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Part II

THEORY OF COMPLEXES IN SOLUTION: II. APPLICATION TO RAMAN SCATTERING FROM IODINE COMPLEXES IN LIQUID SOLUTIONS

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ABSTRACT

Raman scattering from complexes in solution is discussed from the microscopic and statistical point of view. It is shown that the statistical theory proposed in the preceeding paper is successful in explaining the observed anomalies in Raman scattering from iodine complexes in solution. The results indicate that each I_2 can interact simultaneously with two donors, that no particular complex configuration dominates for weak I_2 complexes, and that the shielding effect of inert solvent molecules on complex properties is non-negligible.

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] Benesi and Hildebrand[2] were first to observe that when benzene (or methylated benzene) is added into a solution of iodine in an inert solvent, such as carbontetrachloride, or n-hexane, a new absorption band in the ultraviolet appears. They associated this band with the formation of complexes between iodine and benzene. Mulliken[3] subsequently recognized that these complexes are of the charge-transfer type in which iodine is the acceptor and benzene the donor. The new absorption band is then known as the charge-transfer absorption band of the complex.

By assuming that iodine forms a stable 1:1 complex with benzene, and using the mass action law, Benesi and Hildebrand[2] were able to account for the variation of optical absorption as a function of the benzene concentration in the complex solution by the well-known Benesi-Hildebrand equation. They then deduced from their results the equilibrium constant and the extinction coefficient for a 1:1 complex. However, it was observed that for iodine complexes with methylated benzene, the extinction coefficient of the charge-transfer absorption decreased with increasing methylation. To explain this anomaly, Orgel and Mulliken[4] suggested that there might exist simultaneously in the solution two types of complexes, namely "stable" and "contact" complexes respectively, and they showed that in such a case, the Benesi-Hildebrand equation still holds. Many other

authors have also modified the Benesi-Hildebrand equation by including the effect of inert solvent molecules,[5] the possible dependence of extinction coefficient on donor or acceptor concentrations,[6] the possible existence of stable 1:2 complexes,[7] etc.

In most experiments on charge-transfer complexes, the effort has been concentrated on measurements of the charge-transfer absorption band. There are, however, inherent difficulties in the optical absorption measurements. The large uncertainty in the results often makes the comparison between theory and experiments rather difficult. Moreover, the absorption measurements were usually limited to a single or few discrete frequencies in the charge-transfer band. As Mulliken and Person[8] pointed out, the extinction coefficient which appears in any theory of complexes should not be the one at a certain frequency, but should be the one integrated over the entire charge-transfer band.

Only a few infrared[9] and Raman studies[10] of charge-transfer interaction have been reported. It is quite obvious that complex formation should lead to a change in the vibrational spectrum of the solution.[11] (see Sec. II) With the advent of laser-Raman spectroscopy, Raman measurements could now yield very accurate results on the vibrational spectrum of complexes, and appear to be a useful new method for investigation of charge-transfer complexes.

Our recent measurements[12] of Raman scattering from solutions of iodine in mixtures of benzene (or methylated benzene) and n-hexane showed some anomalous results which cannot be explained by the theories of Benesi-Hildebrand[2] and of Orgel and Mulliken.[4] According to their theories, several discrete fundamental Raman lines of iodine should

appear, one for free iodine molecules, one for the 1:1 stable complexes, and also one for the 1:n contact complexes. While the relative intensities of these lines should vary with the benzene concentration, the positions of the lines for free I_2 and for the stable complexes should not have changed. However, our measurements on I_2 complexes with benzene, toluene, or m-xylene in inert solvent, showed only a single unresolved line. As the benzene (or methylated benzene) concentration increased, this Raman line simply shifted to lower frequencies without appreciable change in its linewidth or lineshape, and the frequency shift for I_2 in 100% benzene was larger than the half width of the line. We can also show, from the model of either Benesi-Hildebrand or Orgel-Mulliken, that the mean vibrational frequency shift as a function of benzene concentration should obey an equation of the Benesi-Hildebrand form.[13] Figure 1, however, shows that our experimental results deviate definitely, although not appreciably, from the theoretical curves of the Benesi-Hildebrand equation. These anomalous results suggest that the simple models of Benesi-Hildebrand and Orgel-Mulliken for complexes in solution are unsatisfactory and should be modified.

From a statistical point of view, there is no *á priori* reason to assume either the existence of only 1:1 stable complexes or the division into stable and contact complexes in a solution. As Orgel and Mulliken[4] pointed out, the observed properties of complexes should be statistical averages over all attainable configurations in thermal equilibrium. This is particularly true for complexes with relatively weak interaction between molecules, e.g., iodine-benzene

charge-transfer complexes. In the preceeding paper (I),[14] we have developed a statistical theory for complexes in solution which takes into account both the statistical distribution of complex configurations and the effect of inert solvent molecules in the solution. We would like to show in this paper that application of our theory to the case of Raman scattering from iodine complexes in solutions can explain all the observed anomalies we mentioned before.

We shall assume that the concentration of I_2 (the acceptors) is small, and we shall consider only the effect of charge-transfer interaction on the Raman spectrum of I_2. To make the discussion complete, we first develope in Sec. II the theory of Raman scattering from a charge-transfer complex. The effect of charge-transfer interaction on the Raman spectrum of the acceptors is calculated. Then in Sec. III, we apply our statistical theory to Raman scattering from charge-transfer complexes in a liquid solution. The results are used in Sec. IV to explain the observed anomalies in Raman scattering from iodine complexes in liquid solutions. Quantitative agreement between theory and experiment is also obtained.

II. RAMAN SCATTERING FROM A CHARGE-TRANSFER COMPLEX

The differential Raman scattering cross-section $d\sigma/d\Omega$ for a material system with eigenstates $|\psi\rangle$ can be obtained from a straightforward second-order perturbation calculation.[15]

$$d\sigma/d\Omega = \frac{e^4\omega_o\omega_s^3}{c^4}\left|\sum_n\left\{\frac{\langle\psi_f|\hat{e}_s\cdot\underset{\sim}{r}|\psi_n\rangle\langle\psi_n|\hat{e}_o\cdot\underset{\sim}{r}|\psi_i\rangle}{\hbar(\omega_o-\omega_{ni})} - \frac{\langle\psi_f|\hat{e}_o\cdot\underset{\sim}{r}|\psi_n\rangle\langle\psi_n|\hat{e}_s\cdot\underset{\sim}{r}|\psi_i\rangle}{\hbar(\omega_o+\omega_{ni})}\right\}\right|^2 . \tag{1}$$

Here, $|\psi_i\rangle$ and $|\psi_f\rangle$ are the initial and the final states in the Raman trasistion, and $|\psi_n\rangle$ are the intermediate states. The unit vectors $\hat{e}_o$ and $\hat{e}_s$ indicate the directions of polarizations of the incoming and the scattered Stokes radiation whose frequencies are given by ω_o and ω_s respectively. The energy difference $(E_n - E_i)$ between the states $|\psi_n\rangle$ and $|\psi_i\rangle$ is abbreviated as $\hbar\omega_{ni}$.

In the case of Raman scattering by molecular vibration, the states $|\psi\rangle$ are eigenstates of the combined electronic and vibrational system of a molecule. With Born-Oppenheimer approximation, one can write

$$|\psi\rangle \equiv |\psi^{ev}\rangle = |\phi\rangle\Big|_{Q=o}|\eta\rangle + \frac{\partial|\phi\rangle}{\partial Q}\Big|_{\underset{\sim}{Q}=o}\underset{\sim}{Q}\,|\eta\rangle + \ldots \tag{2}$$

where $|\phi\rangle$ and $|\eta\rangle$ are the electronic and vibrational states respectively, and $\underset{\sim}{Q}$ is the normal coordinate for the molecular vibration. If we write

$$\mu = \sum_n\left\{\frac{\hat{e}_s\cdot\underset{\sim}{r}|\psi_n\rangle\langle\psi_n|\hat{e}_o\cdot\underset{\sim}{r}}{\hbar(\omega_o-\omega_{ni})} - \frac{\hat{e}_o\cdot\underset{\sim}{r}|\psi_n\rangle\langle\psi_n|\hat{e}_s\cdot\underset{\sim}{r}}{\hbar(\omega_o+\omega_{ni})}\right\} \tag{3}$$

as a Raman transition operator, then we can also expand μ into

$$\mu = \sum_n \left\{ |\eta_n\rangle\langle\eta_n|\gamma_n + Q|\eta_n\rangle\langle\eta_n| \partial\gamma_n/\partial Q + \ldots \right\} \tag{4}$$

with $$\gamma_n = \frac{\hat{e}_s\cdot\underset{\sim}{r}|\phi_n\rangle\langle\phi_n|\hat{e}_o\cdot\underset{\sim}{r}}{\hbar(\omega_o - \omega_{ni})} - \frac{\hat{e}_o\cdot\underset{\sim}{r}|\phi_n\rangle\langle\phi_n|\hat{e}_s\cdot\underset{\sim}{r}}{\hbar(\omega_o + \omega_{ni})} .$$

For fundamental Raman transitions, only terms linear in Q in Eq. (1) contribute. The differential scattering cross-section becomes

$$\frac{d\sigma}{d\Omega} = \frac{e^4\omega_o\omega_s^3}{c^4}|\langle\eta_f|Q|\eta_i\rangle|^2 \left|\frac{\partial\langle\phi_f|}{\partial Q}\gamma|\phi_i\rangle + \langle\phi_f|\frac{\partial\gamma}{\partial Q}|\phi_i\rangle + \langle\phi_f|\gamma\frac{\partial|\phi_i\rangle}{\partial Q}\right|^2 \tag{5}$$

where $$\gamma = \sum_n \gamma_n, \quad \langle\phi_f| = \langle\phi_i| .$$

The above result applies not only to free acceptor molecules, but also to acceptor molecules interacting with donor molecules. In the latter case, the eigenstates of a free acceptor molecule are modified by the charge-transfer interaction with the donor or donors. According to Mulliken,[16,11] the ground state of a 1:1 charge-transfer complex is given by

$$|\psi_g\rangle = a(Q)\,|\psi_o\rangle + b(Q)\,|\psi_1\rangle$$

$$= a_o\,|\phi_o\rangle\,|\eta_g\rangle + b_o\,|\phi_1\rangle\,|\eta_g\rangle$$

$$+\left(\frac{\partial a_o}{\partial Q}|\phi_o\rangle + \frac{\partial b_o}{\partial Q}|\phi_1\rangle + a_o\frac{\partial|\phi_o\rangle}{\partial Q} + b_o\frac{\partial|\phi_1\rangle}{\partial Q}\right)Q|\eta_g\rangle + \ldots \tag{6}$$

where $|\phi_o\rangle$ is the electronic state for the "no-bond" structure (D---A) and $|\phi_1\rangle$ is the "dative" state ($D^+ - A^-$). The coefficients a and b are assumed real and normalized such that $a^2 + b^2 + 2abS = 1$ with $S = \langle\phi_o|\phi_1\rangle$. Since we are only interested in the effect of the charge-transfer interaction on the vibrational spectrum of the acceptor, only the normal coordinate Q of the acceptor is given explicitly in Eq. (16). The case of zero charge-transfer interaction corresponds to a = 1 and b = 0. Similarly, the optical excited states of the molecules should also be modified accordingly by the charge-transfer interaction. In particular, there now exists an excited charge-transfer state described by

$$|\psi_{cT}\rangle = a\,(Q)\,|\psi_1\rangle - b\,(Q)\,|\psi_o\rangle . \tag{7}$$

As a result, the operator γ defined in Eqs. (4) and (5) becomes

$$\gamma = \gamma_o + \Delta\gamma \tag{8}$$

where $\gamma = \gamma_o$ if the charge-transfer interaction is zero. From Eqs. (1), (6), and (8), we find that the differential scattering cross-section for fundamental Raman transitions in a 1:1 charge-transfer complex is given by

$$\frac{d\sigma}{d\Omega} = \frac{e^4\omega_o\omega_s^3}{c^4}|\langle n_f|Q|n_i\rangle|^2|M_{fi}|^2 \tag{9}$$

$$M_{fi} = \left(\frac{\partial a_o}{\partial Q}\langle\phi_o| + \frac{\partial b_o}{\partial Q}\langle\phi_1| + a_o\frac{\partial\langle\phi_o|}{\partial Q} + b_o\frac{\partial\langle\phi_1|}{\partial Q}\right)(\gamma_o + \Delta\gamma)(a_o|\phi_o\rangle + b_o|\phi_1\rangle)$$

$$+ \left(a_o\langle\phi_o| + b_c\langle\phi_1|\right)\left[\frac{\partial}{\partial Q}(\gamma_o + \gamma)\right](a_o|\phi_o\rangle + b_o|\phi_1\rangle)$$

$$+ \left(a_o\langle\phi_o| + b_o\langle\phi_1|\right)(\gamma_o + \Delta\gamma)\left(\frac{\partial a_o}{\partial Q}|\phi_o\rangle + \frac{\partial b_o}{\partial Q}|\phi_1\rangle + a_o\frac{\partial|\phi_o\rangle}{\partial Q} + b_o\frac{\partial|\phi_1\rangle}{\partial Q}\right)$$

we note that $\Delta\gamma$ includes modification on all optical excited states due to charge-transfer interaction. Consequently to a good approximation in evaluating M_{fi}, we could perhaps neglect the modification on the initial and final states due to charge-transfer interaction. We then have

$$M_{fi} \approx M_{fi}^{o} + \Delta M_{fi} \tag{10}$$

where $M_{fi}^{o} = \frac{\partial \langle \phi_o|}{\partial Q} \gamma_o |\phi_o\rangle + \langle \phi_o| \frac{\partial \gamma_o}{\partial Q} |\phi_o\rangle + \langle \phi_o|\gamma_o \frac{\partial |\phi_o\rangle}{\partial Q}$

and ΔM_{fi} has the same expression as M_{fi}^{o} except with γ_o replaced by $\Delta\gamma$. Moreover, if we assume that the major contribution to $\Delta\gamma$ comes from the newly formed charge-transfer band, then the charge-transfer interaction would lead to an increase in the Raman scattering cross-section given approximately by

$$\Delta\left(\frac{d\sigma}{d\Omega}\right) \approx \left(\frac{d\sigma_o}{d\Omega}\right) 2 \left|\frac{\Delta\gamma_o}{\gamma_o}\right| \approx \left(\frac{d\sigma_o}{d\Omega}\right) 2 \frac{f_{CT}}{(\omega_o - \omega_{CT})} \Big/ \sum_n \frac{f_{ni}}{(\omega_o - \omega_{ni})} \tag{11}$$

where f_{CT} and $\hbar\omega_{CT}$ are the oscillator strength and the average energy of the charge-transfer band, and f_{ni} is the oscillator strength for the optical transition between states $|\phi_i\rangle$ and $|\phi_n\rangle$. Here, we have assumed the existence of a 1:1 charge-transfer pair with a definite configuration. More generally, if the acceptor interacts with several donors simultaneously, then in the first-order approximation, we should sum over contributions due to each donor accordingly. For complexes in solution, numerous complex configurations exist and the results should also be averaged over the statistical distribution of

complex configurations as we mentioned earlier. This will be done in the next section.

From the experimental point of view, it is always difficult to measure the absolute scattering (or absorption) cross-section. The vibrational frequencies, however, can be determined with great accuracy by modern Raman spectroscopy.[12] It is well known that interaction between molecules may cause significant changes in the atomic bonding strength. The charge-transfer interaction is particularly effective. It leads to shifts in the vibrational frequencies of both the donor and the acceptor. The theory of the vibrational frequency shifts in donors or acceptors has been formulated by Friedrich and Person.[11] Here, we shall give a brief review of their calculation.

We assume that the potential function for a particular molecular vibration in the charge-transfer complex can be written approximately as

$$W_{CT}(Q) = (a_o^2 + a_o b_o S)\, W_o(Q) + (b_o^2 + a_o b_o S)\, W_1(Q) \qquad (12)$$

where W_o and W_1 are the potential functions for the no-bond (D---A) and the dative ($D^+ - A^-$) structures respectively. The force constant for the molecular vibration in the 1:1 complex is then given by

$$k_{CT} = \partial^2 W_{CT} \Big/ \partial Q^2$$

$$= (a_o^2 + a_o b_o S) k_o + (b_o^2 + a_o b_o S) k_1 \qquad (13)$$

where $k_o = \partial^2 W_o \Big/ \partial Q^2$ and $k_1 = \partial^2 W_1 \Big/ \partial Q^2$. From Eq. (13), we obtain the frequency shift

$$\Delta\omega_v = \frac{1}{2}\,[(k_{CT} - k_o)/k_o]\omega_{vo}$$

$$= \frac{1}{2}\,[(k_1/k_o) - 1]\,(b_o^2 + a_o b_o S)\omega_{vo}. \qquad (14)$$

Here, ω_{vo} is the vibrational frequency for the free acceptor, and we have used the normalization condition $a_o^2 + b_o^2 + 2a_o b_o S = 1$. Since k_1 is usually smaller than k_o,[17] the frequency shift $\Delta\omega_v$ is negative, indicating a decrease in the vibrational frequency.

Again, if the acceptor interacts simultaneously with n donors, the vibrational frequency shift $\Delta\omega_v$ of the acceptor is, in the first-order approximation, the sum of contirubtions from all the n donors. The observed frequency shift for complexes in solution should also be the average of $\Delta\omega_v$ over the statistical distribution of all complex configurations. Equation (14) can be used directly to compare with experimental observations only when there is more or less a definite complex configuration in a solution, as was assumed in Ref. 11. In the following section, we shall find the statistical averages of $\Delta(d\sigma/d\Omega)$ and $\Delta\omega_v$ for complexes in a liquid solution using our theory proposed in I.

III. RAMAN SCATTERING FROM COMPLEXES IN A LIQUID SOLUTION

Equation (2) in I gives a general expression for the statistical average of a certain physical property X of the "A" molecules (the acceptors) dissolved in the solvent mixture of "B" (donor) and "C" (inert solvent) molecules. In a liquid solution, the number of "B" and "C" molecules in the volume V_o should be a constant according to the cell model, and hence, we have n+m = constant = p. We then write

$$\langle X \rangle = \sum_{\substack{n,m \\ n+m=p}} \int_{V_o} X^{(n,m)} \rho^{(n,m)} \, d\underset{\sim}{r}_1 \cdots d\underset{\sim}{r}_n \, d\underset{\sim}{R}_1 \cdots d\underset{\sim}{R}_m \tag{15}$$

with $\rho^{(n,m)}$ given by Eq. (7) in I. The quantity we are often interested in is the change of $\langle X \rangle$ as a function of donor concentration with respect to the solution of pure inert solvent. We have

$$\langle \Delta X \rangle = \langle X \rangle - \langle X^{(o,p)} \rangle . \tag{16}$$

Let X be the differential Raman scattering cross-section $d\sigma/d\Omega$. We then find

$$\langle \Delta(d\sigma/d\Omega) \rangle = \sum_{\substack{n,m \\ n+m=p}} \int_{V_o} [(d\sigma/d\Omega) - \langle d\sigma^{(o,p)}/d\Omega \rangle] \rho^{(n,m)} d\underset{\sim}{r}_1 \cdots d\underset{\sim}{r}_n \, d\underset{\sim}{R}_1 \cdots d\underset{\sim}{R}_m \tag{17}$$

where

$$\langle (d\sigma^{(o,p)}/d\Omega) \rangle \equiv \int_{V_o} (d\sigma^{(o,p)}/d\Omega) \exp[-\beta U^{(o,p)}] d\underset{\sim}{R}' \cdots d\underset{\sim}{R}^{(p)} \times 1 \Big/ \int_{V_o} \exp[-\beta U^{(o,p)}] d\underset{\sim}{R}' \cdots d\underset{\sim}{R}^{(p)} .$$

For the special case of 1:1 complexes in solution, the change of this differential scattering cross-section should obey Eq. (15) in I, which is of the Bensi-Hildebrand form. (see Sec. III of I).

Similarly, let the frequency of a vibrational mode of the acceptor interacting with the n donors and the m inert molecules be

$$\omega_v^{(n,m)} = \omega_v^{(n,m)} (\underset{\sim}{r}_1 \cdots \underset{\sim}{r}_n ; \underset{\sim}{R}_1 \cdots \underset{\sim}{R}_m).$$

If $g(\omega-\omega_v)$ is the lineshape function independent of the interaction, then with $X=g(\omega-\omega_v)\, d\sigma/d\Omega$ in Eq. (15) the observed spectral distribution for

complexes in a liquid solution is given by

$$S(\omega)=\sum_{\substack{n,m\\ n+m=p}} \int_{V_o} g(\omega-\omega_v^{(n,m)})(d\sigma^{(n,m)}/d\Omega)\rho^{(n,m)} d\underset{\sim}{r}_1 \cdots d\underset{\sim}{r}_n d\underset{\sim}{R}_1 \cdots d\underset{\sim}{R}_m . \qquad (18)$$

By definition, the mean vibrational frequency is

$$\langle \omega_v \rangle \equiv \int_{-\infty}^{\infty} S(\omega)\, \omega\, d\omega \Big/ \int_{-\infty}^{\infty} S(\omega)\, d\omega$$

$$= \int_{-\infty}^{\infty} (\omega'+\omega_v^{(n,m)}) S(\omega'+\omega_v^{(n,m)}) d\omega' \Big/ \int_{-\infty}^{\infty} S(\omega'+\omega_v^{(n,m)}) d\omega' . \qquad (19)$$

We also define

$$\langle \Delta\omega_v \rangle = \langle \omega_v \rangle - \langle \omega_v^{(o,p)} \rangle \qquad (20)$$

where we find, from Eqs. (18) and (19)

$$\langle \Delta\omega_v \rangle =$$

$$\sum_{\substack{n,m\\ n+m=p}} \int_{V_o} [\omega_v^{(n,m)} - \langle \omega_v^{(o,p)} \rangle](d\sigma^{(n,m)}/d\Omega)\rho^{(n,m)} d\underset{\sim}{r}_1 \cdots d\underset{\sim}{r}_n d\underset{\sim}{R}_1 \cdots d\underset{\sim}{R}_m$$

$$\times \; 1 \Big/ \sum_{\substack{n,m\\ n+m=p}} \int_{V_o} (d\sigma^{(n,m)}/d\Omega)\rho^{(n,m)} d\underset{\sim}{r}_1 \cdots d\underset{\sim}{r}_n d\underset{\sim}{R}_1 \cdots d\underset{\sim}{R}_m \qquad (21)$$

$$\langle \omega_v^{(o,p)} \rangle \equiv \int_{V_o} dR' \cdots dR^{(p)} \omega g(\omega-\omega_v^{(o,p)})(d\sigma^{(o,p)}/d\Omega) \exp[-\beta U^{(o,p)}]$$

$$\times \; 1 \Big/ \int_{V_o} (d\sigma^{(o,p)}/d\Omega) \exp[-\beta U^{(o,p)}] dR' \cdots dR^{(p)} . \qquad (22)$$

In the case where $(d\sigma/d\Omega)$ does not vary much over various configurations for which $\rho^{(n,m)}$ differs appreciably from zero, the mean frequency shift becomes

$$\langle \Delta\omega_v \rangle \cong \sum_{\substack{n,m \\ n+m=p}} \int_{V_o} [\omega_v^{(n,m)} - \langle \omega_v^{(o,p)} \rangle] \rho^{(n,m)} d\underset{\sim}{r}_1 --- d\underset{\sim}{r}_n d\underset{\sim}{R}_1 --- d\underset{\sim}{R}_m \qquad (23)$$

which is then of the same form as Eq. (17) with $d\sigma/d\Omega$ replaced by ω_v.

In the following section, we shall apply the above general formalism to the special case of I_2 complexes in liquid solutions.

IV. IODINE COMPLEXES IN LIQUID SOLUTIONS

As we mentioned earlier, experimental results have shown that in the solution of I_2 in benzene and n-hexane (or CCl_4), with increasing benzene concentration, the fundamental Raman line of I_2 shifts as a whole to lower frequencies without appreciable change in either its linewidth or lineshape. This cannot be explained by the model of either Benesi-Hildebrand or Orgel-Mulliken. From our statistical theory, however, this is not surprising, since the vibrational frequency ω_v of I_2 is a function of the configuration of benzene and n-hexane around it, and as shown in Eq. (19), the observed spectrum $S(\omega)$ depends on the statistical distribution of the various configurations. That the observed spectrum $S(\omega)$ remains a single unresolved line suggests that the interaction potential between iodine and benzene is rather weak and varies slowly as the relative positions and orientations of iodine with respect to the neighboring benzene and n-hexane molecules change. This agrees with the results of other investigations which indicate that complexes of iodine and benzene (or methylated benzene) in solution are rather loose.[18] If the interaction potential were strong and varied abruptly, then we would expect to see, at least at sufficiently low concentrations of benzene, two resolved Raman lines, one for free

I_2 and the other for I_2 interacting with benzene. This is indeed the case for I_2 and mesitylene in n-hexane. It is known that the charge-transfer interaction between iodine and methylated benzene increases with methylation.[4] While for I_2 complexes with benzene, toluene, and m-xylene, we always observed one single Raman line of I_2 with larger frequency shift corresponding to higher degree of methylation, we did observe for I_2-mesitylene complexes in n-hexane two Raman lines.[12] At low concentrations of mesitylene, the two lines were at approximately 202.5 and 210.1 cm^{-1}, for I_2 bound and unbound to mesitylene respectively. As the mesitylene concentration increases, the free I_2 line diminished and the I_2-complex line increased in strength. At 30% of mesitylene, the free I_2 line almost vanished and the I_2-complex line started to shift towards lower frequencies, indicating that an iodine molecule could now start interacting simultaneously, in the statistical sense, with more than one mesitylene molecule. The above description also applies qualitatively to other I_2-complexes with strong interaction between I_2 and the donors, such as the I_2-pyridine complex.[12]

Quantitatively, since X in Eqs. (15) and (16) can be either the oscillator strength f of the uv absorption band or the Raman scattering cross-section $(d\sigma/d\Omega)$, the quantities $\langle \Delta f \rangle$ and $\langle \Delta(d\sigma/d\Omega) \rangle$ should obey the same equation. Therefore, just as the uv absorption measurements, the measurements of the variation of $\langle \Delta(d\sigma/d\Omega) \rangle$ with the donor concentration can be used to test the theories on complexes in solution. Unfortunately, because of inherent technical difficulties for absolute measurements of scattering cross-section, the experimental results were much too inaccurate to be used for comparison with theories.

Measurements of the vibrational frequency shift in the Raman spectrum can be very accurate, and can actually be used to test quantitatively the theories on complexes in solution. Equations (20)-(22) unfortunately show that the mean frequency shift also depends on the mean Raman scattering cross-section. However, we recall that for I_2-benzene complexes in solution, as the benzene concentration increases, the Raman line simply shifts without appreciable change in the lineshape and the linewidth. As seen from Eq. (18), this suggests that the distribution function $\rho^{(n,m)}$ must always have a single sharp peak shifting with benzene concentration on the frequency scale. Within this narrow peak of $\rho^{(n,m)}$, $d\sigma/d\Omega$ should not have much variation; otherwise the spectral line would be appreciably broadened and distorted. $(\langle d\sigma/d\Omega \rangle)$ changes by about 60% as the benzene concentration varies from 0 to 100%.[12] Therefore, we can use Eq. (23) for $\langle \Delta\omega_v \rangle$ as a good approximation. This is also true for I_2-toluene and I_2-m-xylene complexes in solution. For I_2-mesitylene complexes, we still expect Eq. (23) to be a fairly good approximation since the Raman line is only distorted at low mesitylene concentrations at which $\langle \Delta(d\sigma/d\Omega) \rangle$ is not yet appreciable (probably less than 30%).

Now with Eq. (23) for $\langle \Delta\omega_v \rangle$, if we assume the existence of 1:1 complexes in solution, then the variation of $1/\langle \Delta\omega_v \rangle$ with donor concentration, ρ_D should obey Eq. (15) of I in the Benesi-Hildebrand form (with X and ρ_B replaced by ω_v and ρ_D respectively). Figure 1a shows the experimental data on $1/\langle \Delta\omega_v \rangle$ vs the concentration $1/\rho_B$ of benzene or methylated benzene. We notice that the experimental points fit a curve with definite curvature in the region of small $1/\rho_B$, while Eq. (15) of I should describe a straight line. The case of toluene is more uncertain, because

of larger experimental error caused by the overlapping of the I_2 Raman line with a toluene Raman line. If, however, we still use Eq. (15) of I to fit the experimental data by the least-square method, we can then deduce the coefficients $(\Delta\omega_v)_o$ and K from the slope of the line and the intercept of the line with the vertical axis. The results are shown in Table I, together with K_{eq} deduced from uv absorption measurements.[19] It is seen that K and K_{eq} agree to within 30%.[20]

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 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 this interaction could be shielded considerably by the interaction of the iodine with the first benzene molecule.

Let us therefore assume that each iodine can interact effectively with two benzene molecules simultaneously, but neglect the probability that it can interact with more than two. Equation (23) in I with ΔX replaced by $\Delta\omega_v$ should then describe the mean vibrational frequency shift. In Table II, we show the values of the four parameters, a, b, c, and d, determined from the best fit of the experimental data to Eq. (23) of I for the four cases. Figure 1 shows how well the experimental points fit with the theoretical curves of Eq. (23) in I; there is a definite improvement in comparison with the best-fit Benesi-Hildebrand

curves of Eq. (15) in I. However, the uncertainty in determining the parameters, a, b, c, and d, is quite large,[21] as suggested by the small difference between the two sets of curves in Fig. 1. (The parameter c can be determined rather accurately from the asymptotic slope of $^1/\langle \Delta\omega_v \rangle$ vs $^1/\rho_D$ at small ρ_D.)[21] The least square error in the fitting could, of course, be greatly improved if more experimental data points were available.

Table II shows that a and c increase with the degree of methylation on benzene, while b and d decrease, if the case of toluene is discarded because of the experimental difficulty mentioned earlier. As seen from the expressions for a, b, c, and d in Eq. (24) of I, an increase in a and c implies an increase in the magnitudes of $|U^{(1,1)}|$ and $|\Delta\omega_v{}^{(1,1)}|$. Physically, this suggests that the interaction between I_2 and methylated benzene becomes stronger with methylation, in agreement with the conclusion drawn by others.[2,4] On the other hand, the decrease in b and d implies that $|U^{(2,0)}|$ does not increase as rapidly as $|U^{(1,1)}|$ when the degree of methylation on benzene increases. This suggests that there is an increasing tendency for I_2 to form a 1:1 complex as benzene is methylated. The large errors in a, b, and d, however, make the above interpretation uncertain.

Knowing the values for a, b, c, and d, we can calculate from Eq. (24) of I the values for the following microscopic quantities:

$$\langle U^{(2,0)} - U^{(0,2)} \rangle \equiv (^{-1}/\beta)\log\{(^1/V_o)^2$$

$$\times \int_{V_o} \exp[-\beta(U^{(2,0)} - \langle U^{(0,2)} \rangle)]d\underset{\sim}{r}d\underset{\sim}{r}'\};$$

$$\langle U^{(1,1)} - U^{(0,2)} \rangle \equiv (-1/\beta)\log\{(1/V_o)^2 \times \int_{V_o} \exp[-\beta(U^{(1,1)} - \langle U^{(0,2)} \rangle)]d\underset{\sim}{r}d\underset{\sim}{r}'\};$$

$$\langle (\omega_v^{(2,0)} - \langle \omega_v^{(2,0)} \rangle) \rangle \equiv \int_{V_o} (\omega_v^{(2,0)} - \langle \omega_v^{(0,2)} \rangle) \exp[-\beta(U^{(2,0)} - \langle U^{(0,2)} \rangle)]d\underset{\sim}{r}d\underset{\sim}{r}' \times 1\Big/\int_{V_o} \exp[-\beta(U^{(2,0)} - \langle U^{(0,2)} \rangle)]d\underset{\sim}{r}d\underset{\sim}{r}';$$

$$\langle (\omega_v^{(1,1)} - \langle \omega_v^{(0,2)} \rangle) \rangle \equiv \int_{V_o} (\omega_v^{(1,1)} - \langle \omega_v^{(0,2)} \rangle \exp[-\beta(U^{(1,1)} - \langle U^{(0,2)} \rangle)]d\underset{\sim}{r}d\underset{\sim}{r}' \times 1\Big/\int_{V_o} \exp[-\beta(U^{(1,1)} - \langle U^{(0,2)} \rangle)]d\underset{\sim}{r}d\underset{\sim}{r}'. \tag{24}$$

Equation (24) shows that these quantities are some kind of averages over the volume V_o, which could be quite different from averages over the effective interaction volume. In order to find the latter quantities which are physically more meaningful, we must have knowledge about the effective interaction range, or more exactly, the functional forms of $U^{(2,0)}$, $U^{(1,1)}$, $\omega_v^{(2,0)}$, and $\omega_v^{(1,1)}$. Because the quantities in Eq. (24) are not so meaningful physically, we will not present here their values deduced from the parameters in Table II.

V. CONCLUSION

The theory of Raman scattering from complexes in solution is discussed here from the microscopic and statistical point of view. It

is shown that the models of Benesi-Hildebrand and of Orgel-Mulliken cannot explain the experimental results on Raman scattering from iodine complexes in solution. Our statistical theory proposed in I, which takes into account the statistical distribution of complex configurations and the shielding effect of the inert molecules can, however, explain the results successfully. We show that the distribution of the complex configurations changes as the benzene (or methylated benzene) concentration varies, and that at high benzene concentrations, each iodine molecule is likely to interact with two benzene molecules simultaneously. These conclusions are clearly not in contradiction with the probable geometry of the complexes and the fact that the complexes are loose.

Our approach shows that the effect of inert molecules in the complex solution is important, and that the cases of complexes in gas and in liquid are different. This may explain the anomalies observed by Lang and Strong[22] and by Carter, et al[5] in uv absorption measurements.

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TABLE I

	$(\Delta\omega_v)_o$	K (liters/mole)	K_{eq} (liters/mole)
Benzene	8.6 cm^{-1}	0.17	0.15
Toluene	10.3 cm^{-1}	0.21	0.16
m-xylene	10.5 cm^{-1}	0.40	0.31
Mesitylene	12.8 cm^{-1}	0.62	0.82

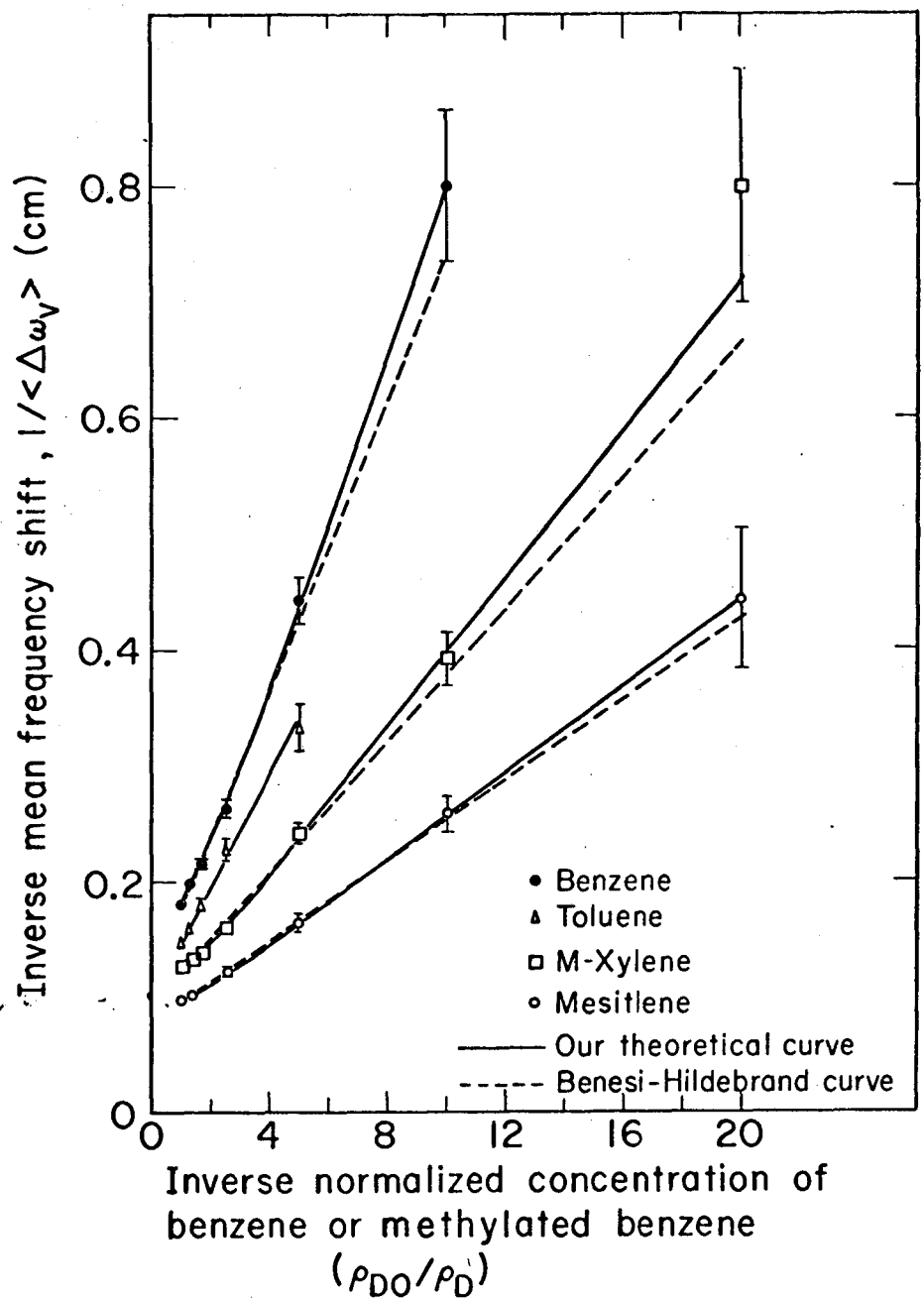

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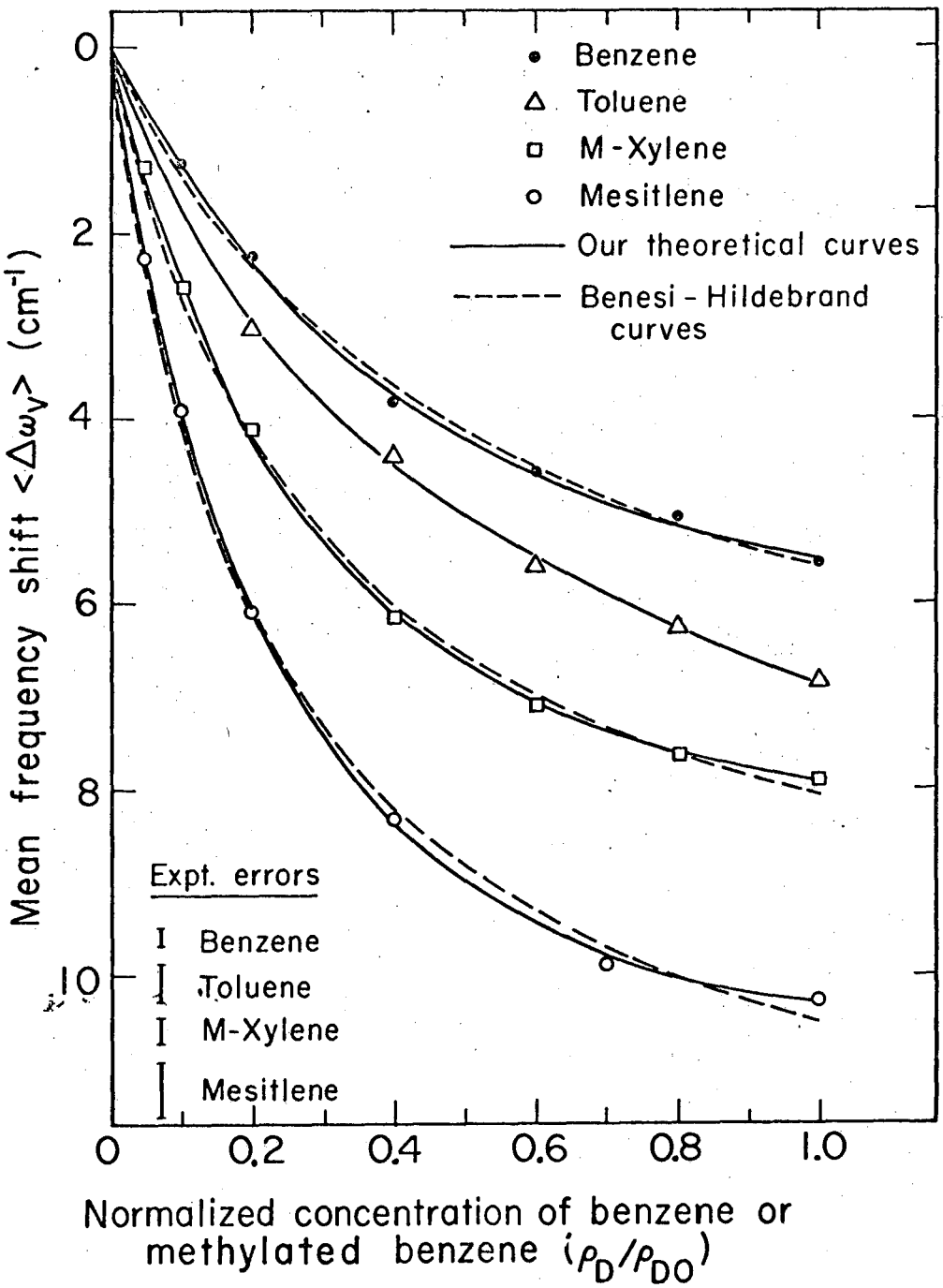
Fig. 1a



XBL697-3277

Fig. 1b

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