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Raman Study of Iodine Complexes in Solutions

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ABSTRACT

Results of Raman measurements on I_2 complexes in various solutions are presented. Emphasis is on the variation of the Raman spectrum of I_2 in mixtures of n-hexane and benzene or methylated benzenes. Our results indicate that each I_2 molecule can probably interact with more than one donor and the effect of inert molecules in the solution should be taken into account.

I. 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.[1] 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.[2] They are generally in qualitative agreement with the charge-transfer theory proposed by Mulliken.[3] However, for weak complexes, the results often show anomalous behavior.[4] For example, since the charge-transfer interaction between 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.[5]

In order to explain the anomalies, various authors have modified the Benesi-Hildebrand theory[2] in a variety of ways.[6-10] In particular, Orgel and Mulliken[10] pointed out that there is no *á 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.[10] This is particularly true for weak I_2 complexes in which the charge-transfer interaction is of fairly long range.[11]

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

of the absorption band. As Mulliken and Person[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[13] and Raman[14,15] experiments on charge-transfer complexes. Raman measurements on I_2 complexes,[14] however, have been limited to the case of I_2 in pure donor solution. No systematic investigation of the changes in the Raman spectrum of I_2 complexes as a function of donor concentration has been reported yet.

In this paper,[16] we would like to report our recent experimental studies on I_2 complexes in solution with modern Raman spectroscopic technique. Emphasis is on the change of the Raman spectrum of I_2 due to charge-transfer interaction between I_2 and various donors. The results indicate that I_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.[10] 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 $\rho(\underset{\sim}{R})$ be the statistical distribution function for a particular configuration (denoted by $\underset{\sim}{R}$) 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

$$\langle X \rangle = \int_{V_o} X(\underset{\sim}{R})\rho(\underset{\sim}{R})\, d\underset{\sim}{R}. \qquad (1)$$

where the volume of integration V_o is chosen large enough to include all molecules interacting with the acceptor. The expression for $\rho(\underset{\sim}{R})$ 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 that Eq. (1) takes the form

$$\langle X \rangle = \frac{a_o + a_1\rho_B + a_2\rho_B^2 + \ldots}{1 + b_1\rho_B + b_2\rho_B^2 + \ldots} \qquad (2)$$

where ρ_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

$$\langle \Delta X \rangle \equiv \langle X \rangle - \langle X \rangle_{\rho_B=0}. \tag{3}$$

From Eq. (2), we obtain

$$\langle \Delta X \rangle = \frac{c_1\rho_B + c_2\rho_B^2 + \ldots}{1 + b_1\rho_B + b_2\rho_B^2 + \ldots}. \tag{4}$$

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,[2]

$$1/\langle \Delta X \rangle = (1/\Delta X_o)(1 + 1/K\rho_B). \tag{5}$$

where ΔX_o 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 ρ_B are also kept, then the equation has the form derived by Deranleau.[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 $\langle d\sigma/d\Omega \rangle$ on the donor concentration ρ_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

$$S(\omega) = \int_{V_o} g(\omega-\omega_v(\underset{\sim}{R}))\ (d\sigma(\underset{\sim}{R})/d\Omega)\ \rho(\underset{\sim}{R})\ d\underset{\sim}{R} \qquad (6)$$

where $g(\omega-\omega_v)$ is the lineshape function. Normally, the distribution of donors and inert molecules has a few most favorable configurations $\underset{\sim}{R}_1$, $\underset{\sim}{R}_2$, etc. If the corresponding $\omega_v(\underset{\sim}{R}_1)$, $\omega_v(\underset{\sim}{R}_2)$, etc. 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

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

From Eq. (6), we can readily find

$$\langle \omega_v \rangle = \int_{V_o} \omega_v(\underset{\sim}{R})(d\sigma(\underset{\sim}{R})/d\Omega)\, \rho(\underset{\sim}{R}) d\underset{\sim}{R} / \int_{V_o} (d\sigma(\underset{\sim}{R})/d\Omega)\, \rho(\underset{\sim}{R}) d\underset{\sim}{R} \tag{8}$$

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

$$\begin{aligned} \langle \Delta\omega_v \rangle &\equiv \langle \omega_v \rangle - \langle \omega_v \rangle_{\rho_B=0} \\ &= \frac{c_1\rho_B + c_2\rho_B^2 + \ldots}{1 + b_1\rho_B + b_2\rho_B^2 + \ldots} . \end{aligned} \tag{9}$$

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.[21] The output of a He-Ne laser (Spectra Physics Model 125), after passing thourgh 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. A photomultiplier (EMI 9558 QA), cooled to -70°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 solutions were obtained with little effort. For example, with a scan speed of 1.Å/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 Å). 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 I_2 complexes is that the Raman lines of I_2 sometimes overlap with Raman lines of the solvent molecules. Decomposition of the lines introduces error and makes the experimental data much less accurate. For examples, the I_2 fundamental overlaps slightly with a toluene line at 214 cm^{-1}, and the first overtone of I_2 overlaps with a weak benzene line at 404 cm^{-1}. In principle, the above difficulty can be avoided by measurements at two different I_2 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 I_2 in Various Solvents

In an iodine solution, interaction of I_2 with solvent molecules always leads to a shift in the frequency of the I_2 stretching vibration. We can usually divide the intermolecular interaction into two types: the long-range van der Waals interaction[22] and the short-range chemical interaction.[23] In the case of I_2 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.[24] 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 $\pm .1\ cm^{-1}$. In Fig. 2, the mean frequency shifts, defined as $\langle\Delta\omega_V^o\rangle \equiv \omega_{Vo} - \langle\omega_V\rangle$ where ω_{Vo}=213.3 cm^{-1} is the vibrational frequency of I_2 in the vapor phase,[25] are plotted against $(n^2 - 1)$.[26] From uv absorption measurements, we know that I_2 has essentially no charge-transfer interaction with n-hexane, n-heptane, and CCl_4.[27] 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.[5,27]

B. Raman Spectra of I_2 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 I_2 in mixtures of n-hexane and benzene or methylated benzenes. In pure n-hexane, the I_2 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 I_2 and benzene, since we recall that there is no charge-transfer interaction between I_2 and n-hexane and that the van der Waals shifts estimated for I_2 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 I_2 and benzene forming 1:1 complexes[2] (allowing each I_2 to interact with only one donor). Such a model would predict two discrete Raman lines of I_2 in the mixed solution, one for I_2 unassociated with benzene, and the other for I_2 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 I_2 in pure benzene, only 60% of I_2 would have formed 1:1 complexes,[2] and the uncomplexed I_2 line would be easily detectable. Our spectra show that, with increasing benzene concentration, the I_2 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.[3] 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 I_2 complexes, I_2 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 I_2 in mixutres of n-hexane and mesitylene.[29] 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 I_2 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 I_2 molecule now starts interacting effectively with more than one donor although the interaction is shielded to some extent by the charge-transfer interaction between I_2 and the first donor. One can also regard the I_2-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 I_2 and pyridine is supposed to be even stronger, we would expect to observe the same phenomenon for I_2 in mixtures of n-hexane and pryidine. 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 cm^{-1} with a linewidth of 15 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 cm^{-1}.[13] In addition, Plyler and Mulliken[13] have observed two infrared absorption bands for I_2 and pyridine in benzene, one at 204 cm^{-1} and one at 174 cm^{-1}. they identify the 204 cm^{-1} line as due to I_2-benzene complexes. They also suggest that the 174 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 cm^{-1} to 174 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 $\langle \Delta\omega_v \rangle$ in the Raman spectrum can be very accurate, and can be used to test quantitatively the theories on complexes in solution. In Fig. 3, $1/\langle \Delta\omega_v \rangle$, the inverse of the mean frequency shift of the I_2 fundamental vibration from its value in pure n-hexane, is plotted against $1/(\rho_B/\rho_{BO})$, the inverse of the normalized concentration of benzene or methylated benzene, where ρ_B is the concentration of benzene

or methylated benzene in the mixture, and ρ_{B0} 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

$$1/\langle \Delta\omega \rangle = (1+\alpha_1 X+\alpha_2 X^2)/(\beta_1 X+\beta_2 X^2) \qquad (10)$$

where $X = \rho_B/\rho_{B0}$ and α_1, α_2, β_1, and β_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

α_1, α_2, β_1, and β_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 β_1 can, however, be determined quite accurately from the asymptotic slope of $1/\langle \Delta\omega_v \rangle$ vs ρ_{B0}/ρ_B at small ρ_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.[15] Thus, measurements of Raman scattering intensity of I_2 as a function of the donor concentration should provide another test on the theories of complexes in solution. Bahnick and Person[15] 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 I_2 in mixtures of benzene and CCl_4. 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 CCl_4 at 217 cm^{-1}. We always measured the Raman line of I_2 together with the 217 cm^{-1} line of CCl_4. We then considered only the relative scattering cross-section of the I_2 line with respect to the CCl_4 line. We found experimentally that in the absence of I_2, the scattering intensity of the 217 cm^{-1} CCl_4 line is proportional to the concentration of CCl_4 in agreement with the results of Bahnick and Person.[15] Therefore, within experimental error, the scattering cross-section of the CCl_4 line should be unaffected by the CCl_4-benzene interaction. Our experimental results in Fig. 6 show that the relative Raman cross-section of I_2 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.[15]

In our case, the accuracy is worse since the CCl_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} CCl_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_2 and pyridine is exceptionally strong. From the infrared absorption spectrum, Lake and Thompson[13] have indeed found the intermolecular mode at 94 cm^{-1} in the I_2-pyridine complex. We have tried to observe the same intermolecular mode from the Raman spectrum. However, from the charge configuration of the I_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.

VI. CONCLUSION

It is demonstrated that Raman spectroscopy can be used to investigate charge-transfer complexes in solution. By measuring the mean frequencies of the I_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_2 Raman spectrum in mixtures of n-hexane and benzene or methylated benzene shows that each I_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_2-fundamental and, in addition, the I_2 overtone spectrum. Results agree qualitatively with what the theory would predict.

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22. We define the van der Waals interaction here to include electrostatic, 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 Liquids (John Wiley and Sons, Inc., New York, 1954) p. 917.

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28. If CCl_4 were used instead of n-hexane, then since CCl_4 and benzene have roughly the same refractive index, the van der Waals shift would presumably remain unchanged with benzene concentration in the CCl_4-benzene mixtures. Unfortunately, the 217 cm^{-1} CCl_4 line overlaps slightly with the I_2 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 CH_2Cl_2 and $CHCl_2$. See Ref. 15.

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31. The values of K_{uv} obtained by different authors are usually different. Our values of K fall within the spread of values of K_{uv} tabulated in G. Briegleb, Electronen-Donor-Acceptor-Komplexes (Springer-Verlag, Berlin, 1961) p. 124. It should be noted that part of the discrepancy between K and K_{uv} could be due to the fact that CCl_4 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 $(\Delta\omega_v)_o$ are around 5 %.

32. With an 85% confidence level, the uncertainties in the values of

α_1, α_2, and β_2 can be as large as 200%, but the uncertainties in the values of β_1 are less than 30%.

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TABLE I

Solvents	Frequency (cm^{-1})
vapor	213.3
n-hexane	210.1 ± 0.1
n-heptane	210.0 ± 0.1
carbontetrachloride	209.7 ± 0.3
chloroform	209.6 ± 0.4
cyclohexane	208.9 ± 0.4
nitrobenzene	208.1 ± 0.4
chlorobenzene	207.1 ± 0.4
bromobenzene	205.9 ± 0.4
benzene	204.6 ± 0.1
toluene	203.6 ± 0.2
m-xylene	202.1 ± 0.15
mesitylene	200.0 ± 0.3

TABLE II

	$(\Delta\omega_v)_o$	K (liters/mole)	K_{uv} (liters/mole)	
Benzene	8.6 cm^{-1}	0.17	0.157	(a)
Toluene	10.3 cm^{-1}	0.21	0.16	(b)
m-xylene	10.5 cm^{-1}	0.40	0.31	(b)
Mesitylene	12.8 cm^{-1}	0.62	.534	(a)

TABLE III

	α_1	α_2	β_1	β_2
Benzene	2.64	4.53	13.20	31.71
Toluene	3.24	1.05	22.0	14.26
m-xylene	3.0	3.6	30.6	29.37
Mesitylene	3.68	0.724	53.11	2.72

FIGURE CAPTIONS

Fig. 1. A typical Raman spectrum (the central line) of the I_2 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 I_2 shows up, while the model of a 1-1 complex would predict two.

Fig. 2. Mean frequency shift of the I_2 fundamental vibration from its value in vapor in various solvents vs $n^2 - 1$, 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 $1/\langle\Delta\omega_v\rangle$ of I_2 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 ρ_{Bo}/ρ_B, where ρ_{Bo} is the density of pure benzene or methylated benzene and ρ_B is the density of benzene or methylated benzene in the mixtures.

Fig. 4. Apparent Raman linewidth of the I_2 fundamental vs the normalized benzene concentration. The instrumental linewidth is 4 cm^{-1}. The true width of the I_2 line in n-hexane obtained by deconvolution of the line with the slit function is 5.1 cm^{-1}.

Fig. 5. Mean frequency shift of the I_2 fundamental as a function of normalized benzene concentration at two temperatures 25°C and 55°C.

Fig. 6. Variation of the Raman scattering cross-section of the I_2 fundamental (normalized against the Raman scattering cross-section of the 217 cm^{-1} line of CCl_4) as a function of the normalized benzene concentration.

Fig. 7. Mean frequency of the I_2 first overtone vs the normalized benzene concentration.

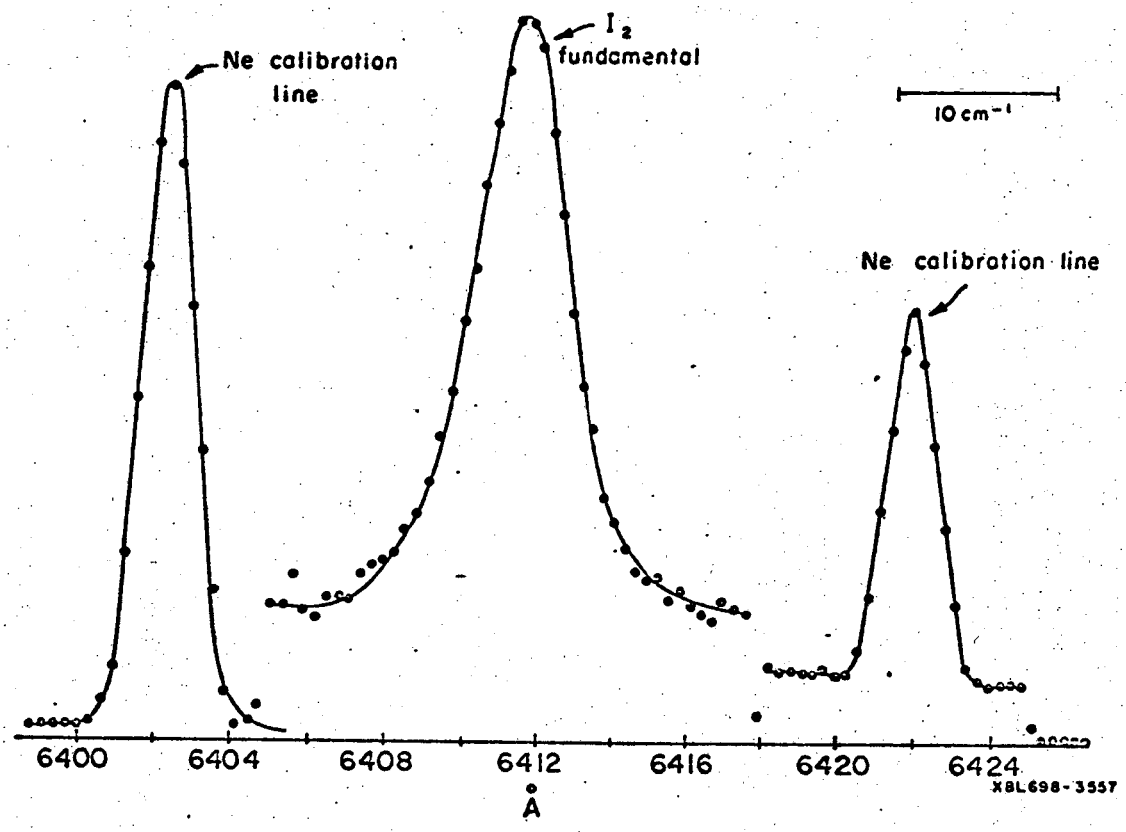
Fig. 8. Variation of $2\omega_f - \omega_o$ as a function of the normalized benzene concentration, where ω_f and ω_o are the mean frequencies of the fundamental and the first overtone of the I_2 vibration respectively.

TABLE CAPTIONS

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

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 III. Values of α_1, α_2, β_1, and β_2 in Eq. (10) derived from the best fit of the experimental data to Eq. (10) as shown in Fig. 3.


Ne calibration line
I_2 fundamental
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Ne calibration line
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Å
XBL698-3557

Fig. 1

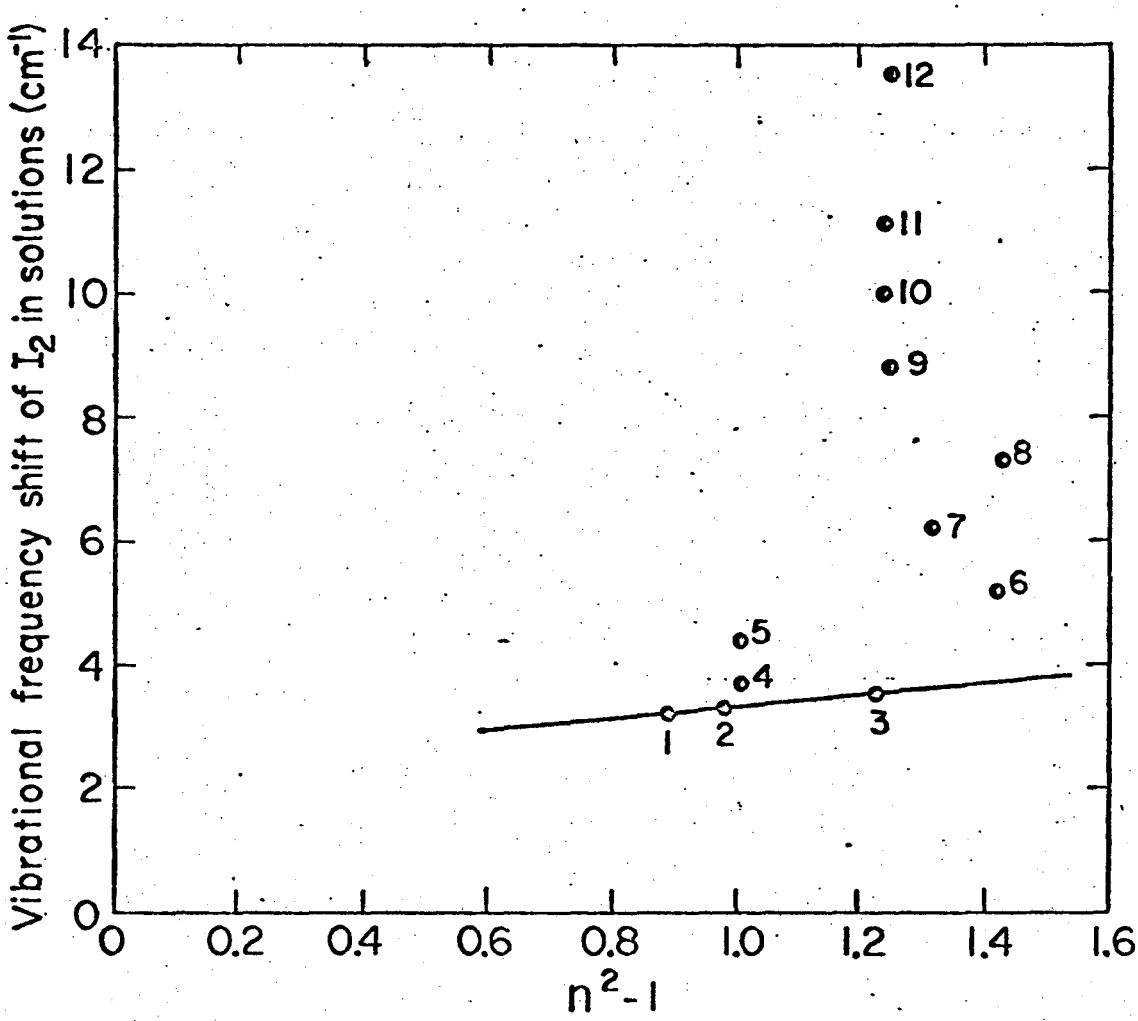

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Fig. 2

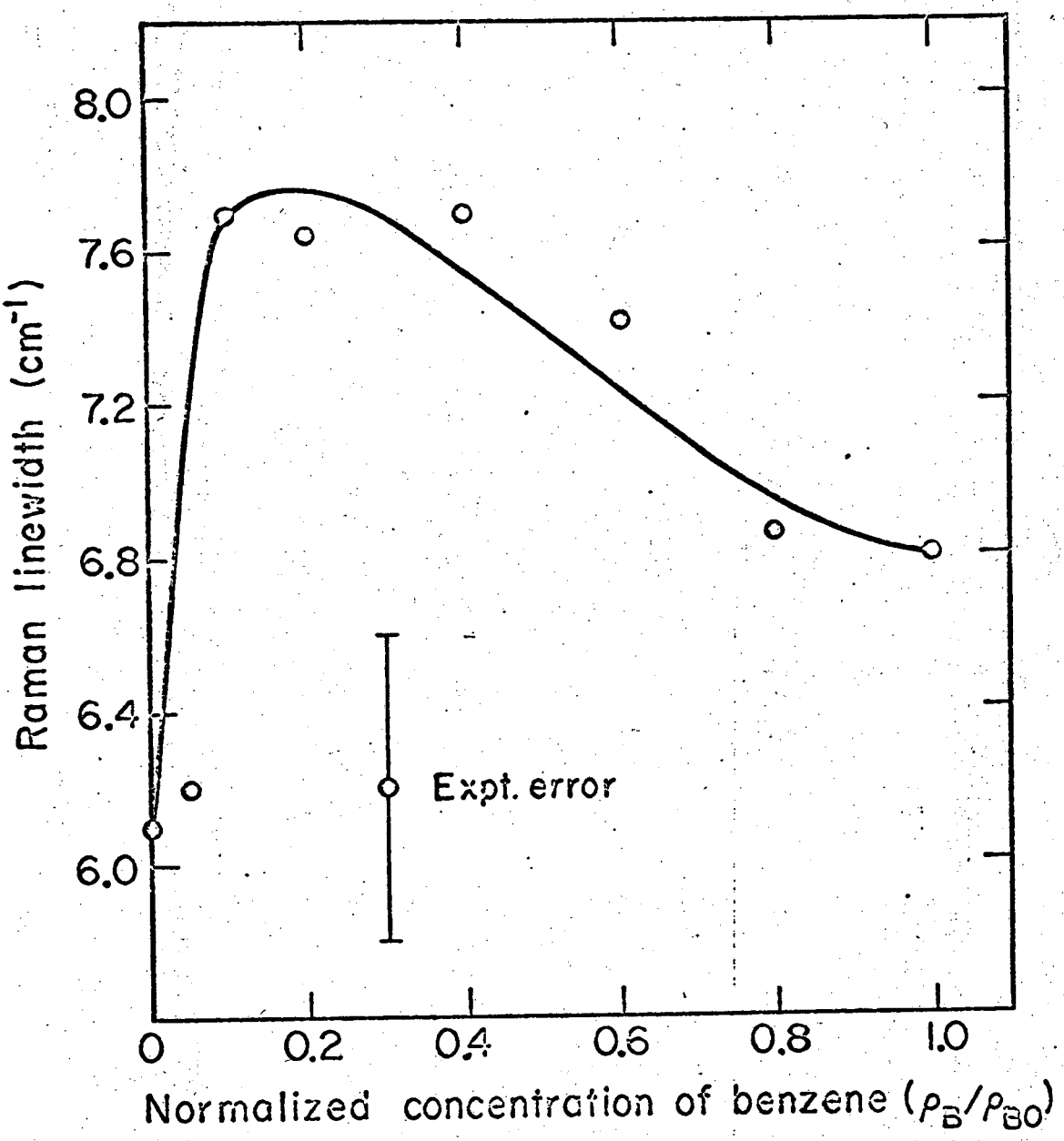

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Fig. 3

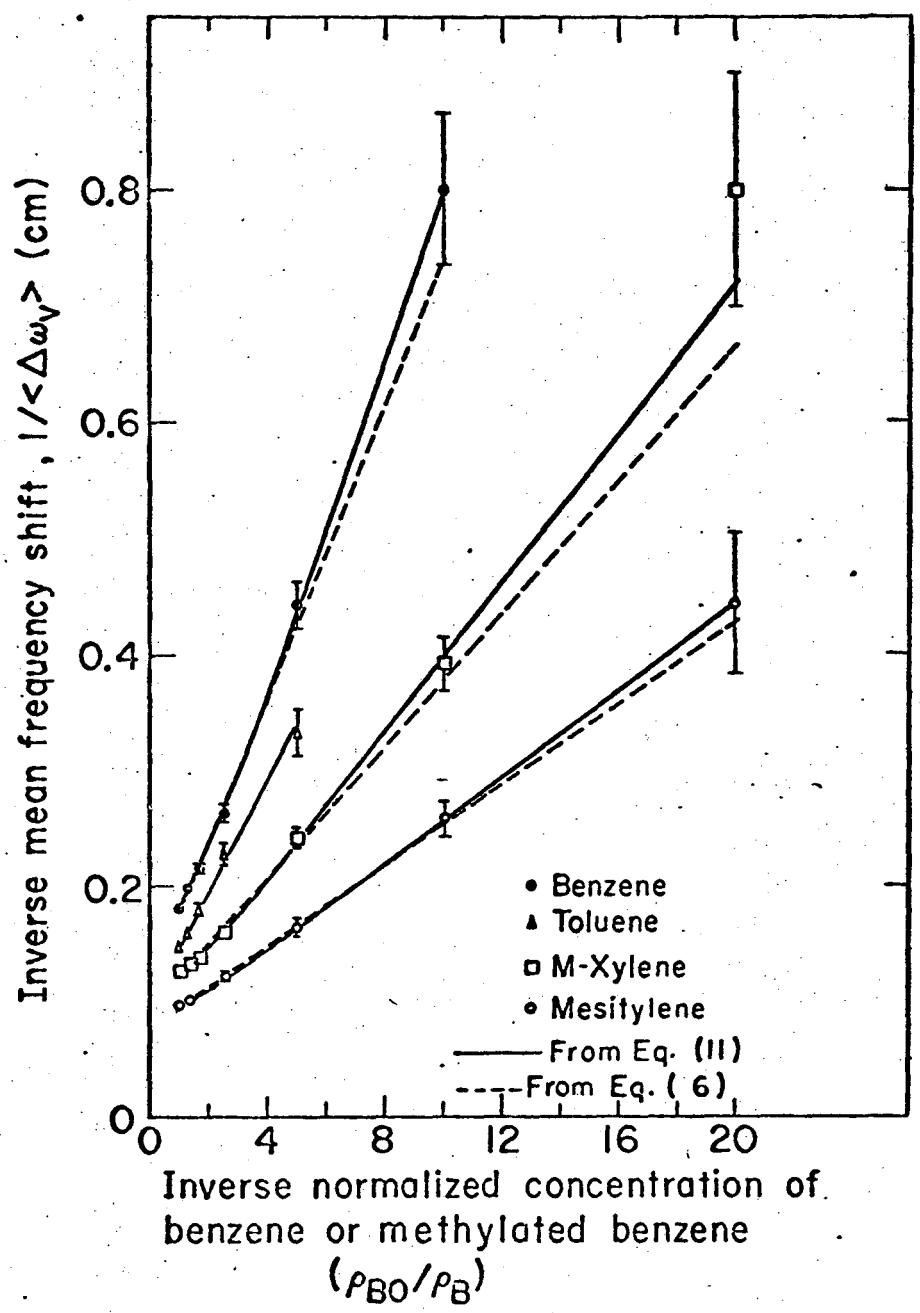

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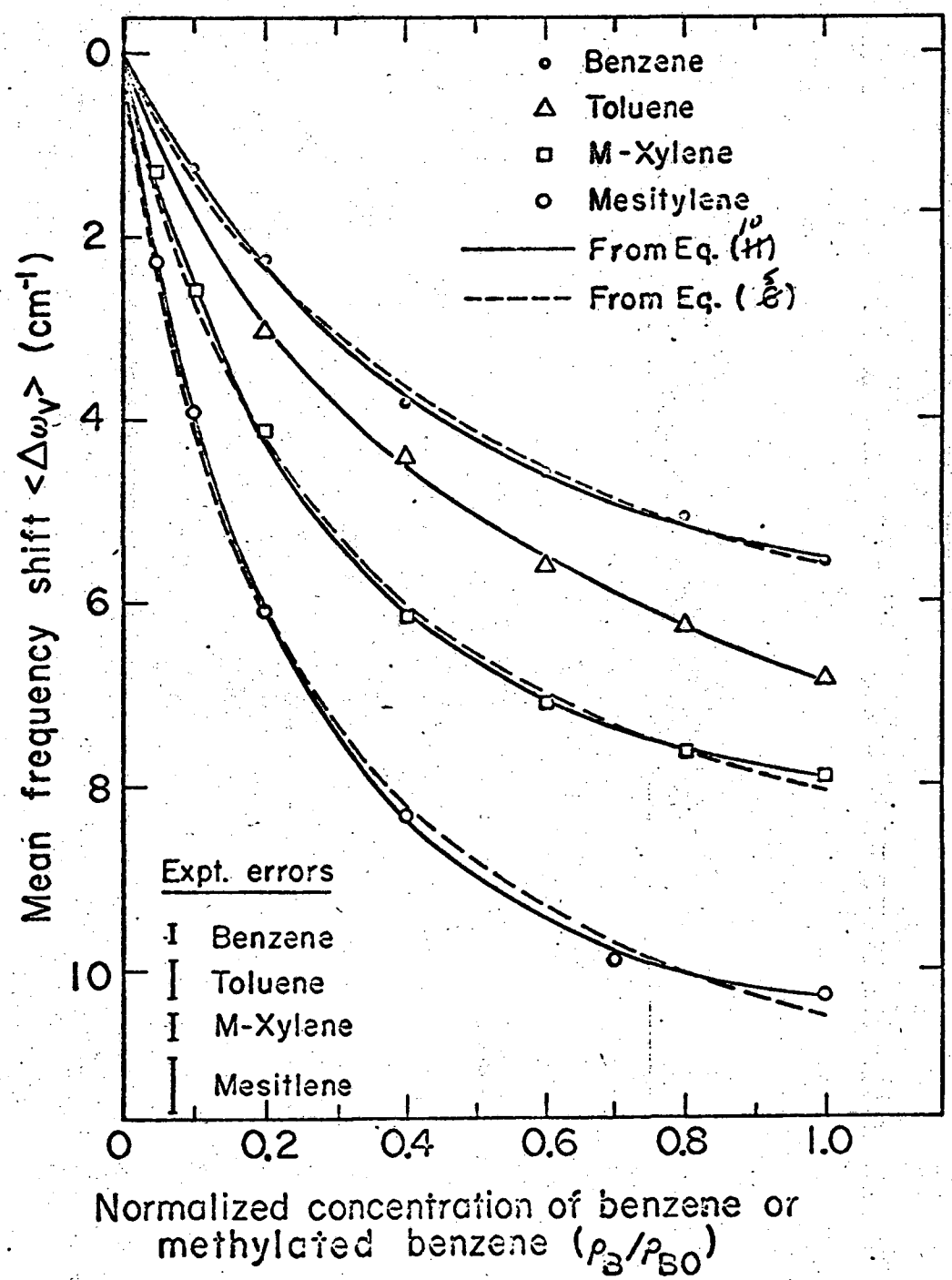
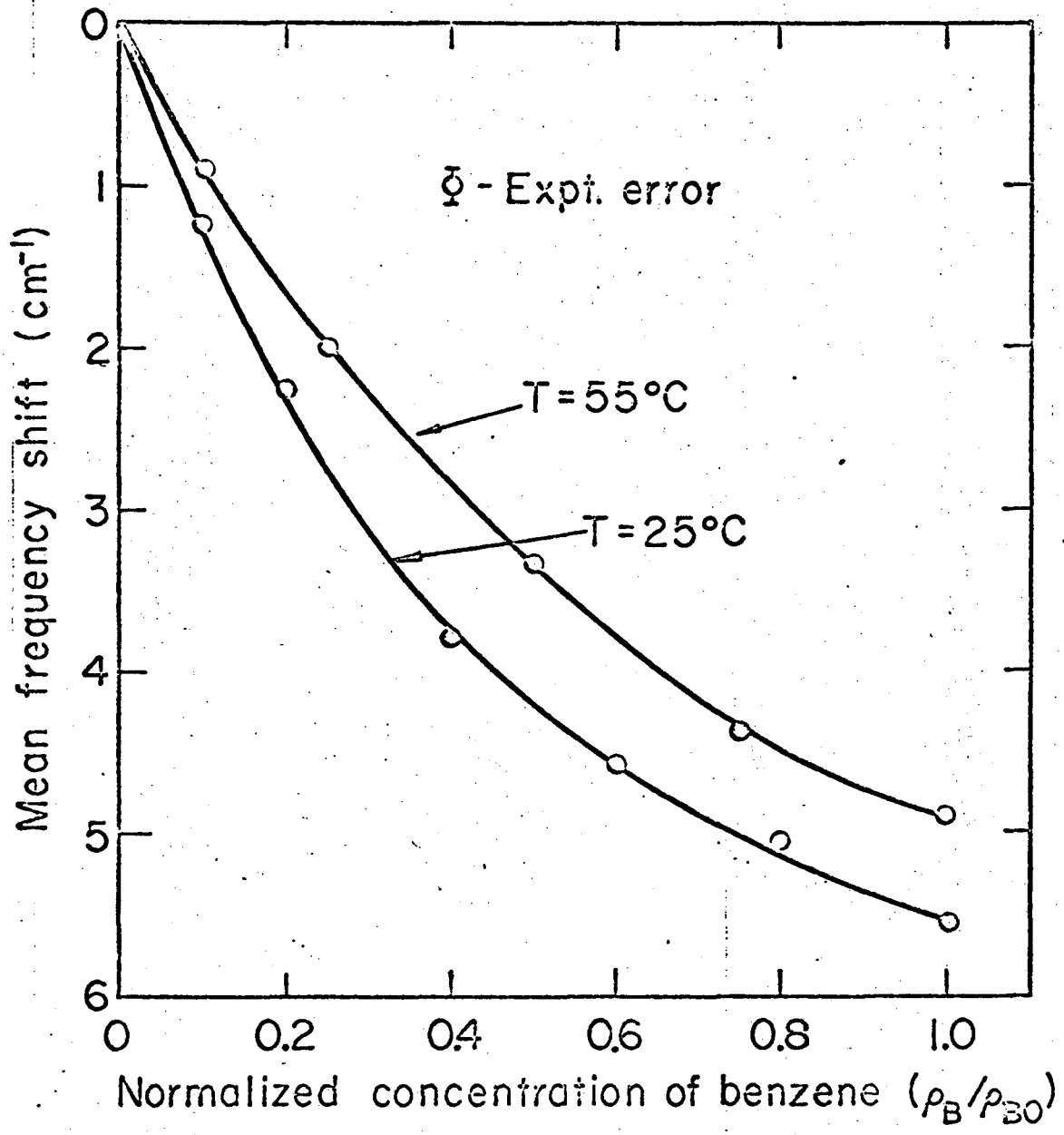
Fig. 4 a



XBL697-3277

Fig. 4 b



XBL697-3332

Fig. 5

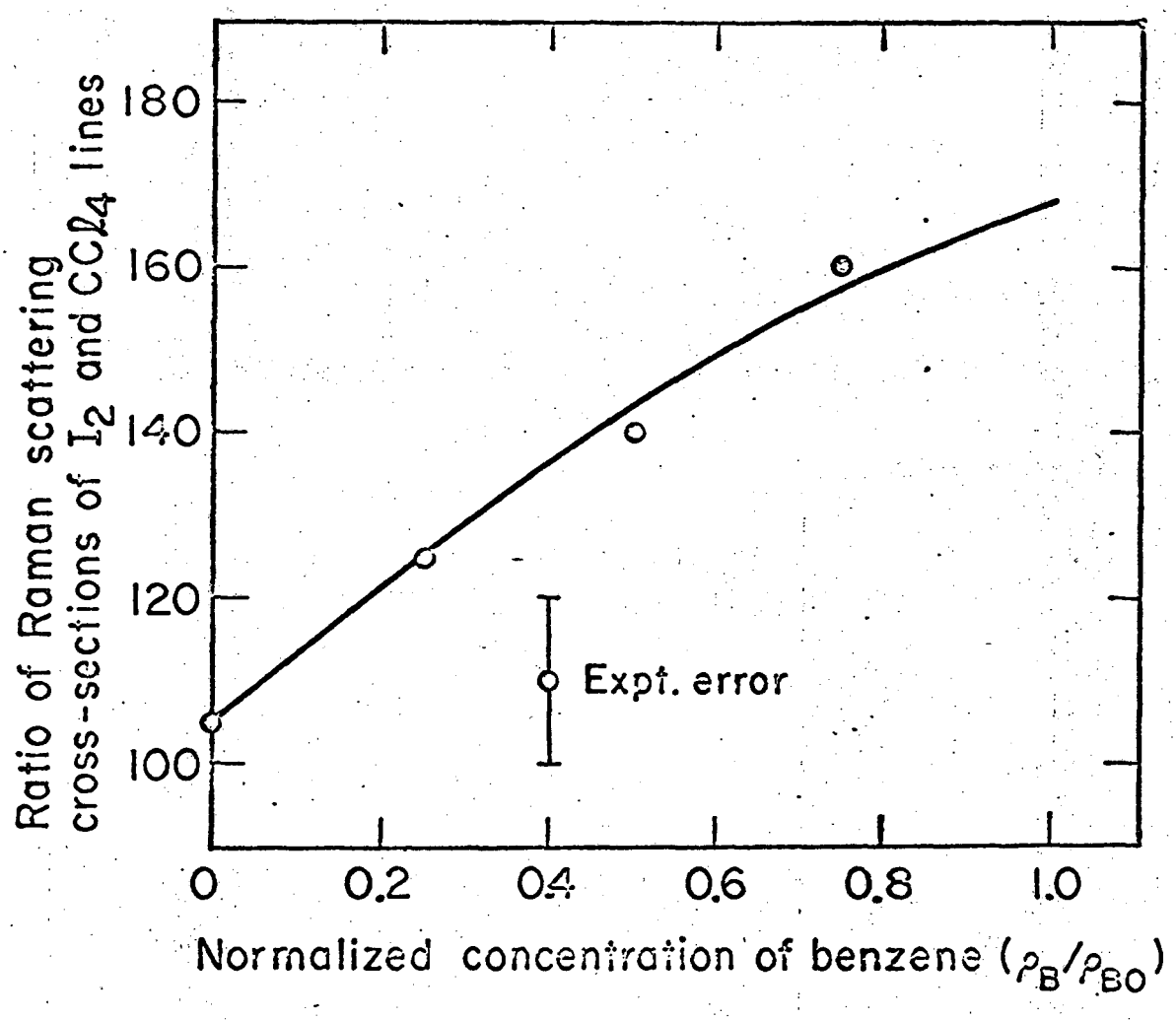


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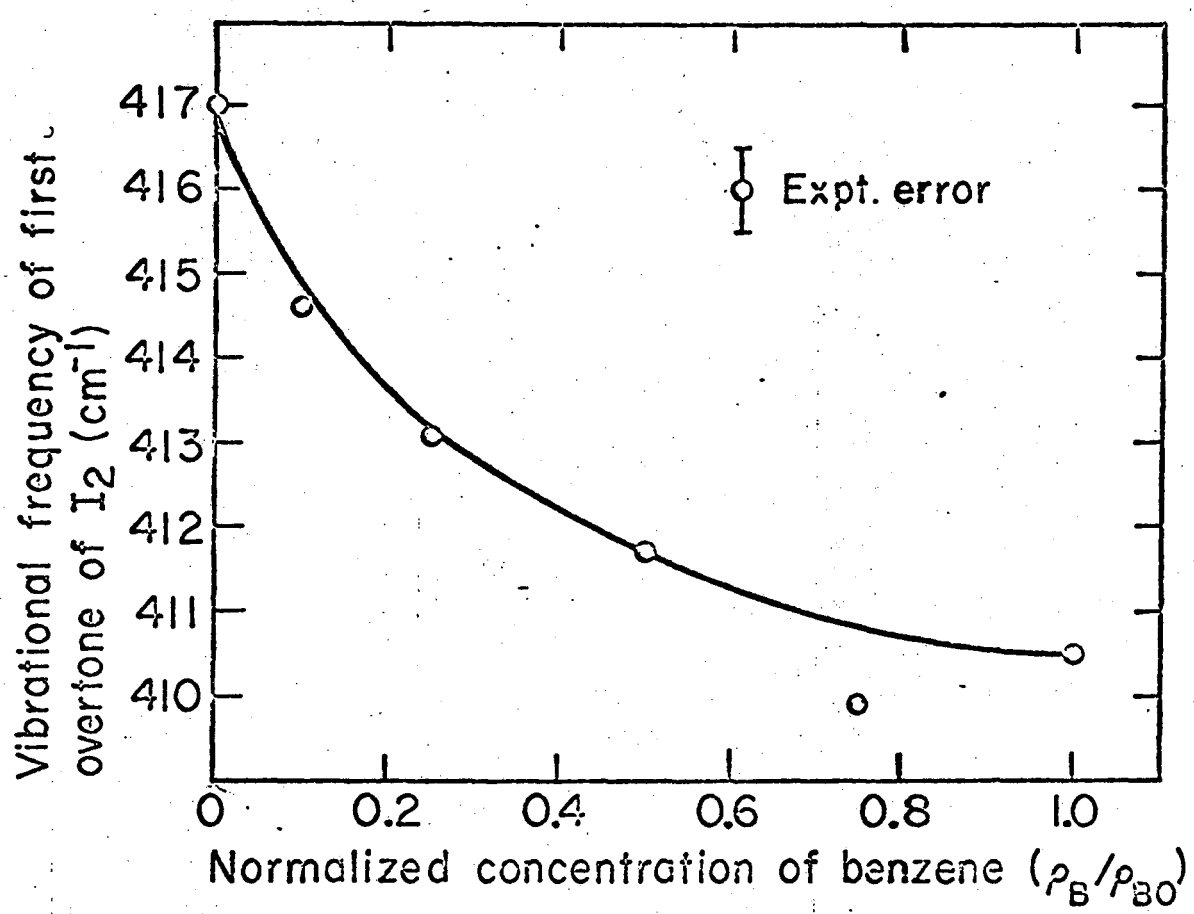
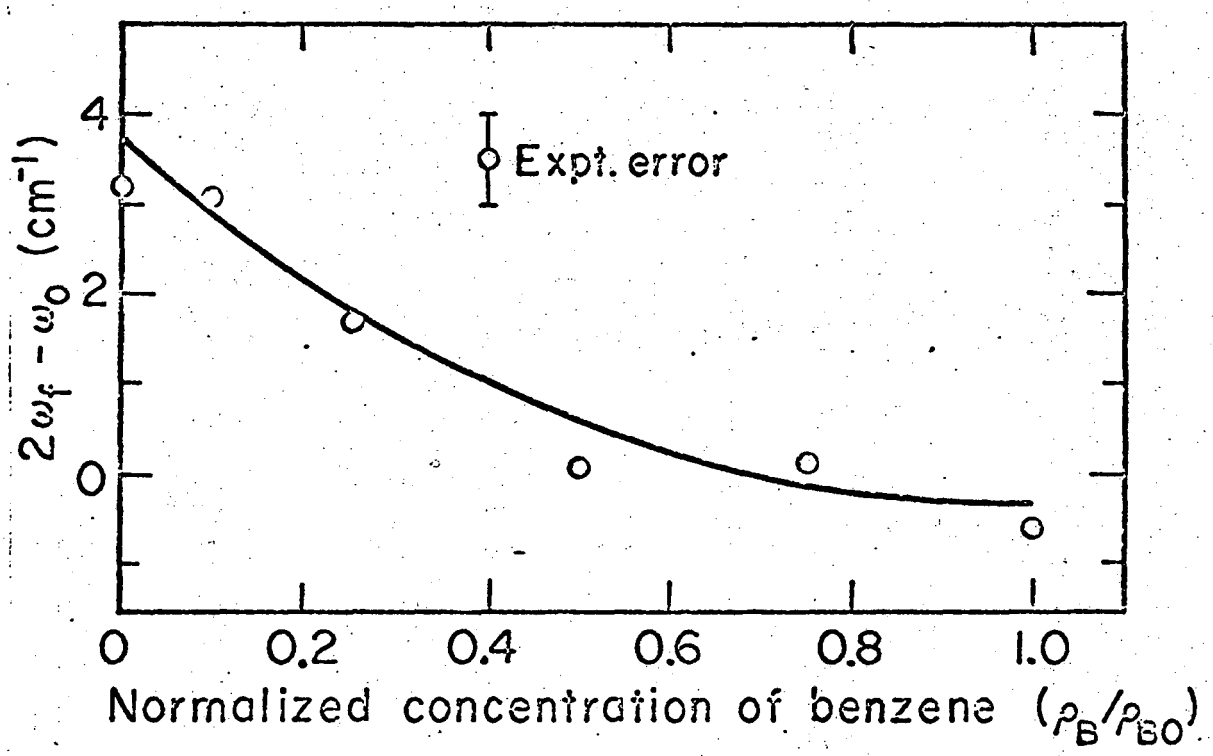
Fig. 6



XBL697-3335

Fig. 7



XBL697-3333

Fig. 8

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