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Speaker

LASER-RAMAN SPECTROSCOPY OF SYNTHETIC POLYMERS

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POLYMERIC materials have become an integral ingredient of modern life. Not only have they substituted for older materials but in many instances have resulted in the creation of entirely new products and even industries. The key to their overwhelming success has been the ability of chemists to tailor-make polymers with properties to satisfy specific requirements. By adeptly manipulating the chemical constitution, the molecular and macromolecular structure of a polymer, they have been able to attain precisely the right chemical, physical and engineering properties for an intended application. For example, different properties are associated with amorphous as opposed to the more ordered regions within a polymer. Randomly oriented regions are more subject to oxidative degradation. They also more readily act as centers for the retention of dyes and permit greater diffusion of small molecules than do the ordered "crystalline" regions. Thus, whether the manufacturer wishes to produce a fiber in which dyes will not run, or wrappers which will keep food fresh, or thousands of other items, he relies eventually on his polymer laboratory.

In any well established polymer laboratory one will find a number of structural methods employed to determine the molecular and macromolecular structure and the presence of chemical discontinuities (end groups, etc.) and also to analyze and control the quality of the products produced. The standard methods normally employed include IR and NMR spectroscopy, x-ray diffraction and electron microscopy. As in so many other areas of physics and chemistry, polymer science is now benefiting from the renaissance in Raman spectroscopy which has occurred in the last five years (1) and we plan in this paper to describe the value of Raman methods in this field.

Vibrations of Polymeric Molecules

The vibrations of polymers are not simply those of the monomer units. Although some vibrations may appear to be associated almost exclusively with pendant groupings or even structural features within a chain, e.g. a para-disubstituted benzene ring, many of the vibrational modes are due to motions of long sequences of atoms, some of which may be in the skeleton of the polymer. The symmetry rules for defining the infrared and Raman activity of molecules and the techniques desired to predict the frequencies of vibration from a knowledge of the appropriate force constants apply equally well to polymers as to smaller molecules. With simple molecules or ions, however, the symmetry rules are fre-

quently applied to species considered in isolation, such as in the gas phase or in dilute solution. By contrast no polymer molecule exists in this idealized situation. Polymer molecules are invariably twisted, folded, bent, intertwined and generally associated with one another even those colloquially referred to as "crystalline polymers" (2) i.e. one must always concern oneself with the polymeric chain entrapped in a small but significant crystalline region and consider the total symmetry. Further, polymer scientists have always to remember that their samples are in the chemical sense impure, i.e. they are always multicomponent mixtures of molecules of varying molecular weight, stereoregularity, degree of branching and identity of chain end-groups.

The vibrations of macromolecules reflect these properties to varying degrees. Thus:-

1. Bands found in the vibrational spectra arise from skeletal motions but their appearance in the infrared or Raman spectrum is governed by the symmetry of the unit cell within which the polymer chains are located. There may well be two or more chains per unit cell and this can complicate the observed spectrum and lead to ambiguities in the interpretation of the observed spectra.

2. The above comment applies only to crystalline regions in a polymer. However, those of its molecules lying in the amorphous region also contribute to the observed vibrational spectrum; they can give rise to new vibrational features or broaden and diffuse one associated with the more regular arrays.

3. End groups, if present in sufficiently high concentration, can also give rise to characteristic spectral features. The concentration of end groups acts as an indicator of either molecule weight or of the degree of chain branching.

4. Vibrations of drawn polymeric materials are similar to those of the bulk specimens, but they frequently show pronounced directional properties which can be invaluable in eliminating ambiguities in the explanation of the origin of the spectra or can be used in reverse to determine local degrees of ordering within a fiber or film.

Full-scale coordinate analyses of perfectly regular infinitely long isolated chains have been successfully completed in a few cases, e.g. polyethylene (3), polypropylene (4), polyoxymethylene (5) and polytetrafluoroethylene (6). In polyethylene (7) and polyoxymethylene (8) attempts have

also been made to predict precisely the effect of inter-molecular forces on the vibrations of molecules within the unit cell. Partial analyses and group frequency explanations of numerous other polymers abound but almost all studies made before the late 1960's have been based on infrared spectra alone. The Raman half of the story has been largely neglected. This was a consequence of the prohibitive difficulty in the determination of Raman spectra from polymers when using discharge lamp sources and the older spectrometric techniques.

Almost all crystalline polymers are highly symmetrical and consequently there are some modes of vibration which give rise to infrared active bands, others to Raman active bands and the remainder to features that appear in both infrared and Raman spectra. From the infrared spectrum alone explanations of the structure can well be intrinsically unreliable, if not misleading, and at best the frequencies of only the majority of vibrations can be determined. Although it may seem a little indelicate to say so, this has led to naive and even erroneous explanations of spectra in the past. Now that Raman spectra of polymers *can* be recorded no one should be content with only half the available information!

Recording the Raman Spectra of Polymers

Several points can gainfully be made about the techniques of recording polymer spectra:

1. Conventional right-angle viewing instruments and their sample holding arrangements are quite adequate for polymer samples. There is great versatility in sampling since the only requirement is for proper optical coupling among laser, sample and spectrometer. Thus, it is convenient to examine powders in bottles or capillaries (since glass has a very weak Raman spectrum), coatings on substrates, pellets, lumps, fibers, films and solutions all with the normal sampling accessories supplied by the instrument maker. No microtoming or sectioning is required, in fact we find that no special preparation of the sample is needed at all. This is a clear advantage over other methods, e.g. IR, NMR, x-ray diffraction, etc. In most cases of Raman study the method is completely non-destructive and the sample can be recovered unharmed. Exceptions to this occur when material is photosensitive or it is essential to melt or dissolve it.

2. By constructing appropriate cells, polymer melts as well as samples maintained at low temperatures and specimens exposed to stress are all easily accessible to Raman study. Again, Raman spectroscopy is favored by great advantage over most other structural techniques.

3. The intrinsic narrowness of Raman lines compared with their infrared counterparts means that strong Raman features do not tend to obscure the weaker ones to the same extent. Hydrogen-bonded systems in particular do not give rise to Raman spectra dominated by the intense, broad and featureless bands characteristic of their infrared spectra.

4. Water has an extremely weak Raman spectrum and in consequence is an excellent solvent for Raman spectroscopy. Thus, solution studies on water-soluble polymers, e.g. adhesives and biopolymers, are becoming relatively commonplace.

5. Depolarization ratios can be easily determined. This familiar practice (1) is, in principle, applicable only to non-oriented transparent materials. Solid polymer samples can give meaningful results if they are essentially non-turbid but since turbidity is characteristic of many polymers the specialized samples appropriate to this type of study may be difficult to prepare.

6. The good spatial resolution of the technique arising from the small area illuminated by the laser and examined by the spectrometer, is of great technological importance in the examination of inhomogeneous samples such as complex moldings, laminates or surface coatings.

7. One major disadvantage of the Raman technique is troublesome. This is the persistent occurrence of fluorescence in some samples. Coping with this problem can tend to take on the mantle of a 'black art' rather than a science but accounts of at least partially successful methods are available (9). A strip chart recorder equipped with powerful and stable zero suppression and a laser with a highly stabilized output are almost essential in this type of work.

8. The desirable characteristics of lasers for obtaining Raman spectra from polymers include:

    a) High output power. This is essential when dealing with polymer samples whose Raman spectra intensity is low, as is so often the case. A powerful laser is also needed for the examination of the subtle differences which frequently appear when comparing the spectra of various specimens of the same polymer. It is also capable of "burning out" excessive fluorescence.

    b) High output amplitude stability, particularly in the time range 0.25 — 20 sec. This is essential when examining weaker features in the spectra and especially when considerable zero suppression is applied.

An argon/krypton ion laser has the advantage of offering several lines of widely differing wavelength. Laser lines whose wavelengths are well removed from the electronic absorption regions are desirable to excite Raman spectra from colored samples. In fact, it is not unknown for an absorbing specimen to burst into flames when exposed to a powerful argon ion laser.

In general we have found that a good, high-power argon ion laser (main lines 5145A, 4880A) is suitable for the excitation of the Raman spectra of polymers which are not deeply colored.

Rather than attempt a comprehensive review of published Raman studies on polymeric systems in this paper, we refer the reader to (10) and (11). We shall confine our attention to some typical systems and attempt to illustrate what types of measurement and analysis are possible with this new and exciting technique.

### Polyethylene (PE) A highly crystalline polymer

It is customary among the most academic practitioners in the polymer world to fall back on this material when all else fails because much more is known of the properties of this chemically simple polymer than any other. However, we shall reverse custom and begin with polyethylene. Its molecular structure is illustrated in Figure 1.

POLYETHYLENE

LINE GROUP AXES

SPACE GROUP AXES

● = C
o = H
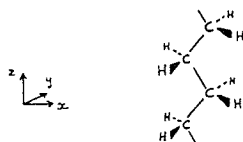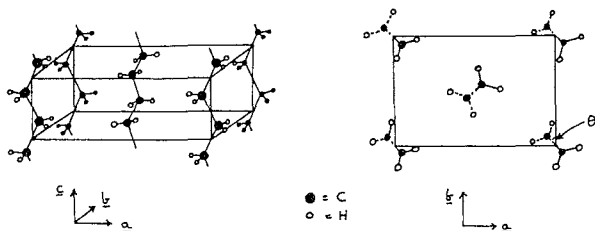
DATA
Θ = 41.2°
Θ = 45°

Fig.1 The molecular structure of crystalline polyethylene. The arrangement of atoms in one chain is shown in Fig. 1a. In a crystallographic unit cell, shown in Fig. 1b, interactions between the two chains are the cause of correlation doubling (i.e., splitting) of bands in the infrared and Raman spectra.

The high symmetry of the polyethylene molecular chain and the crystalline arrangement (line group isomorphous with D_{2h} site group C_{2h} and space group $D_{2h}(16)$ have far reaching consequences for the vibrational spectrum (12). The retention of a center of symmetry means that the rule of mutual exclusion is applicable; only those vibrational modes symmetrical with respect to the center of symmetry are Raman-active and most of the antisymmetrical modes are active solely in the infrared. Since there are two chains per unit cell, correlation doubling occurs. In simple terms, this can be visualized as each of the molecular vibrations of the two chains within the unit cell occurring in-or out-of-phase. The vibrational energies associated with these two modes have slightly different values and so the line group fundamentals are split in the vibrational spectrum of the crystals. The magnitude of this splitting is determined by the strength of the inter-chain interaction. In the infrared spectrum this splitting is well-known and permits determining the degree of crystallinity in polyethylene specimens (13). Careful analysis of the Raman spectrum of polyethylene at liquid nitrogen temperatures shows that some of the bands are close doublets (14). (The low temperature reduces the contribution to the spectrum of vibrational hot bands and increases in strength the interchain interaction following the shrinkage of the unit cell). The analysis of the anisotropic Raman scattering from an oriented specimen of drawn polyethylene closely follows the procedures normally employed for single crystal analysis (15). There is, however, a complication in that one-way drawing causes orientation of the chain axes but not of all the axes of the crystallites, i.e. cylindrical symmetry is adopted by the unit cells within a fiber. As a consequence of this peculiarity, an averaging procedure has to be introduced into the treatment of the observed data. Agreement between predicted and observed anisotropic

behavior can be excellent for really well oriented samples of crystalline polyethylene. Conversely, any deviation from prediction becomes a measure of disorientation in a drawn specimen. There are a number of obvious technological applications of this type of study, e.g. the non-destructive examination of drawn filaments to determine the orientation of the molecules in the core rather than those nearer the skin.

Turning now to randomly oriented crystallites, as found in undrawn bulk specimens, their low depolarization ratios are indicative of bands arising from totally symmetric vibrational modes. However, it is sometimes difficult to prepare a specimen suitable for the determination of depolarization ratios (or for that matter for precise anisotropic scattering studies); unless samples are non-turbid the polarization properties of the laser beam are destroyed and no meaningful results can be obtained. The most successful method of preparing a clear sample is either the rapid quenching of a melt or the preparation of an appropriate solution. With polyethlene the former is to be preferred as the polymer is relatively insoluble. In the more soluble polymers like polystyrene, polymethylmethacrylate or polyvinyl alcohol, precise depolarization data is best obtained with solutions.

TABLE I

Bands Observed in the Raman Spectra of Polyethylenes

$\Delta\nu$ (cm^{-1})		Symmetry (Space Group)	Approximate Description of Mode
2932 m		$A_g + B_{1g}$	ν_{as} CH_2 and ν_s CH_2 and Fermi Resonance interactions with the first overtones and combinations of correlation-doubled δ_{as} CH_2 1468 (b_{3u}) and δ_s CH_2 1440 (a_g) modes
2905 s, sh		$A_g + B_{1g}$	
2884 vs		$A_g + B_{1g}$	
2848 s		$A_g + B_{1g}$	
2725 w		A_g	Overtone/combination
2660 vw			Combination
2617 vw			Combination
2595 vw			Overtone
2430 vw			Combination
2185 vw		A_g	Combination
1672 w			$\nu_{C=C}$ $R-CH=CH_2$ $R\!>\!C=CH_2$ or $R\!>\!C=C\!<\!R'$ $R\!>\!C=C\!<\!R'$
1655 w			
1645 w			
1461 m		$A_g + B_{1g}$	δ_s CH_2 and Fermi Resonance interaction with first overtones and combination of correlation-doubled 725 (b_{2u}) modes
1440 ms		$A_g + B_{1g}$	
1418 m		A_g	
1370 w		$B_{2g} + B_{3g}$	ρ_w CH_2
1306 w	Am		
1296 s		$B_{3g} + B_{2g}$	ρ_r CH_2
1170 w		$B_{1g} + A_g$	ρ_r CH_2
1131 m		$A_g + B_{1g}$	ν_s $C-C$
1080 w	Am		
1063 m		$B_{2g} + B_{3g}$	ν_{as} $C-C$
890 w			Feature of $-(CH_2)_n-CH_3$ when n is small
850 w,br	Am		
725 vw	Am		

Notation: Am refers to bands absent from the spectrum of the most crystalline samples but which increase in intensity as amorphous content increases.

A_g etc. refer to the space group
a_g etc. refer to the line group
as = antisymmetric
s = symmetric
ν = stretching mode

δ = deformation mode
ρ_w = wagging mode
ρ_t = twisting mode
ρ_r = rocking mode

Considerable confusion has existed on the precise origin of the Raman bands in polyethylene mainly due to a lack of adequate appreciation of the importance of correlation effects. Now, however, the combination of the depolarization ratios and anisotropic scattering data makes the assignment of the Raman spectra of polyethylene unambiguous. The table given above contains full details of the Raman spectra of this polymer and contains details of the effects of both correlation and Fermi resonance effects. (The latter arises when, in this case, the first overtone of a fundamental is of appropriate symmetry and has a frequency close to that of another fundamental. Interaction occurs and the observed spectra becomes more complex than would normally be expected).

CAREFUL examination of a number of distinctly different polyethylene specimens (high and low density, drawn and non-oriented, extended chain forms and single crystals obtained from solution) shows that the Raman spectra are sensitive to the following factors:

1. *Degree of crystallinity.* This parameter is of considerable technological importance. Briefly, a crystalline polymer is relatively rigid and a non-crystalline more flexible, while drawn fibers are often more crystalline than undrawn monofilaments. The Raman spectrum of a highly crystalline specimen is sharp and clear while that of one of lower crystallinity is more diffuse. This probably arises from two sources:

   a) a lowering of the site symmetry associated with an amorphous region. Further, it is inevitable that in samples of low crystallinity an appreciable proportion of the CH_2 sequences will be non-planar, i.e., the CH_2-CH_2 orientation will not be of the normal *trans* form but will adopt the *gauche* conformation. The random inclusion of such discontinuities within a regular array removes the molecular center of symmetry and hence distorts the observed vibrational spectra and

   b) strictly, the *gauche* conformational CH_2-CH_2 groups are chemically different from the *trans* species. Although the chemical difference is trivial the vibrations are definitely different and therefore aberration of the spectrum of the pure crystalline polyethylene is inevitable in these cases.

2. *Chain folding.* It is an oddity of polymers that they appear to fold within their crystals (although the exact nature of the fold sequences is not understood) (16). In most bulk polymer samples there is evidence for crystallites of 50-150A dimension in the direction of the polymer chains (2). It has been postulated that these regions are made up of single chains folded at the appropriate interval (16). In polyethylene it is again inevitable that *gauche* conformations are involved in these folds, they are probably highly regular and therefore the symmetry of the specimen is largely retained. In highly crystalline bulk polyethylene sharp bands appear and some features associated with *gauche* structures are probably present as weak features.

3. *Molecular weight* As we have already said, the molecular weight of a polymer is not discrete but rather has a wide distribution. One might expect that the vibrational spectra would be sensitive to molecular weight but this is so only at the lower end of the scale. Thus, a specimen of average

molecular weight 500 produces a spectrum different from that of average value 10^5-10^6, but the latter is identical to that of a specimen of average molecular weight 10^4. It would appear that the observable differences arise from the presence of appreciable concentrations of each group in 'light' molecular species not from fundamental changes in the vibrational behavior of the polymethylene chain* (c.f. the vibrational analysis of wide ranges of straight chain paraffins by Schachtschneider and Snyder (3)). To put it another way the relationship between molecular weight and spectral characteristics becomes a correlation between end group concentration and spectra.

4. *End groups* It is by no means essential that a polyethylene molecule terminate with a methyl group. The laser Raman spectra of many samples contain bands near $\Delta \nu = 1650^{-1}$ cm^{-1} due to vinyl groups and this feature too is included in the Table. Chain branching is also important in polymer science as it tends to produce a non-crystalline material. Low density polyethylene is quite highly branched and one would expect the Raman spectra to contain evidence of this. However, any bands characteristic of groups such as:
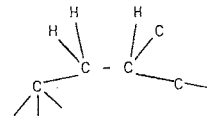
are submerged in the diffuse bands characteristic of the low crystallinity material.

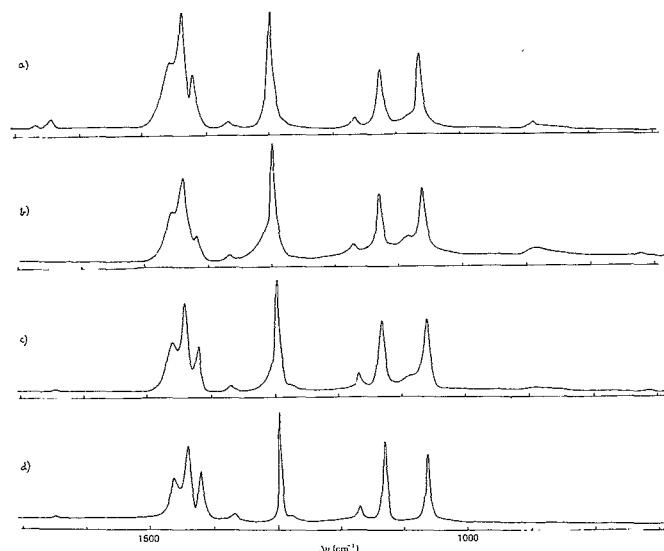Raman spectra from various forms of polyethylene are shown in Figure 2.

Fig. 2 Raman spectra of some polyethylenes. In Fig. 2a the Raman spectrum of a wax lump with a molecular weight around 800 is shown. It melts around 75C. An unoriented film gave the spectrum in 2b. Spectra of high-density, high-melting-point forms with a molecular weight 10^4-10^5 are shown in 2c and 2d. The intensity of the feature at 890 cm^{-1} is a rough inverse indicator of the molecular weight.

Crystallinity, a desirable characteristic from the standpoint of oxidative degradation, is indicated by the sharpness of the bands at 1300 cm^{-1} and 1400 – 1500 cm^{-1}. Thus 2b with a crystallinity of 50% exhibits the widest Raman lines; 2d with almost total crystallinity (the extended chain form) shows the narrowest lines. When molecular chains terminate in a vinyl grouping the features around 1650 cm^{-1} appear.

* In a sense this is not strictly true because series of very low frequency Raman bands have been observed in pure straight-chain hydrocarbons of relatively restricted length (up to $C_{96}H_{194}$) due to accordionlike motions of the planar zig-zag backbone. Their frequencies are sensitive to chain length.

The consideration of molecular weight, degree of crystallinity and so on is not nearly so recondite as might be thought at first. Household items made of polyethylene — buckets, bowls, etc. — have to combine as hard a surface and as high a strength and rigidity as possible with excellent resistance to impact. High density, i.e. highly regular and very crystalline, material satisfies all of the requirements except the last whereas the lower crystallinity of low density polyethylene results in a greater impact resistance but at the expense of hardness. So a plastic with intermediate properties is actually specified. In the construction industry polyethylene sheet is often spread as a water barrier. The material obviously has to be impermeable but also able to stretch over sharp irregularities as it deforms over the rubble beneath the concrete foundation. Oriented (i.e. stretched) polyethylene is clear, strong and impermeable but incapable of stretching. The best choice is farily thick non-drawn sheet. It can deform up to seven times its original length without rupture and since it does not contain plasticizer it does not deteriorate markedly with age. On the other hand oriented polyethylene is popular for packaging since it can be welded easily with a hot metal surface. Further, under heat the orientation relaxes and the film shrinks tightly around the object inside the wrapper.
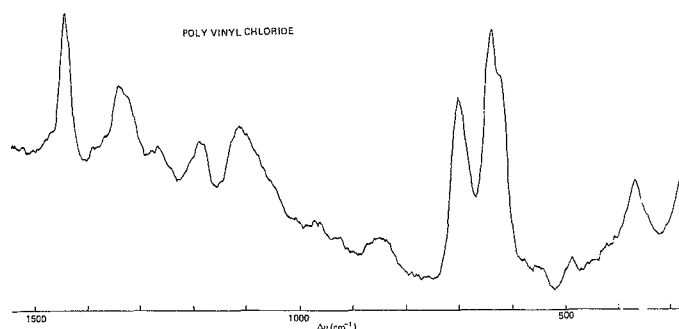

POLY VINYL CHLORIDE

Fig.3 The Raman spectrum of a commercial sample of unplasticized PVC in powder form. The low stereoregularity of the molecules here cause the broadness of the bands in this spectrum. As prepared, PVC is a tough, brittle material completely unlike the synthetic leather and plastic tubing, the most familiarly encountered forms of this polymer. To make PVC soft and resiliant a plasticizer is added (by proportion between 1 and 20%) which acts as an intermolecular lubricant. Plasticizers are liquids, e.g., dioctyl phthalate. Fortunately for the trade they do have some slight volatility; therefore garden hoses left in the sun gradually revert to tough, brittle materials in need of replacement!

Polyvinyl chloride (PVC)

An amorphous stereoirregular material, vinyl polymers are formed from units based on two stero-isomeric units (I) isotactic, (II) syndiotactic, or a mixture producing "heterotactic" specimens.

(I)   (II)
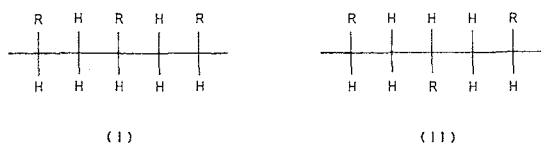
Using specially prepared catalysts it is possible in nonpolar hydrocarbons to restrict the polymerization process to produce one tactic form (e.g. propylene with a Ziegler catalyst yields isotactic polypropylene). When prepared without a stereospecific catalyst the product is of varying structural quality; it oftens tends to be syndiotactic when prepared at low temperatures and of indefinite tacticity at higher temperatures. This heterotacticity tends to give rise to species of low crystallinity.

In general both vinyl and vinylidene polymers give good quality Raman spectra. This is especially so for isotactic hydrocarbon polymers, such as polypropylene (17) and polystyrene (18). A reduction in stereoregularity is normally accompanied by a loss of sharpness in most of the features in the Raman spectrum. In a material such as polyvinyl chloride, which is only commercially obtainable in states of indefinite tacticity and crystallinity (as opposed, for example, to polypropylene), the Raman spectrum contains many broad yet prominent bands. This is illustrated in Figure 3.

A full vibrational analysis in terms of the fundamentals of the space group of the unit cell is not of much value since the unit cell of syndiotactic PVC is only to be found in vanishingly low concentration in the available samples of the polymer. Most of the spectrum arises from the majority of the molecules, i.e., those in a less regular, almost random, arrangement. As a consequence a lower level of rigor is acceptable in the analysis of the vibrational spectra of such polymers. Only slight changes are discernable between the Raman spectra of PVC samples of differing degrees of tacticity and crystallinity (19). Admittedly the range of samples available were very limited but there were no apparent changes in the spectra upon the introduction of applicable amounts of plasticizer (up to 10%), other than bands due to the additive itself.

The naive approach to the description of the origin of the spectra, i.e., one based on characteristic group frequencies appear to work satisfactorily in these PVC samples. Further, the observation of relative insensitivity to plasticizer and crystallinity leads us to presume that the spectral characteristics of these largely random specimens are those characteristic of a short sequence of atom containing all the appropriate functional groups. Chain-chain interactions will be largely random and will therefore contribute to the diffuse nature of the spectra rather than give rise to discrete correlation multiplets.

This situation contrasts with that in polypropylene where samples of widely different tacticity and crystallinity are available. Further, the pure tactic forms are obtainable in highly crystalline states. The Raman spectrum shows marked changes with substantial changes in stereoregularity and this is illustrated in Figure 4.
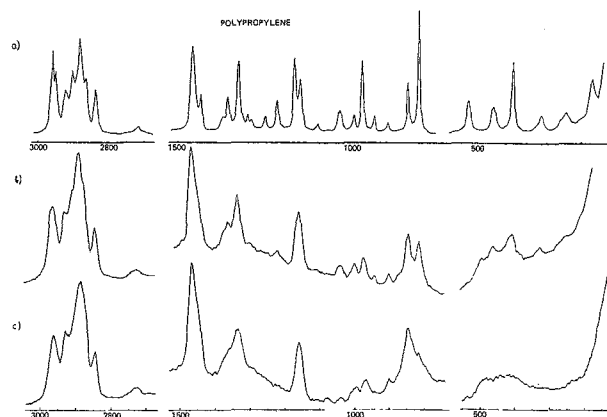

POLYPROPYLENE

Fig. 4 The Raman spectrum of polypropylene. The intensity scale of the first region (around 3000 cm^{-1}) is presented at x½ that of the remainder. Samples with molecular weight around 10^5 give different spectra according to the degree of stereoregularity their molecules possess. In Fig. 4a the spectrum of an oriented and annealed laminate of high crystallinity (≃.90%) isotactic PP contains a series of very sharp bands. An isotactic PP lump of lower crystallinity (≃.60%) gives a more diffuse spectrum as shown in Fig. 4b. The detail in the spectrum is further decreased when an atactic PP lump of very low crystallinity is examined (Fig. 4c).
(Spectra available through the courtesy of Mr. D.S. Watson)

Our detailed knowledge of the vibrational spectra of PVC is limited mainly because it is difficult to produce specimens of good tacticity. Once this is done a detailed analysis of the infrared and Raman spectra will be possible. Careful studies of the spectra of commercially important PVC specimens will give information on the structures involved and, with care, the molecular effects of plasticization may well be revealed in the near future.

Rubbers

The somewhat diffuse Raman spectra of natural rubber, Gutta Percha and synthetic poly *(cis*-isoprene) and poly *(cis* 1,4 butadiene) (20 all of low crystallinity, have been known for some time but our understanding of the spectra is still far from complete. Elastomers, although heavily cross-linked, are known to increase in crystallinity and orientate under stress but no advantage has yet been taken of the Raman method in studying the nature of these phenomena. One would think that the examination of the spectra particularly at high stress and especially those close to rupture could be particulary revealing.

Sulphur-containing compounds are well known to give rise to strong Raman bands and recent attempts at the elucidation of the reactions involved in sulphur vulcanization processes have been reported. It has been long established that compounds containing the S-S link normally produce prominent and polarized Raman bands near $\Delta \nu = 520$ cm^{-1}, while aliphatic C-S links produce features around 600 cm^{-1} (21). Recently, reports of preliminary studies of vulcanized rubber and sulphur containing model compounds have appeared (22). It definitely seems probable that Raman spectroscopy will produce valuable information in this field once extensive and probably protracted studies have been completed on this system, which is already known to be complex. Peroxide vulcanization although currently unfashionable seems to be of recurring interest. This too is accessible to Raman study as the O-O link gives rise to bonds near 860 cm^{-1} and C-O to features around $\Delta \nu = 1100$ cm^{-1}. In combination with infrared examination one should be able to expect equally meaningful conclusions in this field.

The Nylons

The term nylon is a widely accepted generic name for straight chain polyamides. Inevitably, a jargon exists in the trade which can be illustrated as follows:

Nylon 'a' has a repeat -[NH-(CH$_2$)$_{a-1}$-CO]-$_n$; thus Nylon 6 is a polymer prepared from NH$_2$-(CH$_2$)$_5$COOH. Nylon 'ab' has a repeat -[NH-(CH$_2$)$_a$-NH-CO-(CH$_2$)$_{b-2}$-CO]-$_n$ and is thus prepared from condensation of NH$_2$-(CH$_2$)-NH$_2$ and HOOC-(CH$_2$)$_{b-2}$-COOH.

Nylon 6 and 6/6 are tough, resilient, high melting molding materials ideal for gears, wheels and bearings in light machines, but the former is of rather low crystallinity. In addition both form excellent fibers and therefore are very important in the textile industry. Another widely used Inylon is 6/10. The remainder have one or more inferior properties or are uneconomical to manufacture and so are rarely encountered.

Commercial laboratories are frequently called upon for qualitative analysis of a sample thought to be a nylon. If a suitable sample is prepared (by microtoming or casting a film) infrared spectroscopy can confirm that the specimen is a polyamide. But it is by no means easy to distinguish one
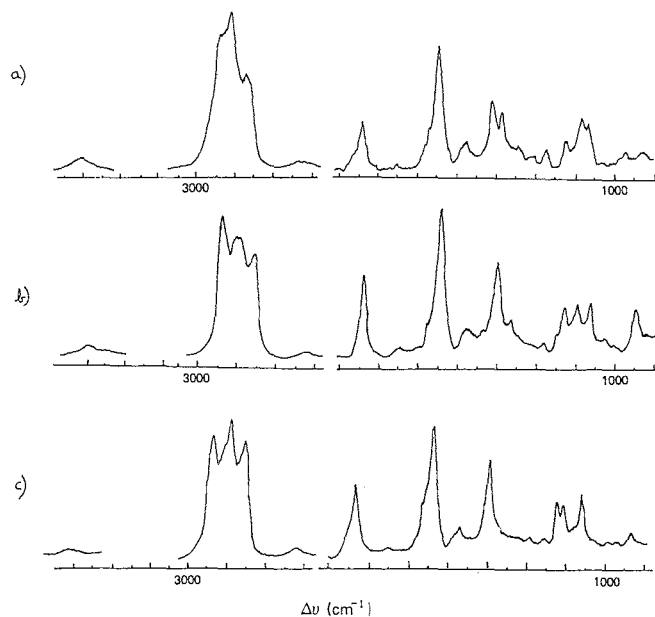

Fig. 5 The Raman spectra of some Nylons. The intensity scale of the region 3300 - 2700 cm^{-1} is presented at x½ that of the region 1700-900 cm^{-1} Chips of some chemically very similar Nylons give quite different Raman spectra in the 1300-1000 cm^{-1} region, which enables them to be easily distinguished. Samples of Nylon 6 (Fig. 5a), Nylon 6/10 (Fig. 5b) and Nylon 11 (Fig. 5c) needed no preparation for examination by this technique.

nylon from another because the infrared spectrum is dominated by bands due to the vibrations of the amide groupings. Here, as with so many other polymers, the Raman spectra are complimentary to the infrared because the Raman bands arise predominantly from the vibrations of the backbone CH$_2$ sequences (23). In consequence, there are considerable differences between the Raman spectra of various nylons, as illustrated in Figure 5. It is worth noting that, in contrast to infrared, no preparation of samples is necessary in the Raman method.

In the solid phase the association of individual chains of the nylons is dominated by the interaction of a C = O group on one chain with an N-H on another through a hydrogen bond. This effect which is, of course, very similar to that found in the association of polyalcohol or polyimine chains is quite different from that normally found in the poly-hydrocarbons or other relatively nonpolar resins. Here chain-chain interactions in the solid phase (which, as we have said, in many ways dominate their mechanical properties) arise from close packing of neighboring chains and weak Van der Waals interaction. As a result, the chains often adopt configurations in the solid phase which are quite different from those found in solution or in the melt. In the nylons the hydrogen bonding acts like a crosslink. Its energy is so high that a regular lattice of hydrogen-bonded amide groups is established and the CH$_2$ sequences simply bridge these in whatever configuration they are constrained. The very strong interchain forces encountered in these nylons make them tough, resilient and of high melting point and tensile strength but the configurations within the CH$_2$ sequences must influence their properties.

Thus, it is of considerable value to determine the orientation of CH$_2$ sequences in these polymers. None of the other structural techniques available to polymer chemists are likely to give information in this particular area; NMR, for example, is restricted mainly to solutions and melts while infrared is burdened by the limitations stated above.

It is known in the polyamides that the carbonyl group lies approximately at right-angles to the backbone axis and this in turn gives rise to the familiar dichroism in the absorptions at approximately 1700 cm^{-1} in the infrared spectrum of an oriented specimen (24). In anisotropic Raman scattering experiments in the same vibrational energy region on oriented nylon 6.6 specimens it was demonstrated that the maximum polarizability change occurs along the C = O bond during this vibration (10). We have already said that it is essential to avoid seeing analogous significance in infrared dichroic and anisotropic scattering data since analysis of the latter, although often very fruitful, is decidedly complex.

However, it would seem that, provided attention is concentrated on vibrations of pendant groups, it is possible to relate the anisotropic data to the orientation of functional groups relative to the draw axis in oriented specimens such as an individual fiber or films. Clearly this observation may well prove invaluable in the study of new polymers or those where our knowledge of their structure is relatively incomplete.
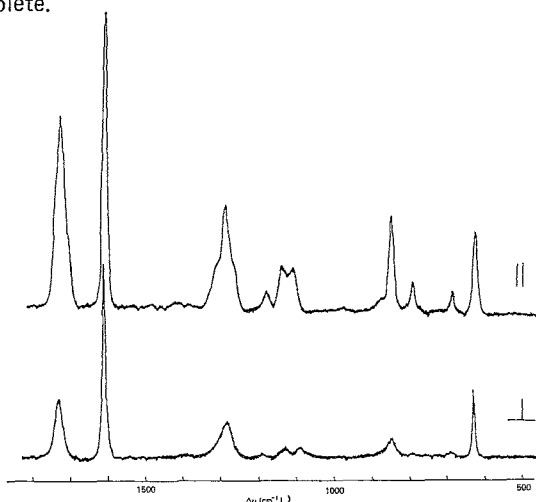

Fig.6 The Raman spectrum from a PET film, thickness 25μ (o.oo1 inch). By analyzing the scattered Raman light with respect to the laser polarization, depolarization ratios of the Raman bands can be obtained. The symbols ‖ and ⊥ denote the relative orientation of laser polarization and analyzer. Depolarization ratios give information about the symmetry of molecular vibrations. Films are easy to study by the Raman technique and thick films, which are hard to examine by infrared spectroscopy, present no problems.

Polyethylene terephthalate (PET)

A large number of the bands in the Raman spectrum of this polymer are due to the *para*-disubstituted benzene ring, but there are important features due to the ester linkages. Part of the spectrum is shown in Figure 6. The overall appearance of the Raman spectrum of PET is quite sensitive to the state of crystallinity of the sample (25). This polymer has a wide range of crystallinity, which can range between 0% (completely amorphous) and 60%. As commercially prepared from the melt, monofilaments and films are always amorphous since rapid quenching occurs as the melt leaves the spineret or slot. Drawing and annealing create and enhance the crystallinity of a sample, improving its textile properties.

A significant contribution would be made to the technology of PET if a reliable and convenient method of crystallinity determination could be devised. It looks as if, with development, Raman spectroscopy may well be able to provide just such a method because the spectrum of the bands primarily associated with the ester groupings are very sensitive to crystallinity and/or orientation (Fig. 7). The

appearance of a doublet with the lower frequency component stronger than the other is indicative of appreciable crystallinity. It is clear that drawing and heat setting are particularly satisfactory at enhancing crystallinity. Further, we find it technically easy to record Raman spectra from fiber bundles, single large diameter fibers and thick or thin films.
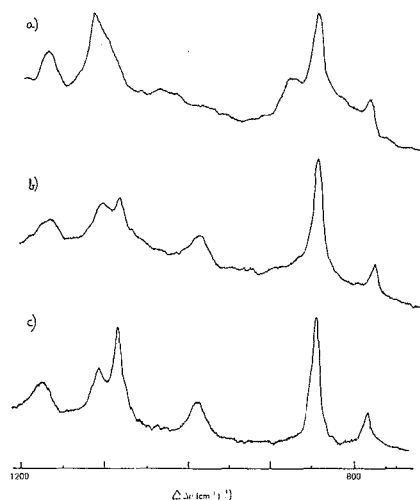

Fig. 7 The partial Raman spectra from some PET fibers. These are very important in the textile industry in that they are "crease resistant" yet permanently creasable. If the fiber is bent and heated above its glass transition temperature (around 100C) and cooled it will set. This is the basis of the permanent pressing process. Body heat and the pressures normally encountered in wear will not permanently deform the fibers. Fig. 7a shows the spectrum from fibers spun from the melt. When these are annealed above the glass transition temperature of PET crystallization sets in, as shown by the sharpening of the Raman bands. (Fig. 7b) Textile fibers are melt spun, drawn (to impart molecular orientation and therefore strength) and annealed (to impart good "wash and wear" characteristics). The Raman Spectrum of such fibers (Fig. 7c) indicates a higher degree of crystallization in them as opposed to 7a and 7b.
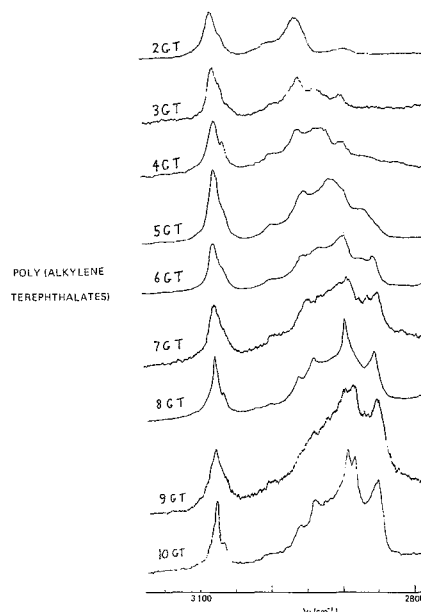

Fig. 8 The Partial Raman spectrum of polyalkylene terephthalate samples in chip form. The notation mGT represents the polymer: -[CO.C$_6$H$_4$.CO.O.(CH$_2$)$_m$.O] $\frac{}{n}$. The Raman bands around 3100 cm^{-1} are associated with the aromatic C-H bonds. The features around 2950 cm^{-1} are due to methylene groups adjacent to oxygen atoms, whereas those bands in the region 2950-2850 cm^{-1} arise from methylene sequences. In the higher members of this series of polymers there are similarities to the Raman spectrum of polyethylene in this last spectral region. Relative intensities of the bands due to aliphatic and aromatic C-H stretching modes can be measured to determine which member of this series is under study.

The polyalkylene terephthalates are of the general types $-[CO.C_6H_6.CO.O.(CH_2)_m.O]_{\bar{n}}$, In PET m has the value of two. An interesting feature in the Raman spectra of these polymers is the information available in the C-H stretching region ($\Delta\nu = 2700 - 3100$ cm^{-1}) (26). Figure 8 shows the spectra from some of these polyesters starting from PET through to polydecamethylene terephthlate. Features due to aromatic CH links, CH_2 groups adjacent to oxygen atoms and extended CH_2 sequences can easily be discerned. The intensity of the bands associated with the aliphatic C-H stretching modes, relative to those of the aromatic species, are found to increase almost linearly with the number of CH_2 groups in the repeat unit. Clearly this is of analytical significance.

Copolymers

Our experience of the Raman spectra of copolymers is much more limited than that of homopolymers, however, some points must be made because the materials are as important as the homopolymers.

A knowledge of the quantitative analysis of a mix of monomers prior to copolymerization does not indicate the composition of the copolymer produced since the reactivities of the components are not identical. As a result it is essential to analyze the copolymer for its constituents and this is frequently tricky. The Raman intensity of bands in a multicomponent system follows a linear relationship with concentration. By contrast in infrared absorption Beer's Law applies and the relationship is exponential.

As a result the Raman method is relatively insensitive to species present in low concentration and so is not as useful for analyzing copolymers containing small quantities of one monomer as infrared spectroscopy.

Most copolymers are valuable because they have a lower crystallinity than their parent homopolymers (and therefore greater flexibility, elasticity and impact- resistance). An example will show the relevence of this characteristic. In the interest of economy many automobile air-filter cases and heater ducts are now made from polyethylene-propylene. The requirements in these applications are a little unusual. The material must be very resistant to vibrational fatigue, dimensionally stable, resistant to heat, gasoline, oil and water. Bakelite was used some years ago for heater ducts but proved very brittle. Plasticized PVC is not appropriate because it swells rapidly in paraffinic solvents and the plasticizer diffuses away if the material is kept hot. On the other hand polyethylene-propylene is cheap, readily obtain- able and satisfies all the requirements. The lowered crystallinity in copolymers results in diffuse Raman spectra and therefore a loss of detailed information.

However, all is not completely lost and preliminary studies (25) have been made on ethylene/propylene, ethylene/butene and ethylene/vinyl chloride copolymers. It is clear that a minority component is not discenrable below ~5% concentration in copolymers formed from two similar, chemically related monomers. When the components of a copolymer are all present in appreciable amounts representa- tive features can be found for each component and the composition of the polymer can be deduced. In block copolymers, where extended arrays of one monomer are present, the tacticity within the blocks is indicated in the Raman spectrum. It is hoped that more structural information will be available after detailed Raman studies.

Biopolymers

There has been much activity of late in the biological applications of laser-Raman spectroscopy. Advantage has been taken of the accessibility of aqueous solutions and gels to this type of study. Systems studied include cellulose and its derivatives (19), DNA, (27) lysozyme and a-chymotrypsins (28), as well as simple polypetides (29). The major biochemically interesting feature appears to be the accessibility of aqueous systems and therefore the lack of necessity for preparing dry crystalline analytical samples. These are hardly typical of the molecules in real life and structural conclusion based on them may be spurious. Thus, for example, DNA specimens examined in aqueous solution but prepared from various sources have been shown to have significantly different Raman spectra (30). It is too early to judge the value of laser-Raman spectroscopy in biochemistry but it seems likely that by taking advantage of its micro-sampling capability and the accessibility of aqueous media highly specific analytical and structural information will be forthcoming in the near future.

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$\mathbb{T}$HERE is little chance that Raman spectroscopy will make a significant contribution to polymer science unless the polymer research institutes and the manufacturing industry are sufficiently convinced of its potential to invest in Raman instrumentation. Certainly the strivings of academic establishments are unlikely to produce significant results rapidly since so few laboratories have the wide range of specialist samples and the ability to provide essential ancillary information about them. As long as the majority of Raman spectrometers remain in the control of academic spectroscopists (many of whom in turn feel that molecules containing more than six atoms are intractable) it is unlikely that very much spectroscopic information will be forth-coming in polymers.

ABOUT THE AUTHORS

Doctors Gall and Hendra are both members of the Chemistry Department at the University of Southampton, SO9 5NH, England, where their polymer work began early in 1967. The studies have aroused substantial interest among other uni-versities, research institutes and industrial concerns en-couraging continued extension of the range of their in-vestigations.

Dr. Hendra is also coauthor with T.R. Gilson of the recently-published LASER RAMAN SPECTROSCOPY. This well-referenced volume is an excellent guide for the chemist interested in laser Raman spectroscopy and concerned about instrument design, sample handling and the necessary theory. The book was published by Wiley-Interscience, London (1970).

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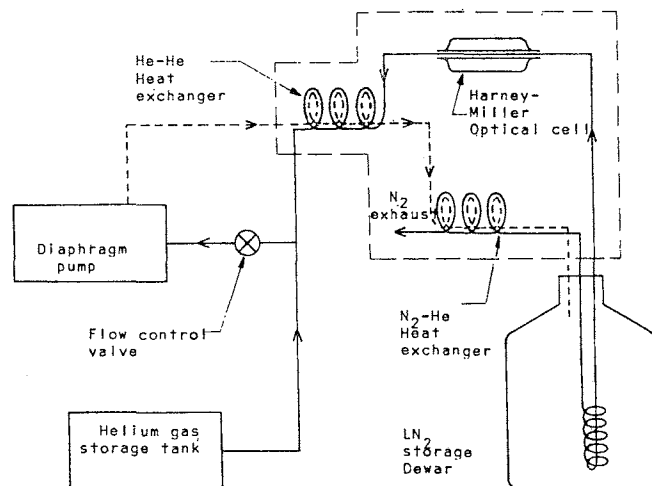30. M.C. Tobin, private communication.

Modification of a Harney-Miller Cryostat for Helium Operation

by Ross H. Freeman, Department of Physics,
University of Illinois, Urbana, Ill. 61801

A persistent problem in Raman scattering from highly polished crystals in the back-scattering geometry has been rotational scattering from oxygen and nitrogen. In a cold nitrogen atmosphere, such as is present around the sample when the Harney-Miller cell is operated conventionally, the problem is even worse than in air. A simple solution is to cool the sample with recirculated helium.

The scheme shown has been devised to cool samples to below 100 K. The heat exchangers are simply two copper tubes, one inside of the other, bent into a few turns of a spiral. Both the liquid nitrogen blow-off gas and the cool helium after it has passed over the sample serve to pre-cool the warm helium from the pump. The flow control valve regulates the sample temperature. The entire system is kept at approximately 1 lb. over-pressure with the helium tank. Tubing within the dash line is all insulated. The exchanger lowered into the LN$_2$ storage dewar is a tightly wound spiral of 1/4" o.d. copper tubing.

In operation, air is first flushed from the He tubes and cooling started as soon as possible. In view of the substantial rate of diffusion of helium through fused silica at room temperature, it is probably unwise to operate this sytem with helium near room temperature. Argon would be a good substitute, but has the problem of liquifying in the tubes at nitrogen temperature.

The system as shown, but without the He-He heat exchanger was somewhat less efficient in LN$_2$ consumption than the usual Harney-Miller scheme. Inclusion of the He-He exchanger should make it more efficient.

THE IODINE FILTER TECHNIQUE IN RAMAN SPECTROSCOPY

OR

HOW LOW CAN YOU GO?

by

Gary Hibler, Joseph Lippert and Warner L. Peticolas
Department of Chemistry, University of Oregon, Eugene, Oregon 97403

Raman spectra below 50 cm^{-1} are difficult to obtain on solid samples other than single crystals because of interference from the intense Rayleigh scattering. Recently a technique which consists of interposing a cell filled with gaseous iodine has been found to attenuate the Rayleigh scattered light up to 2500 times and so allow observation of both Brillouin (1), and Raman (2,3,4) scattered light within 3 cm^{-1} of the 5145.36A argon laser line. This device should be particularly practical for studies of crystals and polymers having vibrations which involve large collections of atoms or molecules so that simply by a mass effect the corresponding frequencies are very low. Indeed, the only reported work with the iodine filter to date involves either crystals (2) or polymers (3,4).

One potential application we believe to be very exciting is the study of low-frequency motions of biological polymers. Our initial work shows that biological macromolecules do possess low-frequency vibrations. These motions must involve at least large parts if not the whole macromolecular structure. The idea that such motions are important in the biological activity of the macromolecule cannot be discounted; nor can a tool for discerning the molecular basis for biological activity.

It is possible that the filter will improve the Raman spectra of either simple liquids or gases despite the fact that they do not possess low-frequency vibrations. However, the filter technique may be of more interest in studying the rotational Raman spectra of gases though several questions such as the possibility of Doppler shifts in the scattered light remain unanswered. Simple liquids possess low-frequency Raman bands arising from intermolecular vibrations, librations, etc. They are very broad, are often quite strong and may extend to very low frequencies. Just how applicable the iodine filter technique will be for liquid materials is, accordingly, difficult to predict.

THEORY OF OPERATION

If one examines the electronic-vibrational-rotational absorption lines of iodine vapor, he finds only two such lines with non-negligible transition probabilities which fall within the frequency range of the gain curve of the 5145.42A laser line (5,6). These transitions have the identical frequency: 19,429.27 cm^{-1} or 5145.42A in air. One of these is a transition from the 12th rotational level of the zeroth vibrational level of the ground electronic state $(X^1 \Sigma_g^+)$ to the 11th rotational level of the 43rd vibrational level of the $B^3 \Pi_{ou}^+$ electronic excited state i.e., O-43 P (12). The other is O-43 R (14) between the same electronic levels. Other rotational-vibrational levels within the frequency range of the gain curve possess too low a transition probability—about 4% of the O-43 P(12), R(14) lines (5)—to provide effective absorption of the laser frequency. For iodine vapor to work as a filter for the Rayleigh scattered argon laser light around 5145.36A the laser must be single-moded and the frequency of the single mode adjusted to fall at 19,429.27 cm^{-1}

Single-moding of the laser is necessary because of the extreme narrowness of the iodine rotational line (250-300 MHz or about 0.01 cm^{-1}).

The Doppler-broadened gain curve of the 5145A line of argon is about 8 GHz. Without an etalon in the cavity 60-80 modes oscillate under this curve with random amplitude and phase; mode separation, as determined by the cavity dimensions is 101 MHz. Insertion of an etalon into the cavity spreads the modes to 8-9 GHz and therefore only one mode at a time can fall under the gain curve and be amplified. The width of the single mode is on the order of 8 MHz; it is easily blocked within the 300 MHz wide rotational line of iodine. Adjusting the etalon changes the cavity length thus sweeping the cavity mode through the gain curve and allowing one to match the cavity mode with the iodine rotational line (Fig. 1). Matching of the iodine absorption with one of the single axial modes is accomplished by adjusting the etalon and watching the 5145A light appear and disappear at the rear of the filter.
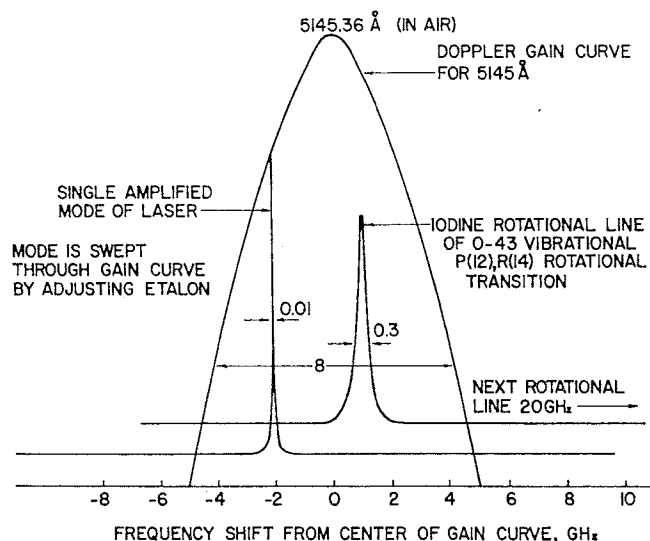

FIG. 1. Intensity of single mode of Ar 5145A vs. frequency as mode is swept through gain curve. About 3/4 of the way through the gain curve the single mode matches the transition and is absorbed.

SINGLE MODING THE LASER

Depending on the laser model, single moding through the insertion of an etalon may or may not be possible. Once the laser is single moded, its output frequency may remain stable for 15 minutes or longer. The latest etalons, fabricated of Cervit with its almost negligible coefficient of expansion, have been found to provide stability of laser operation for hours on end.

After installing the etalon in the cavity at least an hour is needed for some lasers (e.g. CRL Model 53) to reach thermal

equilibrium. Any laser power change, while single-moding, may also require warm-up time. Adjustments of cavity mirrors and etalon have no affect on the stability. We have found that once the laser is stabilized it will remain satisfactorily single-moded for about 30 minutes. The stability of the single mode can be improved by utilizing a beryllium oxide plasma tube. The BeO bore operates at 80C compared with 1000C for the graphite bore. This lower operating temperature reduces the warm-up times to a few minutes and eliminates the microphonics due to boiling of the cooling water. Insertion into the cavity of a piezo-electric mirror mount which automatically maintains single-mode operation by responding to the output of two photodiodes placed on both sides of the filter greatly improves the long-term single mode stability. This technique has been successfully developed by Dr. Paul Lazay at Bell Telephone Laboratories.

Single mode operation reduces the laser power by 50%. This reduction in power may pose a problem in recording weak spectra.

CONSTRUCTION OF THE FILTER

The cell is made of 3 cm diameter Pyrex tubing with optical flats for windows. A 50-mm cell, heated to 80C effects up to 2500X reduction in 5145A light but only a 20-40% reduction in Raman intensity.

To obtain optimum spectra at low frequency the iodine filter should be designed to extinguish the maximum amount of 5145A light with minimum loss of Raman light. We find that a filter temperature of $70 \pm 20C$ yields the best spectra. Above this temperature range the filter absorbs the Raman signal as well as the laser emission. Absorption of the Raman signal is the result of pressure broadening of the iodine rotational lines. Below this temperature range enough laser light passes through the filter to obscure the very low frequency Raman spectra.

The broad temperature range in which the filter will adequately function makes precise temperature control unjustified. Figure 2 shows a series of 3 low-frequency Raman spectra of l-cystine taken at different iodine filter temperatures. Cell temperatures were measured with a digital thermistor thermometer. The thermistor probe was inserted between the cell wall and the heating tape. As the filter temperature is raised one notices an increase in Rayleigh absorption by the filter. The increase in Rayleigh absorption can easily be seen in spectra A, B, and C. Following this reduction of Rayleigh light is a reduction in the ghost intensity at $23 \ cm^{-1}$. The ghost is observed in spectra A and B but is clearly absent in C.

Figure 3 shows the effect of temperature on the Raman intensity as the temperature is raised to 95C after the alignment of the sample was slightly improved. Between 50C (D) and 95C (E) there is considerable reduction in Raman intensity without any noticeable decrease in Rayleigh intensity. Spectrum F is a 5X expansion of E; notice the appearance of a weak emission line at $30 \ cm^{-1}$

The conclusion from these experiments is that temperature control is not a critical factor in obtaining low-frequency Raman spectra of strong Raman scatterers.
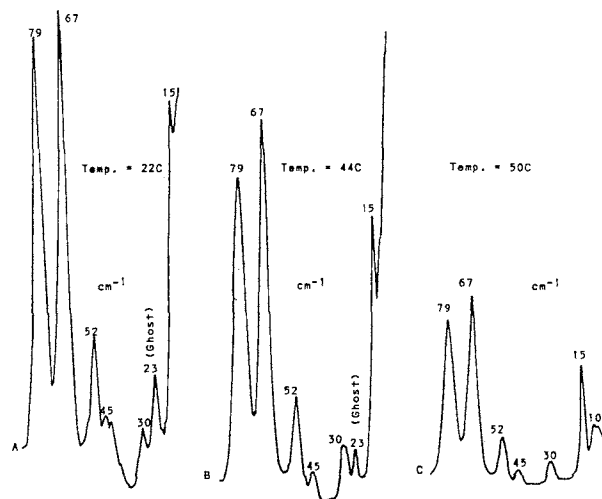

FIG. 2. Low frequency Raman spectra of l-cystine taken at the iodine temperatures marked. Increase in Rayleigh absorption is easily seen.
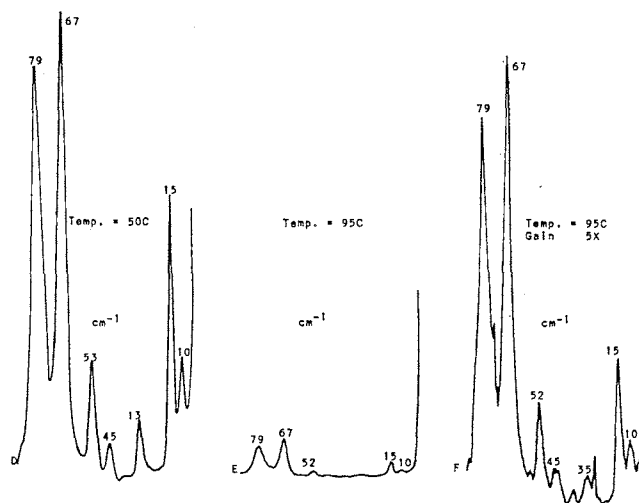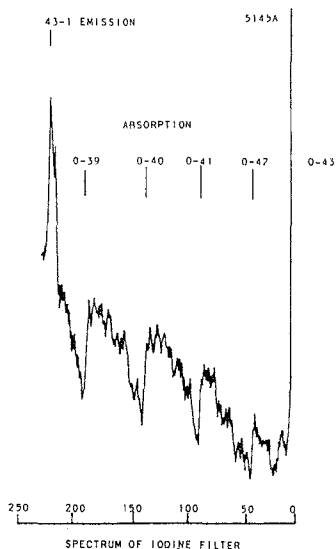

FIG. 3. Low-frequency Raman spectra of l-cystine at iodine temperatures of 50C and 95C showing that the latter temperature is too high. There is a significant reduction in Raman intensity with a negligible reduction in Rayleigh intensity. A 5X change in gain does not yield as good a spectrum as at 50C.

PROBLEMS WITH THE IODINE FILTER

Operation of the filter above 95C causes excessive loss in Raman intensity. This loss can be attributed to pressure broadening of the iodine rotational lines.

Raman spectra beyond 200 cm^{-1} show intense resonance fluorescence bands of iodine (7). The doublet at 213 cm^{-1} in Figure 4 is one of these. These peaks are observable only when the filter is tuned so that the single mode matches the iodine rotational line and are proportional to the amount of Rayleigh light absorbed by the filter. With samples which are low in Rayleigh scattering such as liquids these peaks are too weak to be observed.

43-1 EMISSION   5145A

ABSORPTION

0-39   0-40   0-41   0-47   0-43

250   200   150   100   50   0

SPECTRUM OF IODINE FILTER

FIG. 4. A piece of paper yields an essentially Raman-less spectrum. Thus the spectrum is that of the iodine filter itself. Unless the actual sample is an exceedingly poor Raman scatterer, the iodine spectrum will not interfere.

Fig. 4 is a low frequency spectrum of a piece of white paper aligned so the laser beam is incident on the side of the sample away from the slit of the monochromator. The gradual increase in background intensity can be attributed to a slow drift in the single-mode frequency. The structure in the spectrum between 0 and 200 cm^{-1} is believed to come from absorption of the background signal by the 0-39, 0-40, 0-41 and 0-42 X→B transitions in iodine. This structure should be a problem only for those samples which are exceedingly weak Raman scatterers.

When recording spectra without the iodine filter the etalon should be removed because drifting of the laser power can give a sawtooth appearance to the spectra. This drifting only occurs when the etalon is adjusted so that all spots coincide with the main reflected beam. In this etalon position the light reflects directly back into the cavity and gives nearly full laser power which is critically dependent on etalon angular position. In single mode operation the laser power is quite stable, and smooth spectra can be obtained.
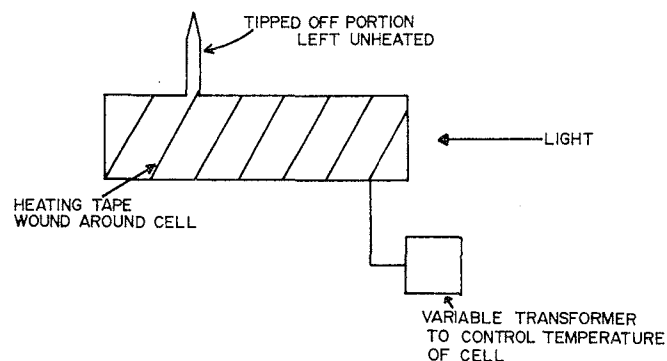
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TIPPED OFF PORTION
LEFT UNHEATED

LIGHT

HEATING TAPE
WOUND AROUND CELL

VARIABLE TRANSFORMER
TO CONTROL TEMPERATURE
OF CELL

FIG. 5 Iodine filter showing tipped-off portion of the cell that is left unheated. Excess iodine crystallizes in this unheated portion preventing iodine from collecting on the windows.

1441 IODINE FILTER CELL, 50-mm long with fused windows 35 mm ϕ; requires heating tape and small autotransformer.   **$100.00**