

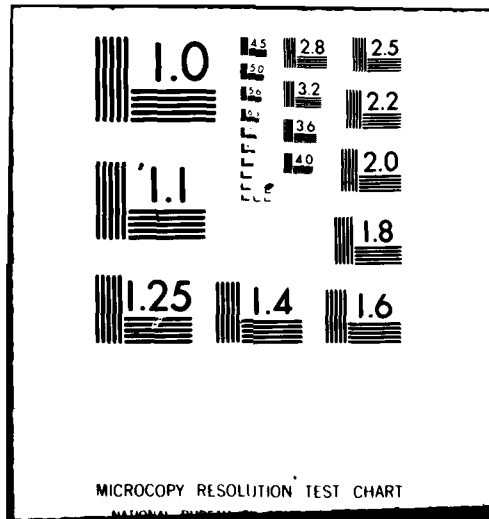
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RAMAN STUDY OF SOLID STATE REACTIONS IN POLYMERIC MATERIALS.(U)
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RAMAN STUDY OF SOLID STATE REACTIONS IN POLYMERIC MATERIALS

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ABSTRACT (Continue on reverse side if necessary and identify by block number)

This research accomplished under this grant focused on intermolecular interaction and reaction dynamics of several monomeric as well as polymeric systems. Specifically the following research areas were investigated: (a) Vibrational relaxation in organic solids. This study was necessitated from a need to formulate conditions under which a selective vibrational as well as a phonon excitation could be used to produce novel products by state selected chemistry. (b) Phonon spectroscopy of reactions in solids. This

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cont novel method was used to determine the mechanism of reactions and the role of phonons in determining reactivity of solids. (c) Raman phonon study of pharmaceutical solids in relation to their bioavailability. The method of Raman phonon spectroscopy was introduced as a convenient method to study various solid state forms of a given drug and their physical and chemical stabilities. (d) Structure and dynamics of the conducting complex: (Benzophenone)₉ (KI)₂ I₇ CHCl₃. Some preliminary work was done on this novel group of conducting materials. (e) Phonon spectroscopy of polymeric alloy. This new method was introduced to determine the molecular homogeneities of polymer blends.

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FINAL REPORT

PROJECT: RAMAN STUDY OF SOLID STATE REACTIONS IN POLYMERIC MATERIALS

SPONSOR: USAFOSR

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GRANT #: AFOSR 800287

PRINCIPAL INVESTIGATOR: Dr. Paras N. Prasad
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RESEARCH ACCOMPLISHED UNDER AFOSR 800287

The research accomplished under this grant focused on inter-molecular interaction and reaction dynamics of several monomeric as well as polymeric systems. Specifically the following research areas were investigated: (a) Vibrational relaxation in organic solids. This study was necessitated from a need to formulate conditions under which a selective vibrational as well as a phonon excitation could be used to produce novel products by state selected chemistry. (b) Phonon spectroscopy of reactions in solids. This novel method was used to determine the mechanism of reactions and the role of phonons in determining reactivity of solids. (c) Raman phonon study of pharmaceutical solids in relation to their bioavailability. The method of Raman phonon spectroscopy was introduced as a convenient method to study various solid state forms of a given drug and their physical and chemical stabilities. (d) Structure and dynamics of the conducting complex: $(\text{Benzophenone})_9 (\text{KI})_2 \text{I}_7 \text{CHCl}_3$. Some preliminary work was done on this novel group of conducting materials. (e) Phonon spectroscopy of polymeric alloy. This new method was introduced to determine the molecular homogeneities of polymer blends.

a) Vibrational Relaxation in Organic Solids:

An important aspect of a dynamical model is to determine specificity in phonon induction of solid state reactions. In order that a large population of selective and coherent vibrational excitation can be achieved to study its effect on reactivity it is necessary that vibrational relaxation be slow. For this reason it is important to investigate and characterize vibrational relaxation and dephasing in organic solids. This study was undertaken during the tenure of the Air Force grant.

Two proto systems were investigated. The dephasing of a localized internal vibration of the naphthalence crystal was investigated by studying the temperature dependence of the line width, the line shape and the line frequency. It was found that at liquid helium temperatures the contribution to dephasing due to physical processes, which are of interest to us, is almost negligible. The observed dephasing can entirely be explained due to inhomogeneities. Even at higher temperatures, the T_1 -relaxation time, which is responsible for decay of the vibrational excitation, is very long. This result is extremely encouraging from the point of view of being able to selectively pump a high degree of vibrational excitation of a given mode. Another system in which we have studied vibrational relaxation is p-bromochlorobenzene. This system in crystalline state exhibits orientational disorder and our motivation was to study phonon relaxation in a structurally disordered system for which both anharmonic interactions and structural disorder provide scattering mechanisms, the study of temperature dependence of linewidths can be used to derive information on phonon relaxations. To discern the effect of disorder, the result on p-bromochlorobenzene was also compared with that on isomorphic p-dichlorobenzene crystal which exhibits no structural disorder. It was found that for both these p-dihalobenzenes the phonon relaxation at liquid helium temperatures is $>10^{-10}$ sec. Vibrational relaxation was also investigated for the lowest frequency phonons in a 1:1 binary solid solution of 1,4-dichlorobenzene and 1-bromo-4-chlorobenzene. Our method using temperature dependence of the line shape and

the linewidth in the Raman spectra shows that the presence of substitutional disorder broadens the line, but the lineshape is still Lorentzian. The observed temperature dependence on the linewidth is, again, in agreement with the T_1 -mechanism which involves the decay of the optical phonon in two acoustic phonons of half the frequency.

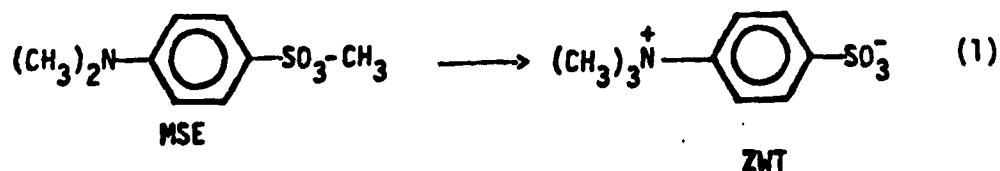
b) Phonon Spectroscopy of Reactions in Solids

Several solid state reactions were investigated by our novel technique of phonon spectroscopy. These studies led us to propose a new concept of phonon-assisted thermal and photochemical reactions in solid. Also, the Raman phonon spectra were found to provide clear information as to if a reaction proceeds by a homogeneous mechanism (the reactant and the product form a solid solution) or a heterogeneous mechanism (the reactant and the product form segregated phases.)

Solid state photodimerization of two modifications of *trans*-cinnamic acids in pure crystals was investigated. The Raman spectra of both the phonon region and the internal vibration region were studied as a function of photodimerization. Figure 1 shows the Raman spectra in phonon region of the *trans*-cinnamic acids and their respective dimers. In this photodimerization we investigated using the phonon spectra, the mechanism of the product lattice formation. As was suggested in the proposal, phonon spectra proved to be conclusive and it was found that the photodimerization proceeds by a heterogeneous mechanism, i.e. no solid solution forms between the reactant and the product. The major thrust of the research has been to derive a dynamical concept of reactivity by considering the role of phonon motions of the lattice in determining reactivity. Large amplitude phonon motions are the analogs of molecular

collisions in the gas phase. The two crystalline modifications of trans-cinnamic acid differ in the degree of reactivity. The β -form is more reactive than the α -form. It can be seen from figure 1 that the β -form has a very low lying phonon transition ($\sim 27 \text{ cm}^{-1}$), whereas for the α -form the lowest phonon transition is at $\sim 52 \text{ cm}^{-1}$. In the 27 cm^{-1} motion the molecules execute large amplitude oscillations which may account for enhanced reactivity.

The thermal rearrangement reaction of methyl-p-dimethylaminobenzene sulfonate (MSE) in pure crystal to form the product p-trimethylammonium benzene sulfonate Zwitterion (ZWT) was also investigated during this period. Detailed studies of the phonon spectra as well as the internal vibration spectra were made as a function of the percentage rearrangement using polycrystalline samples as well as single crystals in different orientations. Figure 2 shows the spectra for the reactant (top Spectrum), the 40% conversion sample (middle spectrum) and the product (bottom spectrum) for the phonon region. Except for the spectral intensity changes due to a difference in orientation, the spectra of the 40% conversion sample can be explained as consisting of unperturbed bands of both the reactant and the product. The same is true for samples of other percentage conversion. From this result we conclude that no solid solution between the reactant and the product is formed when the reaction proceeds. In other words the reaction proceeds by a heterogeneous mechanism. This observation is consistent with the following mechanism:



This mechanism involves an intermolecular transfer of methyl group and, thus, a cooperative rearrangement. When the reaction is induced, it has to occur cooperatively over a large domain, and not just locally.

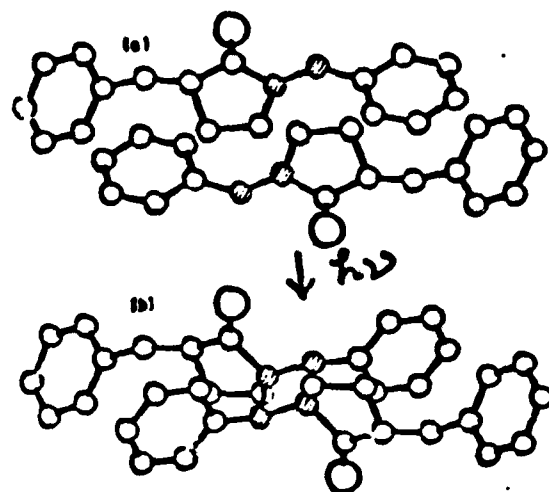
A temperature dependence study of phonons in MSE reveals that phonon transitions broaden rapidly as the temperature is raised from 120°K. There is a low lying phonon at $\sim 30\text{cm}^{-1}$ ($\sim 120^\circ\text{K}$ value). As the sample is warmed from 120°K, this phonon shifts to lower frequencies and rapidly broadens. By 200°K, this transition cannot be distinguished from the Rayleigh background. From this result we conclude that the low lying phonon of MSE represents an over-damped soft mode which, by executing very large oscillations, may be responsible for inducing the thermal rearrangement reaction. This result, again, lends support to a model based on phonon participation in solid state reactions.

The concept of phonon-assisted reactions was also applied to photochemical aggregation (dimerization and polymerization) processes in solids. With the application of electron microscopy for the study of solid state reactions, it has been apparent that there are examples of photochemical reactions in solids that are not sensitive to structural imperfections in the lattice. In such cases, the electron-phonon coupling may play an important role in effectively trapping the excitation energy. Furthermore, a strong electron-phonon coupling in the reactive electronic state, creates a local lattice deformation. The resulting local lattice configuration can, in favorable cases, be a precursor of the photodimer (or the photopolymer) lattice. In other words, a strong electron-phonon coupling can lead to a preformation of the product lattice for a photochemical dimerization or polymerization. Thus, a photochemical reaction

can be phonon-assisted.

Phonon spectroscopy was used to investigate photochemistry in solid state of two systems which are prototypes of two broad classes of compounds. The first reaction is the photodimerization of 2-benzyl-5-benzylidene cyclopentanone (hereinafter abbreviated as BBCP). BBCP belongs to a class of photoreactive compounds which consist of a benzylidene cyclopentanone, or a benzylidene cyclohexanone nucleus. This particular reaction is a single crystal-to-single crystal transformation which proceeds with a minimum rearrangement of the lattice. The second photochemical reaction is the photopolymerization of 2,5-distyrylpyrazine (abbr. as DSP). It represents a class of compounds of the general formula: $AR - C = C - AR' - C = C - AR$. There are two crystallographic modifications of DSP. However, only the α -form grown from solution is photoreactive. The product is a well oriented crystalline polymer. Although, the reaction proceeds by a small molecular rearrangement, but owing to the build-up of mechanical stress, the process ultimately leads to the fracture of the parent crystal.

These reactions were investigated by a combination of two spectroscopic techniques: (i) the laser Raman spectroscopy which probes the phonon spectra as a function of reaction progress; and (ii) the electronic spectroscopy by which the electron-phonon interaction is studied. The laser Raman spectroscopy was also used to obtain intramolecular vibrations of the reactants and the products as well as of the partially converted samples. These intramolecular vibrations were also used to characterize the materials and to study the mechanism of the reaction. The photodimerization of the BBCP crystal can be illustrated as follows:



In the above illustration, (a) presents a pair of monomers in which the hatched circles represent the carbon atoms of the alkene group. The structure (b) represents the photodimer which contains now a cyclobutane ring. In the intramolecular vibration regions, the Raman spectra show that the alkene group modes, at 997 cm^{-1} , 1180 cm^{-1} , 1593 cm^{-1} and 1625 cm^{-1} , disappear during the course of photodimerization, and new modes (due to the cyclobutane ring) appear at 878 cm^{-1} , 979 cm^{-1} and 1001 cm^{-1} . The result is consistent with the mode of chemical transformation shown by equation 2. A rough estimate of the conversion into photodimer was made for each sample by taking a ratio of intensities of the peaks specific to the vibrations of the reactive benzylidene double bond with respect to a peak which is not affected by dimerization. The Raman phonon spectra of the BBCP crystal, monitored as a function of reaction progress, are shown in figure 3. The phonon bands (especially those within the $15\text{-}40\text{ cm}^{-1}$ range) reveal a shift in frequency accompanied by spectral broadening. When the conversion reaches 50%, the interpretation becomes difficult because of the tremendous broadening of the spectral features. When the sample contains more than $2/3$ of the dimer, the

bands, which are specific of the dimer, become predominant. The result of figure 3 clearly shows phonon amalgamation and, therefore, a homogeneous mechanism of photodimerization of BBCP.

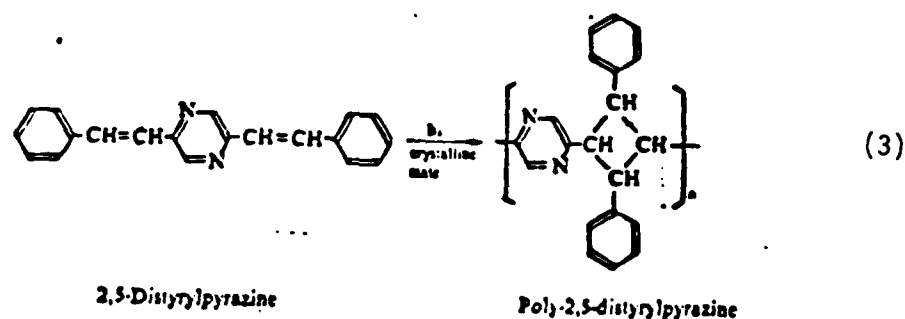
The room temperature electronic absorption spectrum of the BBCP monomer in cyclohexane is shown in figure 4a. The spectrum consists of two distinct bands: a strong absorption band above $30,000\text{ cm}^{-1}$ and a following absorption band below $30,000\text{ cm}^{-1}$. This weak absorption band is found to shift towards higher frequencies and merges with the strong band when a polar solvent is used. A portion of the electronic absorption below $30,000\text{ cm}^{-1}$ (where the weak band is found in non-polar solvent), which was obtained for BBCP in ethanol (a polar solvent), is marked by a dashed line in figure 4a. Because of the shift towards higher frequencies, this weak band cannot be seen in this region. This behavior is specific of an $n \rightarrow \pi^*$ transition, and this transition is found to be capable of photodimerizing the monomer crystal.

The electronic absorption spectrum of the BBCP monomer single crystal at 4.2°K is shown in figure 4b. The spectrum is broad, and again consists of two bands similar to those seen in a non-polar solvent. This lack of any fine structure (usually found in the electronic spectra of organic crystals at 4.2°K) can arise from two possible sources: (i) disorder in the lattice, or (ii) a strong electron-phonon coupling leading to an extremely distorted excited state. Our Raman phonon spectra indicate an ordered lattice for BBCP. Therefore, the broad electronic spectra can be taken as an evidence of a strong electron-phonon coupling in the reactive electronic state. No detectable emission from the monomer single crystal is observed, which suggests that the nonradiative energy-dissipation processes are highly efficient. This

behavior is also consistent with a strong electron-phonon coupling in the BBCP monomer crystal.

The absorption spectrum of the photodimer single crystal, obtained after an exposure to the light of $\lambda > 340$ nm for a few hours, is shown in figure 4c. The weak band disappears; at the same time, a decrease in the absorbance of the long wave portion of the strong band is observed. The photoreactivity of BBCP monomer depends on the temperature. Even a prolonged exposure to uv at 77 K light does not convert BBCP to the dimer in any measureable quantity. This feature allows one to conveniently obtain the absorption spectra of the crystal at low temperatures. This strong temperature dependence of the reactivity also supports the model of a phonon-assisted reaction.

The polymerization of DSP in crystalline state under the irradiation with u.v. light proceeds as follows:



The Raman spectra of α -DSP and the DSP polymer in the intramolecular vibration region are compared in figures 5 and 6. These spectra are significantly different which confirms that α -DSP has undergone a chemical transformation. The peaks (at 860 cm^{-1} , 980 cm^{-1} , 1192 cm^{-1} and 1635 cm^{-1}) owing to the vibrational modes of the alkene group of the

DSP monomer, are absent in the polymer spectra. But the polymer spectra now consist of new bands at 790 cm^{-1} and 970 cm^{-1} which correspond to the vibrations of the cyclobutane ring. This spectroscopic result is in agreement with the polymerization process shown in equation 3.

Figure 7 shows three representative phonon spectra of α -DSP recorded during the polymerization. The phonon spectrum of partially polymerized material is a direct superposition of the monomer and the polymer bands. There is no significant frequency shift. As the reaction proceeds, the monomer peaks diminish in intensity with a concurrent rise in the intensity of the polymer peaks. These results indicate that the solid state photopolymerization of α -DSP involves a heterogeneous mechanism for the entire conversion range sensitive to the Raman technique (product $>1\%$).

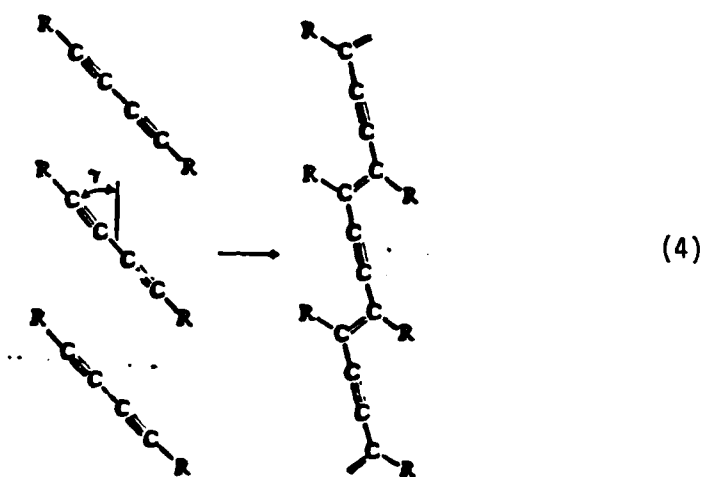
The electronic emission and the photoexcitation spectra of α -DSP monomer, taken at 4.2°K , are shown in figure 8. Both spectra are devoid of fine structures. A large Stokes shift (1200 cm^{-1}) is seen between the photoexcitation maximum and the emission maximum. Both the lack of the fine structure and the large Stokes shift provide a clear evidence of a strong lattice distortion in the excited state and, thus, a strong electron-phonon coupling. The emission spectrum is of excimer nature. The excimer is formed as a result of the strong local lattice deformation which arises from a strong electron-phonon interaction in the excited electronic state (dynamic mode of excimer formation).

Therefore, the Raman phonon spectroscopy clearly shows that photodimerization of the BBCP crystal proceeds by a homogeneous mechanism while the photopolymerization of the α -DSP crystal appears to be heterogeneous in the range of sensitivity of our technique. Both reactive systems show strong electron-phonon interactions in the reactive excited electronic state and, thus, provide support for the model of phonon-assisted

reactivity in the solid state.

Another reaction investigated by Raman phonon spectroscopy is the polymerization of diacetylene in solid state.

Various derivatives of diacetylenes polymerize in the solid state to produce a crystalline polymer according to the following scheme.



The solid state polymerization of diacetylenes of the general formula $R_1-C\equiv C-C\equiv C-R_2$ has been investigated for many systems which differ in the substituent groups R_1 and R_2 . The monomer crystal polymerizes thermally as well as by the action of ultraviolet or higher energy radiation. All these methods of solid state polymerization produce polymers which consist of well aligned chains of form $\left[\begin{array}{c} \text{C} \\ \text{R}_1 \end{array} -C\equiv C-C \begin{array}{c} \text{R}_2 \\ \text{C} \end{array} \right]_n$.

The product is frequently a crystalline material with structural perfection similarly to that of the monomer crystal. The polymer chains are supposed to be uniformly distributed within the reacting phase like a solid solution over the entire conversion range.

The bis-(p-toluene sulfonate)ester of 2,4-hexadiene-1,6-diol (for which $R_1=R_2$ is $-\text{CH}_2-\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3$) has been widely investigated as a model system for the study of solid state polymerization of diacetylenes. From here on, this monomer will be abbreviated as TS (sometimes also abbreviated as TSHD). A freshly crystallized monomer is still slightly pink due to a small amount (estimated to be ~1%) of polymer invariably present even in the untreated sample (without thermal or photopolymerization). The electronic absorption maximum of the polymer at this concentration is at $17,500\text{ cm}^{-1}$. Even at this small concentration (~1%), the resonance enhancement of the polymer Raman bands is so effective that the prominent bands, in Raman spectra of the untreated monomer crystal, belong to the polymer present. The dependence of the low frequency Raman spectra of an untreated TS monomer (which contained ~1% polymer) on the excitation wavelength is shown in figure 9. The spectrum consists of two groups of intense bands in the region $100-280\text{ cm}^{-1}$. The intensities of all these bands change when the excitation frequency approaches the frequency of the electronic transition of the polymer ($\sim 17500\text{ cm}^{-1}$ for ~1% polymer in the monomer matrix). However, upon changing the excitation frequency, no significant frequency shift of the vibrational bands is observed.

The change in the intensities of the vibrational bands on approaching resonance conditions is also exhibited in an experiment during which the excitation frequency is kept constant at a value lower than the absorption maximum of the 1% polymer; but the sample is polymerized further to increase the concentration of the polymer. The increase of the polymer concentration leads to a decrease in the frequency of the electronic absorption maximum. During the course of polymerization,

the excitation frequency comes in resonance when the concentration of the polymer reaches a certain value. Figure 10 shows the low frequency Raman spectra of an untreated TS crystal and a further polymerized TS crystal. The excitation frequency for all the spectra in figure 10 is 16735 cm^{-1} , which is about 800 cm^{-1} below the absorption maximum ($\sim 17500\text{ cm}^{-1}$) of the polymer in the untreated monomer crystal. Comparing the spectral features of figures 9 and 10, it can be seen that the spectrum of an untreated TS crystal, obtained with an excitation frequency of 16988 cm^{-1} , is very similar to the spectrum of a sample containing 5% obtained with an excitation frequency of only 16735 cm^{-1} . Similarly, the spectrum of an untreated TS crystal using an excitation frequency of 17220 cm^{-1} resembles that of a 70% polymerized sample but now with an excitation frequency of 16735 cm^{-1} .

As the polymerization reaction progresses, the low frequency vibration spectrum becomes less distinguishable from the strong fluorescence background. By the time the sample is completely polymerized, the bands in the region $100\text{-}280\text{ cm}^{-1}$ are completely masked by a broad emission background.

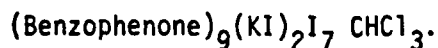
It can be seen from figures 9 and 10 that there are some weak spectral features in the frequency regions $35\text{-}45\text{ cm}^{-1}$. We tentatively assign these modes as phonon modes. Figure 11 shows that these modes shift in frequencies as the polymerization proceeds up to 30% conversion. This behavior is an amalgamation type behavior shown by solid solutions. The result is, therefore, in agreement with the earlier studies which found that the reaction proceeds by a homogeneous mechanism. We find that, beyond 30% conversion, the spectral features show a behavior more complex than a simple amalgamation. Further studies are needed to explain this anomaly.

c) Raman Study of Pharmaceutical Solids:

The Raman phonon spectroscopy was introduced as a convenient method to characterize the solid states of a drug and the study of stabilities of various crystalline modifications of a drug. The interest in such characterization steps from the fact that different crystalline modifications of the same drug have different physical and in some cases different physical and in some cases different chemical properties which may be a serious consideration in manufacturing of the dosage form.

Laser Raman spectroscopy was conveniently used for the characterization of solvates of griseofulvin, investigation of the nature of solute-solvent interactions and the process of desolvation. The spectra of both the lattice vibrations and the intramolecular vibrations were monitored. A new solvate of griseofulvin with bromoform was characterized by Raman spectroscopy. A temperature dependence study of the solvates of griseofulvin with chloroform, bromoform and benzene reveal no phase transformation or chemical change. It was found that, in the benzene solvate, only weak Van der waals interactions exist between the solute and the solvent. However, in the solvates with chloroform and bromoform, a weak hydrogen bonding exists between the proton of the solven and the C=O group of the benzofuran ring in the griseofulvin structure. The study of desolvation process in these solvates reveal that during the desolvation the crystal does not go through any intermediate structure. As the solvent molecule escapes, the lattice reverts to the structure of the unsolvated griseofulvin form.

d) Structure and Dynamics of the Conducting Complex:



The polyiodine complexes have drawn considerable attention during recent years. The interest has been twofold: (i) Many of these complexes show high electrical conductivity. (ii) These complexes also exhibit unusual and varied structural properties in regards to the iodine-iodine topology.

(Benzophenone)₉ (KI)₂ I₇ CHCl₃ belongs to a group of polyiodine complexes between iodine and benzophenone which exhibits the unusual property of a large frequency dependent conductivity, thus, indicating a major contribution due to ionic conductivity.

To elucidate the nature of the iodine column the following was studied: (i) the resonance Raman spectra were obtained to characterize the nature of the iodine species; (ii) a temperature dependence was conducted to investigate the nature of anharmonic interactions in the iodine column, the role of disorder and the possibility of any structural phase transition; (iii) in an effort to understand the role of the solvent, we also studied the nature of the iodine column in BIKI crystal grown from five solvents; (iv) complexes can also be obtained by changing the cation from K⁺ to NH₄⁺, Na⁺ or Li⁺. We investigated the effects of these substitutions and the substitutional disorder (mixed crystals) on the structure and dynamics. It was found that the potassium complex contains two types of iodine species: I₃⁻ and I₃⁻/I₂ complex. A temperature dependence study revealed no phase transition below room temperature, however considerable anharmonicity as well as structural disorder exist in the iodine column. Substitution of cations K⁺ to NH₄⁺ and Na⁺ has small effect on the iodine

column which now shows the presence of I_5^- species in a relatively ordered structure. Although the substitution of the solvent molecule does not influence the nature of the iodine species, it does appear the degree of disorder in the iodine column of the potassium complex.

e) Phonon Spectroscopy of Polymeric Alloy

Some preliminary work was done using a novel application of phonon spectroscopy to determine if a polymer blend is truly homogeneous at the molecular level. In case of a truly homogeneous polymer blend, the observed phonon spectrum of the alloy can not be explained as simply superposition of the unperturbed (unshifted in frequency) phonon bands of the pure polymeric components. With this method, a polymer blend of polystyrene and 2,6-dimethylpolyphenylene oxide was investigated. The result is shown in figure 12. It can be seen that the phonon bands seem in the alloy one shifted in frequency from that of the pure components. Therefore, our phonon spectroscopy shows that this polymer blend is a homogeneous alloy at the molecular level. On the other hand, our method showed that the polymer blend of polyethylene and polypropylene is quite heterogeneous.

FIGURE CAPTIONS

- Figure 1. The Raman phonon spectra at 100°K of α - and β -transcinnamic acids and their respective photodimers, α -truxillic acid and β -truxinic acid.
- Figure 2. The Raman phonon spectra of (a) MSE, (b) a partially converted sample, and (c) ZWT at 152°K.
- Figure 3. The Raman phonon spectra, at 100°K, of the BBCP crystal monitored as a function of the photodimerization progress.
- Figure 4. Absorption spectra of the BBCP in solution and in the solid state: a) $1.2 \cdot 10^{-5}$ M/l BBCP in cyclohexane; curves at frequencies over $30,000 \text{ cm}^{-1}$ were recorded at a hundred fold concentration increase in solution; dashed line refers to the BBCP solution in ethanol. b) The BBCP monomer single crystal at 4.2°K. c) The BBCP single crystal after 2 hours of exposure to the Xenon lamp light of $\lambda > 340 \text{ nm}$ when a total conversion to the dimer occurs.
- Figure 5. In the spectral region $200\text{-}1050 \text{ cm}^{-1}$, the Raman spectra are compared for the α -DSP monomer and its polymer at 100°K.
- Figure 6. The Raman spectra, in the region $100\text{-}1700 \text{ cm}^{-1}$, are compared for the α -DSP monomer and its polymer at 100°K.
- Figure 7. Phonon spectra of α -DSP at $\sim 94^\circ\text{K}$. Shown are monomer (top), partial polymerization (41%), and polymer (bottom). Spectra are shown from 20 cm^{-1} to 200 cm^{-1} .
- Figure 8. The fluorescence and the photoexcitation spectra of the α -DSP monomer crystal at 4.2°K.

Figure 9. The low frequency Raman spectra of an unpolymerized TS crystal shown as a function of the Raman excitation wavelength.

Figure 10. The low frequency ($0-300\text{ cm}^{-1}$) Raman spectra of an untreated crystal (less than 1% of the polymer) are compared with those of a further polymerized crystals obtained with the same excitation wavelength of 16735 cm^{-1} .

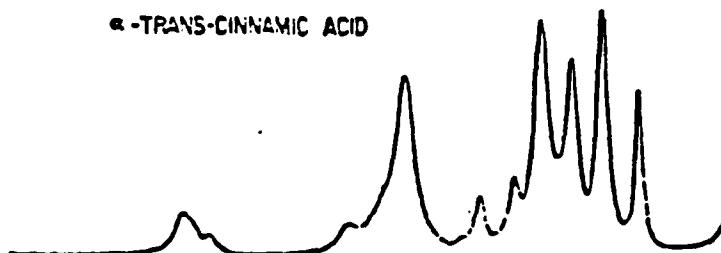
Figure 11. The a higher-dispersion low-frequency Raman spectra, in the spectral region $0-100\text{ cm}^{-1}$, of successively polymerized (thermally) samples obtained with the same excitation frequency of 16735 .

Figure 12. The Raman phonon spectra of polystyrene, (PS); 2,6-dimethylpolyphenylene oxide (PPO); and their polymer blend (PPO/PS) at 100°K .

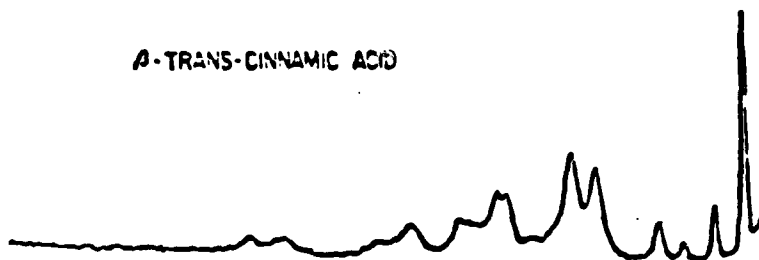
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β -TRANS-CINNAMIC ACID



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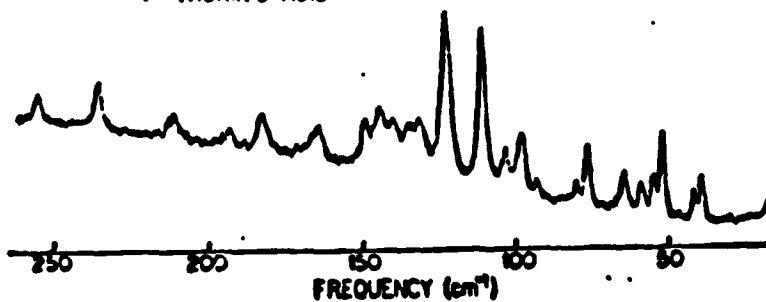


Figure 1

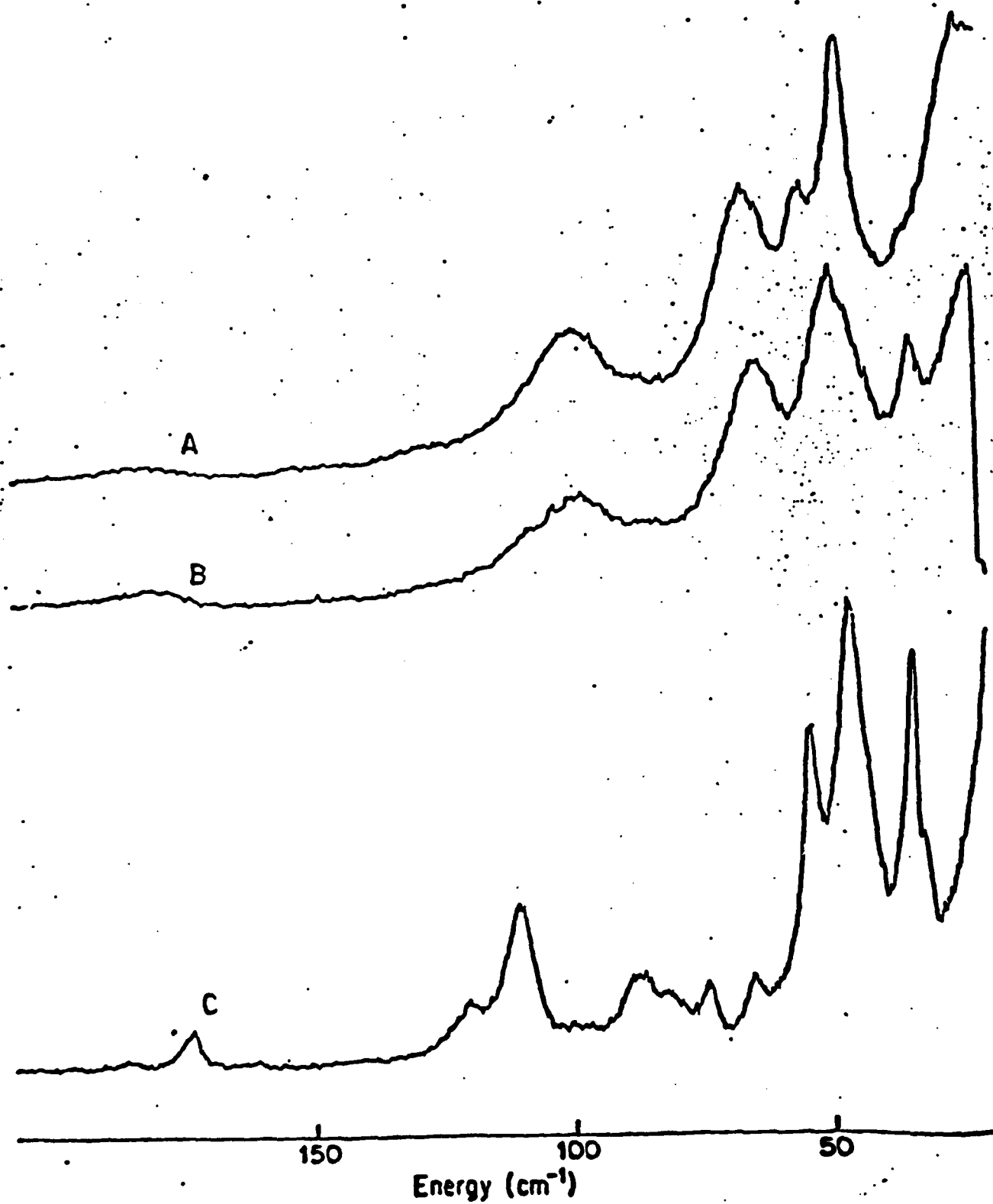


Figure 2.

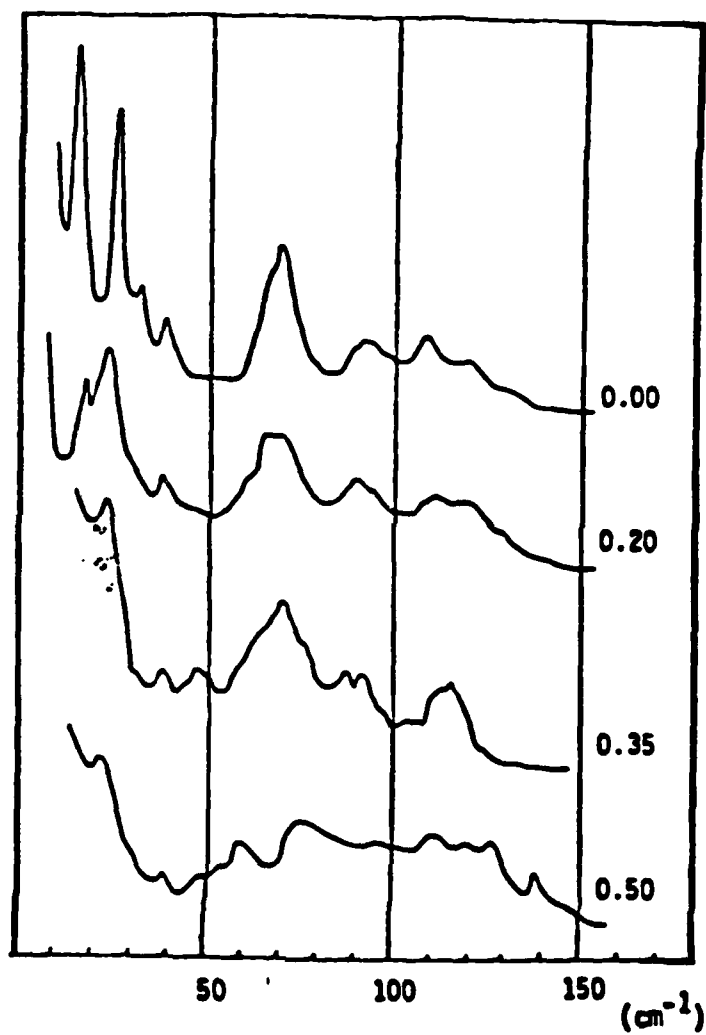


Figure 3

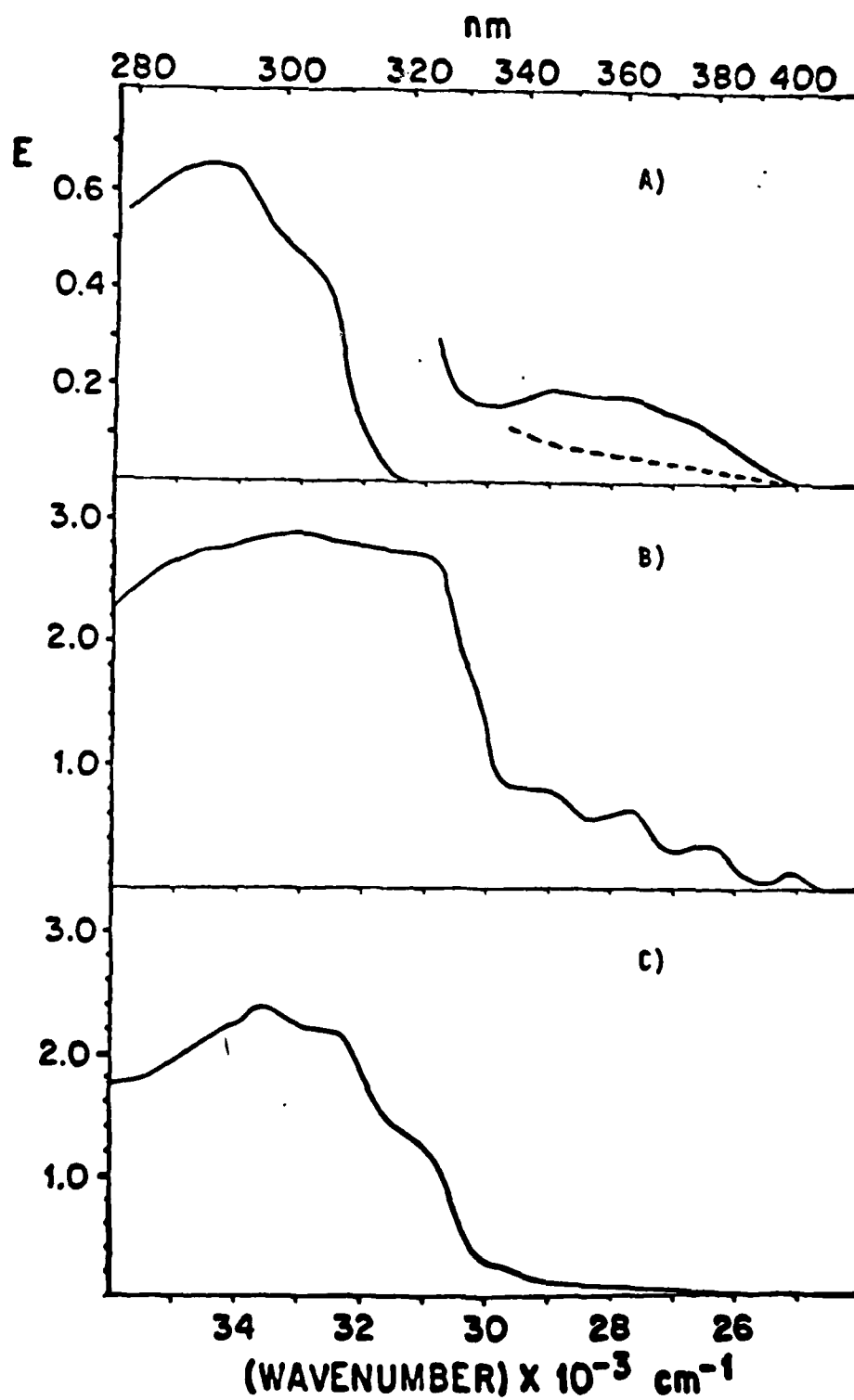


Figure 4

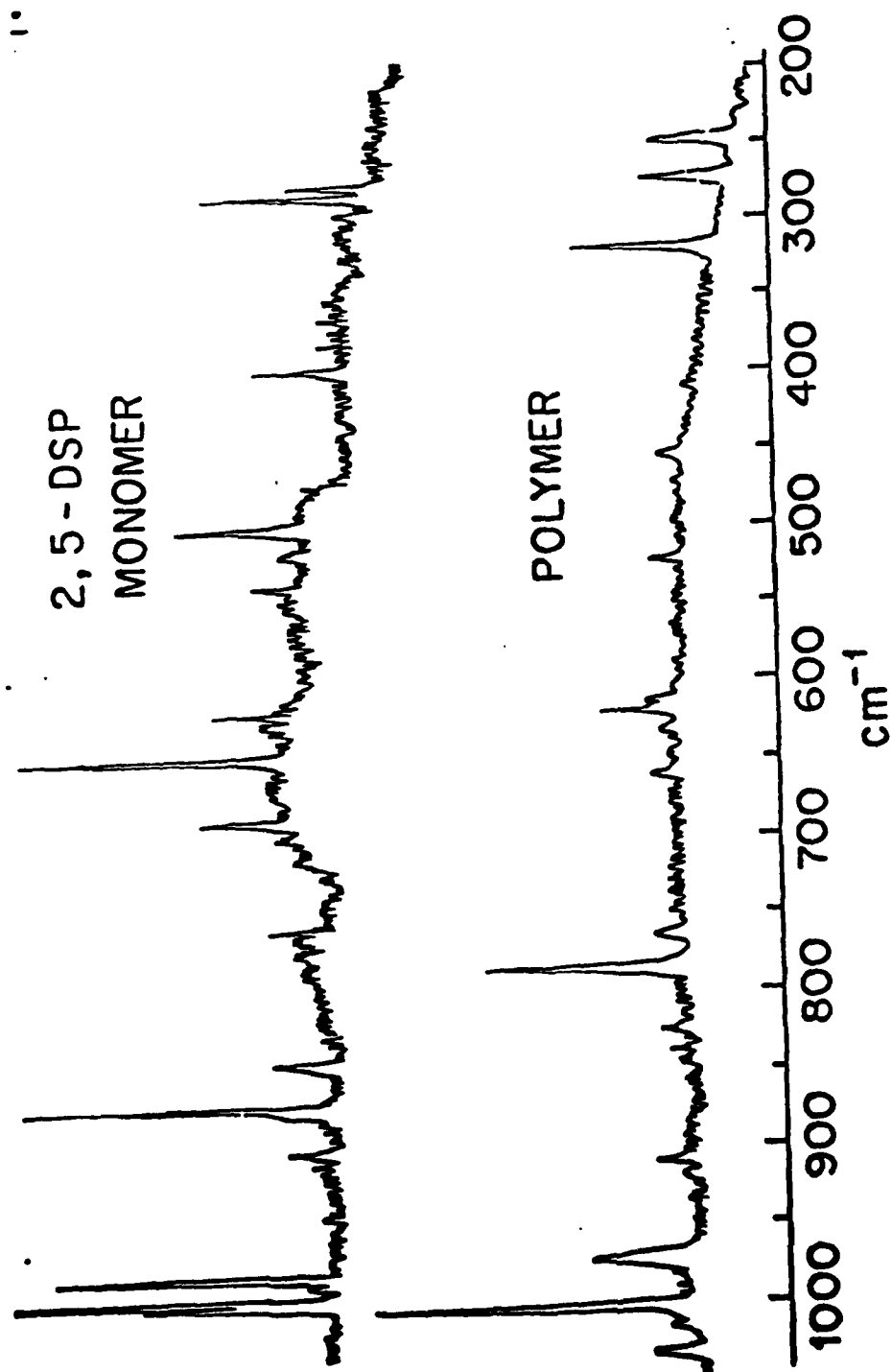


Figure 5

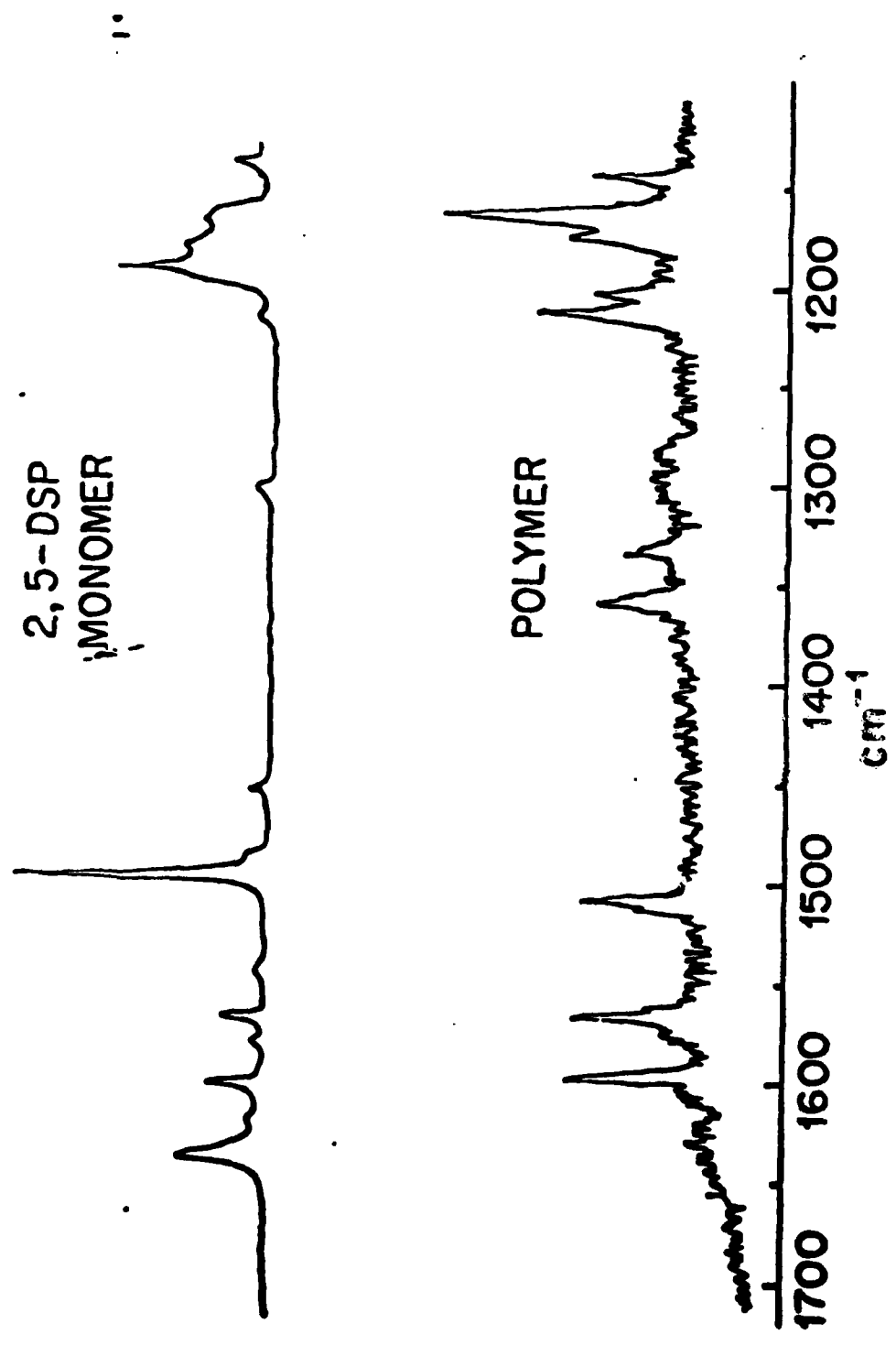
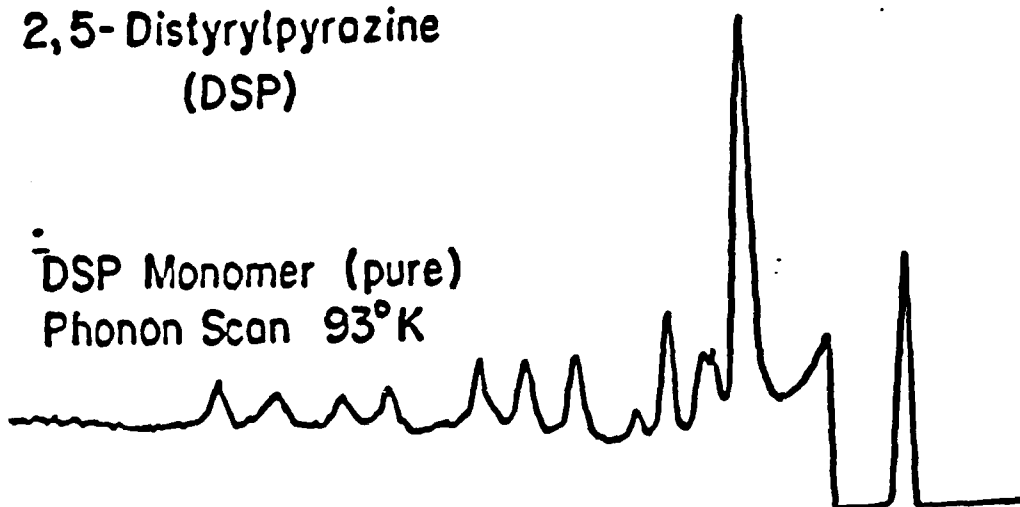


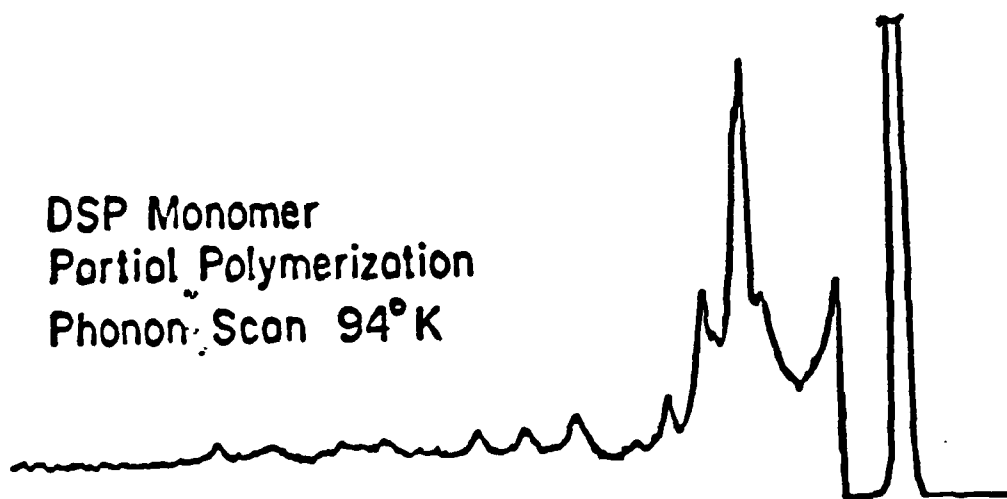
Figure 6

2,5-Distyrylpyrazine
(DSP)

DSP Monomer (pure)
Phonon Scan 93°K



DSP Monomer
Partial Polymerization
Phonon Scan 94°K



DSP Polymer
Phonon Scan 95°K

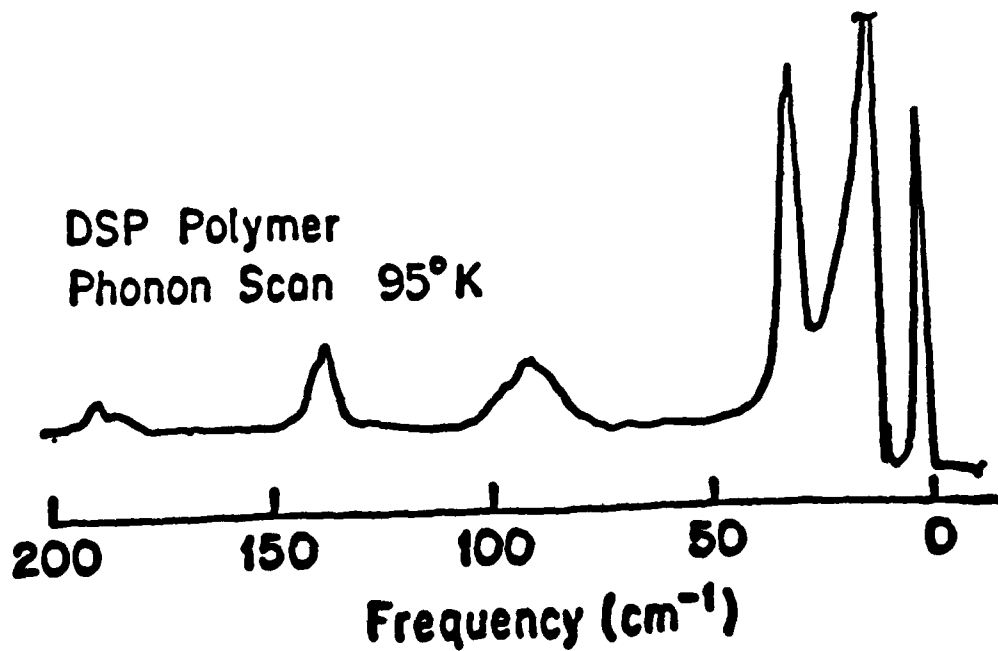
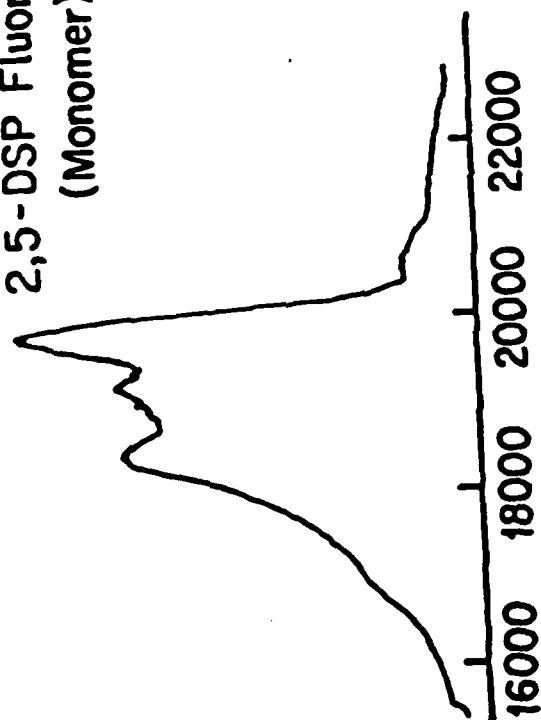


Figure 7

2,5-DSP Fluorescence
(Monomer)



2,5-DSP Photoexcitation Spectra
Monitored at 19850 cm⁻¹

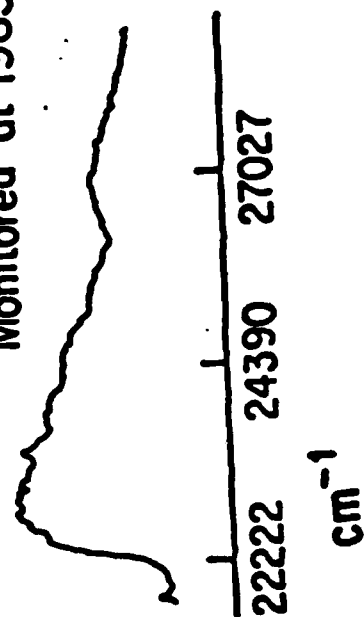


Figure 8

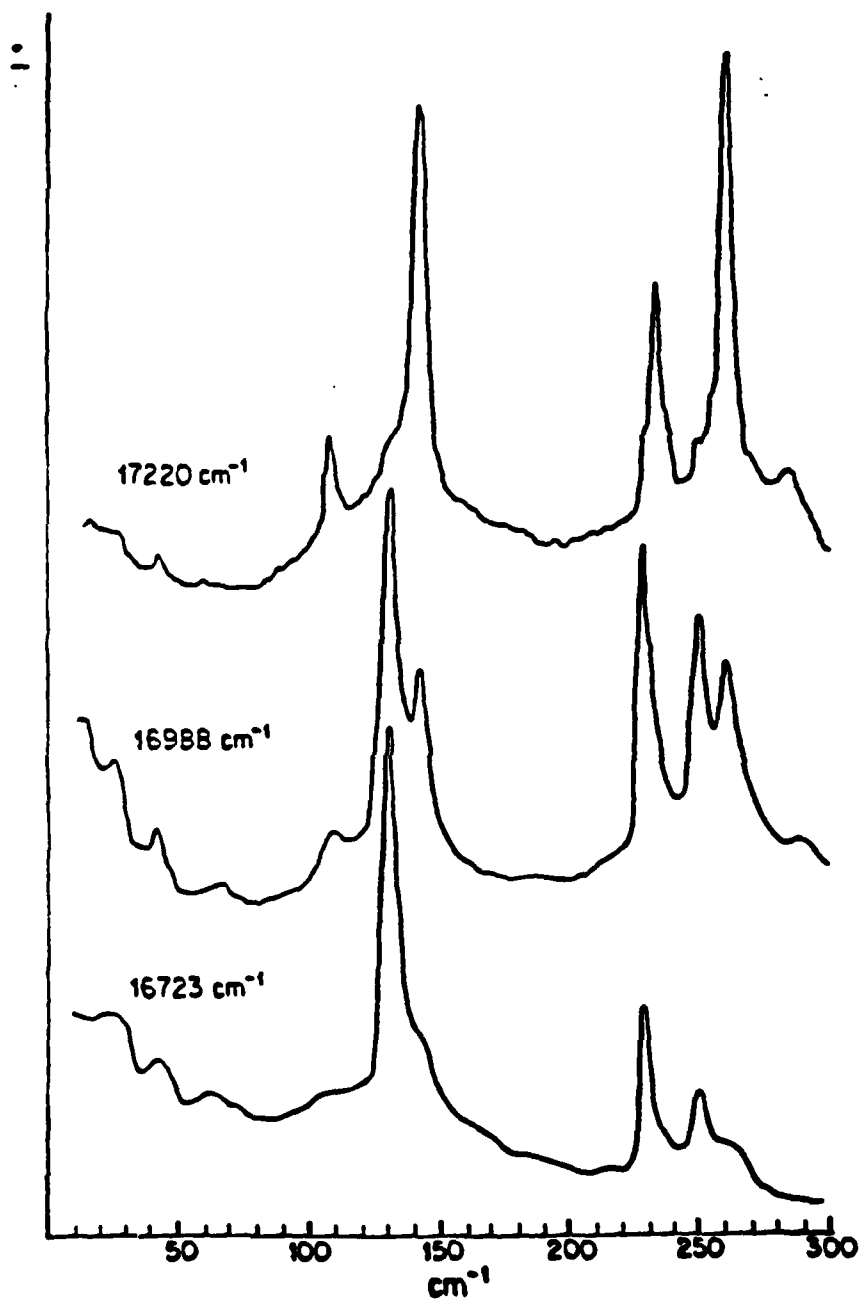


Figure 9

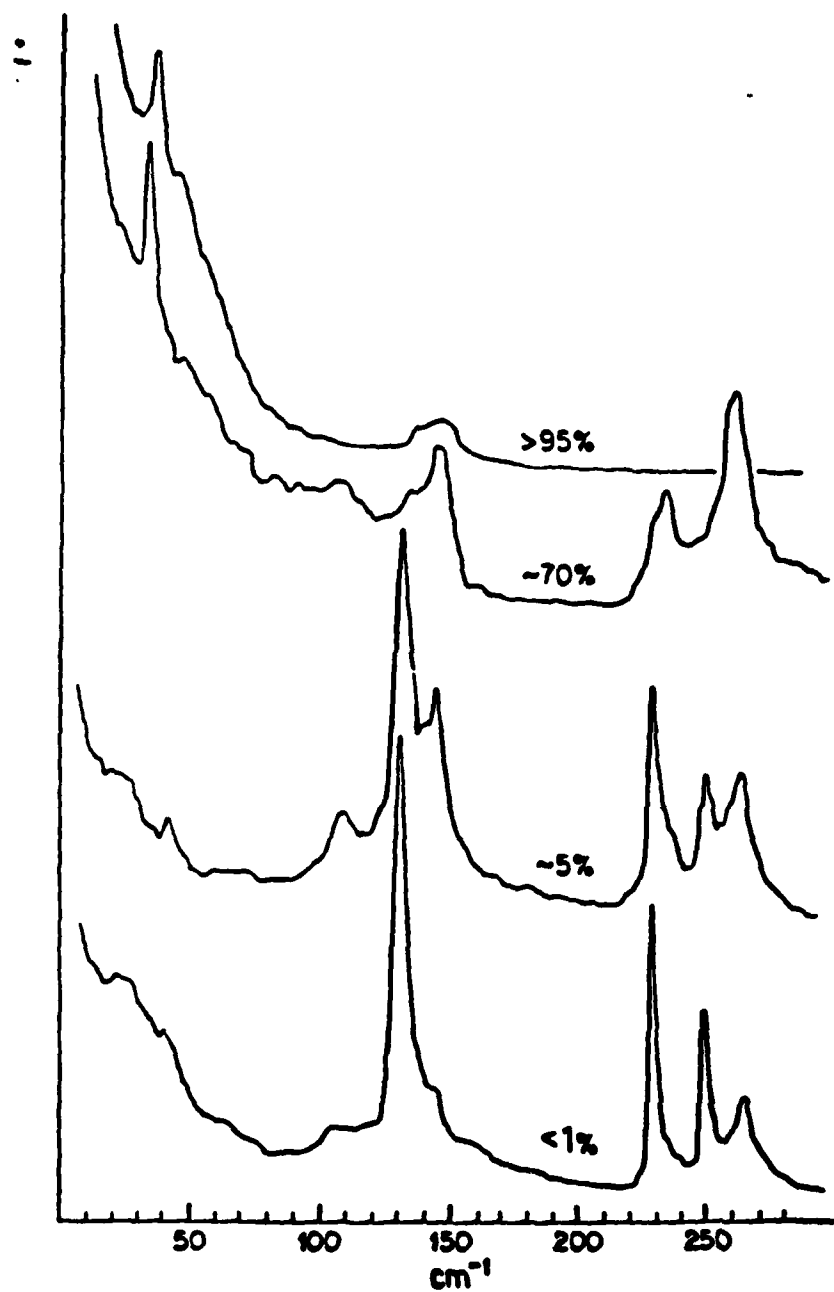


Figure 10

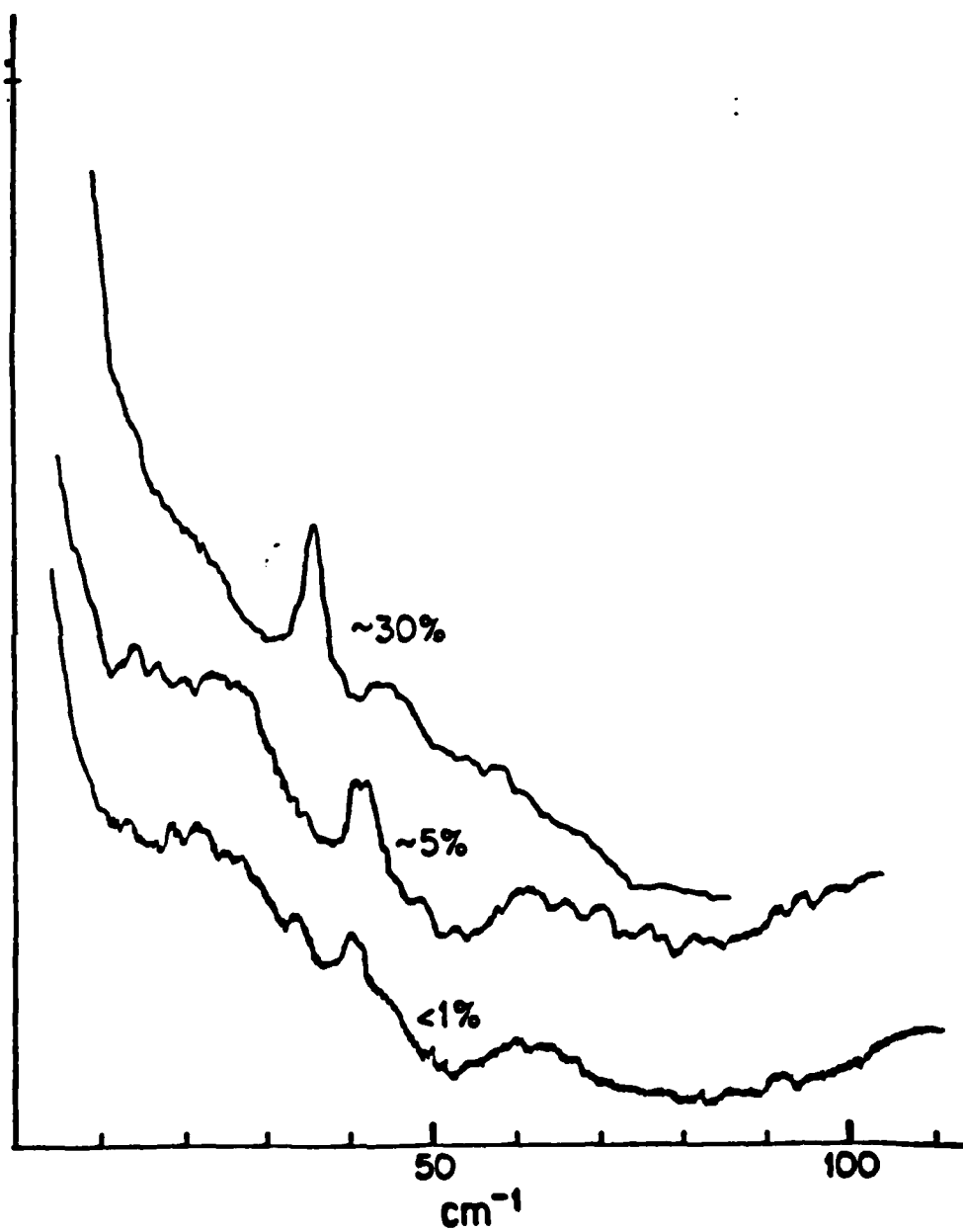


Figure 11

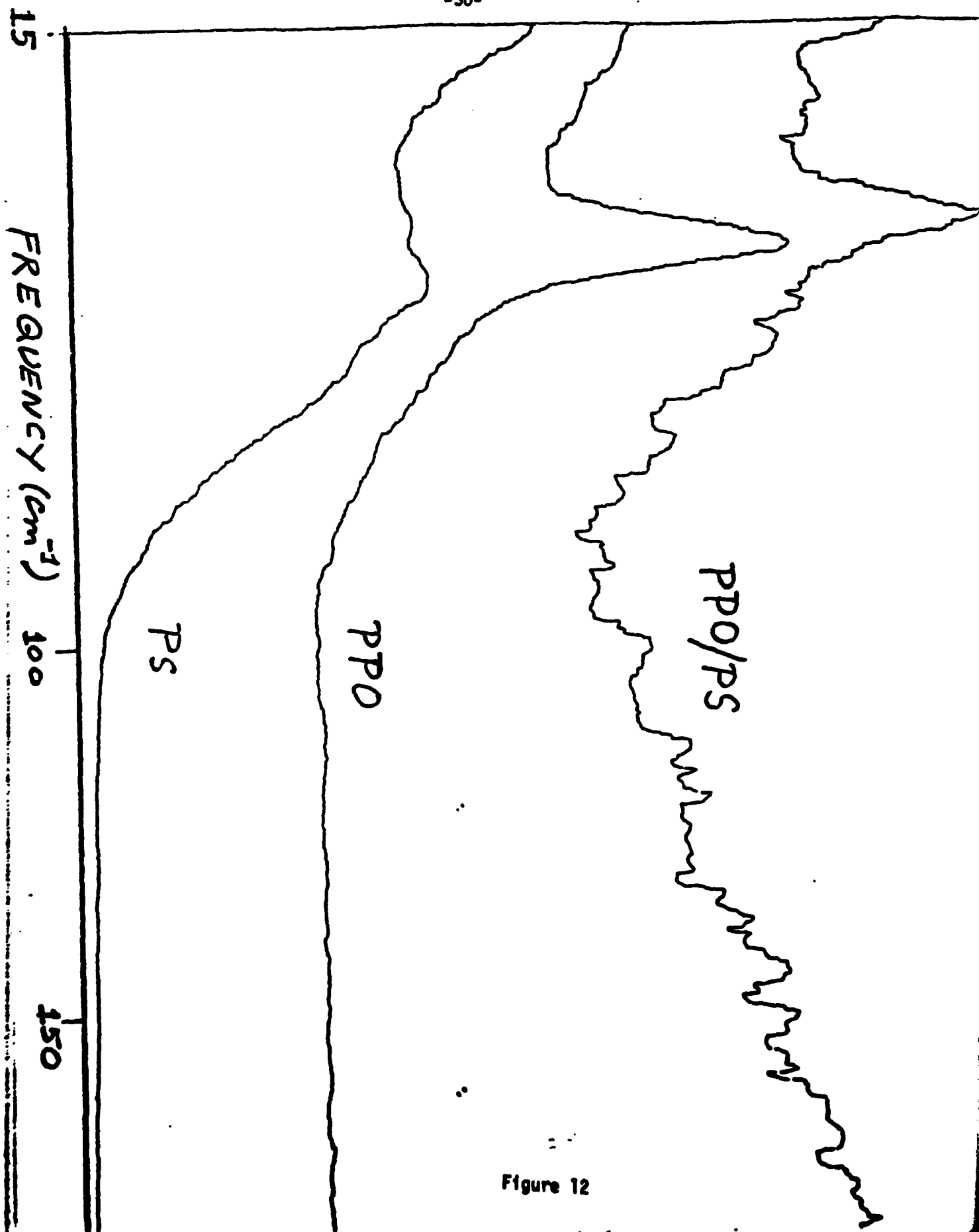


Figure 12

REPORTS OF THE ACCOMPLISHED RESEARCH

I. PUBLICATIONS

1. "Vibrational Relaxation in a Structurally Disordered Solid: Temperature Dependence of Raman Active Phonons in p-Bromochlorobenzene and p-Dichlorobenzene," P. N. Prasad, and R. V. Smith, J. Chem. Phys. 71, 4646 (1979).
2. "Vibrational Dephasing in Organic Solids: Temperature Dependence of a Localized Raman Active Internal Mode of Naphthalene," L. A. Hess and P. N. Prasad, J. Chem. Phys. 72, 573 (1980).
3. "Vibrational Relaxations and Dephasing in Organic Solids," P. N. Prasad, Mol. Cryst. Liq. Cryst. 58, 39 (1980).
4. "Raman Phonon Spectroscopy of Solid State Reactions: Thermal Rearrangement of Methyl-p-Dimethylaminobenzene Sulfonate in Solid State," K. Dwarakanath and P. N. Prasad, J. Am. Chem. Soc. 102, 4254 (1980).
5. "Laser Raman Spectroscopic Investigation of Pharmaceutical Solids, Griseofulvin and its Solvates", B. A. Bolton and P. N. Prasad, J. Pharm. Sci. 70, 789 (1981).
6. "Structure and Dynamics of the Iodine Column in the Polyiodine Canal Complexes (Benzophenone)₉ (KI)₂I₇CHCl₃" B. A. Bolton and P. N. Prasad, Mol Cryst. Liq. Cryst. 76, 309 (1981).
7. "Phonon Spectroscopy of Photochemical Reactions in Organic Solids", J. Swiatkiewicz, G. Eisenhardt, P. N. Prasad, W. Jones J. M. Thomas, and C. R. Theocharis J. Phys. Chem. (in Press) .
8. "Dephasing of Optical Phonons in a Substitutionally Disordered Organic Solid: The Lowest Frequency Raman Active Phonon of a Binary Solid Solution between p-Bromochlorobenzene and p-Dichlorobenzene", L. A. Hess and P. N. Prasad, submitted to J. Phys. Chem.
9. "Low Frequency Raman Spectroscopic Investigation of Polymer Blends", G. Eisenhardt, B. A. Bolton and P. N. Prasad, manuscript under preparation.
10. "Phonon Spectroscopy of Dynamics of Solid State Polymerization Process", J. Swiatkiewicz and P. N. Prasad, manuscript under preparation.

II. ORAL PRESENTATIONS AT SCIENTIFIC MEETINGS

1. "Laser Raman Study of Solid State Reactions," P. N. Prasad. Presented on April 2, 1979 at the American Chemical Society Symposium in Honolulu.
2. "Laser Raman Study of the Thermal Rearrangement of Methyl p-Dimethyl-Aminobenzene Sulfonate in Solid State," K. Dwarakanath, R. V. Smith and P. N. Prasad, Molecular Spectroscopy Symposium, June 12, 1979 at Columbus, Ohio.
3. "Vibrational Relaxation and Dephasing of Raman Active Modes in Molecular Solids and Crystalline Molecular Complexes," L. A. Hess and P. N. Prasad, Molecular Spectroscopy Symposium, June 12, 1979 at Columbus, Ohio.
4. "Dephasing of Optical Excitations in Disordered Organic Solids," L. A. Hess and P. N. Prasad, Molecular Spectroscopy Symposium, June 16, 1980 at Columbus, Ohio.
5. "Raman Study of Solid State Reactions," G. Eisenhardt and P. N. Prasad, Molecular Spectroscopy Symposium, June 14, 1980 at Columbus, Ohio.
6. "Raman Investigation of Structure and Dynamics of Conducting Polyiodine Canal Complex (Benzophenone)₉ (KI)₂I₇CHCl₃," B. A. Bolton and P. N. Prasad, Molecular Spectroscopy Symposium June 19, 1980 at Columbus, Ohio.
7. "Phonons and Phonon Interactions in Organic Solids," P. N. Prasad, Ninth International Molecular Crystal Symposium, Aparthotel, Kleinwalsertal, Austria, September 28, 1980.
8. University of Pennsylvania Symposium on Molecular Spectroscopy and Dynamics, April 10, 1981, "Dynamics of Phonon Interactions".
9. 28th Congress, International Union of Pure and Applied Chemistry, Vancouver, British Columbia, August 18, 1981, "Phonon Spectroscopy of Solid State Reactions", P. N. Prasad, J. Swiatkiewicz, T. N. Misra, and G. Eisenhardt.
10. International Conference on Phonon Physics, Bloomington, Indiana, September 2, 1981, "Dynamics of Phonon Interactions in Organic Solids", P. N. Prasad.

III. INVITED SEMINARS

1. University of Groningen, Netherlands, September 23, 1980, "Dynamics of Phonon Interactions in Organic Solids".
2. University of Amsterdam, Netherlands, September 24, 1980, "Dynamics of Molecular Motions in Molecular Solids".
3. University of Frankfurt am Main, W. Germany, Department of Physical Chemistry, Laboratory of Professor Keilm, October 3, 1980, "Organic Solid State Spectroscopy".
4. Cambridge University, Department of Physical Chemistry, Research Group of Professor Thomas, Cambridge, England, October 15, 1980, "Phonon Spectroscopy of Solid State Reactions".
5. Oxford University, Department of Physical Chemistry, October 18, 1980, "Phonons and Phonon Interactions in Organic Solids".
6. University of Lille, Lille, France, Department of Physics, Laboratory for Dynamics of Molecular Crystals, October 21, 1980, "Dynamics of Molecular Motions in Organic Solids".
7. Tata Institute of Fundamental Research, Bombay, India, December 22-24, 1980, invited to give three lectures.
8. Indian Institute of Technology, Kanpur, India, December 26, 1980, "Dynamics of Physical and Chemical Transformations in Solids".
9. Chulalongkorn University, Bangkok, Thailand, January 19, 1981, "Laser Raman Spectroscopy of Organic Solids".
10. Hong Kong University, Hong Kong, January 24, 1981, "Laser Raman Spectroscopy of Organic Solids".
11. Tohoku University, Sendai, Japan, January 28, 1981, "Vibrational Dephasing in Organic Solids".
12. IBM, San Jose, California, February 5, 1981, "Phonon Spectroscopy of Organic Solids".
13. Xerox, Webster, New York, February 19, 1981, "Dynamics of Molecular Motions in Organic Solids".
14. Emory University, Department of Physics, Atlanta, Georgia, March 6, 1981, "Dynamics of Molecular Motions in Organic Solids".
15. Stanford University, Department of Chemistry, March 26, 1981, "Dynamics of Molecular Motions in Organic Solids".

16. University of California at Los Angeles, Department of Chemistry.
April 6, 1981, "Dynamics of Molecular Motions in Organic Solids".
17. University of California at Davis, Department of Chemistry.
April 7, 1981, "Dynamics of Excitations in Organic Solids".