and Figure 8) in benzene, in which it is cryoscopically monomeric in dilute solution (24), and in acetonitrile, in which it is effectively a non-conductor (25), are closely similar to that of gaseous TeCl<sub>4</sub> (24). The presence of two polarized bands in the stretching region and two polarized bands in the deformation region strongly favor a C<sub>2v</sub> structure. The observed spectrum in the gas phase differs strikingly from the melt and solid state spectra.

TABLE 3

THE RAMAN SPECTRUM OF TELLURIUM TETRACHLORIDE IN THE GAS PHASE AND IN SOLUTION IN BENZENE AND METHYL CYANIDE\*

Vapor 350°C	Benzene Solution	MeCN Solution	CD <sub>3</sub> CN Solution
382(7.5p)	372vs(p) 344vwsh 316w	378vs(p) 357sh	376vs(p) solvent
290(10p)	278s(p)	280s(p)	282s(p)
158(3.7p)			
130wsh			
72w(p)			

\* Reference 24

TABLE 4

THE GAS PHASE RAMAN SPECTRA OF VOCl<sub>3</sub> AND NbOCl<sub>3</sub>

VOCl <sub>3</sub> † 120°C	NbOCl <sub>3</sub> * † 330°C	Assignment
1042(1.8p)	997(1.8p)	ν <sub>2</sub>
502(2.0)	448(0.3)	ν <sub>4</sub>
408(10.0p)	395(8.0p)	ν <sub>1</sub>
249(1.5)	225(0.7)	ν <sub>5</sub>
164(0.8p)	106(4.0p)	ν <sub>3</sub>
125(3.8)	110(sh)	ν <sub>6</sub>

\* Weak polarized band at ~340 cm<sup>-1</sup> (~0.1) ν<sub>5</sub>+ν<sub>6</sub>

† Reference 27, 28

\*Water is an example of C<sub>2v</sub> symmetry. The single O atom is centered between two symmetrically opposed H atoms. If an axis C<sub>2</sub> is drawn through O, two identical configurations will result for every 360° rotation of the H atoms about this axis.

**Niobium Oxide Trichloride:** In the solid state  $\text{NbOCl}_3$  consists of infinite (double) chains based on *trans*-oxygen bridges and *cis*-chlorine bridges (26). Single crystal Raman polarization data have been used to assign the vibrational modes of the crystal (27). Table 4 and Figure 9 contain data for gaseous  $\text{NbOCl}_3$  (27, 28). Correspondence with the Raman spectra of liquid (27,28) and gaseous (27)  $\text{VOCl}_3$  is striking and suggests the presence of discrete monomeric  $\text{NbOCl}_3$  molecules.† The depolarization ratio for the M-O stretching mode is close to zero for both  $\text{NbOCl}_3$  and  $\text{VOCl}_3$ , while the frequency of the Nb-O stretching mode agrees with that previously found by infrared spectroscopy (29).

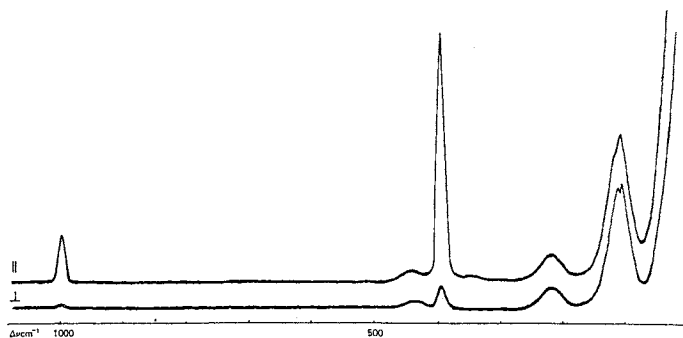


Figure 9. The gas-phase Raman spectrum of  $\text{NbOCl}_3$  at  $330^\circ\text{C}$ .



Figure 10. The gas-phase Raman spectrum of  $\text{NbBr}_5$ .

†Although it is known that  $\text{NbOCl}_3$  decomposes (30,31) to some extent to  $\text{NbCl}_5$  and  $\text{Nb}_2\text{O}_5$  the results here refer to a temperature of approximately  $330^\circ$  when decomposition should be slight. We note, however, that the most intense (polarized) band of molecular  $\text{NbCl}_5$  lies (32) at  $394\text{cm}^{-1}$ .

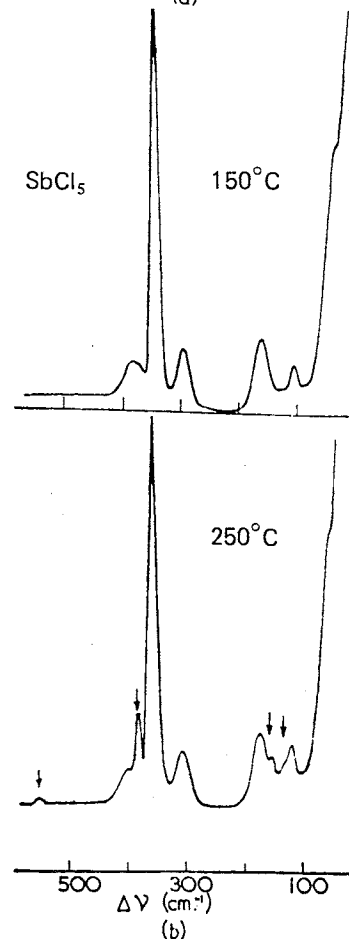
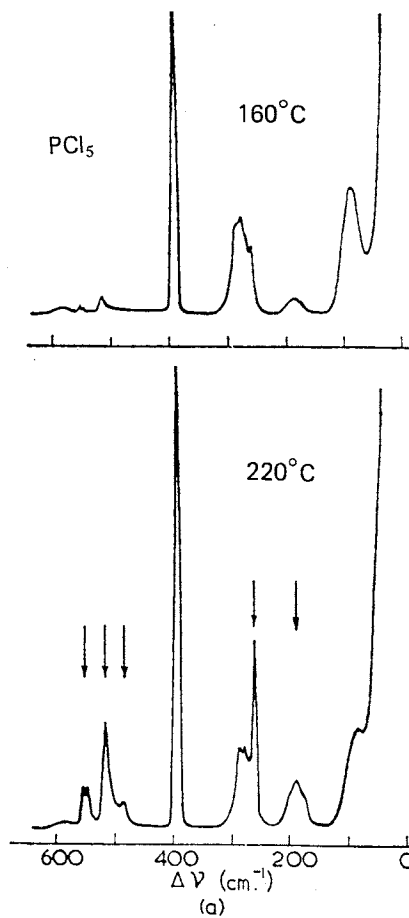


Figure 11. Raman spectra of  $\text{PCl}_5$  and  $\text{SbCl}_5$ . Arrows indicate bands due to  $\text{PCl}_3$ ,  $\text{SbCl}_3$  and  $\text{Cl}_2$ .

## MX<sub>5</sub> SPECIES

**Niobium and Tantalum Pentabromides:** There is some dispute about the structure of the pentabromides of niobium and tantalum in the solid state (33). In the gas phase, electron diffraction data (34) suggest the presence of a trigonal bipyramidal species. The Table 5 and Figure 10 Raman data for NbBr<sub>5</sub>, TaBr<sub>5</sub>, (32) and [SnBr<sub>5</sub>]<sup>-</sup> ion, (35), are consistent with the presence of a discrete monomeric formulation for the vapor.

**Phosphorus and Antimony Pentachloride:** The gas phase Raman spectra of PCl<sub>5</sub> and SbCl<sub>5</sub> are in agreement with the presence of discrete trigonal bipyramidal species (32). As the temperature of the vapor is gradually raised the temperature sensitive dissociation



TABLE 5

THE GAS PHASE RAMAN SPECTRA OF NbBr<sub>5</sub> AND TaBr<sub>5</sub> AND THE RAMAN SPECTRUM OF THE SnBr<sub>5</sub><sup>-</sup> ion\*\*

Assignment	NbBr <sub>5</sub>	TaBr <sub>5</sub>	SnBr <sub>5</sub> <sup>-</sup> *
ν <sub>5</sub> (e')			257m
ν <sub>1</sub> (a <sub>1</sub> ' )	234s(p)	240s(p)	202vs
ν <sub>2</sub> (a <sub>1</sub> ' )	178w(p)	182w(p)	154m
ν <sub>6</sub> (e')	119w	110w	109m
ν <sub>8</sub> (e'')	101w	93w	103m
ν <sub>7</sub> (e')	67w	70w	

\* This spectrum is taken from the infrared and Raman study of reference 35 where only the bands assigned to fundamentals of SnBr<sub>5</sub><sup>-</sup> are reported in the above table.

\*\* Reference 32

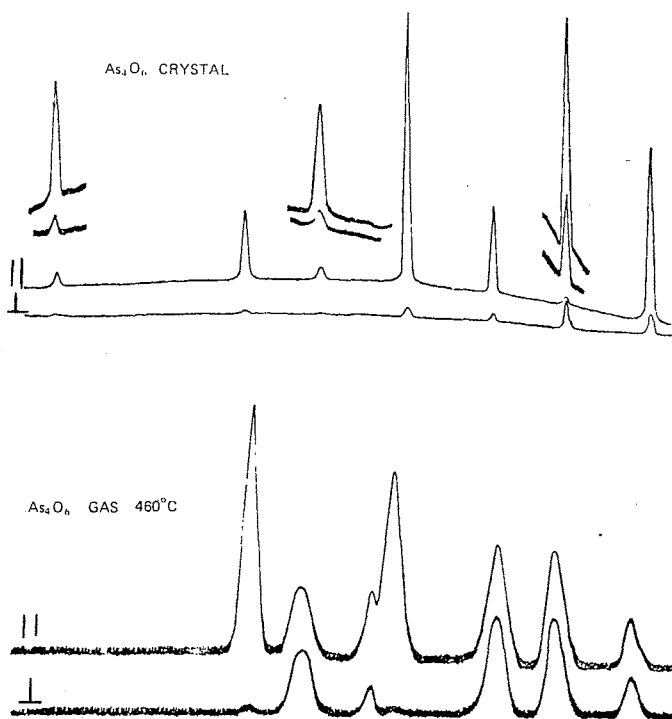


Figure 12. The Raman spectra of As<sub>4</sub>O<sub>6</sub> from the gas and crystal.

can readily be observed from gas-phase Raman data. In Figure 11, Raman spectra of PCl<sub>5</sub> and SbCl<sub>5</sub>, bands due to PCl<sub>3</sub> and Cl<sub>2</sub> or SbCl<sub>3</sub> and Cl<sub>2</sub> are absent in the lower of the two temperature observations.

## MORE COMPLEX SPECIES

**As<sub>4</sub>O<sub>6</sub> and P<sub>4</sub>O<sub>10</sub>:** Single crystal Raman polarization data have been used to assign the vibrational modes of arsenolite which contains As<sub>4</sub>O<sub>6</sub> molecules (36). Owing to the low solubility of As<sub>4</sub>O<sub>6</sub> and P<sub>4</sub>O<sub>10</sub>, gas phase Raman studies offer a unique solution to the problem of polarization measurements on the discrete molecular species which retain their identity in the gas phase (37,38). In the case of As<sub>4</sub>O<sub>6</sub> (Figure 12) the predicted two polarized bands at 556 and 381 cm<sup>-1</sup> closely agree with the isotropic modes of the single crystal at 560 and 370 cm<sup>-1</sup>.

In P<sub>4</sub>O<sub>10</sub>, the presence of four 'extra' terminal oxygens compared with M<sub>4</sub>O<sub>6</sub> introduces one extra totally symmetric mode. Data in Table 6 clearly identify the three expected polarized bands at 1440, 717 and 553 cm<sup>-1</sup>. The Raman spectrum of gaseous P<sub>4</sub>O<sub>10</sub> is essentially the same as that of crystalline phosphoric oxide for the molecular form.

It is perhaps worth mentioning here that by adopting the oriented gas phase approximation it is frequently possible to calculate the derived polarizability tensor components measured on the crystal. In this way the relative intensity and depolarization ratio of bands in the gas phase spectrum (or solution spectrum) can formally be calculated (39).

TABLE 6

THE RAMAN SPECTRUM OF GASEOUS PHOSPHORUS PENTOXIDE AT 660°C\*

P <sub>4</sub> O <sub>10</sub> (gas 660°C)**	
1440 (4.0p)	a <sub>1</sub>
1406sh (1.2)	f <sub>2</sub>
~824 (~0)	
~764 (~0)	
717 (4.2p)	a <sub>1</sub>
~684 (~0.1p?)	
~662 (~0.1)	
~583sh (0.1)	
553 (10p)	a <sub>1</sub>
529 (2.4p)	
411 (3.8)	f <sub>2</sub>
~277sh (~0.2)	
264 (8.4)	f <sub>2</sub>
254sh (4.0)	e
~240sh (1.2)	

$$\Gamma_{\text{vib.}} = 3a_1 + 3e + 6f_2$$

\* Reference 6

\*\* Assignments follow those of reference 49

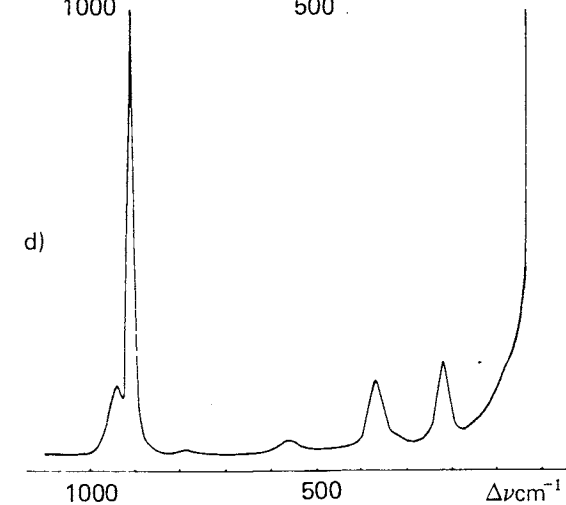
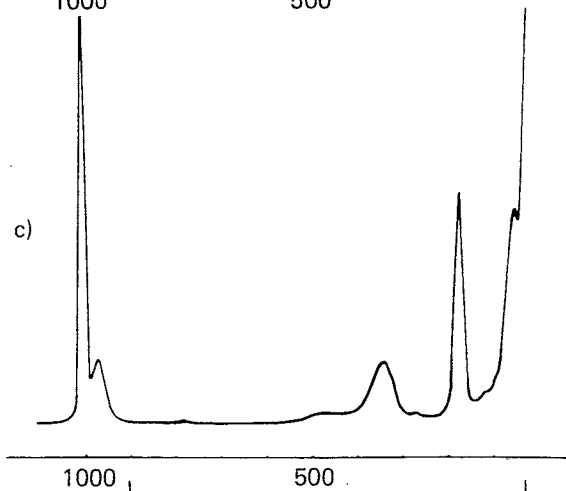
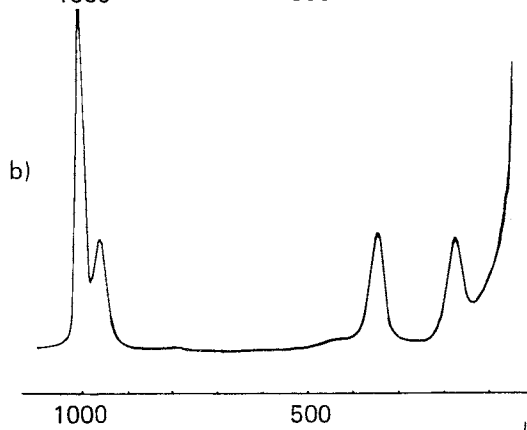
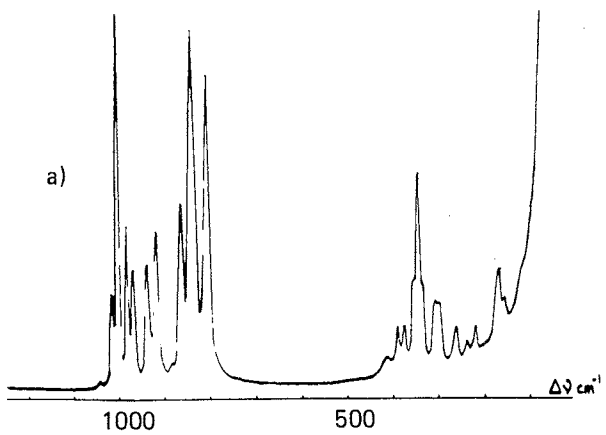


Figure 13. The Raman spectra of  $\text{Re}_2\text{O}_7$  (a) solid (b) gas (c) melt. The Raman spectrum of a saturated aqueous solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  is shown at (d).

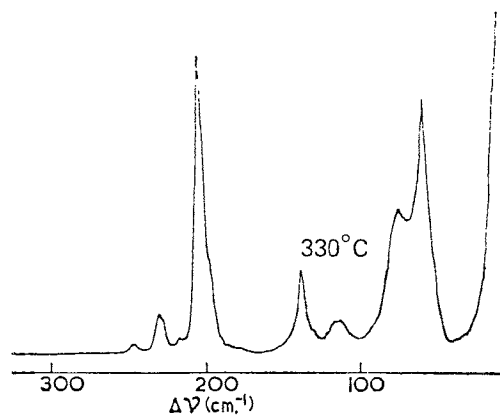
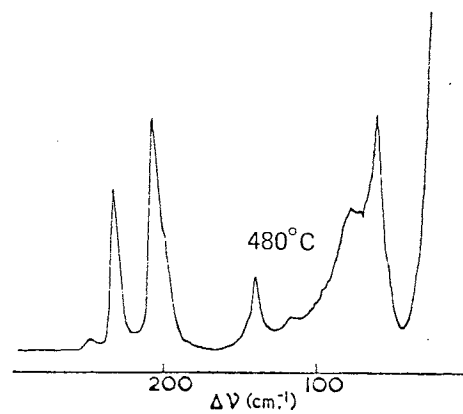
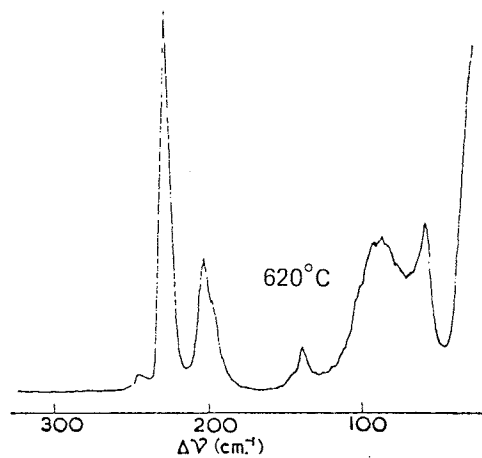
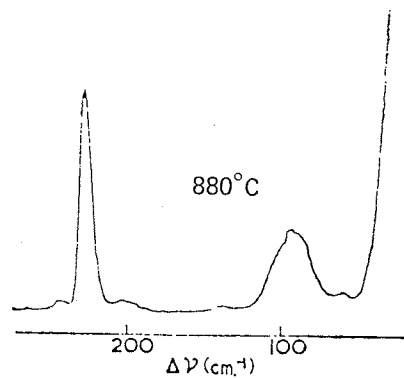
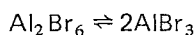


Figure 14. The Raman spectrum of gaseous aluminum tribromide at  $880^\circ\text{C}$ ,  $620^\circ\text{C}$ ,  $480^\circ\text{C}$ ,  $330^\circ\text{C}$ .



$\text{Re}_2\text{O}_7$ : Attractive for Raman studies, this nearly colorless compound has a low melting ( $220^\circ$ ) and boiling point ( $362^\circ$ ) and does not attack glass. The solid is polymeric and is based on linked  $\text{ReO}_4$  tetrahedra and  $\text{ReO}_6$  octahedra (40). By contrast measurements show the vapor to be monomeric (41-44). Raman spectra of solid, melt and gas define the major structural change which occurs between the solid, melt or vapor (45). Data for the melt and gas confirm the presence of a monomeric species in each case (Figure 13). The Raman data for  $\text{Re}_2\text{O}_7$  in the melt or gas phase are closely similar to that of the dichromate ion in aqueous solution (46,47). Related data on  $\text{Tc}_2\text{O}_7$  will be of particular interest in view of the recent X-ray structure determination showing a linear Tc-O-Tc bridge (48).

$(\text{MX}_3)_n$  Species: In Figure 14 we show (2) an example of the equilibrium:



At  $880^\circ$  the spectrum is essentially that of pure monomeric  $\text{AlBr}_3$ . By contrast at  $330^\circ$  the spectrum is essentially that of the dimer. For  $\text{ReCl}_3$  the results are more confusing. The effusion cell mass spectroscopy technique, indicates the predominant species present in the gas-phase to be the trimeric unit  $\text{Re}_3\text{Cl}_9$ . We cannot be certain that under the conditions of our gas-phase Raman experiment the same polymer unit will predominate as that found in the mass spectroscopy experiment, but it is probable that this will be so. Certainly there is considerable evidence that in contrast to  $\text{Al}_2\text{Br}_6$ ,  $\text{Al}_2\text{I}_6$ ,  $\text{Ga}_2\text{Cl}_6$ ,  $\text{Ga}_2\text{Br}_6$ ,  $\text{Ga}_2\text{I}_6$  and  $\text{In}_2\text{I}_6$  the preferred unit for species containing rhenium and halogen contains an  $\text{Re}_3$  triangle.

TABLE 7

THE RAMAN SPECTRA OF SOLID AND GASEOUS RHENIUM TRICHLORIDE, AND GASEOUS IRON, GALLIUM AND INDIUM TRICHLORIDES

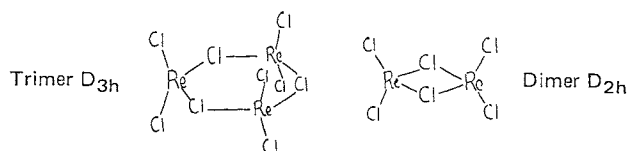
$(\text{ReCl}_3)_{2 \text{ or } 3}$	$\text{ReCl}_3$ (solid)**	$\text{Fe}_2\text{Cl}_6$ (gas)**	$\text{Ga}_2\text{Cl}_6$ (liquid)*	$\text{In}_2\text{Cl}_6$ (liquid)†
427wsh		455wsh	462m	400w
401s(p)		426s(p)	413s(p)	368s(p)
382wsh(p)	336msh	373wsh(p)	344m(p)	
	323wsh			
308w(p)	308s	310w(p)	318mw(p)	298mw(p)
270w	278w		268w(p)	
241wsh			231w	
213m			215sh	
190wsh	202w			
162mw(p)	176s	163vww	167m(p)	
120w		127vww	128sh	
102w(p)	106w		113sh	118wsh
			100s	
				76wsh
				68vs(p)

\* Reference 51

\*\* Reference 50

† Reference 2

The Raman spectrum of this blue gas, Table 7 and Figure 15 (50) bears a striking resemblance to that of  $\text{Fe}_2\text{Cl}_6$ , (50)  $\text{Ga}_2\text{Cl}_6$  (51) and presumed  $\text{In}_2\text{Cl}_6$  (2). The point of interest here is that the local symmetry at the rhenium atom for either dimer or trimer is similar; they are both based on approximately tetrahedrally coordinated rhenium with two terminal and two bridging chlorines. The Raman differentiation between dimer and trimer would therefore be expected to be difficult unless excellent well-resolved spectra are obtained. This problem is not unique and had been noted previously for molten  $\text{InCl}_3$  (2). Put formally, the difference between the  $\text{D}_{2h}$  dimer



and the  $\text{D}_{3h}$  trimer is (for Raman active modes)

$$\Gamma_{\text{vib}} = 4a_{1g} + 2b_{1g} + 2b_{2g} + b_{3g} \quad (\text{dimer})$$

$$\Gamma_{\text{vib}} = 4a_1' + 6e' + 4e'' \quad (\text{trimer})$$

yielding four totally symmetric modes in each case with either 5 (dimer) or 10 (trimer) non-totally symmetric modes. Accidental degeneracies or low intensities could easily lead to erroneous assignments. The difference in the Raman spectra of gaseous  $\text{ReCl}_3$  and solid  $\text{ReCl}_3$  (Table 7) clearly shows a considerable reorganization of the trimer unit on passage from the crystal to the gas (assuming that the trimer unit is retained in gas phase).

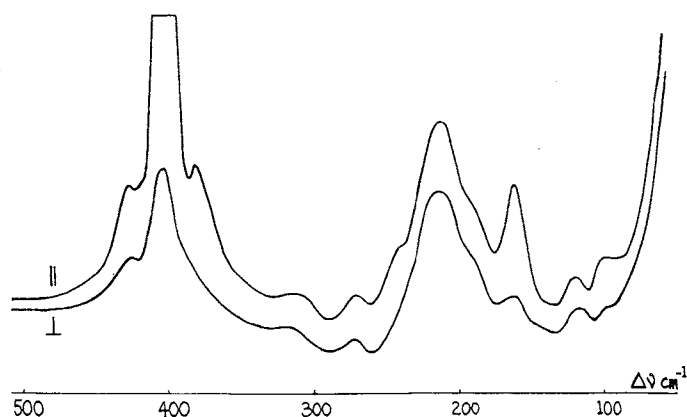


Figure 15. The gas-phase Raman spectrum of  $\text{ReCl}_3$ .

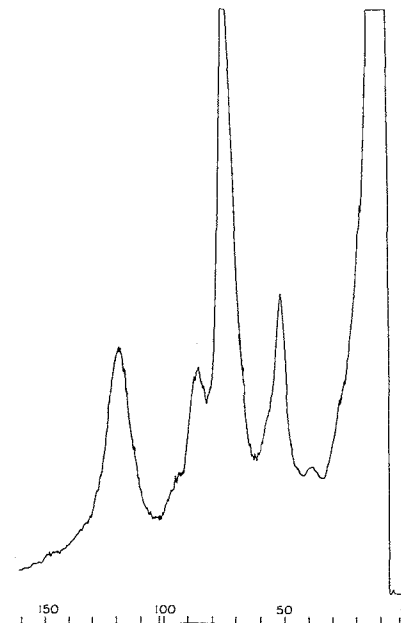
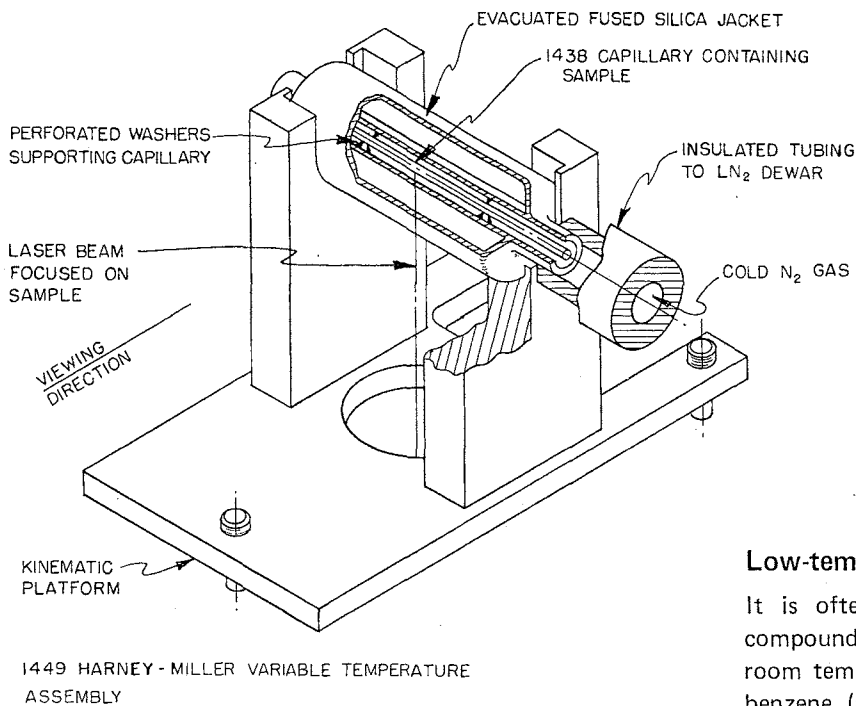
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*We wish to thank our authors of this issue for their extraordinary efforts in meeting our already over-extended deadline with this roundly substantiated, pertinent and timely article. These Britishers have us wondering what took us so long (14 years) to internationalize the SPEAKER.*

*Ian Beattie arrived at his Southampton Professorship via the steep ladder of industrial and academic research as well as teaching positions. Geoffrey Ozin, fresh from being a post-doctoral Fellow at Southampton is now making tracks of his own at Erindale College of the University of Toronto. We are most grateful to both gentlemen for the grace with which they accomplished the awkward long distance cooperation it took, triangularly, to coordinate facts, figures and a bit of trimming.*

—ED.



### Low-temperature Studies

It is often desirable to record the vibrational spectra of compounds in states other than those in which they exist at room temperature. The low-temperature Raman spectrum of benzene (at 77°K) shows lines in the low-frequency region observed only for the solid phase. These lines are therefore indicative of the crystal structure of solid benzene.

Raman spectra of samples at low-temperatures are relatively simple to record since glass apparatus may be used in all major parts of the system and Raman is a scattering rather than an absorption process.

## 1449 HARNEY-MILLER VARIABLE TEMPERATURE ASSEMBLY

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The sample will be cooled even if the heater is not on; 77°K can be attained within ten minutes when the autotransformer is turned up. The temperature at a given setting will then remain stable subject to the voltage stability of the autotransformer.

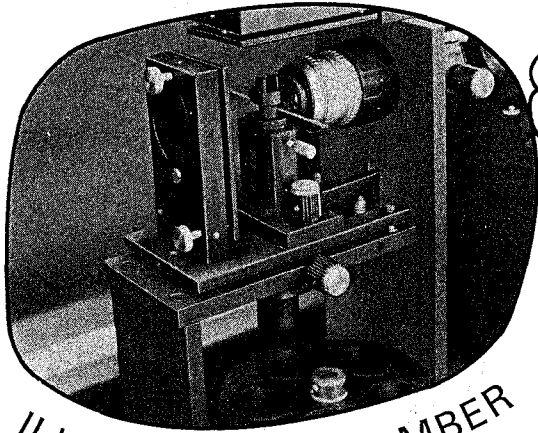
The sample itself, nestled inside the 1 mm  $\phi$  glass capillary may be as small as 0.1  $\mu$ l. A thermistor with an approximate calibration is provided. It may be easily removed for more exacting calibration against liquid nitrogen, ice water, salt-ice-water and other familiar referencing media.

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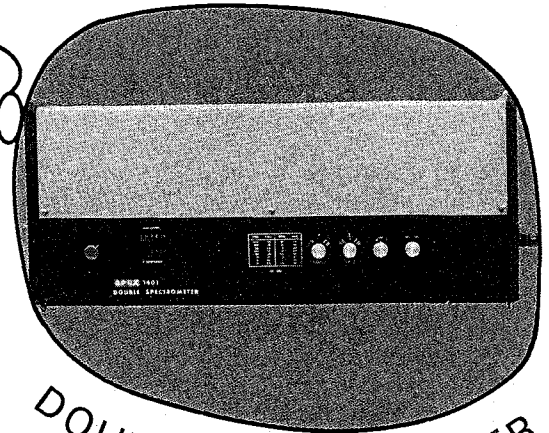
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