Vibrational energy transfer in solutions: From diffusive to impulsive binary collisions

Rony Granek and Abraham Nitzan

School of Chemistry, The Sackler Faculty of Science, Tel Aviv University, Tel Aviv 69978, Israel

Eric Weitz

Department of Chemistry, Northwestern University, Evanston, Illinois 60208

The effect of diffusion on energy transfer from excited donor to acceptor molecules in liquid solutions is studied with particular attention focused on vibrational energy transfer between solute molecules in dilute solutions. Such processes are often discussed in the independent binary collision (IBC) framework and diffusion effects are assumed to be negligible. We introduce the concept of diffusive collisions (encounters between acceptor and donor molecule within an effective energy transfer range) and investigate the conditions under which the cross section for the energy transfer process may be affected by the cross section for the diffusive collision as opposed to the more common fast diffusion limit where the energy transfer is dominated by direct binary collisions. We conclude that while in most common situations vibrational energy transfer is indeed dominated by binary collision events, pronounced diffusion effects should exist at moderately high pressures. Explicit estimates are provided for the HCl/Xe system.

I. INTRODUCTION

The process of energy transfer from an excited (donor) molecule to an acceptor molecule can proceed in one (or a combination) of two pathways: (a) long range energy transfer by dipolar or exchange interaction,[1,2] or (b) short range "contact" collisions between the donor and acceptor molecules when both are found within the same solvent "cage." In addition, diffusion of the donor and/or the acceptor molecules, when possible, may strongly affect the rate of energy transfer both because of the strong distance dependence of long range energy transfer and because of the proximity required for collisional energy transfer.

When the energy transfer process involves electronic excitations, the usually large dipole–dipole coupling together with the fact that the time duration of the overall processes is limited by the lifetime (typically 10^{-9} s for an allowed transition) of an excited molecule imply that long range energy transfer, sometimes modified by diffusion, is the dominant mechanism. In the absence of diffusion this leads to[1,3-6]

$$C_{B^*}(t) = C_{B^*}^0 \exp[-t/\tau_{B^*} - 4\pi C_A (\pi a t)^{1/2}/3],$$
$$(1.1)$$

where $C_{B^*}(t)$ is the concentration of excited donor molecules at time t, $C_{B^*}^0$ is the same quantity at time $t = 0$, C_A is the concentration of acceptor molecules (assumed constant), τ_{B^*} is the lifetime of B* for all processes except intermolecular energy transfer. Intermolecular energy transfer is assumed to take place via the dipole–dipole interaction, i.e., the transfer rate is given by

$$W(r) = \frac{\alpha}{r^6}.$$
$$(1.2)$$

The effect of diffusion on this process has been studied by many authors. These studies have been recently reviewed.[7] If we disregard spontaneous decay of the donor and focus on the energy transfer process described by

$$\frac{dC_{B^*}}{dt} = -k(t)C_{B^*}C_A,$$
$$(1.3)$$

then good approximations for $k(t)$ are available in the extreme limit of strong and weak diffusion defined according to $Z_0 \ll 1$ or $Z_0 \gg 1$, respectively, where

$$Z_0 = \frac{1}{2}\sqrt{\frac{\alpha}{D}}/a^2.$$
$$(1.4)$$

a is the contact distance between the donor and acceptor within which energy transfer is assumed to occur instantaneously. In the first case ($Z_0 \ll 1$) one obtains the usual result for diffusion controlled reactions,[8]

$$k(t) = 4\pi Da(1 + a/\sqrt{\pi Dt}),$$
$$(1.5)$$

while in the other limit ($Z_0 \gg 1$),[9] at long time

$$k(t \to \infty) = 2.704\pi D(\alpha/D)^{1/4}.$$
$$(1.6)$$

For intermediate times and intermediate values of Z_0 full numerical solutions of the distribution function $P(r,t)$

$$\frac{\partial P(r,t)}{\partial t} = D\nabla^2 P - \frac{\alpha}{r^6}P$$
$$(1.7)$$

may be used and good agreement with experiment is usually obtained.[10]

While the physical ingredients in the case of vibrational energy transfer are similar to those discussed above for electronic energy transfer, the different time scales associated with the former process often makes the actual physical behavior different for this case. First, the transition dipole for vibrational energy transfer is ~3 orders of magnitude smaller than for electronic energy transfer, making long range dipole–dipole coupling 6 orders of magnitude slower. Secondly, the spontaneous relaxation time due to infrared radiative decay and to solvent induced relaxation can be

quite long, especially for small molecules and low temperatures.[11] It is therefore not surprising that in many situations and provided that the acceptor concentration is not too low, energy transfer may be dominated by close collisional encounters by the donor and acceptor molecules. Indeed, independent binary collision (IBC) models[12,13] have been used successfully to account for vibrational energy transfer in liquids, mostly in situations involving energy transfer to the solvent[14] but also in processes where donor and acceptor molecules exist in relatively low concentrations in an inert solvent.[15]

In the IBC model one assumes that the energy transfer process (or generally the bimolecular reaction) in solution proceeds via independent binary collisions between donor and acceptor molecules (reactants), and that the cross section is identical to that of the gas phase process. Under this assumption, the bimolecular reaction rate in solution is given by

$$k(\text{solution}) = k(\text{gas})g(\rho,T,\chi;a)/g(0,T,\chi;a), \qquad (1.8)$$

where $g(\rho,T,\chi;a)$ is the radial pair distribution function for the two reactants at contact distance, $r = a$, for total density ρ, and composition χ (χ denotes the set of molar fractions of the components). $\rho = 0$ is the zero density limit. Obviously this model assumes that the occurrence of the chemical reaction does not disturb the thermal equilibrium in the solution and, when applied to energy transfer, neglects long range transfer. The assumption of thermal equilibrium corresponds to the fast diffusion limit where mixing of the reactants overcomes their depletion by the reaction.

In this paper we generalize the treatment of energy transfer in solutions and develop a framework which yields the IBC model and the diffusion controlled kinetics as particular limits (Sec. III), thus making it possible to predict the conditions under which the finite diffusion rates of donors and acceptors start to affect the observed energy transfer rate. Since vibrational energy transfer in solutions is primarily controlled by binary encounters, it is convenient to cast the whole process, including the long range energy transfer mechanism in the framework of collisional processes. For this purpose, in Sec. II we introduce the concept of diffusive collisions and show that a stochastic theory of such collisions leads to standard results for the fast diffusion reaction rate in the low concentration limit. Short range collisions and cage effects are considered within this framework in Sec. III. In Sec. IV we use this theory to develop a unified picture of energy transfer kinetics in solutions. We conclude by making some numerical estimates and predictions for vibrational energy transfer in solutions.

II. DIFFUSIVE COLLISIONS

Consider a system in which reactant molecules B and A diffuse in an inert solvent and react with each other with a distance dependent bimolecular rate constant $W(r)$ for $r \geqslant a$. For $r = a$ we take reflective boundary conditions for the diffusion process (we shall later consider more general situations). r is the instantaneous distance between the donor (B) and acceptor (A) molecules. The reaction or energy transfer process is assumed irreversible. We also assume that the con-
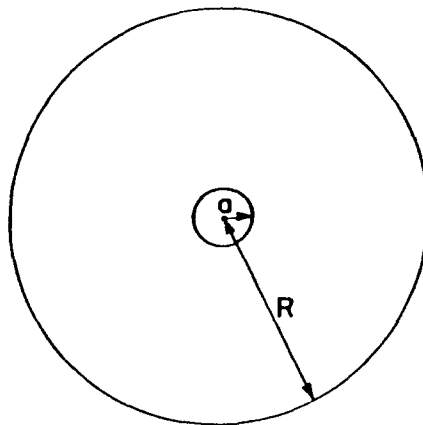

FIG. 1. Schematic of the collisional diffusion model as described in Sec. II. R is the assumed range of the interaction and a is the "reaction" radius.

centration of A and B molecules is low enough, so that at any instant, for a particular A (or B) molecule, at most one (nearest neighbor) B (or A) molecule has to be considered as a candidate for reaction. Focusing on a particular A molecule taken to be at the origin, we consider a sphere of radius R large enough so that reactive events occurring at distances larger than R are negligible (see Fig. 1). (The average distance d between A molecules has to be large enough for $R < d/2$ to satisfy this requirement. The specific value of R is otherwise unimportant.) We also assume the B molecules to react with A independently of each other (implying low concentration of B) and that, upon reaction, B disappears but A remains intact. [This corresponds to energy transfer from donor (B) molecules to acceptor (A) molecules followed by fast relaxation of A.] Note that with the coordinate system defined above, the diffusion coefficient D used henceforth is the sum of the diffusion coefficient of the two species.[10]

The model presented above corresponds to a reaction which may occur with some probability once a "collision" occurs. Note that this model assumes that diffusion is fast enough; otherwise, as is the case in solids, for long enough times energy transfer will be dominated by long range $r > R$ events.

Let $\gamma(R)$ be the probability that given that a B molecule entered the sphere of radius R, it reacts with the center A molecule before exiting the sphere. Also let $J_{\text{in}}(R)$ be the steady state flux of B molecules into this sphere. The steady state bimolecular reaction (or energy transfer) rate per unit volume is then

$$\Gamma = \gamma(R)J_{\text{in}}(R)C_{\text{A}}, \qquad (2.1)$$

where C_{A} is the concentration of A. Obviously $J_{\text{in}}(R)$ is proportional to C_{B}. The bimolecular rate constant is thus

$$k = \gamma(R)J_{\text{in}}(R)/C_{\text{B}} \qquad (2.2)$$

and should not depend on the arbitrarily chosen R ($R \gg a$ is always implied). Before we calculate $\gamma(R)$ and $J_{\text{in}}(R)$ we consider some general properties of diffusive collisions. We shall use continuous diffusion theory, however some of our intermediate results will be expressed in terms of a minimum length l (conveniently thought of as the mean free path) for

the diffusion process. Thus, a molecule B is considered to have entered the interaction sphere of radius R surrounding A when its distance from A becomes $r = R - l$. This molecule B has left the sphere when its distance from the center becomes $r = R$. A more rigorous calculation based on a discrete random walk model leads to results identical to those obtained below.[16]

In Appendix A we calculate some properties of diffusive collisions. Here we present the results needed for the rest of our analysis:

(a) The average duration $T(R)$ of a diffusive collision, namely the average time elapsed between entering the interaction sphere and leaving it for the first time is given by

$$T(R) = \frac{Rl}{3D}.\qquad(2.3)$$

(b) The average time spent by the diffusing molecule at the distance range $r...r + dr$ from the center during a single diffusive collision is

$$\tau(r;R)dr = \frac{lr^2}{DR^2}\,dr.\qquad(2.4)$$

Note that $\int_a^R dr\,\tau(r;R)$ gives $T(R)$ of Eq. (2.3) if we use $R \gg a$.

Consider now the reaction probability $\gamma(R)$ per diffusive collision. It is given by

$$\gamma(R) = 1 - P_s(R)$$
$$= 1 - \left\langle\exp\left(-\int_o^T dt\, W[r(t)]\right)\right\rangle_{\substack{r(0) = R - l}},\qquad(2.5)$$

where T is the first exit time [time for which $r(T) = R$ for the first time]. Note that both T and $r(t)$ in Eq. (2.5) are stochastic variables. Equation (2.5) may also be written as a moment expansion

$$\gamma(R) = \sum_{n=1} \frac{(-1)^{n-1}}{n!}\,U_n(R - l),\qquad(2.6)$$

$$U_n(x) = \left\langle\left(\int_o^T dt\, W[r(t)]\right)^n\right\rangle_{r(0) = x}.\qquad(2.7)$$

The moments $U_n(x)$ are solutions of the following boundary value problem[17(a)]

$$D\frac{1}{x^2}\frac{d}{dx}\left(x^2\frac{dU_n}{dx}\right) + nU_{n-1}(x)W(x) = 0\qquad(2.8a)$$

with

$$U_n(R) = 0(n > 0); \quad \frac{dU_n}{dx}(x = a) = 0; \quad U_0 = 1.\qquad(2.8b)$$

Next consider $J_{in}(R)$, the flux of the excited donor (B) molecules into the interaction sphere. Note that this is not the net steady state flux, but the total flux into (and in the absence of reaction also out of) the sphere. This flux is independent of the particular reaction mechanism as long as equilibrium velocity distribution is maintained. To find it we consider the simple case

$$W(r) = \begin{cases} 0, & r > a \\ \infty, & r \leqslant a \end{cases}\qquad(2.9)$$

for which the steady state rate is obtained from the theory of diffusion controlled reactions

$$\Gamma = kC_A C_B = 4\pi DaC_A C_B.\qquad(2.10)$$

This rate can be also calculated using Eq. (2.1). For this case the reaction probability $\gamma(R)$ per diffusive collision is the probability that the diffusing particle, once it enters the sphere (i.e., starts at $r = R - l$) will reach $r = a$ before reaching $r = R$ for the first time. This probability is [cf. Eq. (A14) with $x = R - l$ using $R \gg l, a$] $\gamma(R) = la/R^2$, whence from Eq. (2.1),

$$\Gamma = \frac{la}{R^2}\,J_{in}(R)C_A.\qquad(2.11)$$

Comparing Eqs. (2.10) and (2.11) yields

$$J_{in}(R) = 4\pi R^2 C_B\,\frac{D}{l}.\qquad(2.12)$$

We note in passing that in Eq. (2.12) the quantity D/l plays the role of the thermal velocity v. Even though the quantity l was loosely defined, requirements of consistency force us to choose $l = D/v$.

A consistency check on these results is provided by the observation that the average number $N(R)$ of particles in the sphere, the incoming flux $J_{in}(R)$ and the average time $T(R)$ spent by a particle in the sphere per diffusive collision are related by

$$T(R) = N(R)/J_{in}(R).\qquad(2.13)$$

Using $N(R) = (4/3)\pi R^3 C_B$ and $J_{in}(R)$ from Eq. (2.12) we obtain again Eq. (2.3).

The results obtained above apply, under the conditions discussed, to any binary reactive process involving diffusion and long range reaction probability. For the familiar (albeit rarely relevant to vibrational energy transfer in solution) case of dipole–dipole energy transfer rate [Eq. (1.2)], Eq. (2.8) yields (for $R \gg l, a$)

$$U_1(R - l) = \frac{1}{3}\frac{la}{R^2}\,\epsilon,\qquad(2.14a)$$

$$U_2(R - l) = \frac{1}{7}\frac{la}{R^2}\,\epsilon^2,\qquad(2.14b)$$

$$U_3(R - l) = \frac{21}{220}\frac{la}{R^2}\,\epsilon^3,\qquad(2.14c)$$

$$U_4(R - l) = \frac{23}{270}\frac{la}{R^2}\,\epsilon^4,\qquad(2.14d)$$

$$U_5(R - l) = \frac{16\,901}{177\,840}\frac{la}{R^2}\,\epsilon^5,\qquad(2.14e)$$

and so on where

$$\epsilon = \frac{\alpha}{Da^4} = \frac{(D/a^2)^{-1}}{(\alpha/a^6)^{-1}}.\qquad(2.15)$$

These and higher order moments are easily generated using computer programs for symbolic manipulations such as MACSYMA or REDUCE. It is seen that Eq. (2.6) is an expansion in the parameter ϵ which is the ratio between the diffusion time across the distance a and the energy transfer time at this distance. This parameter is small for small energy transfer rates and relatively fast diffusion—a typical situation in processes involving vibrational energy transfer in li-

quids (it is also quite small for most electronic energy transfer processes in normal liquids). Note also that all moments (of any order) are linear in the small parameter al/R^2.

These results, Eqs. (2.14), together with Eqs. (2.2) and (2.12) lead to

$$k = 4\pi \frac{\alpha}{a^3} \left(\frac{1}{3} - \frac{1}{14} \epsilon + \frac{7}{440} \epsilon^2 \right.$$
$$\left. - \frac{23}{6480} \epsilon^3 + \frac{16\,901}{21\,340,800} \epsilon^4 - ... \right). \qquad (2.16)$$

The first two terms in this expansion about the fast diffusion limit have been previously obtained by Sibani and Pedersen.[18] Equations (2.6)–(2.8) provide a systematic way for generating higher order terms in this expansion. Note that this final result does not depend on the arbitrary choice of R or on the discretization parameter l.

III. BRIDGING BETWEEN THE DIFFUSION AND THE COLLISION CONTROL LIMITS

In Sec. II we focused on the role played by the diffusion process and by the long range distance dependent reaction rate. We now modify the model of Sec. II in the following way: In addition to the sphere of radius R in which diffusive motion and long range energy transfer occur, we define a cage sphere of radius r_c also surrounding the acceptor molecule (Fig. 2). Within the cage the relative motion of the A and B molecules is ballistic even if random, and energy transfer is dominated by the short range collisions. The cage radius r_c satisfies

$$a < r_c < a + l. \qquad (3.1)$$

In a somewhat loose way we make the model assumption that entering the cage corresponds to hopping from $r = a + l$ to $r = a$, while leaving it involves the opposite hop. When the particle entered the cage (reached $r = a$) it has a probability q to exit it (to $r = a + l$). For $r < r_c$ we assume that the evolution is governed by independent binary collisions (IBCs) whose efficiency will determine the exit probability q.

As before we consider a single diffusive collision (the diffusing particle starts at $r_0 = R - l$). We consider first the
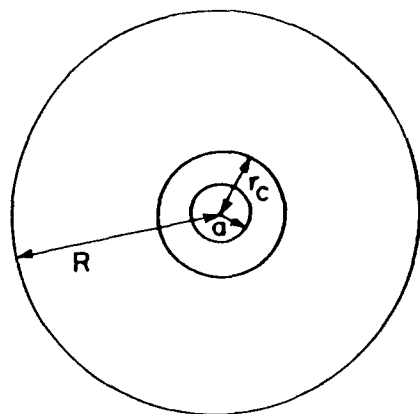

FIG. 2. Schematic of a model including diffusive collisions and cage formation. r_c is the cage radius.

situation where there is no long range reaction: all energy transfer occurs in the cage $r < r_c$. Let $P(r_0 \to R)$ be the probability that the particle goes from r_0 to R (and terminates the diffusive collision) without going through $r = a$. Similarly $P(r_0 \to a)$ denotes the probability that in a single diffusive collision (without going through R) the particle reaches a. Also $P(a + l \to R)$ and $P(a + l \to a)$ are the probabilities that a particles which starts just outside the cage ($r = a + l$) will exit ($r = R$) without ever entering the cage, or enter the cage ($r = a$) before ever exiting, respectively. Note that

$$P(r_0 \to a) + P(r_0 \to R) = 1, \qquad (3.2)$$

$$P(a + l \to R) + P(a + l \to a) = 1. \qquad (3.3)$$

In terms of these quantities, and the probability q to leave the cage, the probability P_s to survive a diffusive collision is

$$P_s = P(r_0 \to R) + P(r_0 \to a)q \; [P(a + l \to R)$$
$$\qquad + P(a + l \to a) \; q[P(a + l \to R)$$
$$\qquad + P(a + l \to a)q[...[...]$$
$$= P(r_0 \to R) + \frac{P(r_0 \to a)qP(a + l \to R)}{1 - qP(a + l \to a)}. \qquad (3.4)$$

The probability $\gamma(R) = 1 - P_s$ to react during the diffusive collision is

$$\gamma(R) = P(r_0 \to a) \frac{1 - q}{1 - qP(a + l \to a)}. \qquad (3.5)$$

To get Eq. (3.5) we have used Eqs. (3.2) and (3.3). The probabilities $P(r_0 \to a)$ and $P(a + l \to a)$ may be calculated from the continuum diffusion formalism of Sec. II: Starting from position x, $a < x < R$, the probability to reach $r = a$ before reaching $r = R$ is [cf. Eq. (A14)] $(R - x)a/(R - a)x$. Putting $x = R - l$ we get (using $R \gg a,l$)

$$P(r_0 \to a) = \frac{la}{R^2} \qquad (3.6)$$

while putting $x = a + l$ leads to

$$P(a + l \to a) = \frac{a}{a + l}. \qquad (3.7)$$

Using Eqs. (3.5)–(3.7), and denoting by $W = 1 - q$ the probability for reaction when the diffusing particle has been trapped in the well we get

$$\gamma(R) = \frac{la(a + l)W}{R^2(l + aW)}. \qquad (3.8)$$

Next we estimate the cage reaction probability W assuming the validity of the IBC model. This probability is governed by two times: τ_{esc}, the mean time for a particle in the cage to escape the cage and τ_{relx}—the energy relaxation time for the donor in the cage. An estimate for τ_{esc} may be obtained as follows: It should be proportional to the diffusion time l^2/D and to the donor–acceptor radial pair distribution function at distance $r = a$, $g_{AB}(a)$ (g depends also on the solution density and composition).

$$\tau_{esc} = \lambda \frac{l^2}{D} g_{AB}(a). \qquad (3.9)$$

l^2/D measures the time for negotiating the cage in free diffusion. The factor $g_{AB}(a)$ arises from detailed balance consid-

erations. It takes into account the fact that the average escape time should be proportional to the average donor concentration in the cage. The parameter λ is of order 1 (see Appendix B).

Assuming an exponential distribution for the escape time, the reaction (or energy transfer) probability is

$$W = \frac{\tau_{esc}}{\tau_{esc} + \tau_{relx}} = \frac{\theta}{1 + \theta}, \qquad (3.10)$$

where

$$\theta = \frac{\tau_{esc}}{\tau_{relx}} = \frac{\lambda l^2 g_{AB}(a)}{D\tau_{relx}}. \qquad (3.11)$$

In terms of θ the rate k [using Eqs. (2.2), (2.12), (3.3), and (3.10)] is

$$k = 4\pi Da \frac{(a+l)\theta}{l + (a+l)\theta}. \qquad (3.12)$$

In the fast diffusion limit $\theta(a + l)/l \ll 1$ and $k = 4\pi Da\theta(a + l)/l$. Under the IBC assumption this should be equal to $k_0 g_{AB}(a)$, where k_0 is the ideal gas limit $[g_{AB}(a) = 1]$ of the bimolecular rate coefficient. This implies

$$\theta = \frac{k_0 g_{AB}(a)}{4\pi Da} \frac{l}{l + a}. \qquad (3.13)$$

This, with Eq. (3.11) provides some information on the parameter τ_{relx}. Indeed, taking λ from Eq. (B7) leads to

$$\frac{1}{\tau_{relx}} = \frac{k_o}{\frac{4}{3}\pi[(a+l)^3 - a^3]} \qquad (3.14)$$

providing an explicit estimate $\tau_{relx} \sim V_c/k_o$ for the cage relaxation time in terms of the cage free volume V_c and the ideal gas phase bimolecular rate coefficient. More relevant to the present discussion is the fact that Eqs. (3.12) and (3.13) lead to

$$\frac{1}{k} = \frac{1}{k_0 g} + \frac{1}{4\pi Da} \qquad (3.15)$$

which says that in this model, which has neglected long range energy transfer, the total donor relaxation time (per unit volume) is the sum of the diffusion and the collisional times.

Two comments should be made at this place: (a) The IBC result can be trivially generalized by replacing the relaxation $k_{IBC} = k_0 g$ by $k = k_0 g\lambda_c$ where λ_c is a correlation factor which accounts for the possibility of correlation between consecutive collisions in the cage. λ_c is an empirical

parameter which can also be estimated from numerical simulations. Recent simulations of vibrational relaxation of iodine in solutions[19] indicate that λ_c may be considerably larger than 1 under certain circumstances. Equation (3.15) is then replaced by

$$\frac{1}{k} = \frac{1}{k_0 g\lambda_c} + \frac{1}{4\pi Da} \qquad (3.15a)$$

(b). The result (3.15) could be derived from the theory of diffusion controlled reactions with radiative boundary condition at the contact distance a, by setting the boundary condition parameter such that the IBC rate is obtained in the infinite diffusion rate limit. In fact, the calculation given above is little more than performing this derivation in the diffusive collision framework. This becomes convenient when we next include long range energy transfer.

IV. THE COMBINED SOLUTION

In the previous sections we have focused on the diffusion effects on (a) the short range energy transfer rate, via IBC model (Sec. III), and (b) the long range (e.g., dipole–dipole) coupling rate, with the contact distance taken as an inert reflective boundary (Sec. II). In the present section we will derive a unified expression, which will combine both the short and long range effects. Long range, i.e., dipole–dipole, energy transfer is usually not important for vibrational energy transfer because of the small transition matrix element involved. However, for very low concentrations of donors and acceptors and for low diffusion rates this channel cannot be ruled out because of the long time it takes the molecules to approach each other. The results obtained below are of course valid also for electronic energy transfer.

Focusing again on a donor particle which starts at $r_0 = R - l$ we denote by $P_s(r_0 \to a)$ the conditional probability that a donor particle that diffused from $r = r_0$ to $r = a$ without exiting the R sphere (namely without passing through $r = R$) still remained excited upon reaching a. $P_s(r_0 \to R)$ is the probability that an excited donor that starts at r_0 and reaches R without passing through $r = a$ is still excited. [Note that $P(r_0 \to a)P_s(r_0 \to a)$ and $P(r_0 \to R)P_s(r_0 \to R)$ are the corresponding joint probabilities.] Similarly $P_s(a + l \to a)$ and $P_s(a + l \to R)$ are the corresponding excitation survival probabilities given that the donor which started at $r = a + l$ reached $r = a$ (without passing through R) or $r = R$ (without passing through a), respectively. Using these quantities, the probability to survive a diffusive collision can be written in the form

$$P_s = P(r_0 \to R)P_s(r_0 \to R) + P(r_0 \to a)P_s(r_0 \to a)q[P(a + l \to R)P_s(a + l \to R)$$

$$+ P(a + l \to a)P_s(a + l \to a)q[P(a + l \to R)P_s(a + l \to R) + ...[...[\quad]...]$$

$$= P(r_0 \to R)P_s(r_0 \to R) + \frac{qP(r_0 \to a)P_s(r_0 \to a)P(a + l \to R)P_s(a + l \to R)}{1 - qP(a + l \to a)P_s(a + l \to a)}. \qquad (4.1)$$

The probability $\gamma(R) = 1 - P_s$ to react during a diffusive collision is therefore [using Eq. (3.2)]

$$\gamma(R) = 1 - P_s(r_0 \to R) + P(r_0 \to a)\left[P_s(r_0 \to R)\right.$$
$$\left. - \frac{qP_s(r_0 \to a)P(a + l \to R)P_s(a + l \to R)}{1 - qP(a + l \to a)P_s(a + l \to a)}\right].$$
(4.2)

The calculation of the various survival probabilities up to second order in ϵ [Eq. (2.5)] is performed in Appendix A 3. Using Eqs. (A21a)–(A21c) for these quantities with Eqs. (3.3), (3.6), and (3.7) we find (with $l, a \ll R^2$)

$$\gamma(R) \simeq \frac{la}{R^2}\left(\frac{\epsilon}{30} - \frac{11}{12\,600}\epsilon^2\right.$$
$$\left. + 1 - \frac{lq\left(1 - \frac{\epsilon}{20} + \frac{91}{50\,400}\epsilon^2\right)^2}{lq\left(1 + \frac{\epsilon}{5} - \frac{\epsilon^2}{225}\right) + W(a + l)}\right).$$
(4.3)

Neglecting terms of high order than ϵ^2, we get after some algebra,

$$\gamma(R) \simeq \frac{la}{R^2}\left(\frac{\epsilon}{30} - \frac{11}{12\,600}\epsilon^2\right.$$
$$\left. + \frac{lq\left(\frac{3}{10}\epsilon - \frac{133}{12\,600}\epsilon^2\right) + W(a + l)}{lq\left(1 + \frac{\epsilon}{5} - \frac{\epsilon^2}{225}\right) + W(a + l)}\right).$$
(4.4)

Using also Eqs. (2.2), (2.12), and (3.10) we find the bimolecular rate in the form (with $\theta = \tau_{\rm esc}/\tau_{\rm relx}$)

$$k \simeq 4\pi Da\left[\frac{\epsilon}{30} - \frac{11}{12\,600}\epsilon^2\right.$$
$$\left. + \frac{\frac{3}{10}\epsilon - \frac{133}{12\,600}\epsilon^2 + \frac{a + l}{l}\theta}{1 + \frac{\epsilon}{5} - \frac{\epsilon^2}{225} + \frac{a + l}{l}\theta}\right].$$
(4.5)

Using Eq. (3.13) for θ, the rate in terms of IBC model is given by

$$k \simeq 4\pi\frac{\alpha}{a^3}\left(\frac{1}{30} - \frac{11}{12\,600}\epsilon\right)$$
$$+ \left(\frac{4\pi\frac{\alpha}{a^3}\left(\frac{3}{10} - \frac{133}{12\,600}\epsilon\right) + k_0 g_{\rm AB}(a)}{1 + \frac{\epsilon}{5} - \frac{\epsilon^2}{225} + \frac{k_0 g_{\rm AB}(a)}{4\pi Da}}\right).$$

with $\epsilon = \alpha/Da^4$. As mentioned in Sec. III, correlations between binary collisions may be phenomenologically taken into account by inserting a correlation factor λ_c that multiplies k_0.

To end this discussion, the fast and slow diffusion limits (compared to the short range transfer rate) should be examined. These are determined by the parameter x

$= k_0 g_{\rm AB}(a)/4\pi Da$. In the fast diffusion limit, $x \ll 1$, we get

$$k \simeq 4\pi\frac{\alpha}{a^3}\left(\frac{1}{3} - \frac{\epsilon}{14}\right) + \frac{k_0 g_{\rm AB}(a)}{1 + \frac{\epsilon}{5} - \frac{\epsilon^2}{225}}.$$
(4.7)

This is simply the sum of the long range contribution when the contact distance is treated as a reflective boundary [first two terms in Eq. (2.16)] and the short range (IBC) rate (modified by a factor which is usually only slightly less than unity). In the slow diffusion limit, $x \gg 1$, it can be easily seen that

$$k \simeq 4\pi\frac{\alpha}{a^3}\left(\frac{1}{30} - \frac{11}{12\,600}\epsilon\right) + 4\pi Da$$
(4.8)

which is the sum of the diffusion limited rate with quenching at contact and the long range energy transfer rate as can be seen by putting $q = 0$ in Eq. (4.2). Using the identity $4\pi\alpha/a^3 = 4\pi Da\epsilon$, Eq. (4.8) can be also written as

$$k \simeq 4\pi Da\left(1 + \frac{\epsilon}{30} - \frac{11}{12\,600}\epsilon^2\right).$$
(4.9)

The first two terms in this expansion were already derived by Sibani and Pedersen.[18]

V. EXPERIMENTAL IMPLICATIONS

While for electronic energy transfer in liquids diffusion effects have been observed experimentally, no such effects have been seen for vibrational energy transfer in solutions. In the latter systems the IBC model has been widely used. The results obtained in the previous sections show that indeed most processes of this kind correspond to the large diffusion rate situation. It is however of interest to explore the limits to this fast diffusion assumption, both because its failure may affect the interpretation of observed vibrational energy transfer and relaxation kinetics and for predictions of possible diffusion effects. The estimates provided below are for V–V energy transfer in the system HCl in Xe that was recently studied experimentally.[15(b)] From Eq. (3.15) written in the form

$$k = \frac{k_{\rm IBC}}{1 + x},$$
(5.1)

where

$$k_{\rm IBC} = k_0 g; \quad k_0 = \frac{k({\rm gas})}{g({\rm gas})};$$

and (using $D = 2D_{12}$) $x = \dfrac{k_0 g}{8\pi D_{12}a}$
(5.1a)

with D_{12} is the diffusion coefficient of HCl in Xe, we can predict deviations from the IBC model rate due to finite diffusion rate, with the factor $1/(1 + x)$ determining the deviation.

Data on transport properties of high density Xe may be found in Refs. 20–22. From Fig. 1 in Ref. 20 we find that the self-diffusion coefficient D_0 of Xe, at the temperature 298 K, in the density range 6.2 to 21.4 mol/ℓ varies approximately between 4.1×10^{-4} to 5.4×10^{-5} cm^2/s. For the diffusion coefficient D_{12} of HCl in Xe, we get from Ref. 23 Eqs. (8.2-

44,46) and (9.3–38).

$$
D_{12} = D_0 \left[\frac{1}{2}\left(1 + \frac{m_{Xe}}{m_{HCl}}\right)\right]^{1/2} \left(\frac{\sigma_{Xe}}{\sigma_{12}}\right)^2
$$

$$
\times \frac{\Omega^{(1,1)*}(T^*)\,Y(\rho;\sigma_{Xe})}{\Omega_{12}^{(1,1)*}(T_{12}^*)\,Y_{12}(\rho,\chi;\sigma_{12})} \tag{5.2}
$$

with $T^* = k_B T/\epsilon_{Xe}$, $T_{12}^* = k_B T/\epsilon_{12}$; where m_{Xe} and m_{HCl} are the molecular masses, χ is the molar fraction of HCl in the HCl/Xe mixture, and ρ is the total density; σ_{Xe}, σ_{12}, ϵ_{Xe}, ϵ_{12} are molecular (Lennard-Jones) potential energy parameters (effective diameters and well depths) characterizing the Xe–Xe and HCl–Xe interaction, respectively. Following Ref. 23 (Eqs. 3.6-8,9) we take $\sigma_{12} = \sigma_{Xe} + \sigma_{HCl}$; $\epsilon_{12} = \sqrt{\epsilon_{Xe}\epsilon_{HCl}}$ where σ_{HCl}, ϵ_{HCl} are the Lennard-Jones parameters for HCl–HCl interaction. The factors Y and Y_{12} are essentially the Xe–Xe and Xe–HCl radial pair distribution functions at contact and for low concentrations of HCl are approximately equal. Their ratio in Eq. (5.2) is taken as 1. The parameters $\Omega^{(1,1)*}$ are related mainly to the attractive part of the interaction and are available from Ref. 23 (Table I-M in the Appendix). From Ref. 23 (Tables 8.4-1 and 8.6-1) we have $\epsilon_{HCl}/k_B = 218$ K, $\sigma_{HCl} = 3.506$ Å, $\epsilon_{Xe}/k_B = 229$ K, $\sigma_{Xe} = 4.005$ Å.[24] At room temperature $T = 298$ K we have $T^* = 1.301$ and $T_{12}^* = 1.334$, whence $\Omega^{(1,1)*} = 1.273$ and $\Omega_{12}^{(1,1)*} = 1.260$. From this data we find that at 298 K, in the density range 6.2 to 21.4 mol/ℓ, D_{12} varies between 7.1×10^{-4} to 9.4×10^{-5} cm^2/s.

In Eq. (5.1a) we take a, the average hard sphere diameter of HCl, as twice the sum of H and Cl covalent radiuses; $a = 2.6$ Å. The contact values of the radial pair distribution function are [from Ref. 12(a) using the parameter values given above]: g(gas, 298 K) $= \exp(218/298)$, and (for low HCl concentration in high density Xe) $g = (1 - \mu/2)/(1 - \mu)^3$ with $\mu = (\pi/6)\rho\sigma_{Xe}^3$.[25] The value of k(gas) at 298 K is taken from Ref. 26 to be 0.90×10^5 s^{-1} Torr^{-1} or 1.17×10^{12} cm^3 mol^{-1} s^{-1} for the process

$$
\text{HCl}(v=2) + \text{HCl}(v=0) \rightarrow 2\text{HCl}(v=1).
$$
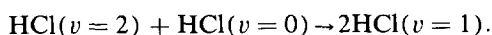
Using these and the semiempirical values of D_{12} we find that in the density range 6.2 to 21.4 mol/ℓ (studied experimentally in Ref. 20) the factor $1/(1+x)$ varies between 0.997 to 0.939. This variation is not sufficient for a clear cut experimental study. However, using the equation of state for Xe given in Ref. 27, we find that a pressure of ~ 7000 atm corresponds to Xe density of 45 mol/ℓ, and $1/(1+x) \sim 0.5$. While this is a rough and uncertain estimate, it suggests that observations of deviations from the IBC behavior is possible with modest high pressure systems.

To end this discussion we note that these corrections will be more pronounced if the correlation factor λ_c [Eq. (3.15a)] is considerably larger than 1. (We should keep in mind, however, that the density dependence of λ_c will make it difficult to interpret deviations from IBC behavior purely in terms of the theory advanced here.) Also, smaller diffusion rates and therefore larger deviations from the fast diffusion (IBC) limit may be obtained using other solute molecules (e.g., replacing HCl by HBr or HI).

APPENDIX A: SOME CONSEQUENCES OF THE DIFFUSION EQUATION

1. The exit problem for the diffusion equation in a sphere

Here we derive some properties of first exit problems for the diffusion process in a sphere. In particular we consider the spherical region $a \leqslant r \leqslant R$ (Fig. 1).

(a) Let

$$
U_n(x) = \left\langle \left(\int_0^T k\,[r(t)]\,dt\right)^n \right\rangle_{r(0)=x}, \tag{A1}
$$

where $r(t)$ is the position of the diffusing particle, T is the first exit time, $k(r)$ is an arbitrary function, and x is the starting position. r and T are stochastic variables. The average should be performed over all possible (infinite) trajectories.

Consider first regular diffusion where $r = R$ is the exit boundary and $r = a$ is a reflective boundary. Following Karlin,[17(a)] the U_n moment can be shown to obey the recursive differential equation

$$
D\frac{d^2 U_n}{dx^2} + \frac{2D}{x}\frac{dU_n}{dx} = -nk(x)U_{n-1}(x) \tag{A2}
$$

with

$$
\frac{dU_n}{dx}(x=a) = 0; \quad U_n(R) = 0\,(n>0); \quad U_0 = 1.
$$

It is convenient to use the Green function, defined as the solution of

$$
D\frac{d^2 G(x,r)}{dx^2} + \frac{2D}{x}\frac{dG(x,r)}{dx} = -\delta(x-r) \tag{A3}
$$

with

$$
\frac{dG}{dx}(x=a) = 0, \quad G(R) = 0.
$$

Using this Green function, the U_n moment can be expressed in terms of the U_{n-1} moment

$$
U_n = n\int_a^R G(x,r)k(r)U_{n-1}(r)\,dr. \tag{A4}
$$

In particular

$$
U_1(x) = \left\langle \int_0^T k\,[r(t)]\,dt \right\rangle_{r(0)=x} = \int_a^R G(x,r)k(r)\,dr. \tag{A5}
$$

From this relation we can see that $G(x,r)dr$ is the time spent in the interval $r...r + dr$ before exit. This Green function is

found to be

$$G(x,r) = \begin{cases} \dfrac{r^2}{D}\left(\dfrac{1}{r} - \dfrac{1}{R}\right), & a \leqslant x \leqslant r \leqslant R \\[2mm] \dfrac{r^2}{D}\left(\dfrac{1}{x} - \dfrac{1}{R}\right), & a \leqslant r \leqslant x \leqslant R \end{cases} \tag{A6}$$

Next we define a "conditioned diffusion" process.[17(b)] This process is built from regular diffusion, when it describes only trajectories that do not pass through a certain boundary, called an "entrance boundary." This condition is translated into a special drift term, which prevents the process to pass through the entrance boundary; however, it can start as close as we want to this boundary. Consider first $r = a$ as the entrance boundary, while $r = R$ is the exit. For the conditional process, the U_n moment defined in Eq. (A1) satisfies[17(b)]

$$D\frac{d^2 U_n}{dx^2} + \frac{2D}{x}\left(1 + \frac{a}{x-a}\right)\frac{dU_n}{dx} = -nk(x)U_{n-1}(x) \tag{A7}$$

and the related Green function, defined as the solution G_* of

$$D\frac{d^2 G_*}{dx^2} + \frac{2D}{x}\left(1 + \frac{a}{x-a}\right)\frac{dG_*}{dx} = -\delta(x-r) \tag{A8}$$

is found to be[17(c)]

$$G_*(x,r) = \begin{cases} \dfrac{(R-r)(r-a)}{D(R-a)}, & a \leqslant x \leqslant r \leqslant R \\[2mm] \dfrac{(R-x)(r-a)^2}{D(x-a)(R-a)}, & a \leqslant r \leqslant x \leqslant R \end{cases} \tag{A9}$$

Similarly, for the case when $r = a$ is the exit, and $r = R$ is the entrance, the related Green function is found to be[17(c)]

$$G_*(x,r) = \begin{cases} \dfrac{(x-a)(R-r)^2}{D(R-x)(R-a)}, & a \leqslant x \leqslant r \leqslant R \\[2mm] \dfrac{(R-r)(r-a)}{D(R-a)}, & a \leqslant r \leqslant x \leqslant R \end{cases} \tag{A10}$$

(b) Let $f(x)$ be the probability to arrive at $r = R$ for the first time before arriving at $r = a$, if the starting position is $r = x$. Similarly, $g(x)$ is the probability to arrive at $r = a$ for the first time without passing through $r = R$. It is therefore clear that

$$f(x) + g(x) = 1. \tag{A11}$$

$f(x)$ is the solution of the boundary value problem[17(d)]

$$\frac{d}{dx}\left(x^2\frac{df}{dx}\right) = 0 \tag{A12}$$

with $f(R) = 1$ $f(a) = 0$. This leads to

$$f(x) = \frac{R(x-a)}{a(R-a)}, \tag{A13}$$

$$g(x) = \frac{a(R-x)}{(R-a)x}. \tag{A14}$$

2. Diffusive collisions

Here we derive some of the properties related to diffusive collisions. A "diffusive collision" is defined as the event

in which a diffusive particle enters and leaves the interaction zone once. The fact of entering is established when the particle's distance from the center is $R - l$ where l is a typical hopping distance, and where the interaction is assumed to vanish for $r > R$.

First consider the average time spent by the diffusing particle at the distance range $r...r + dr$ in one collision. Using $x = R - l$ in Eq. (A16) with $R \gg l$, this time is

$$\tau(r;R)dr = \frac{l}{D}\frac{r^2}{R^2}dr \tag{A15}$$

while the total time of the diffusing collision is just

$$T(R) = \int_a^R \tau(r;R)dr = \frac{l(R^3 - a^3)}{3DR^2} \tag{A16}$$

for $R \gg a$

$$T(R) \simeq \frac{lR}{3D}. \tag{A17}$$

If we are interested only in trajectories that do not pass through $r = a$, we put $x = R - l$ in Eq. (A9) to get (using $R \gg l, a$)

$$\tau_*(r;R) = \frac{l}{D}\frac{(r-a)^2}{R^2}dr \tag{A18}$$

which gives the same $T(R)$ as in Eq. (A17) if we use $R \gg a$.

3. Survival probabilities for long range energy transfer

In this part we give some details of the calculation for the various survival probabilities needed in Sec. IV. The definitions given in Sec. IV are translated into the following: The quantities $P_s(R - l \to R)$ and $P_s(a + l \to R)$ are associated with conditional diffusion processes of the type discussed in Part II where $r = a$ is the entrance boundary, $r = R$ is the exit, and where the starting positions are $R - l$ and $a + l$, respectively; $P_s(R - l \to a)$ and $P_s(a + l \to a)$ are related to conditional diffusion processes where $r = R$ is the entrance, $r = a$ is the exit, and the starting positions are $R - l$ and $a + l$, respectively. Therefore, the appropriate Green functions are Eq. (A9) for $P_s(R - l \to R)$ and $P_s(a + l \to R)$, and Eq. (A10) for $P_s(R - l \to a)$ and $P_s(a + l \to a)$. Using these Green functions, the first and second moment (as a function of the starting position x) are, by Eq. (A4),

$$U_1(x) = \int_a^R G_*(x,r)k(r)dr, \tag{A19a}$$

$$U_2(x) = 2\int_a^R G_*(x,r)k(r)U_1(r)dr. \tag{A19b}$$

We set $x = R - l$ for the calculation of $P_s(R - l \to R)$ and $P_s(R - l \to a)$ and $x = a + l$ for $P_s(a + l \to R)$ and $P_s(a + l \to a)$; $R \gg a, l$ is always used. Finally, since by moment expansion

$$P_s(x) = \left\langle \exp\left(-\int_0^l k[r(t)]dt\right)\right\rangle_{r(0) = x}$$

$$= \sum_{n=0}^{\infty} \frac{(-1)^n}{n!}U_n(x) \tag{A20}$$

the surviving probabilities up to order ϵ^2 (where $\epsilon = \alpha/$

Da^4) are given by

$$P_s(a + l \rightarrow R) = P_s(R - l \rightarrow a)$$

$$\simeq 1 - \frac{\epsilon}{20} + \frac{91}{50\,400} \epsilon^2 + O(\epsilon^3), \text{(A21a)}$$

$$P_s(a + l \rightarrow a) \simeq 1 - \frac{l}{5a} \epsilon + \frac{1}{225} \frac{l}{a} \epsilon^2 + O(\epsilon^3),$$
$$\text{(A21b)}$$

$$P_s(R - l \rightarrow R) \simeq 1 - \frac{1}{30} \frac{la}{R^2} \epsilon$$

$$+ \frac{11}{12\,600} \frac{la}{R^2} \epsilon^2 + O(\epsilon^3). \quad \text{(A21c)}$$

APPENDIX B

Here we find τ_{esc}, the escape time from the cage, for the model considered in Sec. III. Consider a large sphere of radius R around the acceptor, containing one donor in it. The sphere is taken to be closed (reflecting boundary conditions at $r = R$). From equilibrium statistical mechanics, the probability of the donor and acceptor to be within the distance range $a \ldots a + l$, is

$$W(a, a + l) = \frac{\int_a^{a+l} 4\pi r^2 g_{\text{AB}}(r)dr}{\frac{4}{3}\pi R^3}, \quad \text{(B1)}$$

where $g_{\text{AB}}(r)$ is the radial pair distribution function. This probability should be also equal to the fraction of time for which the acceptor and donor are in this distance range during an infinitely long period. If τ_{in} is the average time to get back into the cage for the first time after escaping from it, then this fraction f is just $\tau_{\text{esc}}/(\tau_{\text{in}} + \tau_{\text{esc}})$. Assuming $g_{\text{AB}}(r)$ to vary slowly between a and $a + l$, we can approximate

$$\int_a^{a+l} 4\pi r^2 g_{\text{AB}}(r)dr \simeq \frac{4}{3} \pi[(a + l)^3 - a^3]g_{\text{AB}}(a)$$
$$\text{(B2)}$$

and therefore τ_{esc} can be obtained from

$$\frac{(a + l)^3 - a^3}{R^3} g_{\text{AB}}(a) \simeq \frac{\tau_{\text{esc}}}{\tau_{\text{in}} + \tau_{\text{esc}}} \quad \text{(B3)}$$

if τ_{in} is known. τ_{in} can be easily found by solving for the time to arrive at $r = a$ for the first time starting at $r = x$ [using $n = 1$ and $k = 1$ in Eq. (A1), (A2) with a difference in the boundary conditions].

$$D \frac{1}{x^2} \frac{d}{dx} \left(x^2 \frac{dT}{dx} \right) = -1 \quad \text{(B4)}$$

with $T(a) = 0$, $dT/dx|_R = 0$ and setting $\tau_{\text{in}} = T(a + l)$,

since right after escaping the distance is $a + l$. This leads to

$$\tau_{\text{in}} = \frac{R^3 l}{3Da(a + l)} - \frac{l(2a + l)}{6D}. \quad \text{(B5)}$$

Using it in Eq. (B3) and solving for τ_{esc}, we get (using $R \gg a, l$)

$$\tau_{\text{esc}} = \frac{l^2}{D} g_{\text{AB}}(a) \left[1 + \frac{l^2}{3a(a + l)} \right]. \quad \text{(B6)}$$

The parameter λ, defined in Eq. (3.9), is therefore

$$\lambda = 1 + \frac{l^2}{3a(a + l)} \quad \text{(B7)}$$

and is of order 1 in most situations.

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