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Hal J. Rosen
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LIGHT SCATTERING FROM LIQUIDS AND LIQUID CRYSTALS

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LIGHT SCATTERING FROM LIQUIDS AND LIQUID CRYSTALS

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ABSTRACT

In this thesis three separate investigations using the light scattering technique will be presented. In Section II results of Raman measurements on I\textsubscript{2} complexes in various solutions are reported. Emphasis is on the variation of the Raman spectrum of I\textsubscript{2} in mixtures of n-hexane and benzene or methylated benzenes. Our results indicate that each I\textsubscript{2} molecule can probably interact with more than one donor and the effect of inert molecules in the solution should be taken into account. In Section III we present a Raman study of the phase transitions of the nematic liquid crystal, Para-Azodyanisole. The intensities of several Raman modes were shown to change abruptly at the phase transitions, but no detectable frequency shift of any mode was observed. Our results suggest that the Raman spectrum of Para-Azodyanisole is only affected by short range ordering. Qualitative interpretation of the results is given. Finally, in Section IV, we present our Brillouin scattering measurements of the
propagation of hypersonic waves in a cholesteric medium at the liquid-to-liquid-crystal transition. Contrary to the results obtained by others, we have found no anomalous change in either the velocity or the attenuation of the hypersonic waves at the transition.
I. INTRODUCTION

Light scattering is a spectroscopic technique for investigating low frequency excitations. Although this technique has been known for almost 60 years most of the work in this field has been done since 1961 when the laser was invented. Such diverse excitations as: rotational, vibrational and electronic energy levels, phonons (acoustic and optic), entropy and pressure fluctuations, magnons, plasmons, polaritons and rotons have been studied. These excitations range in frequency from a few Hertz to $10^{14}$ Hertz.

It is instructive to make a comparison between the light scattering technique and the infra-red absorption technique. First consider an absorption process. One can cause transitions between two energy levels $a$ and $b$ by shining in radiation whose frequency matches the energy spacing, $\Omega$. The cross-section for this process is calculated from first order perturbation theory and is typically $10^{-21}$ cm$^2$. In a light scattering experiment one causes transitions by a second order or Raman process. For such a process a photon of frequency $\omega$ is absorbed and a scattered photon of frequency $\omega-\Omega$ is emitted with the material system making a transition from $a$ to $b$. By detecting the scattered radiation one can determine the energy spacing $\Omega$ of the two levels of the system. Of course, the cross-section for this second order process is much smaller than the absorption cross-section and is typically $10^{-30}$ cm$^2$. However, with a laser source one can easily detect such modes. The light scattering technique has a major advantage over the infra-red absorption technique in that one does not have to match the frequency of the source to the energy spacing. In principle, one can measure any low frequency
excitation with a single frequency source. Actually the two techniques are complementary in the sense that the two processes have complementary selection rules. Some modes can be detected via Raman processes (tensor selection rules) while others are only infra-red active (vector selection rules).

In this thesis I will report on three separate investigations using the light scattering technique. In the first investigation the interaction between iodine and benzene (methylated benzenes) was studied by carefully monitoring the vibrational frequency of $I_2$ as the benzene (methylated benzene) concentration was changed. The results of this investigation are presented in Sec. II. In Sec. III a Raman study of the nematic liquid crystal Para-Azoxydianisole at its phase transitions is presented. Finally, in Sec. IV an investigation of the propagation of sound at the liquid crystal-liquid phase transition using the Brillouin scattering technique will be presented.
SECTION II
RAMAN STUDY OF IODINE COMPLEXES IN SOLUTIONS

1. Introduction

For the past two decades, the subject of charge-transfer interaction between molecules has attracted much attention. In particular, charge-transfer complexes of iodine have been investigated by many research workers. Among the many properties of charge-transfer complexes, the uv absorptivity has been investigated most thoroughly. Results are often analyzed using the Benesi-Hildebrand equation. They are generally in qualitative agreement with the charge-transfer theory proposed by Mulliken. However, for weak complexes, the results often show anomalous behavior. For example, since the charge-transfer interaction between \( \text{I}_2 \) and methylated benzenes increases with methylation, one would expect the uv extinction coefficient of the complex also to increase with methylation, but the opposite was found.

In order to explain the anomalies, various authors have modified the Benesi-Hildebrand theory in a variety of ways. In particular, Orgel and Mulliken pointed out that there is no \( \text{a priori} \) reason to assume the existence of only 1:1 stable complexes in solution. The observed properties of complexes in solution should be statistical averages over all attainable complex configurations in thermal equilibrium. This is particularly true for weak \( \text{I}_2 \) complexes in which the charge-transfer interaction is of fairly long range.

There has also been criticism on the uv absorption measurements. The measurements were usually carried out at a single frequency in the charge-transfer band, ignoring the possible shift and change of profile

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of the absorption band. As Mulliken and Person\textsuperscript{12} pointed out, the extinction coefficient which goes into any theory of complexes should be the one integrated over the entire charge-transfer band. Unfortunately, there are technical difficulties in making absorption measurements over the whole band to a good degree of accuracy. It is therefore important to perform measurements on other properties of complexes to offer an independent test of the theories. Infrared and Raman studies serve this purpose.

There have been several reports of infrared\textsuperscript{13} and Raman\textsuperscript{14,15} experiments on charge-transfer complexes. Raman measurements on I\textsubscript{2} complexes,\textsuperscript{14} however, have been limited to the case of I\textsubscript{2} in pure donor solution. No systematic investigation of the changes in the Raman spectrum of I\textsubscript{2} complexes as a function of donor concentration has been reported yet.

In this paper,\textsuperscript{16} we would like to report our recent experimental studies on I\textsubscript{2} complexes in solution with modern Raman spectroscopic technique. Emphasis is on the change of the Raman spectrum of I\textsubscript{2} due to charge-transfer interaction between I\textsubscript{2} and various donors. The results indicate that I\textsubscript{2} can simultaneously interact with more than one donor. In Section II, a brief theoretical discussion on the average properties of complexes in solution is given. Then in Section III, we describe the experimental setup and procedure briefly. Finally, in Section IV, the experimental results are presented and interpreted.
II. Theoretical Discussion

Properties of a molecule are generally affected by molecular interaction with its surrounding molecules. For complexes in solution, the observed properties of the complexes should correspond to statistical averages over all possible complex configurations, as suggested by Orgel and Mulliken. Consider a solution of complexes, with a small amount of acceptors dissolved in a mixture of donors and inert solvent molecules. The concentration of acceptors is so low that the interaction between acceptors can be neglected. Therefore, the properties of an acceptor in the solution are affected only by its interactions with the neighboring donors and inert molecules. We shall not make any prejudgment on what types of interactions they are, although it is believed that the interaction between acceptors and donors is mainly due to charge-transfer interaction. Let \( \rho(R) \) be the statistical distribution function for a particular configuration (denoted by \( R \)) of donors and inert molecules around the acceptor. Then, for a certain property \( X \) of the acceptors, such as the uv absorption coefficient, Raman scattering cross-section, etc., the corresponding observed quantity is given by

\[
\langle X \rangle = \int_{V_0} X(R)\rho(R) \, dR. \tag{1}
\]

where the volume of integration \( V_0 \) is chosen large enough to include all molecules interacting with the acceptor. The expression for \( \rho(R) \) can be obtained from simple statistical mechanics.

If we allow an acceptor to interact simultaneously with several surrounding molecules, then we can show from statistical treatment (see Appendix I for details) that Eq. (1) takes the form

\[
\langle X \rangle = \frac{a_0 + a_1 \rho_B + a_2 \rho_B^2 + \ldots}{1 + b_1 \rho_B + b_2 \rho_B^2 + \ldots} \tag{2}
\]
where $\rho_B$ is the donor concentration in the solution, and $a_n$ and $b_n$ are constant coefficients.

In experimental investigation, it is more interesting to compare the observed property of acceptors at finite donor concentrations with the same property at zero donor concentration (corresponding to pure inert solvent). Therefore, the quantity of interest is

$$\langle \Delta X \rangle = \langle X \rangle - \langle X \rangle_{\rho_B=0}. \quad (3)$$

From Eq. (2), we obtain

$$\langle \Delta X \rangle = \frac{c_1 \rho_B + c_2 \rho_B^2 + \cdots}{1 + b_1 \rho_B + b_2 \rho_B^2 + \cdots}. \quad (4)$$

where $c_n$ and $b_n$ are constant coefficients.

When only the linear terms are kept in both the numerator and the denominator, the above equation reduces to the well-known Benesi-Hildebrand equation,

$$\frac{1}{\langle \Delta X \rangle} = \frac{1}{\Delta X_0} \left(1 + \frac{1}{K \rho_B}\right). \quad (5)$$

where $\Delta X_0$ and $K$ are constants depending on the properties of the complexes. In the Benesi-Hildebrand model, $K$ represents the equilibrium constant, but this is not true here as is seen from the derivation of Eq. (5).
If the terms quadratic in \( \rho_B \) are also kept, then the equation has the form derived by Derrahau.\(^9\)

We now consider the case of Raman scattering from complexes in solution. Because of interaction between donors and acceptors (mainly due to charge-transfer interaction), Raman scattering from a vibrational mode of the acceptor is changed through changes of energies and wave functions of the eigenstates of the acceptor. The scattering cross-section could either increase or decrease, but if the newly created, strong charge-transfer band happens to be near the frequency of the exciting field, it is likely to have a noticeable enhancement.\(^{18}\) With \( X \) replaced by \( (d\sigma/d\Omega) \) in the above equations, we then have the functional dependence of the observed differential scattering cross-section \( (d\sigma/d\Omega) \) on the donor concentration \( \rho_B \).

Interaction between donors and acceptors also loosens up the interatomic bonding in an acceptor. As a result, the vibrational frequencies of the acceptor usually shift to lower values.\(^{19,20}\) For complexes in solution, the observed spectral distribution for a Raman mode is given by

\[
S(\omega) = \int_{V_0} g(\omega - \omega_v(R)) \frac{d\sigma(R) d\Omega}{d\Omega} \rho(R) dR \tag{6}
\]

where \( g(\omega - \omega_v) \) is the lineshape function. Normally, the distribution of donors and inert molecules has a few most favorable configurations \( R_1, R_2, \ldots \). If the corresponding \( \omega_v(R_1), \omega_v(R_2), \ldots \) are separated by more than a linewidth, then several distinct peaks would be observed for the same mode in the spectrum. This happens, for example, in the
case of strong 1:1 complexes in solution. There, two well-separated Raman lines could be observed for an acceptor mode, one for complexed and one for uncomplexed acceptor molecules.

We can also measure the mean vibrational frequency defined as

$$\langle \omega_v \rangle = \int_{-\infty}^{\infty} S(\omega) \omega \, d\omega / \int_{-\infty}^{\infty} S(\omega) \, d\omega.$$  \hspace{1cm} (7)

From Eq. (6), we can readily find

$$\langle \omega_v \rangle = \int_{V_o} \omega_v (R) \left( \frac{d\sigma(R)}{d\Omega} \right) \rho(R) \, dR / \int_{V_o} \left( \frac{d\sigma(R)}{d\Omega} \right) \rho(R) \, dR$$  \hspace{1cm} (8)

which can also be expressed in the form of Eq. (2). The mean vibrational frequency shift is then given by

$$\langle \Delta \omega_v \rangle = \langle \omega_v \rangle - \langle \omega_v \rangle_{\rho_B=0} = \frac{c_1 \rho_B + c_2 \rho_B^2 + \ldots}{1+b_1 \rho_B + b_2 \rho_B^2 + \ldots}$$  \hspace{1cm} (9)

where $b_n$ and $c_n$ are constants. Again, in special cases, the above equation reduces to the simple form of the Benesi-Hildebrand equation, Eq. (5), although the physical meanings of the coefficients would be different.

We shall apply these results to the case of Raman scattering from $I_2$ complexes in solution in Section IV.
III. Experimental Arrangement

The construction of the Raman spectrometer was the same as that of Landon and Porto. The output of a He-Ne laser (Spectra Physics Model 125), after passing through an interference filter, was focused on the sample with a microscope objective. Scattered radiation from the sample in a direction perpendicular to the incoming beam was collected with a projector lens and focused on the entrance slit of a double monochromator (Spex Model 1400). For detection, the photon counting technique was adopted. (See Appendix II for details). A photomultiplier (EMI 9558 QA), cooled to \(-70^\circ C\) with dry nitrogen, was used to detect single photons in the form of current pulses. These pulses were then amplified, shaped, and finally registered on a multichannel analyzer.

This setup proved to be both convenient and sensitive. Excellent Raman spectra of \(I_2\) in solution were obtained with little effort. For example, with a scan speed of 1 A/min and a slit width of 4 cm\(^{-1}\) on the monochromator, the fundamental Raman line of \(I_2\) in a 0.06 molar solution appeared with a signal-to-noise ratio greater than 50. A typical spectrum is shown in Fig. 1. Iodine absorbs rather strongly at the laser frequency (6328 A). To avoid heating effects, it is necessary not to focus the laser beam too strongly into the \(I_2\) solution. One must also properly choose the concentration of \(I_2\) and the distance the scattered radiation travels through the solution in order to optimize the signal-to-noise ratio. In our experiments, the \(I_2\) concentration was usually taken to be 0.06 M, and the laser was focused at approximately 1 mm away from the cell window through which the scattered radiation was collected. For frequency calibration, spectral lines from a Ne lamp were used.
A major difficulty in our Raman studies on I₂ complexes is that the Raman lines of I₂ sometimes overlap with Raman lines of the solvent molecules. Decomposition of the lines introduces error and makes the experimental data much less accurate. For example, the I₂ fundamental overlaps slightly with a toluene line at 214 cm⁻¹, and the first overtone of I₂ overlaps with a weak benzene line at 404 cm⁻¹. In principle, the above difficulty can be avoided by measurements at two different I₂ concentrations, so that the part due to solvent molecules in the observed spectrum can be subtracted out. No such correction procedure was made in our experiments.

The chemicals used were all of the Reagent grade. High purity of the solvents is not important here, since the effect of impurities on iodine should be small. We saw no observable effects from the small quantities of impurities in our experiments. Solutions were prepared the same day they were measured. Errors in the concentrations of solutions were estimated to be ±2%. Unless specified, all measurements were made at 25°C.

IV. Experimental Results and Discussion

A. Raman Spectra of I₂ in Various Solvents

In an iodine solution, interaction of I₂ with solvent molecules always leads to a shift in the frequency of the I₂ stretching vibration. We can usually divide the intermolecular interaction into two types: the long-range van der Waals interaction and the short-range chemical interaction. In the case of I₂ complexes, the chemical interaction is presumably dominated by the charge-transfer interaction. In many cases, it is important to separate the effect of the charge-transfer interaction from that of the van der Waals interaction.
In order to estimate the effect of van der Waals interaction, we have measured the Raman spectra of I$_2$ dissolved in various solvents. While a true microscopic theory for the vibrational frequency shifts due to van der Waals interaction is not available, it is generally assumed, from Onsager's reaction field model, that the frequency shift $\Delta \omega_V$ for a solute molecule is a function of $n^2$ where $n$ is the refractive index of the solvent. For a narrow range of $n^2$, we would then expect that $\Delta \omega_V(n^2)$ can be approximated by a straight line. The results of our Raman measurements on the fundamental vibration of I$_2$ in various solvents are given in Table I. Here, the mean vibrational frequency $\langle \omega_V \rangle$ is defined as the center of gravity of the Raman line with respect to the exciting laser frequency. Our measurements on this mean frequency could be as accurate as $\pm 0.1$ cm$^{-1}$. In Fig. 2, the mean frequency shifts, defined as $\langle \Delta \omega_V^0 \rangle \equiv \omega_{V0} - \langle \omega_V \rangle$ where $\omega_{V0}=213.3$ cm$^{-1}$ is the vibrational frequency of I$_2$ in the vapor phase, are plotted against $(n^2 - 1)$. From uv absorption measurements, we know that I$_2$ has essentially no charge-transfer interaction with n-hexane, n-heptane, and CCl$_4$. Figure 2 shows that the frequency shifts for I$_2$ in these three solvents are small, and the three respective points indeed fall on a straight line. The frequency shifts in the other solvents are partly due to charge-transfer interaction, and Fig. 2 indicates that the charge-transfer interaction between I$_2$ and solvent molecules increases in the following order: chloroform, cyclohexane, nitrobenzene, chlorobenzene, bromobenzene, benzene, toluene, m-xylene, and mesitylene. This result on the relative strengths of the charge-transfer interaction between I$_2$ and different donors is consistent with the uv measurements.
B. Raman Spectra of I₂ in Mixtures of n-hexane and Benzene or Methylated Benzenes

For a better understanding of charge-transfer complexes in solution, we have made a systematic investigation of the Raman spectrum of I₂ in mixtures of n-hexane and benzene or methylated benzenes. In pure n-hexane, the I₂ Raman line has a mean vibrational frequency of 210.1 cm⁻¹, and an apparent full width at half maximum of 6.0 cm⁻¹. (The corresponding true full width is 5.1 cm⁻¹, obtained from deconvolution of the line with the slit function.) With increasing benzene concentration in the mixture, the line gradually shifts to lower frequencies (see Fig. 3) with little change in the line profile, and finally reaches a mean frequency of 204.6 cm⁻¹ in pure benzene. This shift is primarily due to charge-transfer interaction between I₂ and benzene, since we recall that there is no charge-transfer interaction between I₂ and n-hexane and that the van der Waals shifts estimated for I₂ in pure n-hexane and in pure benzene differ only by 0.4 cm⁻¹ as seen from Fig. 2.28

This observation cannot be explained by the model of I₂ and benzene forming 1:1 complexes² (allowing each I₂ to interact with only one donor). Such a model would predict two discrete Raman lines of I₂ in the mixed solution, one for I₂ unassociated with benzene, and the other for I₂ complexed with benzene. As the benzene concentration increases, the frequencies of the two lines would remain unchanged, but their relative intensity would change. Even for I₂ in pure benzene, only 60% of I₂ would have formed 1:1 complexes,² and the uncomplexed I₂ line would be easily detectable. Our spectra show that, with increasing benzene concentration, the I₂ line shifts as a whole to lower frequencies. The shift from pure n-hexane to pure benzene is greater than the half width of the line. It is impossible to decompose the line into two lines, one for
complexed $I_2$ and one for uncomplexed $I_2$, as required by the above model. We did observe a small change ($<25\%$) in the linewidth as shown in Fig. 4, but it does not affect our conclusion. Similar results were obtained for $I_2$ in mixtures of n-hexane and toluene or m-xylene. Our results suggest that the charge-transfer interaction between $I_2$ and the donors is weak, and each $I_2$ molecule can interact simultaneously with more than one donor. The observed spectrum $S(\omega)$ is a statistical average over all complex configurations as indicated by Eq. (6).

Microscopic pictures also seem to suggest that an $I_2$ molecule could interact effectively with more than one donor. Mulliken has discussed various models of a 1:1 $I_2$-benzene complex. According to him, the most compact and most probable model has the iodine molecule resting on the benzene molecule with its axis parallel to the plane of the benzene ring and its center on the sixfold axis of the benzene. In all the models, it seems obvious that we cannot rule out the possibility of having a second benzene molecule interacting with the iodine from the other side, although the interaction could be shielded considerably by the interaction of the iodine with the first benzene molecule. This shielding should be more effective for stronger charge-transfer interaction, since the $I_2$ molecule is more negatively charged in the complex formation with the first donor, and therefore reduces its
ability to interact with other donors. We then expect that for sufficiently
strong I₂ complexes, I₂ and donor molecules would actually form 1:1 complexes
with a more or less definite configuration at low donor concentrations.
Correspondingly, two Raman lines should appear with their relative
intensity changing with donor concentration. This is indeed the case
for I₂ in mixtures of n-hexane and mesitylene. At low concentrations
of mesitylene, two lines at 210.1 cm⁻¹ and 202.5 cm⁻¹ can be observed.
With increasing mesitylene concentration, the complexed I₂ line
(202.5 cm⁻¹) increases in intensity and the uncomplexed line (210.1 cm⁻¹)
diminishes. For mesitylene concentration higher than 40%, only the
complex line remains and gradually shifts as a whole to lower frequencies
with increasing mesitylene concentration. This gradual shift again
indicates that each I₂ molecule now starts interacting effectively
with more than one donor although the interaction is shielded to some
extent by the charge-transfer interaction between I₂ and the first donor.
One can also regard the I₂-mesitylene complex as a unit which
now interacts weakly with surrounding donors to form higher-order
complexes in various attainable configurations.

Since the charge-transfer interaction between I₂ and pyridine is
supposed to be even stronger, we would expect to observe the same
phenomenon for I₂ in mixtures of n-hexane and pyridine. We found that
there are indeed two lines at 210.1 cm⁻¹ and 185 cm⁻¹ for pyridine
concentrations less than 0.2%. With increasing pyridine concentration
above 0.2%, the uncomplexed line disappears and the complexed line
gradually shifts to lower frequencies with increasing linewidth.
Finally, in pure pyridine, the line appears at $174 \text{ cm}^{-1}$ with a linewidth of $15 \text{ cm}^{-1}$. Infrared measurements on I$_2$-pyridine (Py I$_2$) complexes in inert solvents with small concentrations of I$_2$ and pyridine have also revealed an absorption band around $184 \text{ cm}^{-1}$.

In addition, Plyler and Mulliken$^{13}$ have observed two infrared absorption bands for I$_2$ and pyridine in benzene, one at $204 \text{ cm}^{-1}$ and one at $174 \text{ cm}^{-1}$. They identify the $204 \text{ cm}^{-1}$ line as due to I$_2$-benzene complexes. They also suggest that the $174 \text{ cm}^{-1}$ line could be due to the formation of double complexes Benzene-PyI$_2$ of donor-acceptor character, or due to PyI$_2$ in "contact" donor-acceptor interaction with the benzene molecules around it.

Our observation of a gradual shift of the complexed I$_2$ line from $185 \text{ cm}^{-1}$ to $174 \text{ cm}^{-1}$, which has also been observed in the infrared work of Ginn and Wood$^{13}$, leads us to believe that the shift is the result of interaction between the PyI$_2$ complex and neighboring molecules in the statistical sense. The interaction could be of donor-acceptor character, but since the PyI$_2$ complex has a large permanent dipole moment, van der Waals interaction between PyI$_2$ and surrounding molecules could also be appreciable. Further studies of the PyI$_2$ complex in different solvents could help determine which type of interaction is more important.

Our remark here also applies to the case of PyI$_2$ in benzene.

As we mentioned earlier, measurements of the mean vibrational frequency shift ($\Delta \omega_v$) in the Raman spectrum can be very accurate, and can be used to test quantitatively the theories on complexes in solution. In Fig. 3, $1/\Delta \omega_v$, the inverse of the mean frequency shift of the I$_2$ fundamental vibration from its value in pure n-hexane, is plotted against $1/(\rho_B/\rho_{B0})$, the inverse of the normalized concentration of benzene or methylated benzene, where $\rho_B$ is the concentration of benzene.
or methylated benzene in the mixture, and \( p_{BO} \) the concentration of pure benzene or methylated benzene. The results look very much the same as those obtained from the uv measurements with the extinction coefficient replaced by the mean frequency shift. This is not unexpected since both the average uv extinction coefficient (integrated over the entire charge-transfer band) and the mean frequency shift should have the form of Eq. (4) in Section II. In fact, if we use the Benesi-Hildebrand equation, or Eq. (5), to fit the experimental data by the least-square method, we find that the constant \( K \) deduced from our measurements is within 25% of the value of \( K_{uv} \) deduced from uv absorption measurements\(^5,30,31\) (see Table II). This gives us further assurance that the vibrational frequency shifts of \( I_2 \) in these mixtures from its value in pure n-hexane is primarily due to charge-transfer interaction.

In Fig. 3, while the Benesi-Hildebrand equation yields a straight line, the experimental data show some evidence of curvature. From Eq. (9), we realize that a better approximation should be

\[
\frac{1}{\langle \Delta \omega \rangle} = \frac{(1+\alpha_1 x + \alpha_2 x^2)}{(\beta_1 x + \beta_2 x^2)}
\]

where \( x = p_B / p_{BO} \) and \( \alpha_1, \alpha_2, \beta_1, \) and \( \beta_2 \) are constant parameters. In Fig. 3, the theoretical curves obtained from a least-square fit of both Eq. (10) and the Benesi-Hildebrand equation are shown. It is seen that Eq. (10) appears to give a better description of the experimental data. The values of
\( \alpha_1, \alpha_2, \beta_1, \) and \( \beta_2 \) are given in Table III. However, the uncertainty in determining these parameters is quite large,\(^{32}\) as suggested by the small difference between the two sets of curves in Fig. 3. (The parameter \( \beta_1 \) can, however, be determined quite accurately from the asymptotic slope of \( 1/(\Delta \omega_\nu) \) vs \( \rho_{BO}/\rho_B \) at small \( \rho_B \)).\(^{32}\) The least-square error in the fitting could of course be greatly improved if more experimental data points are available.

C. Temperature Dependence of Raman Spectra of I\(_2\) in Mixtures of Benzene and n-Hexane

Generally, thermal agitation decreases the probability of interaction between molecules. Therefore, the vibrational frequency shift of I\(_2\) in solution should be smaller at higher temperatures. In Fig. 5, we show the variation of the frequency shift as a function of the benzene concentration in mixtures of benzene and n-hexane at 25°C and 55°C. For a given benzene concentration, the shift is indeed smaller at the higher temperature.

D. Variation of Raman Scattering Intensity with Benzene Concentration in Mixtures of Benzene and CCl\(_4\)

For complexes in solution, the variation of the Raman scattering cross-section I\(_2\) should have the same functional dependence on the
donor concentration as the extinction coefficient for charge-transfer absorption. Thus, measurements of Raman scattering intensity of I₂ as a function of the donor concentration should provide another test on the theories of complexes in solution. Bahnick and Person have in fact made such measurements on several charge-transfer complexes. The equilibrium constants deduced from their results by assuming 1:1 complexes agree with those obtained from uv measurements. We have measured the integrated Raman cross-section of I₂ in mixtures of benzene and CCl₄. In order to eliminate possible variations of collection efficiency, change of absorptivity with benzene concentration, long-term instability of the Raman spectrometer, etc., we need an internal intensity calibration for scattering cross-section measurements. This is provided by the strong Raman line of CCl₄ at 217 cm⁻¹. We always measured the Raman line of I₂ together with the 217 cm⁻¹ line of CCl₄. We then considered only the relative scattering cross-section of the I₂ line with respect to the CCl₄ line. We found experimentally that in the absence of I₂, the scattering intensity of the 217 cm⁻¹ CCl₄ line is proportional to the concentration of CCl₄ in agreement with the results of Bahnick and Person. Therefore, within experimental error, the scattering cross-section of the CCl₄ line should be unaffected by the CCl₄-benzene interaction. Our experimental results in Fig. 6 show that the relative Raman cross-section of I₂ increases with the benzene concentration. This behavior agrees qualitatively with what we would predict since a strong charge-transfer band appears in the near uv (see Section II). Unfortunately, there is inherent inaccuracy in the measurements of integrated intensity. The same difficulty clearly exists also in the measurements of Bahnick and Person.
In our case, the accuracy is worse since the CC$_4$ line overlaps slightly with the I$_2$ line. Consequently, the results in Fig. 6 cannot be used for a quantitative test on the different theories of complexes in solution.

E. First Raman Overtone of I$_2$ in Mixtures of Benzene and n-hexane.

We have also measured the relative scattering cross-section of the I$_2$ first overtone with respect to the fundamental as a function of benzene concentration. Usually, one would expect the overtones to be much weaker than the fundamental. However, we found in pure n-hexane that the first overtone is only 4 times less intense than the fundamental. This anomaly is probably due to resonance enhancement, since the exciting laser frequency is at the lower edge of the visible absorption band of I$_2$. Because of this resonance Raman effect, the I$_2$ Raman line is exceptionally strong (100 times more intense than the 217 cm$^{-1}$ CC$_4$ line), and it would not be surprising even if the first overtone happened to be more intense than the fundamental.$^{33}$ As the benzene concentration increases, the relative cross-section becomes smaller, and finally in pure benzene, the overtone is approximately 8 times weaker than the fundamental. This is presumably because the visible absorption band of I$_2$ has a blue shift resulting from the charge-transfer interaction between I$_2$ and benzene.$^{2,34}$ Here again, the results are not accurate enough for a more detailed quantitative discussion.

Anharmonicity in a molecular vibration should be reflected in the overtone spectrum of the vibration. Thus, measurements of the overtone spectrum of I$_2$ complexes in solution should yield information
about how the anharmonicity of the I-I intramolecular potential is changed by the charge-transfer interaction. We have measured the first Raman overtone of $I_2$ in mixtures of benzene and n-hexane. Just as for the fundamental, the mean frequency of the overtone shifts to lower frequencies as the benzene concentration is increased (see Fig. 7). The overtone line is roughly symmetric, with a linewidth of about 18 cm$^{-1}$ which increases slightly with higher benzene concentrations. Qualitatively, these results are expected if we take into account the statistical distribution of complex configurations in solution, and consider the fact that the overtone line is usually broader than the fundamental.

To show explicitly the change of anharmonicity, we have plotted in Fig. 8 the difference between twice the mean fundamental frequency and the mean-overtone frequency as a function of the benzene concentration. In pure n-hexane the anharmonicity is 2.5 times greater than the value found in vapor$^{25}$ and as the benzene concentration increases, the "average" anharmonicity of the vibration decreases, approaching zero for benzene concentrations greater than 50%. The difference between the anharmonicity in pure n-hexane and in vapor is presumably due to van der Waals interaction between $I_2$ and n-hexane which enhances the anharmonicity. On the other hand, the charge-transfer interaction apparently tends to make the $I_2$ vibration more harmonic.

F. Intermolecular Mode of $I_2$, Complexes

In addition to a change in the Raman spectrum of $I_2$, the charge-transfer interaction between $I_2$ and the donor could also induce a new intermolecular mode. Frequencies of intermolecular modes are generally low, higher for stronger interaction. The charge-transfer interaction
between I\textsubscript{2} and pyridine is exceptionally strong. From the infrared absorption spectrum, Lake and Thompson\textsuperscript{13} have indeed found the intermolecular mode at 94 cm\textsuperscript{-1} in the I\textsubscript{2}-pyridine complex. We have tried to observe the same intermolecular mode from the Raman spectrum. However, from the charge configuration of the I\textsubscript{2}-pyridine complex, this intermolecular mode is probably more infrared-active than Raman-active. Because of this and also because of the relatively large scattering background near the exciting laser line, we have not been successful in detecting this intermolecular mode.

V. Conclusions

It is demonstrated that Raman spectroscopy can be used to investigate charge-transfer complexes in solution. By measuring the mean frequencies of the I\textsubscript{2} stretching vibration in various solvents, the frequency shift due to van der Waals interaction can be separated from that due to charge-transfer interaction. Investigation of the I\textsubscript{2} Raman spectrum in mixtures of n-hexane and benzene or methylated benzene shows that each I\textsubscript{2} molecule can probably interact simultaneously with more than one donor in the statistical sense. We have also measured, for various donor concentrations, the temperature variation, the linewidth, and the scattering cross-section of the I\textsubscript{2}-fundamental and, in addition, the I\textsubscript{2} overtone spectrum. Results agree qualitatively with what the theory would predict.
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E. K. Plyler and R. S. Mulliken, J. Am. Chem. Soc. 81, 823 (1959);
H. Yada, J. Tanaka, and S. Nagakura, J. Mol. Spectry. 2, 461 (1962);
14. P. Klaboe, J. Am. Chem. Soc. 89, 3667 (1967);  

15. D. A. Bahnick and W. B. Person, J. Chem. Phys. 48, 1251 (1968);  
48, 5637 (1968); J. Phys. Chem. 73, 2309 (1969).

16. Preliminary results of the experiments were reported in Y. R. Shen,  

17. See, for example, J. O. Hirschfelder, C. F. Curtiss, and B. B. Bird,  
Molecular Theory of Gases and Liquids (John Wiley and Sons, Inc.,  

18. See, for example, G. Placzek, Marx's Handbuch der Radiologie VI, 2,  
209 (1934).


22. We define the van der Waals interaction here to include electro-
static, induction and dispersion forces between molecules. See  
Ref. 23.

23. This classification is somewhat arbitrary; See J. O. Hirschfelder,  
C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and  

24. See, for example, A. D. Buckingham, Proc. Roy. Soc. (London), A248,  
169 (1958).


26. Indices of refraction for the solvents are obtained from *Handbook of Chemistry and Physics* (Chemical Rubber Co., Cleveland, 1963) p. 766.


28. If CCl₄ were used instead of n-hexane, then since CCl₄ and benzene have roughly the same refractive index, the van der Waals shift would presumably remain unchanged with benzene concentration in the CCl₄-benzene mixtures. Unfortunately, the 217 cm⁻¹ CCl₄ line overlaps slightly with the I₂ line, making accurate frequency measurements more difficult.

29. The same phenomenon was observed by Bahnick and Person for ICN forming charge-transfer complexes with tetrahydrofuran in a mixed solvent of CH₂Cl₂ and CHCl₃. See Ref. 15.


31. The values of Kᵥᵥ obtained by different authors are usually different. Our values of K fall within the spread of values of Kᵥᵥ tabulated in G. Bricgleb, *Electronen-Donor-Acceptor-Komplexes* (Springer-Verlag, Berlin, 1961) p. 124. It should be noted that part of the discrepancy between K and Kᵥᵥ could be due to the fact that CCl₄ is used as the inert solvent in the uv measurements, while n-hexane is used in our case. The estimated errors in our determination of K and (Δωᵥ₀) are around 5%.

32. With an 85% confidence level, the uncertainties in the values of
$\alpha_1, \alpha_2,$ and $\beta_2$ can be as large as 200%, but the uncertainties in the values of $\beta_1$ are less than 30%.


Table I. Mean frequencies of the $I_2$ fundamental vibration in various solvents.

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Frequency (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>vapor</td>
<td>213.3</td>
</tr>
<tr>
<td>n-hexane</td>
<td>210.1 ± 0.1</td>
</tr>
<tr>
<td>n-heptane</td>
<td>210.0 ± 0.1</td>
</tr>
<tr>
<td>carbontetrachloride</td>
<td>209.7 ± 0.3</td>
</tr>
<tr>
<td>chloroform</td>
<td>209.6 ± 0.4</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>208.9 ± 0.4</td>
</tr>
<tr>
<td>nitrobenzene</td>
<td>208.1 ± 0.4</td>
</tr>
<tr>
<td>chlorobenzene</td>
<td>207.1 ± 0.4</td>
</tr>
<tr>
<td>bromobenzene</td>
<td>205.9 ± 0.4</td>
</tr>
<tr>
<td>benzene</td>
<td>204.6 ± 0.1</td>
</tr>
<tr>
<td>toluene</td>
<td>203.6 ± 0.2</td>
</tr>
<tr>
<td>m-xylene</td>
<td>202.1 ± 0.15</td>
</tr>
<tr>
<td>mesitylene</td>
<td>200.0 ± 0.3</td>
</tr>
</tbody>
</table>
Table II. Values of $(\Delta \omega_v)_o$ and $K$ in Eq. (5) derived from the best fit of the experimental data to Eq. (5) as shown in Fig. 3. The equilibrium constants $K_{uv}$ deduced from the uv absorption measurements are obtained from (a) R. M. Keefer and L. J. Andrews, Ref. 30 and (b) L. J. Andrews and R. M. Keefer, Ref. 5.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$(\Delta \omega_v)_o$ (cm$^{-1}$)</th>
<th>$K$ (liters/mole)</th>
<th>$K_{uv}$ (liters/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>8.6</td>
<td>0.17</td>
<td>0.157</td>
</tr>
<tr>
<td>Toluene</td>
<td>10.3</td>
<td>0.21</td>
<td>0.16</td>
</tr>
<tr>
<td>m-xylene</td>
<td>10.5</td>
<td>0.40</td>
<td>0.31</td>
</tr>
<tr>
<td>Mesitylene</td>
<td>12.8</td>
<td>0.62</td>
<td>0.534</td>
</tr>
</tbody>
</table>
Table III. Values of $\alpha_1$, $\alpha_2$, $\beta_1$, and $\beta_2$ in Eq. (10) derived from the best fit of the experimental data to Eq. (10) as shown in Fig. 3.

<table>
<thead>
<tr>
<th></th>
<th>$\alpha_1$</th>
<th>$\alpha_2$</th>
<th>$\beta_1$</th>
<th>$\beta_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>2.64</td>
<td>4.53</td>
<td>13.20</td>
<td>31.71</td>
</tr>
<tr>
<td>Toluene</td>
<td>3.24</td>
<td>1.05</td>
<td>22.0</td>
<td>14.26</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>3.0</td>
<td>3.6</td>
<td>30.6</td>
<td>29.37</td>
</tr>
<tr>
<td>Mesitylene</td>
<td>3.68</td>
<td>0.724</td>
<td>53.11</td>
<td>2.72</td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS

Fig. 1. A typical Raman spectrum (the central line) of the I₂ fundamental vibration in pure benzene at 55°C. The dots correspond to the number of counts in the channels of the multichannel analyzer. The two side lines are Ne calibration lines at 6402.25 Å and 6421.71 Å. The instrumental linewidth is 4 cm⁻¹. Note that only one spectral line of I₂ shows up, while the model of a 1:1 complex would predict two.

Fig. 2. Mean frequency shift of the I₂ fundamental vibration from its value in vapor in various solvents vs. n² - 1, where n is the refractive index of solvent.
1 - n-hexane; 2 - n-heptane; 3 - carbon tetrachloride;
4 - chloroform; 5 - cyclohexane; 6 - nitrobenzene;
7 - chlorobenzene; 8 - bromobenzene; 9 - benzene;
10 - toluene; 11 - m-xylene; 12 - mesitylene.

Fig. 3. Comparison of the theoretical curve of Eq. (10) and the Benesi-Hildebrand curve of Eq. (5) with the experimental data. The inverse mean vibrational frequency shifts 1/(Δω) of I₂ in solutions of benzene or methylated benzene and n-hexane, with respect to the frequency in pure n-hexane, are plotted as a function of inverse normalized concentration of benzene or methylated benzene p_B₀/p_B, where p_B₀ is the density of pure benzene or methylated benzene and p_B is the density of benzene or methylated benzene in the mixtures.
Fig. 4. Apparent Raman linewidth of the I\textsubscript{2} fundamental vs the normalized benzene concentration. The instrumental linewidth is h cm\textsuperscript{-1}. The true width of the I\textsubscript{2} line in n-hexane obtained by deconvolution of the line with the slit function is 5.1 cm\textsuperscript{-1}.

Fig. 5. Mean frequency shift of the I\textsubscript{2} fundamental as a function of normalized benzene concentration at two temperatures 25\textdegree C and 55\textdegree C.

Fig. 6. Variation of the Raman scattering cross-section of the I\textsubscript{2} fundamental (normalized against the Raman scattering cross-section of the 217 cm\textsuperscript{-1} line of CCl\textsubscript{4}) as a function of the normalized benzene concentration.

Fig. 7. Mean frequency of the I\textsubscript{2} first overtone vs the normalized benzene concentration.

Fig. 8. Variation of $2\omega_f - \omega_o$ as a function of the normalized benzene concentration, where $\omega_f$ and $\omega_o$ are the mean frequencies of the fundamental and the first overtone of the I\textsubscript{2} vibration respectively.
Fig. 1
Fig. 2
From Eq. (10)

Fig. 3

Inverse normalized concentration of benzene or methylated benzene
($\rho_{DO}/\rho_D$)
Fig. 4
Fig. 5

- Expt. error

\[ T = 55^\circ C \]

\[ T = 25^\circ C \]

Mean frequency shift (cm⁻¹)

Normalized concentration of benzene \( (\rho_D/\rho_{DO}) \)
Fig. 6
Fig. 7

Vibrational frequency of first overtone of I₂ (cm⁻¹) vs. Normalized concentration of benzene ($\rho_D/\rho_{DO}$)

- Expt. error
Fig. 8

Normalized concentration of benzene \((\rho_D/\rho_{DO})\) vs. \(2\omega_4 - \omega_0\) (cm\(^{-1}\))

Expt. error

XBL697-3333
SECTION III
RAMAN STUDY OF PARA-AZOXIDIANISOLE AT THE PHASE TRANSITIONS

Using Raman scattering technique, we have investigated the phase transitions of the nematic liquid-crystalline substance p-azoxydianisole (PAA). Although Raman spectra of this substance have previously been obtained, no systematic investigation of the temperature dependence of the Raman modes has been reported. Furthermore, to our knowledge, no investigation of the low-frequency Raman modes has ever been made. In this note, we would like to report the results of our measurements of the temperature dependence of the Raman modes in two spectral regions: 30-100 and 1225-1300 cm\(^{-1}\). The intensities of these modes change significantly during the phase transitions. Our results indicate that the Raman spectrum of PAA is affected mainly by short-range interaction between neighboring molecules, and that Raman scattering, in general, can be used to probe the change of short-range ordering during the phase transitions.

The experimental setup was the same as that described by Landon and Porto, with a 40 mW He-Ne laser as the exciting source. The PAA sample was recrystallized three times for purity. For better temperature control, the sample cell was inserted in a copper block and then immersed in an oil bath. The sample temperature was monitored constantly, and temperature fluctuations were less than 0.035°C.

A spectral range of ±1900 cm\(^{-1}\) about the laser line was investigated. There are around 30 strong Raman lines (of the same order as the 992 cm\(^{-1}\) line of pure benzene) in that range. As the substance changes phases from solid to nematic and into isotropic liquid, some of the lines disappear, but most of them decrease in intensity and become broader. Three

of the lines, however, show little change (<10%) in their integrated intensities. In particular, the line at 1095 cm⁻¹ also shows essentially no change in its linewidth. It was, therefore, chosen as the internal calibration line in our intensity measurements. Generally speaking, the spectra of the nematic phase resemble those of the isotropic liquid more than those of the solid. None of the observed Raman lines show any detectable frequency shift in the phase transformation. For the high-frequency Raman modes, our spectra have general resemblance to those obtained by others¹,² but the detailed structure is quite different, especially for nematic and liquid phases. The difference may be attributed to the better quality of our spectra.⁴

Two spectral regions show more significant changes under phase transformation (see Fig. 1). The first region from 1225 to 1300 cm⁻¹ was first investigated by Freymann and Servant.¹ They reported observing two lines at 1247 and 1276 cm⁻¹ in the solid and nematic phases and that the line at 1247 cm⁻¹ disappeared in the liquid phase. Our spectrum for solid PAA in Fig. 1a, however, indicates that the composite spectrum of this region can be decomposed into four symmetric lines at 1246 (±2), 1252, 1261, and 1276 cm⁻¹, with the respective intensity ratio of 3.7:1:4.2:6.3. The strongest line is roughly 1/2 as strong as the 992 cm⁻¹ line of benzene. As the temperature increases through the solid-nematic transition, the three lines at lower frequencies decrease sharply in intensity and merge into a single broad peak. However, assuming that the lines are always symmetric, we can still decompose the spectrum into four lines at approximately the same frequencies as before. In figure 2a, we
plotted the normalized integrated intensity of the 1246 cm\(^{-1}\) (calibrated against the intensity of the 1095 cm\(^{-1}\) line) as a function of temperature.\(^5\)

It is seen that the curve has the characteristic quasidiscontinuity at the solid-nematic phase transition. However, no such discontinuity occurs at the nematic-isotropic transition. The integrated intensity of the 1276 cm\(^{-1}\) line remains unchanged through the phase transitions, but the linewidth changes as shown in Fig. 2b. Again, the variation of the linewidth with temperature has a quasidiscontinuity at the solid-nematic transition.

The low-frequency region from 30 to 100 cm\(^{-1}\) is also of interest. The spectrum of solid PAA shows three Raman modes at 40 (±2), 52, and 72 cm\(^{-1}\) located on the tail of the central scattering component, as shown in Fig. 1. The intensity ratio is 1:1.4:2.4, respectively, the 72 cm\(^{-1}\) mode being 1/4 as intense as the 1276 cm\(^{-1}\) mode. In transition from solid to the nematic phase, the 72 cm\(^{-1}\) mode vanished completely, and the intensities of the modes at 40 and 52 cm\(^{-1}\) drop sharply with their intensity ratio becoming 4:1. The latter two modes also disappear suddenly at the nematic-to-liquid transition. While the intensities vary, the frequencies and the linewidths of the three modes remain unchanged. Figure 3 shows the variation of the normalized integrated intensities of the three modes with temperature. Here again, the curves exhibit the characteristic discontinuities at the phase transitions.

To explain our results qualitatively, we can use the simple model suggested for PAA.\(^6,7\) In the solid phase, the molecules CH\(_3\)O-(C\(_6\)H\(_4\))-N\(_2\)O-(C\(_6\)H\(_4\))-CH\(_3\)O are all aligned and fixed in regular positions. Two neighboring molecules are half overlapped, with the benzene rings facing
each other and the CH$_3$O groups in close contact with the N$_2$O groups. In the nematic phase, the long axes of the molecules are still essentially aligned, but the molecules are no longer rigidly fixed in position and they can rotate more or less freely about their own long axes. The rotation of the benzene-ring groups is presumably less hindered because no permanent dipole moment is attached to the benzene ring. Finally, in the liquid phase, disordering in the molecular alignment sets in.

As suggested by Freyman and Servant, the Raman lines around 1260 cm$^{-1}$ should arise from the vibrational modes of the CH$_3$O-(C$_6$H$_4$)-N$_2$O group. These modes are likely to be strongly affected by intermolecular interaction when neighboring molecules are overlapping in a manner described above for the solid phase. In the nematic phase, since the molecules can move and can rotate about their long axes, the probability of finding two neighboring molecules with this particular relative position and orientation is smaller than that of the solid phase. Consequently, the intensities of these modes drop sharply. That the mode frequencies remain unchanged suggests that here only the optical excited states are modified by the intermolecular interaction. The sudden increase in the linewidth of the Raman modes at the phase transition indicates the onset of rotational freedom the molecules acquire in going to the nematic phase.

The same model can be used to explain the observation of the low-frequency modes. Unlike the soft lattice modes in ferroelectrics, these modes do not change in frequency during the phase transition. They are most likely the intermolecular modes arising from interaction between the CH$_3$O-(C$_6$H$_4$)-N$_2$O groups of two neighboring molecules and
should be affected primarily by short-range ordering. The $72 \, \text{cm}^{-1}$ mode may depend strongly, and the other two less strongly, on the relative position and orientation of the neighboring molecules. As a result, the $40$ and $52 \, \text{cm}^{-1}$ modes persist in the nematic phase although their intensities decrease. It is interesting to note from Fig. 3 and the modes with higher frequencies show more drastic changes at the solid-nematic transition. This seems to suggest that the modes with higher frequencies have deeper but narrower intermolecular potential wells. These intermolecular modes do not have sidebands due to rotation or libration of individual molecules. Consequently, little change in their linewidths should be expected at the phase transition.

In an attempt to study the influence of magnetic field on ordering in PAA, we applied a field of $4.0 \, \text{kOe}$ on the sample and varied the temperature. The field is strong enough to induce macroscopic alignment and, hence, saturation of the dielectric constant in PAA. We have, however, seen no effect of the field on the phase-transition temperatures of PAA. The Raman spectrum, after calibration against the $1095 \, \text{cm}^{-1}$ line, also showed no field dependence at any temperature. The field is apparently not strong enough to modify the short-range interaction between molecules. This is in agreement with the conclusion drawn by others that in nematic substances a magnetic field has effect only on a macroscopic scale but not on local individual molecules.

We also observed in our experiment abrupt broadening of the central Rayleigh-wing component at both solid-to-nematic and nematic-to-liquid phase transitions. This is clearly due to the onset of rotation and libration of the molecules at the phase transitions. However, systematic investigation on this Rayleigh-wing scattering is yet to be performed.
We have shown here that Raman scattering can be used to probe phase transitions and short-range ordering in liquid crystalline materials. Combination of Raman studies with other methods of investigation, such as NMR, etc. may yield a better picture of intermolecular interaction in these materials. We are extending our study to the other members of the homologous series of the 4, 4'-bis (alkoxy) azoxybenzenes. Preliminary results indicate that, in general, the temperature dependence of both the low-frequency and the high-frequency Raman modes conform with the results obtained from PAA. A full report of the investigation will be published elsewhere.
REFERENCES


4. Zhdanova et al. reported in Ref. 2 the disappearance of several high-frequency Raman modes in the nematic and isotropic-liquid phases. However, we were unable to confirm their observation. Our complete Raman spectra of PAA in the three phases will be published elsewhere.

5. Because of inaccuracy caused by decomposition of the spectrum, the quantitative results of intensity variation of the other two lines are not presented here.


7. For example, see G. Meier and A. Saupe, Mol. Cryst. 1, 515 (1966).


FIGURE CAPTIONS

Fig. 1  Raman spectra of PAA from 30 to 100 cm$^{-1}$ and from 1225 to 1300 cm$^{-1}$ in the three phases a) solid phase at T = 113.9°C; b) nematic phase at T = 116.8°C; c) liquid phase at T = 134.8°C. The slit width is 2 cm$^{-1}$.

Fig. 2  a) Normalized integrated intensity of the 1246 cm$^{-1}$ line as a function of temperature. b) Variation of the linewidth of the 1276 cm$^{-1}$ Raman mode with temperature.

Fig. 3  Normalized integrated intensity of the low-frequency Raman modes as a function of temperature.
Fig. 1

(a) $T = 113.9^\circ C$

(b) $T = 116.8^\circ C$

(c) $T = 134.8^\circ C$

Intensity (arbitrary units)
(a) Solid–nematic transition

(b) Nematic–liquid transition

Fig. 2
Fig. 3

- Solid-nematic transition
- Typical error
- 40 cm⁻¹
- 52 cm⁻¹
- 72 cm⁻¹

Normalized intensity vs. Temperature (°C)

XBL702-2298
SECTION IV

BRILLOUIN SCATTERING FROM A CHOLESTERIC MEDIUM AT ITS LIQUID-TO-LIQUID CRYSTAL TRANSITION

I. INTRODUCTION

There have been many investigations of the acoustic properties of substances in the phase transition region. Such diverse transitions as the liquid-vapor, order-disorder, superconducting, ferroelectric and ferromagnetic have been studied rather thoroughly over a wide range of frequencies. These studies have yielded a great deal of information about the dynamical properties of these systems in the transition region. One would hope that similar investigations of the liquid crystal-liquid transition could be just as fruitful. However, so far, there have been only a few reports in existence on the subject.

Hoyer and Nolle, using the standard ultrasonic technique have investigated the liquid crystal-liquid transition of p-azoxyanisole (P.A.A.) and cholesteryl benzoate in a frequency range of .5 to 6 MHz. They observed almost a two order of magnitude increase in the attenuation and a 10% dip in the velocity of the sound waves at the transition. Hoyer and Nolle attributed these effects to structural relaxation and were able to quantitatively interpret their results. Zvereva and Kapustin obtained similar results in the same frequency range for p,p'-nonoxybenzaltoluidine, cholesteryl caprate and cholesteryl caprinate.

Durand and Rao have extended the investigation of the liquid crystal-liquid transition to hypersonic frequencies (10 GHz) using the Brillouin scattering technique. Their investigation of cholesteryl 2-(2 ethoxy ethoxy) ethyl carbonate (CEC) showed that the sound wave became highly damped (large broadening of the Brillouin line) in the transition region, and that its velocity changed by approximately
These effects appear similar to those observed at lower frequencies. However, since in this case, the liquid crystal had domain sizes comparable to the wavelength of the acoustic excitation, we suspect that these effects could be due to an increase of scattering loss induced by the small domains at the transition rather than structural relaxation.

In order to minimize the scattering loss, we should therefore choose a sample with sufficiently large domains. In this paper, we would like to report on our Brillouin scattering measurements at the liquid crystal-liquid phase transition of a thin film sample which has domain sizes approximately one hundred times greater than the wavelength of the hypersonic waves. Contrary to the results obtained by Durand and Rao, we have found no anomalous behavior in the attenuation or in the velocity of the hypersonic wave at the transition.
II. EXPERIMENTAL METHODS

Figure 1 shows our experimental set-up which is similar to that of Durand and Pine's. A coherent Radiation Model 52 argon laser with a 100 mW single-mode output at 5145 Å was used as the light source. The laser beam was focused on the sample by a condensing lens \( L_1 \) via a small reflecting mirror (4 x 3 mm). The sample was surrounded by a copper block which acted like a thermal reservoir and was temperature controlled to \( \pm 0.01^\circ C \). The back-scattered radiation from the sample was spectrally analyzed by a combined set of a Fabry-Perot and a double monochromator. It was collected by the lens \( L_2 \), and focused on a 500 \( \mu \)m pinhole after passing through an \( I_2 \) absorption cell. The pinhole was located at the focus of the third lens \( L_3 \). Then, the parallel rays from \( L_3 \) were incident on a piezoelectrically scanned Fabry-Perot interferometer whose plates were \( \lambda/100 \) flat and had a 97.8\% reflectivity. The output from the Fabry-Perot was focused by the lens \( L_4 \) on the slit of a Spex double monochromator with a bandpass of 20 cm\(^{-1}\) centered at 5145Å. Detection was accomplished using the photon counting method in conjunction with a multichannel analyzer.

In this experiment the Fabry-Perot was used in a multiscanning mode to improve the signal-to-noise ratio. A sawtooth voltage applied to the piezoelectric disks periodically scanned the mirrors, in synchronization with the scan of the multichannel analyzer. A typical spectrum was taken in about 2 minutes and consisted of 20 scans. The integration time per channel was 0.4 seconds which yielded a signal to noise ratio of 20:1. The Fabry-Perot was aligned before each run and typically had a finesse of 70 over its 1.85 cm aperture. After 20 scans the effective finesse was degraded to approximately 60 which corresponded to a
resolution of 0.016 cm$^{-1}$ for the free spectral range of 0.960 cm$^{-1}$ used in our experiments.

The major difficulty often encountered in Brillouin scattering experiments is in the discrimination against elastic scattering from the sample. For clean liquids and homogeneous crystals, the elastic scattering is about 100 times stronger than inelastic scattering and hence the typical discrimination factor of 1000 of a Fabry-Perot interferometer is sufficient. However, in our case the elastic scattering from the liquid crystal was about seven orders of magnitude stronger than the inelastic scattering and detection of the Brillouin signal would have been impossible without much higher discrimination. Recently, Devlin et al. found that the argon laser frequency at 5145 Å can be tuned to coincide with a strong, but narrow (0.05 cm$^{-1}$) absorption line of I$_2$ vapor. One can therefore use an I$_2$ cell as a very effective filter for the elastically scattered light. Using such a cell at a temperature of 67°C we were able to attenuate the elastic scattering from our sample by five orders of magnitude. Unfortunately I$_2$ has other absorption lines nearby which may distort the Brillouin lines and make the spectral analysis more difficult. We shall discuss in detail how the observed Brillouin spectra were analyzed in the next section.

The liquid crystal sample used in our experiments was a mixture of 34% cholesteryl nonanoate, 34% cholesteryl oleyl carbonate and 32% cholesteryl chloride (by weight). This mixture was in the cholesteric phase from 20°C to 56°C with corresponding pitch in the infrared varying from 1.4μ to 2.8 μ. With this mixture it was relatively easy to
make thin film samples 250 μ thick which appeared homogeneous and transparent to the naked eye. Under a polarizing microscope, we could however see domains of about 30 μ in size. The samples were prepared by pressing a few drops of the mixture between two glass slides. Initially, the sample was hazy, but it became transparent after a few days. The chemicals were obtained from Eastman Kodak and were used without further purification.
III. RESULTS AND DATA ANALYSIS

In a liquid medium, the spectrum of Brillouin scattering has two components \(^{10}\) shifted on either side of the exciting frequency \(\omega_0\) by the frequency of the hypersonic excitation \(^{11}\)

\[ \Omega = (2\omega_0 n v / c) \sin(\theta/2) \]  

(1)

where \(v\) is the acoustic velocity, \(n\) is the refractive index, \(c\) is the light velocity in vacuum, and \(\theta\) is the angle between the directions of incident and scattered radiation. In obtaining Eq. (1), we have assumed that each wave propagating in the medium is characterized by a single wave vector. This is not quite true in cholesteric liquid crystals. There, even for waves propagating along the helical axis, each eigenmode is a linear combination of waves with wave vectors \(k\) and \(k + 4\pi/p\) where \(p\) is the helical pitch of the liquid crystal. \(^{12}\) However, if the wavelengths involved are far from the periodicity \(p/2\), then the component with the wave vector \(k + 4\pi/p\) in each eigenmode has a negligibly small amplitude. \(^{12}\) In that limit, Eq. (1) is a very good approximation. This is the case for our experiments.

We chose to investigate Brillouin scattering in the backward direction \((\theta = \pi)\), corresponding to an acoustic excitation with a frequency of approximately 10 GHz. By varying \(\theta\), we can also study the characteristics of the acoustic excitations at lower frequencies. We have not yet carried out such an experiment completely.

In Fig. 2 we show a typical Brillouin spectrum of the liquid crystal taken at room temperature. The Stokes component is distorted by the \(I_2\) absorptions, but the anti-Stokes component, on the other hand, is in a flat region of the absorption spectrum and is undistorted.
As the temperature increases, the distortion of the Stokes component becomes greater while distortion of the anti-Stokes component remains small. We therefore chose to analyze only the anti-Stokes component and were able to determine its frequency to $\pm 1\%$ and its linewidth to $\pm 10\%$.

We have measured the temperature dependence of the Brillouin shift, $\Omega$, and the Brillouin linewidth, $\Gamma$, in the cholesteric liquid crystalline phase and through the liquid crystal-liquid phase transition. Typical values for $\Omega$ and $\Gamma$ are $0.375$ cm$^{-1}$ and $0.06$ cm$^{-1}$. The corresponding value for the acoustic velocity $v$ deduced from Eq. (1) is $1.9 \times 10^5$ cm/sec. As the temperature of the liquid crystal increased from 20°C and through the phase transition in steps of 0.1°C, $\Omega$ gradually decreased (see Fig. 3) and $\Gamma$ remained constant within the experimental error. Contrary to the results of the ultrasonic measurements$^{2-5}$ and those of Durand and Rao, $^6$ no anomalous change in either $v$ or $\Gamma$ was observed in the transition region (see Figs. 3 and 4).

In order to determine the frequency shift and the linewidth of the Brillouin mode accurately, it was necessary to take into account the effects of the $I_2$ absorption cell which we used to eliminate the elastic scattering. Let $G(\omega)$ be the true Brillouin spectrum and $T(\omega)$ is the transmissivity of the $I_2$ cell. Then, the observed Brillouin spectrum $S_B(\omega)$ is given by

$$S_B(\omega) = \int_{-\infty}^{\infty} I_B(\omega - \omega_o) T(\omega_o) G(\omega_o) \, d\omega_o$$ (2)
where $I_B(\omega)$ is the instrumental function of the Fabry-Perot spectrometer set-up, and was obtained in our experiment by using a single-mode laser beam as the incoming source.

We are interested in knowing $G(\omega)$. To find $G(\omega)$, we must first obtain the transmissivity $T(\omega)$ of the $I_2$ cell. This was done by measuring the transmission of the $I_2$ cell with broadband radiation shining on the Fabry-Perot spectrometer setup. The spectrometer limited the radiation to a band narrower than the free spectral range of the Fabry-Perot. If $I_T(\omega)$ is the instrumental linewidth in this measurement, the measured transmissivity $S_T(\omega)$ is related to the true transmissivity $T(\omega)$ by the equation

$$S_T(\omega) = \int_{-\infty}^{\infty} I_T(\omega - \omega_0) T(\omega_0) d\omega_0.$$  \hspace{1cm} (3)

Then, through deconvolution of Eqs. (2) and (3), we can find $T(\omega)$ and $G(\omega)$.

The standard technique of deconvolution is to substitute a known functional form for the spectral function and vary the parameters in the function until the integral gives a spectrum which fits well with the measured spectrum. In our case, this would be quite difficult since $T(\omega)$ does not have a known functional form. Here, we used the Fourier transform technique to deconvolve our spectra. It is well known that the Fourier transform of a convolution integral

$$\int_{-\infty}^{\infty} A(X - X_0) B(X_0) dX_0$$ is the product of the Fourier transforms of $A(X)$ and $B(X)$. Therefore, by Fourier-transforming Eqs. (2) and (3), we can find the Fourier transforms of $G(\omega)T(\omega)$ and $T(\omega)$, if the
Fourier transforms of the instrumental functions are known. Then, the
inverse Fourier transforms enable us to determine the spectral functions
G(\omega) and T(\omega) separately.

In our analysis, the instrumental functions were approximated by
Airy functions. The fast Fourier transform technique was used to carry
out the Fourier transformations on a 6600 Control Data computer. (See
Appendix III for details.) In order to reduce random fluctuations in
the spectra, an observed spectrum was first approximated by the best
polynomial fit (typically a 20th-order polynomial) and then used in the
analysis. Since the sharp structure of the I\textsubscript{2} absorption spectrum
coincides with the Brillouin-Stokes frequency, the accuracy of our
analysis for the Stokes component was much worse than that for the anti-
Stokes component. We therefore chose to analyze only the anti-Stokes
component. We were able to determine its peak position to \pm 1\% and
its linewidth to \pm 10\%.
IV. DISCUSSION

Except for the gradual decrease in \( \Omega \) or \( \nu \) with increasing temperature which is presumably due to thermal expansion, our results are quite different from those obtained in the Brillouin measurements of Durand and Rao\(^6\) or the ultrasonic studies of Hoyer and Nolle,\(^2\) and Zverera and Kapustin.\(^3\)\(^-\)\(^5\) All these workers observed intense acoustic attenuation as well as changes in the velocity of the sound wave in the transition region.

We believe that the difference between our results and those of Durand and Rao\(^6\) can be explained by the difference in the domain sizes of the samples in the two cases. We realize that scattering of acoustic waves by domain walls increases the damping constant of the acoustic waves. If the domain size is much larger than the mean free path or the attenuation length \( \lambda_\alpha \) of the acoustic waves, then most of the acoustic waves excited in a domain decay away before hitting the domain walls, and hence the effect of the domain walls can be neglected. If the domain size is comparable with \( \lambda_\alpha \), then the effective damping constant increases as the domain size decreases. We have observed that at the liquid-crystal-to-liquid transition, the domain size of liquid crystals changes rapidly. It decreases by a factor larger than 2 in a pre-transitional region of about 3°C and then within 0.1°C of the transition, suddenly disappears. This behavior is similar to that of the order parameter.\(^1\) In our case, the domain size in the liquid crystal phase was about 30 \( \mu \)m, and the attenuation length obtained from \( \lambda_\alpha = \nu/\Gamma \) was about 0.2 \( \mu \)m. Therefore, it is clear that we should not expect to observe any change in the acoustic damping constant due to scattering by domain walls in the pre-transition region. Since in our
experiment, the temperature was raised in steps of 0.1°C, we were also unable to resolve any change which happened within 0.1°C of the transition. In the case of Durand and Rao, the domain size of their sample was about 0.2 μm, which was comparable to λ. Then, in the pre-transition region, the acoustic damping constant should increase as the domain size decreased. Finally, after the transition, the domains disappeared in the liquid phase, and the acoustic damping returned to its normal value. This explains why Durand and Rao observed the anomalous increase of acoustic damping and the corresponding dispersion of acoustic velocity at the transition.

The difference between our results and those of the ultrasonic studies can be explained by the difference in the acoustic frequencies in the two cases. The ultrasonic studies have been carried out in the frequency range of 0.5 to 15 MHz. They typically show almost a two order-of-magnitude increase in the ultrasonic attenuation in the transition region. Away from the transition the results of Hoyer and Nolle fit the classical absorption coefficient which has an ω² frequency dependence. However, in the transition region the acoustic attenuation appears to have a frequency dependence of ω²/(1+ω²τ²) which is characteristic of a relaxational process with τ being the relaxation time. Hoyer and Nolle suggested that this attenuation was due to structural relaxation and using Frenkel's heterophase fluctuation theory, we were able to explain their results fairly well.

The model of structural relaxation is based on the supposition that an increase of pressure can convert a fluid to a more compact local molecular arrangement (larger order parameter) which has a smaller specific
volume. This induced change is more pronounced at the phase transition since the pressure affects the equilibrium between the two phases. However, the response of this structural change to the pressure cannot be instantaneous, but has a finite relaxation time $\tau$. Therefore, as a sound wave propagates in the medium, the induced change in the order parameter or in the volume lags in phase behind the pressure wave, and consequently, causes attenuation of the sound wave. The acoustic attenuation constant $\xi (= \Gamma /v)$ due to structural relaxation can be written as

$$\frac{\xi}{\omega^2} = \frac{1}{2} \frac{v_o^2 - v_\infty^2}{v_o^2 v_\infty^2} \frac{\tau \nu(\omega)}{1 + \omega^2 \tau^2} \quad (4a)$$

$$v^2(\omega) = \frac{1 + \omega^2 \tau^2}{\left(\frac{1}{v_o}\right)^2 + \left(\frac{\omega \tau}{v_\infty}\right)^2} \quad (4b)$$

Here $v_\infty$ is the sound velocity at very high frequencies and has no contribution from structural relaxation since the structure or volume change can not respond to a high-frequency pressure wave. $v_o$ is the sound velocity at very low frequencies and its value depends on how the structure responds to the pressure wave. Since $v_o$ is not very different from $v_\infty$, the frequency dependence of $v(\omega)$ is weak and hence $\xi/\omega^2$ is proportional to $\tau/(1+\omega^2 \tau^2)$ approximately. As the medium approaches the liquid crystal-to-liquid transition, the decrease of $v_o$ with temperature due to structural relaxation becomes large. This leads to the large acoustic attenuation and the corresponding dip in the velocity $v(\omega)$ at the transition as Hoyer and Nolle have observed. From their results, they found $\tau = 3.5 \times 10^{-8}$ sec at the transition.
In our case, the hypersonic wave probed by the Brillouin scattering was at about 10 GHz. At such a high frequency, $\xi/\omega^2$ should nearly vanish since we do not expect the structural relaxation time to vary much with frequency. Then, the classical acoustic attenuation, which is proportional to $\omega^2$, should dominate. This was indeed the case. Using Eq. (4) with values of $v_o$, $v_\infty$, and $\tau$ given by Hoyer and Nolle, we found that in our case the linewidth of the Brillouin mode due to structural relaxation should be about $3 \times 10^{-5}$ cm$^{-1}$, and the change of acoustic velocity at the transition is less than one part in $10^5$. These effects are of course too small to be observed in the Brillouin scattering measurements.
CONCLUSIONS

We have used Brillouin scattering to study the hypersonic properties of a cholesteric mixture in the liquid crystal-liquid phase transition region. Contrary to the results of similar measurements by Durand and Rao and the results of the ultrasonic studies, we have found no anomalous change in either the velocity or the attenuation of the hypersonic waves at the transition. We realize that in the case of Durand and Rao, the anomalous change is due to acoustic scattering by the small domains in their sample, and in the case of the ultrasonic studies, it is due to structural relaxation. Neither of these mechanisms has any appreciable effect in our case.
References
10. Actually one would expect to see four modes since viscous fluids are known to have transverse as well as longitudinal acoustic waves. (See G. I. A. Stegeman and B. P. Stoicheff, Phys. Rev. Letters 21, 202 (1968). However, the transverse modes are much weaker than the longitudinal modes and were not observed in this experiment.


16. It is clear that this frequency dependence can not be explained by acoustic scattering which should have an \( \omega^4 \) dependence since the domains in the sample are much smaller than the ultrasonic wavelength.


18. The relaxation time \( \tau \) increases by a factor of about two at the transition. In the frequency range of interest, \( \omega \tau \lesssim 1 \).
**FIGURE CAPTIONS**

Fig. 1. Schematic of experimental setup. S-sample; \( L_1, L_2, L_3, L_4 \) - lenses with respective focal lengths of 8, 8, 31, and 15 cm; M - small mirror; \( I_2 \) - iodine absorption cell; P - 500μm pinhole; FP - Fabry-Perot interferometer; SPEC- SPEX Double monochrometer; PM - EMI 9558 photomultiplier, PCE - Standard photon counting electrons; MCA - multichannel analyzer; SCAN - sawtooth generator for scanning the Fabry-Perot.

Fig. 2. A typical Brillouin spectrum of the cholesteric mixture of 34% cholesteryl nonanoate, 34% cholesteryl oleyl carbonate and 32% cholesteryl chloride taken at 20°C. The Stokes component is somewhat distorted by the \( I_2 \) absorptions but the anti-Stokes component is almost undistorted. The structure in the background is due to \( I_2 \) absorption lines.

Fig. 3. Brillouin frequency shift of the cholesteric mixture of 34% cholesteryl nonanoate, 34% cholesteryl oleyl carbonate and 32% cholesteryl chloride as a function of temperature in the liquid crystal phase and through the liquid crystal-to-liquid phase transition. The insert shows the Brillouin frequency shift in the transition region.

Fig. 4. Brillouin linewidth of the cholesteric mixture of 34% cholesteryl nonanoate, 34% cholesteryl oleyl carbonate and 32% cholesteryl chloride as a function of temperature in the liquid crystal-to-liquid transition region.
Fig. 2

Anti-Stokes Component

Stokes Component

$\times 50$

0.960 cm$^{-1}$
Fig. 3

Transitions in Bragg frequency shift (cm$^{-1}$) as a function of temperature (°C). The experimental error and transition region are indicated.
EXPERIMENTAL ERROR

Fig. 4
APPENDIX I

Statistical Theory Complexes in Solution

ABSTRACT

A statistical theory of complexes in solution is presented. It takes into account the statistical distribution of all attainable complex configurations and the effect of inert solvent molecules in a solution. The formalism should be generally applicable to problems involving physical and chemical reaction in solution.
I. INTRODUCTION

When different molecular species are brought in contact with each other, molecular complexes may appear as a result of intermolecular interaction. This often happens in the process of physical or chemical reaction of the species. The subject of molecular complexes in solution has always been of great interest to many research workers. In particular, charge-transfer complexes in solution have been the subject of active research in recent years. ¹

While experimental reports on the subject of complexes in solution have been numerous, no satisfactory theory has yet been developed. The usual approach is to assume reaction equilibrium for complex formation, and then use the mass-action law to find the concentrations of complex and uncomplexed molecules. There are two obvious shortcomings of this approach. First, one usually assumes that only a few definite complex configurations exist in a solution. For each complex configuration, there is a corresponding reaction rate equation. However, it is conceivable that in a general case, many attainable complex configurations could appear with comparable probabilities. This happens particularly with weak complexes. Only in special cases, where the interaction energy is much stronger for a few complex configurations than for the others, can we consider it as a good approximation to assume the existence of only these few complex configurations. Second, one usually assumes that the equilibrium constant in the mass-action law is a constant independent of the molecular concentrations, but this is true only in the case of ideal gases. ² Furthermore, one usually neglects, in the above approach, the effect of inert molecules present in the solution in order to simplify
the calculations.

From what we have discussed here, it is clear that the usual equilibrium approach is certainly unsatisfactory for describing weak complexes in solution, although it might be sufficient for describing strong complexes in some cases. A correct theory must take into account the statistical distribution of all attainable complex configurations and the effect of inert molecules if present. It is the purpose of this paper to construct such a statistical theory, and to show that in the ideal limiting case our results agree with those obtained from the equilibrium approach. We present the general formalism in Sec. II. We then apply the formalism to the special cases of 1:1 complexes in solution and 1:1 and 1:2 complexes in solution respectively in Secs. III and IV. The theory is used to interpret the experimental results of Raman scattering from iodine complexes in solutions in the following paper.

II. GENERAL FORMALISM

Consider a solution composed of a small amount of "A" molecules dissolved in a solvent mixture of molecular species "B" and "C". In general, all the three molecular species can interact with one another, and our formalism developed in the following can account for this. However, in order to restrict our discussion to molecular complexes, we assume that only "A" molecules interact with "B" molecules to form complexes, with "C" molecules present as inert molecules interacting only weakly with both "B" and "C" molecules. For charge-transfer complexes in solution, we may have "A" molecules acting as acceptors, "B" as donors, and "C" as inert solvent molecules.

Thus, in a solution, each "A" molecule may interact with zero, one,
or more "B" molecules depending on the relative positions and orientations
of the "A" molecule with the surrounding "B" molecules. The strength
of interaction between an "A" molecule and a "B" molecule should also
be a function of the relative position and orientation of the two
molecules. The inert "C" molecules, although ineffective in interacting
with other molecules, may still affect the interaction of "A" and "B"
molecules by shielding one from the other. This is particularly true
for solutions of weak complexes, where around an "A" molecule, no
specific configuration of "B" and "C" molecules dominates. Our formalism
must therefore take into account all possible configurations around an
"A" molecule with proper statistical average.

Let us imagine that at any instant the region around an "A" molecule
can be divided into cells of equal volumes. Each cell is normally
filled with zero or one molecule. The probability of a cell being
occupied by more than one molecule can be neglected. Let $V_o$ be some
volume which covers the entire effective interaction volume around the
"A" molecule and contains an integer number of cells of volume $V_c$. Then,
the $n$ "B" molecules within $V_o$ at $r_1, \ldots, r_n$ with respect to the "A"
molecule could interact with the "A" molecule and the $m$ "C" molecules
at $r_1, \ldots, r_m$ within $V_o$ could affect the interaction between the "A"
molecule and the "B" molecules. (Here, the notations $r$ and $R$ are generalized
to indicate not only the positions but also the relative orientations
for "B" and "C" molecules with respect to the "A" molecule.) If $X$
represents a certain physical property of the "A" molecule, e.g., the
oscillator strength of a certain UV absorption band, then since the "A"
molecule is under the influence of both the "B" and "C" molecules, the
quantity \( X \) should be a function of the positions and orientations of "B" and "C" molecules in \( V_o \),

\[
X = X^{(n,m)}(r_1 \cdots r_n; R_1 \cdots R_m).
\]  

(1)

The corresponding observed quantity should, however, be given by the statistical average over all possible configurations of "B" and "C" molecules in \( V_o \),

\[
\langle X \rangle = \sum_{n,m} \int_{V_o} X^{(n,m)}(r_1 \cdots r_n; R_1 \cdots R_m) \times
\]

\[
\times \rho^{(n,m)}(r_1 \cdots r_n; R_1 \cdots R_m) \, dr_1 \cdots dR_m
\]  

(2)

where \( \rho^{(n,m)}(r_1 \cdots r_n; R_1 \cdots R_m) \) is the probability distribution function for the \( n \) "B" molecules at \( r_1 \cdots r_n \), and \( m \) "C" molecules at \( R_1 \cdots R_m \), and we have the normalization condition

\[
\sum_{n,m} \int_{V_o} \rho^{(n,m)} \, dr_1 \cdots dr_n dR_1 \cdots dR_m = 1.
\]

From statistical mechanics, the probability distribution function

\[
\rho^{(N,M)}(r_1 \cdots r_N; R_1 \cdots R_M)
\]

for \( N \) "B" molecules and \( M \) "C" molecules in the entire solution is given by

\[
\rho^{(N,M)}(r_1 \cdots r_N; R_1 \cdots R_M)
\]

\[
= \left[ \frac{1}{N! M!} Q_{N,M} \right] \exp\left[ -\beta \Phi^{(N,M)}(r_1 \cdots r_N; R_1 \cdots R_M) \right]
\]

(3)

where

\[
\beta = \frac{1}{kT}
\]

\[
Q_{N,M} = \left( \frac{1}{N! M!} \right) \int_V \exp\left[ -\beta \Phi^{(N,M)} \right] \, dr_1 \cdots dr_N dR_1 \cdots dR_M
\]
and \( \phi^{(N,M)}(r_1 \cdots r_N; R_1 \cdots R_M) \) is the potential function for the particular distribution of "B" molecules at \( r_1 \cdots r_N \) and M "C" molecules at \( R_1 \cdots R_M \).

The normalization condition for \( \rho^{(N,M)} \) in a solution of volume \( V \) is

\[
\int_V \rho^{(N,M)} \, dr_1 \cdots dr_N \, dR_1 \cdots dR_M = 1. \tag{4}
\]

Then, the function \( \rho^{(n,m)} \) can be derived from \( \rho^{(N,M)} \) as

\[
\rho^{(n,m)}(r_1 \cdots r_n; R_1 \cdots R_m) = \frac{1}{(N-n)! \, (M-m)! \, n! \, m!} \exp[-\beta U^{(n,m)}] \int_{V-V_o} \rho^{(N,M)} \, dr_{n+1} \cdots dr_N \, dR_{m+1} \cdots dR_M. \tag{5}
\]

As a simplifying assumption, we neglect the correlation between the system of molecules inside \( V_o \) and the system of molecules outside \( V_o \). Then, the potential \( \phi^{(N,M)} \) can be written as

\[
\phi^{(N,M)} = U^{(n,m)}(r_1 \cdots r_n; R_1 \cdots R_m) + \phi^{(n,m)}(r_1 \cdots r_n; R_{n+1} \cdots R_{n+m}) \tag{6}
\]

where \( U^{(n,m)}(r_1 \cdots r_n; R_1 \cdots R_m) \) is the interaction potential for the particular distribution of \( n \) "B" molecules at \( r_1 \cdots r_n \) and \( m \) "C" molecules at \( R_1 \cdots R_m \) in \( V_o \), and \( \phi^{(n,m)} \) is the remaining part of \( \phi^{(N,M)} \) depending only on coordinates of molecules outside the volume \( V_o \). We then have, from Eq. (5),

\[
\rho^{(n,m)} = \frac{1}{(N-n)! \, (M-m)! \, n! \, m!} \left( \frac{1}{N!M!Q_{NM}} \right) \exp[-\beta U^{(n,m)}] \int_{V-V_o} \exp[-\beta \phi^{(n,m)}] \, dr_{n+1} \cdots dr_N \, dR_{m+1} \cdots dR_M \tag{7}
\]

where \( Q_{NM} \) can also be written in the form
\[ q_{nm} = \left( \frac{1}{N!M!} \right) \sum_{n,m} \left[ \frac{1}{(N-n)! (M-m)! n! m!} \right] \]
\[ \times \int_{V} \exp[-\beta U(n,m)] dr_{1} \cdots dr_{n} dR_{1} \cdots dR_{m} \]
\[ \times \int_{V-V} \exp[-\beta U'(n,m)] dr_{n+1} \cdots dr_{N} dR_{m+1} \cdots dR_{M}. \] (8)

With Eqs. (7) and (8), we can now obtain from Eq. (2) an expression for the observed quantity \((X)\) in terms of \(X^{(n,m)}\) and interaction potentials. For a specified \(V_o\), the maximum value of \((n+m)\) is given by \((V_o/V_c)\). The expression for \((X)\) can be greatly simplified if \((n+m)_{\text{max}}\) is a small number. In liquid solutions which are nearly incompressible, we can assume that each cell is occupied by one and only one molecule; the probability of being otherwise should be negligible. Then, for a specific \(V_o\), the number \((n+m)\) is always equal to \((V_o/V_c)\). In the following sections, we consider the special cases of \((n+m)_{\text{max}}\) being 1 and 2. They appear as good approximation to many physical cases one encounters in practice.

III. ONE-TO-ONE COMPLEXES IN SOLUTION

Let us first consider the special case where the volume \(V_o\) is of one cell volume \(V_c\) (or \((n+m)_{\text{max}}=1\)). Each "A" molecule can interact with at most one "B" molecule. This is the case for 1:1 complexes in solution. Note, however, that our picture is quite different from the usual picture of 1:1 complexes often assumed in the literature. Here, the 1:1 complexes have no definite configuration in general. The relative position and orientation of the two molecules in a complex may vary. Only in the limiting case, would a particular complex configuration dominate.
From Eq. (7), we find

\[ \rho^{(1,0)}(r) = \left( \frac{N}{Z} \right) \exp[-\beta U^{(1,0)}(r)] \]  

(9)

\[ \rho^{(0,1)}(r) = \left( \frac{MC}{Z} \right) \exp[-\beta U^{(0,1)}(r)] \]

where

\[ Z = c_1 + N \int_{V_0} \exp[-\beta U^{(1,0)}(r)] \, dr + c_2 M \int_{V_0} \exp[-\beta U^{(0,1)}(r)] \, dr \]

\[ c_1 = \int_{V-V_0} \exp[-\beta \phi^{(0,0)}(r)] \, dr \int_{V-V_0} \exp[-\beta \phi^{(1,0)}(r)] \, dr \]

\[ c_2 = \int_{V-V_0} \exp[-\beta \phi^{(0,1)}(r)] \, dr \int_{V-V_0} \exp[-\beta \phi^{(1,0)}(r)] \, dr \]

To find \( c_1 \) and \( c_2 \), we notice that in the absence of the "A" molecule, we would expect \( U^{(1,0)}(r) = U^{(0,1)}(r) = \Delta \phi \) and we should have \( \frac{1}{V_0} \int_{V_0} \rho^{(1,0)}(r) \, dr = \rho_B = \frac{N}{V} \) and \( \frac{1}{V_0} \int_{V_0} \rho^{(0,1)}(r) \, dr = \rho_C = \frac{M}{V} \). Using Eq. (9) together with these conditions, we find readily

\[ c_1 = V(1 - \rho_B V - \rho_C V) \exp[-\beta \Delta \phi] \]

(10)

\[ c_2 = 1 \]

where

\[ \exp[-\beta (\Delta \phi)] = \left( \frac{1}{V_0} \right) \int_{V_0} \exp(-\beta \Delta \phi) \, dr \]

We therefore obtain, from Eqs. (2) and (9)

\[ \langle x \rangle = \left\{ \rho_B \int_{V_0} x^{(1,0)} \exp[-\beta (U^{(1,0)} - \langle \Delta \phi \rangle)] \, dr + \right. \]

\[ \left. \rho_C \int_{V_0} x^{(0,1)} \exp[-\beta (U^{(0,1)} - \langle \Delta \phi \rangle)] \, dr \right\} \]
\[ + \rho_C \int_{V_0} \chi^{(0,1)} \exp[-\beta(U^{(0,1)} - \langle \Delta \phi \rangle)]d\mathcal{R} \]
\[ \times \frac{1}{\{(1 - \rho_B V_0 - \rho_C V_0) + \rho_B \int_{V_0} \exp[-\beta(U^{(1,0)} - \langle \Delta \phi \rangle)]d\mathcal{R} + \rho_C \int_{V_0} \exp[-\beta(U^{(0,1)} - \langle \Delta \phi \rangle)]d\mathcal{R} \}^2} \]

In the case of liquid solution of constant volume \( V \), there exists the relation \((\rho_B/\rho_{B_0}) + (\rho_C/\rho_{C_0}) = 1\), with \( \rho_{B_0} \) and \( \rho_{C_0} \) being the densities of pure donor and pure inert solvents respectively. If we recall that the liquid is nearly incompressible, then we expect that in the cell model every cell in the liquid should be occupied, and hence \( 1 - (\rho_B + \rho_C)V_0 \approx 0 \) in Eq. (11). Physically, we are often interested in the variation of the quantity

\[ \langle \Delta X \rangle = \langle X \rangle - \langle X_C \rangle \]  

as a function of \( \rho_B \), where \( \langle X_C \rangle \) is the value of \( \langle X \rangle \) in the case of pure inert solvent \( (\rho_B = 0) \). In the present case, we have

\[ \langle X_C \rangle = \langle X^{(0,1)} \rangle = \int_{V_0} \chi^{(0,1)} \exp[-\beta U^{(0,1)}]d\mathcal{R}/\int_{V_0} \exp[-\beta U^{(0,1)}]d\mathcal{R} \]

and hence from Eq. (11), we can write

\[ \langle \Delta X \rangle = \frac{\rho_B \int_{V_0} [X^{(1,0)} - \langle X_C \rangle] \exp[-\beta U^{(1,0)}]d\mathcal{R}}{\rho_B \int_{V_0} \exp[-\beta U^{(1,0)}]d\mathcal{R} + [1 - \rho_B/\rho_{B_0}] \rho_C \int_{V_0} \exp[-\beta U^{(0,1)}]d\mathcal{R}} \]

becomes equal to \( K_{eq} \).

The usual equilibrium constant, \( K_{eq} \), is obtained from the mass-action
Inversion of the above equation leads to the form

\[ \frac{1}{\Delta X} = \left( \frac{1}{\Delta X_0} \right) + \left( \frac{1}{K \Delta X_0} \rho_{Bo} \right) \left( \frac{\rho_{Bo}}{\rho_B} \right) \]  

(15)

where

\[ \Delta X_0 = \int_V \left[ x^{(1,0)} - \langle x_C \rangle \right] \exp[-\beta U^{(1,0)}] d\zeta \]

\[ \times \left[ \frac{1}{\rho_{C_0}} \int_{V_0} \{ \exp[-\beta U^{(1,0)}] - \left( \frac{\rho_{Co}}{\rho_{Bo}} \right) \exp[-\beta U^{(0,1)}] \} d\zeta \right] \]

\[ K = \int_V \{ \exp[-\beta U^{(1,0)}] - \left( \frac{\rho_{Co}}{\rho_{Bo}} \right) \exp[-\beta U^{(0,1)}] \} d\zeta \]

\[ \times \frac{1}{\rho_{Co}} \int_{V_0} \exp[-\beta U^{(0,1)}] d\zeta \]

Equation (15) is in the form of the Benesi-Hildebrand equation. The quantities \( \langle \Delta X \rangle \), \( \Delta X_0 \), and K in Eq. (15) correspond respectively to the observed uv extinction coefficient \( \langle \epsilon \rangle \), the uv extinction coefficient for complexes \( \epsilon_c \), and the equilibrium constant \( K_{eq} \) in their equation. However, the physical meanings of \( \Delta X_0 \) and K in our case are rather different from those of \( \epsilon_c \) and \( K_{eq} \). The Benesi-Hildebrand equation was originally derived using the mass-action law for 1:1 stable complexes and neglecting the effect of inert molecules. Here, from our more general model, \( \Delta X_0 \) corresponds to some kind of average uv extinction coefficient for complexes over the interaction volume, with the effect of inert molecules taken into account. The quantity K also depends on the presence of inert molecules, and is clearly different from \( K_{eq} \). We can, however, show that in the ideal limiting case, K becomes equal to \( K_{eq} \).

The usual equilibrium constant, \( K_{eq} \), is obtained from the mass-action
law, assuming absence of inert molecules \( \rho_C = 0 \),

\[
K_{eq} = \frac{\rho_K}{(\rho_A - \rho_K)\rho_B} \tag{16}
\]

for the case where the density of "B" molecules, \( \rho_B \), is much larger than the density of "A" molecules, \( \rho_A \). The density of complex molecules is \( \rho_K \). From our picture, a 1:1 complex is defined as an "A" molecule with its interaction volume \( V_I \) filled by a "B" molecule. Then the complex concentration can be written as

\[
\rho_K = \rho_A \int_{V_I} \rho^{(1,0)} d_2 \tag{17}
\]

With the help of Eqs. (9) and (10) (with \( \rho_C = 0 \)), we can now find from Eqs. (17) and (16)

\[
\rho_K = \frac{\rho_A \rho_B \int_{V_I} \exp[-\beta(U^{(1,0)} - \langle \Delta \phi \rangle)] \bar{d}_2}{(1 - \rho_B \bar{V}_o) + \int_{V_o} \exp[-\beta(U^{(1,0)} - \langle \Delta \phi \rangle)] \bar{d}_2}
\]

\[
K_{eq} = \int_{V_I} \exp[-\beta(U^{(1,0)} - \langle \Delta \phi \rangle)] \bar{d}_2 / (1 - \rho_B V_I). \tag{18}
\]

On the other hand, if we let \( \rho_C = 0 \) in Eq. (11), we still have Eq. (15), but with

\[
\Delta X_o = \frac{\int_{V_o} \bar{A}^{(1,0)} \exp[-\beta(U^{(1,0)} - \langle \Delta \phi \rangle)] \bar{d}_2}{\int_{V_o} \{\exp[-\beta(U^{(1,0)} - \langle \Delta \phi \rangle)] - 1\} \bar{d}_2}
\]

\[
K = \int_{V_o} \{\exp[-\beta(U^{(1,0)} - \langle \Delta \phi \rangle)] - 1\} \bar{d}_2. \tag{19}
\]

From Eqs. (18) and (19), we find

\[
K_{eq} = (K + V_I) / (1 - \rho_B V_I) \tag{20}
\]
we then recognize that in the limit $V_I \to 0$, the equilibrium constant $K_{eq}$ reduces to $K$. This is just the limit of ideal gases. For non-ideal gases, $V_I \neq 0$, the mass action law leads to an equilibrium constant which depends on $\rho_B$ as shown in Eq. (20).

In gas mixtures, we can also have $\rho_C = \text{constant}$, but vary $\rho_B$. For this case, Eq. (15) still holds if we define $\langle X_C \rangle = \langle X \rangle$. The expression for $\Delta X_0$ and $K$ would, of course, change accordingly.

IV. ONE-TO-ONE AND ONE-TO-TWO COMPLEXES IN SOLUTION

We now apply our formalism to the case where each "A" molecule can interact with two molecules. We consider here only complexes in liquid solution. With $n+m=2$ in Eq. (7) and (8). An "A" molecule can interact with zero ($n=0$), one ($n=1$), or two ($n=2$) "B" molecules. The $n=1$ and $n=2$ cases correspond to 1:1 and 1:2 complexes respectively, but again the complexes here do not have definite configurations in general.

With two molecules in $V_0$, Eqs. (7) and (8) yield

\[
\rho^{(2,0)} = \left[ \frac{N(N-1)/2Z_2}{Z_2} \right] \exp[-\beta U^{(2,0)}] \int_{V-V_0} \exp[-\beta \Phi^{(2,0)}(r)] dr_{\text{r}_3} dr_{N} dr_{-1} dr_{-1} dr_{-M}.
\]

\[
\rho^{(1,1)} = \left[ \frac{NM/Z_2}{Z_2} \right] \exp[-\beta U^{(1,1)}] \int_{V-V_0} \exp[-\beta \Phi^{(1,1)}(r)] dr_{\text{r}_2} dr_{N} dr_{-2} dr_{-M}.
\]

\[
\rho^{(0,2)} = \left[ \frac{M(M-1)/2Z_2}{Z_2} \right] \exp[-\beta U^{(0,2)}] \int_{V-V_0} \exp[-\beta \Phi^{(0,2)}(r)] dr_{\text{r}_1} dr_{N} dr_{-3} dr_{-M}.
\]

(21)

where

\[
Z_2 = (N!M!)^2 Z_{NM} |_{n+m=2}.
\]

Again, we are often interested in the quantity
\( \langle \Delta X \rangle = \langle X \rangle - \langle X_C \rangle \)

\[
= \sum_{n,m} \int_{V_0} [x^{n,m} - \langle X_C \rangle] \rho^{n,m}(x) dr_1 dr_2 dr_3 \tag{22}
\]

with

\[
\langle X_C \rangle = \langle x^{0,2} \rangle = \int_{V_0} x^{0,2} \exp[-\beta U^{0,2}] dr'dr''
\]

\[
\times \frac{1}{\int_{V_0} \exp[-\beta U^{0,2}] dr'dr''}
\]

we can obtain from Eq. (2), after some straightforward manipulation,

\[
\frac{1}{\langle \Delta X \rangle} = \left[ 1 + a \left( \frac{\rho_B}{\rho_B^0} \right)^2 + b \left( \frac{\rho_B}{\rho_B^0} \right)^2 \right] \left[ c \left( \frac{\rho_B}{\rho_B^0} \right) + d \left( \frac{\rho_B}{\rho_B^0} \right)^2 \right]^{-1}
\]

\[
(23)
\]

where

\[
a = 2 \int_{V_0} \left\{ \frac{\rho_B}{\rho_C} \exp[-\beta (U^{1,1} - \langle u^{0,2} \rangle)] - 1 \right\} dr'dr''
\]

\[
b = \int_{V_0} \left\{ \frac{\rho_B}{\rho_C} \exp[-\beta (U^{2,0} - \langle u^{0,2} \rangle)] \right\}
\]

\[
-2 \left( \frac{\rho_B}{\rho_C} \right)^2 \exp[-\beta (U^{1,1} - \langle u^{0,2} \rangle)] + 1 \right\} dr'dr''
\]

\[
c = 2 \int_{V_0} \left\{ \frac{\rho_B}{\rho_C} \left[ x^{1,1} - \langle x_C \rangle \right] \exp[-\beta (U^{1,1} - \langle u^{0,2} \rangle)] \right\} dr'dr''
\]

\[
d = \int_{V_0} \left\{ \frac{\rho_B}{\rho_C} \left[ x^{2,0} - \langle x_C \rangle \right] \exp[-\beta (U^{2,0} - \langle u^{0,2} \rangle)] \right\}
\]

\[
-2 \left( \frac{\rho_B}{\rho_C} \right)^2 \left[ x^{1,1} - \langle x_C \rangle \right] \exp[-\beta (U^{1,1} - \langle u^{0,2} \rangle)] \right\} dr'dr''
\]

\[
(24)
\]
with \( \langle U(0,2) \rangle \) defined by the relation

\[
\exp[-\beta U(0,2)] = \frac{1}{V_0} \int_{V_0} \exp[-\beta U(0,2)] \, \text{d}x_1 \text{d}x_2.
\]

We recall that in the present case, \( V_0 \) contains two cells. It may happen that the "B" molecule in the second cell is shielded from interaction with the "A" molecule by either "B" or "C" molecule in the first cell. One would expect that if the shielding is strong, then the "B" molecule in the second cell cannot interact effectively with the "A" molecule, and our Eq. (23) should approach the Benesi-Hildebrand form of Eq. (15). In the limit where the shielding is perfect, Eq. (23) should reduce to Eq. (15). This can be seen by letting \( U^{(2,0)} \rightarrow U^{(1,0)} \), \( U^{(0,2)} \rightarrow U^{(0,1)} \), \( x^{(2,0)} \rightarrow x^{(1,0)} \) in Eq. (24), and \( U^{(1,1)} \rightarrow U^{(1,0)} \), \( x^{(1,1)} \rightarrow x^{(1,0)} \) if the "B" molecule is in the first cell.

In the other limit, we assume no shielding, so that \( x^{(2,0)} = 2x^{(1,1)} \) and \( U^{(2,0)} = 2U^{(1,1)} \). We also assume that the interaction potential between "A" and "B" is much larger than "A" and "C" (\( U^{(2,0)} \gg U^{(1,1)} \gg U^{(0,2)} \)). This is equivalent to neglecting the effect of inert molecules. By keeping only the leading terms in the expressions in Eq. (24), we can again show that Eq. (23) reduces to the Benesi-Hildebrand form of Eq. (15). Physically, these assumptions mean that the two molecules in the two cells are uncorrelated.

If we plot \( 1/\langle \Delta x \rangle \) vs \( \rho _{Bo}/\rho _{B} \), then Eq. (15) yields a straight line, but Eq. (23) gives a curve with definite curvature. However, in practice, experimental errors of \( 1/\langle \Delta x \rangle \) at small \( \rho _{B} \) are often large, so that with the least-square fit, the discrimination between Eq. (15) and Eq. (23) is difficult, unless the curvature of Eq. (23)
is large. This happens, for example, when a and c in Eq. (23) are sufficiently small.

Recently, Deranleau has derived an equation similar to our Eq. (23) for charge-transfer complexes in solution using the usual equilibrium approach. He assumes that an acceptor can interact with one or two different sites. He then sets up three rate equations for the formation of the three possible complex configurations. This enables him to calculate the average uv extinction coefficient as a function of donor concentration. His approach, however, has not taken into account the statistical distribution of complex configurations and the effect of inert solvent molecules.

V. DISCUSSION AND CONCLUSION

The main assumption in our derivation is that the molecules within the volume \( V_0 \) around an "A" molecule are uncorrelated with molecules outside the volume. We believe that this is a reasonable approximation in most cases. The approximation would, of course, be better if the volume \( V_0 \) contains more molecules.

We have derived from our general formalism the results of two special cases where an "A" molecule can interact with at most one and two "B" molecules respectively. We can, of course, extend the calculations to the more general case where an "A" molecule can interact with at most \( p \) "B" molecules. The general expression for \( 1/\langle \Delta X \rangle \) with \( p \) molecules in \( V_0 \) should be a quotient with \( p^{th} \)-order polynomials of \( (\rho_B/\rho_{B_0}) \) in both the numerator and the denominator.

What we should emphasize in our statistical theory is that we have taken into account both the statistical distribution of complex
configurations and the effect of inert solvent molecules. While our equations for \( \frac{1}{\Delta A} \) vs \( \frac{\rho_{B_0}}{\rho_B} \) appear to be the same as, or close to those of others, the physical pictures are quite different. Thus, for example, if the spectrum for a complex depends on the complex configuration, then by assuming only one complex configuration, we should find for complexes in solution two spectra, one for unassociated molecules and one for complexes. However, if there is a distribution of complex configurations, then we should find a group of spectra, one for each complex configuration, superimposed on one another according to the statistical distribution of complex configurations. A practical example is given in Sec. I, where we apply our theory to Raman scattering from iodine complexes in solutions.
REFERENCES


4. Since we assume low concentration of "A" molecules, we can neglect the probability that a "B" molecule can interact simultaneously with more than one "A" molecule.


7. We let the potentials be infinite when two molecules appear in the same cell.

APPENDIX II

Photon Counting Electronics

In this appendix I will give a detailed description of the photon counting electronics\textsuperscript{1} used in my experiments. The current pulses produced by the photon pulses from an EMI 9558A photomultiplier\textsuperscript{2,3} cooled to dry ice temperatures were sent to amplifier which had an input impedance of 50 $\Omega$. The negative voltage pulse developed across this impedance ranged between $-1$ mv to $-30$ mv and was approximately 25 nanasec wide. The positive output of this amplifier ranged in voltage from 100 mV to 3V and had the same width as the input pulse. This output pulse was passed through an inverter (transformer) and then into a constant delay discriminator. The discriminator produced a constant negative output pulse which was $-0.5$ V high and 25 NS wide whenever the input pulse was above a preset threshold. The threshold was chosen to optimize signal to noise (i.e. the dark current and amplifier noise had a different pulse height distribution than the signal). Typically the threshold was chosen to be 200 mv which corresponds to a setting of 600 on the discriminator dial. With this setting approximately 30% of the signal counts are lost. The output of the discriminator goes to an inverter and then to another amplifier. The positive 10 V, 50 ns output of the amplifier then goes to a Delay Gate. The width of the $-4$V output pulse of the Delay Gate can be adjusted from 1 $\mu$s to 1 s. For weak signals 100 counts/sec or less the delay gate can be used to improve signal to noise. For a cooled photomultiplier the dark current pulses tend to come in groups which are less than 0.1 ms long. By choosing the output pulse of the delay gate to be 1 ms or greater one can count this
group of pulses as a single pulse and therefore improve signal to noise. For example, if one chooses a 1 ms setting rather than a 1 μsec setting, the dark current goes down approximately by a factor of three and is typically 6 counts/sec. For normal operation, however, the 1 μs setting should be used so that one can measure count rates over a large dynamic range. The output of the delay gate goes to an amplifier whose -12 V output goes into the data input of the multichannel analyzer.

References


APPENDIX III

Computer Programs for Deconvolving Spectra

In this appendix the computer programs used in my analysis of the Brillouin scattering measurements will be presented and described. In order to use the Fourier transform technique to deconvolve a spectrum it is first necessary to smooth the data. This was done using Program CRSFIT. For a given order Legendre polynomial (1-40) Program CRSFIT finds the polynomial coefficients which minimize Chi-Square for this order of fit. Chi-Square is defined as

\[ \sum_{i=1}^{I=IMAX} \frac{(FIT(I) - ARG(I))^2}{(DARG(I))^2} \]

where ARG(I) is the value of the \( I^{th} \) data point, FIT(I) is the value of the polynomial fit for the \( I^{th} \) data point, DARG(I) is the error in the \( I^{th} \) data point and IMAX is the number of data points. In practice one simply reads in ARG(I), DARG(I), IMAX, MAXP which the maximum order of the polynomial to be fit and NCAS the number of spectra to be fit and the program will print out the polynomial coefficients which minimize Chi-Square for each order of fit up to MAXP. For the best fit at each order it will also print out Chi-Square and FIT(I). One can then either use Chi-Square tables or one's own judgment to determine which order of fit should be used.

Once the spectrum is fit to a polynomial one can use Program BRILL to deconvolve it. For Program BRILL one reads in the polynomial coefficients, C(I), the order of the polynomial fit which is called MAXP in this program, the free spectral range of the Fabry-Perot, TCHA, and
the full width at 1/2 max of the Fabry-Perot instrumental function, WA. The output of this program will be a Cal Comp plot of the deconvolution of the polynomial fit.

Program BRILL works in the following way. The Real Fast Fourier Transform subroutine is used to find the real and imaginary parts of the Fourier transform of the polynomial fit and of an Airy Function with a finesse given by TCHA/WA. Using the fact that the Fourier transform of a convolution integral is the product of the Fourier transform of the integrands we can now determine the real and imaginary parts of the Fourier transform of the deconvolution of the polynomial fit. They are given respectively by:

\[ G_1(\tau) = \frac{(S_1(\tau)I_1(\tau) + S_2(\tau)I_2(\tau))}{I_1^2(\tau) + I_2^2(\tau)} \]
\[ G_2(\tau) = \frac{(S_2(\tau)I_1(\tau) - S_1(\tau)I_2(\tau))}{I_1^2(\tau) + I_2^2(\tau)} \]

where \( S_1(\tau), S_2(\tau) \) are the real and imaginary parts of the Fourier transform of the polynomial fit and \( I_1(\tau), I_2(\tau) \) are the real and imaginary parts of the Fourier transform of the instrumental function. We can now use the inverse Real Fast Fourier Transform Subroutine to determine the deconvolved spectrum.
PROGRAM CRSFIT

PROGRAM CRSFIT (INPUT, OUTPUT, PUNCH, TAPE 2=INPUT, TAPE 3=OUTPUT,
1 TAPE 4=PUNCH)

OC0002 DIMENSION CHSQQ(40), FIT(40), CRSEC(80), DCPRSEC(80)
OC0002 COMMON FIT, ARG(40), DARG(40), X(40), C(40), C2(40)

C READ N. OF CASES TO BE FIT
OC0002 READ 20, I,CAS
OC0010 20 FORMAT(I2)
OC0010 C READ MAX ORDER OF KNOWN CCEFF, MAX NO. OF PTS. TO FIT AND MAX
OC0010 C ORDER OF POLYFIT
OC0010 100 READ, IMAX, MAX, MAXP, IFIX
OC0002 1 FORMAT(4I2)
OC0002 2 FORMAT(16F5.1)
OC0003 DC 99 J=1, IMAX
OC0004 99 CARG(I)=1.0C
OC0004 DC 4 I=1, IMAX
OC0005 X(I)=1.0+2.0*(1-1)/(IMAX-1)
OC0006 4 CONTINUE
OC0006 40 MAX=MAX+1
OC0007 40 FORMAT(4I2)

C FIND CHI SQUARE AND PRINT RESULTS
OC0004 DO 40 J=1, MAXP
OC0006 IF(20-J)40, 11, 40
OC0007 11 CALL POLYFIT(KK, J, IMAX)

C CALC. CHI SQUARE FOR THIS ORDER FIT
OC0007 CHISQ(J)=0.0
OC0007 13 Ji=1, KM
OC0007 FIT(J)=0.0
OC0007 Ji=1, J
OC0007 FIT(J)=FIT(J)+C!NI*ARG(J)
OC0007 CONTINUE
OC0007 CHISQ(J)=CHISQ(J)+(FIT(J)-ARG(J)**2)/(DARG(J)**2)
OC0007 CONTINUE
OC0007 FORMAT(16H LAB MOVENTUM=, F10.4)
OC0010 PRINT15, J
OC0010 15 FORMAT(19H CADER OF THIS FIT=, I2)
OC0010 IFD=IMAX-J
OC0010 PRINT16, CHSQQ(J), IDF, KM, NFICT, FUFAC
OC0017 16 FORMAT(12H CHI SQUARE=, F10.4, 5X, 9H D=0.0, F=, 12, 5X, 1CH REAL PTS=,
*. 12, 5X, 7H NFICT=, 12, 5X, 9H FUFAC=, F10.5)
OC0017 DO62 L=1, J
OC0017 62 FORMAT(16H CILI=, F10.4, 10X, 6H ZC2(L)=, F10.4)
OC0017 CONTINUE
OC0017 PRINT17, L, C(L), C2(L), L=1, J
OC0020 17 FORMAT(3/ H L=1,2, 4X, 6H C(L)=, F10.4, 10X, 9H ZC2(L)=, F10.4)
OC0020 PUNCH 103, (C(L), L=1, MAXP)
OC0025 103 FORMAT(8F9.5)
OC0025 DO 10 L=1, IMAX
OC0025 10 FORMAT(2I5)
OC0016 62 CONTINUE
OC0016 40 CONTINUE
OC0020 17 CONTINUE
OC0025 PRINT18, L, C(L), C2(L), L=1, J
OC0025 18 FORMAT(3/ H L=1, 2, 4X, 6H C(L)=, F10.4, 10X, 9H ZC2(L)=, F10.4)
OC0025 PUNCH 103, (C(L), L=1, IMAX)
OC0025 103 FORMAT(8F9.5)
OC0025 DO 10 L=1, IMAX
OC0025 10 FORMAT(2I5)
OC0016 62 CONTINUE
OC0020 17 CONTINUE
OC0025 PRINT18, L, C(L), C2(L), L=1, J
OC0025 18 FORMAT(3/ H L=1, 2, 4X, 6H C(L)=, F10.4, 10X, 9H ZC2(L)=, F10.4)
OC0025 PUNCH 103, (C(L), L=1, IMAX)
OC0025 103 FORMAT(8F9.5)
SUBROUTINE POLYFIT(IYPE,ICORDER,NMEAS)
  C S.R. POLYFIT FITS A SET OF MEASUREMENTS TO A SERIES EXPANSION
  C OF ORDER (ICORDER) USING (LEGENDRE,ASSOC. LEGENDRE) POLYNOMIALS
  C IF IYPE=1,2,
  C THERE ARE NMEAS MEASUREMENTS—QMEAS+//-ZQMEAS AT ABCISSA X
  C THE FITTED COEF. ARE C(N)+//-ZC(N)...ZC2(N) ARE ERROR SQUARE
  C Z(N) ARE ALWAYS A,B,0 ARE USED IN THE SOLUTION—SEE NOTES
  C F(N,I) IS THE VALUE OF THE N-TH POLYNOMIAL AT X=X(I)

000005 COMMON/FIT/QMEAS(40),ZQMEAS(40),X(40),C(40),ZC(40)
000006 DIMENSION C(40),A(40,40),SCRATCH(900),A(10,80),F(10,80)
000007 IF(ICORDER.GT.40) ICORDER=40
000010 DO3 I=1,NMEAS
000011 NC N=1,ICORDER
000013 NC NC=1,ICORDER
000015 1 F(N,I)=POLYCPM(IYPE,N,X(I))
000017 DO2 J=1,ICORDER
000019 IF IYPE .EQ. 1, 2
000020 2 F(N,I)=POLYCPM(IYPE,N+1,X(I))
000021 CONTINUE
000022 DO 30 I=1,NMEAS
000024 30 CONTINUE
000025 L=40
000027 CONTINUE
000028 C INVERT MATRIX EQU B*C=D TO GET EXPANSION COEFFICIENTS C
000029 CALL LINEFIT(B,A,ICORDER,M,DET,IEX,CNR,SINGUL,L,SCRATCH)
000030 IF(SINGUL) GO TO 30
000031 GO TO 31
000032 IF (ICORDER .GT. 100)
000033 CONTINUE
000034 DO 45 N=1,ICORDER
000035 45 CONTINUE
000036 RETURN
000037 END

C COMMON/FIT/QMEAS(40),ZQMEAS(40),X(40),C(40),ZC(40)
C DIMENSION C(40),A(40,40),SCRATCH(900),A(10,80),F(10,80)
C IF(ICORDER.GT.40)ICORDER=40
C DO3 I=1,NMEAS
C NC N=1,ICORDER
C NC NC=1,ICORDER
C 1 F(N,I)=POLYCPM(IYPE,N,X(I))
C DO2 J=1,ICORDER
C IF IYPE .EQ. 1, 2
C 2 F(N,I)=POLYCPM(IYPE,N+1,X(I))
C CONTINUE
C DO 30 I=1,NMEAS
C 30 CONTINUE
C L=40
C CONTINUE
C C INVERT MATRIX EQU B*C=D TO GET EXPANSION COEFFICIENTS C
C CALL LINEFIT(B,A,ICORDER,M,DET,IEX,CNR,SINGUL,L,SCRATCH)
C IF(SINGUL) GO TO 30
C GO TO 31
C IF (ICORDER .GT. 100)
C CONTINUE
C DO 45 N=1,ICORDER
C 45 CONTINUE
C RETURN
C END
FUNCTION POLYNOMIALTYPE, ORDER, X)
DIMENSION POLY(2)
ORDER=1 FOR L=0 ETC
GO TO (1, 2), ITYPE

1 POLY(1)=1.
1=0
POLY(2)=X
GO TO 25

2 POLY(1)=0.
1=1
POLY(2)=SQR(1-2**2)

25 DO 26 J=1,2
IF (ORDER/=J) GO TO 27
26 GO TO 25

27 POLYCNMPOLY(J)
RETURN

25 CONTINUE

DO 30 L=0, ORDER

30 POLY(2)=

RETURN

END

SUBROUTINE LIMIT(A, R X, N, DET, EX, Cnr, SINGUL, L, SCR)
DIMENSION ALT(L), B(L), X(L), SCR(L, 1)

drive A AND B TO SCRATCH AREA

N=MINT(N)
IF (N .LT. 1) GO TO 4

DO 3 1=1, L
DO 2 J=1, N

2 CONTINUE

DO 1 CONTINUE

IF (3 .LT. 1) GO TO 3

DO 3 1=1, L
DO 2 J=1, N

2 CONTINUE

K=2*N+4+J

SCR(1, K)=R(1, J)

2 CONTINUE

CALL LINEAR(SCR(1, 1), SCR(1, 2*N+5), X, A, M, DET, EX, Cnr, SINGUL, L

X, SCR(1, 1), SCR(1, 2*N+1), SCR(1, 2*N+2), SCR(1, 2*N+3), SCR(1, 2*N+4)

RETURN

END
SUBROUTINE LINEAR(A,B,X,K,M,DET,EX,CAR,SINGUL,L) 
X = US*PIVOT*Y, *S,MULT
C
C PROCEDURE LIINEAR SYSTEII# 0021
C 6600 6600 6600 6600 6600 6600 6600 6600 6600 6600
C NORDER, P=NH SIDES, M=II OF NH SIDES, X=ANSWERS,
C (DET**2)=DETEIIIIAY, CNR=CONDITION, SINGUL=FALSE, IF OK.
C
C.....LINEAR IS BASED ON ALGORITHII 135, EACH NOVEM:-ER 1962 PAGE 553,
C AS CORRRECTED EACH JULY 1964 PAGE 421.
C IT USES CROUT'S METHOD WITH ROW EQUILIBR/ATION, ROW INTERCHANGES,
C AND ITERATIVE IMPROVEMENT FOR SOLVING THE MATRIX EQUATION A*X=B,
C WHERE A IS M BY N, X AND B ARE A BY M. IN CASE M<.L.E. N ONLY THE
C DETERMINANT OF A IS EVALUATED. FOR M=N, THE SLAQOUTINE SOLVES A
C SYSTEM OF LINEAR EQUATIONS IN N UNKNOWNS. FOR M=N AND N=THE
C IDENTITY MATRIX, X IS SET TO THE INVERSE OF A.
C IF A IS NEARLY SINGULAR, *SINGUL# IS SET TO .TRUE.
C
C DATA EPS / C 1.6077777777777777 / 0022
C SINGUL=.FALSE.
C CNR=1.0 0023
C DET=.0 0024
C X=0 0025
C IF (N.GE.1) AND (N.LT.L1) GO TO 1000
C SINGUL=.TRUE.
C RETURN 0026
C 1000 CONTINUE 0027
C
C REMOVE APPROPRIATE FACTORS FROM THE ROWS OF A.
C CALL EQUILIBRATE 0028
C
C IF(SINGUL) RETURN 0029
C
C SAVE THE RESULT FOR COMPUTATION OF RESIDUALS DURING ITERATION.
C DO ICOZ=1,N 0030
C IF (1.GE.ICOZ) CONTINUE 0031
C LU(I,J)=1(I,J) 0032
C 1001 CONTINUE 0033
C DO ICOZ=1,N 0034
C
C DECOMPOSE THE MATRIX INTO TRIANGULAR FACTORS.
C CALL CROUT# 0035
C
C IF (SINGUL) RETURN 0036
C
C EVALUATE THE DETERMINANT IN THE FORM (DET**2)*EX
C DO ICOZ=1,N 0037
C Y(I)=LU(I,1)**MULT11 0038
C 1003 CONTINUE 0039
C
C DET=DET*PRODUIT(I,N,EX) 0040
C
C DO BEGIN TO PROCESS RIGHT HAND SIDES.
C IF (M.LT.1) RETURN 0041
C DO ICOZ=1,N 0042
C PK=FLCAT(K) 0043
C SCALE THE RIGHT HAND SIDES
C RES(I,I)=RES(I,I)*MULT11 0044
C 0045
C SUBROUTINE LINEAR(A,B,X,K,M,DET,EX,CAR,SINGUL,L) 
X = US*PIVOT*Y, *S,MULT
C
C PROCEDURE LIINEAR SYSTEII# 0021
C 6600 6600 6600 6600 6600 6600 6600 6600 6600 6600
C NORDER, P=NH SIDES, M=II OF NH SIDES, X=ANSWERS,
C (DET**2)=DETEIIIIAY, CNR=CONDITION, SINGUL=FALSE, IF OK.
C
C.....LINEAR IS BASED ON ALGORITHII 135, EACH NOVEM:-ER 1962 PAGE 553,
C AS CORRRECTED EACH JULY 1964 PAGE 421.
C IT USES CROUT'S METHOD WITH ROW EQUILIBR/ATION, ROW INTERCHANGES,
C AND ITERATIVE IMPROVEMENT FOR SOLVING THE MATRIX EQUATION A*X=B,
C WHERE A IS M BY N, X AND B ARE A BY M. IN CASE M<.L.E. N ONLY THE
C DETERMINANT OF A IS EVALUATED. FOR M=N, THE SLAQOUTINE SOLVES A
C SYSTEM OF LINEAR EQUATIONS IN N UNKNOWNS. FOR M=N AND N=THE
C IDENTITY MATRIX, X IS SET TO THE INVERSE OF A.
C IF A IS NEARLY SINGULAR, *SINGUL# IS SET TO .TRUE.
C
C DATA EPS / C 1.6077777777777777 / 0022
C SINGUL=.FALSE.
C CNR=1.0 0023
C DET=.0 0024
C X=0 0025
C IF (N.GE.1) AND (N.LT.L1) GO TO 1000
C SINGUL=.TRUE.
C RETURN 0026
C 1000 CONTINUE 0027
C
C REMOVE APPROPRIATE FACTORS FROM THE ROWS OF A.
C CALL EQUILIBRATE 0028
C
C IF(SINGUL) RETURN 0029
C
C SAVE THE RESULT FOR COMPUTATION OF RESIDUALS DURING ITERATION.
C DO ICOZ=1,N 0030
C IF (1.GE.ICOZ) CONTINUE 0031
C LU(I,J)=1(I,J) 0032
C 1001 CONTINUE 0033
C DO ICOZ=1,N 0034
C
C DECOMPOSE THE MATRIX INTO TRIANGULAR FACTORS.
C CALL CROUT# 0035
C
C IF (SINGUL) RETURN 0036
C
C EVALUATE THE DETERMINANT IN THE FORM (DET**2)*EX
C DO ICOZ=1,N 0037
C Y(I)=LU(I,1)**MULT11 0038
C 1003 CONTINUE 0039
C
C DET=DET*PRODUIT(I,N,EX) 0040
C
C DO BEGIN TO PROCESS RIGHT HAND SIDES.
C IF (M.LT.1) RETURN 0041
C DO ICOZ=1,N 0042
C PK=FLCAT(K) 0043
C SCALE THE RIGHT HAND SIDES
C RES(I,I)=RES(I,I)*MULT11 0044
C 0045
CONTINUE
C BEGIN THE ITERATION LOOP. THE NUMBER OF ITERATIONS IS DETERMINED
C DURING THE FIRST ITERATION.

CONTINUE
C COMPUTE THE RESIDUALS OF THE SOLUTION Y.
C CALL *RESIDUALS.
C FIND NEXT INCREMENT TO THE SOLUTION.
C CALL *SOLVE.
C CALL SOLVE(LU,N,RES,PIVOT(Y,L))
C SET UP TERMINATION CONDITIONS.

IF (KCOUNT .NE. 1) GO TO 1007

IF (DYNORM .LE. 0.0) GO TO 1009

IF (ET .LE. 2.0) GO TO 1010

SINGUL = .TRUE.

RETURN

CONTINUE
C LIMIT=FIX(ALOG(EPS)/ALOG(1.0/T))

CONTINUE
C STORE THE NEW APPROXIMATION

DO 1011 I2=1,N

1011 KOUNT=KOUNT+1

IF (KCOUNT .LE. LIMIT) GO TO 1012

RETURN

END
SUBLRUTINE EQUILIT(A,K,MUL,T,SINGUL,L)
C PROCEDURE =EQUILITATE#
C N=ORDER, MUL=MULTIPLZERS
000007 REAL MUL, K, A(K), X
000007 LOGICAL SINGUL
000007 DIMENSION A(K, L)
X(MUL)
C SCALING THE ROWS OF THE MATRIX (A) TO ROUGHLY THE SAME MAXIMUM
C MAGNITUDE ALLOWS THE PROCEDURE (COUNTER) TO SELECT EFFECTIVE
C GROWTH ELEMENTS FOR GAUSSIAN DECOMPOSITION OF THE MATRIX, A
C POWER OF 2 IS USED INSTEAD OF THE ACTUAL LARGEST ELEMENT TO
C REDUCE ROUNDING ERROR IN THE DIVISION.
C SEE WILKINSON, JACK JULY 1961 PAGE 224.

000067 DATA MASK / 1 1 1 1 1 1 1
000067 DO 2001 I = 1, N
000067 K = I + 1
C FIND THE LARGEST ELEMENT
000011 DO 2002 K = 1, N
000012 IF (ABS(A(I, J)) .GT. M(K)) MX = M(A(I, J))
000012 CONTINUE
000025 IF (M(K) .EQ. 0) GO TO 2903
000029 SINGUL = TRUE.
000033 RETURN
000034 2003 CONTINUE
C HOW STORE THE MULTIPLIER AND SCALE THE ROW.
000034 MUL(I) = MX(I, K)
000046 IF (MUL(I) .EQ. 1) GO TO 2004
000042 DO 2005 K = 1, N
000056 I(I, J) = A(I, J) / MUL(I)
000057 2005 CONTINUE
000063 2004 CONTINUE
000063 2001 CONTINUE
000066 RETURN
000066 END

SUBROUTINE SOLVE(A, N, V, PIVOT, Y, L)
C PROCEDURE =SOLVE#
C N=ORDER, V=RH VECTOR, PIVOT=PERMUTATION VECTOR, Y=ANSWER.
000010 INTEGER PIVOT,
000010 DIMENSION A(N, N)
X(PIVOT), W(N), Y(N)
C PROCESSES A = RHS VECTOR AND THEN BACK-SLVES FOR Y USING THE L*U
C DECOMPOSITION PRODUCED BY (EUCUT).
000010 00 6001 K = 1, N
000011 00 6001 J = PIVOT(K)
000013 00 6001 T = V(J)
000014 00 6001 V(J) = V(K)
000016 00 6001 K + K - 1
000020 00 6001 IF (K + K1 .LT. 1) GO TO 6102
000022 00 6001 DO 6002 P = 1, KML
000024 00 6001 T = - A(KM1, P) * V(P)
000026 00 6002 CONTINUE
000028 00 6002 CONTINUE
000041 V(K) = T
C HAVING MODIFIED Y BY L INVERSE...
000043 00 6001 CONTINUE
C HOW THE BACK SOLUTION FOR Y.
000045 00 6001 DO 6005 K = 1, N
000047 00 6001 K = K1 - NK
000051 00 6001 T = V(K)
000053 00 6001 K1 = K1
000054 00 6001 IF (K1 .LT. A) GC TO 6005
000057 00 6001 DO 6004 P = K1, N
000067 00 6001 T = - A(KM1, P) * Y(P)
000069 00 6004 CONTINUE
000071 00 6004 CONTINUE
000076 Y(K) = T / A(K, K)
C C00103 6003 CONTINUE
C C00106 RETURN
C C00108 END

-97-
SUBROUTINE CHOUT(A,N,PVOT,SG,SINGUL,L)
C PROCEDURE CHOUT
C ORDER, PVOT=PVOTS, SG=INTERCHANGES.
C
OC0010 INTEGER PVICT,P
OC0010 DOUBLE PRECISION D
OC0010 LOGICAL SINGUL
OC0010 DIMENSION A(L,11)
XC*PVICT(1)

C ROUNTE'S METHOD WITH RCM INTERCHANGES FOR A=L*U WITH L(K,K)=1.0.
C (PVICT) STORES THE PERMUTATION MATRIX.
C
OC0010 SG=1.0
C
OC0011 DO 3001 K=1,N
OC0012 T=0.0
OC0013 DO 3002 I=K,N
OC0014 C COMPUTE L.
OC0015 KM1=K-1
OC0016 D=DBLE(A(I,KI))
OC0017 IF (KM1.LT.1) GO TO 3003
OC0018 DO 3004 P=1,KMI1
OC0019 O=D-DBLE(A(I,P))*DBLE(A(I,KPI))
OC0020 CONTINUE
OC0020 1003 COMPUTE A (I,KI) = SINGLE(A/I,KI)
OC0021 IF (IABS(A/I,KI).LE.T) GO TO 3005
OC0022 T=ABS(A/I,KI)
OC0023 IAX=I
OC0024 CONTINUE
OC0025 3004 CONTINUE
OC0026 3003 CONTINUE
OC0027 A(I,KI)=SINGUL*T
OC0028 RETURN
OC0029
OC0030 1165 CONTINUE
C A(IAX,KI) IS LARGEST ELEMENT IN REMAINDER OF COLUMN K.
C INTERCHANGE COLUMNS IF NECESSARY.
C
OC0030 PVICT(KI)=IAX
OC0031 IF (IAX.EQ.K1) GO TO 3006
OC0032 SG=SG
OC0033 DO 3007 J=1,N
OC0034 OC0035 T=A(I,J)
OC0036 A(I,J)=A(IAX,J)
OC0037 A(IAX,J)=T
OC0038 CONTINUE
OC0039 3007 CONTINUE
OC0040 3006 CONTINUE
C
OC0040 DO 3009 J=KPI,N
OC0041 D=DBLE(A(I,J))
OC0042 IF (KPI.LT.K1) GO TO 3010
OC0043 DO 3008 I=KPI,N
OC0044 A(I,J)=A(I,KPI)*D
OC0045 CONTINUE
OC0046 CC0020 3008 CONTINUE
OC0047 CC0020 CONTINUE
C AND COMPUTE A ROW OF U
C
OC0048 DO 3000 J=KPI,N
OC0049 CC0020 3010 CONTINUE
OC0049 CC0020 3011 CONTINUE

REAL FUNCTION PRODUC(FAC, S, F, EX)
C PROCEDURE #PRODUCT
C S=START, F=FINISH, EX=EXponent
C 000006 INTEGER S, F, EX
C 000006 DIMENSION FACTOR(1)
C ..., MULTIPLIES FACTOR(S) THROUGH FACTOR(F), CORRECTING TO PREVENT
C OVERFLOW. THE ABSOLUTE VALUE OF THE RESULT IS BETWEEN 0.1 AND 1.0
C AND THE EXPONENT APPEARS IN EX.
C 000006 EX=0.0
C 000006 P=1.0
C 000007 IF (S .GE. F) GO TO 4004
C 000008 DO 4009 I=S, F
C 000009 D=FACTOR(I)
C 000010 IF (IA(D) .GE. 0.1) GO TO 4002
C 000011 D=10.0*D
C 000012 EX=EX-1
C 4002 CONTINUE
C 000020 P=P*D
C 000021 IF (IP .LT. 0.1) GO TO 4003
C 000022 P=P*D
C 000023 EX=EX+1
C 4003 CONTINUE
C 4004 CONTINUE
C 4005 CONTINUE
C 4006 IF (ABS(P) .GE. 0.1) GO TO 4004
C 000033 P=P1
C 000034 EX=EX-1
C 000035 GO TO 4004
C 000036 4007 CONTINUE
C 000037 4008 CONTINUE
C 000038 4009 CONTINUE
C 000040 PRODUC=P
C 000041 RETURN
C 000042 END
C SUBROUTINE RESIDUAL(A, N, B, K, X, RES)
C PROCEDURE #RESIDUALS#
C N=ORDER, B=RHS SIDES, K=COLUMN OF R, X=APPROXIMATE SOLUTION,
C RES=RESIDUALS
C 000011 DIMENSION A(L), B(L), K(L), X(L)
C 000011 X(RES)
C 000011 INTEGER P
C 000011 DOUBiE PRECISION D
C ..., COMPUTES E(.,K)-A*X(.,K)
C 000011 DO 5001 I=1, N
C 000012 D=DBL E(A(I, K))
C 000013 IF (N .LT. I) GO TO 5003
C 000014 D=DBL E(A(I, P))
C 000015 D=D-DBL (A(I, P)) *DBL E(X(P, K))
C 000016 5002 CONTINUE
C 000017 5003 CONTINUE
C 000018 5004 CONTINUE
C 000019 RES(I)=SNGL(D)
C 000020 RETURN
C 000021 END
PROGRAM BRILL

PROGRAM BRILL (INPUT,OUTPUT,PUNCH+TAPE 9@,PLOT,TAPE 9@,PLOT)
DIMENSION C(43),A(106),FPA(1026),X(A),Y(1026),AM(1026),AT(1026),
Z(1026),Y(100),AK(1026),ATP(120),INV(300),SA(300)
COMMON/CCPOOL/XMIN,XMAX,YMIN,YMAX,CCXMIN,CCXMAX,CCYMIXN,CCYMAX
COMMON/CCFACT/FACTOR

10 CONTINUE
READ 1,KPUP,IMAX,MAXP
1 FORMAT(3I2)
1 IF(IMAX.LE.0+0)GO TO 18
READ 3(A(I),I=1,IMAX)
3 FORMAT(18F5.1)
2 CONTINUE
READ 2(C(I),I=1,MAXP)
2 FORMAT(8F9.5)
READ 4,TCHA,WA
4 FORMAT(2F10.2)
KK=1
DO 75 I=1,1024
AM(I)=0.0
DO 76 I=1,MAXP
Z(I)=1.0+T(I)*(I-1)/1023
75 CONTINUE
DO 13 I=1,1025
AM(I)=AM(I)+C(I)*POLYOM(KK,L,Z(I))
13 CONTINUE
AM=0.0
AT=1.0
DO 100 I=1,1026
FPA(1)=1.0/(1.0+0.4058*(TCHA*SIN(XA(I))/WA)*
*(TCHA*SIN(XA(I))/WA))
100 CONTINUE
DO 18 I=1,1026
CALL RFFT(9,FPA,INV,SA,IE)
18 CONTINUE
DO 200 I=1,1026
AMIN=0.0
AMIN=AM(1)
99 IF(ABS(AM(1))/LE.AM)AM(I)=0.0
99 CONTINUE
AM=0.0
AT=0.0
DO 225 I=1,1026
AT=AT+AM(I)*FPA(I)
225 CONTINUE
AT=AT+AM(I)*FPA(I)
200 CONTINUE
DO 325 I=1,1026
Y(I)=AM(I)*FPA(I)
325 CONTINUE
DO 425 I=1,1026
XMIN=I-1.0
XMIN=AM(I)
425 CONTINUE
DO 425 I=1,1026
YMIN=I-1.0
YMIN=AM(I)
425 CONTINUE
DO 625 I=1,1026
XMAX=AM(I)
XMAX=AM(I)
625 CONTINUE
DO 625 I=1,1026
YMAX=AM(I)
YMAX=AM(I)
625 CONTINUE
CALL CCPL0T(Z,I,AM(1)+HJOIN)
CALL CCPL0T(Y,I,AM(1)+HJOIN,80+1)
CALL CCNEXT
DO 675 I=1,103
675 CONTINUE
K=10*I-9
80 ATP(I)=AT(9)
80 CONTINUE
PUNCH 78+(ATP(I)+I*103)
78 FORMAT(13F6.1)
GO TO 18
CALL CCEND
STOP
END
FUNCTION POLYNOM(IYTP+ORDER,X)  
DIMENSION POLY(2)  
C NORDER=1 FOR L=0 ETC  
C GO TO (1,2)+ITYPE  
C LEGEND FOR FUNCTION  
1 POLY(1)=1.

M=0  
POLY(2)*X  
GO TO 25  
2 POLY(1)*0.  
M=1  
POLY(2)*SQRT(1.-X**2)  
25 DO 28 J=1,2  
28 POLY(J)=POLY(J)  
GO TO 26  
26 RETURN  
27 POLYNOM=POLY(J)  
28 CONTINUE  
29 DO 30 ORDER  
P=((-2*L-1)*X+POLY(2)+(L+M-2)*POLY(1))/(L=M+1)  
30 RETURN  
31 P=POLY(2)*P  
32 CONTINUE  
33 RETURN  
34 END

SUBROUTINE FFT(M+INVS,IFSET,IFERR)  
DIMENSION A(1),L(3),INV(1),S(1)  
DATA PI/1721 6220 7732 5042 0550 8/  
IFERR=1  
IF(NIFORM+EQO) GO TO 20  
20 RETURN  
21 P=PI/FLOAT(M)  
22 IF(IFSET+EQO) GO TO 20  
23 RETURN  
24 DO 10 L=0,NT  
10 CONTINUE  
25 A=2*FLOAT(M)
A(1)=TA
A(2)=0.
A(NT+1)=TB
A(NT+2)=0.
RETURN

DO 30 I=2,NT+2
J=I+1
JJ=J+1
K=NT-I+1
KK=K+1
A(J)=.5*A(J)
A(JJ)=.5*A(JJ)
A(K)=.5*A(K)
A(KK)=.5*A(KK)
A1R=A(J)+A(K)
A1I=A(JJ)-A(KK)
ARG=FLOAT(I)*P
C=COS(ARG)
D=SIN(ARG)
TA=A(J)-A(K)
TB=A(JJ)+A(KK)
A2R=TA*C-TB*D
A2I=TA*D+TB*C
A(J)=A1R-A2I
A(JJ)=A1I+A2R
A(K)=A1R+A2I
A(KK)=A2R-A1I
CONTINUE

A(1)=.5*A(1)
A(NT+1)=.5*A(NT+1)
A(2)=A(1)-A(NT+1)
A(1)=A(1)+A(NT+1)
CALL CFFT(L,A,INV,S,IFSET,IFERR)
RETURN
END
SUBROUTINE CFFT(M,INV,S,IFSET,IFERR)
DIMENSION A(1),INV(1),S(1),N(3),M(3),NP(3),W(2),W2(2),W3(2)
DATA PI/172/7732,502,0560,8/
000010 033277 10 IF IABS(IFSET) = 1 900x+900x+12
000013 033302 12 MT=MAX0(M(1)+M(2)+M(3)) -2
000022 033311 13 IF(MT=1) 13x+11+1
000024 033313 11 MSUM=M(1)+M(2)+M(3)
000027 033316 15 IF(MSUM=15) 15x+15x+13
000031 033320 19 ROOTZ = SQRT(2).
000033 033322 13 IFERR=1
000036 033325 RETURN
000044 033333 14 IFERR=0
000045 033334 M1=M(1)
000046 033335 M2=M(2)
000047 033336 M3=M(3)
000051 033340 N1=2*M1
000055 033344 N2=2*M2
000061 033350 N3=2*M3
000065 033354 16 IF(IFSET) 20+18+18
000067 033356 18 NX= N1+N2+N3
000072 033361 FN=NX
000074 033363 DO 19 I = 1,NX
000107 033376 20 A(2*I-1) = A(2*I-1)/FN
000110 033377 19 A(2*I) = -A(2*I)/FN
000116 033405 20 NP(1)=N1/2
000120 033407 N1=NP(1)*N1
000122 033411 NP(2)=NP(1)*N2
000124 033413 NP(3)=NP(2)*N3
000126 033415 IL = NP(3)-NP(1)
000130 033417 IL=IL+1
000132 033421 MI = M(ID)
000133 033422 IF (MI) 250,250,30
000136 033425 30 IDF=NP(ID)
000136 033425 KBIT=NP(ID)
000137 033426 MEV = 2*(MI/2)
000141 033430 IF (MI) MEV 160+60+40
000143 033432 40 KBIT=KBIT/2
000144 033433 KLBIT=KBIT/2
000146 033435 DO 50 I=1,IL1,10IF
000147 033436 KLAST=KLI
000150 033437 DO 50 KI=1,KLAST,2
000160 033447 KD=KBIT
000161 033450 T(A(KD))
000162 033451 A(KD)=A(KD)-T
000163 033452 A(KD)=A(KD)-T
000165 033454 T(A(KD))=A(KD)=T
000166 033455 A(KD)=A(KD)==T
000170 033457 50 A(K+1)=A(K+1)+T
000172 033457 IF (MI) 1250,250,52
000174 033467 52 LFIRST =3
000180 033474 JLAST=JLAST+1
000206 033475 GO TO 70
000207 033476 60 LFIRST = 2
000210 033477 JLAST=0
000211 033500 70  DO 240 I=1, FIRST+MI+2
000213 033502  JD01IF=KBIT
000214 033503  KBIT=KBIT/4
000215 033504  KL=KBIT-2
000216 033505  DO 80 I=1, IL, IDIF
000220 033507  KLAST=I+KL
000221 033510  DO 80 K=I,KLAST+2
000223 033521  K1=K*KBIT
000233 033522  K2=K1*KBIT
000234 033523  K3=K2*KBIT
000235 033524  T=K(2)
000236 033525  A(K2)=A(K)+T
000237 033526  A(K)=A(K)+T
000240 033527  T=A(K2+1)
000241 033530  A(K2+1)=A(K)+T
000244 033533  A(K+1)=A(K)+T
000246 033535  T=A(K3)
000247 033536  A(K3)=A(K)+T
000251 033540  A(K1)=A(K1)+T
000252 033541  T=A(K3+1)
000253 033542  A(K3+1)=A(K1+1)+T
000256 033545  A(K1+1)=A(K1+1)+T
000261 033550  T=A(K1)
000262 033551  A(K1)=A(K)+T
000263 033552  A(K)=A(K)+T
000264 033553  T=A(K1+1)
000265 033554  A(K1+1)=A(K)+T
000270 033557  A(K+1)=A(K)+T,
000272 033561  R=A(A(K3+1))
000273 033562  T=A(K3)
000275 033564  A(K3)=A(K2)-R
000277 033566  A(K2)=A(K2)+R
000300 033567  A(K3+1)=A(K2+1)+T
000303 033572  80 A(K2+1)=A(K2+1)+T
000320 033607  IF (LAST) 235,235,82
000321 033610  82 J=J+IOIF +1
000323 033612  ILAST=c IL +JJ
000325 033614  DO 85 I = JJ, ILAST, IOIF
000326 033615  KLAST = KL+I
000327 033616  DO 85 K=I,KLAST+2
000340 033627  K1 = K*KBIT
000341 033630  K2 = K1*KBIT
000342 033631  K3 = K2*KBIT
000344 033633  T = A(K2)
000346 033635  A(K2) = A(K)+R
000350 033637  A(K) = A(K)+R
000351 033640  A(K2+1)=A(K)+T
000353 033642  A(K+1)=A(K)+T
000355 033644  AWR=A(K1)-A(K1+1)
000357 033646  AWI = A(K1+1)*A(K1)
000361 033650  R=A(A(K3+1))
000364 033653  T=A(K3)=A(K3+1)
000366 033655  A(K3)=(AWR+R)/ROOT2
000371 033660  A(K3+1)=(AWI+T)/ROOT2
000373 033662  A(K1)=(AWR+R)/ROOT2
000376 033665  A(K1+1)=(AWI+T)/ROOT2
000401 033670  T= A(K1)
000402 033671  A(K1)=A(K)+T
000403 033672  A(K)=A(K)+T,
000410 033677  A(K+1) = A(K+1) + T
000412 033701  R = A(K+1)
000413 033702  T = A(K3)
000415 033704  A(K3) = A(K2) - R
000417 033706  A(K2) = A(K2) + T
000420 033707  A(K3+1) = A(K2+1) + T
000423 033712  85 A(K2+1) = A(K2+1) + T
000440 033727  IF(JLAST = 1) 235, 235, 90
000442 033731  90 JJM = JJ + JJDF
000444 033733  DO 230 JM2, JLAST
000445 033734  96 I = INV(J+1)
000447 033736  98 IC = NT - I
000451 033740  W(1) = S(1C)
000452 033741  W(2) = S(1)
000454 033743  I2E = *I
000455 033744  I2C = NT - I2
000457 033746  IF(I2C = 120, 110, 100
000461 033750  W2(1) = S(I2C)
000463 033752  GO TO 130
000464 033753  110 W2(1) = 0.
000465 033754  W2(2) = 1.
000467 033756  GO TO 130
000467 033756  120 I2CC = I2C+NT
000471 033760  I2C = I2C
000471 033760  W2(1) = S(I2C)
000473 033762  W2(2) = S(I2C)
000475 033764  130 I3 = I+12
000477 033766  I3C = NT - I3
000500 033767  IF(I3C = 190, 180, 170
000502 033771  W3(1) = S(I3C)
000504 033773  W3(2) = S(I3)
000506 033775  GO TO 200
000507 033776  150 W3(1) = 0.
000510 033777  W3(2) = 1.
000512 034001  GO TO 200
000512 034001  160 I3C = I3C+NT
000514 034003  IF(I3C = 190, 180, 170
000515 034004  I3C = I3C
000516 034005  W3(1) = S(I3C)
000520 034007  W3(2) = S(I3C)
000522 034011  GO TO 200
000523 034012  180 W3(1) = 1.
000524 034013  W3(2) = 0.
000525 034014  GO TO 200
000526 034015  190 I3CCC = NT + I3CC
000530 034017  I3CC = I3CC
000530 034017  W3(1) = S(I3CCC)
000532 034021  W3(2) = S(I3CCC)
000535 034024  200 ILAST = IL+JJ
000537 034026  DO 220 I = *ILAST, IDIF
000540 034027  KLAST = KL+1
000541 034030  DO 220 K = 1, KLAST, 2
000552 034041  K1 = K*KBIT
000553 034042  K2 = K1*KBIT
000554 034043  K3 = K2*KBIT
000555 034044  K4 = K(K2)*W2(1) + A(K2+1)*W2(2)
000560 034047  T = (A(K2)*W2(2) + A(K2+1)*W2(1))
000564 034053  A(K2) = A(K) = R
000566 034055  A(K) = A(K) + R
000567 034056  A(K2+1) = A(K+1) + T
000571 034060  A(K+1) = A(K+1) + T
00073 034262  DO 870 JP3=1,MINV3
00073 034263  GO TO (610,620),IG03
001002 034271  610 JP3=INV(J,J)3*N3VNT
001006 034275  GO TO 630
001006 034275  620 JP3=INV(JP3)/NTVN3
001012 034301  630 I3=(JPP3+IP3)*N2
001016 034305  700 JJ=1
001017 034306  DO 870 JPP2=1,N2VNT
001021 034310  IPP2=INV(JJ2)+I3
001023 034312  DO 860 JP2=1,MINN2
001025 034314  GO TO (710,720),IG02
001033 034322  710 JP2=INV(JP2)*N2VNT
001037 034326  GO TO 730
001037 034326  720 JP2=INV(JP2)/NTVN2
001043 034332  730 I2=(JPP2+IP2)*N1
001047 034336  800 JJ=1
001050 034337  DO 860 JPP1=1,N1VNT
001052 034341  IPP1=INV(JJ1)+I2
001054 034343  DO 850 JP1=1,MINN1
001056 034345  GO TO (610,620),IG01
001064 034353  810 JP1=INV(JP1)/N1VNT
001070 034357  GO TO 830
001070 034357  820 JP1=INV(JP1)/NTVN1
001074 034363  830 I2=(JPP1+IP1)*N1
001077 034366  IF (J=1) 840,845,845
001113 034402  840 T=A(I)
001114 034403  A(I)=A(J)
001115 034404  A(J)=T
001117 034406  T=A(I-1)
001120 034407  A(I+1)=A(J+1)
001121 034410  A(J+1)=T
001122 034411  845 CONTINUE
001122 034411  850 J=J+2
001126 034415  860 JJ=JJ+JU1
001135 034424  870 JJ2=JJ2+JJ2
001143 034432  880 JJ3=JJ3+JJ3
001147 034436  890 IF (IFSET) 895,895,891
001151 034440  891 DO 892 I = 1,NX
001157 034446  892 A(2*1) = A(2*1)
001165 034454  895 RETURN
001165 034455  900 MT=MXXO(M(1)+M(2)+M(3))-2
001175 034464  901 IF (MT=1) 905,905,903
001177 034466  903 MT = MAXO(2*4)
001203 034472  904 IF (MT=13) 906,906,905
001206 034475  905 IFERR = 1
001207 034476  GO TO 895
001210 034477  906 IFERR=0
001211 034500  NT=2*MT
001214 034503  NT2=NT/2
001215 034504  PFNT2=PI/FLOAT(2*NT)
001217 034506  DO 950 L=1,NT
001221 034510  SL=SIN(FLOAT(L)*PFNT2)
001231 034520  950 CONTINUE
001233 034522  960 MTLEXP=NTV2
001234 034523  LMEXP=1
001235 034524  INV(I)=0
001237 034526  DO 980 L=1,MT
001240 034527  INV(LMEXP)=MTLEXP
001242 034531  DO 970 J=2,LM1EXP
001250 034537  JJJ=LM1EXP
001251 034540  970 INV(JJJ)=INV(J)+MTLEXP
001254 034543  MTLEXP=MTLEXP/2
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