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Speaker

THE IMPACT OF LASER-RAMAN SPECTROSCOPY ON INORGANIC CHEMISTRY

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THE introduction of the laser source has stimulated and revolutionized Raman spectroscopy. Nowhere has this revolution been felt more strongly than in inorganic chemistry, principally because such a large proportion of inorganic compounds are colored. With the older mercury arc sources only colorless or yellow compounds had in general been amenable to study. A few more deeply colored compounds (usually red) had provided spectra with excitation such as He 6678A. With the advent of the He-Ne laser (6328A) and subsequently the argon ion laser (4579, 4658, 4727, 4765, 4880, 4965, 5017 and 5145A) and the krypton ion laser (4762, 4825, 5208, 5308, 5682, 6471 and 6764A) it has become possible to choose excitation frequencies which largely or completely avoid electronic transitions in the molecules. This has enabled Raman studies of great numbers of inorganic compounds to be carried out for the first time.

But it is not in this respect alone that great developments have been made; many new areas have been opened up, some of which overlap considerably the fields of interest of both physical chemists and physicists. The following account of the areas of Raman spectroscopy impinging on inorganic chemistry which have developed most rapidly in recent years necessarily constitutes a personal assessment of the situation and it is not intended to be a complete review. Eight main areas will be discussed in the present account. Omitted subjects such as metals, doped alkali halides, semiconductors, polymers, etc., have been regarded as more within the domain of physics and/or physical chemistry.

Determination of the Fundamental Frequencies of Colored Compounds

Raman spectra of molecular metal halides, MX_4 (M = C, Si, Ge, Ti, or Sn; X = F, Cl, Br or I), are readily obtained from samples in Pyrex or silica tubes. Not only does one thus obtain all four fundamentals expected for molecules of T_d symmetry, $\nu_1 (a_1)$, $\nu_2 (e)$, $\nu_3 (t_2)$ and $\nu_4 (t_2)$ (only the two t_2 fundamentals are ir active), but problems of hydrolysis of certain of the halides are more easily coped with in Raman than ir. Colors of the above compounds were not sufficiently restrictive to prevent the fundamentals of all but one, titanium tetraiodide (Figure 1), to have been established with mercury or helium exciting lines.

In a similar vein, only three of the four fundamentals of the deep red-brown liquid vanadium tetrachloride had been established with the mercury arc source. Recent work[3] with 6471A excitation led to the complete assignment of the spectrum, the four fundamentals being found to occur at 385, 111, 483, and 128, cm^{-1}.

This in conjunction with vapor phase Raman work with zirconium and hafnium halides, has contributed to the calculation of the force constants of all the molecular tetrahalides of group IVA for comparison with those of group IVB. Moreover and more interestingly, calculations of the thermodynamic parameters of these halides also become possible with the measurement of all the fundamental frequencies, and allow for the first time detailed thermodynamic comparisons of these halides, and in particular of the (chemically very similar) zirconium and hafnium tetrahalides.

Vanadium oxytribromide is a further molecule which obstinately defied Raman studies in pre-laser days. However, its spectrum can be recorded[4] satisfactorily when laser-excited at 6471A; polarization confirms the assignments, made originally from ir studies[5], for the six fundamentals. Results are given in Table 1, together with those for vanadium oxytrifluoride and vanadium oxytrichloride.

Normal vibrations of a tetrahedral MX_4 molecule.

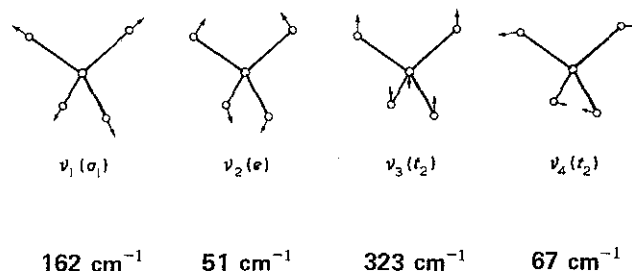| $\nu_1 (\sigma_1)$	$\nu_2 (e)$	$\nu_3 (t_2)$	$\nu_4 (t_2)$
162 cm^{-1}	51 cm^{-1}	323 cm^{-1}	67 cm^{-1}

Fig. 1. The spectrum of titanium tetraiodide, which has a very deep red-brown color associated with strong (ϵ = 6000-10,000) charge transfer bands in the visible region, was obtained with 6471 and 6764A Kr^+ laser excitation[1], as well as 6943A excitation of a quasi-continuous ruby laser[2]. These fundamentals occur at 162, 51, 323, and 67 cm^{-1} and are fully in accord with the values expected for a tetrahedral molecular tetraiodide of a metal atom of atomic weight 48. Only one component of each of the degenerate fundamentals is shown.

Table 1

**Vapor Phase Values for the Fundamentals
of the Vanadium Oxytrihalides as determined
from Raman Measurements (cm^{-1})***

Assignment	Description	VOF$_3$ (175C)	VOCl$_3$ (200C)	VOBr$_3$†
$\nu_1(a_1)$	V = O stretch	1055.0 s	1042.5 m	1029.0 w
$\nu_2(a_1)$	sym. VX$_3$ stretch	720.5 vs	409.5 vs	272.0 vs
$\nu_3(a_1)$	sym. VX$_3$ bend	256.0 s	163.0 w	118.5 w
$\nu_4(e)$	asym. VX$_3$ stretch	801.0 vw	503 vw,br	401.0 wm
$\nu_5(e)$	X$_3$VO rock	309 m	248 w	213.0 w
$\nu_6(e)$	asym. VX$_3$ bend	204.0 s	124.5 ms	82.0 wm

*Ref. 4. The frequencies of the Q-branches only are given in the Table.

†Measured in cyclohexane solution owing to thermal decomposition in the vapor state by the laser beam.

Tungsten hexachloride is of interest as it is one of the very few established neutral metal hexachlorides; very deeply colored, it crystallizes in a metastable deep red-brown form, which reverts on gentle heating to a deep blue form. Again, it was not possible to obtain a Raman spectrum of this molecule prior to the introduction of the laser source, although very approximate values for its Raman-active fundamentals, $\nu_1(a_{1g})$, $\nu_2(e_g)$ and $\nu_5(t_{2g})$, had been deduced from infrared-active combination bands[6]. This compound is extremely difficult to obtain free from oxytetrachloride impurity, which scatters at similar frequencies to the hexachloride. However, it is now reasonably certain[7,8] that the above three fundamentals occur at 410 s, 315 vw, and at about 170 w,br cm^{-1} respectively (6328A excitation). Force constant calculations on this molecule, both on the basis of the modified Urey-Bradley force field as well as of the generalized valence force field are available[7]. The WCl stretching force constant in the latter is 2.23 md/A.

The above discussion has all been confined to molecular species, but of course a great number of colored ionic solids have now also become amenable to study. Examples include[7,9] the various salts of the TiCl$_6$$^{2-}$, TiBr$_6$$^{2-}$, ZrCl$_6$$^{2-}$, ZrBr$_6$$^{2-}$, HfCl$_6$$^{2-}$, HfBr$_6$$^{2-}$, NbCl$_6$$^-$, NbBr$_6$$^-$, TaCl$_6$$^-$ and TaBr$_6$$^-$ ions. The metal halogen stretching force constants for these ions fall in the order MX$_6$ > MX$_6$$^-$ > MX$_6$$^{2-}$. Even Raman experiments with the deeply blue or green anions CoX$_4$$^{2-}$ (X = Cl, Br, or I) have been successful to the extent that the totally symmetric stretching fundamental, $\nu_1(a_1)$, has been located for each[10].

In the field of coordination chemistry, vast numbers of compounds are colored, even deeply colored, and Raman work on many of these has been undertaken to provide values for the Raman-active fundamentals which, with the values for the ir-active fundamentals, provides a basis for force constant

calculations. Examples include studies of the square planar platinum and palladium complexes of the type MX$_2$(SR$_2$)$_2$ (X = Cl, Br or I; R = Me, Et, isopropyl, etc.)[11,12].

The major hindrance to Raman studies of the above kind on colored samples has been local heating of the solid or solution caused by partial absorption of the laser beam even when employing the most satisfactory excitation line, i.e., the one which is furthest removed from the electronic absorption bands in the compound. Local heating may produce bubbles in solutions or may cause decomposition of the sample. Decomposition products may fall to the bottom of the sample cell and reduce the laser power, or they may act as intense hot spots. Great further advances in understanding the structure of deeply colored compounds now seem possible with the discovery that local heating may be obviated by rotating the sample at up to 3000 rpm. With blue excitation lines, attendant advantages occur in signal/noise ratio owing to photomultiplier response, as well as the fourth power frequency factor. A modified version of R.J. Gillespie's liquid cell[13] is illustrated in Figure 2.

Modification of the procedure is expected to improve greatly the chances of obtaining a good Raman spectrum of deeply colored solids (e.g., potassium permanganate). Metal carbonyls and substituted metal carbonyls in particular may be better analyzed in this way, as these compounds are very thermally sensitive and readily lose carbon monoxide on irradiation.
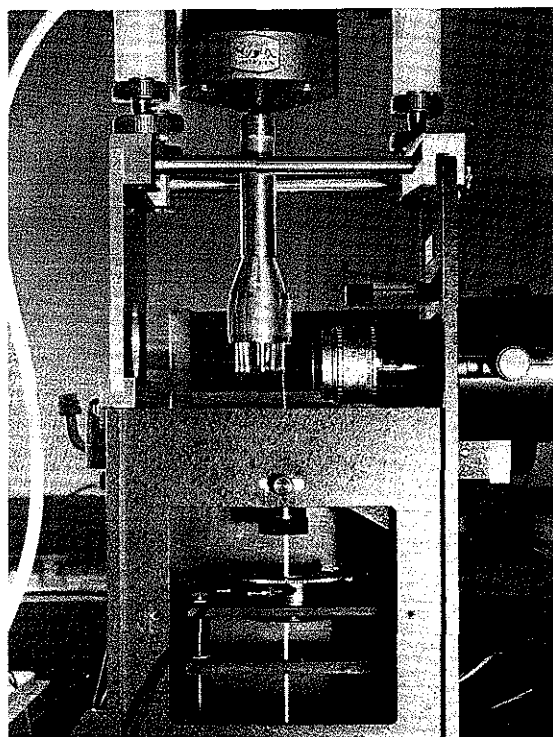

Fig. 2. In this rotating cell designed for deeply colored liquids[13] the focused laser beam is kept as close as possible to the cylindrical window to minimize self-absorption of the scattered radiation. The technique does not prevent photochemical decomposition, however, or fluorescence of the sample, problems which can only easily be overcome by changing the exciting frequency — generally towards the red.

Structural Changes of Molecules on Change of State

By contrast with organic molecules, which rarely undergo structural changes on change of state, a great many inorganic molecules do so with respect to both their stereo-chemistry and the coordination number of the central metal atom. Here Raman spectroscopy is rather well suited because, with relatively minor sampling modifications, spectra may be obtained on samples in the solid, liquid and vapor states, as we are about to exemplify.

Metal pentahalides are a group of compounds which usually have different structures in different states. As a solid at room temperature, phosphorus pentachloride has an ionic structure consisting of PCl_4^+ and PCl_6^- ions[14]. Infrared and Raman studies have, however, demonstrated that the solid formed by a rapid cooling of the vapor is molecular, and contains five-coordinate trigonal bipyramidal molecules[15]. The compound also occurs in molecular form in non-coordinating solvents such as carbon disulfide or dichloroethane. Thus the molecular solid has the same structure as the vapor, that already established by electron diffraction[16]. Recent Raman spectra of the vapor, metastable molecular solid, and stable ionic solid have confirmed[8,17,18] these conclusions. Particularly dramatic is the sudden and irreversible change in the Raman and ir spectra of solid molecular phosphorus pentachloride as it warms up and passes through the transition temperature whereupon it converts to the ionic form.

By contrast to phosphorus pentachloride, phosphorus pentabromide crystallizes in the form $PBr_4^+Br^-$ (as demonstrated by x-ray work)[19], and Raman spectroscopic evidence is consistent with this[20]; however it is also a trigonal bipyramidal monomer in the vapor phase.

Other pentahalides behave in yet other ways on change of state. Some, like niobium and tantalum crystallize as dimeric units, M_2X_{10}, which consist of two octahedra with a shared edge (e.g., Nb_2Cl_{10})[21]. In solution in non-polar solvents, these halides retain this structure[22], but as melts a monomer-dimer equilibrium is set up[23]. In the gas phase, electron diffraction studies have demonstrated that these molecules are all monomeric and trigonal bipyramidal[24,25]; Raman data have been fully in accord with these conclusions[8].

The tetrahalides MX_4 (M = Zr or Hf, X = Cl or Br) consist in the solid state of zig-zag chains, each metal atom being octahedrally coordinated to six halogen atoms, four of which are bridging and two terminal[26] viz $[MX_{4/2}X_2]_\infty$. Electron diffraction data have demonstrated that the two tetrachlorides are monomeric and tetrahedral in the vapor state[27]. Raman spectroscopic studies of these four halides in the vapor phase at 380-420C have shown conclusively that these four halides, as well as zirconium and hafnium tetraiodides, are all tetrahedral in the vapor phase[28] (four bands were observed, one polarized with $\rho \sim 0$ and with no rotational structure, the other three depolarized and with pronounced rotational structure, two of the depolarized bands being coincident with infrared-active fundamentals).

In the solid state, vanadium pentafluoride consists of infinite chains of molecules linked by cis-bridging fluorine atoms with an approximately octahedral arrangement of fluorine atoms around each vanadium atom[29]. The Raman spectrum of liquid vanadium pentafluoride[30] indicates that this too is polymeric, in agreement with earlier conclusions based on the high viscosity and high Trouton constant of the compound. The spectra indicate that at room temperature monomeric vanadium pentafluoride molecules are present, but as minor constituents; as the temperature is raised, however, the proportion of monomeric species present increases as evidenced by the increase in the intensities of two of the characteristic bands of the monomer, 719 cm^{-1} (pol) and 608 cm^{-1} (dp). In the vapor state, the molecule appears to be exclusively monomeric and its spectrum has been assigned on the basis of D_{3h} molecular symmetry[31], (compare PF_5 and AsF_5 in the vapor phase).

Structural changes on change of state also occur in metal trihalides. Aluminum trichloride and indium trichloride crystallize with a distorted close-packed layer structure the cations occupying one third of the octahedral sites[32]. Raman spectra of the solids differ greatly from those of the melts and vapors[33]. For instance, the melt and vapor (at 225C) spectra of aluminum trichloride are consistent with the presence of chlorine-bridged dimeric molecules of the Al_2Br_6 type. However, on raising the temperature of aluminum trichloride vapor to 820C, the Raman spectrum changes further, and becomes characteristic of monomeric trigonal planar molecules, i.e., at this temperature aluminum trichloride is isostructural with the boron trihalides. With 1000C furnaces[34], it is possible to obtain quantitative data on a wide range of depolymerization reactions in the gas phase.

Likewise, many metal dihalides (ZnX_2, HgX_2, SnX_2) have three dimensional polymeric structures in the solid state[35,36], are extensively polymerized as melts[37,38], but vaporize as linear (ZnX_2, HgX_2) or bent (SnX_2) monomeric species. Not surprisingly, spectral changes on change of state are very dramatic, the vapor phase spectra of these molecules[39,40] being particularly simple and readily interpretable. Linear molecules have only one Raman-active fundamental whereas the bent molecules have three, and this is one of the criteria for distinguishing between the two structural possibilities.

Among metal oxyhalides, it is essentially the norm to find structural changes on change of state, and very many instances have been defined through Raman analysis[8,41]. Vanadium oxytrifluoride for one, crystallizes with vanadium atoms linked into pairs through di-μ-fluoro bridges, linked into sheets by cis-bridging fluorine atoms. There is thus a distorted octahedral arrangement around each vanadium atom[42]. The Raman spectrum of the solid[43] is much more complicated than that found[43,44] for the vapor at 120C, which is

recognizable as that of a monomeric molecular species. Thus, the molecules VOF_3, $VOCl_3$ and $VOBr_3$ are isostructural in the vapor phase, in contrast with the solid state in which the oxychloride and oxybromide alone are molecular.

Clearly, Raman spectroscopy is very valuable for defining structural changes, particularly for its versatility and applicability over enormous temperature ranges (about 4K to 1000C).

Vapor Phase Raman Spectra and Raman Band Contours

High resolution Raman spectroscopy, which began to make great strides in the 1950s with the work of Welsh, Stoicheff, Weber and a few others, is concerned principally with the rotational structure in spectra of gases and vapors. Detailed analysis of rotational fine structure allows the calculation of moments of inertia and hence internuclear distances and interbond angles. It also yields information on molecular symmetry, vibration-rotation interactions and occasionally on nuclear spin and statistics.

High resolution pre-laser studies were confined to such simple molecules as[45,46,47] H_2, HD, D_2, N_2, O_2, F_2, CO_2, CS_2, C_2H_2, C_2N_2, C_4H_2, C_3O_2, C_6H_6, C_3H_4, C_2H_6, C_3H_6, CF_4. With the introduction of powerful laser sources, many more complicated molecules have now been studied. However, line spacings of most molecules are too small to allow resolution of the inherent fine structure of Raman bands, and thus work is limited to band contours.

It is well established that the infrared band contours of triply degenerate fundamentals of spherical top molecules depend markedly on the Coriolis (vibration-rotation) forces in the molecules. If the rotational fine structure of these bands can be resolved in either ir or Raman, the Coriolis constants (ζ) may be evaluated directly from line spacings in the rotational branches, or, although with less accuracy, from the separations of the P and R branch maxima in the ir based on the relationship[48]

$$\Delta\nu_{PR} = 4 \, (BkT/hc)^{1/2} \, (1 - \zeta)$$

where B is the rotational constant, and the other symbols have their usual meanings. This equation has been applied successfully to the determination of Coriolis constants of a large number of spherical top molecules such as CF_4, SiF_4, GeF_4, $SiCl_4$, $GeCl_4$, $SnCl_4$. Experimental difficulties, principally associated with the lack of suitable window materials, have so far precluded the recording of the vapor phase infrared spectra of metal tetrabromides and tetraiodides, for which no Coriolis constants have been calculated. On the other hand, vapor phase Raman spectra of such molecules can readily be obtained on samples sealed in Pyrex or silica tubes, because the latter form suitable window materials at all likely exciting frequencies. Only the intensity of color of such molecules poses problems.

Because less restrictive selection rules in Raman allows changes in the rotational quantum number of, in general, $\Delta J = 0, \pm 1$, or ± 2, and permit O, P, Q, R and S branches, band contours are more complicated in Raman than in ir. The original theory of Raman band contours, by Placzek and Teller[49], was confined to totally symmetric stretching fundamentals of symmetric top molecules. Theory has recently been extended to both the doubly[50,51] and the triply degenerate fundamentals of spherical top molecules[52-54].

Treatment for doubly degenerate fundamentals of spherical top molecules leads to the expression[53] (strictly true only for B = O).

$$\Delta\nu_{OP,RS} = 4.412 \, (BkT/hc)^{1/2}$$

Triply degenerate fundamentals involve the appropriate Coriolis constant, which can accordingly be evaluated by a computer simulation of the band contour or by other means. The Coriolis constants then serve[55] to assist in the evaluation of more accurate force constants for the molecules than were previously attainable from vibrational frequencies and constrained force fields alone[53,54].

The vapor phase spectrum of 22C silicon tetrafluoride[49,52], is given in Figure 3. Coriolis constants calculated from $\Delta\nu_{OP,RS}$ values found for the t_2 fundamentals are compared in Table 2 in three cases with the values found from ir band contour analyses. Note, excellent agreement is found, and it would appear that the Raman method for obtaining these constants[53] is important for heavy molecules. It is particularly satisfying that the experimentally determined zeta value (−0.35) for carbon tetrafluoride from ir and Raman-based contour analyses is in agreement with that determined by an analysis of the rotational fine structure of an ir-active band; this is the only
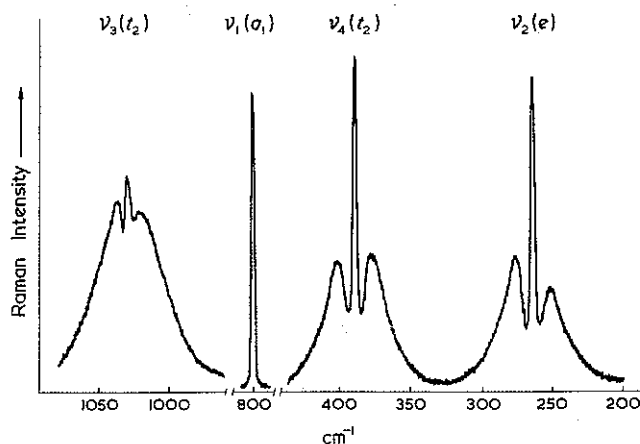

Fig. 3. **Vapor phase Raman spectrum of silicon tetrafluoride[50] at 22C. In accord with the selection rules for tetrahedral molecules of the type MX_4, the $\nu_1(a_1)$ fundamental consists solely of a Q branch, whereas the $\nu_2(e)$, $\nu_3(t_2)$ and $\nu_4(t_2)$ fundamentals all show OPQRS structure. Calculated and observed $\Delta\nu_{OP,RS}$ values for the e fundamental of nearly all tetrahedral molecules are in excellent agreement (to $\pm$ 0.5 cm^{-1})[53].**

	CF$_4$		SiF$_4$		GeF$_4$	
	ν_3	ν_4	ν_3	ν_4	ν_3	ν_4
$\Delta\nu_{PR}$ (cm^{-1})	4.65	34.2	10.3	23.0	16	13
ζ	0.82	−0.35	0.53	−0.07	0.20	0.35
$\Delta\nu_{OP,RS}$ (cm^{-1})	27.0	12.9$_5$	14.6	23.2	23.9$_5$	8.7
ζ	0.83	−0.36	0.63	−0.08	~0.2	0.35

metal tetrahalide for which the fine structure has been resolved, and hence the only one for which a strict test of the contour methods can be applied. Unfortunately, the Raman Contour method suffers an intrinsic weakness of the range ζ = 0.0–0.35, because $\Delta\nu_{OP,RS}$ is an insensitive function of ζ in this range.

Other types of spherical top molecule which have yielded good vapor phase Raman spectra in which the rotational branch contours are clearly evident and understandable in terms of these theories are[56] SF$_6$, SeF$_6$, and TeF$_6$ (Figure 4) and P$_4$ and As$_4$.

Such band contour analyses have recently been extended to prolate symmetric top molecules, vastly increasing the number of molecules amenable to study[57]. Moreover, advances are probable on the experimental side with the development of computer-averaging techniques, multipass arrangements and in-cavity techniques, always with the object of improving signal-to-noise ratios. Other advances, which exploit[58] the enhanced resolution available with laser sources and modern instrumentation are increasing the number of molecules successfully studied.

Raman Intensities and Bond Polarizability Derivatives

Precise determination of absolute intensities of Raman bands is a notoriously difficult operation[59-63]. Difficulties arise partly in the avoidance of Tyndall scattering by impurities in a liquid and from the walls of the Raman tube, and partly from the intensity calibration procedure: not only does the response of the instrument depend strongly on the blaze wave length of the grating, typically 5000A, but also on the 4500A peak spectral sensitivity of the typical photomultiplier. The spectral response of the instrument may be determined by referencing a standard lamp calibrated by the National Bureau of Standards. A controversial subject relates to the relative merit of internal and external intensity standards. An external standard poses problems with corrections for differing sample geometries, refractive indices, extinction coefficients, etc., of sample and standard[59,60],
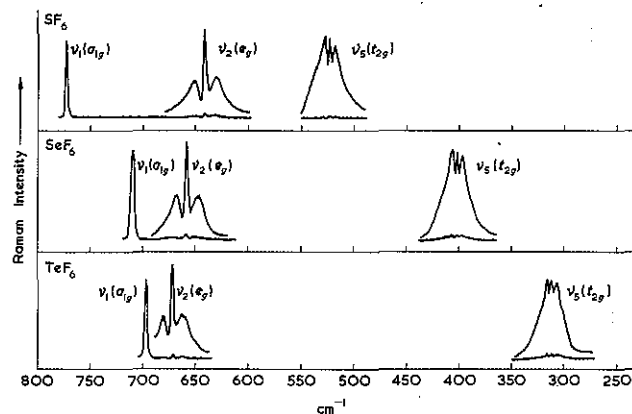

Fig. 4. Vapor phase Raman spectra of sulfur, selenium and tellurium hexafluorides at 23C, depict rotational branch contours[56].

and of fluctuating intensities of the exciting line. Internal standards (even if non-polar) pose problems of intermolecular interactions. Relative Raman intensities have been placed on an absolute basis by their comparison[62,63] with either Rayleigh line intensities or with the hydrogen pure rotational line J = 3 ← 1. Fortunately, the Optical Society of America has convened a committee to consider and make recommendations as to the most appropriate procedures for future Raman intensity measurements.

If the excitation beam is plane-polarized (as with a laser) with its electric vector at right angles to the direction of scattering, the intensity of the scattered light for the ith normal mode of vibration of the molecule, $(I_p)_i$, can be shown to be given by the expression[63,64]

$$(I_p)_i = \frac{KMI_0}{\mu} \cdot \frac{(\nu_0 - \nu_i)^4}{\nu_i[1-\exp(-h\nu_i/kT)]} \cdot [45(\bar{\alpha}')^2 + 7(\gamma')^2]$$

$$= \frac{KMI_0}{\mu} \cdot \frac{(\nu_0 - \nu_i)^4}{\nu_i[1-\exp(-h\nu_i/kT)]} \cdot [45(\bar{\alpha}')^2] \cdot \frac{3(1+\rho_p)}{(3-4\rho_p)}$$

where K   is a constant, depending on geometric and other factors

M   is the molar concentration of the molecule

I_0 is the intensity of the incident light beam

μ is the reduced mass

ν_0 is the excitation frequency (in cm^{-1})

ν_i is the Raman shift of normal mode Q$_i$ (in cm^{-1})

$\overline{\alpha}''$ is the derivative of the mean molecular polarizability with respect to the ith normal mode of vibration, i.e. $\gamma\overline{\alpha}/\gamma\,Q_i$

γ' is the corresponding derivative of the anisotropy of the polarizability

ρ_p is the depolarization ratio for the ith normal mode (polarized incident light)

This expression is strictly applicable only to gases at low pressures, since it is based on the assumption of randomly oriented, non-associated molecules; for the liquid phase the dependence of the cross section on the refractive index of the scattering medium (the "internal field effect") must be taken into consideration[65]. With internal standardization the constant terms disappear. Band intensities are better determined from band areas than from peak heights; the output of the photomultiplier over the applicable frequency range may be fed into a single-channel analyzer, and finally a counter.

Thus the above expressions for the intensities of Raman bands provide a means for deriving mean molecular polarizability derivatives, $\overline{\alpha}'$, and via defined transformations, the appropriate bond polarizability derivatives, $\overline{\alpha}'_{MX}$, i.e., $\delta\overline{\alpha}_{MX}/\delta r$. The theory on the basis of which these calculations became possible involves a number of assumptions, which have been discussed by Hester[66]. The chemical interest in $\overline{\alpha}'_{MX}$ values derives from their relationship to the degree of covalent character of the MX bonds involved in the vibration. Thus from Raman intensity measurements one may estimate, albeit crudely, degrees of covalent character of chemical bonds. Unfortunately the theoretical relationships[67] between these quantities are not yet well defined. In particular, it is not strictly possible to separate effects caused by change in the degree of covalent character of bonds from those caused by change in bond order.

Such studies involve a further complication: the exciting frequency (ν_0) may not be well removed from the frequency of the first allowed electronic transition (ν_e) in the molecule under study. Here it becomes necessary to correct for resonance enhancement of Raman band intensities, usually by plotting $\overline{\alpha}'_{MX}$ values against the function[68] $[1 + (\nu_0/\nu_e)^2]/[1 - (\nu_0/\nu_e)^2]^2$, the frequency function of Shorygin.

Recent studies of the intensities of the totally symmetric (a_1) bands of molecular tetrahalides[69] have shown that $\overline{\alpha}'_{MCl} < \overline{\alpha}'_{MBr} < \overline{\alpha}'_{MI}$ consistent with the increase in the percentage covalent character of the MX bonds in this order $(a_1(CCl_4):a_1(SnI_4) = 1:54$ for 5145A excitation), and that the resonance enhancement of the a_1 bands is much more pronounced for metal tetrabromides and metal tetraiodides than for metal tetrachlorides (consistent with the much smaller $(\nu_0-\nu_e)$ values for the former). The $\overline{\alpha}'_{MX}$ values range from $\overline{\alpha}'_{CCl}$ (2.04A^2) to $\overline{\alpha}'_{SnI}$ (6.86A^2). The resonance
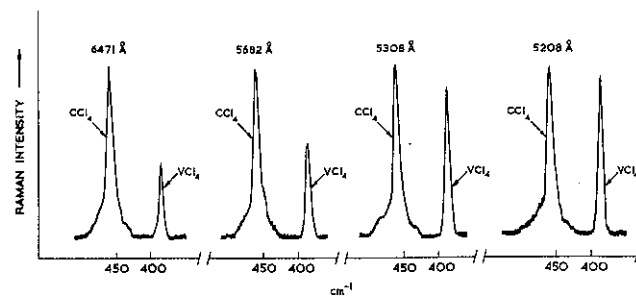

Fig. 5. Relative intensities of the a_1 bands of carbon and vanadium tetrachlorides at different exciting frequencies[3]. Note the enhancement of the a_1 band of vanadium tetrachloride as the exciting frequency approaches that of its first allowed electronic transition (24,800 cm^{-1}).

enhancement of an a_1 band as $(\nu_0-\nu_e)$ decreases is best illustrated for vanadium tetrachloride (Figure 5).

Additional studies along the above lines have led to the determination of $\overline{\alpha}'$ values for metal oxyanions[70], metal cyanoanions[71], boron halides[72], and metal thiocyanate complexes (from which it was found possible to distinguish sulfur from nitrogen bonded thiocyanate groups)[73], as well as for metal-metal bonded molecules such as $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ or metal hexacarbonyls $M(CO)_6$ (M = Cr, Mo or W)[74].

A particularly interesting recent indication is that, at least with metal tetrahalides and with certain substituted metal carbonyls, it is the totally symmetric metal-ligand stretching frequencies which show the resonance enhancement as the exciting frequency approaches that of the first allowed electronic transition in the molecule. If this conclusion can be generalized, it would appear that for complicated molecules which are not soluble in suitable solvents, one may thereby have acquired a potential technique for the identification of these particular fundamentals.

Redistribution Reactions, Dissociation Reactions, and Equilibria

A redistribution reaction is one in which two or more different compounds, on being mixed, redistribute their ligands so that mixed-ligand compounds are formed in the mixture together with the originally mixed compounds. In some instances, the mixed species may be isolated from the mixture, but in others this is impossible. This type of reaction takes place very widely in inorganic chemistry, and particularly so among metal halides.

The redistribution reaction has been recognized for a very long time, and one of the first techniques applied to study such reactions was photographic Raman spectroscopy. Delwaulle and co-workers demonstrated in this way the existence of chlorobromides of carbon and silicon (which are isolatable) and of titanium, germanium and tin (which are not). Subsequent work demonstrated the existence of chloro-iodides[75], and bromoiodides[76] of silicon, germanium and tin with similar properties.

A characteristic feature of each halide and mixed halide — indeed frequently the sole criterion for the existence of the latter — is a very strong and highly polarized Raman band attributed to the symmetric stretching of the metal-halogen bonds. As expected from mass considerations, this band moves progressively to lower frequencies as bromine or iodine replaces chlorine in the mixed species (Figure 6). [77]
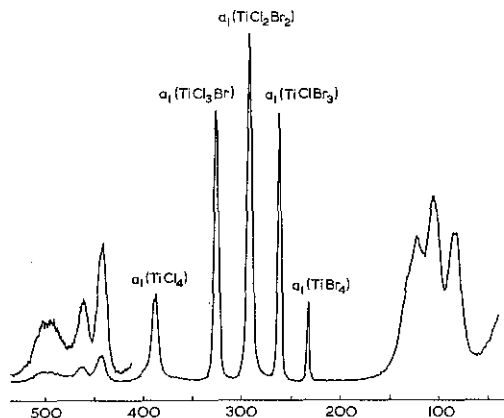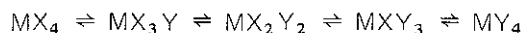

Fig. 6. Raman spectrum of a neat mixture of titanium tetrachloride and titanium tetrabromide at a mole ratio 59:41 over the range 50-550 cm^{-1} at 23C; excitation 6471A [69]. Mixed halides of germanium, tin and titanium may simply be formed by mixing the appropriate parent tetrahalides, either neat or in non-polar solvents, at room temperature. The nine "triple-mixed" species, MX$_2$YZ, have also been identified [77] for silicon, germanium and tin by recognition of the unique values for their symmetric stretching frequencies.

Recent work on these halide systems [69] has been aimed at establishing whether, in the mixtures, there is a preference for the formation of mixed halides, for the retention of the parent halides, or for the setting up of a random distribution of halogen atoms. The equilibria can be represented thus,

$$MX_4 \rightleftharpoons MX_3Y \rightleftharpoons MX_2Y_2 \rightleftharpoons MXY_3 \rightleftharpoons MY_4$$

and they are defined in terms of the equilibrium constants

$$K_1 = \frac{[MX_4][MX_2Y_2]}{[MX_3Y]^2}$$

$$K_2 = \frac{[MX_3Y][MXY_3]}{[MX_2Y_2]^2}$$

$$K_3 = \frac{[MX_2Y_2][MY_4]}{[MXY_3]^2}$$

which take the values $K_1 = K_3 = 0.375$ and $K_2 = 0.444$ for a random distribution. Quantitative Raman studies of TiCl$_4$/TiBr$_4$ mixtures, both neat and in cyclohexane solutions, have led to the conclusion that the distribution of chlorine and bromine atoms is either random or very closely so [69]. Similar conclusions have been reached for VOCl$_3$/VOBr$_3$ mixtures (Figure 7) from Raman studies [4], and for SnCl$_4$/SnBr$_4$ mixtures from ^{119}Sn nmr studies [78]. It is of interest that only a single resonance is observed [79] for TiCl$_4$/TiBr$_4$ mixtures by ^{47,49}Ti nmr spectroscopy, the resonance position varying in accord with the Cl:Br ratio of the mixture. This clearly demonstrates the differing time scales of the Raman and nmr experiments. Further research with mixtures of MX$_4$ and M'Y$_4$ molecules is expected to establish the order of preference of metal atoms for different halogen atoms [80], a matter of considerable interest to inorganic chemists.

In the vapor phase, many redistribution reactions take place and may be recognized by Raman investigation of appropriate mixtures. HgClBr, HgClI and HgBrI have been recognized as existing in the vapor above mixtures of the parent HgX$_2$ molecules [34].

Another intriguing recent study is that of the Raman spectra of mixed phosphorus and arsenic vapor. Redistribution to form P$_3$As, P$_2$As$_2$, and PAs$_3$ was clearly evident [81], the necessary reactions presumably taking place by way of a dissociative-associative redistribution involving diatomic species.

In a similar way it is possible to study dissociation phenomena, such as the temperature-sensitive process

$$MCl_5 \rightleftharpoons MCl_3 + Cl_2$$

where M = P or Sb. The vapor phase spectrum of phosphorus pentachloride at 160C contains bands assignable only to the molecule itself, but by 220C new bands attributable to the presence of both phosphorus trichloride as well as chlorine are clearly apparent [18].

Further examination of dissociation phenomena, appears worthwhile.

Factor Group Studies of Molecular Crystals

Because of intermolecular interactions, the symmetry of a molecule is in general lower in crystals than in solutions or vapors. Reduction in symmetry may split degenerate vibrations as well as activate infrared or Raman inactive vibrations. Moreover, solid state spectra also exhibit lattice modes, which arise from translational or librational motions of the molecules within the lattice. In the method known as factor group analysis, normal vibrations of the entire Bravais
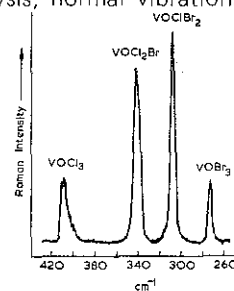

Fig. 7. Raman spectrum of a mixture of vanadium oxytrichloride and vanadium oxytribromide in the region of the $\nu_2(a_1)$ fundamental — the VX$_3$ symmetric stretching fundamental — [4], with evident random distribution of chlorine and bromine atoms.

unit cell are considered in relationship to the symmetry elements of the cell. These elements define a group, the factor group, which governs the selection rules pertaining to the molecules in the crystalline state. The factor group is derived from the space group by setting the primitive translation operation equal to the identity operation. A change of solid phase will in general be associated with a change in the relevant factor group, and accordingly the selection rules governing the appearance or non-appearance of various fundamentals will change with the phase change. Solid-state phase changes can in general be readily recognized from the ir or Raman spectrum of the compound over the relevant temperature range. One object of factor group studies is, then, to define phase changes, particularly those occuring in molecular crystals. Another consideration is the establishment of how well the selection rules (ir and Raman) hold for compounds in which the factor group had been assigned by x-ray; conversely, if the factor group is not known it may, in favorable cases, be determined from the detailed ir and Raman spectra of the compound[82]. Other investigations especially those in the low frequency region are aimed at the determination of lattice frequencies and of barriers to internal rotation.

Low temperatures, 77K or lower, are desirable to minimize the broadening influence of hot bands on fundamentals; this cannot be neglected because factor group splittings may be as small as 1 cm^{-1}, and such splittings, critical to the establishment of the factor group, may well be obscured at higher temperatures.

Recent examples[83] are of boron trichloride, boron tribromide, and boron triiodide; these molecules are isomorphous and crystallize in the centrosymmetric space group $P6_3/m = C_{6h}^2$ with two molecules per unit cell. The structure in fact consists very nearly of hexagonal close packing of halogen atoms with the boron atoms inserted interstitially in the appropriate places and numbers. The site symmetry of the boron atoms is C_{3h} and the factor group is C_{6h} (a centrosymmetric group). Following the rule of mutual exclusion, it follows that the selection rules pertaining to crystalline solids are effectively the same as those for isolated molecules. The observed Raman spectra of sublimed films of these halides at about 77C are found to be in complete agreement with the above factor group analysis. However, considerable isotopic structure to some or all of the bands is both expected and found due to the presence in natural abundance of two isotopes of boron (^{10}B = 19.78%, ^{11}B = 80.22%), two isotopes of chlorine (^{35}Cl = 75.53%, ^{37}Cl = 24.47%), and two isotopes of bromine (^{79}Br = 50.54%, ^{81}Br = 49.46%). Halogen isotopic splitting is most evident for the a_1' fundamental of each molecule, in which the boron atom does not move (Figure 8). The fact that there is only one stable isotope of iodine is consistent with observation of only a single component to the a_1' band of boron triiodide. The isotopic splitting of the a_1' band of boron trichloride amounts to 4.2 cm^{-1} and of boron tribromide to 1.2 cm^{-1}, in complete agreement with the calculated values; the intensity patterns are similar to those calculated on the basis of the known abundances of the isotopically different atoms.
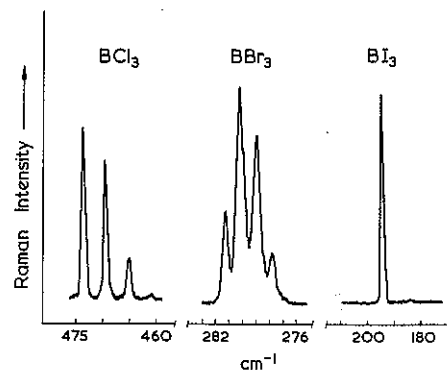

Fig. 8. Raman spectra of crystalline boron trichloride, boron tribromide and boron triiodide at about 77K, in the region of the totally symmetric fundamentals. Chlorine and bromine isotope splitting is evident in contrast with the single iodine isotope[83].

Similarly with the tetrahalides of carbon, silicon, titanium, germanium, tin, and lead[84-86], the isotopic splittings of the a_1 bands are, on average, 3.15, 2.85, 2.75, 2.7, 2.5, and 2.15 cm^{-1} respectively. The isotopic splitting pattern, however, deviates appreciably from the calculated pattern for the heavier halides. For the other fundamentals, both factor group splitting and isotopic splitting are of comparable magnitude, and can only be adequately understood by comparison with an isotopically pure molecule[87], e.g., $C^{35}Cl_4$, at temperatures sufficiently low (50K) that the influence of hot bands on the spectrum is insignificant.

Many of these globular molecules readily undergo phase changes which should provide information about intermolecular forces operating in condensed phases[88]. Titanium tetrabromide, for instance, probably occurs in three different forms between room temperature and 77K.

Investigations of other substances, however, such as solid sulphur hexafluoride did not lead to a firm conclusion as to its factor group[89], but solid ethylene[90] has been found to belong to the space group $P2_1/n| = C_{2h}^5$. Raman analysis is noteworthy for simple compounds containing hydrogen atoms, since the latter may not be detected by x-ray diffraction. The value of factor group analyses has been well illustrated by the far ir work on hydrogen and deuterium halides, in which not only were conclusions drawn as to the likely factor groups of the solid molecules, but intermolecular force constants were also calculated[91].

Assignment of translational and librational lattice modes has long been the forte of far ir. Complementary spectra of the Raman-active lattice modes has been hampered by the presence of grating ghosts, but with the development of interferometrically ruled gratings and triple monochromator systems, difficulties on this score could well be overcome.

That more precise structural and spectroscopic information is now obtained with single crystals in which the individual Raman tensor components can be isolated, is a subject, that has already been treated in the Spex Speaker[92].

Metal-Metal Bonded Systems

Vibrations of very polarizable groupings such as $C \equiv C$, $C \equiv N$, $O = O$, $S - S$ give rise to intense Raman bands, and from the point of view of group frequencies, such moieties can often be better identified by Raman than by infrared measurements. It has similarly been demonstrated that metal-metal bonding in compounds can frequently be recognized by way of the often intense Raman activity of the metal-metal stretching fundamentals. The first such fundamental to be assigned was the Hg-Hg stretch of aqueous solutions of mercurous nitrate; the appropriate band was found by Woodward[93] in 1934 to occur at 169 cm^{-1}. Subsequently, the metal-metal stretching frequencies in $Mn_2(CO)_{10}$, $MnRe(CO)_{10}$, and $Re_2(CO)_{10}$ have been identified[94] at 160, 157, and 122 cm^{-1} respectively; Pb-Pb in compounds such as R_6Pb_2 (R = Me or Ph)[95,96] at ~ 110 cm^{-1} the Sn-Sn at ~ 200 cm^{-1} [97]. The metal-mercury stretching frequencies in compounds $M(CO)_4(HgCl)_2$ (M = Fe, Ru or Os) have also been identified. [98]

It is perhaps more important that Raman spectroscopy has offered structural guidance for complicated molecules — metal cluster compounds like $Bi_6(OH)_{12}^{6+}$, $Tl_4(OEt)_4$, $Nb_6O_{19}^{8-}$, $Pb_4(OH)_4^{4+}$, $Rh_4(CO)_{12}$, $Os_4O_4(CO)_{12}$, $Ir_4(CO)_{12}$, $Mo_6Cl_8^{4+}$, and systems based on the Os_3 triangular nucleus [99,100]. The metal-metal stretching frequencies in these compounds generally lie in the 100-200 cm^{-1} region.

Unusual ions in sulfuric acid systems have also been identified. Selenium, present as the unusual cation Se_4^{2+}, dissolves in sulfuric and fluorosulfuric acids in the presence of oxidizing agents to form intense green or yellow solutions. This ion, as present in the salt $Se_4(HS_2O_7)_2$, has been shown by x-ray diffraction to have a square planar structure with D_{4h} symmetry. Spectroscopic investigations of this ion have led to the assignments[101] a_{1g} (327 cm^{-1}), e_u (306 cm^{-1}) and b_{2g} (188 cm^{-1}), and hence (using a Se-Se distance of 2.3A) to Urey-Bradley force constants of K = 2.2, H = 0.12, and F = 0.15 md/A.

Complex Ions in Aqueous Solution

Complex ions in solution, have long been recognized as significant and ideal Raman subjects. Although water is a good solvent for many inorganic compounds, the very large changes in dipole moment accompanying its vibrations lead to intense interfering ir absorption. On the other hand, polarizability changes associated with its vibrations are only small, leading to very weak Raman scattering, facilitating identification of ions in solution, determination of their structures and detection of cation-anion association phenomena as well as determination of relevant equilibrium constants by Raman spectroscopy. In this connection, in view of the low frequency of most metal-ligand vibrations, the ease with which such shifts may be detected is most welcome. Moreover, as the intensity of a Raman band is directly proportional to the concentration of the relevant molecule, the evaluation of equilibrium constants may readily be accomplished.

Interaction between a polyatomic anion, such as the SO_4^{2-}, ClO_4^-, or NO_3^- ions, and a cation in solution (through the intervening solvent molecules of the first coordination sphere of either ion, or more importantly, by way of direct coordination) leads to a reduction in the point symmetry of the anion. In general, this results in splitting of degenerate vibrations of the isolated anion, and activation of otherwise inactive bands. For ion pairs, no bands associated with cation-anion stretching vibrations have yet been detected, principally due to the highly ionic character of the cation-anion interaction.

Metal ion — oxyanion associations have been reported by Irish[102], and others investigating metal sulfates, perchlorates, and nitrates[103,104].

Melts

Many melts make particularly suitable Raman samples. Pyrex to 550C and silica to 1400C are generally adequate as window materials for pure molten nitrates and halides (except lithium salts), although in the presence of water or hydroxide severe corrosion may set in. Molten fluorides, hydroxides and carbonates, however, readily attack these materials; nickel containers have been found satisfactory for fluorides, and metals such as molybdenum, tungsten or tantalum or boron nitride, sapphire or alumina[105].

Similar to aqueous solutions, melts may be analyzed by characteristic vibrational frequencies and establishment of the local symmetries of the ions. Melts are found to vary widely in nature, from predominantly ionic (formed by alkali metal halides) to predominantly molecular (formed, for example, by mercuric halides and inorganic polymers). Studies of ionic melts have been directed towards the strength and symmetry of nearest-neighbor interactions and thus to the theory of the liquid state; hydroxides, chlorates, perchlorates, sulfates, bisulfates, thiocyanates, and in particular nitrates have been studied from these viewpoints[105,106]. By contrast, the vibrational spectra of molten mercuric chloride and mercuric bromide are consistent with the presence in the melts of linear triatomic molecules, with less than 0.01% of ionic species HgX^+, HgX_3^-, and HgX_4^{2-} present to account for the finite electrical conductance of the melts. Symmetric stretching frequencies of the HgX_2 molecules in the melts occur[107] at 313 cm^{-1} ($HgCl_2$) and 195 cm^{-1} ($HgBr_2$). These are, however, considerably reduced from the gas phase values for these fundamentals, 358 cm^{-1} ($HgCl_2$), and 222 cm^{-1} ($HgBr_2$) and this may imply that the above interpretation is an over-simplification. Raman spectra of molten zinc and cadmium halides are less simple than those of mercury halides, and there is no doubt that polymeric species are predominant at least in "low" temperature melts.

It is interesting that gallium dichloride and gallium dibromide[108], provide Raman spectra nearly identical with those of aqueous solutions of the $GaCl_4^-$ and $GaBr_4^-$ ions respectively, leaving no doubt that in the melts, these halides have disproportionated to the ions $Ga^+[GaX_4]^-$.

SIGNIFICANT technical discoveries of the last few years in Raman spectroscopy have given research on vibrational spectra of inorganic molecules a new lease on life. Exploitation of these advances is still at an early stage, much important work may confidently be expected in the near future.

Acknowledgment

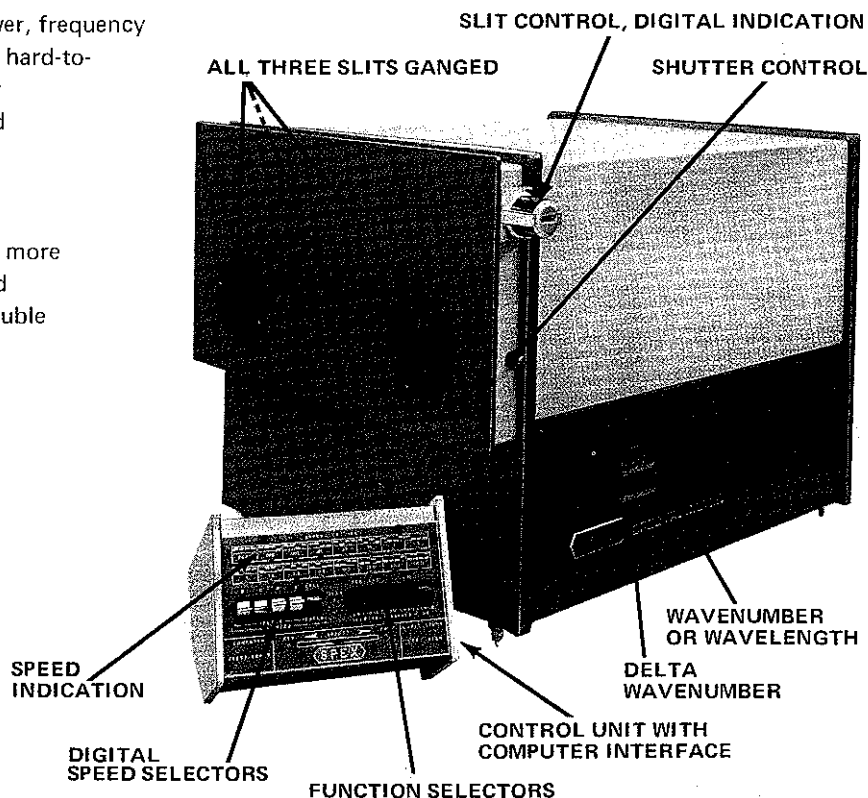## REFERENCES

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SPEED INDICATION

All performance characteristics below are cast in terms of 1200 g/mm gratings in first order.

OPTICAL SPECIFICATIONS

DOUBLE SPECTROMETER:
0.5-meter Czerny-Turner system, double dispersing

APERTURE:
f/7

MIRRORS:
Protected coatings, reflectivity exceeding 90%.

GRATINGS:
68x68x10 mm in kinematic quick-change mounts with three orthogonal adjustments, 1200 groove/mm 5000A blaze standard. (Optionally, 1800 to 8 grooves/mm with blaze from 1500A to 112 microns).

Efficiencies are typically greater than 70% at blaze; resolution typically 70-95% of theoretical. Standard 1200 g/mm gratings are essentially ghost-free with root structure almost undetectable in line images.
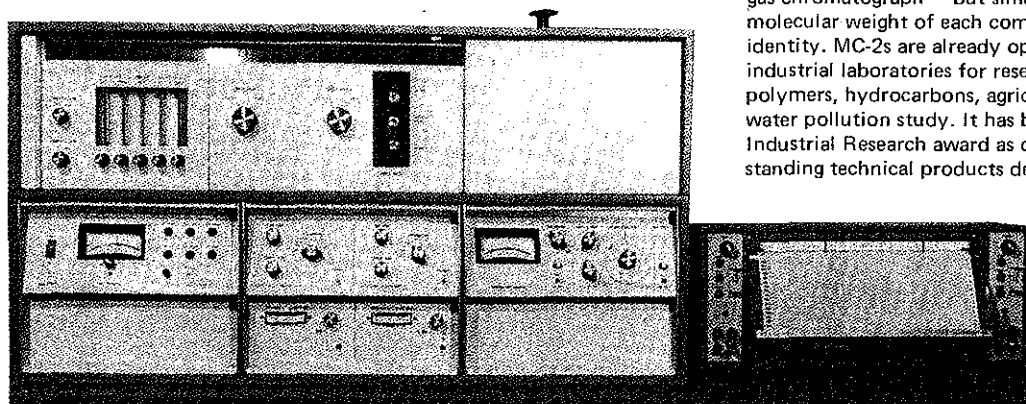
SPECTRAL PURITY:
With a monochromatic source, I/I_0 is less than 10^{-11} at 100 cm^{-1} separation from input light.

SLITS:
Three, bilaterally opening from 10 microns to 3 mm. Height 2 to 20 mm. Ganged with direct reading in microns on 4-digit counter.

MASS CHROMATOGRAPH

This MC-2 Mass Chromatograph is one of two highly innovative instruments developed at Chromalytics Corporation, which was acquired by Spex Industries, Inc. in February, 1973. The MC-2 not only separates complex mixtures into their components — the basic function of any gas chromatograph — but simultaneously spells out the molecular weight of each component, a relevant clue as to its identity. MC-2s are already operating in university and industrial laboratories for research and quality control of polymers, hydrocarbons, agricultural products as well as a water pollution study. It has been patented and received the Industrial Research award as one of the 100 most outstanding technical products developed during 1971.
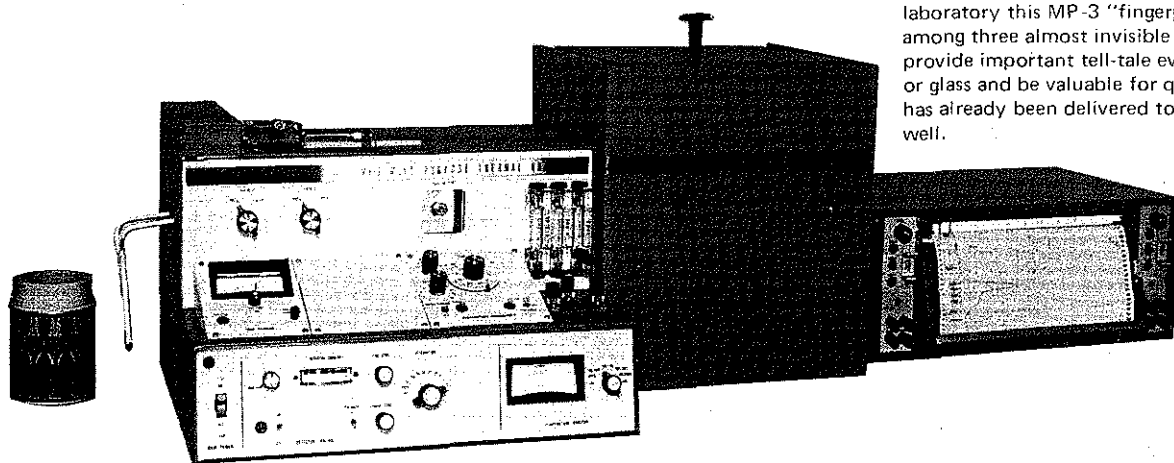
INTRODUCING

MASS
AND
THERMAL

CHROMATOGRAPHY

THERMAL CHROMATOGRAPH

Demonstrated early in its career at a state police forensic laboratory this MP-3 "fingerprinted" and differentiated among three almost invisible paint chips. It can likewise provide important tell-tale evidence with plastic, hair, cloth or glass and be valuable for quality control and research. One has already been delivered to an atomic energy installation as well.

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