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thesis entitled MOLECULAR DYNAMICS OF A LIQUID CRYSTAL THROUGH BAND SHAPE ANALYSIS; A STUDY OF 4-CYANO-4'-PENTYLBIPHENYL (5CB) WITH A COMPUTERIZED RAMAN SPECTROMETER

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MOLECULAR DYNAMICS OF A LIQUID CRYSTAL THROUGH BAND SHAPE ANALYSIS; A STUDY OF 4-CYANO-4'-PENTYLBIPHENYL (5CB) WITH A COMPUTERIZED RAMAN SPECTROMETER

By

Stephen Michael Gregory

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ABSTRACT

MOLECULAR DYNAMICS OF A LIQUID CRYSTAL THROUGH BAND SHAPE ANALYSIS; A STUDY OF 4-CYANO-4'-PENTYLBIPHENYL (5CB) WITH A COMPUTERIZED RAMAN SPECTROMETER

By

Stephen Michael Gregory

This work was undertaken to understand more about the nature of liquids and the forces that hold liquid molecules together. The type of liquid system that was chosen for this study was a nematic liquid crystal system. The system was probed by Raman spectroscopy and viscosity measurements. The nematic liquid crystal system that was the most fruitful was 4-cyano-4'-pentylbiphenyl (5CB).

The Raman spectrometer used in this work was computerized for the project and software was written for both a minicomputer and a large computer to analyze the data. 5CB was synthesized from 4-bromobiphenyl for the experiments.

The Raman lineshape analysis of 5CB was not very conclusive due to experimental difficulties. The viscosity measurements were converted to reorientational relaxation times by use of several modified Stokes-Einstein equations. These results covered a range of one magnitude around 1 x 10^{-10} seconds. The analysis indicated that sticking boundary conditions with a microviscosity correction came the closest to the Raman lineshape results, but there was a one order of magnitude difference, with the Raman results being the shortest. To Joyce

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I. INTRODUCTION

In order to understand the nature of liquids and the forces that hold liquid molecules together one must find a suitable probe into the interactions within the liquid state. This work deals with the selection of such a probe and the determination of its efficacy in answering some of the questions raised by theory and other experiments.

The probe chosen for this work was Raman spectroscopy. The lineshape contribution to a vibrational Raman band from molecular rotations can be separated out and measured.¹ The functional form used to reproduce the rotational (or reorientational) contribution to the overall bondshape can possibly shed some light on the liquid state being studied. One such mathematical model is a Lorentzian function, which corresponds to random rotational behavior and has a half-width that is related to the rotational correlation time (the l/e decay time). If rotation in the liquid under study is not random then some other functional form will better fit the experimental data.

One question this work has attempted to address is what happens to the rotational motion, and also to the rotational bandshape, when a liquid passes from an isotropic state to an anisotropic state? Nematic liquid crystals were chosen as prototypic systems. The theoretical development for such a system suggests that the true rotational reorientation function will be a sum of Lorentzians, which would not necessarily be matchable with a single Lorentzian.² The liquid crystal that proved to be the most fruitful, and was therefore studied in most detail, was 4-cyano-4'-pentylbiphenyl (5CB). Its reorientational time, as

determined from the shape of the $C \equiv N$ stretching mode, was found to be very slow; in fact, it was so slow that a distinction between single or multiple Lorentzian lineshapes could not be drawn within the experimental error. However, there do appear to be significant differences between the bandshapes in the isotropic and nematic phases. The data obtained were good enough to show that this system behaves like others of similar size³ and that its overall correlation function is dominated by vibrational relaxation on a short time scale (<5 psec).

The same experiment from which data for the rotational lineshape calculations is collected also provides sufficient data for calculation of the vibrational lineshape. From the vibrational lineshape for each liquid phase the vibrational correlation times were calculated and found to be consistant with studies of other liquid crystals. In order to obtain information about flow characteristics, the temperature dependence of the apparent flow viscosity of 5CB was determined and reorientational times were calculated using the Stokes-Einstein equation with a variety of boundary conditions.

Because Raman intensity data are difficult to measure precisely, and because good data are required at closely spaced intervals well into the wings of a Raman band, traditional strip-chart recording of a Raman spectrum was not feasible for these studies. Therefore, as part of this dissertation research, an interface between a minicomputer and a Raman instrument was designed and constructed. This interface will be described, as will the software and the operating parameters which must be defined for efficient utilization of the computerized Raman spectrophotometer.

II. LIQUID CRYSTAL SYSTEMS

Liquid crystals have been studied since the middle of the 19th century. Most of the early work was devoted to describing the liquid systems; it was not until the 1920's that a quantitative theory for liquid crystals was presented. It was also during that period that the first works on the viscosity behavior of liquid crystals were presented.⁴

Liquid crystals can be divided into two categories: thermotropic and lyotropic. Lyotropic liquid crystals are prepared by mixing two or more components, one of which generally has polar molecules. These systems can exhibit many structures, with one of the most common systems being a lipid-water system. Thermotropic liquid crystals are prepared by heating certain organic or organometallic compounds. The two classes of thermotropic liquid crystals are called smectic (from the Greek word meaning grease or slime) and nematic (from the Greek word meaning thread).⁵

In a smectic liquid crystal the molecules are arranged in layers with their long axes parallel to each other. The molecules can move in two directions in the plane, and they can rotate about one axis. Within the layers they can be arranged either in neat rows or randomly distributed. The layers can slide, without much hindrance, over neighboring layers.

In a nematic liquid crystal the only structural restriction is that the molecules maintain a parallel or nearly parallel arrangement to one another. The molecules are mobile in three directions and can rotate freely about one axis. This molecular arrangement can be compared to

a long box of pencils where the pencils can roll and slide back and forth, but they remain parallel to one another in the direction of their long axes.

Liquid crystals also exhibit an isotropic liquid state. There is a well defined transition point as these compounds pass from a liquid crystalline state to an isotropic liquid state. The temeprature at this point is denoted T_c and it is called the clearing point, since all cloudiness in the liquid vanishes. There can also be transitions between different liquid crystalline states, such as from a smectic state to a nematic state,

Molecular structure plays an important role in the liquid crystalline states that a molecule exhibits. Small alterations in the structure will sometimes greatly affect the properties of the liquid crystal compound.⁶ Changes that increase lateral separation and decrease lateral attractions tend to decrease the thermal stabilities of liquid crystalline states. If the change increases the polarity and/or polarizability of the molecule, then the thermal stability will be increased.

Modification of the alkyl tail length on liquid crystalline molecules has two opposing effects. The longer molecules are less readily rotated out of the ordered states and their overall polarizability is increased. These two factors will increase the thermal stability of the system. On the other hand, the aromatic centers are further apart, and this tends to result in a decrease in thermal stability.

Many theories have been proposed that try to describe the various liquid crystalline states; some of them will be briefly discussed here.⁷⁻¹⁴ Ericksen⁷ suggests a continuum theory that describes the macroscopic behavior of nematic liquid crystals, and has used this theory to investigate the propagation of orientation waves and viscosity. In this model, the nematic fluids are considered to be incompressible and thermal effects are ignored. It was found that associated with any discontinuity in orientation there is a discontinuity in motion, which promotes dissipation of the orientation wave. The continuum theory predicts that the fluid will behave as a Newtonian fluid at high shear rates. If the shear rate is low, then there will be some small differences in the normal stress. These stress effects should be similar to those found in polymer solutions.

Franklin⁸ has modified Kirkwood's diffusion theory to take into account anisotropic viscosity, molecular order, and the detailed geometry of the molecules. This theory adopts the assumption that the molecules are rigid rods, and predicts a Stokes-Einstein like behavior for the relationship between the rotational diffusion of a liquid crystal and its viscosity. It also predicts a temperature dependence of the broadening of Rayleigh peaks.

Wadati and Isihara⁹ present a theory based on cluster expansions for a non-uniform system. They obtained good success in predicting phase transitions of rod-like molecules in two dimensions. They predict that the mechanism for the nematic-smectic phase transition is the same as that for hard-sphere particles.

Freed¹⁰ has looked at a stochastic-molecular theory for spin relaxation of liquid crystals. He has shown that the statistical independence between the overall molecular reorientational motion and the order fluctuations can be removed.

Cotter¹¹⁻¹⁴ has developed a theory in which the short range intermolecular repulsions are represented by repulsions between hard spherocylinders and the intermolecular attractions are treated self-consistently in the mean field approximation. This attraction tends to align the molecular axes in space and provides a uniform background potential. This model suggests that short range anisotropic intermolecular repulsions play a major role in stabilizing nematic mesophases.

Raman spectroscopy has been used to delve into the molecular structure and forces that characterize liquid crystal systems. Schnur¹⁵ noticed new Raman bands that changed as the liquid crystal phase changes for alkoxyazobenzens. These low frequency bands were attributed to an accordian mode of the alkyl tail of the molecules under study. The temperature dependence of these bands indicate that a greater number of conformations of the tail are allowed as the order of the fluid decreases.

Priestley and Pershun¹⁶ and Jen et al.¹⁷ have developed a formalism by which the order parameter of a nematic liquid crystal can be obtained using depolarization ratios of Raman bands. The technique used has shown promise for being able to study the internal structure of various smectic phases, since the limitations are how well the incident beam can be focused and how selectively the scattered light can be collected.

A good discussion of the vibrational spectroscopy of liquid crystals has been presented by Bullkin.¹⁸ He has noticed pretransitional effects in both the infrared and Raman spectra of nematic liquid crystals. The indication is a "softening" of a mode that arises from a hindered rotation or translation of the system. Calculations made on these modes have shown that there exists strong coupling among the modes along certain axes, while much weaker coupling exists along others.

Gray and Mosley¹⁹ have looked at the Raman spectra of 5CB and 5CB-d₁₁. They assigned the observed Raman bands to various vibrational modes of the molecules. They also explained some of the frequency shifts and intensity changes observed upon transition from one phase to another. Most of these changes were due to a freeing of translational and rotational modes.

Many investigators have studied the viscosity of liquid crystals.²⁰⁻³⁴ Fisher and Fredrickson²⁰ investigated the effect of interfacial orientation on the viscosity of p-azoxyanisole. They found that if the molecules were oriented perpendicular to the walls of a capillary tube there was a much more pronounced non-Newtonian behavior of the viscosity than if the molecules were parallel to the walls. Martinoty and Candau²¹ studied the viscosity coefficients using shear wave reflectance equations. Gahwiller²² determined five independent viscosity coefficients using a combination of the flow velocity and changes in birefringence induced by laminar flow in a magnetic field. Wahl and Fisher²³ looked at shear flow using rotating glass plates. With this method they were able to obtain elastic and viscosity constants of N-(p-methoxybenzylidene)-pbutylamine (MBBA).

Brochard²⁴ studied the effect of rotation of the molecular axis on some effective viscosity coefficients. He was also able to determine some of the Leslie coefficients using this technique. Gruler and Meier²⁵ determined the splay and bend constants of a series of 4,4'-di(n-alkoxy)azoxybenzenes by means of changes in birefringence of parallel oriented samples in a magnetic field. Porter et al.²⁶ studied the viscosity of blends of cholesteryl acetate and myristate. These studies showed that the viscosity was Newtonian in the isotropic phase, but non-Newtonian in the cholesteric and smectic phases. DeGennes²⁷ calculated the effect of shear flows on critical fluctuations in fluids. Kim et al.²⁸ measured the anisotropic shear viscosity in CBOOA. They found that if the molecules are aligned parallel to the walls, the smectic phase showed nearly Newtonian flow, and the temperature dependence had an Arrhenius behavior.

Karat and Madhusudana²⁹⁻³¹ looked at the elastic properties of a series of 4'-n-Alkyl-4-Cyanobiphenyls. The constants showed the oddeven effect. Bata et al.³² obtained rotary motion of liquid crystal molecules about their short axes from splay viscosity measurements. The relaxation time showed a Stokes-Einstein type of behavior. Kawamura and Iwayanagi³³ obtained a complex shear viscosity in the isotropic and nematic phases of nematic liquid crystals. They noticed Newtonian behavior in both phases. White et al.³⁴ measured the apparent viscosity of MBBA, hexyloxybenzylidene amino benzonitrile (HBAB), and cyanobenzylidene octyloxyaniline (CBOOA). They showed that the measured viscosities fit all the standard relations. A good review of the physical properties of liquid crystals can be found in a book written by DeGennes.³⁵

III. THEORETICAL

In describing the expected shape of a Raman band one must start from the basic equation that describes the transition between energy levels, taken from the Schrodinger picture of a molecular transition. In the Schrodinger viewpoint, the intensity of a Raman band can be written using the polarization formula for non-resonant Raman scattering:³⁶

$$I(\omega) = \sum_{i} \rho_{i} \sum_{f} |\langle i | \varepsilon^{I} \cdot \alpha^{\vee} \cdot \varepsilon^{S} | f \rangle |^{2} \delta(\omega^{S} - \omega^{I} + \omega_{\vee} + \omega_{f} - \omega_{i}), \qquad (1)$$

where i and f correspond to the initial and final rotation-translation states of the molecule, respectively. The ω 's are the frequencies of the radiation, with: ω^{I} the frequency of the incident photon, ω^{S} the scattered frequency, and ω_{ν} , ω_{f} , and ω_{i} corresponding to the energies of the vibration, the final state, and the initial state, respectively. The polarization is given by α^{ν} , and ε^{I} and ε^{S} are the incident and scattered unit, polarized, electric vectors, respectively.

To convert to the Heisenberg picture the first assumption that is made is that the sample is in thermal equilibrium before each photon is scattered, so that

$$\rho_{i} = e^{-\hbar} i^{/kT} \sum_{i} e^{-\bar{h}\omega_{i}/kT}.$$
(2)

The delta function in Equation 1 is expressed as a Fourier integral with the form

$$\delta(\omega) = (1/2\pi) \int_{-\infty}^{\infty} e^{i\omega t} dt$$
(3)

Using Equation 3, Equation 1 becomes

$$I(\omega) = (1/2\pi) \sum_{i} \sum_{i} \langle i | \varepsilon^{I} \cdot \alpha^{\vee} \cdot \varepsilon^{S} | f > \langle f | \varepsilon^{I} \cdot \alpha^{\vee} \cdot \varepsilon^{S} | i >$$

$$X \int_{-\infty}^{\infty} e^{i(\omega^{S} - \omega^{I} + \omega_{\nu})t} e^{i\omega} f^{t} e^{-i\omega} i^{t} dt. \qquad (4)$$

The next step in the transformation is to express the rotationtranslation energies as eigenvalues of the Hamiltonian, \hat{H} , acting on the states |i> and |f>, and to sum over the complete set of final states. Equation 4 becomes

$$I(\omega) = (1/2\pi) \sum_{i} \sum_{i} \sum_{f} |\epsilon^{I} \cdot \alpha^{v} \cdot \epsilon^{S}| f \ge f |e^{i\hat{H}t/\hbar} \epsilon^{I} \cdot \alpha^{v} \cdot \epsilon^{S}$$

$$X_{e}^{-i\hat{H}t/\hbar} |i \ge \int_{-\infty}^{\infty} e^{i(\omega^{S} - \omega^{I} + \omega_{v})t} dt$$

$$= (1/2\pi) \int_{0}^{\infty} dt e^{-i\omega t} \sum_{i} |\epsilon^{i}| (\epsilon^{I} \cdot \alpha^{v} \cdot \epsilon^{S}) \frac{i\hat{H}t/\hbar}{\epsilon} (\epsilon^{I} \cdot \alpha^{v} \cdot \epsilon^{S})$$

$$X_{e}^{-i\hat{H}t/\hbar} |i \ge, \qquad (5)$$

where $\omega = \omega^{I} - \omega^{S} - \omega_{v}$ and is the displacement from the center of the Raman band. Equation 5 can be simplified by using the solution to the Heisenberg equation of motion

$$d\alpha | dt = i [\hat{H}, \alpha] / \bar{h}, \qquad (6)$$

which upon integration with respect to time yields

$$\begin{array}{l} \alpha(t) = e^{i\widehat{H}t/\hbar} \alpha(0)e^{-i\widehat{H}t/\hbar}. \end{array}$$

$$\begin{array}{c} (7) \end{array}$$

Substituting Equation 7 into Equation 5 yields

$$I(\omega) = (1/2\pi) \int_{-\infty}^{\infty} < [\varepsilon^{I} \cdot \alpha^{\vee}(0) \cdot \varepsilon^{S}] [\varepsilon^{I} \cdot \alpha^{\vee}(t) \cdot \varepsilon^{S} > e^{-i\omega t} dt. (8)$$

If the sample is isotropic, Equation 8 can be simplified to

$$I(\omega) = (1/2\pi) \int_{-\infty}^{\infty} (1/3) < \alpha^{\nu}(0) \alpha^{\nu}(t) > e^{-i\omega t} dt.$$
(9)

The factor of 1/3 can be omitted by normalizing the intensity.

To obtain an expression for the time correlation function, the inverse Fourier transform is taken of Equation 9, and the correlation function can be written as

$$\Phi(t) = \langle \alpha^{\vee}(t) \alpha^{\vee}(0) \rangle = \int_{-\infty}^{\infty} I(\omega) e^{i\omega t} d\omega.$$
(10)

The polarizability taken into account has been the total polarizability of the sample. If this is transformed to the polarizability of individual molecules, the correlation function becomes, when looking at one component:

$$\Phi_{jk}(t) = \sum_{B} \langle \alpha_{jk}^{A}(t) \alpha_{jk}^{B}(0) \rangle, \qquad (11)$$

where the superscripts A and B label the molecules of the system.

Equation 11 can be simplified by expanding $\alpha_{jk}(t)$ in a Taylor series in powers of the normal coordinate $q^{\nu}(t)$, 37

$$\alpha_{jk}(t) = \alpha_{jk}^{0}(t) + \sum_{\nu} \alpha_{jk}^{\nu}(t) q^{\nu}(t) + \dots , \qquad (12)$$

where $\alpha_{jk}^{\nu}(t) = dx_{jk}(t)/dq^{\nu}(t) |q^{\nu} = 0$. Substituting Equation 12 into Equation 11 and keeping terms to first order only, the correlation function can be written as

$$\Phi_{jk}(t) = \sum_{B} \left[\langle \alpha_{jk}^{OA}(t) \alpha_{jk}^{OB}(0) \rangle + \sum_{\nu} \langle \alpha_{jk}^{\nu A}(t) \alpha_{jk}^{\nu B}(0) \rangle \right]$$

$$X \langle q^{\nu A}(t) q^{\nu B}(0) \rangle], \qquad (13)$$

where the assumption is made that the internal vibrations are not coupled to the orientation of the molecule, and thus the cross terms can be neglected.

The correlation function can be split up into terms that depend only on molecule A, a "self" part, and into terms that depend on the interaction between A and B, a "distinct" part.³⁸ When this is done the correlation function becomes

$$\Phi_{jk}(t) = \langle \alpha^{A}_{jk}(t) \alpha^{A}_{jk}(0) \rangle t \sum_{B \neq A} \langle \alpha^{A}_{jk}(t) \alpha^{B}_{jk}(0) \rangle.$$
(14)

The assumption is now made that the phases of vibrations in different molecules are random, that is, $q^{\nu A}(t)q^{\nu B}(0) = 0$. Using this assumption and combining Equations 13 and 14, the correlation function can be written as

$$\Phi_{jk}(t) = \langle \alpha_{jk}^{OA}(t) \alpha_{jk}^{OA}(0) \rangle + \sum_{\substack{B \neq A}} \langle \alpha_{jk}^{OA}(t) \alpha_{jk}^{OB}(0) \rangle$$

+
$$\sum_{\nu} \langle \alpha_{jk}^{\nu A}(t) \alpha_{jk}^{\nu A}(0) \rangle \langle q^{\nu A}(t) q^{\nu A}(0) \rangle, \qquad (15)$$

where the three terms are the single-particle Ragleigh, cooperative Rayleigh, and single-particle Raman scattering, respectively.

Any of the three terms in Equation 15 can be used to extract reorientational information from a lineshape measurement of the sample in question. Since the Raman scattering arises from normal vibrational modes of the molecule, it can be used to probe how different vibrational modes reorient, and thus, by careful selection of the mode, the reorientation about the different molecular axes can be sampled. Therefore, the single-particle Raman scattering term of Equation 15 will be analyzed. The superscripts denoting the molecule will be dropped since it is a single-particle process. The terms α_{jk}^{ν} can be separated into an isotropic part and an anisotropic part. The two parts are, respectively,

$$\alpha^{\vee} = (1/3) \sum_{j} \sum_{j} \alpha^{\vee}_{jj},$$

$$\beta^{\vee}_{jk} = \alpha^{\vee}_{jk} - \alpha^{\vee} \delta_{jk}.$$
 (16)

Since the anisotropic part does not commute with the rotational kinetic energy, 39 it is this part that contains the rotational information. Thus the orientational component of the spectrum is: 38

$$I_{jk}^{OR} = \int_{-\infty}^{\infty} \langle \beta_{jk}^{\nu}(A) \beta_{jk}^{\nu}(0) \rangle e^{-i\omega t} dt, \qquad (17)$$

where the intrinsic width has been neglected.

In order to extract reorientational information from Equation 17, the form of $\langle \beta_{jk}^{\nu}(t)\beta_{jk}^{\nu}(0) \rangle$ must be determined. Viewed in the molecular frame of reference the β_{jk}^{ν} 's are constants that are dependent only on the structure of the molecule. Written in spherical notation, they become:³⁸

$$\beta_{0}^{v} = [(6)^{1/2}/2]\beta_{zz}^{v},$$

$$\beta_{\pm 1}^{v} = (1/2)(\mp \beta_{xz}^{v} - i\beta_{yz}^{v}),$$

$$\beta_{\pm 2}^{v} = (1/2)(\beta_{xx}^{v} - \beta_{yy}^{v})\pm i\beta_{xy}^{v}.$$
(18)

The molecular frame is different from the laboratory frame and the relation between the two can be described by a rotation in terms of Eulerian angles, $\Omega(\alpha,\beta,\gamma)$.⁴⁰ The transformation from the molecular frame to the laboratory frame can be performed by³⁸

$$\beta_{n}^{\nu}(\Omega) = \sum_{m=-2}^{2} D_{nm}^{(2)}(\Omega) \beta_{m}^{\nu}(MF), \qquad (19)$$

where $D_{nm}^{(2)}(\Omega)$ is the Wigner rotation matrix of the second order and is described by ⁴¹

$$D_{nm}^{j}(\Omega) = e^{-in\alpha} e^{-in\gamma} \sum_{s} (-1)^{s} [(j+m)!(j+n)!(j-m)!(j-n)!]^{1/2}$$

$$X[s!(j-s-n)!(j+m-s)!(n+s-m)!]^{-1} [\cos(\beta/2)]^{2j+m-n-2s}$$

$$X[-sin(\beta/2)]^{h-m+2s}, \qquad (20)$$

with the sum over ^s starting where all the factorials in the denominator are positive. The $\beta_m^{\nu}(MF)$'s are the spherical polarizability elements in the molecular frame.

Now that there is a relation between the laboratory frame and the molecular frame, a laboratory coordinate system must be chosen. Let the light be incident along the Y axis, and view the 90° scattering along the X axis. The polarization perpendicular to this scattering plane is called V and the polarization in the plane H.³⁸ From this arrangement there are four possible combinations of the incident and scattered polarizations for the system: VV, VH, HV, and HH, where the first letter indicates the polarization of the incident beam and the second letter the polarization of the scattered light. In the laboratory frame a single element of the polarizability tensor, $\beta_{ik}^{\nu}(\Omega)$, is selected for

each of the four spectra. The equations can be exemplified using the VH scattering geometry. The $\beta_{ik}^{\nu}(\Omega)$ selected by VH scattering is

$$\beta_{yz}^{\nu}(\Omega) = i [\beta_{1}^{\nu}(\Omega) + \beta_{-1}^{\nu}(\Omega)] = i \sum_{m} [D_{1m}^{(2)}(\Omega) + D_{-1m}^{(2)}(\Omega)] \beta_{m}^{\nu}(MF),$$
(21)

where the appropriate terms are obtained from Equations 18 and 19. From Equation 21 the time correlation function becomes

In order to proceed further with the evaluation of the correlation function one must evaluate the probability that in any time t a molecule will have rotated through an angle between $\Delta\Omega$ and $\Delta\Omega$ + d($\Delta\Omega$) from its initial orientation Ω ; that is, some form must be given for the single particle orientational probability density, P($\Delta\Omega$,t). Here the implicit assumption is that the probability density depends only on the change in angle and not the initial angle. The probability density provides information about the reorientational motion of the molecule. In fact, any experiment that can be devised to gain some understanding about the rotations will probe P($\Delta\Omega$,t). One possible functional form for P($\Delta\Omega$,t) is an expansion in terms of a sum of products of the Wigner matrices and an arbitrary function of time, $f_k^{(\ell)}(t)$.³⁸ P($\Delta\Omega$,t) then becomes

$$P(\Delta\Omega,t) = \sum_{kk} D_{kk}^{(\ell)}(\Delta\Omega) f_{k}^{(\ell)}(t).$$
(23)

The D matrices will operate on one another to give the following transformation property:

$$D_{nm}^{(2)*}(\Omega') = \sum_{\varrho} D_{n\ell}^{(2)*}(\Omega) D_{\ell m}^{(2)*}(\Delta \Omega), \qquad (24)$$

which along with Equation 23 will change Equation 22 into

Upon integration over Ω and $\Delta\Omega$ and application of the orthogonality condition for the D matrices,⁴¹ Equation 25 simplifies to

$$\langle \beta_{yz}^{\nu}(\Omega')\beta_{yz}^{\nu}(\Omega) \rangle = C_{o_{m=-2}}^{2} |\beta_{m}^{\nu}(MF)|^{2} f_{m}^{(2)}(t).$$
 (26)

Up to this point nothing has been assumed about the molecular reorientation mechanism. As a molecule rotates in a liquid, the sharp vibrational transitions seen for an isolated molecule will be broadened due to the changing interactions with the other molecules in the liquid. The broadening is therefore characteristic of the liquid and of the method of molecular rotation. The functional form of the broadened transition is described by Equation 26, which, as written, is independent of any choice of model. By selecting a model that is appropriate for the experimental data collecting technique, Equation 26 can be written in a form that will yield the reorientational correlation function from the collected data. Symmetric top molecules are reasonably simple ones to consider when finding an explicit expression for Equation 26, since $f_m^{(2)}(t) = f_{-m}^{(2)}(t)$. If the major symmetry axis is taken to be the Z axis in the molecular frame, then $f_0^{(2)}(t)$ is the correlation function for the tumbling of the major axis of the molecule. The two functions $f_1^{(2)}(t)$ and $f_2^{(2)}(t)$ contain information about both the tumbling motion and the reorientation about the major axis. The problem is to determine the functional form of $f_m^{(2)}(t)$ by using a model for the reorientation of the molecule.

For symmetric top molecules there is one feature that makes the evaluation of $f_m^{(2)}(t)$ somewhat simpler. Vibrations can be chosen where only one $|\beta_m^{\nu}(MF)|^2 \neq 0$, and since the $|\beta_m^{\nu}(MF)|^2$'s are the coupling coefficients for the correlation function, information can be obtained about the $f_{(m)}^{(2)}(t)$ that corresponds to the nonzero $|\beta_m^{\nu}(MF)|^2$. The symmetry of the molecule lets one choose the vibrations which provide this information.

The symmetry of the appropriate vibrations very often determines the form of $\beta^{\nu}(MF)$. Bartoli and Litovitz give a table of the polarizability elements that are nonzero for the different symmetry species of the various point groups of symmetric top molecules.³⁸ In some cases each $f_m^{(2)}(t)$ can be determined separately, but in others linear combinations of $f_m^{(2)}(t)$ arise.

The next step in the problem is to assume a model for the rotational motion. A specific form for Equation 26 has been obtained by assuming a small-step rotational diffusion model.³⁸ This model is applicable only to symmetric top molecules. With this assumption Equation 26 becomes

$$\langle \beta_{yz}^{\nu}(\Omega')\beta_{yz}^{\nu}(\Omega) \rangle = \alpha \sum_{m=-2}^{2} |\beta_{m}^{\nu}(MF)|^{2} e^{-t/\tau} \tau_{m}^{(2)}$$

$$(27)$$

where $f_m^{(2)}(t)$ is expressed as an exponential whose time constant is

$$\tau_{\rm m}^{(2)} = \left[6D_{\underline{1}} + (D_{11} - D_{\underline{1}})_{\rm m}^2 \right]^{-1}$$
(28)

and depends only on the principal rotational diffusion constants of the molecule. From Equations 28 and 27 the rotational diffusion tensor can be determined by studying the reorientational spectra of any two Raman lines that arise from different symmetry vibrations. The reorientational lineshape is seen to be a Lorentzian function with a half-width at half-height (HWHH) that is the reciprocal of the correlation time, $\tau_m^{(2)}$. With these equations, the reorientational motion about an axis perpendicular to the major symmetry axis and about an axis parallel to the symmetry axis, ³⁸ can be studied.

If, instead of assuming an isotropic medium with small-step rotational diffusion, the case of an anisotropic medium, where there exists a preferential molecular orientation, is considered, it is found that there is a different form for $f_m^{(2)}(t)$.² The difference in form arises because the rotational motion is no longer random, but there is a driving force that tends to rotate the molecules back toward an aligned state. Such a motion leads to a mathematical form for the correlation function that looks like:

$$f_{m}^{(2)}(t) = \sum_{i} C_{i} e^{-\lambda mi} t_{i}^{(2)},$$
 (29)

so that Equation 26 becomes

$$\langle \beta_{yz}^{\vee}(\Omega')\beta_{yz}^{\vee}(\Omega) \rangle = \alpha \sum_{m=-2}^{2} |\beta_{m}^{\vee}(MF)|^{2} \sum_{i=1}^{2} C_{i} e^{-\lambda_{mi}^{(2)}t}.$$
(30)

Since Equation 30 contains an infinite sum of exponentials, the reorientational lineshapes may be drastically altered. One might expect that these lineshapes would be non-Lorentzian, and that through a suitable experiment this change could be detected as the medium changes from isotropic to anisotropic.

Another way of obtaining reorientational relaxation times is to use the Stokes-Einstein relation between the shear viscosity of a liquid and the reorientational correlation time. Bloemberger et al.⁴² presented the following equation for spherical-top molecules:

$$\tau_2 = 4\pi a^3 n/3kT;$$
 (31)

where a is the hydrodynamic rotational radius of the molecule, η is the viscosity of the fluid, and τ_2 is the reorientational correlation time. Equation 31 uses sticking boundary conditions and there has been much discussion as to the agreement with experimental data.⁴³⁻⁴⁸ It is therefore appropriate to consider the consequences of choosing other boundary conditions.

Hu and Żwanzig have presented a formulation for calculating a weighting factor based on the degree of slipping that a molecular system will undergo as it rotates.⁴³ This slipping gives rise to a relaxation time that is shorter than that calculated with sticking boundary conditions, so the weighting factor is less than unity. Alms et al.⁴⁹⁻⁵¹ introduced a nonzero intercept into the correlation expression to reproduce their experimental data. This intercept is very similar to the free-rotor correlation time given by Bartoli and Litovitz^{1,38} as

$$\tau_{\rm FR} = 2\pi (41/360) (1/kT)^{1/2}, \qquad (32)$$

where I is the moment of inertia for that rotation,

Fury and Jonas⁴⁴ obtained an expression for τ_2 of the form

$$\tau_{2}(T,n) = C(T)n + \tau_{0}(T),$$
 (33)

where $\tau_0(T)$ is the free-rotor correlation time. Applying the slip/ stick ratio obtained from Hu and Zwanzig⁴³ they obtained the following expression for C(T):

$$C(T) = (4\pi a^3/3kT)\theta_{eff}$$
, (34)

where θ is the effective slip/stick ratio and can be estimated in three different ways;

$$\theta_{\text{eff}} = \frac{(1/3)\Sigma\theta(\rho_i)}{i}, \qquad (35a)$$

$$\theta_{\text{eff}} = (2/3)\theta(\rho_{xy}), \qquad (35b)$$

$$\theta_{\text{eff}} = \sum_{i}^{\Sigma \omega} i^{(\rho_i)}, \qquad (35c)$$

where i = (x, y_z) and ρ_i represents the deviation from sphericity. ω_i is a weighting factor that is given by

$$\omega_{i} = \rho_{i}^{2} (\sum_{i} \rho_{i}^{2})^{-1}$$
(36)

and is related to an inverse of the area swept out by rotation about the ith axis. As the molecule becomes more spherical Equation 35c approaches the value of Equation 35a, so the difference in the two is related to the non-spherical nature of the molecule and will be reflected in the resulting correlation times. Assink and Jonas⁵² have presented another modification to the Stokes-Einstein relation, which is:

$$\tau_2 = (4\pi a^3 n/3kT) f_R, \qquad (37)$$

where f_R is the rotational microviscosity factor and is equal to 0.163 for a neat liquid.

The expressions derived using slipping boundary conditions work well when there is a reasonable degree of sphericity to the molecular system. It is more likely that the behavior of liquid crystal systems will follow sticking boundary conditions, since they are composed of long, rodlike molecules. Therefore, the equation used by Gierke and Flygare⁵³ in the investigation of reorientational relaxation of p-methoxybenzylidinen-butylaniline (MBBA) was formulated from sticking boundary conditions and a nonzero intercept. The equation they used was a modified form of Equation 31,

$$\tau_2 = V^* \eta / kT + \tau_2^0.$$
(38)

V* is the effective molecular volume and can be calculated from density measurements and τ_2^0 is the zero viscosity intercept given by Equation 32.

IV, EXPERIMENTAL

The experimental data were collected using a laser Raman system built from components to suit a variety of experimental needs. 54,55 Figure 1 shows a block diagram of this instrument. Excitation is provided by either a Spectra-Physics model 165 krypton ion on a Spectra-Physics model 164 argon ion gas laser, each permitting a choice of several excitation wavelengths. The laser emission is sent through a Spectra-Physics model 310-21 polarization rotator to define the incident electric vector, and the light scattered from the sample is passed through a piece of Polaroid film to select the polarization to be analyzed. The scattered light is then focused onto the entrance slit of a Jarrell-Ash model 25-100 double monochromator, and the dispersed radiation is detected by an RCA model C31034A photomultiplier tube cooled to -30°C by a Products for Research model TE-104TS thermoelectric cooler. The electrical output of the photomultiplier tube is sent either to a picoammeter which detects and amplifies the average current, or to a photon counting system which counts the number of current pulses per unit time. The photon counting system can be interfaced to a minicomputer, and that part of the system will be described in some detail in the next chapter.

The sample cell used for simple isotropic liquids is shown in Figure 2. It is fabricated of glass and has optically flat ends so that the laser light enters without being defocused by the air-glass or glassliquid interfaces. For samples where the temperature needed to be controlled or monitored, a quartz cuvette of dimensions 7mm x 7mm x 25.4mm

FIGURE 1. A BLOCK DIAGRAM OF THE LASER RAMAN SYSTEM USED FOR THIS WORK.



FIGURE 1

FIGURE 2. THE GLASS RAMAN CELL USED FOR SIMPLE LIQUIDS



FIGURE 2
was employed. Temperatures near 25°C were maintained by the copper holder shown in Figure 3. The block is hollow to allow circulation of a thermostatting liquid. Because of its high heat capacity, water was normally chosen as the temperature-controlling liquid; it was circulated by a pump from a reservoir which also contained an immersion heater and thermostat. The sample temperature was monitored at a slot in the cuvette holder by means of a copper-constantan thermocouple (see Figure 3). Raman scattered radiation was gathered from a slit in the copper block. Figure 4 shows the holder used for temperatures above 100°C. The optical features are the same as the circulating holder for the cuvette, but this high-temperature block is solid copper, warmed by means of a resistive heater. The temperature is controlled by placing a thermistor in a feedback loop which controls the current to the heater. In both of the sample holders a glass cover plate is placed over the cuvette.

The data analysis can be simplified by the following definition of the scattering geometry (see Figure 1). The incident laser light is along the y-axis and the 90° scattered light is along the x-axis. The polarization of the electric vectors of both the incident and the scattered light can be related to the xy scattering plane. Polarization perpendicular to the scattering plane, i.e., in the z direction, is designated as V polarization; polarization in the xy plane is denoted as H polarization. Four possible spectroscopic combinations result;¹ VV, VH, HV, and HH, where the incident polarization is designated by the first letter. The VV scattering geometry yields a polarized spectrum, while the other three scattering geometries provide depolarized spectra.

FIGURE 3. THE COPPER CUVETTE HOLDER USED FOR RAMAN EXPERIMENTS RUN AT TEMPERATURES AROUND 25°C.





Side View

.



Front View

FIGURE 3

FIGURE 4. THE COPPER CUVETTE HOLDER USED FOR RAMAN EXPERIMENTS RUN AT TEMPERATURES ABOVE 100°C.



Top View



Side View



Front View



In order to obtain meaningful lineshape measurements, the resolution of the monochromotor was set at a spectral slit width of 1.0 cm^{-1} . The dispersion of the monochromator varies with absolute frequency, but over a small interval (less than 100 cm^{-1}) the dispersion does not vary sufficiently to change the spectral slit width significantly. The resolution was chosen to be roughly five to ten times smaller than the half-widths of the isolated Raman bands that were analyzed. In order to obtain enough data points to properly define the overall shape of a Raman band, the sampling interval was chosen to be 0.05 cm^{-1} , or one step on the monochromator stepping motor. The range of a scan was 50 cm^{-1} , or 1000 data points, chosen as the optimum compromise between computational time on the CDC 6500 computer and determination of the lineshape in the wings of a Raman band. The limiting factor in this decision was the core size of the CDC 6500 computer (150K octal words).

The instrumental function was measured by using a candle to scatter the incident radiation. A non-lasing fluorescence transition of the argon ion plasma was chosen. With the laser in resonance at 5145\AA , the plasma line at 4880 Å was viewed. Since this electronic transition is essentially a delta function, the only contribution to the overall shape is due to the instrument function. As with the sample data, the slit width was 1.0 cm^{-1} and the range of the scan was 50 cm^{-1} .

Density measurements were made using a 1.0 ml pycnometer. Since changes in weight were observed in the 10-100 mg range for neighboring temperatures, the sample was weighed four times on a Mettler 0.1 milligram balance to obtain an average weight. Pure water was weighed

at the same temperatures to correct for expansion of the pycnometer. The viscosities were measured with a Cannon Instrument Company Ostwald viscometer, number 75/K280, which has a flow constant of 0.00794 centistokes/second. An average of two runs was used to obtain the flow times. The viscometer was kept at a constant temperature in a water bath with a blade heater and a thermoregulator. For both the density and the viscometer water baths the temperature was controlled to $\pm 0.1^{\circ}$ C.

V. INSTRUMENTAL

With the greater availability of minicomputers and microprocessors it has become apparent that interfacing a Raman spectrometer to such a device has many advantages, $^{56-58}$ One such advantage is the ability to utilize multiple scans or longer integration times, thus increasing the signal-to-noise ratio (S/N) and thereby extracting weak signals from the background noise. Another advantage is the ability to perform repeated, sequential scans of a region of the spectrum and consequently to follow the time development of the system. Also, any data analysis that must be performed on a large region of the spectrum, such as lineshape fitting, is easier and more convenient if the data are collected in digital form in real time. 59

The computer interface between Digital Equipment Corporation PDP 8/I or PDP 8/M minicomputers and the Raman instrument described previously, designed and constructed as part of this dissertation work, is outlined in Figure 5. The interface consists of six circuit cards in a Vector card cage. The cards are located in slots two through seven, counting from left to right as viewed from the front of the cage. The cards cannot be interchanged in the cage, since the wiring on the back connectors differs depending on the particular slot. The interface comprises three distinct parts: photon counter, stepping motor, and control logic.

The photon counting portion consists of two 12-bit counters with an overflow flag on each counter. This allows up to three 12-bit words (2^{35} pulses) in the minicomputer to be used to count the number

FIGURE 5. THE OVERALL SCHEMATIC OF THE INTERFACE BETWEEN A PDP 8/I MINICOMPUTER AND A JARRELL-ASH RAMAN SPECTROMETER.

•



FIGURE 5

•

of photons striking the detector, thus enabling longer integration times before the counter overflows. The stepping motor control connects the minicomputer to the RTL electronics in the Raman instrument stepping motor control circuitry, It consists of a flip-flop (the output level defining the direction of motor rotation) and a monostable multivibrator that shapes the pulses used to drive the stepping motor. A capacitor and a resistor connected to the monostable limit the pulse rate to less than 400Hz, thus insuring that the stepping motor control will not become overloaded and start skipping steps. The control logic is used to sample the contents of each 12-bit counter separately, clear the counters, check the overflow flags, run the stepping motor, and turn the counter on or off. The input pulses to the control logic and the contents of the counters are transported between the minicomputer and the Raman spectrometer along two 70 foot, 34 line, ribbon cables with every alternate line connected to common. The +5 volt signal from the interface power supply is also sent along the ribbon cable to activate the line receivers connected to the minicomputer bus line.

The data acquisition programs are listed in Appendix A and a flowchart is provided in Figure 6. Some of the subroutines used, but not listed in Appendix A, were obtained from E. J. Darland.⁶⁰ The runtime parameters are defined in an interactive mode. First the minimum count time, which fixes the time the counter will be open for an initial measurement of the strength of the signal, is set. A calculation is then performed on the initial count rate to determine whether the preset number of counts (chosen to attain a certain S/N) will be reached within the preset maximum count time interval. Usually 0.1 to 0.2 seconds is

FIGURE 6. A FLOWCHART OF PROGRAM DATCOL.SV



FIGURE 6

sufficient for the initial count time. The next parameter to be set is the maximum count time, the longest interval for which the counter will be open to collect the pulses from the photomultiplier tube at a given data point. Longer count times will allow weaker signals to be detected and separated from the background noise. A count time of one to five seconds is adequate for a long survey scan, but count times up to forty seconds can be used to collect very weak signals. Next the limits of the scan are entered. Both the starting point and the ending point are entered as Stokes shifted frequencies $(\Delta \bar{\nu}'s)$ in wavenumbers.

Next the total number of counts desired is entered. This determines the signal-to-noise ratio that will be obtained during the run, since for random noise the S/N is the square root of the total number of counts.⁶¹ Usually for a quick survey run the number of counts entered should be between 1000 and 5000, depending on the background level. The total number of counts is coupled with the maximum count time, and care must be taken to set the two so that the background is not treated as part of the Raman signal and thus integrated for a long period of time. This is done by setting the maximum number of counts high enough so that the background counts will never reach that number within the maximum count time. If the background is treated as part of the Raman signal the quick survey scan could last for a few hours. For higher resolution scans over a small region of the spectrum, 10,000 counts or higher is adequate, depending on the strength of the Raman signal.

The next parameter to be entered is the spacing between data points. Since each step of the stepping motor moves the spectrometer 0.05cm⁻¹, the spacing entered must be a multiple of this number. The spacing

should be chosen so that an adequate number of data points, usually four or five, is collected per spectral slit width. The next parameter set is the number of scans desired over the region of interest. This enables the operator to collect many data sets for signal averaging without having to reenter the input parameters. Next the strip chart recorder parameters are set. These are maximum counts per second and wavenumbers per inch. Both parameters are selected according to the operator's discretion regarding the data display in real time; they have no influence on how the data are collected or stored. For example, if the pen goes off scale the data are still stored by the computer as collected. Finally the filenames are entered in the form DEVI:FINAME, where DEVI is a standard OS/8 device name (RKB1, FLP2, DTA0, SYS, etc.) and FINAME is a six character file name. An extension of .DA is automatically appended to the filename.⁶⁰ If it becomes necessary to change parameters during a data run the program can be interrupted by striking a CONTROL G (^G) on the terminal. If the program is continued it will ask the operator which parameters he or she would like to change. Following this pause the program will continue to collect data.

After the run-time parameters are entered the program opens the counter for the minimum count time and samples the counters. The computer then performs a calculation to determine if the predetermined number of counts will be reached within the specified integration time.⁶¹ If this condition is not met the program will store the counts/second calculated and then step the motor to move the grating the preset distance. If the above condition is met, the program will calculate how long the counter should be active to reach the predetermined number of counts.

Once this is done the program opens the counter for that calculated length of time, samples the counter, calculates the counts/second, and steps the stepping motor. If the predetermined number of counts has been exceeded in the initial count period, the computer will calculate the count/second and step the stepping motor. After each step there is a software wait loop of about five milliseconds to let the moving parts settle down and also to keep the electronics from becoming overloaded. The data are stored as counts/second versus Stokes wavenumber in A6 format on a mass storage device, the choice being a hard disk, floppy disk, or Dectape.

Before the data collection is initiated, the spectrometer should be positioned at the desired starting frequency. This is accomplished by a program called MOVE, which is listed in Appendix B; the flowchart is given in Figure 7. This program will direct the stepping motor to move the grating of the Raman Spectrometer from one frequency to another, and will also calibrate the system by scanning over the laser excitation line. The spectrometer must first be positioned about five wavenumbers to the blue of the excitation wavenumber and precautions MUST be taken to insure that very little light strikes the detector. This is done by setting the laser output power at 100 milliwatts, the voltage on the photomultiplier tube at 1100 volts, and the slits at 10-20-10 microns. The computer then scans the grating through the excitation frequency, collects the counts/second, and finds the maximum signal. The position of the maximum is defined as zero and is used as the reference point for the Stokes-Shifted Raman scattering. The computer then inquires of the operator the starting wavenumber shift for the Raman scan and moves the spectrometer to that point.

FIGURE 7. A FLOWCHART OF PROGRAM MOVE.SV



FIGURE 7

The data are analyzed with a PDP 8/I, a PDP 8/M, or a CDC 6500 computer. The PDP 8 programs are listed in Appendix C and a flowchart is provided in Figure 8. These programs include baseline correction, smoothing, normalization of individual bands, peck location, signal averaging, and plotting of data on either a CRT display terminal or a strip chart recorder. The programs are all designed to use a minimum number of core locations, and are therefore somewhat slow when operating on a large amount of data.

The baseline correction program assumes a linear baseline function and performs a least squares fit of a preset number of data points to a general straight line equation.⁶² The calculated straight line is then subtracted from the entire data set and the new data are stored in another file.

The smoothing routine uses a 17-point polynomial fit to calculate a better value for the central point. The weighting coefficients incorporated in the program were derived from a table published by Sovitzky and Golay.⁶³ The smoothing routine should be used with caution, since some distortion arises from any type of data smoothing.⁶⁴ Smoothing will make the Raman bands look sharper and will thus enhance any parameters that are extracted by way of human interaction, such as obtaining peak locations from a plot of the spectrum.

The normalization program scales the entire Raman spectrum so that the maximum intensity of the strongest band in the desired region is assigned a value of unity. This routine is useful for preparing the data for bandshape measurements, and also can be used to scale spectra for background subtraction, enabling changes in relative band intensities under varying experimental conditions to be easily discerned.

FIGURE 8. A FLOWCHART OF PROGRAM CRUNCH.SV



FIGURE 8

The peak location routine finds all the local maxima above a preset level within a specified region of the data file. The program checks whether the difference between the maximum and minimum values within a twenty point region around the maximum is greater than the signal-tonoise ratio. If the difference is not greater, then the maximum is really part of the background. Also the maximum must be the central point in the twenty point region. Twenty points were chosen as an adequate tradeoff between finding all the shoulders and sidebands and rejecting noise spikes in the background.

The signal averaging routine will either add or subtract data files. Up to 100 data files can be added together to improve the signal-to-noise ratio. The subtraction feature is useful to remove the effects of background and solvent bands.

The data plotting routine plots all or part of a data file on either a Tektronix model 4010 terminal or a strip chart recorder. The program first scans the region to be plotted to find the extrema within that region. If the plot is to be on the terminal the program will ask the operator to choose either point or line plot options. It also asks for the tick interval on the x-axis. When the file is plotted out crosshairs appear. The x and y values of the intersection of the crosshairs are printed when any key is struck. To exit this part of the program a CONTROL G (^G) must be struck. If the plot is to be on the strip chart recorder the program asks the operator to input the spacing on the chart in wayenumbers/inch.

Another option in the package is a routine that will take the data files from the format used for storage on the PDP 8's (A6) and translate

the numbers to a standard format (E15.7). The transfer can be made with a two character data tag placed at the beginning of each line of data. Once the data are in the E format they are in a form suitable for use on the Cal Data 135 minicomputer in the CEMCOMGRAF facility. This minicomputer is configured like a Digital Equipment Corporation PDP 11 and uses the same software. The Cal Data 135 computer has a phone line interface with the University's CDC 6500 computer, and the data files are transferred between them as batch jobs.

The data analysis programs used on the CDC 6500 computer are lineshape determination programs. They are listed in Appendix D and the flowchart is shown in Figure 9. These programs were obtained from D. A. Wright⁶⁵ and modified to suit the Raman data obtained in this dissertation work. The rotational lineshape is assumed to be a Lorentzian function and is convolved with the isotropic line and fit to the anistotropic line. The convolution is performed as a Simpson's rule integration, and the fit is made by a least-squares method of minimizing the sum of the squared residuals between the calculated and experimental functions as the half-width of the Lorentzian function is varied. The final results of this program are sent back to the Cal Data 135 minicomputer for display on a matrix plotter. To obtain the vibrational function only minor modifications were made to the programs.

Sometimes instruments and electronic components seem to have minds of their own, and it becomes necessary to perform some troubleshooting. For the Raman system described in this dissertation experience has shown that several of the problems that may arise can be solved fairly readily.

FIGURE 9. A FLOWCHART OF PROGRAM LNSHP.



FIGURE 9

.

One such problem is the stepping motor not taking the specified number of steps. A symptom of this problem is the program not returning the spectrometer to the correct starting frequency. The step line leading from the interface to the spectrometer is the first place that an oscilloscope should be inserted to check out the system. The following diagnostic program should then be toggled into the minicomputer from the switch register:

This program will send pulses to the stepping motor at a rate that is determined by the setting on the switch register. To run the routine just below the limit of the monostable multivibrator the switch register should be set to 2000_8 . The pulses should be regularly spaced with no jitter when viewed on the oscilloscope. The usual source of step line problems is either a faulty flip-flop or monostable multivibrator on the card in slot seven of the cage.

If the step line is working well, the problem might be in the level line which controls the direction of the spectrometer. This can also be checked with an oscilloscope. The following little program will test the level line circuitry:

0200 6614 0201 6615 0202 5200

This routine will change the state of a flip-flop on card seven and cause the output to be a series of pulses that should be jitter-free when viewed on the oscilloscope. The jitter that has been seen in the past at this flip-flop has resulted from some high frequency noise on the inputs to the flip-flop. The noise was coming from some partial solder bridges on the circuit card. Also, at one time the unused inputs of the flip-flop were not properly terminated.

Sometimes one of the counters will be stuck in one state, or an integrated circuit associated with the counters might fail. To test the counters, a pulse generator is placed at the count input to the interface cage, either program from Appendix E is toggled into the computer, and the AC display on the computer is monitored as it counts up. If the circuitry is not counting properly, the malfunctioning bit can be retraced through the interface circuitry until the problem is spotted. If both programs show that the same bit is malfunctioning, the problem is probably in the final latch circuitry. If a bit is not working properly on only one program, then the problem is on the appropriate counter card.

Occasionally problems have arisen due to a difference in ground connections between the interface cage at the Raman instrument and the interface cage at the computer. These differences will set up a ground loop that can cause enough noise on the ribbon cable to degrade the signals. Ground loops are sometimes very difficult to trace down and solve, ⁶⁶ but in the past just a simple switch of a power cord from one outlet to another has worked.

VI. LINESHAPE ANALYSIS OF SIMPLE LIQUIDS

The reorientational lineshapes of several simple, isotropic liquids were measured to serve as standards for the lineshape analysis of an anisotropic system. Acetonitrile (CH_3CN) and chloroform ($CHCl_3$) were chosen as the sample liquids, and the computer programs written to collect and analyze the data were tested on them. These liquids have been subjects of many experiments, and there are sufficient results in the literature to enable easy comparison.^{1,38,48,67-70} The method of analysis chosen was similar to that used by Bartoli and Litovitz in their analysis of polarized Raman bands.¹

The liquid that gave the best results was acetonitrile. Its Raman spectrum is shown in Figure 10. The band that is the easiest to analyze is the C=N stretch at 2250 cm⁻¹. This is an A_1 vibration and is strongly polarized. Figure 11 shows the isolated vibrational band that was used as input for the lineshape analysis program described previously. The peak labeled P is the polarized scattering, and that labeled D is the depolarized scattering. The crude depolarization ratio for this band was measured to be 0.070. After correction for analyzer efficiency and polarization leakage the depolarization ratio became 0.057. The results of the lineshape calculation are shown in Figure 12. The peak labeled D is again the depolarized scattering. The curve labeled C is a convolution of the polarized scattering and a Lorentzian function used to approximate the reorientational correlation function. The program, which ceases iteration when the half-width change in two successive cycles is less than 0.01cm⁻¹, converged to a reorientational

FIGURE 10. SURVEY SCAN OF THE RAMAN SPECTRUM OF ACETONITRILE



FIGURE 11. THE 2250 cm⁻¹ VIBRATIONAL BAND OF ACETONITRILE, USED AS INPUT TO PROGRAM LNSHP.





FIGURE 11

FIGURE 12. THE OUTPUT OF PROGRAM LNSHP FOR THE 2250 cm⁻¹ VIBRATIONAL BAND OF ACETONITRILE.



 ${\rm cm}^{-1}$ band of ${\rm CH}_{3}{\rm CN}$

half-width of 3.0 \div 0.5 cm⁻¹. This number compares favorably with the half-width obtained by Bartoli and Litovitz using the same experimental and computational methods (3.5 cm⁻¹).¹ The reorientational lifetimes calculated through $\tau = 1/(2\pi CW_{OR})$, corresponding to an W_{OR} of 3.0 cm⁻¹ is 1.8 \pm 0.3 psec. This may be compared to the value Patterson and Griffiths obtained from depolarized Rayleigh scattering (1.8 psec).⁶⁹ Whittenburg and Wang obtained similar results in a more recent work from half-widths of Raman bands.⁴⁸

The analysis program was debugged and characterized using acetonitrile and other simple liquids. Some of the pitfalls that were observed while using this technique will be discussed in a later chapter. It should be noted at this point that the technique is very sensitive with regard to the strength of the transition being analyzed. Although this is true of most forms of spectroscopy, the effects become even more apparent when one is dealing with a quantity that results from the difference of two very similar experimental measurements.

VII, LIFETIME STUDY OF LIQUID CRYSTAL SYSTEMS

As was noted in the previous chapter, much work has been done on lineshape analysis of simple liquids, where the overall environment is isotropic and the reorientational bandshape is Lorentzian. It is possible that different theoretical predictions apply when the overall environment is anistotropic, as was shown in Chapter III. In order to test this prediction experimently, a suitable choice of an anisotropic environment must be made. Liquid crystals offer both isotropic and anisotropic media, depending on the temperature chosen.

The liquid crystal systems utilized in this study all have a nematic phase, that is, a phase where the long molecules line up like rods. This means that there is a preferential direction in the liquid system, while random disorder remains along the other two axes. Since any nematic liquid crystal could be used to provide an anisotropic medium for Raman bandshape analysis, some choices must be made, based upon work in isotropic liquids, in order to attempt to understand what is happening in the nematic liquid crystal phase. One consideration is whether to use a vibrational band of the liquid crystal itself, or to use some probe molecule to sense the environment. Both types of lineshape measurements have been made in this work. Another requirement is to find a suitable band that is isolated from other vibrations, and if it is a vibration of the liquid crystal molecule, to select one that is not significantly coupled with other vibrational modes, A third consideration is the temperature range of the phase transitions. The three liquid crystal systems that were studied are:
p-[(p-ethoxybenzylidene)-amino] benzonitrile (EBB), 4-cyano-4'pentylbiphenyl (5CB), and n-(p-methoxybenzylidene)-p-butylamine (MBBA).
Their structures are shown in Figure 13.

Work was first attempted on n-(p-methoxybenzylidene)-p-butylamine (MBBA); see Figure 13-C. Figure 14 shows the Raman spectra of MBBA in both the nematic liquid crystal (bottom) and isotropic liquid (top) phases. This molecule seemed ideal for use as an anisotropic environment for a suitable guest. Since there is no host scattering around 2200 cm^{-1} , acetonitrile (CH_zCN) was chosen as the guest. Unfortunately, addition of very little acetonitrile (five percent by volume) was enough to effectively break up the liquid crystal order. At that concentration the liquid crystal phase covered a span of only 0.5°, from 15.0° to 15.5°C. At higher concentrations no nematic phase could be observed, and at lower concentrations the C≡N vibrational scattering from acetonitrile was hidden in the background fluorescence of the liquid crystal. Even at the five percent concentration the acetonitrile peak at 2225 cm⁻¹ was difficult to discern above the background. Since the probe molecule produced such a weak signal on top of fairly strong fluorescence, even data collected for long periods of time (two days for each polarization) still contained so much noise that the lineshape analysis program would not converge. This method might prove fruitful under different conditions, as will be outlined in the next chapter.

The second liquid crystal system chosen, commercially available from Kodak, was p-[(p-ethoxybenzylidene)-amino]-benzonitrile (EBB), shown in Figure 13-A. It was selected because it has a C=N group at

FIGURE 13. STRUCTURES OF EBB, 5CB, AND MBBA



p-[(p-Ethoxybenzylidene)-amino]benzonitrile

ς.



4-cyano-4'-pentylbiphenyl



N-(p-methoxybenzylidene)-p-butylamine

FIGURE 14. SURVEY RAMAN SPECTRA OF MBBA. TOP: ISOTROPIC PHASE (45°C). BOTTOM: NEMATIC PHASE (25°C)

•



FIGURE 14

one end that has a stretching mode which is not strongly coupled with any of the other vibrational modes. Unfortunately, this particular molecule was not very well suited for lineshape analysis because its high fluorescence background almost completely washed out the relatively weak C=N stretch scattering.

The next molecule chosen was 4-cyano-4'-pentylbiphenyl (5CB), shown in Figure 13-B. This molecule turned out to be the most suitable of the systems chosen. The published Raman spectra of both the unsubstituted and the deuterated compounds showed that the C=N stretch was strong and isolated.¹⁹ The greatest problem with this compound is that it is not readily available. It was therefore necessary to synthesize 5CB before any spectroscopic measurements could be made.

The synthesis was carried out using a modified procedure based on preparations published by Gray et al. ⁷¹ and by Sadashiva and Subba Rao.⁷² The first step was a Friedel-Crafts reaction between 4-bromobiphenyl and pentanoyl chloride to give 4-bromo-4'-pentanoylbiphenyl:

$$C_4H_9COC1 + C_6H_5 \cdot C_6H_4Br ----- C_4H_9CO \cdot C_6H_4 \cdot C_6H_4Br.$$
 (39)

The melting point for this product was 95.5° - 96.5°C which was considered close enough to the published melting point (98°C) to continue.⁷¹ Next the carbonyl group was reduced with lithium aluminum hydride in an eighteen hour reflux, with a mixture of diethyl ether and chloroform used as solvent, to yield 4-bromo-4'-pentylbiphenyl:

$$C_{4}H_{9}CO \cdot C_{6}H_{4} \cdot C_{6}H_{4}Br \xrightarrow{A1C1_{2}/E_{2}O}_{LiA1H_{4}/CHC1_{3}} C_{5}H_{1} \cdot C_{6}H_{4} \cdot C_{6}H_{4}Br$$
 (40)

To be certain that the isolated compound was the correct one, the infrared spectrum of the product was taken and no carbonyl band was observed. The melting point of the compound was $90^{\circ} - 92^{\circ}C$ (literature value $95^{\circ} - 96^{\circ}C$).⁷¹ The third and final step was a substitution reaction whereby the bromine was replaced with a cyano group. This was accomplished by reacting the product from the previous step with cuprous cyanide:

$$C_{5}H_{11} \cdot C_{6}H_{4} \cdot C_{6}H_{4}Br + CuCN ---- C_{5}H_{11} \cdot C_{6}H_{4} \cdot C_{6}H_{4}CN + CuBr.$$
 (41)

After purification by means of column chromatography, a Raman spectrum of the compund was taken to verify that it was the desired material, 5CB. Figure 15 shows the Raman spectra that were obtained, and they do match the published spectra of 5CB very well.¹⁹ The three traces, from bottom to top, are the solid (15° C), nematic liquid (25° C), and isotropic liquid (45° C) phases.

In the spectra of Figure 15, note that the C=N stretch, at 2225cm⁻¹, is a strong, isolated band and is therefore suitable for lineshape analysis. Another feature, not observed by Gray and Mosley because of experimental limitations,¹⁹ is the C-H stretching region between 2900 and 3200cm⁻¹, which gives the appearance of a plateau because of the many overlapping bands arising from the different types of C-H stretching modes in 5CB. The survey spectra show that this molecule does not have the high background scattering that plagued the other two liquid crystal systems,

Figures 16 and 17 show the raw data from the 2225cm⁻¹ scattering used for the rotational and vibrational lineshape analysis. As with

FIGURE 15. SURVEY RAMAN SPECTRA OF 5CB. BOTTOM: SOLID PHASE (15°C); CENTER: NEMATIC PHASE (25°C); TOP: ISOTROPIC LIQUID PHASE (45°C).



FIGURE 16. 2225cm⁻¹ SCATTERING FOR 5CB IN THE NEMATIC PHASE (25°C).



5CB CN Stretch N-phase

FIGURE 17. 2225cm⁻¹ SCATTERING FOR 5CB IN THE ISOTROPIC PHASE (45°C)



5CB CN Stretch I-phase

FIGURE 17

the simple liquids, the line labeled P is the polarized scattering and D is the depolarized line. Figure 16 depicts the nematic phase $(25^{\circ}C)$ and Figure 17 shows the isotropic phase $(45^{\circ}C)$. The instrumental function required for the vibrational lineshape analysis is measured from a plasma fluorescence line, and is shown in Figure 18, with the frequency axis shifted to correspond to the SCB 2225cm⁻¹ line. The depolarization ratio, after corrections for detector efficiency and polarization leakage are made, is 0.28 for the nematic phase and 0.36 for the isotropic phase. These values, which are larger than that for the 459 cm⁻¹ band of carbon tetrachloride, indicate that the vibration is not completely symmetric.⁷³ This means that the center of mass of the vibration moves with respect to the center of mass of the molecule during a vibrational period.

The fit of a convolved Lorentzian with the polarized line to the depolarized line for the isotropic phase is shown in Figure 19. The apparent frequency shift is an artifact of the display portion of the computer program used for the convolution and has no bearing on the results. The Lorentzian function has a half-width of 0.19 ± 0.10 cm⁻¹, corresponding to a reorientational correlation time of 28 \pm 15 psec. The corresponding fit for the nematic phase is shown in Figure 20. In this phase the Lorentzian has a half-width of 0.13 ± 0.10 cm⁻¹, corresponding to a reorientational correlation time of 41 \pm 30 psec. Note that the fit for the nematic phase data is not quite as good, which could be due to the true reorientational function being a sum of Lorentzians rather than a single Lorentzian. However, the experimental error is so large that one cannot critically evaluate this possibility.

FIGURE 18. INSTRUMENT FUNCTION FOR THE JARRELL-ASH SPECTROMETER: Ar LASER PLASMA LINE AT 4850Å.



FIGURE 19. LINESHAPE FIT FOR THE 2225cm⁻¹ RAMAN BAND OF 5CB IN THE ISOTROPIC PHASE (45°C).



FIGURE 20. LINESHAPE FIT FOR THE 2225cm⁻¹ RAMAN BAND OF 5CB IN THE NEMATIC PHASE (25°C).



5CB CN Stretch N-phase

FIGURE 20

Even though the numbers appear to fall within the common error range, the student t-test 74 indicates that they are statistically different.

Since the overall correlation function for large molecules is dominated by vibrational relaxation,⁷⁵ the vibrational correlation time for 5CB in each liquid phase was calculated by convolving a Lorentzian function with the instrument function of the Raman spectrometer described earlier, and then fitting the resulting function to the vibrational scattering (the polarized band). Figure 21 shows the results for the isotropic phase (45°C) of 5CB. The Lorentzian halfwidth is 3.7 ± 0.3 cm⁻¹, corresponding to a vibrational correlation time of 1.4 ± 0.2 psec. Figure 22 shows the result for the nematic phase (25°C) of 5CB. The Lorentzian half-width for this phase is 3.9 ± 0.3 cm⁻¹, also corresponding to a vibrational correlation time of 1.4 ± 0.2 psec. It is not too surprising that the vibrational relaxation time for the two different phases is the same, since the local environment does not change a great deal on either side of the phase transition.³

When this work was started it was hoped that the local environment would change enough during a phase transition to produce a significant change in the reorientational correlation times and functions. It is possible that such a change did in fact take place, but the experimental error was large enough that the change could not be detected by the method used. Perhaps another method could be used that would give results with less error, and some possibilities will be discussed in the next chapter. It is also possible that another approach might be useful both as a check, and as a way of extracting

FIGURE 21. VIBRATIONAL LINESHAPE FIT TO THE 2225cm⁻¹ RAMAN BAND OF 5CB IN THE ISOTROPIC PHASE (45°C).





FIGURE 22. VIBRATIONAL LINESHAPE FIT TO THE 2225 cm⁻¹ RAMAN BAND OF 5CB IN THE NEMATIC PHASE (25°C)



5CB CN Stretch N-phase

different information from the system. It was in this light that density and viscosity measurements were made.

Since other researchers have had good success using a Stokes-Einstein relation (as outlined in Chapter III) to compare rotational correlation times to viscosities,^{44,48,49,53,76,77} this relation was applied to the reorientational correlation times obtained for 5CB. At this point there are two ways that the analysis could have been made. One would have been to calculate the viscosities from the experimental correlation times and to match those to the experimental viscosities. The other was to use the measured viscosities to calculate correlation times and to match those to the times obtained from the lineshape measurements. The second method was chosen since it was easy to obtain viscosities over a wide temperature range.

The viscometer used measured the viscosity in units of centistokes, so the density of 5CB had to be obtained at the various temperatures to convert to units of centipoise. The measured densities are tabulated in Table 1 and compare favorably with those reported by Karat and Madhusudana.²⁹ After the unit conversion the measured viscosities were fit to an Arrhenius type activation energy^{33,34} using a linear least-squares routine.⁶² Both the experimental viscosities and those calculated from the Arrhenius equation are given in Table 2. For the isotropic phase (T $\stackrel{>}{\sim}$ 35°C) the calculated viscosity equation is:

 $\eta = (1.33 \pm 0.3) \times 10^{-5} \exp [(4340 \pm 120)/T]$ centipoise; (42)

	TA	B	LE	1
--	----	---	----	---

T(°C)	D(gm/ml)	T(°C)	D(gm/ml)
15.0	1.023	33.0	.9764
16.0	1.061	34.0	.9881
17.0	1.012	35.0	.9887
18.0	1.014	36.0	.9965
19.0	1.025	37.0	.9749
20.0	1.022	38.0	.9695
21.0	1.012	39.0	.9798
22.0	1.018	40.0	.9927
23,0	1.018	41.0	.9991
24.0	.9984	42.0	.9730
25.0	1.037	43.0	.9672
26.0	1.024	44.0	.9556
27.0	1.061	45.0	.9410
28.0	1.044	46.0	.9085
29.0	1.054	47.0	.9096
30.0	1.017	48.0	.8950
31.0	1.030	49.0	.8843
32.0	1.021	50.0	.8563

Density of 4-cyano-4'-pentylbiphenyl

TABLE 2

Experimental and Calculated Viscosities of 4-cyano-4'-pentylbiphenyl

T(°C)	ŋ(cp)	calc.n(cp)
17.0	55.7	54.2
20.0	44.1	44.9
23.0	35.9	37.4
26.0	34.5	31.3
29.0	27.9	26.2
31.0	24.2	23.3
33.0	19.4	20.8
35.0	17.8	17.4
38.0	15.2	15.1
40.0	14.4	13.9
43.0	12.5	12.2
46.0	10.4	10.7
49.0	9.46	9.4
	-	

for the nematic liquid crystal phase (15°C \leq T \leq 35°C) the equation is:

$$n = (6.11 \pm 3.0) \times 10^{-7} \exp [(5310 \pm 220)/T]$$
 centipoise. (43)

It seems reasonable that as the liquid becomes more ordered the activation energy for viscous flow would increase, since there would be a greater hinderance to movement in an ordered system.

The reorientational correlation times were calculated using both sticking and slipping boundary conditions. Equation 38 was used for the sticking boundary condition. The unweighted equation is a modification of Equations 33 and 35a and is the form:

$$\tau_{2} = (V^{*}\eta/kT) (1/3) (\Sigma \theta(\rho_{1})) + 2\pi (41/360) (I/kT)^{1/2}.$$
 (44)

- --

. . . .

The weighted slip equation is taken from Equations 33 and 35c and is:

$$\tau_{2} = (V * n/kT) (\Sigma W_{i}^{\theta}(\rho_{i})) + 2\pi (41/360) (I/kT)^{1/2}.$$
(45)

The fourth equation used is a modification of Equation 37 which incorporates the microviscosity factor and is:

$$\tau_{2} = (V^{*}n/kT) (0.163) + 2\pi (41/360) (I/kT)^{1/2}.$$
 (46)

The calculated relaxtion times are summarized in Table 3 along with calculated viscosities and effective molecular volumes. The volumes were calculated from the densities and are comparable to ones calculated for molecules of similar size, 53,78 The calculated reorientational correlation times from all four equations are longer than those obtained from the Raman lineshape analysis. Those calculated with the microvis-cosity factor (Equation 46) are the closest, but they are still one

40.0	39.0	38.0	37.0	36.0	35.0	34.0	33.0	32.0	31.0	30.0	29.0	28.0	27.0	26.0	25.0	24.0	23.0	22.0	21.0	20.0	19.0	18.0	17.0	16.0	15.0				T(°C)	
0.139	0.145	0.151	0.159	0.166	0.174	0.197	0.208	0.220	0.233	0.247	0.262	0.278	0.295	0.313	0.332	0.352	0.374	0.398	0.423	0.449	0.478	0.509	0.542	0.577	0.615				n(poise)	
4.171	4.226	4.271	4.247	4.155	4.188	4.191	4.241	4.056	4.020	4.071	3.929	3.966	3.903	4.044	3.993	4.048	4.147	4.067	4.092	4.052	4.040	4.084	4.092	3.903	4.048	X10 ²²	1		V*(cm ³)	a
1.35	1.43	1.51	1.58	1.62	1.72	1.95	2.09	2.12	2.24	2.41	2.47	2.66	2.78	3.07	3.22	3.48	3.80	3.98	4.27	4.50	4.79	5.18	5.54	5.65	6.26	X10 ⁹		stick	т(sec)	
0.513	0.544	0.574	0.603	0.617	0.654	0.743	0.796	0.808	0.851	0.916	0.940	1.01	1.06	1.17	1.23	1.32	1.44	1.51	1.62	1.71	1.82	1.97	2.10	2.14	2.38	Х10 ⁹	slip	unweight	τ(sec)	
1.16	1.23	1.30	1.37	1.40	1.48	1.65	1.81	1.84	1.93	2.08	2.14	2.30	2.41	2.65	2.79	3.01	3.28	3.44	3.69	3.89	4.14	4.47	4.79	4.88	5.41	01X	slip	weight	τ(sec)	Þ
0.223	0.236	0.249	0.261	0.268	0.284	0.322	0.345	0.350	0.368	0.396	0.407	0.437	0.547	0.504	0.529	0.571	0.623	0.652	0.699	0.737	0.785	0.848	0.906	0.924	1.02	⁹ X10	cosity	microvis-	ı(sec)	•

Viscosities, Effective Molecular Volumes, and Relaxation Times for 4-cyano-4'-pentylbiphenyl TABLE 3

TABLe 3 (continued)

	49.0 0.0943 4.682 0.997 0.381	48.0 0.0984 4.626 1.03 0.394	47.0 0.103 4.552 1.07 0.407	46.0 0.107 4.558 1.11 0.424	45.0 0.112 4.400 1.13 0.430	44.0 0.117 4.333 1.16 0.444	43.0 0.122 4.281 1.20 0.458	42.0 0.127 4,256 1.25 0.476	41.0 0.133 4.144 1.28 0.486
0.376	0.381	0.394	0.407	1 0.424	3 0.430	6 0.444	0 0.458	0.476	0.486
0.852	0.862	0.892	0.921	0.961	0.974	1.01	1.04	1.08	1.10
0.164	0.166	0.172	0.177	0.185	0.187	0.193	0.199	0.202	0.212

order of magnitude longer. It is interesting to note that the weighted slip correlation times are closer to the sticking boundary condition than the unweighted slip times are. This is just the opposite of what Fury and Jonas observed,⁴⁴ and indicates that sticking boundary conditions may better describe 5CB.

Since sticking boundary conditions may do a better job of describing the reorientational behavior of systems comprised of long, rod-like molecules such as 5CB, the question arises as to why the results from Equation 38 are two orders of magnitude longer than those calculated from the Raman lineshapes. The Stokes-Einstein relation assumes that the molecules are in a fluid of continuous viscosity.⁷⁹ This continuous medium assumption is not valid in a neat liquid and therefore a correction should be made. Gierer and Wirtz⁸⁰ postulated a model involving concentric solvent shells, which for a neat liquid reduces to Equation 37 and contains the microviscosity term. This explains why Equation 46 does a better job in matching the Raman results.

It is still bothersome that the results of Equation 46 and the Raman results differ by one order of magnitude. One possible explanation for this discrepancy may be that the hydrodynamic models were developed using spherical, or nearly spherical, molecules. Elongated liquid crystal molecules are not spherical and will probably behave somewhat differently when undergoing rotations. If this is the case, then one might wonder about the validity of attempting to match the hydrodynamic results to the lineshape results. Since other researchers were able to obtain satisfactory results with the two methods,

it was assumed that similar agreement could be obtained using 5CB. Since this is not the case it might be interesting to look into the differences more at a later date.

VIII, CONCLUSIONS

In this work attempts were made to observe two different types of relaxation processes involving anisotropic media. One process was the relaxation of a liquid crystal molecule in both the nematic and isotropic phases. The other was the relaxation of a guest molecule surrounded by molecules of a liquid crystal. Results for the first process, only, could be obtained. These results include both reorientational and vibrational relaxation from Raman lineshapes. Reorientational correlation times were also obtained for the liquid crystal system from viscosity measurements.

The reorientational lifetimes obtained from Raman lineshapes which are reported here can only be considered as approximate values, due to the magnitude of the error associated with them. However, they do indicate that more work must be done on the applicability of hydrodynamic theory for calculating correlation times in complex fluids, since the correlation times calculated from viscosity data differ from the Raman results by more than the combined experimental error. This study does reinforce the vibrational relaxation work of other researchers, which indicate that on a short time scale the total correlation function is dominated by vibrational relaxation.³,⁷⁵

Since this research is just one piece in a large puzzle, it is appropriate to suggest other experiments that could be performed, and also experiments that should not be attempted. It would be very interesting to obtain the rotational and possibly the vibrational relaxation of a guest molecule in an anisotropic host, as was attempted

here with acetonitrile in MBBA. In order for this type of experiment to succeed one must keep the guest concentration low enough to insure that the host still has an anisotropic phase. At such low concentrations any host fluorescence becomes a problem that cannot be ignored. The most obvious solution to this problem is to find a suitable host that does not fluoresce, or to find a suitable quencher that can be inserted into the host in very low concentrations. Since most liquid crystal systems are aromatic, some fluorescence is likely in almost every case. One way to reduce the fluorescence is to find a molecule that has an electron withdrawing group, such as NO₂, on the aromatic ring.⁸²

One could obviate the fluorescence background problem by preforming Coherent Anti-Stokes Raman Scattering (CARS) experiments. Since anti-Stokes scattering is monitored, fluorescence would be minimized.⁸³ Another method would be to use a pulsed laser source and gated detection electronics. This experimental setup is useful since the lifetime of the Raman scattering is shorter than the risetime of the fluorescence signal.

As was mentioned earlier, there are a number of pitfalls associated with extracting the reorientational function from a Raman band. One problem arises from truncation error when Lorentzian functions are deconvulated by Fourier transformation.⁸⁴ This problem could possibly be overcome by using the solution of a Fredholm integral equation of the first kind,^{85,86} in which a finite time range of the data is exactly accounted for. With this approach it might be possible to obtain differences in the correlation functions arising from both vibrations and rotations at longer times.

Another problem is caused by overlapping bands, and this is particularly severe when the bands have different polarization characteristics. Any attempt to mathematically separate overlapping bands will change the overall shape of each individual band, and this effect will more than likely be different for depolarized scattering than for polarized scattering. This is the main reason why care should be taken when choosing a Raman band for analysis.

Weak bands pose another problem. In order to obtain reliable lineshapes, the relative signal-to-noise ratio must be high; that is, the noise level must be many times smaller than the difference between the baseline and the peak maximum. Some ways of experimently dealing with this problem have been outlined by Griffiths.⁸⁷ As a last resort, weak bands with a low S/N can be digitally smoothed. However, this technique may also change the overall shape of a Raman band⁶⁴ and thus could change the final results unless an appropriate correction is used. APPENDICES
APPENDIX A

PROGRAM DATCOL

A FORTRAN/SABR program that controls a Jarrell-Ash Raman spectrometer and collects counts from the photomultiplier tube.

•

PROGRAM DATCOL.FT

CCCCC	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC	
C C C	PROGRAM DATCOL		
C	RAMAN DATA TAKING PROGRAM		
	PROGRAM WILL CO WELL AS COLLECT IT WILL TAKE UP WHEN THE ENDING BE PUT BACK AT BACKLASH IN THE THE STARTING FR THIS WILL NOT A IS LESS THAN 70 THE COUNT TIME EACH DATA FILE THE PROGRAM CAN THEN HAS THE OP STOPPING, OR ST IF THE PROGRAM OF CHANGING SOM	NTROL THE JARRELL-ASH RAMAN SPECTROMETER AS THE COUNTS COMING FROM THE PMT. TO 100 SCANS OVER A REGION OF INTEREST. FREQUENCY IS REACHED, THE GRATING WILL THE STARTING FREQUENCY. GEARS IS TAKEN CARE OF BY COING 50 CM-1 BY EQUENCY AND COMING BACK TO IT. UTOMATICALLY HAPPEN IF THE STARTING FREQUENCY CM-1. CAN BE VARIED FROM 100 MSEC TO 40 SEC. IS ENDED WITH A NEGATIVE NUMBER. BE INTERRUPTED BY A CONTROL G. THE OPERATOR TION OF CONTINUING, CLOSING THE FILE AND OPPING WITHOUT CLOSING THE FILE. IS CONTINUED, THE OPERATOR HAS THE OPTION E OF THE PARAMETERS.	
C	WHEN THE RUN IS	OVER, THE OPERATOR HAS THE OPTION TO	
C	RESTART, MOVE T	HE GRATING, OR CRUNCH DATA.	
C	COMMON VARIABLE	S USED IN THIS PROGRAM	
C	AN	MAVININ NINDED OF COUNTS DESIDED	
C	SN YNII	CURRENT ERFOUENCY INSTURMENT IS AT	
č	YCNT	COUNTS/SEC AT XNU	
č	ISTEP	NUMBER OF STEPS STEPPING MOTOR WILL TAKE	
Č		BETWEEN DATA POINTS	
C	TIME	MAXIMUM COUNT TIME	
C	TMIN	MINIMUM COUNT TIME	
C	SNU	STARTING FREQUENCY	
C	FNU	ENDING FREQUENCY	
C	NSTEP	NUMBER OF STEPS RECORDER WILL TAKE	
C		BEIWEEN DATA PUTNIS	
C	INTERNAL VARIAB	lfs	
C	0.017		
C		OUTPUT STURAGE DEVICE	
	FILE	DESIDED EDECHENCY INTERVAL RETWEEN	
č	RESUL	DATA POINTS	
č	YMAX	MAXIMUM COUNT/SEC RANGE FOR PLOT	
č	IY	INTEGER Y COORDINATE FOR PLOT	
ā	NTIMES	NUMBER OF SCANS OVER REGION	
C	ITEMP	TEMPORARY ISTEP STORAGE	
C	AY	TEMPORARY STORAGE FOR PLOT PARAMETER	
С	IMO	MONTH	
C	IDAY	DAY	
C	IYR	YEAR	
C	XDONE	LAST X VALUE	
U C	idure Otto	LADI I VALUE CM-1/INCH RECORDER WILL MOVE	
č	JIEF Ivat	CHARACTER STORACE	
č	IC	FLAG FOR CONTROL C	
č	IG	FLAG FOR CONTROL G	
č	~~		
Č	SUBROUTINES USE	D	
č	OOPENID	EV.FILE)	
č	SCST(I)		
Ĉ	SAMPLE		
C	SCAN(J)		
C	SCPLT(N	STEP, I)	
C	OCLOSE		
C	BELL		

C SCEND C EXIT C LIMIT(IL, RVAR, IH) Ĉ ERASE Ĉ YESNO(IVAL) CHAIN CCCC KCHEK(IDUM) FILE(DEV, FIL, IMODE) Č CHANCE LETIN(IVAL, IC, IG) C C STEPHEN M. GREGORY Ĉ APRIL 17, 1978 C COMMON SN, XNU, YCNT, ISTEP, TIME, TMIN, NSTEP, SNU, FNU, YMAX DIMENSION DEV(100), FNAME(100) С Ĉ GET DATE WORD C S DUMMY DATE S TAD I DATE S DCA TEMP S TAD TEMP S AND (7 I YR 9 DCA S TAD TEMP S RAR s RTR s AND (37 S DCA **iDAY** ŝ TAD TEMP S CLL RAL ŝ RTL S RTL s AND (17 S DCA i MO GO TO 1 CPAGE S 3 DATE, S 6211 S 7666 s TEMP. 0 IF(IMO)2.2,3 1 2 WRITE(1,100) GO TO 29 С С SET UP INITIAL VALUES Ĉ CALL BELL 3 IYR= IYR+8 WRITE(1,101) IMO, IDAY, IYR WRITE (1,102) READ (1, 103) TIME, TMIN READ (1, 104) SNU, FNU READ (1, 105) SN READ (1,106) RESOL READ (1,107) NTIMES READ(1,108) STEP READ(1, 109) YMAX XNU= SNU ISTEP= IF IX(RESOL*20.) STEP=300.*RESOL/STEP NSTEP=LIMIT(1,STEP,2047) DO 5 I=1, NTIMES I MODE=0 4

	WRITE(1,110) I
	CALL FILE(DEV(I), FNAME(I), IMODE)
	17800E=17800E+3 CO TO (3 9 4 8) IMODE
5	CONTINUE
-	CALL ERASE
CCCCCC	
C	
C	COLLECT DATA
	CALL OOPEN(DEV(I), FNAME(I))
	CALL SCST(0)
6	IF(XNU-FNU)7,7,15
7	CALL SAMPLE
	CALL SCAR(1) AVE VCNT25047 /VMAX
	IY=LIMIT(0,AY,2047)
	CALL SCPLT(INSTEP, IY)
	CALL KCHEK(IDUM)
0	IF(IDUED 19, 14, 8 WDITE(1 11) VNHT WEET
0	CALL YESNO(IVAL)
	IF(IVAL-89)11,9,11
9	WRITE(1,112)
	CALL YESNO(IVAL)
10	IF(IVAL-89)19,10,19 CALL CHANCE
10	GO TO 14
11	WRITE(1,113)
	CALL YESNO(IVAL)
	IF(IVAL-89) 13, 12, 13
12	WRITE(4, 114) XNU, YGNT YWTT- WRITEFEON
13	XNU= XNU+ RESOL
	CALL SCEND
	GO TO 16
19	WRITE (9,119) XNU, ICNT VNTIL VNTIL DESOL
	GO TO 6
15	XDONE=-1000.
	YDONE=0.
	WRITE(4, 114) XDONE, YDONE
	CALL OCLOSE
CCCCCC	
C	
C	MOVE GRATING BACK TO STARTING POINT
C	
16	XNU= XNU-RESOL
	CALL SCAN(2)
	IF(XNU-SNU) 17, 17, 16
17	ITEMP=ISTEP
10	IF(SNU-70.) 18, 18, 19
10	CALL DELL BEAD(1.115) IBLOCK
19	ISTEP=1000
	CALL SCAN(2)
	CALL SCAN(1)
	ISTEP=ITEMP
20	
	WRITE(1,116)
	CALL YESNO(IVAL)
_	IF(IVAL-89)21,29,21
21	WRITE(1,117)

.

DATCOL, CONT.

.'

	CALL LETIN(IVAL.IC.IG)
	IF(IC-1)22,29,22
22	IF(IG-1)23,21,23
23	IF(IVAL-210)24,26,24
24	IF(IVAL-847)25,27,25
25	IF(IVAL-257)21,28,21
26	CALL ERASE
	CALL CHAIN('CRUNCH')
27	CALL ERASE
	CALL CHAIN('MOVE')
28	CALL ERASE
	GO TO 3
29	CALL EXIT
CCCCCC	
C	
C	FORMAT STATEMENTS
C	
CCCCCC	266666666666666666666666666666666666666
100	FORMAT(' ENTER CURRENT DATE AND RESTART PROGRAM')
101	FORMAT(' DATE IS ',2X, I2, '/', I2, '/197', I1)
102	FORMAT(' RAMAN DATA TAKING PROGRAM')
103	FORMAT(' MAX COUNT TIME IN SEC = ', F10.4/' MIN COUNT TIME
	1 IN SEC = ',F10.4)
1 04	FORMAT(' STARTING POINT = ',F10.4/' ENDING POINT = ',F10.4)
1 05	FORMAT(' DESIRED NUMBER OF COUNTS = ', F10.4)
106	FORMAT(' SPACING BETWEEN DATA POINTS = ',F10.4)
107	FORMAT(' HOW MANY SCANS ? ', I3)
108	FORMAT(' CM-1/INCH ON RECORDER = ', F10.4)
109	FORMAT(MAXIMUM COUNT/SEC ON RECORDER = ', F10.4)
110	FORMAT(' OUTPUT FILE ', 12)
111	FORMAT(' CURRENT FREQUENCY IS ', F10.4/' CURRENT COUNTS/SEC
	1 ARE ', E10.4/' DO YOU WANT TO CONTINUE ?')
112	FORMAT(' DO YOU WANT TO CHANGE ANY OF THE PARAMETERS ?')
113	FORMAT(' DO YOU WANT TO SAVE THE COLLECTED DATA ?')
114	FORMAT(2A6)
115	FORMAT(' BLOCK THE SLITS AND HIT RETURN', 11)
116	FURMAT(' DUNE ?')
117	FURMAT(' CRUNCH, MOVE, OR DATCOL ?')
	END

SUBROUTINE SAMPLE.FT

ccccc	SUBROUTINE S	AMPLE CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
	SUBROUTINE TO INITIAL COUNT	D COUNT PHOTONS I PERIOD IS 100 MSEC AND IT WILL COUNT UP TO 40 SEC
CC	COMMON VARIA	BLES USED
C	YCNT	COUNTS/SEC.
C	SN	SIGNAL/NOISE
C	TIME	COUNT TIME
C C	THIN	MINIMUM COUNT TIME
Č	INTERNAL VAR	IABLES
ā	IXH	HIGH OVERFLOW STORAGE
ā	IYL	LOW ORDER COUNT STORAGE
Ē	IYH	HIGH OBDER COUNT STORAGE
č	AYL	FLOATING LYL
ā	AYH	FLOATING LYH
ā	AXH	FLOATING IXH
ē	YC	TEMP COUNTS/SEC
č	TMAX	MAXIMUM COUNTING TIME

102

•

SAMPLE, CONT.

C		ITC	INTEGER COUNT TIME
C		NYL	STORAGE FOR MSB OF LOW COUNT
C		NYH	STORAGE FOR MSB OF HIGH COUNT
C		NXH	STORAGE FOR MSB OF OVERFLOW WORD
C			
C	SUBROUT	INES CALI	LED
C			
C		DFIX (R	VAR, IH, IL)
C		DFLOT ()	(H, IL, RVAR)
C			
C	OPERATIO	DNS DEFII	VED
C			
C		LPSET	LOAD PRESET REGISTER
G		SIPGA	START PROGRAM CLOCK
C		LCTRL	LUAD CUNTRUL REGISTER
C		PUSKP	PGM OFLOW SKIP
G		CLRCT	CLEAR RAMAN COUNTER
C		COUNT	START PHOTON COUNTING
G		STPCT	STOP COUNTING
G		LIGIR	LATCH COUNTER INTO COMPUTER
C		CLRLO	CLEAR LOW OVERFLOW
G		СНКНО	CHECK HIGH OVERFLOW
C		CLRHO	CLEAR HIGH OVERFLOW
C		SMPLL	SAMPLE LOW COUNT
C		SMPLH	SAMPLE HIGH COUNT
C		DRIVE	DRIVE INTO AC
C			
C	STEPHEN	M. GREGO	DRY
C	APRIL 12	2, 1978	
C			· · · · · · · · · · · · · · · · · · ·
CCCCCC	CCCCCCCCC	CCCCCCCCC	
S	OPDEF	LPSET	6121 /LOAD PRESET REGISTER
S	OPDEF	STPGM	6123 /START PROGRAM CLOCK
S	OPDEF	LCTRL	6131 /LOAD CONTROL REGISTER
S	SKPDF	POSKP	6132 /PGM OFLOW SKIP
8	OPDEF	CLRCT	6601 /CLEAR RAMAN COUNTER
S	OPDEF	COUNT	6602 /START PHOTON COUNTING
S	OPDEF	STPCT	6603 /STOP COUNTING
S	OPDEF	LTCTR	6604 /LATCH COUNTER INTO COMPUTER
S	OPDEF	CLRLO	6606 /CLEAR LOW OVERFLOW
S	SKPDF	СНКНО	6607 /CHECK HIGH OVERFLOW
S	OPDEF	CLRHO	6611 /CLEAR HIGH OVERFLOW
S	OPDEF	SMPLL	6612 /SAMPLE LOW COUNT
S	OPDEF	SMPLH	6613 /SAMPLE HIGH COUNT
S	OPDEF	DRIVE	6617 /DRIVE INTO AC
	COMMON S	SN, XNU, YO	CNT, ISTEP, TIME, TMIN, NSTEP, SNU, FNU, YMAX
CCCCCC	CCCCCCCCC	CCCCCCCCC	
C			
C	INITIAL	IZE	
U COORCO	00000000		
3			
3	LA CLL		
	IAN-0		
	NUL-0		
	IVI-0		
	I IL-U		
	JAL-U	100	
	CALL DE	LINA LUU. Ivi Tmine I	151 TMTN)
	CALL DE	OT IT I	The trains
	TMIN-TH	501 (10, 11 [N[/100	111, 11117
a		14/ 144.	
3	TAD	(
3	I AD	\ 77 04	
3			
2	GLRLU		
2	ULKHU		
2	ULA CLL		

SAMPLE, CONT.

TAD IMIN S S CIA S LPSET S CLA CLL С Ĉ COUNT FOR TMIN SEC C S STPCM 88 COUNT Β, **CHKHO /CHECK HIGH OVERFLOW** SS JMP С JMP D 5 5 5 C, POSKP **/CHECK CLOCK OVERFLOW** JMP В S STPCT **/STOP COUNTING** СНКНО S JMP F ISZ i XH SSS NOP **CLRHO** S F, CLA CLL LTCTR SMPLL NOP DRIVE DCA i YL SMPLH NOP DRIVE DCA i YH JMP Е D, ISZ i XH NOP CLRHO JMP С ŝ E, NOP 1H=0 CALL DFLOT(IYH, IYL, AY) CALL DFLOT(IH, IXH, AXH) Ĉ CALCULATE COUNT/SEC C YCNT=AY+AXH*8192. IF(YCNT-SN) 1, 12, 12 YC=YCNT/TMIN 1 IF(YCNT)2, 12,2 2 TMAX= ABS(SN/YC) IF(TMAX-TMIN)3,4,4 3 TMAX=TMIN IF(TMAX-TIME)5.5.12 4 5 TI=TIME*100. IF(TI-4096.)7.7.6 TI=4096. 6 7 TM=TMAX*100. IF(TM-4096.)9,9,8 8 TM=4096. IF(TM-TI) 11, 11, 10 9 10 TM=TI 11 CALL DFIX(TM, IH, ITC) I H= 0 CALL DFLOT(IH, ITC, TM TMAX= TM/ 100. CLRCT S S **CLRHO** S CLRLO

SAMPLE, CONT.

S CLA CLL TAD **iTC** CIA LPSET CLA CLL IXH=0 NYL=0 NYH=0 IYL=0 IYH=0 NXH=0 S CLA CLL С Ĉ START COUNTING C STPCM COUNT BB. СНКНО JMP CC JMP DD POSKP CC, JMP BB STPCT СНКНО JMP FF ISZ i XH NOP CLRHO FF, CLA CLL LTCTR SMPLL NOP DRIVE DCA iYL SMPLH NOP DRIVE i YH DCA JMP EE ISZ iXH DD, NOP CLRHO JMP CC NOP EE, IH=0 C C C CALCULATE COUNT/SEC YCNT=AY+AXH*8192. GO TO 13 YCNT= YCNT/TMIN 12 GO TO 14 13 YCNT= YCNT/TMAX 14 RETURN END

SUBROUTINE SCAN.FT

SUBROUTINE SCAN(IWAY) Ĉ SUBROUTINE TO DRIVE STEPPING MOTOR COMMON VARIABLES USED ISTEP NUMBER OF STEPS INTERNAL VARIABLES IWAY **1 FOR FORWARD 2 FOR REVERSE** SUBROUTINES CALLED NONE **OPERATIONS DEFINED** REVS MOVE GRATING IN REVERSE DIRECTION FORWD MOVE GRATING FORWARD STEP STEP THE STEPPING MOTOR ONCE Ū C STEPHEN M. GREGORY APRIL 12. 1978 C S OPDEF REVS 6614 **/REVERSE** \mathbf{S} OPDEF FORWD 6615 **/FORWARD** С Ĉ MOVES THE GRATING A DISTANCE OF RESOL C DO 4 I=1, ISTEP GO TO (1,2) IWAY CONTINUE 1 S FORWD **GO TO 3** 2 CONTINUE S REVS CONTINUE 3 s STEP C C C A WAIT LOOP TO LET EVERYTHING SETTLE DOWN. STEPPING MOTOR CANNOT STEP FASTER THAN 441, 50L C S CLA CLL TAD (2000 CIA -A, IAC SŻA JMP A S NOP CONTINUE 4 RETURN END

SUBROUTINE CHANGE.FT

SUBROUTINE CHANGE C Č C SUBROUTINE TO CHANGE PARAMETERS DURING A RAMAN DATA RUN. Ĉ COMMON VARIABLES USED MAXIMUM NUMBER OF COUNTS DESIRED SN NUMBER OF STEPS STEPPING MOTOR WILL TAKE ISTEP BETWEEN DATA POINTS MAXIMUM COUNT TIME MINIMUM COUNT TIME TIME TMIN NSTEP NUMBER OF STEPS RECORDER WILL TAKE BETWEEN DATA POINTS STARTING FREQUENCY ENDING FREQUENCY SNU FNU YMAX MAXIMUM COUNTS/SEC ON RECORDER INTERNAL VARIABLES DESIRED FREQUENCY INTERVAL BETWEEN DATA RESOL POINTS CM-1/INCH RECORDER WILL MOVE STEP IVAL CHARACTER STORAGE SUBROUTINES USED ERASE YESNO(IVAL) LIMIT(IL, RVAR, IH) STEPHEN M. GREGORY С APRIL 12, 1978 C COMMON SN, XNU, YCNT, ISTEP, TIME, TMIN, NSTEP, SNU, FNU, YMAX CALL ERASE C C MAXIMUM COUNT TIME C WRITE(1,100) CALL YESNO(IVAL) IF(IVAL-89)2,1,2 READ(1,101) TIME С C MINIMUM COUNT TIME. C WRITE(1,102) CALL YESNO(IVAL) IF(IVAL-89)4,3,4 READ(1,101) TMIN 3 C С STARTING FREQUENCY C WRITE(1,103) CALL YESNO(IVAL) IF(IVAL-89)6,5,6 READ(1,101) SNU 5 C Ĉ ENDING FREQUENCY C CHANGE, CONT.

WRITE(1,104) 6 CALL YESNO(IVAL) IF(IVAL-89)8,7,8 READ(1,101) FNU 7 С TOTAL NUMBER OF COUNTS С C WRITE(1.105) 8 CALL YESNO(IVAL) IF(IVAL-89)10,9,10 READ(1,101) SN C SPACING BETWEEN DATA POINTS С С WRITE(1,106) CALL YESNO(IVAL) 10 IF(IVAL-89)12,11,12 11 READ(1,101) RESOL ISTEP= IF IX(RESOL*20.) C CM-1/INCH ON RECORDER С С WRITE(1.107) 12 CALL YESNO(IVAL) IF(IVAL-89)14,13,14 13 **READ(1, 101) STEP** STEP=300.*RESOL/STEP NSTEP=LIMIT(1,STEP,2047) С MAXIMUM COUNTS/SEC ON RECORDER C С WRITE(1.108) 14 CALL YESNO(IVAL) IF(IVAL-89)16,15,16 15 READ(1,101) YMAX CALL ERASE 16 RETURN С С FORMAT STATEMENTS С FORMAT(' MAXIMUM COUNT TIME ?') FORMAT('? ',F10.4) 100 101 FORMAT(' MINIMUM COUNT TIME ?') 102 FORMAT(' STARTING FREQUENCY ?') FORMAT(' ENDING FREQUENCY ?') 103 104 FORMAT(' TOTAL NUMBER OF COUNTS ?') 105 FORMAT(' SPACING BETWEEN DATA POINTS ?') 106 FORMAT(' CM-1/INCH ON RECORDER ?') 107 FORMAT(' MAXIMUM COUNTS/SEC ON RECORDER ?') 108 END

APPENDIX B

PROGRAM MOVE

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A FORTRAN/SABR program to move the grating of a Jarrell-Ash Raman spectrometer. It will also calibrate the system with respect to the excitation frequency.

С С PROGRAM MOVE Č C THIS PROGRAM WILL MOVE THE GRATING OF THE RAMAN SPECTROMETER TO A NEW FREQUENCY. IF THE STARTING FREQUENCY HAS NOT BEEN С С DETERMINED, THEN THIS PROGRAM WILL RUN OVER THE EXCITING LINE AND SET THE CRATING THE DESIRED DISTANCE AWAY. MONOCHROMETER MUST BE SET UP SO THAT IT IS 5 CM-1 ABOVE THE C Č C EXCITING FREQUENCY WHEN CALIBRATING. С С COMMON VARIABLES USED C С SN MAXIMUM NUMBER OF COUNTS DESIRED C C XNU CURRENT FREQUENCY INSTRUMENT IS AT COUNTS/SEC AT XNU YCNT Ĉ NUMBER OF STEPS STEPPING MOTOR WILL TAKE ISTEP BETWEEN DATA POINTS Ĉ TIME MAXIMUM COUNT TIME CM-1/INCH RECORDER WILL MOVE STEP Ĉ MINIMUM COUNT TIME TMIN C C INTERNAL VARIABLES Ċ C Y ARRAY FOR COUNT/SEC STORAGE ITOP INDEX FOR MAXIMUM IN Y ARRAY Ĉ FREQUENCY TO BE SET XSET DISTANCE TO BE MOVED DIST C C MONTH IMO IDAY DAY С IYR YEAR C C SUBROUTINES USED С С SAMPLE C C C C C SCAN(J) BELL ERASE LETIN(IVAL, IC, IG) С YESNO(IVAL) С CHAIN С KCHEK(IDUM) Ĉ С STEPHEN M. GREGORY C APRIL 17, 1978 С COMMON SN, XNU, YCNT, ISTEP, TIME, TMIN, NSTEP, SNU, FNU, YMAX DIMENSION Y(200) С Ĉ GET DATE WORD С WRITE(1,100) S DUMMY DATE S TAD I DATE ŝ DCA TEMP S S TAD TEMP AND (7 S DCA 1YR S TEMP TAD \mathbf{S} RAR S RTR (37 S AND s DCA IDAY S TAD TEMP S CLL RAL $\bar{\mathbf{S}}$ RTL

MOVE. CONT. S RTL (17 S AND S DCA i MO GO TO 1 CPAGE 3 S S DATE. 6211 S 7666 S TEMP, 0 IF(IMO)2,2,4 1 CALL BELL 2 WRITE(1,101) 3 STOP CALL BELL 4 IYR=IYR+8 WRITE(1,102) IMO, IDAY, IYR С C BRANCH TO DESIRED ROUTINE C WRITE(1,103) 3 CALL LETIN(IVAL, IC, IG) IF(IC-1)6,3,6 IF(IC-1)7,5,7 6 IF(IVAL-847)8,9,8 7 IF(IVAL-193)5,29,5 8 С SET DISTANCE TO BE MOVED С С 9 READ(1, 104) XNU 10 READ(1,105) XSET CALL ERASE DIST=XSET-XNU IF(DIST)11,22,12 11 J=2 DIR=-1. GO TO 13 12 J=1 **DIR=1**. C MOVE GRATING С C 13 DMOVE=.05*DIR ISTEP=1 14 CALL SCAN(J) CALL KCHEK(IDUM) IF(IDUM) 15, 15, 17 IF(ABS(DMOVE)-ABS(DIST))16,18,18 15 DMOVE=DMOVE+.05*DIR 16 GO TO 14 17 XD=XNU+DMOVE WRITE(1,106) XD CALL YESNO(IVAL) IF(IVAL-89)22,15,22 18 IF(DIR) 19,22,22 С MOVE GRATING TO RELEAVE BACKLASH С C 19 IF(XSET-70.)20,20,21 20 READ(1, 107) IBLOCK 21 **ISTEP=1000** CALL SCAN(2) CALL SCAN(1)

MOVE, CONT.

22 WRITE(1,108) CALL LETIN(IVAL, IC, IG) IF(IC-1)23,3,23 23 IF(IG-1)24,22,24 24 IF(IVAL-210)25,27,25 25 IF(IVAL-847)26,5,26 IF(IVAL-257)22,28,22 26 27 CALL ERASE CALL CHAIN('CRUNCH') CALL ERASE CALL CHAIN('DATCOL') 28 С RUN OVER EXCITING LINE С C 29 CALL ERASE ISTEP=1 SN=10000. TIME=3. TMIN=.1 DO 30 I=1,200 CALL SAMPLE Y(I) = YCNT30 CALL SCAN(1) YMAX=Y(1) DO 32 I=2,200 IF(Y(I)-YMAX) 32,31,31 31 YMAX=Y(I) ITOP= I 32 CONTINUE XNU=FLOAT(200-ITOP) *.05 CALL BELL GO TO 10 С C FORMAT STATEMENTS С FORMAT(' PROGRAM TO MOVE THE GRATING') FORMAT(' ENTER CURRENT DATE AND RESTART PROGRAM') 100 101 FORMAT(' DATE IS ', 12, '/', 12, '/197', 11) 102 FORMAT(' DATE IS , 12, ', 12, ', 14, ', 11) FORMAT(' DO YOU WANT TO MOVE OR CALIBRATE ?') FORMAT(' WHAT FREQUENCY ARE YOU AT NOW ? ', F10.4) FORMAT(' WHAT FREQUENCY DO YOU WANT ? ', F10.4) FORMAT(' CURRENT FREQUENCY IS ', F10.4/' DO YOU WANT TO 103 104 105 106 1 CONTINUE ?') FORMAT(' HIT RETURN AFTER BLOCKING LASER BEAM', I1) FORMAT(' CRUNCH, MOVE, OR DATCOL ?') 107 108 END

APPENDIX C

PROGRAM CRUNCH

A FORTRAN/SABR program that will help in the analysis of Raman spectra. The features include plotting, smoothing of spectra, baseline substraction, normalization of peaks, scale expansion on plots, signal averaging, background subtraction, and peak location.

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PROGRAM CRUNCH. FT

Č C IMODE

C C **PROGRAM CRUNCH** CCCCC PROGRAM TO CRUNCH RAMAN DATA STEPHEN M. GREGORY c C APRIL 17, 1978 CCCC THIS IS THE TRAFFIC DIRECTOR FOR A SET OF PROGRAMS DESIGNED TO DISPLAY AND ANALYZE RAMAN DATA OPTIONS ARE CHOSEN BY TYPING IN THE NAME OF THE OPTION DESIRED. WHEN A QUESTION IS ASKED THAT REQUIRES A YES OR Č C NO ANSWER, RESPOND WITH A Y/N DEPENDING ON YOUR ANSWER. OPTIONS THAT THE PROGRAM HAS ARE PLOTTING, SMOOTHING, č CORRECTING FOR A LINEAR BASELINE DRIFT, NORMALIZATION OF SINCLE PEAKS, SCALE EXPANSION OF PLOTS, PRINTING, C TRANSLATING TO E FORMAT, AVERAGEING OF MANY SPECTRA. OR PEAK SUBTRACTION. С Ċ C INITIAL DIALOGUE IS NOT NEEDED FOR TRANSLATING. C VARIABLES USED IN THIS PROGRAM AND SUBROUTINES C Č C XMIN COMMON MINIMUM FREQUENCY FOR THIS RUN XMAX MAXIMUM FREQUENCY FOR RUN MINIMUM VALUE OF Y IN RANGE MAXIMUM VALUE OF Y IN RANGE YMIN YMAX FREQUENCY INTERVAL BETWEEN DATA POINTS DELX ITYPE = **1 FOR PLOT** FOR SMOOTHING 2 FOR BASELINE CORRECTION 3 FOR NORMALIZATION 4 5 FOR SCALE EXPANSION FOR SIGNAL AVERAGEING 6 FOR PRINTING 7 8 FOR TRANSLATION **9 FOR PEAK LOCATION** DEV1 DEVICE INPUT DATA IS STORED ON DEVICE OUTPUT DATA IS TO BE STORED ON DEV2 FILE1 INPUT FILE NAME OUTPUT FILE NAME 1 FOR STRIP CHART RECORDER FILE2 IPLOT =**2 FOR TERMINAL** IDONE FLAG RAISED WHEN PROGRAM IS FINISHED LAST FREQUENCY VALUE READ FROM INPUT FILE Х Y LAST COUNT VALUE READ FROM INPUT FILE IPST **1 IF PLOT HAS STARTED** ALSO INDEX FOR PEAKS IBASE 1 FOR CALCULATION OF SUMS IF ALL POINTS HAVE BEEN READ IN FOR BASELINE 2 CALCULATION **3** IF SLOPE AND INTERCEPT HAVE BEEN CALCULATED INORM 1 IF SCALE HAS BEEN DETERMINED NTST **0** UPON ENTERING NORM 1 WHEN YMAX HAS BEEN READ IN -1 WHEN SCALING HAS STARTED Č C ISIG =**1 FOR ADDITION 2 FOR SUBTRACTION** c c INTERNAL VARIABLES CCCCCCCC IVAL USED FOR CHARACTER STORAGE USED AS A FLAG FOR CONTROL C USED AS A FLAG FOR CONTROL G IC IG I MO MONTH IDAY DAY IYR YEAR

I/O MODE AND RETURN FLAG

C			07	CALL	
č			UN	A:	OUTPUT IS INTENDED TO THE
č				•••	DEV AND FIL ENTERED
Č				1:	INPUT IS INTENDED FROM THE DEV AND FIL ENTERED
č			ON	RETURN:	
č			•••	-2:	G ENCOUNTERED
č				-1:	C ENCOUNTERED
Ċ				0:	SYNTAX ERROR OR INAPPROPRIATE
Č					DEVICE
Ĉ				1:	EVERYTHING IS OKAY.
Č				-	
Č	SUBR	OUT	INES CALLED		
Ċ					
Ċ			BELL		
C			YESNO(IVAL))	
C			LETIN(IVAL,	IC, IG)	
C			RDAT		
С			ERASE		
C			FILE(DEV,FI	(L, IMODE)	
C					
CCCCCC	COMM	ICCCC ION X	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
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3	AND		(17		
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G					-
C	GET	FILE	NAMES AND	INITIAL VALUE	8
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CCCCCC		CCCC			
ა	CALL	BEL	ц С		
	I YH=	1 YK+	·8		
	TUON	L=0	101) 190		
	WEIT	LLI, Trei	IVIJ INU, IL	AI, IIM	
	TATT	LUL,	IUZJ		
	UALL		MULIVAL)		
	IFCI	VAL-	.84,8		
4	YMAX	=0			
	YMIN	= 0			

CRUNCH, CONT.

5 IMODE = 1WRITE(1,103) CALL FILE(DEV1, FILE1, IMODE) IMODE= IMODE+3 CO TO (3,49,5,6) IMODE IMODE=0 6 WRITE(1,104) CALL FILE(DEV2, FILE2, IMODE) IMODE= IMODE+3 GO TO (3,49,6,7) IMODE READ(1,105) XMIN, XMAX, DELX 7 WRITE(1,106) 8 CALL LETIN(IVAL, IC, IG) С С SET UP ITYPE FOR BRANCHING С IF(IC-1)9,49,9 IF(IG-1)10,3,10 9 10 IF(IVAL-1036)11,22,11 IF(IVAL-1229)12,23,12 11 12 IF(IVAL-129)13,24,13 IF(IVAL-911)14,25,14 13 14 IF(IVAL-344) 15,26,15 IF(IVAL-1042) 16,21,16 15 16 IF(IVAL-1298) 17,20,17 IF(IVAL-1225) 18,27,18 17 18 IF(IVAL-1029)8, 19,8 19 ITYPE=9 GO TO 40 20 ITYPE=8 GO TO 40 ITYPE=7 21 GO TO 40 ITYPE=1 22 GO TO 34 23 ITYPE=2 GO TO 40 ITYPE=3 24 GO TO 40 25 ITYPE=4 GO TO 40 26 ITYPE=5 GO TO 40 27 ITYPE=6 С С SET UP ISIG C 28 WRITE(1,107) CALL LETIN(IVAL. IC. IG) IF(IC-1)29,49,29 29 IF(IG-1)30,3,30 30 IF(IVAL-68)31,32,31 31 IF(IVAL-1237)28,33,28 32 ISIC=1 CO TO 40 33 ISIG=2 GO TO 40 С C SET UP IPLOT C 34 WRITE(1,108) CALL LETIN(IVAL, IC, IG) IF(IC-1)35,49,35

CRUNCH, CONT.

35	IF(IG-1)36.3.36
36	IF(IVAL-1236) 37, 38, 37
37	IF(IVAL - 1285) 34, 39, 34
38	
30	
40	
70	
	IF (IDONE) 41, 41, 49
41	WRILE(1, 109)
	CALL LETIN(IVAL, IC, IG)
	IF(IC-1)42,49,42
42	IF(IG-1)43,41,43
43	IF(IVAL-210)44,48,44
44	IF(IVAL-847)45,46,45
45	IF(IVAL-257)41,47,41
46	CALL ERASE
	CALL CHAIN('MOVE')
47	CALL ERASE
	CALL CHAIN('DATCOL')
48	CALL_ERASE
	CO TO 3
49	STOP
CCCCCC	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C	
C	FORMAT STATEMENTS
C	
CCCCCC	
100	FORMAT(ENTER CURRENT DATE AND RESTART PROGRAM)
101	FORMATC' DATE IS ',2X, 12, '/', 12, '/197', 11)
102	FORMAT(' PROGRAM TO CRUNCH RAMAN DATA'//' DO YOU WANT
	1 INITIAL DIALOGUE ?')
103	FORMAT(' INPUT_FILE_')
104	FORMAT(' OUTPUT FILE ')
103	FORMAT(' MIN FREQUENCY = ',F10.4/' MAX FREQUENCY = ',F10.4/
	1' SPACING BETWEEN POINTS = ',F10.4)
106	FORMAT(' OPTIONS FOR THIS RUN ARE; '/' PLOT; SMOOTH;
	1 BASELINE CORRECTION; NORMALIZE; '/' EXPAND; PRINT; TRANSLATE
	2 TO E FORMAT; PEAK LOCATE; OR SIGNAL AVERAGE'/
	3' WHAT IS YOUR CHOICE?')
107	FORMAT(' ADD OR SUBTRACT? ')
108	FORMAT(' STRIP CHART OR TERMINAL?')
109	FORMAT(' CRUNCH, MOVE, OR DATCOL ?')
	END

SUBROUTINE RDAT.FT

-

	SUBROUTINE RD.	AT
CCCCCC	CCCCCCCCCCCCCCC	
C		
C	SUBROUTINE TO	READ ONE LINE OF DATA FROM THE INPUT FILE AND
C	BRANCH TO THE	APPROPRIATE ROUTINE.
C		
C	COMMON VARIAB	LES USED
C		
C	IBASE	BASELINE CORRECTION BRANCHING PARAMETER
C	INORM	NORMALIZATION BRANCHING PARAMETER
C	IPST	PLOT STARTING BRANCHING PARAMETER
C	DEV1	INPUT DEVICE
C	FILE1	INPUT FILE
C	Х	CURRENT FREQUENCY
C	Y	CURRENT COUNTS/SEC.
C	XMIN	MINIMUM FREQUENCY
C	XMAX	MAXIMUM FREQUENCY
С	YMAX	MAXIMUM COUNTS/SEC.

RDAT, CONT.

C		ITYPE	BRANCHING PARAMETER
C		IPLOT	PLOT BRANCHING PARAMETER
C		IDONE	TEST FOR END
č	INTERNAT	WADIAD	IFC
č		- VARIADA	
č		IPEND	FLAG FOR END OF PLOT
č		YSC	Y STORAGE FOR NORM
C		В	SUM STORAGE FOR BASE
C		NT	TOTAL NUMBER OF POINTS READ IN
C		1 VAL	CHARACTER STORAGE
C		ISTEP	NUMBER OF STEPS/POINT ON STRIP CHART
C		IP	PLOT TYPE STORAGE
C			
C	SUBROUT	INES CALI	LED
		LODER DI	
č		DI OT(IS	CV,fILD/ TED)
č		CHAIN	
č		BASE(B.I	TT)
ā		NORM(SC	ALE. YSC)
C		EXPAND	
C		SCEND	
C		LABEL	
C		OCLOSE	
C		BELL	
C		YESNOC IV	VAL)
u c		PRINT	
Č		PEAKS(VI	רטיוט סיעס ארסי
č		I LANS(A	, , 1 ° , 11 7
č	STEPHEN	M. GBECO	JBY
č	APRIL 12	1978	
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č cccccc			222222222222222222222222222222222222222
č cccccc	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
č cccccc	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC	CCCCCCCCC MIN, XMAX PLOT, IDO	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
č cccccc	CCCCCCCCC COMMON 2 1 1 DIMENSIC	CCCCCCCCC MIN, XMAX PLOT, IDC N B(6), Y	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
	CCCCCCCCC COMMON 2 1 I DIMENSIC CCCCCCCCCC	CCCCCCCCC MIN,XMAX PLOT,ID N B(6),Y CCCCCCCCC	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
č cccccc c c	CCCCCCCCCC COMMON 2 1 I DIMENSIC CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC	CCCCCCCCC MIN, XMAD PLOT, ID N B(6), 3 CCCCCCCCC	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
č cccccc c c c c c c c c c c c c c c c	CCCCCCCCCC COMMON 3 1 1 DIMENSIC CCCCCCCCCCCC READ IN	CCCCCCCCC MIN,XMAX PLOT,IDO N B(6),Y CCCCCCCCCCCCC DATA PO	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
	CCCCCCCCCC COMMON 3 1 I DIMENSIC CCCCCCCCCCCC READ IN	CCCCCCCCC MIN, XMA PLOT, IDC N B(6), 3 CCCCCCCCC DATA PO	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
	CCCCCCCCCC COMMON 3 1 I DIMENSIC CCCCCCCCCCC READ IN CCCCCCCCCCC LPEND=0	CCCCCCCCC MIN, XMA PLOT, IDC N B(6), 3 CCCCCCCCC DATA PO	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
	CCCCCCCCCC COMMON 3 1 DIMENSIC CCCCCCCCCCC READ IN CCCCCCCCCCC IPEND=0 IBASE=1	CCCCCCCCC MIN, XMAX PLOT, IDC N B(6), Y CCCCCCCCCC DATA PO	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
	CCCCCCCCCC COMMON 3 1 I DIMENSIC CCCCCCCCCCC READ IN CCCCCCCCCCC IPEND=0 IBASE=1 INORM=0	CCCCCCCCC MIN, XMAX PLOT, IDC N B(6), Y CCCCCCCCC DATA PO	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
	CCCCCCCCCC COMMON 3 1 I DIMENSIC CCCCCCCCCCC READ IN CCCCCCCCCCC IPEND=0 IBASE=1 INORM=0 IPST=1	CCCCCCCCC MIN, XMAX PLOT, IDC N B(6), Y CCCCCCCCCC DATA PO CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
	CCCCCCCCCC COMMON 3 1 DIMENSIC CCCCCCCCCCC READ IN CCCCCCCCCCC IPEND=0 IBASE=1 INORM=0 IPST=1 ITRAN=1	CCCCCCCCC MIN, XMAX PLOT, IDC N B(6), Y CCCCCCCCC DATA PO	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
	CCCCCCCCCC COMMON 3 1 DIMENSIC CCCCCCCCCCC READ IN CCCCCCCCCCC IPEND=0 IBASE=1 INORM=0 IPST=1 ITRAN=1 NP=1	CCCCCCCCC MIN, XMAX PLOT, IDC N B(6), Y CCCCCCCCC DATA PO	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
	CCCCCCCCCC COMMON > 1 I DIMENSIC CCCCCCCCCCC READ IN CCCCCCCCCCC IPEND=0 IBASE=1 INORM=0 IPST=1 ITRAN=1 NP=1 DO 1 I=1	CCCCCCCCC MIN, XMAN PLOT, IDC N B(6), T CCCCCCCCC DATA PO CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
	CCCCCCCCCC COMMON > 1 I DIMENSIC CCCCCCCCCCC READ IN CCCCCCCCCCC IPEND=0 IBASE=1 INORM=0 IPST=1 ITRAN=1 NP=1 DO 1 I=1 YSC(I)=0	CCCCCCCCC MIN, XMAX PLOT, IDC N B(6), Y CCCCCCCCC DATA PO CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
	CCCCCCCCCC COMMON 2 1 1 DIMENSIC CCCCCCCCCC READ IN CCCCCCCCCCC IPEND=0 IBASE=1 INORM=0 IPST=1 ITRAN=1 NP=1 DO 1 I=1 YSC(I)=0 DO 2 I=1	CCCCCCCCC MIN, XMAD PLOT, IDC N B(6), 7 CCCCCCCCCC DATA PO CCCCCCCCCC 0 3 CCCCCCCCCCCCCC ,5 ,6	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
	CCCCCCCCCC COMMON 2 1 1 DIMENSIC CCCCCCCCCC READ IN CCCCCCCCCCC IPEND=0 IBASE=1 INORM=0 IPST=1 ITRAN=1 NP=1 DO 1 I=1 YSC(I)=0 DO 2 I=1 B(I)=0.	CCCCCCCCC MIN, XMA PLOT, IDC N B(6), 7 CCCCCCCCCC DATA PO CCCCCCCCCCC 0 ATA PO CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
	CCCCCCCCCC COMMON 2 1 1 DIMENSIC CCCCCCCCCC READ IN CCCCCCCCCCC IPEND=0 IBASE=1 INORM=0 IPST=1 ITRAN=1 NP=1 DO 1 I=1 YSC(I)=0 DO 2 I=1 B(I)=0. GO TO (3 CALL 100	CCCCCCCCC MIN, XMAN PLOT, IDC N B(6), 7 CCCCCCCCCC DATA PO CCCCCCCCCCC 0 .5 .6 .6 .16, 3, 3,	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
č cccccc c c c c c c c c c c c c c c c	CCCCCCCCCC COMMON 2 1 1 DIMENSIC CCCCCCCCCC READ IN CCCCCCCCCC IPEND=0 IBASE=1 INORM=0 IPST=1 ITRAN=1 NP=1 DO 1 I=1 YSC(I)=0 DO 2 I=1 B(I)=0. GO TO (3 CALL IOF NT=0	CCCCCCCCC MIN, XMAN PLOT, IDC N B(6), 7 CCCCCCCCCC DATA PO CCCCCCCCCCC 0 3 CCCCCCCCCCCCCCCC 0 16, 3, 3 EN(DEV1,	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
Č CCCCCCC C C C C C C C C C C C C C C C	CCCCCCCCCC COMMON 2 1 1 DIMENSIC CCCCCCCCCC READ IN CCCCCCCCCC IPEND=0 IBASE=1 INORM=0 IPST=1 ITRAN=1 NP=1 DO 1 I=1 YSC(I)=0 DO 2 I=1 B(I)=0. GO TO (3 CALL IOP NT=0 READ(4.1	.5 .6 .16,3,3, .00) X.Y	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
Č CCCCCCC C C C C C C C C C C C C C C C	CCCCCCCCCC COMMON 2 1 1 DIMENSIC CCCCCCCCCC READ IN CCCCCCCCCC IPEND=0 IBASE=1 INORM=0 IPST=1 ITRAN=1 NP=1 DO 1 I=1 YSC(I)=0 DO 2 I=1 B(I)=0. GO TO (3 CALL IOF NT=0 READ(4,1 CALL KCE	CCCCCCCCC MIN, XMAN PLOT, IDC N B(6), Y CCCCCCCCCC DATA PO CCCCCCCCCC 0 16, 3, 3, EN(DEV1, 00) X, Y EK(IDUM	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
Č CCCCCCC C C C C C C C C C C C C C C C	CCCCCCCCCC COMMON 2 1 1 DIMENSIC CCCCCCCCCC READ IN CCCCCCCCCC IPEND=0 IBASE=1 INORM=0 IPST=1 ITRAN=1 NP=1 DO 1 I=1 YSC(I)=0 DO 2 I=1 B(I)=0. GO TO (3 CALL IOP NT=0 READ(4,1 CALL KCH IF(IDUM)	.5 .6 .16,3,3, .6 .16,3,3, .00) X,Y .2 .2 .2 .2 .2 .2 .3 .3 .3 .3 .3 .3 .3 .3 .3 .3 .3 .3 .3	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
Č CCCCCCC C C C C C C C C C C C C C C C	CCCCCCCCCC COMMON 2 1 1 DIMENSIC CCCCCCCCCC READ IN CCCCCCCCCC IPEND=0 IBASE=1 INORM=0 IPST=1 ITRAN=1 NP=1 DO 1 I=1 YSC(I)=0 DO 2 I=1 B(I)=0. GO TO (3 CALL IOP NT=0 READ(4,1 CALL KCH IF(IDUM) WRITE(1,	.5 .6 .16,3,3, .6 .16,3,3, .6 .16,3,3, .6 .16,3,3, .16,3,3, .16,3,3, .10) X,Y	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
č cccccc c c c c c c c c c c c c c c c	CCCCCCCCCC COMMON 2 1 1 DIMENSIC CCCCCCCCCC READ IN CCCCCCCCCC IPEND=0 IBASE=1 INORM=0 IPST=1 ITRAN=1 NP=1 DO 1 I=1 YSC(I)=0 DO 2 I=1 B(I)=0. GO TO (3 CALL IOP NT=0 READ(4,1 CALL KCE IF(IDUM) WRITE(1, CALL YES	.5 .6 .16,3,3, .6 .16,3,3, .6 .16,3,3, .6 .16,3,3, .16,3,3, .16,3,3, .10) X,Y .100) X,Y .100) X,Y .101) X,Y .101) X,Y	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
Č CCCCCCC C C C C C C C C C C C C C C C	CCCCCCCCCC COMMON 2 1 I DIMENSIC CCCCCCCCCC READ IN CCCCCCCCCC IPEND=0 IBASE=1 INORM=0 IPST=1 ITRAN=1 NP=1 DO 1 I=1 YSC(I)=0 DO 2 I=1 B(I)=0. GO TO (3 CALL IOP NT=0 READ(4.1 CALL KCE IF(IDUM) WRITE(1, CALL YES IF(IVAL-	.5 .6 .6 .10, 3, 3, . .6 .16, 3, 3, . .10) X, Y 	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C C C C C C C C C C C C C C C C C C C	CCCCCCCCCC COMMON 2 1 I DIMENSIC CCCCCCCCCC READ IN CCCCCCCCCC IPEND=0 IBASE=1 INORM=0 IPST=1 ITRAN=1 NP=1 DO 1 I=1 YSC(I)=0 DO 2 I=1 B(I)=0. GO TO (3 CALL IOP NT=0 READ(4,1 CALL XCE IF(IDUM) WRITE(1, CALL YES IF(IVAL- IF(X)24.	CCCCCCCCC MIN, XMAN PLOT, IDC N B(6), Y CCCCCCCCC DATA PO CCCCCCCCC DATA PO CCCCCCCCCC ,5	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C C C C C C C C C C C C C C C C C C C	CCCCCCCCCC COMMON 2 1 I DIMENSIC CCCCCCCCCC READ IN CCCCCCCCCC IPEND=0 IBASE=1 INORM=0 IPST=1 ITRAN=1 NP=1 DO 1 I=1 YSC(I)=0 DO 2 I=1 B(I)=0. GO TO (3 CALL IOP NT=0 READ(4.1 CALL XCH IF(IDUM) WRITE(1, CALL YES IF(IVAL- IF(X-XMI) IF(X-XMI)	CCCCCCCCC MIN, XMAN PLOT, IDC N B(6), Y CCCCCCCCC DATA PO CCCCCCCCCC DATA PO CCCCCCCCCCC 0 4, 16, 3, 3, EN(DEV1, 00) X, Y EK(IDUMD 6, 6, 5 101) X, Y NO(IVAL) 89) 36, 6, 7, 7 N) 4, 9, 9 V 4, 9, 9	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C C C C C C C C C C C C C C C C C C C	CCCCCCCCCC COMMON 2 1 DIMENSIC CCCCCCCCCC READ IN CCCCCCCCCC IPEND=0 IBASE=1 INORM=0 IPST=1 ITRAN=1 NP=1 DO 1 I=1 YSC(I)=0 DO 2 I=1 B(I)=0. GO TO (3 CALL IOP NT=0 READ(4.1 CALL XCH IF(IDUM) WRITE(1, CALL YES IF(IVAL- IF(X-XMI IF(X-XMI IF(X-XMI)	CCCCCCCCC MIN, XMAN PLOT, IDC N B(6), Y CCCCCCCCC DATA PO CCCCCCCCC DATA PO CCCCCCCCCC 0 4,16,3,3, EN(DEV1, 00) X, Y EK(IDUMD 6,6,5 101) X, Y EK(IDUMD 6,6,5 101) X, Y NO(IVAL) 89)36,6, 7,7 N)4,9,9 X)4,24,2	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

RDAT, CONT.

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CCCCCC	
C C C	BRANCH
CCCCCC	000000000000000000000000000000000000000
	GO TO (10, 16, 17, 18, 19, 20, 21, 22, 23) ITYPE
10	IF(IPEND) 11, 11, 15
11	IF(YMAX-Y) 12, 13, 13
12	$I \square A A^{-1} I$
13	IF(Inin-I)0,0,14
1-9	
15	CALL PLOT(ISTEP, IP) GO TO 8
16	CALL CHAIN('SMOOTH') GO TO 36
17	CALL BASE(B, NT) GO TO 8
18	CALL NORM(SCALE, YSC) GO TO 8
19	CALL EXPAND IF(ITYPE-1)24,3,24
20	CALL CHAIN('SIGAV') GO TO 36
21	CALL PRINT GO TO 8
22	CALL CHAIN('MERGE') GO TO 8
23	CALL PEAKS(XP,YP,NP) GO TO 8
CCCCCC	000000000000000000000000000000000000000
C	BRANCH TO TIE UP LOOSE ENDS BEFORE RETURNING TO CALLING
u	RUOTINE.
č	ROTINE.
cccccc	
C C CCCCCC 24 25	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C C CCCCCC 24 25 26	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C CCCCCC 24 25 26	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C CCCCCCC 24 25 26 27	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C CCCCCC 24 25 26 27 28	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C CCCCCC 24 25 26 27 28	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C CCCCCCC 24 25 26 27 28 29	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C CCCCCCC 24 25 26 27 28 29	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C CCCCCCC 24 25 26 27 28 29	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C CCCCCCC 24 25 26 27 28 29 30	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C CCCCCCC 24 25 26 27 28 29 30 31	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C CCCCCCC 24 25 26 27 28 29 30 31	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
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C CCCCCCC 24 25 26 27 28 29 30 31 32	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C CCCCCCC 24 25 26 27 28 29 30 31 32 33	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
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C CCCCCCC 24 25 26 27 28 29 30 31 32 33 33 33 34 35 36	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C CCCCCCC 24 25 26 27 28 29 30 31 32 33 33 34 35 36	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C CCCCCCC 24 25 26 27 28 29 30 31 32 33 33 34 35 36	ROUTINE. CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C CCCCCC 24 25 26 27 28 29 30 31 32 33 33 34 35 36 37	<pre>R0011NE. CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC</pre>
C CCCCCC 24 25 26 27 28 29 30 31 32 33 33 34 35 36 37 38	TWOUTTME. CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC

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RDAT, CONT.

SUBROUTINE PLOT.FT

SUBROUTINE PLOT(ISTEP. IP) С SUBROUTINE WILL PLOT OUT A DATA FILE ON EITHER THE STRIP CHART RECORDER IF IPLOT=1, OR ON THE TERMINAL IF IPLOT=2 IF THE PLOT IS MADE ON THE TERMINAL, THEN LABEL IS ENTERED TO USE THE CROSSHAIRS TO LABEL INTERESTING FEATURES OF THE PLOT. A TERMINAL PLOT CAN EITHER BE A LINE PLOT OR A POINT PLOT. COMMON VARIABLES USED **IPLOT** BRANCHING PARAMETER IPST START PARAMETER FOR STRIP CHART CURRENT COUNTS/SEC. CURRENT FREQUENCY Y Х YMAX MAXIMUM COUNTS/SEC. MINIMUM COUNTS/SEC. YMIN MAXIMUM FREQUENCY XMAX XMIN MINIMUM FREQUENCY DELX SPACING BETWEEN DATA POINTS INTERNAL VARIABLES INTEGER Y VALUE INTEGER X VALUE IY IX ISTEP INTERVAL BETWEEN POINTS ON RECORDER TEMPORARY FLOATING ISTEP TEMPORARY FLOATING IX TEMPORARY FLOATING IY STEMP AX AY IP **1 FOR LINE PLOT** -1 FOR POINT PLOT SUBROUTINES GALLED SCST(IY) SCPLT(ISTEP, IY) EBASE FDIS(I, IX, IY) LIMIT(IL, RVAR, IH) LETIN(IVAL, IC, IG) BELL HOME Ĉ STEPHEN M. GREGORY APRIL 12, 1978 С COMMON XMIN, XMAX, YMIN, YMAX, DELX, ITYPE, DEV1, DEV2, FILE1, FILE2, IPLOT, IDONE, X, Y, IPST, IBASE, INORM, NTST, ISIG GO TO (1,4) IPLOT

120

PLOT, CONT.

С С PLOTS ON RECORDER С GO TO (2,3) IPST IPST=2 2 CALL BELL READ(1, 100) STEP CALL ERASE STEMP=DELX*300./STEP ISTEP=LIMIT(0, STEMP, 2047) AY=(Y-YMIN) *2047./(YMAX-YMIN) IY=LIMIT(0,AY,2047) CALL SCST(IY) RETURN AY=(Y-YMIN) *2047./(YMAX-YMIN) 3 IY=LIMIT(0, AY, 2047) CALL SCPLT(ISTEP, IY) RETURN С С PLOTS ON TERMINAL C GO TO (5,17) IPST 4 IPST=2 5 CALL BELL 6 WRITE(1,101) CALL LETIN(IVAL, IC, IG) IF(IC)8,8,7 7 STOP IF(IG)9,9,6 8 IF(IVAL-1039)10,11,10 IF(IVAL-777)6,12,6 Q 10 С С POINT PLOT С IP = -111 GO TO 13 С С LINE PLOT С 12 IP=1 READ(1,102) XMARK 13 CALL ERASE С Ċ SET UP X AXIS MARKINGS С XM=XMARK*1024./(XMAX-XMIN) MARK=LIMIT(1, XM, 1024) CALL FDIS(0,0,0) IX=-MARK IX=IX+MARK 14 IF(IX-1024)15,15,16 CALL FDIS(1, IX, 0) 15 CALL FDIS(1, IX, 10) CALL FDIS(1, IX, 0) GO TO 14 16 CALL FDIS(0,0,0)

PLOT, CONT.

С C PLOT DATA Č AX=(X-XMIN)*1024./(XMAX-XMIN) 17 IX=LIMIT(0, AX, 1024) AY=(Y-YMIN) *768./(YMAX-YMIN) IY=LIMIT(0, AY, 768) CALL FDIS(IP, IX, IY) CALL HOME RETURN C FORMAT STATEMENTS С С 100 FORMAT(' SPACING ON RECORDER IN CM-1/INCH = '.F10.4) 101 FORMAT(' POINT OR LINE PLOT ?') FORMAT(' MARKINGS IN CM-1 = '.F10.5) 102 END

PROGRAM SMOOTH.FT

C c c PROGRAM SMOOTH PROGRAM DOES A 17 POINT SMOOTH ON REAL DATA. THIS PROCRAM IS USED WITH THE RAMAN PACKAGE. IT IS CALLED BY THE STATEMENT CALL CHAIN('SMOOTH') COMMON VARIABLES USED INPUT DEVICE INPUT FILE DEV1 FILE1 OUTPUT DEVICE OUTPUT FILE DEV2 FILE2 MAXIMUM FREQUENCY XMAX MINIMUM FREQUENCY XMIN DELX SPACING BETWEEN DATA POINTS INTERNAL VARIABLES NUMBER OF DATA POINTS NUMBER OF DATA POINTS FOR EACH PASS NP NR XNU FREQUENCY VALUES YCN COUNTS SMOOTHING POLYNOMIAL Р SUM SMOOTHING FACTOR IVAL CHARACTER STORAGE IDUM CHECK FOR INTERAUPTION SUBROUTINES CALLED IOPEN(DEV, FILE) OOPEN(DEV, FILE) OCLOSE CHAIN BELL YESNO(IVAL) KCHEK(IDUM)

С STEPHEN M. GREGORY C APRIL 12, 1978 С COMMON XMIN, XMAX, YMIN, YMAX, DELX, ITYPE, DEV1, DEV2, FILE1, FILE2, IPLOT, IDONE, X, Y, IPST, IBASE, INORM, NTST, ISIG, XNU, YCN DIMENSION XNU(512), YCN(512), P(17) С Ĉ OPEN DATA FILES AND READ IN С CALL IOPEN(DEV1, FILE1) CALL OOPEN(DEV2, FILE2) NP=IFIX((XMAX-XMIN)/DELX)+1 IF(NP-512)2.2.3 NR=NP 2 GO TO 4 3 NR=512 DO 5 I=1.NR READ(4, 100) XNU(1), YCN(1) 5 CALL KCHEK(IDUM) IF(IDUM) 7,7,6 WRITE(1, 101) XNU(1), YCN(1) 6 CALL YESNO(IVAL) IF(IVAL-89)16.7.16 N=NR-16 7 DO 8 I=1.16 P(I+1) = YCN(I)R С SMOOTH С С DO 10 J=1,N DO 9 K=1,16 9 P(K) = P(K+1)P(17) = YCN(J+16)SUM=43.*P(9)+42.*(P(8)+P(10))+39.*(P(7)+P(11))+34.*(P(6)+P(12)) SUM=SUM+27.*(P(5)+P(13))+18.*(P(4)+P(14))+7.*(P(3)+P(15)) SUM=SUM-6.*(P(2)+P(16))-21.*(P(1)+P(17)) 10 YCN(J) = SUM/323. L= N DO 11 K=1,N YCN(L+8)=YCN(L) 11 L=L-1 DO 12 K=1,8 J = N + 8 + K - 1L = N + K - 112 YCN(J) = YCN(L)С **READ ONTO OUTPUT FILE** С DO 13 I=1,NR 13 WRITE(4,100) XNU(1), YCN(1) IF(NR-NP) 14, 15, 15 NP=NP-NR 14 CO TO 1 15 XDONE=-1000. YDONE=0. WRITE(4,100) XDONE, YDONE CALL OCLOSE CALL BELL WRITE(1,102) 16 CALL YESNO(IVAL) IF(IVAL-89)17,25,17 17 WRITE(1,103)

SMOOTH, CONT.

	CALL LETIN(IVAL, IC, IG)
	IF(IC-1)18,25,18
18	IF(IG-1)19,17,19
19	IF(IVAL-210)20,22,20
20	IF(IVAL-847)21,23,21
21	IF(IVAL-257)17,24,17
22	CALL ERASE
	CALL CHAIN('CRUNCH')
23	CALL ERASE
	CALL CHAIN('MOVE')
24	CALL ERASE
	CALL CHAIN('DATCOL')
25	STOP
CCCCCC	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C	
C	FORMAT STATEMENTS
C	
CCCCCC	.00000000000000000000000000000000000000
100	FORMAT(2A6)
101	FORMAT(' CURRENT FREQUENCY IS ', F10.4/' CURRENT COUNTS/SEC
	1 ARE ',E10.4/' DO YOU WANT TO CONTINUE ?')
102	FORMAT(' DONE ? ')
103	FORMAT(' CRUNCH, MOVE, OR DATCOL ?')
	END

SUBROUTINE BASE.FT

SUBROUTINE BASE(B, NT) С SUBROUTINE TO CORRECT FOR A LINEAR BASELINE DRIFT AFTER GOING THROUGH THE FIRST HALF OF THE PROGRAM, EXPAND IS ENTERED SO THAT THE FREQUENCY LIMITS CAN BE CHANGED TO INCLUDE ANY PEAKS THAT NEED TO HAVE THE BASELINE ADJUSTED COMMON VARIABLES USED DEV2 OUTPUT DEVICE FILE2 OUTPUT FILE BRANCH PARAMETER IBASE Х CURRENT FREQUENCY Y CURPENT COUNTS/SEC. INTERNAL VARIABLES USED TO HOLD ALL SUMS DENOMONATOR FOR SLOPE CALC В D NEW VALUE OF Y NUMBER OF POINTS YN NT SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED OOPEN(DEV, FILE) STEPHEN M. CRECORY APRIL 12, 1978 C COMMON XMIN, XMAX, YMIN, YMAX, DELX, ITYPE, DEV1, DEV2, FILE1, FILE2, IPLOT, IDONE, X, Y, IPST, IBASE, INORM, NTST, ISIG DIMENSION B(6) GO TO (1,2,3) IBASE

BASE, CONT.

C B(1) IS THE SUM OF ALL X, B(2) IS THE SUM OF ALL Y, B(3) IS THE SUM OF ALL X*X, B(4) IS THE SUM OF ALL X*Y, B(5) IS THE SLOPE, B(6) IS THE INTERCEPT C C C C B(1) = B(1) + X1 B(2) = B(2) + YB(3)=B(3)+X*X B(4) = B(4) + X * YRETURN С Ĉ CALCULATE SLOPE AND INTERCEPT С IBASE=3 2 D=FLOAT(NT) *B(3) -B(1) *B(1)B(5)=(FLOAT(NT)*B(4)-B(1)*B(2))/D B(6) = (B(3) * B(2) - B(1) * B(4)) / DCALL OOPEN(DEV2, FILE2) YN = Y - B(5) * X - B(6)3 WRITE(4, 100) X, YN RETURN 100 FORMAT(2A6) END SUBROUTINE NORM. FT SUBROUTINE NORM(SCALE, YSC) C C SUBROUTINE WILL NORMALIZE ONE OR MORE RAMAN PEAKS Ċ C IT USES THE FIVE POINTS AROUND YMAX TO CALCULATE THE SCALING FACTOR С č COMMON VARIABLES USED C BRANCHING PARAMETER INORM NTST TEST FOR FINISH Y CURRENT COUNTS/SEC. CURRENT FREQUENCY Х DEV2 OUTPUT DEVICE OUTPUT FILE FILE2 INTERNAL VARIABLES YSC STORAGE FOR Y VALUES USED TO CALCULATE SCALE MIDPOINT OF YSC TEMPORARY Y STORAGE YMD ΥI SCALE SCALING FACTOR SUBROUTINES CALLED **OOPEN(DEV.FILE)** STEPHEN M. GREGORY C APRIL 12, 1978 С COMMON XMIN, XMAX, YMIN, YMAX, DELX, ITYPE, DEV1, DEV2, FILE1, FILE2, IPLOT, IDONE, X, Y, IPST, IBASE, INORM, NTST, ISIG 1 DIMENSION YSC(3) IF(INORM) 1, 1, 11

.

NORM, CONT.

CCCCC	000000000000000000000000000000000000000
C	CALCULATE SCALING FACTOR
1	
2	$\begin{array}{c} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 $
4	
U	
	DO 5 [=2.5
	$\mathbf{F}(\mathbf{YI} - \mathbf{YMD})5, 5, 4$
4	
-	K= I
5	CONTINUE
	IF(K-3)9,6,9
6	IF (YMD-YMA209,7,10
7	NTST= 1
	SCALE=0.
	DO 8 I=1,5
8	SCALE=SCALE+YSC(I)
	SCALE=SCALE/5.
	WRITE(1,100) SCALE
9	RETURN
10	YMAX= YMD
	GO TO 7
CCCCCC	
C	
C	NORMALIZE
C	
CCCCCC	
11	IF(NTST) 13, 14, 12
12	N1S1=-1
	CALL OOPEN(DEV2, FILE2)
13	YN=Y/SCALE
	WRITE(4, 101) X, YN
14	RETURN
	FORMAT STATEMENTS
100	$FORMAT(I) \in CALINC FORMOP = \mathcal{FORMAT}(I)$
100	FORMAT(SCALING FACTOR = (,,FIG.4)
101	
SUBBO	ITINE EXPAND. FT
0.00110	
	SUBROUTINE EXPAND
CCCCCC	
C	
C	SUBROUTINE TO CHANCE MAXIMUM AND MINIMUM VALUES OF BOTH
С	FREQUENCY AND COUNTS/SEC
C	AFTER LEAVING THIS ROUTINE SUBROUTINE PLOT CAN BE ENTERED USING
C	THE NEW VALUES AND PLOTTING ON THE TERMINAL
C	
C	COMMON VARIABLES USED:
C	
C	XIIN MINIMUM FREQUENCY VALUE
U C	XTIAN MAXIMUM FREQUENCY VALUE
u a	THIN MININUM COUNTS/SEC.
U C	ITTAX MAXIMUM COUNTS/SEC.
G	ITYPE BRANCHING PARAMETER
L L	IFLUI FLUIIING FARATEIER

EXPAND, CONT.

С C INTERNAL VARIABLES С С IVAL USED FOR CHARACTER STORAGE С SUBROUTINES CALLED CCCCCC YESNO(IVAL) ERASE BELL C STEPHEN M. CREGORY С APRIL 12, 1973 С COMMON XMIN, XMAX, YMIN, YMAX, DELX, ITYPE, DEV1, DEV2, FILE1, FILE2, IPLOT, IDONE, X, Y, IPST, IBASE, INORM, NTST, ISIG CALL ERASE CALL BELL WRITE(1,100) XMIN, XMAX, YMIN, YMAX WRITE(1,101) CALL YESNO(IVAL) IF(IVAL-89)2,1,2 READ(1,102) XMIN WRITE(1,103) CALL YESNO(IVAL) 2 IF(IVAL-89)4,3,4 READ(1,102) XMAX 3 4 WRITE(1,104) CALL YESNO(IVAL) IF(IVAL-89)6,5,6 READ(1,102) YMIN 5 WRITE(1,105) 6 CALL YESNO(IVAL) IF(IVAL-89)8,7,8 READ(1,102) YMAX 7 8 WRITE (1,106) CALL YESNO(IVAL) IF(IVAL-89)10,9,10 9 ITYPE=1 IPLOT=2 CALL ERASE 10 RETURN C C FORMAT STATEMENTS С FORMAT(' CURRENT VALUES'/' MINIMUM FREQUENCY = ', F10.4/ 1' MAXIMUM FREQUENCY = ', F10.4/' MINIMUM COUNT = ', E15.8/ 100 2' MAXIMUM COUNT = ',E15.8) 101 FORMAT(' WHICH ONES DO YOU WANT TO CHANGE ?'/' MINIMUM 1 FREQUENCY ?') FORMAT(' ? ', F10.4) 102 FORMAT(' MAXIMUM FREQUENCY ?') 103 FORMAT(' MINIMUM COUNT/SEC ?') FORMAT(' MAXIMUM COUNT/SEC ?') 104 105 FORMAT(' DO YOU WANT TO PLOT EXPANDED RESULTS ?') 106 END

PROGRAM SIGAV.FT

C CCCC PROGRAM SIGAV PROGRAM WILL EITHER ADD OR SUBTRACT UP TO 100 SETS OF SPECTRA C C ISIG =**1 FOR ADDITION** Ĉ C **2 FOR SUBTRACTION** COMMON VARIABLES USED OUTPUT DEVICE OUTPUT FILE DEV2 FILE2 DEV1 FIRST INPUT DEVICE FILE1 FIRST INPUT FILE ISIG BRANCHING PARAMETER MINIMUM FREQUENCY XMIN XMAX MAXIMUM FREQUENCY DELX SPACING BETWEEN DATA POINTS INTERNAL VARIABLES NUMBER OF DATA FILES TO BE AVERAGED DEVICE EACH DATA FILE IS ON NDAT DEV STORAGE FOR FILE NAMES FIL TEMPORARY FREQUENCY STORAGE TEMPORARY Y STORAGE TEMPORARY STORAGE FOR XMIN XDAT YDAT XTEMP ARRAY FOR FREQUENCY STORAGE XЭ ARRAY FOR COUNT/SEC YS: IDUM CHECK FOR INTERUPTION SUBROUTINES CALLED OOPEN(DEV, FILE) IOPEN(DEV, FILE) BELL ERASE OCLOSE YESNO(IVAL) FILE(DEV, FIL, IMODE) KCHEK(IDUND STEPHEN M. GREGORY APRIL 12, 1978 С COMMON XMIN. XMAX, YMIN, YMAX, DELX, ITYPE, DEV1, DEV2, FILE1, FILE2, 1 IPLOT, IDONE, X, Y, IPST, IBASE, INORM, NTST, ISIG DIMENSION DEV(100), FIL(100), XS(300), YS(300) CALL OOPEN(DEV2, FILE2) CALL BELL READ(1,100) NDAT DEV(1) = DEV1FIL(1) = FILE1DO 2 I=2, NDAT IMODE = 11 WRITE(1,101) I CALL FILE(DEV(I), FIL(I), IMODE) IMODE= IMODE+3 GO TO (19,27,1,2) IMODE CONTINUE 2 CALL ERASE XTEMP=XIIIN GO TO (3,28) ISIG

SIGAV, CONT.

•

	ADDITION
00000	
3	DO 4 I=1.300
4	YS(I) = 0.
-	DO 13 I=1, NDAT
	CALL IOPEN(DEV(I), FIL(I))
	J= 1
5	READ(4,102) XDAT,YDAT
	CALL_KCHEK(IDUM)
_	
6	WRITE(1,103) I, XDAT, YDAT
	CALL YESNO(IVAL)
-	IF(IVAL-89)18,7,18
6	IF(ADAT/10,6,6
0	IF(ADAT-ATIN) 3 , 3 , 3
10	$V_{X}(1) = V_{A}T$
10	YS(J) = YS(J) + YTAT
	IF(SDAT) 13, 11, 11
11	IF(J-300) 12, 13, 13
12	J=J+1
	CO TO 5
13	CONTINUE
	XMIN= XDAT+DELX
	DO 14 I=1,J
	YI=YS(1)
	YI=YI/FLOAT(NDAT)
14	$\begin{array}{c} \text{WRIIE}(4, 102) \text{XS}(1), \text{II} \\ \text{IE}(4) \text{ATA} = 0 \text{ ATA} = 16 ATA$
1	IF(ADAT-ATRAX) 13,10,10 IF(VDAT)14,2,3
16	IF (ADAL) IV, S, S WHINS YTEMD
17	
••	CALL BELL
18	WRITE(1,104)
	CALL YESNO(IVAL)
	IF(IVAL-89)19,27,19
19	WRITE(1,105)
	CALL LETIN(IVAL, IC, IG)
00	
20	IF(1G-1)21, 19, 21
21	IF(IVAL=210)22,29,22
23	IF(1VAL -257) 19 26 19
24	CALL EBASE
	CALL CHAIN('CRUNCH')
25	CALL ERASE
	CALL CHAIN('MOVE')
26	CALL ERASE
	CALL CHAIN('DATCOL')
27	STOP
Č	SIBTRACTION
č	Submaction
ccccc	000000000000000000000000000000000000000
28	CALL IOPEN(DEV(1), FIL(1))
	J=1
29	READ(4,102) XDAT,YDAT
	CALL KCHEK(IDUD)
~ ~	IF(IDUD)31,31,30
30	WRITE(1, 103) I, XDAT, YDAT
	UALL IESTUUIVAL)
21	IFV IVAL-07/10,01,10 IFV TVAT 02,00,20
30	$\begin{array}{c} 1 & 1 \\$
33	XS(J) = XDAT
~ ~	

SIGAV, CONT.

	YS(J) = YDAT	
	IF(XDAT) 37, 34, 34	
34) 95	IF(XDA1~XTAX) 35, 37, 37 IF(1_940) 36, 37, 37	
36	I=J=J=	
	CO TO 29	
37	DO 42 I=2, NDAT	
	CALL IOPEN(DEV(I), FIL(I))	
~~	DO 42 K=1, J	
38	READ(4,102) XDAT, IDAT CALL VCDEV(IDDM)	
	LALL KUMERC IDONS	
39	WRITE(1, 103) I. XDAT, YDAT	
	CALL YESNO(IVAL)	
	IF(IVAL-89)18,40,18	
40	IF(XDAT)42,41,41	
41	1F(xDAT-xMIN) 38, 42, 42	
42	$I \supset (K) = I \supset (K) = I \cup A I$	
	DO 43 K=1.J	
43	WRITE(4,102) XS(K), YS(K)	
	IF(XDAT)45,44,44	
44	IF(XDAT-XMAX)37,45,45	
45	XMIN=XTEMP	
ccccc	- 60 - 10 - 17 Procence concerce concer	
C		
č	FORMAT STATEMENTS	
Ē		
CCCCC	CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC	
100	FORMAT(' HOW MANY DATA FILES ? ', 13)	
101	FORMAT(' INPUT FILE ', 12)	
102	FURTAI(2A0) Format('Fiif'' 137' CIRRENT ERFOIFTCY IS 'F10 47' CIRRENT	
100	1 CONTS/SEC ARE ', E10.4/' DO YOU WANT TO CONTINUE ?')	
104	FORMAT(' DONE ?')	
105	FORMAT(' CRUNCH, MOVE, OR DATCOL ?')	
	END	
SSUBR	OUTINE PRINT.FT	
CCCCC		
C		
ē	SUBROUTINE TO PRINT OUT A LINE OF DATA ON THE TTY	
С	NORMALLY USED TO CHECK THE DATA THAT IS BEING WRITTEN	
C	ON THE OUTPUT FILE.	
C		
C	COMMON VARIABLES USED	
C	V CIEDENT EDECIFICY	
C	Y CIRBENT COUNTS/SEC	
č		
Č	SUBROUTINES USED	
C		
C	NONE	
C	OTTEN M ODECODY	
C C	STEPHEN M. GREGURY MAY 16 1077	
Č	THI 10, 17((
u		
CCCCC	000000000000000000000000000000000000000	

COMMON XMIN, XMAX, YMIN, YMAX, DELX, ITYPE, DEV1, DEV2, FILE1, FILE: 1 IPLOT, IDONE, X, Y, IPST, IBASE, INORM, NTST, ISIG PRINT, CONT.

PROGRAM MERGE.FT

C C **PROGRAM MERGE** C PROGRAM TO MERGE FILES TOGETHER. PROGRAM CAN HANDLE EITHER E OR A FORMATTED FILES, WITH OR WITHOUT DATA TAGS. THE PROGRAM WILL MERGE UP TO 10 INPUT FILES C C С VARIABLES USED NUMBER OF INPUT FILES **NFILE** MINIMUM X ARRAY XMIN XMAX MAXIMUM X ARRAY INPUT DEVICE ARRAY INPUT FILE ARRAY DEV FIL IMODE I/O MODE AND RETURN FLAG OUTPUT DEVICE DEVO FILO OUTPUT FILE CHARACTER STORAGE IVAL IC FLAG FOR CONTROL C FLAG FOR CONTROL G IG X VALUE TO BE TRANSFERED Y VALUE TO BE TRANSFERED Х Y FINAL X VALUE FINAL Y VALUE XEND YEND FLAG FOR OUTPUT FILE DATA TAG ITG OUTPUT DATA TAG TG FLAG FOR INPUT FILE DATA TAG ITAG OLD (INPUT FILE) DATA TAG OTG IDUM FLAG FOR INTERRUPT SUBROUTINES CALLED FILE(DEV, FIL, IMODE) OOPEN(DEV,FIL) LETIN(IVAL, IC, IG) IOPEN(DEV, FIL) YESNO(IVAL) **OCLOSE** KCHEK(IDUM) STEPHEN M. GREGORY Ē APRIL 12, 1973 С DIMENSION DEV(10), FIL(10), XMIN(10), XMAX(10) 1 READ(1,100) NFILE DO 2 I=1,NFILE WRITE(1,101) I READ(1, 102) XMIN(I), XMAX(I) 2 DO 4 I=1,NFILE WRITE(1,101) I з IMODE=1

MERGE, CONT.

CALL FILE(DEV(I), FIL(I), IMODE) IMODE= IMODE+3 GO TO (69,78,3,4) IMODE CONTINUE 4 5 WRITE(1,103) I MODE=0 CALL FILE(DEVO, FILO, IMODE) IMODE= IMODE+3 GO TO (69,78,5,6) IMODE CALL OOPEN(DEVO, FILO) 6 WRITE(1,104) CALL LETIN(IVAL, IC, IG) 7 IF(IC-1)8,78,8 IF(IG-1)9,69,9 я IF(IVAL-65)10,13,10 9 IF(IVAL-69)11,22,11 10 IF(IVAL-321)12,36,12 11 IF(IVAL-325)7,49,7 12 C С A TO A FORMAT С 13 CALL ERASE DO 20 I=1, NFILE CALL IOPEN(DEV(I), FIL(I)) READ(4, 105) X, Y 14 CALL KCHEK(IDUM) IF(IDUMD 17, 17, 15 15 WRITE(1,106) 1,X,Y CALL YESNO(IVAL) IF(IVAL-89)69,16,69 16 CALL ERASE IF(X) 20, 18, 18 17 18 IF(X-XMIN(I)) 14, 19, 19 WRITE(4, 105) X, Y 19 IF(X-XMAX(I))14,29,20 20 CONTINUE 21 XEND=-1000. YEND=0. WRITE(4, 105) XEND, YEND GO TO 68 С С A TO E FORMAT C 22 WRITE(1,107) CALL YESNO(IVAL) IF(IVAL-89)23,24,23 23 ITC=1 GO TO 25 ITC=2 24 READ(1, 108) TG CALL ERASE 25 DO 35 I=1,NFILE CALL IOPEN(DEV(I), FIL(I)) READ(4, 105) X, Y 26 CALL KCHEK(IDUND IF(IDUM) 29, 29, 27 27 WRITE(1,106) I,X,Y CALL YESNO(IVAL) IF(IVAL-89)69,28,69 CALL ERASE 28 29 IF(X)35,30,30 30 IF(X-XMIN(1))26,31,31 31 GO TO (32,33) ITG 32 WRITE(4,109) X,Y GO TO 34

MERCE, CONT.

33 WRITE(4,110) TG,X,Y IF(X-XMAX(I))26.35.35 34 35 CONTINUE GO TO 68 С С E TO A FORMAT C WRITE(1.111) 36 CALL YESNO(IVAL) IF(IVAL-89)37,38,37 37 ITAG=1 GO TO 39 ITAG=2 38 39 CALL ERASE DO 48 I=1,NFILE CALL IOPEN(DEV(I), FIL(I)) GO TO (41,42) ITAG 40 READ(4, 109) X, Y 41 GO TO 43 READ(4, 110) OTG. X. Y 42 CALL KCHEK(IDUM) 43 IF(IDUMD 46, 46, 44 WRITE(1,106) I,X,Y 44 CALL YESNO(IVAL) IF(IVAL-89)69,45,69. CALL ERASE IF(X-XMIN(I))40,47,47 45 46 WRITE(4,105) X,Y 47 IF(X-XMAX(I))40,48,48 48 CONTINUE CO TO 21 С С E TO E FORMAT C 49 WRITE(1,111) CALL YESNO(IVAL) IF(IVAL-89)50,51,50 50 ITAG= 1 GO TO 52 ITAG=2 51 WRITE(1,107) 52 CALL YESNO(IVAL) IF(IVAL-89)53.54.53 53 ITG=1GO TO 53 ITG=2 54 READ(1, 198) TG 55 CALL ERASE DO 67 I=1,NFILE CALL IOPEN(DEV(I),FIL(I)) 56 GO TO (57,58) ITAG 57 READ(4, 106) X, Y GO TO 59 58 READ(4, 110) OTG, X, Y CALL KCHEK(IDUM) 59 IF(IDUM) 62, 62, 60 60 WRITE(1, 106) I, X, Y CALL YESNO(IVAL) IF(IVAL-89)69.61.69 CALL ERASE 61 IF(X-XMIN(1))56.63,63 62 63 CO TO (64,65) ITC 64 WRITE(4,109) X,Y CO TO 66 65 WRITE(4,110) TG, X, Y
MERGE, CONT.

66 IF(X-XMAX(I))56,67,67 67 CONTINUE С C CLOSE FILES С 68 CALL OCLOSE 69 WRITE(1,112) CALL YESNO(IVAL) IF(IVAL-89)70,78,70 70 WRITE(1,113) CALL LETIN(IVAL, IC, IG) IF(IC-1)71,78,71 71 IF(IG-1)72,70,72 72 IF(IVAL-210)73,75,73 IF(IVAL-847)74,76,74 73 74 IF(IVAL-257)70,77,70 75 CALL ERASE CALL CHAIN('CRUNCH') CALL ERASE 76 CALL CHAIN('MOVE') 77 CALL ERASE CALL CHAIN('DATCOL') 78 STOP С С FORMAT STATEMENTS C FORMAT(' HOW MANY INPUT FILES ? ', 12) 100 FORMAT(' FILE ', 12) FORMAT(' FILE ', 12) FORMAT(' MIN X = ', F10.4/' MAX X = ', F10.4) FORMAT(' OUTPUT FILE') 101 102 103 FORMAT(' OUTPUT FILE') FORMAT(' I/O OPTIONS ARE:'/' A FORMAT TO A FORMAT (AA); A 1 FORMAT TO E FORMAT (AE);'/' E FORMAT TO A FORMAT (EA); 2 E FORMAT TO E FORMAT (EE)'/' WHAT IS YOUR CHOICE ?') 104 105 FORMAT(2A6) FORMAT(' FILE ', 12/' FREQUENCY = 5719.4/' COUNTS/ 1SEC = ', E10.4/' DO YOU WANT TO CONTINUE ?') FORMAT(' IS THERE AN OUTPUT DATA TAG ?') FORMAT(' DATA TAG = ', A2) 106 107 108 109 FORMAT(2E15.7) FORMAT(A2,2E15.7) 110 111 FORMAT(' IS THERE AN INPUT DATA TAG ?') FORMAT(' DONE ?') 112 FORMAT(' CRUNCH, MOVE, OR DATCOL ?') 113 END SUBROUTINE PEAKS.FT SUBROUTINE PEAKS(XP, YP, NP)

С C SUBROUTINE TO FIND AND PRINT OUT THE VALUES OF ALL RAMAN PEAKS THAT HAVE AN INTENSITY ABOVE A MINIMUM VALUE C С COMMON VARIABLES USED C C C IPST BRANCHING PARAMETER Ċ C MINIMUM COUNTS/SEC CURRENT FREQUENCY YMIN Х С Y CURRENT COUNTS/SEC С YMAX TOTAL COUNTS WHEN DATA WAS COLLECTED С

PEAKS, CONT.

INTERNAL VARIABLES CCCCCCCCCCCCCC XP FREQUENCY ARRAY YP COUNTS/SEC ARRAY NP ARRAY POINTER YTOP MAX COUNTS/SEC IN ARRAY FREQUENCY OF YTOP XTOP POINTER FOR YTOP MAX MIN COUNTS/SEC IN ARRAY SQUARE ROOT OF YMAX YLOW YSORT YDIFF YTOP - YLOW STEPHEN M. GREGORY Ĉ APRIL 12, 1978 C COMMON XIIIN, XMAX, YMIN, YMAX, DELX, ITYPE, DEV1, DEV2, FILE1, FILE2, IPLOT, IDONE, X. Y. IPST, IBASE, INORM, NTST, ISIG 1 DIMENSION XP(21), YP(21) GO TO (1,2,5) IPST С C FILL UP ARRAY C READ (1,100) YMIN, YMAX 1 CALL ERASE IPST=2 2 XP(NP) = XYP(NP) = YIF(NP-21)3,4,4 NP = NP + 13 RETURN IPST=3 4 GO TO 6 XP(21)=X 5 YP(21) = YС C FIND MAXIMUM AND MINIMUM IN ARRAY С 6 YTOP=YP(1) XTOP=XP(1) YLOW=YP(1) DO 10 I=2.21 IF(YTOP-YP(I))7,8,8 7 YTOP=YP(1) XTOP=XP(I) MAX= I IF(YLOW-YP(I))10,10,9 8 YLOW=YP(I) 10 CONTINUE IF(MAX-11) 14, 11, 14 IF(YTOP-YMIN) 14, 12, 12 11 12 YSGRT=SQRT(YMAX) YDIFF=YTOP-YLOW IF(YDIFF-YSQRT) 14, 13, 13 WRITE(1, 101) XTOP, YTOP 13 14 DO 15 I=1,20 XP(I) = XP(I+1)15 YP(I) = YP(I+1)RETURN

PEAKS, CONT.

С С FORMAT STATEMENTS С FORMAT(' MINIMUM COUNTS/SEC FOR PEAK = ', F10.4, ' MAXIMUM COUNTS 100 1 FOR DATA SET = ', F10.4) FORMAT(' FREQUENCY = ', F10.4, 5X, ' COUNTS/SEC = ', E15.8) 101 END SUBROUTINE LABEL.FT SUBROUTINE LABEL C č SUBROUTINE TO LABEL POINTS ON THE TERMINAL HIT A CONTROL G TO RETURN TO CALLING PROGRAM CROSSHAIRS ARE PUT ON THE SCREEN AND A + IS PUT AT THE INTERSECTION OF THE CROSSHAIRS WHEN A CHARACTER ON THE KEYBOARD IS HIT. ALSO THE X AND Y VALUES OF THAT POINT ARE PRINTED OUT. COMMON VARIABLES USED MAXIMUM FREQUENCY XMAX XMIN MINIMUM FREQUENCY YMAX MAXIMUM COUNTS/SEC. MINIMUM COUNTS/SEC. YMIN INTERNAL VARIABLES X COORDINATE OF CROSSHAIRS NX Y COORDINATE OF CROSSHAIRS NY CHARACTER STORAGE FREQUENCY CORRESPONDING TO NX NC XP YP COUNTS CORRESPONDING TO NY SUBROUTINES CALLED JOY(NX, NY, NC) FDIS(I, IX, IY) ALPHA HOME ERASE STEPHEN M. GREGORY MAY 16, 1977 C COMMON XMIN, XMAX, YMIN, YMAX, DELX, ITYPE, DEV1, DEV2, FILE1, FILE2, IPLOT, IDONE, X, Y, IPST, IBASE, INORM, NTST, ISIG CALL JOY(NX, NY, NC) 1 IF(NC-489)2,3,2 NX=NX-142 С С PUT + ON SCREEN С CALL FDIS(9, NX-5, NY) CALL FDIS(1,NX+5,NY) CALL FDIS(0, NX, NY-5) CALL FDIS(1,NX,NY+5) XP=FLOAT(NX) ×(YMAX-XMIN)/1024.+XMIN YP=FLOAT(NY) *(YMAX-YMIN) /768.+YMIN

LABEL, CONT.

CALL FDIS(0, NX, NY)

C C

PRINT OUT X AND Y COORDINATES

С

WRITE(1,100) XP, YP

- GO TO 1 CALL HOME CALL ERASE 3
 - RETURN

С

FORMAT STATEMENTS C

С 100 FORMAT(F10.4.3X.E15.8)

END

APPENDIX D

PROGRAM LNSHP

A FORTRAN program that calculates the reorientational half-width from the polarized and depolarized spectra of a Raman band.

```
PROGRAM LNSHP(INPUT, OUTPUT, RPLOT, TAPE60= INPUT, TAPE61=OUTPUT,
     1TAPE10=RPLOT)
C
      A PROGRAM TO OBTAIN A REORIENTATION LINESHAPE FOR A RAMAN LINE AND
CCCCC
      COMPARE THIS LINESHAPE TO A LORENTZIAN. DATA IS READ AS
      ANGSTROM COORDINATES AND TRANSFERED TO WAVENUMBERS BEFORE BEING
      PLOTTED OUT.
      DIMENSION X1(1024), Y(1024), C(3), TL(18), IFSMO(4)
      COMMON/AMP/SCALE(8), ICF(8), RHO, POLEFF, GAIN(8)
      COMMON/DATA/AXIS(1024)
      COMMON/CONV/Q(4, 1024), ERROR(4), SCALC(8)
      COMMON/SPECT/S(4, 1024)
      COMMON/SEARCH/XHWDTH, XMSTEP, ISKIP
      COMMON P(5, 1024), D(1024), IGONE(1024)
C
C
      READ IN DATA
č
      READ (60, 1000) NJOB
 1000 FORMAT (1814)
      DO 15 KGRP=1, NJOB
      READ (60,1001) (TL(N), N=1,18)
 1001 FORMAT (18A4)
      READ (60, 1000) NDATA, NPPS, NBASE, ISKIP
      READ(60,1000) (IFSMO(I), I=1, NDATA)
      WRITE (61, 1002) (TL(N), N=1, 18)
 1002 FORMAT (1H1, 1844//)
      WRITE (61, 1003) NDATA, NPPS
 1003 FORMAT (14H DATA CONTAINS, 14, 2X, 10HLINES WITH, 14, 2X, 15HPOINTS PER
     1LINE)
      READ (60, 1004) XHWDTH, XMSTEP
      DO 15 KK=1, NDATA
      READ (60, 1004) GAIN(KK)
 1004 FORMAT (2E15.7)
      DO 1 K=1, NPPS
    1 READ (60, 1004) AXIS(K), S(KK, K)
С
С
      REMOVE NOISE SPIKES
С
      IF(IFSMO(KK).NE.1) GO TO 4
      OLDPNT=S(KK, 1)
      OLDSLP=.05
      IDELETE=0
      DO 3 K=1, NPPS
      XNEWPNT=S(KK,K)
      XNEWSLP=ABS(XNEWPNT-OLDPNT)
      IF(XNEWSLP.EQ.0) XNEWSLP=OLDSLP
      FOS=OLDSLP*500.
      IF(XNEWSLP.GT.FOS) GO TO 2
      OLDSLF=XNEWSLP
      OLDPNT=XNEWPNT
      GO TO 3
    2 XNEWSLP=OLDSLP
      XNEWPNT=OLDPNT
      S(KX,K)=OLDPNT
      IDELETE= IDELETE+1
      IGONÉ(IDELETZ) =K
    3 CONTINUE
      IF(IDELETE.NE.0) WRITE (61,1005) (IGONE(K),K=1,IDELETE)
 1005 FORMAT (35H THE FOLLOWING POINTS WERE DELETED. /30(1X, I3))
      IF(IDELETE.GT.5) GO TO 13
      CALL SMOOTH(KX, NPPS)
С
С
      TAKE MAX VALUE FOR MDPNT
Ĉ
    4 MAX=S(KK, 1)
      XMDPNT=AXIS(1)
      MDPNT=1
      DO 5 K=2, NPPS
```

PROGRAM LNSHP

LNSHP, CONT.

```
IF(S(KK, K).LE.XMAX) GO TO 5
       XMDPNT=AXIS(K)
       XMAX=S(KK,K)
       MDPNT=K
    5 CONTINUE
С
Ū
C
       CALCULATE BASELINE
      L=0
       IUP=NPPS-NBASE
      DO 6 K=1, NBASE
       L=L+1
       X1(L) = AXIS(K) - XMDPNT
    6 \quad Y(L) = S(KK, K)
       DO 7 K=IUP, NPPS
       L=L+1
       X1(L) = AXIS(K) - XIDPNT
    7 Y(L) = S(KK, K)
       NP=2*NBASE
      CALL BASE(NP, X1, Y, C)
ICF(KX) = MDPNT
       IF(KGRP.EQ.1.A.KK.EQ.1) READ (60,1004) RHO, POLEFF
       DO 8 K=1,NPPS
    8 S(KK, K) = S(KK, K) - C(1) * (AXIS(K) - XMDPNT) - C(2)
       BLCOR=S(KK, 1)
       DO 9 K=2, NPPS
       IF(BLCOR.LT.S(KK,K)) GO TO 9
       BLCOR=S(KK,K)
    9 CONTINUE
       DO 10 K=1, NPPS
   10 S(KK, K) = S(KK, K) - BLCOR
С
С
       NORMALIZE
С
       CALL_NORM(S, KK, NPPS, MDPNT, SCALE(KK))
       WRITE(61, 1006) XMDPNT, SCALE(KK)
 1006 FORMAT(//23H AFTER NORMALIZATION AT, T44, 17HCENTER FREQUENCY=, F10.4
      1,8X,19HTHE SCALING FACTOR=,E13.5)
       SCALE( KK) = SCALE( KK) *GAIN( KK)
С
С
       GET 2 SPECTRA BEFORE ENTERING INTNCOR AND MINN
С
       IF(KK.NE.1) GO TO 12
       DO 11 K=1, NPPS
   11 D(K) = S(KK, K)
       GO TO 15
   12 CALL INTNCOR(KK, NPPS)
       IF(KK.NE.2) GO TO 14
       DO 13 K=1, NPPS
   13 S(1,K)=S(1,K)-(4./3.)*S(KK,K)*SCALE(KK)/SCALE(1)
       CALL NORM(S, 1, NPPS, MDPNT, XMAX)
   14 CALL MINN(KK, NPPS)
   15 CONTINUE
       STOP
       END
```

SUBROUTINE PLOT

SUBROUTINE PLOT(J,N,NW) С SUBROUTINE PLOT CAN PLOT OUT UP TO SEVEN DATA SETS ON THE LINE С C C PRINTER. * IS THE FIRST DATA SET AND F IS THE SEVENTH. J IS THE NUMBER OF DATA SETS AND N IS THE NUMBER OF DATA POINTS. Č C TO PRINT OUT PLOTTED DATA, SET NW = 3. TO WRITE DATA INTO A FILE NUMBERED 10, SET NW = 2. C TO DO BOTH, SET NW = 4. TO DO NEITHER, SET NW = 1. С COMMON/DATA/AXIS(1024) COMMON P(7, 1024) DIMENSION Y(121), D(10), NP(7) DATA D/1H , 1H+, 1H=, 1H*, 1HA, 1HB, 1HC, 1HD, 1HE, 1HF/ DATA TC/2HRD/ Ĉ SET UP Y AXIS YMAX=0. YMIN=0. DO 2 I=1,J DO 2 K=1,N IF(P(I,K).LE.YMAX) GO TO 1 YMAX=P(I, K) 1 IF(P(I,K).GE.YMIN) GO TO 2 YMIN=P(I,K) 2 CONTINUE XMIN=AXIS(2)-AXIS(1) WRITE(61, 100) J.N.AXIS(1), AXIS(N), XMIN, YMIN, YMAX 100 FORMAT(1H1,26HSUBROUTINE PLOT PLOTTING OUT,2X,12,2X,14HFUNCTIONS W 11TH,2X,14,2X,11HDATA POINTS/18H X AXIS GOES FROM ,F9.2,2X,2HTO, 2F9.2,2X,11HBY STEPS OF ,F5.2/18H Y AXIS GOES FROM ,F7.2,2X,2HTO, 3F7.2//) С C SET UP EACH LINE OF PLOT Ē DO 6 I=1,N DO 3 KKK=1,121 Y(KKK) = D(1)3 Y(1) = D(2)DO 4 K=1,J YP=(P(K, I)-YMIN)/(YMAX-YMIN) YP=YP*120.+1. 4 NP(K) = IF IX(YP) DO 5 K=1,J Y(NP(K)) = D(K+3)IF(K.EQ.1) GO TO 5 IF(NP(K).EQ.NP(K-1)) Y(NP(K))=D(3) IF(K.EQ.2) GO TO 5 IF(NP(K), EQ, NP(K-2)) Y(NP(K)) = D(3)IF(K.EQ.3) GO TO 5 IF(NP(K), EQ, NP(K-3)) Y(NP(K)) = D(3)IF(K.E2.4) GO TO 5 IF(NP(K), EQ, NP(K-4)) Y(NP(K)) = D(3)IF(K.EQ.5) GO TO 5 IF(NP(K).EQ.NP(K-5)) Y(NP(K))=D(3)IF(K.EQ.6) GO TO 5 IF(NP(K).EQ.NP(K-6)) Y(NP(K))=D(3) **5** CONTINUE 6 WRITE (61, 101) (Y(NN), NN=1, 121) 101 FORMAT(1H , 121A1) GO TO (11,9,7,7) NW 7 DO 3 I=1,N 8 WRITE (10, 192) TG, AXIS(1), (P(K, I), K=1, J) 102 FORMAT(A2,8E15.7) IF(NW.NE.4) GO TO 11 9 WRITE (61,193) 103 FORMAT(1H1) DO 10 I=1,N 10 WRITE (61, 104) AXIS(1), (P(K, I), K=1, J)

PLOT, CONT.

104 FORMAT(1H ,8(3X,E12.6)) 11 RETURN END

SUBROUTINE NORM

SUBROUTINE NORM(F, M, NPPS, ICF, SCALE) COMMON P(7, 1024) DIMENSION F(4, 1024) MLO=ICF-2 MHI=ICF+2 SCALE=0. DO 1 K=MLO, MHI 1 SCALE=SCALE+F(M, K) SCALE=SCALE/5. DO 2 K=1,NPPS 2 F(M, K)=F(M, K)/SCALE RETURN END

SUBROUTINE MINN

```
SUBROUTINE MINN(M, NPPS)
    COMMON/SPECT/S(4, 1024)
    COMMON/CONV/C(4, 1024), ERROR(4), SCALC(8)
    COMMON/AMP/SCALE(8), ICF(8), RHO, POLEFF
    COMMON/SEARCH/XHWDTH, XMSTEP, ISKIP
    COMPION P(7, 1024)
    DIMENSION X1(4). WT(3)
    CPOINT= XHWDTH
    STEP=XMSTEP
    CTST=0.001
    NTIMES=1
    MORE=0
  1 DO 2 K=1.3
    XSTEP=(K-2)*STEP
    CALL CONVOLV(K, NPPS, CPOINT, XSTEP, ICF(M), M, ISKIP)
    WT(K) = 1.
  2 X1(K) = CPOINT+XSTEP
    CALL PARABOL(X1, ERROR, P1, P2, P3)
    X1(4) = -P2/(2.*P1)
    IFOUR=4
    XDIFF=X1(4)-CPOINT
    CALL CONVOLV( IFOUR, NPPS, CPOINT, XDIFF, ICF( MD, M, ISKIP)
    KFLAG=0
    ERRNIN=ERROR(4)
    DO 3 K=1,3
    IF(ERROR(K)-ERRMIN.LE.9) KFLAG=K
    IF(ERROR(K)-ERRMIN.LE.O) ERRMIN=ERROR(K)
    IF(ABS(XDIFF).LT.CTST) KFLAG=4
  3 CONTINUE
    STDEV=SQRT(ERROR(4)/FLOAT(NPPS))
    WRITE(61,100) NTIMES, X1(4), STDEV
100 FORMAT(/40X, 5HCYCLE, 13, 18HOF SUBROUTINE MINN,//60X, 23HTHE MINIMUM
1HALF-WIDTH=, F19.5/60X, 23HTHE STANDARD DEVIATION=, E15.9)
    IF(KFLAG.NE.0) GO TO 4
    CPOINT=X1(4)
    STEP=STEP/2.
    NTIMES=NTIMES+1
    GO TO 1
  4 IF(MORE.EC. 1.0. KFLAG.EQ.4) GO TO 5
```

MINN, CONT.

```
MORE= 1
    WRITE (61,101)
101 FORMAT(//36H PROGRAM IS DIVERGING, TRY DIFFERENT STARTING PARAMETE
   1RS)
    CPOINT=X1(KFLAG)
    STEP=STEP*2.
    NTIMES=NTIMES+1
    CO TO 1
 5 KALL= 1
    XDIFF=X1(KFLAG)-CPOINT
    CALL CONVOLV(KFLAG, NPPS, CPOINT, XDIFF, ICF(M), M, KALL)
    STDEV=SQRT(ERROR(KFLAG)/FLOAT(NPPS))
    WRITE (61,102) NTIMES, X1(KFLAG), STDEV
102 FORMAT(//40X, 5HAFTER, 13, 21HCYCLES THE VALUES ARE, //40X, 16HBEST HAL
   1F-WIDTH=, F10.5/40X, 23HTHE STANDARD DEVIATION=, E15.9)
    DO 6 I=1, NPPS
    P(1, I) = S(1, I)
    P(2, I) = S(M, I)
 6 P(3, I)=C(KFLAG, I)
    CALL PLOT(3, NPPS, 4)
    RETURN
    END
```

SUBROUTINE INTNCOR

SUBROUTINE INTNCOR(M. NPPS) С С CORRECTS SPECTRA ACCORDING TO FORMULA С I(DEPOL, ACTUAL) = I(DEPOL, EXP) / POLEFF-I(POL, EXP) *RHO С COMMON/SPECT/S(4, 1024) COMMON/AMP/SCALE(8), ICF(8), RHO, POLEFF, GAIN(8) COMMON P(5, 1024), D(1024), REP(1024) RAWDPR=SCALE(M)/SCALE(1) SCALE(M) = SCALE(M) *POLEFF IOFFSET= ICF(1) - ICF(M) ISHIFT=NPPS-IABS(IOFFSET) IF(IOFFSET.EQ.0) GO TO 7 IF(IOFFSET.LT.0) GO TO 4 DO 1 K=1, ISHIFT 1 REP(K+IOFFSET)=S(M,K)-RHO*D(K+IOFFSET)*(SCALE(1)/SCALE(M)) DO 2 K=1, IOFFSET 2 S(M, K) = REP(K+IOFFSET) DO 3 K=1, ISHIFT 3 S(M, K+IOFFSET) = REP(K+IOFFSET) GO TO 9 4 DO 5 K=1, ISHIFT 5 S(M, K) = S(M, K-IOFFSET) - RHO * D(K) * (SCALE(1) / SCALE(M))**IUP=ISHIFT+IOFFSET+1** DO 6 K=IUP, ISHIFT 6 S(M, K-IOFFSET) = S(M, K)GO TO 9 7 DO 8 K=1, NPPS 8 $S(M, K) = S(M, K) - RHO \times D(K) \times (SCALE(1) / SCALE(M))$ 9 ICF(M) = ICF(1)CALL NORM(S, M, NPPS, ICF(M, SCOR) SCALE(M) = SCALE(M) *SCOR REALDPR=SCALE(M)/SCALE(1) WRITE (61, 101) RHO, POLEFF, GAIN(MD, IOFFSET, RAWDPR, SCALE(MD, REALDPR 101 FORMAT(/32H AFTER INTENSITY CORRECTION WITH, T40, 21HPOLARIZATION LE 1AKAGE=, F6.4/T41, 19HDETECTOR EFFICENCY=, F5.3/T42, 14HRECORDER GAIN=, 2E11.3/T46, 14HCENTER OFFSET=, 13/T34, 27HCRUDE DEPOLARIZATION RATIO=, 3F7.5, 10X, 19HTHE SCALING FACTOR=, E13.7/T74, 25HTHE DEPOLARIZATION RA 4TIO=, F7.5) SLOSS=(1.-SCOR)*100.

INTNCOR, CONT.

```
LOSS=IFIX(SLOSS)
WRITE (61,102) LOSS
102 FORMAT(///.30H THIS CORRECTION ACCOUNTED FOR,13,36HPER CENT OF THE
1 TOTAL LINE INTENSITY)
RETURN
END
```

SUBROUTINE CONVOLV

```
SUBROUTINE CONVOLV(M, NPPS, XHWDTH, XCHNGE, ICF, L, ISKIP)
С
C
C
C
C
      SUBROUTINE CONVOLV CONSTRUCTS A CONVOLUTION OF A LORENTZIAN
      AND THE POLARIZED LINE, AND MATCHES IT TO A DEPOLARIZED LINE
      DIMENSION WOR(3000), XAXIS(3000)
      COMMON/SPECT/S(4, 1024)
      COMMON/CONV/C(4, 1024), ERROR(4), SCALC(8)
      COMMON/DATA/AXIS(1024)
      COMMON P(7, 1024)
      NPTT= ICF * 4 + 40
      JJ=1
      DEL=AXIS(2)-AXIS(1)
      XAXIS(1)=AXIS(1)
      NPTTP=NPTT+1
      DO 1 K=1, NPTTP
    1 XAXIS(K+1) = XAXIS(K) + DEL
      DO 2 K=1,NPTT
      J= ICF*2
      XJ=XAXIS(K)-XAXIS(J)
    2 WOR(K) = 1./(1.+(XJ*XJ)/(XHWDTH+XCHNGE)**2)
      DO 3 K=1,NPPS
    3 C(M, K) = 0.
С
C
      SIMPSONS RULE INTEGRATION
      NSIMPSN=4
      NADJ = -2
      DO 4 K=1, NPPS, ISKIP
      DO 4 N=1, NPPS, ISKIP
      KKK=K+2*ICF-N
      NSIMPSN=NSIMPSN+NADJ
      COEFF=FLOAT(NSIMPSN)
      NADJ=-NADJ
       IF(N.EQ.1.O.N.EQ.NPPS) COEFF=1.
    4 C(M, K) = C(M, K) + WOR(KKK) *S(JJ, N) *COEFF
      NBSLINE=5*ISKIP
      IUP=NPPS-4*ISKIP
      BLCORR=0.
      DO 5 K=1, NESLINE, ISKIP
    5 BLCORR=BLCORR+C(M,K)
      DO 6 K=IUP, NPPS, ISKIP
    6 BLCORR=BLCORR+C(M,K)
      BLCORR=BLCORR/10.
    DO 7 K=1, NPPS, ISKIP
7 C(M, K) = C(M, K) - BLCORR
      YMAX=C(M, 1)
      DO 8 K=1, NPPS, ISKIP
       IF(C(M, K).LE.YMAX) GO TO 8
      YMAX=C(M,K)
       IRCENT=K
    8 CONTINUE
       IDIFF=IRCENT-ICF
       IDIFF=(IDIFF/ISKIP)*ISKIP
       IF(IDIFF)13,18,14
   13 DO 15 K=1, NPPS, ISKIP
```

CONVOLV, CONT.

15	P(1, K-IDIFF) = C(M, K)
	IAD= IABS(IDIFF)
	DO 16 K=1, IAD, ISKIP
16	P(1, K) = P(1, K+ IAD)
	DO 17 K=1, NPPS, ISKIP
17	C(M, K) = P(1, K)
	GO TO 18
14	IOFF=((NPPS-IDIFF)/ISKIP)*ISKIP
	DO 19 K=1, IOFF, ISKIP
19	C(M, K) = C(M, K+IDIFF)
	DO 20 K= IOFF, NPPS, ISKIP
20	C(M, K) = C(M, K-IDIFF)
18	IF(ISKIP.EQ.1) GO TO 10
	ICENTL= IRCENT-2
	ICENTH= IRCENT+2
	DO 9 K= ICENTL, ICENTH
9	C(M, K) = C(N, IRCENT)
	GO TO 11
10	IRCENT= ICF
11	CALL NORM(C, M, NPPS, IRCENT, SCALC(M))
	ERROR(M) = 0.
	DO 12 K=1, NPPS, ISKIP
12	ERROR(M) = ERROR(M) + (S(L, K) - C(M, K)) * (S(L, K) - C(M, K))
	RETURN
	END

SUBROUTINE SMOOTH

```
SUBROUTINE SMOOTH(KK, NPPS)
  COMMON/SPECT/S(4,1024)
COMMON PP(7,1024)
  DIMENSION P(17)
  NPPS=NPPS-16
  DO 1 K=1,16
1 P(K+1) = S(KK, K)
DO 3 J=1,NPPS
DO 2 K=1,16
2 P(K)=P(K+1)
  P(17) = S(KK, J+16)
  SUM=43.*P(9)+42.*(P(8)+P(10))+39.*(P(7)+P(11))+34.*(P(6)+P(12))+27
 1*(P(5)+P(13))+18.*(P(4)+P(14))+7.*(P(3)+P(15))-6.*(P(2)+P(16))-21.
 2*(P(1)+P(17))
3 S(KK, J) = SUM/323.
  L=NPPS
  DO 4 K= 1, NPPS
S(KK, L+3) = S(KK, L)
4 L=L-1
  DO 5 K=1,8
J=NPPS+8+K-1
  L=NPPS+K-1
5 S(KK, J) = S(KK, L)
  NPPS=NPPS+16
  RETURN
  END
```

SUBROUTINE PARABOL

SUBROUTINE PARABOL(X,V,A,B,C) COMMON P(7,1024) DIMENSION X(3),V(3),Y(3),ERROR(3),ERRSQ(3) WRITE(61,100) PARABOL, CONT.

```
100 FORMAT(1H1, T24, 68HSUBROUTINE PARABOL FITS 3 POINTS TO THE PARABOLI
   1C CURVE Y=AX**2+BX+C)
    TM1=(X(1)-X(2))*(V(2)-V(3))
    TM2=(X(2)-X(3))*(V(1)-V(2))
    ALPHA=-TM1+TM2
    BETA=TM1*(X(1)+X(2))-TM2*(X(2)+X(3))
    D=-(X(1)-X(2))*(X(2)-X(3))*(X(3)-X(1))
    IF(ALPHA.EQ.0.0) ALPHA=1.0E-20
    IF(D.EQ.0.0) D=1.0E-20
    A=ALPHA/D
    B=BETA/D
    C=V(1)-A*X(1)*X(1)-B*X(1)
    WRITE(61,101) A,B,C
101 FORMAT(///20X, 12HCOEFFICIENTS//20X,4HA = ,E13.7/20X,4HB = ,E13.7/2
   10X, 4HC = , E13.7)
    CHISQ=0.
    WRITE(61,102)
102 FORMAT(///10X,7HRESULTS//15X,8HVARIABLE,T30,14HEXPERIM. VALUE,T45,
112HTHEOR. VALUE,T60,10HDIFFERENCE,T73,13HDIFF. SQUARED)
    DO 1 K=1,3
    Y(K) = A * X(K) * X(K) + B * X(K) + C
    ERROR(K) = Y(K) - V(K)
    ERRSQ(K) = ERROR(K) * ERROR(K)
    CHISQ=CHISQ+ERRSQ(K)
  1 WRITE(61, 103) X(K), V(K), Y(K), ERROR(K), ERRSQ(K)
103 FORMAT( 14X, E13.7, T32, E13.7, T46, E13.7, T59, E13.7, T75, E13.7)
    WRITE(61, 104) CHISQ
104 FORMAT(//10X, 26HTOTAL CHI SQUARED VALUE = ,E13.7)
    RETURN
    END
```

SUBROUTINE BASE

```
SUBROUTINE BASE(N, X, Y, C)
С
C
      THIS SUBROUTINE FINDS THE BEST STRAIGHT LINE THROUGH N POINTS
ē
      COMMON P(7, 1024)
      DIMENSION X(1024), Y(1024), C(3)
      WRITE(61,200) N
  200 FORMAT (1H1, T10, 42HSUBROUTINE BASE FITTING A STRAIGHT LINE TO ,
     114,12H DATA POINTS//)
      SX=0.
      SY=0.
      SX2=0.
      SXY=0.
C
      SX = SUM OF ALL X, SY = SUM OF ALL Y, SX2 = SUM OF ALL X*X.
С
С
      SXY = SUM OF ALL X*Y
С
      DO 1 I=1,N
      SX=SX+X(I)
      SY=SY+Y(I)
      SXY=SXY+X(I)*Y(I)
    1 SX2=SX2+X(I)*X(I)
      FN=FLOAT(N)
      D=FN*SX2-SX*SX
      C(1)=(FN*SXY-SX*SY)/D
      C(2) = (SX2*SY-SX*SXY)/D
      WRITE(61,201) (NN,C(NN),NN=1,2)
  201 FORMAT(//10X, 12HCOEFFICIENTS,/(T11,*C(*, 12,*) = *,E15.9))
      H=Ø.
      DO 2 I=1,N
      YC=C(1) *X(1)+C(2)
    2 H=H+(Y(I)-YC)*(Y(I)-YC)
```

BASE, CONT.

STDEV=SQRT(H/(FN-2.)) WRITE(61,202) H.STDEV 202 FORMAT(/4X,26HTOTAL CHI SQUARED VALUE = ,E15.9//9X,21HSTANDARD DEV 21ATION = ,E15.9/) RETURN END

APPENDIX E

TEST ROUTINE

A test routine to be input with the switch register on a PDP 8 minicomputer that is designed to troubleshoot the two counters in the Ramn interface.

LOW COUNTER TEST PROGRAM

0200	7300	∕CLEAR AC AND LINK
0201	6601	CLEAR RAMAN COUNTER
0202	66 06	CLEAR LOW OVERFLOW
0203	6602	START COUNTING
0204	6604	/LATCH COUNTER
0205	6612	SAMPLE LOW COUNT
0206	7300	✓CLEAR AC AND LINK
0207	6617	/DRIVE INTO AC
0210	6695	✓CHECK LOW OVERFLOW
0211	5204	∕GO TO 204
0212	7402	✓HALT

HIGH COUNTER TEST PROGRAM

0200	7300	✓CLEAR AC AND LINK
0201 .	6601	CLEAR RAMAN COUNTER
0202	6611	CLEAR HIGH OVERFLOW
0203	6602	START COUNTING
0204	6604	/LATCH COUNTER
0205	6613	SAMPLE HICH COUNT
0206	7300	CLEAR AC AND LINK
0207	6617	/DRIVE INTO AC
0210	6607	CHECK HIGH OVERFLOW
0211	5204	∕GO TO 204
0212	7402	✓HALT

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