Energy and angular momentum diffusion theory of dissociation rate constants[a)]

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We evaluate the dissociation rate constant of a molecule in the low pressure and the weak collision limit. We take the full coupling between energy and angular momentum into account by asymptotic techniques. We applied this result to a diatomic molecule using the Kramers frictional Fokker–Planck model. The predicted temperature dependence of the recombination rate constant is in agreement with experimental data on iodine recombination at high temperatures.

I. INTRODUCTION

Early versions of unimolecular rate theory in the low pressure regime where the energy activation step is rate limiting were formulated using the "strong collision approximation,"[1,2] an approximation which rests on the assumption that the average energy transferred per collision $\langle \Delta E \rangle$ is large compared to the thermal energy. Even though this assumption is always justified at low enough temperatures it will eventually break down as the temperature is increased. This often happens even at room temperature. In this case the opposite "weak collision limit" is of interest. Here each collision can change the energy only by a small amount. In this case one often approximates the action of the collisions by a one-dimensional diffusion in energy space[1,2] although the validity of such an approximation is not trivial.[3] The reason why one only focuses on the energy is that in the absence of collisions the energy is a conserved variable. Therefore, when the collisions are infrequent the energy will relax much slower than any other internal dynamical variable-like positions or momenta. However, this simple picture can be only qualitatively correct since in a real molecule the angular momentum is also a conserved variable. The angular momentum will therefore also relax slowly and one has to consider the coupled diffusion of energy and angular momentum to obtain a more realistic description of the dissociation process in the weak collision limit. Even though the importance of this effect has been emphasized repeatedly[1,4] it is difficult to evaluate rate constants for such models explicitly.[5] To our knowledge only one very special model of this kind has been solved.[6]

Recently asymptotic methods have been developed to evaluate mean first passage times for diffusion processes in several dimensions.[7] In this communication we show how to use these methods to account for the full coupling between energy and angular momentum in the dissociation of a molecule in the weak collision limit. As an illustration we focus on the dissociation of a diatomic molecule and represent the action of the collisions by a simple Fokker–Planck model which is characterized by a single friction parameter ζ.[8] However, the method is much more general since it allows evaluation of rate constants in different situations: Dissociation of polyatomic molecules, effects of non-Markovian (frequency dependent)[10] friction, and situations where quantities like average energy or angular momentum transferred per collision, $\langle \Delta E \rangle$ or $\langle \Delta J \rangle$, are known from trajectory calculations[11] can all be treated in a very similar way.

II. ENERGY AND ANGULAR MOMENTUM DIFFUSION

A diatomic molecule in the center of mass frame is described by the Hamiltonian[12]

$$H = \frac{p_r^2}{2\mu} + V_{\text{eff}}(r, J)\,, \tag{1}$$

where p_r is the radial component of the momentum $\mathbf{p}$, r is the bond length, μ is the reduced mass, and

$$V_{\text{eff}}(r, J) = V(r) + \frac{J^2}{2\mu r^2} \tag{2}$$

is the effective rotational potential which depends on the magnitude J of the angular momentum $\mathbf{J}$. The interaction potential $V(r)$ approaches the constant value of dissociation energy D_e as $r \to \infty$. The effective potential $V_{\text{eff}}(r, J)$ has a metastable minimum at an energy $E_0(J)$ and goes through a maximum located at $r = r_m(J)$ at an energy $Q(J)$ {i.e., $Q(J) = V_{\text{eff}}[r_m(J), J]$}. As we increase the angular momentum J the metastable well of $V_{\text{eff}}(r, J)$ disappears at a critical value J_c. If the diatom feels weak friction all the "conserved variables" will decay slowly. Because $\mathbf{J}$ is always perpendicular to the bond vector $\mathbf{r}$ we choose the following set of slowly relaxing variables: The total energy E and the two rotational energies $R_\theta = J_\theta^2/2\mu r_e^2$ and $R_\phi = J_\phi^2/2\mu r_e^2$, where J_θ and J_ϕ are components of the angular momentum along the unit vectors $\hat{\theta}$ and $\hat{\phi}$ in spherical polar coordinates. By r_e we denote the equilibrium bond length of the diatomic molecule.

We assume that the distribution function $P(E, R_\theta, R_\phi, t)$ evolves according to a diffusion equation which can be completely specified (using detailed balance) by the equilibrium distribution function and a symmetric diffusion matrix. The equilibrium distribution is

$$P_{\text{eq}}(E, R_\theta, R_\phi) = \left\langle \delta(E - H)\,\delta\!\left(R_\theta - \frac{J_\theta^2}{2\mu r_e^2}\right)\delta\!\left(R_\phi - \frac{J_\phi^2}{2\mu r_e^2}\right)\right\rangle, \tag{3}$$

where the canonical average $\langle \ldots \rangle$ must be restricted to the region of the phase where the diatomic cannot dissociate[9] [i.e., $J < J_c$ and $r < r_m(J)$]. If we denote ω_0 the angular frequency near the minimum at $r = r_e$ of the potential $V(r)$, Eq. (3) becomes

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$$P_{\rm eq}(E,R_\theta,R_\phi)=\frac{\beta^2\omega_0}{4\pi}\frac{\Omega_J(E)}{(R_\theta R_\phi)^{1/2}}e^{-\beta E}, \tag{4}$$

where $\beta = 1/k_B T$,

$$\Omega_J(E)=\int_{r<r_m(J)} dr\,dp_r\,\delta\left[\frac{p_r^2}{2\mu}+V_{\rm eff}(r,J)-E\right] \tag{5}$$

is the density of states of the effective potential and the magnitude of J is obtained from $R_\theta + R_\phi = J^2/2\mu r_e$. The diffusion coefficients can be evaluated from the second moments of the transition probability density. For the Kramers model we can obtain the diffusion coefficients explicitly. We follow the procedure which was used to obtain the energy diffusion coefficient in the case of several degrees of freedom[9] yielding the generalization

$$D_{EE}=\frac{\zeta}{\beta\mu^2}\langle p^2\rangle_{E,R_\theta,R_\phi}, \tag{6}$$

where

$$\langle p^2\rangle_{E,R_\theta,R_\phi}=2\mu r_e^2(R_\theta+R_\phi)\langle r^{-2}\rangle_{E,J}+\frac{\mu}{\Omega_J(E)}\int_{E_0(J)}^{E}dE'\,\Omega_J(E'). \tag{7}$$

The average $\langle\ldots\rangle_{E,R_\theta,R_\phi}$ is analogous to the ordinary microcanonical average with the difference that besides E also R_θ and R_ϕ are held fixed. The notation $\langle\ldots\rangle_{E,J}$ indicates that $\langle\ldots\rangle_{E,R_\theta,R_\phi}$ depends on E and J only. Similarly one finds

$$D_{ER_i}=\frac{2\zeta}{\beta\mu}R_i \quad \text{for } i=\theta,\phi. \tag{8}$$

The remaining diffusion coefficients must also be evaluated but we will not need the explicit results.

At this point we have completely characterized the diffusion in this three-dimensional E, R_θ, and R_ϕ space by finding the diffusion coefficients and the equilibrium distribution function. The dissociation rate constant can be evaluated from the inverse of the mean first passage time from $E=0$ to the dissociation threshold defined by $E=Q(J)$ (absorbing boundary). Note that the motion is constrained since the energies E, R_θ, and R_ϕ must be positive and the total energy E at a given J must always exceed the potential minimum at given angular momentum $E_0(J)$ (reflecting boundaries).

An explicit solution of this problem can be achieved for large dissociation energies ($\beta D_e \gg 1$) using asymptotic techniques. For details of the procedure the reader is referred to the Appendix. The final expression for the dissociation rate constant becomes

$$k\sim\frac{\beta^3\omega_0}{\mu r_e^2}\int_0^{J_c}dJ\,Je^{-\beta E}\Omega_J(E)\times\left(D_{EE}-D_{EJ}\frac{dQ(J)}{dJ}\right)\Bigg|_{E=Q(J)}, \tag{9}$$

where $D_{EJ}=\zeta J/\beta\mu$. The result for k consists of two separate terms: The first and more important one is essentially the second term of Eq. (7) and corresponds physically to one-dimensional energy diffusion at fixed angular momentum averaged over the equilibrium distribution of angular momenta at the dissociation threshold. The second less important term which could be neglected in an approximate treatment originates from vibration–rotation coupling. Note that the rate constant is proportional to the friction ζ. It might be helpful to point out that even though for continuous potentials $\Omega_J(E)$ diverge at the dissociation threshold the integrand entering Eq. (9) is well behaved.

We have evaluated numerically Eq. (9) for the Morse potential

$$V(r)=D_e[1-e^{-b(r-r_e)}]^2, \tag{10}$$

where $b=(\mu\omega_0^2/2D_e)^{1/2}$. The dissociation rate constant can be approximated quite accurately (to a few percent) by the simple formula

$$k\simeq\frac{\zeta}{\mu}A(\beta D_e)^\alpha e^{-\beta D_e} \tag{11}$$

for a fixed value of $r_e b$. We have summarized several values of the prefactor A and the exponent α as a function of $r_e b$ in Table I. One can see that for large $r_e b$ the dissociation rate constant approaches the result of one-dimensional energy diffusion without the coupling to the angular momentum[13]

$$k\sim\frac{\zeta}{\mu}2\beta D_e e^{-\beta D_e}. \tag{12}$$

In this case of large br_e the angular momentum contribution to the effective potential [Eq. (2)] will be negligible. Therefore, the dissociation threshold $Q(J)$ does not depend on J anymore and the diffusion process becomes one-dimensional.

III. CONCLUSION AND COMPARISON WITH EXPERIMENTS

We have evaluated the dissociation rate constant at low pressures in the weak collision regime taking the full coupling between energy and angular momentum into account. We applied this result to the dissociation of a diatomic molecule representing the action of the collisions by the frictional Fokker–Planck model. The asymptotic result for the dissociation rate constant [Eq. (9)] can be accurately approximated by Eq. (11) for the case where the atoms interact through a Morse potential. For a large, stiff diatomic the contribution of the rotational degrees of freedom is negligible and the rate constant is given by one-dimensional energy diffusion. However, as the molecule becomes smaller or less

TABLE I. Exponent α and prefactor A of the dissociation rate constant [Eq. (11)] of a diatomic molecule interacting by a Morse potential. The last line for $r_e b \to \infty$ are the corresponding quantities of Eq. (12).

$r_e b$	A	α
1	29.95	1.346
2	16.03	1.232
3	10.09	1.200
4	7.46	1.182
5	6.09	1.166
6	5.27	1.153
10	3.85	1.116
40	2.54	1.035
∞	2.00	1.000

stiff the rate constant increases in magnitude and decreases more strongly with temperature. It is interesting to note that the influence of rotational degrees of freedom is much smaller in the weak collision limit than in strong collision models.[2,14]

One would like to compare the prediction of this model with experimental data. Let us consider iodine recombination as an example. Since for iodine[14] $r_e b \simeq 5.0$ and the equilibrium constant is proportional to $T^{-1/2}$ one finds from Table I that the present model predicts that the ratio of the recombination rate constant $k_{\rm rec}$ and the friction ζ is proportional to $T^{-0.67}$. It is known that at low temperatures the recombination of iodine atoms proceeds by the bound complex mechanism and not by the energy transfer mechanism considered here.[1,14,15] However, at higher temperatures ($\sim$700 K) the recombination proceeds mainly by the energy transfer mechanism. Even though the recombination rate constants are not too accurately known at such high temperatures plotting the available data[16] as $k_{\rm rec}/\zeta$ vs the temperature one finds for a wide variety of bath gases that $k_{\rm rec}/\zeta \propto T^{-a}$ where $a = 0.6 \pm 0.2$. The friction constant ζ can be estimated from $\zeta \simeq \zeta_{\rm I}/2$ where the friction on a single iodine atom $\zeta_{\rm I}$ is calculated from the Enskog expression for a Lennard-Jones interaction potential (using tabulated potential parameters).[17] The experimentally observed temperature dependence is in agreement with the model presented here. However, if one compares the absolute value of the low pressure rate constant with experimental data the theory severely overestimates the rate constant. However, this is not surprising since one must include electronic degeneracy factors[1,14,15] and furthermore, the Kramers model uses a delta-correlated friction which is an appropriate model of hard sphere interactions only. Because soft collisions are not instantaneous the friction has a correlation time of the order of a duration of one collision. A finite correlation time of the friction is known to significantly reduce the rate constant for one degree of freedom in the low pressure regime[13] and one has to expect that this effect is important in the case of dissociation of diatomics too.

We now comment on how well these experimental data compare with simpler theories. If one neglects the coupling to the angular momentum and considers a one-dimensional energy diffusion equation (or $r_e b \rightarrow \infty$) we find from Eq. (12) that $k_{\rm rec}/\zeta \propto T^{-1/2}$. Obviously both models are able to explain the experimentally observed temperature dependence. A strong collision model on the other hand predicts that $k_{\rm rec}$ is approximately independent of temperature[14] which is in substantial disagreement with experimental data.[16]

In our treatment we neglected the role of the conserved center of mass momentum. However, the above arguments apply if one includes the relaxation of the kinetic energy of the center of mass. It turns out that this mode completely decouples from the total energy and rotational energies and does not affect our results.

At this point one can approximately evaluate the rate constant for the Fokker–Planck model for arbitrary friction ζ since the rate constant is known in three different limits: First, the rate constant in the low friction limit was evaluated in this communication. Second, the transition state rate constant is given by canonical transition state theory. Third, the high friction (diffusive) limit is equivalent to Smoluchowski theory of diffusion controlled reactions with a diffusion coefficient $D = 1/\beta\zeta$. With the exception of the low friction limit these results were considered in detail in connection with a different collisional model.[14] Given these three limiting expressions the rate constant for arbitrary friction can be evaluated from a simple Padé-like approximant.[16] The dissociation or recombination rate constant of a diatomic molecule exhibits the characteristic maximum as pointed out by Kramers[8] for a single degree of freedom model.

Recently the same problem was considered by reducing the Langevin equations for each atom to a one-dimensional equation for the bond length r which is solved in a standard fashion.[18] However, the elimination of rotational degrees of freedom involves the assumption that the orientational average of the square of the angular velocity for a given r immediately relaxes to its equilibrium value $2/\beta\mu r^2$. While this assumption is correct in the high friction limit (where r is a slow variable) it breaks down in the low friction limit where r is a fast variable. Therefore we believe that such an approach is not entirely correct at low frictions.

In conclusion let us summarize our results. We have evaluated the dissociation rate constant in the low pressure regime and in the weak collision limit taking the full coupling of the relaxation of the energy and angular momentum into account. The asymptotic result valid for large dissociation energies is evaluated for the Kramers frictional Fokker–Planck model. The temperature dependence of the recombination rate constant predicted by the Kramers model is in agreement with experiments on iodine recombination at high temperatures.

APPENDIX

There has been considerable activity in applying asymptotic techniques for evaluation of escape rate constants. Since most of the arguments have become quite standard[7,19] we give only a brief summary of the ideas involved.

Before specializing to the problem of the dissociating diatomic considered in the text let us outline the general solution the diffusion equation[19]

$$\frac{\partial}{\partial t} P(\mathbf{x}, t) = LP(\mathbf{x}, t)\,, \tag{A1}$$

where

$$L = -\epsilon \sum_i \frac{\partial}{\partial x_i} [a_i(\mathbf{x})\ldots] + \frac{\epsilon^2}{2} \sum_{i,j} \frac{\partial^2}{\partial x_i \partial x_j} [b_{ij}(\mathbf{x})\ldots] \tag{A2}$$

and detailed balance gives for even quantities x_i even under time reversal[19]

$$a_i(\mathbf{x}) = \frac{\epsilon}{2P_{\rm eq}(\mathbf{x})} \sum_j \frac{\partial}{\partial x_i} [b_{ij}(\mathbf{x}) P_{\rm eq}(\mathbf{x})] \tag{A3}$$

and a symmetric matrix b_{ij}. Suppose that the equilibrium distribution is of the form

$$P_{\rm eq}(\mathbf{x}) = K(\mathbf{x}) e^{-\psi(\mathbf{x})/\epsilon}\,, \tag{A4}$$

where $\psi(\mathbf{0}) = 0$.

The mean first passage time $T(\mathbf{x})$ from a point $\mathbf{x}$ out of a domain Ω with a surface $\partial\Omega$ which has an absorbing part $\partial\Omega_{\text{abs}}$ and a reflecting part $\partial\Omega_{\text{ref}}$ can be calculated by solving[19]

$$L^{+}T(\mathbf{x}) = -1\,, \tag{A5}$$

where

$$L^{+} = \epsilon \sum_i a_i(\mathbf{x}) \frac{\partial}{\partial x_i} + \frac{\epsilon^2}{2} \sum_{i,j} b_{ij}(\mathbf{x}) \frac{\partial^2}{\partial x_i \partial x_j} \tag{A6}$$

is the adjoint operator of L and Eq. (A5) has to be solved with the boundary conditions

$$\begin{aligned} &T(\mathbf{x}) = 0\,, && \mathbf{x}\in\partial\Omega_{\text{abs}}\,, \\ &\sum_{i,j} b_{ij}(\mathbf{x}) n_i \frac{\partial T}{\partial x_j} = 0\,, && \mathbf{x}\in\partial\Omega_{\text{ref}}\,, \end{aligned} \tag{A7}$$

where n_i are the components of the outer normal unit vector $\hat{n}$ of $\partial\Omega$. Such problems can be solved asymptotically in the $\epsilon \to 0$ limit using boundary layer techniques.[7,19] One sets $T(\mathbf{x}) = Cv(\mathbf{x})$ where the maximum of $v(\mathbf{x})$ is unity for $\mathbf{x}\in\Omega$. As we show later [cf. Eq. (12)] for $\epsilon \to 0$ the constant C becomes exponentially large so that Eq. (A5) becomes

$$L^{+}v(\mathbf{x}) \sim 0\,. \tag{A8}$$

Deep inside Ω the function $v(\mathbf{x}) = 1$ and drops rapidly to zero in boundary layer near $\partial\Omega_{\text{abs}}$. To evaluate $v(\mathbf{x})$ with the boundary layer we transform to local orthogonal coordinates with the origin at $\partial\Omega$ where one of these coordinates is

$$z = \hat{n} \cdot (\mathbf{x} - \mathbf{x}_s)\,, \tag{A9}$$

where $\mathbf{x}_s$ is a vector pointing to the surface $\partial\Omega$. The boundary layer solution is obtained by introducing the stretched variable $\eta = z/\epsilon$ and expanding the coefficients of Eq. (A8) around $\mathbf{x}_s$. To lowest order in ϵ the resulting equation for v involves only the variable z. The solution of this equation becomes

$$v(z) = 1 - e^{-\gamma\eta}\,, \tag{A10}$$

where

$$\gamma = -2 \frac{\Sigma_i n_i a_i(\mathbf{x}_s)}{\Sigma_{i,j} n_i b_{ij}(\mathbf{x}_s) n_j}\,. \tag{A11}$$

This holds if $\Sigma_i n_i a_i < 0$ which is the case of interest here. Given the function $v(\mathbf{x})$ the constant C is determined by multiplying Eq. (A5) by $P_{\text{eq}}(\mathbf{x})$ and integrating over Ω. Using Gauss' divergence theorem and Eq. (A7) we obtain

$$C = -\frac{\int_\Omega dx^n\, P_{\text{eq}}(\mathbf{x})}{\frac{1}{2}\epsilon^2 \int_{\partial\Omega_{\text{abs}}} dS\, P_{\text{eq}}(\mathbf{x})\, \Sigma_{i,j}\, n_i b_{ij}(\mathbf{x}) (\partial v/\partial x_j)|_{\mathbf{x}=\mathbf{x}_s}}\,. \tag{A12}$$

The rate constant is evaluated from the inverse of C which becomes using Eq. (A9),

$$k \sim \frac{1}{C} \sim -\epsilon \int_{\partial\Omega_{\text{abs}}} dS\, P_{\text{eq}}(\mathbf{x}_s) \sum_i n_i a_i(\mathbf{x}_s)\,. \tag{A13}$$

Taking Eq. (A3) into account one finally obtains

$$k \sim \frac{\epsilon}{2} \int_{\partial\Omega_{\text{abs}}} dS\, P_{\text{eq}}(\mathbf{x}_s) \sum_{i,j} n_i b_{ij}(\mathbf{x}_s) \frac{\partial\psi}{\partial x_i}\bigg|_{\mathbf{x}=\mathbf{x}_s}\,. \tag{A14}$$

Returning to our problem of a dissociating diatomic we identify $\epsilon = 1/\beta D_e$ and the variables by $x_1 = E/D_e$, $x_2 = R_\theta/D_e$, and $x_3 = R_\phi/D_e$. The b_{ij}'s are proportional to the diffusion coefficients; i.e., $b_{11} = 2\beta^2 D_{EE}$, $b_{12} = 2\beta^2 D_{ER_\theta}$, etc. The final result [Eq. (9)] is obtained by rewriting the surface integral as an integral over R_θ and R_ϕ which can be transformed to polar coordinates to give a single integration over J.

One should point out that the present derivation of Eq. (A14) assumes a finite $K(\mathbf{x})$ in Eq. (A4) at the boundary $\partial\Omega_{\text{abs}}$ even though the case considered in text has a weak logarithmic divergence. However using very similar arguments it is possible to rederive Eq. (A14) for this more general case.

For applications of the expressions derived here in the case where average energy and angular momentum transferred per collision, $\langle \Delta E \rangle$ or $\langle \Delta J \rangle$, are known from a trajectory calculation, Eq. (A13) is more useful in evaluating the rate constant since these quantities are essentially the a's which enter Eq. (A13). Note that the major advantage of Eq. (A13) is that quantities like $\langle \Delta E \rangle$ or $\langle \Delta J \rangle$ enter only in the linear combination $\Sigma_i\, n_i a_i$ and furthermore even though this quantity depends on the energy E and angular momentum J of the molecule prior to the collision one only needs this quantity evaluated along the absorbing boundary [in this case for $E = Q(J)$]. This fact should reduce the computational effort enormously. In a trajectory calculation one would therefore have to start the calculation with an excited molecule at the dissociation threshold and after a thermal collision sample directly the quantity $\Sigma_i\, n_i a_i$ for different angular momenta.

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