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THEORY OF COMPLEXES IN SOLUTIONS.
I. STATISTICAL THEORY

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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[3] 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.[4] 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 $\underset{\sim}{r}_1$, ---, $\underset{\sim}{r}_n$ with respect to the "A" molecule could interact with the "A" molecule and the m "C" molecules at $\underset{\sim}{R}_1$ ---$\underset{\sim}{R}_m$ within V_o could affect the interaction between the "A" molecule and the "B" molecules. (Here, the notations $\underset{\sim}{r}$ and $\underset{\sim}{R}$ are generalized to indicate not only the positions but also the relative orientations fo "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,

$$X = X^{(n,m)}(\underset{\sim}{r}_1 \text{ --- } \underset{\sim}{r}_n;\ \underset{\sim}{R}_1, \text{ ---} R_m). \tag{1}$$

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

$$\langle X \rangle = \sum_{n,m} \int_{V_o} X^{(n,m)}(\underset{\sim}{r}_1 \text{ --- } \underset{\sim}{r}_n;\ \underset{\sim}{R}_1 \text{ ---} \underset{\sim}{R}_m) \times$$

$$\times\ \rho^{(n,m)}\ (\underset{\sim}{r}_1 \text{ ---} \underset{\sim}{r}_n;\ \underset{\sim}{R}_1 \text{ ---} \underset{\sim}{R}_m)\ d\underset{\sim}{r}_1 \text{ ---} dR_m \tag{2}$$

where $\rho^{(n,m)}(\underset{\sim}{r}_1 \text{ ---} r_n;\ \underset{\sim}{R}_1 \text{ ---} \underset{\sim}{R}_m)$ is the probability distribution function for the n "B" molecules at $\underset{\sim}{r}_1 \text{ ---} \underset{\sim}{r}_n$, and m "C" molecules at $\underset{\sim}{R}_1$, --- $\underset{\sim}{R}_m$, and we have the normalization condition

$$\sum_{n,m} \int_{V_o} \rho^{(n,m)}\ d\underset{\sim}{r}_1 \text{ ---} d\underset{\sim}{r}_n d\underset{\sim}{R}_1 \text{ ---} dR_m = 1.$$

From statistical mechanics, the probability distribution function $\rho^{(N,M)}(\underset{\sim}{r}_1 \text{ ---} r_N;\ \underset{\sim}{R}_1 \text{ ---} \underset{\sim}{R}_M)$ for N "B" molecules and M "C" molecules in the entire solution is given by [5]

$$\rho^{(N,M)}(r_1 \text{ ---} r_N;\ R_1 \text{ ---} R_M)$$

$$= [{}^1/N!M!\ Q_{N,M}]\ \exp[-\beta\Phi^{(N,M)}(\underset{\sim}{r}_1 \text{ ---} \underset{\sim}{r}_N;\ \underset{\sim}{R}_1 \text{ ---} \underset{\sim}{R}_M)] \tag{3}$$

where $\beta = {}^1/kT$

$$Q_{N,M} = \left({}^1/N!M!\right) \int_V \exp[-\beta\Phi^{(N,M)}]\ d\underset{\sim}{r}_1 \text{ ---} d\underset{\sim}{r}_N d\underset{\sim}{R}_1 \text{ ---} d\underset{\sim}{R}_M$$

and $\Phi^{(N,M)}(\underset{\sim}{r}_1 --- \underset{\sim}{r}_N; \underset{\sim}{R}_1 ---\underset{\sim}{R}_M)$ is the potential function for the particular distribution of "B" molecules at $\underset{\sim}{r}_1 --- \underset{\sim}{r}_N$ and M "C" molecules at $\underset{\sim}{R}_1 --- \underset{\sim}{R}_M$. The normalization condition for $\rho^{(N,M)}$ in a solution of volume V is

$$\int_V \rho^{(N,M)} d\underset{\sim}{r}_1 --- d\underset{\sim}{r}_N d\underset{\sim}{R}_1 --- d\underset{\sim}{R}_M = 1. \tag{4}$$

Then, the function $\rho^{(n,m)}$ can be derived from $\rho^{(N,M)}$ as[5]

$$\rho^{(n,m)}(\underset{\sim}{r}_1---\underset{\sim}{r}_n; \underset{\sim}{R}_1---\underset{\sim}{R}_m) = [{}^1/(N-n)!\ (M-m)!\ n!\ m!]$$
$$\times \int_{V-V_o} \rho^{(N,M)} d\underset{\sim}{r}_{n+1}---d\underset{\sim}{r}_N d\underset{\sim}{R}_{m+1}---d\underset{\sim}{R}_M. \tag{5}$$

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

$$\Phi^{(N,M)} = U^{(n,m)}(\underset{\sim}{r}_1---\underset{\sim}{r}_n; \underset{\sim}{R}_1---\underset{\sim}{R}_m) + \Phi'^{(n,m)}(\underset{\sim}{r}_{n+1}---\underset{\sim}{r}_N; \underset{\sim}{R}_{m+1}---\underset{\sim}{R}_M) \tag{6}$$

where $U^{(n,m)}(\underset{\sim}{r}_1---\underset{\sim}{r}_n; \underset{\sim}{R}_1---\underset{\sim}{R}_m)$ is the interaction potential for the particular distribution of n "B" molecules at $\underset{\sim}{r}_1,---,\underset{\sim}{r}_n$ and m "C" molecules at $\underset{\sim}{R}_1,---,\underset{\sim}{R}_m$ 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),

$$\rho^{(n,m)} = \left[{}^1/(N-n)!\ (M-m)!\ n!\ m!\right]\left({}^1/N!M!Q_{NM}\right)\exp[-\beta U^{(n,m)}]$$
$$\times \int_{V-V_o} \exp[-\beta\Phi'^{(n,m)}] d\underset{\sim}{r}_{n+1}---d\underset{\sim}{r}_N d\underset{\sim}{R}_{m+1}---d\underset{\sim}{R}_M \tag{7}$$

where Q_{NM} can also be written in the form

$$Q_{NM} = \left({}^{1}/N!M!\right) \sum_{n,m} \left[{}^{1}/(N-n)!\ (M-m)!\ n!\ m!\right]$$
$$\times \int_{V_o} \exp[-\beta U^{(n,m)}] d\underset{\sim}{r}_1 \text{---} d\underset{\sim}{r}_n d\underset{\sim}{R}_1 \text{---} d\underset{\sim}{R}_m$$
$$\times \int_{V-V_o} \exp[-\beta \Phi'^{(n,m)}] d\underset{\sim}{r}_{n+1} \text{---} d\underset{\sim}{r}_N d\underset{\sim}{R}_{m+1} \text{---} d\underset{\sim}{R}_M . \qquad (8)$$

With Eqs. (7) and (8), we can now obtain from Eq. (2) an expression for the observed quantity $\langle X \rangle$ 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 $\langle X \rangle$ can be greatly simplified if $(n+m)_{max}$ 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 $(n+m)_{max}$ 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 $(n+m)_{max}=1$). 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

$$\rho^{(1,0)}(\underset{\sim}{r}) = (N/Z)\ \exp[-\beta U^{(1,0)}(\underset{\sim}{r})]$$

$$\rho^{(0,1)}(\underset{\sim}{R}) = (MC_2/Z)\ \exp[-\beta U^{(0,1)}(\underset{\sim}{R})] \tag{9}$$

where

$$Z = C_1 + N\int_{V_o} \exp[-\beta U^{(1,0)}]\ d\underset{\sim}{r} + C_2 M\int_{V_o} \exp[-\beta U^{(0,1)}]d\underset{\sim}{R}$$

$$C_1 = \int_{V-V_o} \exp[-\beta\Phi'^{(0,0)}]d\underset{\sim}{r}_1 --- d\underset{\sim}{R}_M / \int_{V-V_o} \exp[-\beta\Phi'^{(1,0)}]d\underset{\sim}{r}_2 --- d\underset{\sim}{R}_M$$

$$C_2 = \int_{V-V_o} \exp[-\beta\Phi'^{(0,1)}]d\underset{\sim}{r}_1 --- d\underset{\sim}{r}_N d\underset{\sim}{R}_2 --- d\underset{\sim}{R}_M / \int_{V-V_o} \exp[-\beta\Phi'^{(1,0)}]d\underset{\sim}{r}_2 --- d\underset{\sim}{R}_M.$$

To find C_1 and C_2, we notice that in the absence of the "A" molecule, we would expect $U^{(1,0)}(\underset{\sim}{r}) \approx U^{(0,1)}(\underset{\sim}{R}) = \Delta\Phi$ and we should have $(1/V_o) \int_{V_o} \rho^{(1,0)} d\underset{\sim}{r} = \rho_B = N/V$ and $(1/V_o) \int_{V_o} \rho^{(0,1)} d\underset{\sim}{R} = \rho_C = M/V$. Using Eq. (9) together with these conditions, we find readily

$$C_1 = V(1-\rho_B V_o - \rho_C V_o)\ \exp[-\beta\langle \Delta\Phi \rangle]$$

$$C_2 = 1 \tag{10}$$

where

$$\exp[-\beta \langle \Delta\Phi \rangle] \equiv (1/V_o)\int_{V_o} \exp(-\beta\Delta\Phi)d\underset{\sim}{r}.$$

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

$$\langle X \rangle = \Big\{\rho_B\int_{V_o} X^{(1,0)} \exp[-\beta(U^{(1,0)} - \langle \Delta\Phi \rangle)]d\underset{\sim}{r} +$$

$$+ \rho_C \int_{V_o} X^{(0,1)} \exp[-\beta(U^{(0,1)} - \langle \Delta\Phi \rangle)] d\underset{\sim}{R} \Big\}$$

$$\times \; {}^{1}/\Big\{(1 - \rho_B V_o - \rho_C V_o) + \; .$$

$$+ \rho_B \int_{V_o} \exp[-\beta(U^{(1,0)} - \langle \Delta\Phi \rangle)] d\underset{\sim}{r} + \rho_C \int_{V_o} \exp[-\beta(U^{(0,1)} - \langle \Delta\Phi \rangle)] d\underset{\sim}{R} \Big\} \tag{11}$$

In the case of liquid solution of constant volume V, there exists the relation $(\rho_B/\rho_{Bo}) + (\rho_C/\rho_{Co}) = 1$, with ρ_{Bo} and ρ_{Co} 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 $1 - (\rho_B + \rho_C)V_o \approx 0$ in Eq. (11). Physically, we are often interested in the variation of the quantity

$$\langle \Delta X \rangle = \langle X \rangle - \langle X_C \rangle \tag{12}$$

as a function of ρ_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

$$\langle X_C \rangle = \langle X^{(0,1)} \rangle = \int_{V_o} X^{(0,1)} \exp[-\beta U^{(0,1)}] d\underset{\sim}{R} / \int_{V_o} \exp[-\beta U^{(0,1)}] d\underset{\sim}{R} \tag{13}$$

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

$$\langle \Delta X \rangle = \frac{\rho_B \int_{V_o} [X^{(1,0)} - \langle X_C \rangle] \exp[-\beta U^{(1,0)}] d\underset{\sim}{r}}{\rho_B \int_{V_o} \exp[-\beta U^{(1,0)}] d\underset{\sim}{r} + [1 - {}^{\rho_B}/\rho_{Bo}] \rho_{Co} \int_{V_o} \exp[-\beta U^{(0,1)}] d\underset{\sim}{R}} \; . \tag{14}$$

Inversion of the above equation leads to the form

$$1/\langle \Delta X \rangle = (1/\Delta X_o) + (1/K\Delta X_o \, \rho_{Bo})(\rho_{Bo}/\rho_B) \tag{15}$$

where

$$\Delta X_o = \int_{V_o} [X^{(1,0)} - \langle X_C \rangle] \exp[-\beta U^{(1,0)}] d\underset{\sim}{r}$$
$$\times \, 1/\int_{V_o} \{\exp[-\beta U^{(1,0)}] - (\rho_{Co}/\rho_{Bo}) \exp[-\beta U^{(0,1)}]\} d\underset{\sim}{r}$$

$$K = \int_{V_o} \{\exp[-\beta U^{(1,0)}] - (\rho_{Co}/\rho_{Bo}) \exp[-\beta U^{(0,1)}]\} d\underset{\sim}{r}$$
$$\times \, 1/\rho_{Co} \int_{V_o} \exp[-\beta U^{(0,1)}] d\underset{\sim}{r}.$$

Equation (15) is in the form of the Benesi-Hildebrand equation.[6] The quantities $\langle \Delta X \rangle$, ΔX_o, and K in Eq. (15) corresponds respectively to the observed uv extinction coefficient $\langle \varepsilon \rangle$, the uv extinction coefficient for complexes ε_C, and the equilibrium constant K_{eq} in their equation. However, the physical meanings of ΔX_o and K in our case are rather different from those of ε_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, ΔX_o 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 ($\rho_C = 0$),

$$K_{eq} = \rho_K/(\rho_A - \rho_K)\rho_B \tag{16}$$

for the case where the density of "B" molecules, ρ_B, is much larger than the density of "A" molecules, ρ_A. The density of complex molecules is ρ_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

$$\rho_K = \rho_A \int_{V_I} \rho^{(1,0)} d\underset{\sim}{r}. \tag{17}$$

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

$$\rho_K = \frac{\rho_A \rho_B \int_{V_I} \exp[-\beta(U^{(1,0)} - \langle \Delta\Phi \rangle)] d\underset{\sim}{r}}{(1 - \rho_B V_o) + \int_{V_o} \exp[-\beta(U^{(1,0)} - \langle \Delta\Phi \rangle)] d\underset{\sim}{r}}$$

$$K_{eq} = \int_{V_I} \exp[-\beta(U^{(1,0)} - \langle \Delta\Phi \rangle)] d\underset{\sim}{r}/(1 - \rho_B V_I). \tag{18}$$

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

$$\Delta X_o = \frac{\int_{V_o} \Delta X^{(1,0)} \exp[-\beta(U^{(1,0)} - \langle \Delta\Phi \rangle)] d\underset{\sim}{r}}{\int_{V_o} \{\exp[-\beta(U^{(1,0)} - \langle \Delta\Phi \rangle)] - 1\} d\underset{\sim}{r}}$$

$$K = \int_{V_o} \{\exp[-\beta(U^{(1,0)} - \langle \Delta\Phi \rangle)] - 1\} d\underset{\sim}{r}. \tag{19}$$

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 ρ_B as shown in Eq. (20).

In gas mixtures, we can also have ρ_C = constant, but vary ρ_B. For this case, Eq. (15) still holds if we define $\langle X_C \rangle = \langle X \rangle_{\rho_{B=0}}$. The expression for ΔX_o 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_o, Eqs. (7) and (8) yield

$$\rho^{(2,0)}=[N(N-1)/2Z_2]\exp[-\beta U^{(2,0)}]\int_{V-V_o}\exp[-\beta\Phi'^{(2,0)}]d\underset{\sim}{r}_3\cdots d\underset{\sim}{r}_N d\underset{\sim}{R}_1\cdots d\underset{\sim}{R}_M.$$

$$\rho^{(1,1)}=[NM/Z_2]\exp[-\beta U^{(1,1)}]\int_{V-V_o}\exp[-\beta\Phi'^{(1,1)}]d\underset{\sim}{r}_2\cdots d\underset{\sim}{r}_N d\underset{\sim}{R}_2\cdots d\underset{\sim}{R}_M.$$

$$\rho^{(0,2)}=[M(M-1)/2Z_2]\exp[-\beta U^{(0,2)}]\int_{V-V_o}\exp[-\beta\Phi'^{(0,2)}]d\underset{\sim}{r}_1\cdots d\underset{\sim}{r}_N d\underset{\sim}{R}_3\cdots d\underset{\sim}{R}_M. \tag{21}$$

where

$$Z_2 = (N!M!)^2 Q_{NM}\big|_{n+m=2}.$$

Again, we are often interested in the quantity

$$\langle \Delta X \rangle = \langle X \rangle - \langle X_C \rangle$$

$$= \sum_{\substack{n,m \\ n+m=2}} \int_{V_o} [X^{(n,m)} - \langle X_C \rangle] \rho^{(n,m)} d\underset{\sim}{r}_1 --- d\underset{\sim}{r}_n d\underset{\sim}{R}_1 --- d\underset{\sim}{R}_m \qquad (22)$$

with

$$\langle X_C \rangle = \langle X^{(0,2)} \rangle = \int_{V_o} X^{(0,2)} \exp[-\beta U^{(0,2)}] d\underset{\sim}{R} d\underset{\sim}{R}'$$

$$\times \, 1 \Big/ \int_{V_o} \exp[-\beta U^{(0,2)}] d\underset{\sim}{R} d\underset{\sim}{R}'$$

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

$$1/\langle \Delta X \rangle = [1 + a\,(\rho_B/\rho_{Bo}) + b(\rho_B/\rho_{Bo})^2]/[c(\rho_B/\rho_{Bo}) + d\,(\rho_B/\rho_{Bo})^2] \qquad (23)$$

where

$$a = 2\int_{V_o} \left\{ (\rho_{Bo}/\rho_{Co}) \exp[-\beta(U^{(1,1)} - \langle U^{(0,2)} \rangle)] - 1 \right\} d\underset{\sim}{r} d\underset{\sim}{r}'$$

$$b = \int_{V_o} \left\{ (\rho_{Bo}/\rho_{Co})^2 \exp[-\beta(U^{(2,0)} - \langle U^{(0,2)} \rangle)] \right.$$

$$\left. -2(\rho_{Bo}/\rho_{Co}) \exp[-\beta(U^{(1,1)} - \langle U^{(0,2)} \rangle)] + 1 \right\} d\underset{\sim}{r} d\underset{\sim}{r}'$$

$$c = 2\int_{V_o} \left\{ (\rho_{Bo}/\rho_{Co}[X^{(1,1)} - \langle X_C \rangle] \exp[-\beta(U^{(1,1)} - \langle U^{(0,2)} \rangle)] \right\} d\underset{\sim}{r} d\underset{\sim}{r}'$$

$$d = \int_{V_o} \left\{ (\rho_{Bo}/\rho_{Co})^2 [X^{(2,0)} - \langle X_C \rangle] \exp[-\beta(U^{(2,0)} - \langle U^{(0,2)} \rangle)] \right.$$

$$\left. -2(\rho_{Bo}/\rho_{Co})[X^{(1,1)} - \langle X_C \rangle] \exp[-\beta(U^{(1,1)} - \langle U^{(0,2)} \rangle)] \right\} d\underset{\sim}{r} d\underset{\sim}{r}'$$

(24)

with $\langle U^{(0,2)} \rangle$ defined by the relation

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

We recall that in the present case, V_o 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 $U^{(2,0)} = 2U^{(1,1)}$.[7] We also assume that the interaction potential between "A" and "B" is much larger than "A" and "C" ($U^{(2,0)} >> U^{(1,1)} >> U^{(0,2)}$). 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 ρ_{Bo}/ρ_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 ρ_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[8] 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_o 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_o 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_o should be a quotient with p^{th}-order polynomials of (ρ_B/ρ_{Bo}) 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 $^{1}/\langle \Delta X \rangle$ vs ρ_{Bo}/ρ_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 the following paper, where we apply our theory to Raman scattering from iodine complexes in solutions.

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