ORIGINAL PAPER

Collisional energy transfer with statistical energy exchange: an analytical solution in the statistical limit

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Abstract   Collisional energy transfer between highly vibrationally excited molecules and bath gas is considered with a statistical kernel, describing energy exchange in complex-forming collisions. Knowledge of the bilinear formula for the Laguerre polynomials offers a means for determining eigenvalues and eigenfunctions of the kernel. An exact solution to master equation for the conditional probability is given as an expansion in terms of these eigenfunctions. The bulk averages of internal energy moments and energy transfer moments are calculated analytically.

1 Introduction

Highly vibrationally excited molecules are of importance in many non-equilibrium processes such as combustion and atmospheric photochemistry. The details of energy transfer depend on the type of excited and bath molecules, on their state densities, on the level of excitation, and on the interaction potential. Recently, much experimental [1–6] and theoretical [7–9] attention has been focused on the nature of a small subset of collisions in which inordinately large amounts of energy are transferred in a single collision. In this case, the collisional energy transfer probability function $P(E \rightarrow E')$ exhibits a tail at high $\Delta E = E - E'$ energies. These large energy-changing collisional encounters are called "supercollisions".

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The behavior of a non-equilibrium system, depending on energy-transfer processes, may be found out from a master equation [10–13] that may be solved by using the $P(E \to E')$ probability of transitions from the state with the initial energy E to that with the final energy E' near $E' + dE'$ that, until recently, was the unknown quantity. The simplest possible prediction of this probability is based on the assumption of the fully micro-canonical energy equilibration occurring at collisions. The statistical theory is simply a complex-forming model in which the large amount of energy can be transferred due to the energy shared among the internal modes of the hot molecule, the transition modes in the collision complex, and in all degrees of freedom of the bath molecule [14–17]. It is now appreciated that a long tail of $P(E \to E')$ for very large initial energies E was the expected feature related to the statistical fluctuations of energy excess in these collisions. Experiments clearly indicate that the main contribution to $P(E \to E - \Delta E)$ is made by the change in state density with ΔE [3–6] which is a strong argument in favor of the statistical character of the energy-transfer mechanism with large ΔE [18].

The collisional probability of transitions can be readily derived in the framework of the statistical theory and expressed in terms of the state densities of colliding particles [14–17]. Assuming harmonic intramolecular potentials and decoupling among the different degrees of freedom, the key expression for $P(E \to E')$ is easily deduced from combinatorial arguments similar to those of Kassel [19]. The aim of this work is to build up a representation in which the well-known collisional kernel is expressed in terms of its eigenfunctions and eigenvalues. The solution to the master equation is then written as an expansion in terms of these eigenfunctions and the bulk (or ensemble) averages are calculated in the analytical form so as all the moments of the energy transferred. The modified theory of this kind gives a systematic understanding of the energy-transfer processes in which substantial amounts of energy are transferred in a single collision.

2 Energy transfer in complex-forming collisions

The simplest approach, in which the dynamics of scattered particles are ignored completely, assumes that the collision partners are trapped in the potential field of the complex, and during the lifetime of the complex, the energy is randomly distributed in all of the internal modes of the collision complex. The statistical transition probability for the active molecule is given in [14–16]

$$P(E \to E') = \int_{\Delta}^{\infty} \frac{\rho_A(E')\rho_B(E'' + E - E')}{\rho_{AB}(E'' + E)} N_B^{eq}(E'') dE'', \tag{1}$$

where $\Delta = \max(0, E' - E)$; ρ_A and ρ_B are the state densities of the active and bath molecules, respectively, ρ_{AB} is their state density in the complex, and $N_B^{eq}(E'')$ is the thermal distribution of the energy of the bath molecules. In order to explicitly evaluate the transition probability, we use the harmonic approximation for molecular vibrations and take the rotations to be separable. The errors introduced by the approx-

imation are discussed in details in [14–17,20]. To avoid cumbersome expressions, it is convenient to introduce the reduced energy variables (energy in units of $k_B T$, where T is the heat-bath temperature). The above assumptions together with the conditions of completeness and detailed balance lead to the kernel [20]

$$P(x \to y) = \frac{y^{a-1}}{B(a,b)} \int_\Delta^\infty \frac{(\varepsilon + x - y)^{b-1}}{(\varepsilon + x)^{a+b-1}} \frac{\varepsilon^{b-1} e^{-\varepsilon} d\varepsilon}{\Gamma(b)}, \qquad (2)$$

where $a = n_V + n_R/2$ is the number of internal degrees of freedom of the active molecule (i.e., including vibrations and rotations), and $b = n_V + (n_R + n_T)/2$ is the number of all degrees of freedom of the bath molecule (including translations). Upon substitution of the variable $\varepsilon + x = w$, Eq. (2) is reduced to the following equation

$$P(x \to y) = N^{eq}(y) \frac{\Gamma(a+b)}{\Gamma(b)^2} \int_z^\infty [(w-x)(w-y)]^{b-1} e^{-w+x+y} \frac{dw}{w^{a+b-1}}, \qquad (3)$$

where $z = \max(x, y)$, and $N^{eq}(y)$ is the thermal distribution of the energy of the active molecules

$$N^{eq}(y) = \frac{y^{a-1} e^{-y}}{\Gamma(a)} \qquad (4)$$

It is worth noting that Eq. (3) may be based on the combinatorial considerations using the complex of $a + b$ oscillators in which the chosen a oscillators gain energy y, if initially it was x.

Further, we use the Laguerre polynomials that are orthonormalized with a weight function $N^{eq}(y)$:

$$\hat{L}_k^{(a-1)}(y) = \left[\frac{\Gamma(a)k!}{\Gamma(k+a)} \right]^{\frac{1}{2}} L_k^{(a-1)}(y) \qquad (5)$$

The completeness property for these polynomials is given by the expression

$$N^{eq}(y) \sum_{k=0}^\infty \hat{L}_k^{(a-1)}(x) \hat{L}_k^{(a-1)}(y) = \delta(x - y) \qquad (6)$$

We make use of the well-known equation that maps a Laguerre polynomial to another polynomial with a different parameter [21]

$$L_k^{(a-1)}(x) = \frac{1}{\Gamma(b)} \int_x^\infty L_k^{(a+b-1)}(w)(w-x)^{b-1} e^{-w+x} dw, \quad b > 0 \qquad (7)$$

With Eq. (7) we try to evaluate the series

$$
\sum_{k=0}^{\infty} \frac{k!}{\Gamma(k+a+b)} L_k^{(a-1)}(x) L_k^{(a-1)}(y)
$$

$$
= \frac{1}{\Gamma(b)^2} \int_x^{\infty} (w-x)^{b-1} e^{-w+x} dw \int_y^{\infty} (w'-y)^{b-1} e^{-w'+y} dw'
$$

$$
\times \sum_{k=0}^{\infty} \frac{k!}{\Gamma(k+a+b)} L_k^{(a+b-1)}(w) L_k^{(a+b-1)}(w') \tag{8}
$$

Now we give Eq. (6) in more detail with regard to the $L_k^{(a+b-1)}(w)$ polynomials

$$
\frac{w^{a+b-1} e^{-w}}{\Gamma(a+b)} \sum_{k=0}^{\infty} \frac{k! \, \Gamma(a+b)}{\Gamma(k+a+b)} L_k^{(a+b-1)}(w) L_k^{(a+b-1)}(w') = \delta(w-w') \tag{9}
$$

Substituting Eq. (9) in the right-hand side of Eq. (8), we get

$$
\sum_{k=0}^{\infty} \frac{k!}{\Gamma(k+a+b)} L_k^{(a-1)}(x) L_k^{(a-1)}(y)
$$

$$
= \frac{1}{\Gamma(b)^2} \int_z^{\infty} [(w-x)(w-y)]^{b-1} e^{-w+x+y} \frac{dw}{w^{a+b-1}} \tag{10}
$$

Now we are in a position to find our principal result. Equations (3)–(5) and (10) imply the following relation

$$
P(x \to y) = N^{eq}(y) \sum_{k=0}^{\infty} \lambda_k \hat{L}_k^{(a-1)}(x) \hat{L}_k^{(a-1)}(y), \tag{11}
$$

where

$$
\lambda_k = \frac{\Gamma(a+b)\Gamma(k+a)}{\Gamma(a)\Gamma(k+a+b)} \tag{12}
$$

This representation of $P(x \to y)$ makes it clear that $\hat{L}_k^{(a-1)}(x)$ are the eigenfunctions and λ_k are the eigenvalues of the kernel

$$
\int_0^{\infty} P(x \to y) \hat{L}_k^{(a-1)}(y) dy = \lambda_k \hat{L}_k^{(a-1)}(x) \tag{13}
$$

The full characterization of transition probability is the knowledge of all the moments of internal energy transferred per collision

$$\langle (y - x)^n \rangle = \sum_{m=0}^{n} \binom{n}{m} (-x)^{n-m} \langle y^m \rangle, \tag{14}$$

where the mth moment of $P(x \to y)$ is defined as usual. Note that $\langle y^m \rangle$ is the average over all possible outcomes of a single collision with the initial energy x. As a result, $\langle y^m \rangle$, like $P(x \to y)$, is a microscopic property that reflects an intrinsic characteristic of the molecule of interest. Now, to perform an actual averaging, we write y^m as a finite series in terms of the orthonormalized Laguerre polynomials [22]

$$y^m = \Gamma(m + a) \sum_{k=0}^{m} (-1)^k \binom{m}{k} \left[\frac{k!}{\Gamma(a)\Gamma(k + a)} \right]^{\frac{1}{2}} \hat{L}_k^{(a-1)}(y) \tag{15}$$

The desired moment $\langle y^m \rangle$ is readily calculated and expressed in terms of the finite series which may be folded with the summation formula [23]

$$\sum_{k=0}^{m} \frac{(-1)^k}{(m-k)!\Gamma(k+a+b)} L_k^{(a-1)}(x) = \frac{(-1)^m}{\Gamma(m+a+b)} L_m^{(-m-b)}(x) \tag{16}$$

Finally, using this relation we get

$$\langle y^m \rangle = (-1)^m m! \lambda_m L_m^{(-m-b)}(x) \tag{17}$$

It must be emphasized that the mth moment of the kernel is proportional to its eigenvalue. The dependence of λ_m on the parameters a and b is explicit from the recurrent relation

$$\lambda_{m+1} = \lambda_m \left(1 + \frac{b}{a+m} \right)^{-1}, \quad m = 0, 1, 2, \ldots \tag{18}$$

where $\lambda_0 = 1$. Another remarkable feature of relation (17) is that the x-dependence of the moments is defined by the parameter b only, the number of degrees of freedom of the heat-bath molecules.

Now we calculate the moments of the internal energy transferred per collision from Eqs. (14) and (17). In particular, the average energy transferred per collision is

$$\langle \Delta E(E) \rangle = -(1 - \lambda_1)(E - \langle E \rangle_T) \tag{19}$$

where $\langle E \rangle_T$ is the mean thermal energy. For convenience, in this case, E is used instead of x, because the only difference in these variables is the constant reduced in both of the parts of Eq. (19). The case $\lambda_1 \approx 0$ (or $b/a \gg 1$) corresponds to the limit of strong collisions whereas at $\lambda_1 \approx 1$ ($b/a \ll 1$) the collisions are weak. Thus, the statistical

theory predicts that the amount of energy transferred per collision, depends on the size of colliding particles or, more precisely, on their ratio. Another useful average is $\langle \Delta E^2 \rangle$ which characterizes the width of the energy-transfer probability distribution

$$\left\langle \Delta E^2(E) \right\rangle = (1 - \lambda_1) \left\langle \Delta E^2 \right\rangle_T + \left(1 - \lambda_1 - \frac{\lambda_1 - \lambda_2}{\lambda_1} \right) E^2$$
$$+ (1 - \lambda_1) \frac{\lambda_1 - \lambda_2}{\lambda_1} (E - \langle E \rangle_T)^2 , \tag{20}$$

where $\left\langle \Delta E^2 \right\rangle_T$ is the variation of thermal energy. For strong collisions, the first and the third terms are the values of the same order of magnitude, whereas the second is much smaller. In the case of weak collisions, the first term is the leading one, while the second and the third terms are the small corrections. The second term is always smaller than the third one. Thus, the approximation in which the second moment is energy-independent, will be sufficient for weak collisions in which only the small amounts of energy are transferred. In this case, the energy-transfer probability distribution is a very narrow function of energy.

3 Bulk averages

If $N(x, t)$ is the time-dependent population density, i.e., the fraction of hot molecules per unit energy at energy x and time t, the populations satisfy the master equation [10–13]

$$\frac{\partial}{\partial t} N(x, t) = -\nu N(x, t) + \nu \int_0^\infty P(y \to x) N(y, t) dy, \tag{21}$$

where ν is the collision frequency. Inasmuch as the eigenfunctions and the eigen-values of the kernel are known, the solution to the master equation is easily found as the eigenfunction expansion

$$N(x_i, x; t) = N^{eq}(x) \sum_{k=0}^\infty \exp\left[-(1 - \lambda_k) \nu t \right] \hat{L}_k^{(a-1)}(x_i) \hat{L}_k^{(a-1)}(x) \tag{22}$$

with the initial condition $\delta(x - x_i)$. Physically, $N(x_i, x; t)$ is the density of conditional probability that the random variable $x(t)$ takes the value x at time t provided it was x_i at previous time $t_i = 0$. Now we use the solution to the master equation to study the relaxation process.

Let us employ the conditional probability to calculate the time evolution of the nth bulk moment of internal energy

$$\left\langle \left\langle x^n (x_i, t) \right\rangle \right\rangle = \int_0^\infty N(x_i, x; t) x^n dx \tag{23}$$

A bulk average is a macroscopic property, and will be represented by a doublet bracket to distinguish it from a per collision average represented by a single bracket. The x^n power, where n is the integer, may be given in terms of the finite sum of the orthonormalized Laguerre polynomials (see, Eq. (15)). Hence, Eq. (23) becomes

$$\langle\langle x^n (x_i, t)\rangle\rangle = \Gamma(a+n) \sum_{k=0}^{n} (-1)^k \left[\frac{k!}{\Gamma(a)\Gamma(a+k)} \right]^{\frac{1}{2}} e^{-(1-\lambda_k)vt} \hat{L}_k^{(a-1)}(x_i)$$

(24)

In particular, the average energy at time t is

$$\langle\langle E (E_i, t)\rangle\rangle = E_i \exp[-(1-\lambda_1)vt] + \langle E\rangle_T \{1 - \exp[-(1-\lambda_1)vt]\} \quad (25)$$

It is seen that during the time of order of $1/v(1-\lambda_1)$ the initial condition (energy E_i) is "forgotten" and the system relaxes to the equilibrium energy value.

Thus, the energy decay is characterized by the average time Z/v and the mean number of collisions Z necessary to reach equilibrium. Here Z is of the form

$$Z = \frac{1}{1-\lambda_1} = 1 + \frac{a}{b}$$

(26)

Thus, the mean transferred energy may be written as

$$\langle\Delta E(E)\rangle = -\frac{E - \langle E\rangle_T}{Z}$$

(27)

It is worth noting that the linear dependence of $\langle\Delta E(E)\rangle$ on E is the necessary and sufficient condition for a simple exponential relaxation [24]. Usually, experimental data are given just in this form. A comparison of the observable values Z_V with the predictions of the statistical theory indicates that the Z_V/Z ratio is too large (typically 10–100 times). This is not surprising, since the collision complex exists only for a short period. A fraction of collisions, in which a complete statistical energy exchange occurs, varies from 1 to 10 % of the total number of collisions under normal conditions [16]. A fraction of supercollisions does not exceed 1 % [7–9]. The statistical theory holds well for these collisions.

Finally, the time evolution of the nth bulk moment of energy transfer is given in terms of the conditional probability

$$\langle\langle \Delta x^n (x_i, t)\rangle\rangle = \int_{0}^{\infty} N(x_i, x; t) \langle\Delta x^n(x)\rangle dx$$

(28)

There is no need to evaluate this integral directly, because the result is derived from Eq. (28) by formally substituting any power x^k by $\langle\langle x^k\rangle\rangle$. Actually, all the moments

can be determined analytically, but the resulting expressions are very cumbersome. However, the bulk-average energy transfer at time t is given by the simple relation

$$\langle\langle\Delta E\left(E_i, t\right)\rangle\rangle \;=\; -\frac{E_i - \langle E\rangle_T}{Z}\exp\left(-\frac{vt}{Z}\right) \tag{29}$$

The result $\langle\langle\Delta E\left(E_i, \infty\right)\rangle\rangle = 0$ means that at equilibrium there is no net energy transfer in the bulk or macroscopic system. The initial $\langle\langle\Delta E\left(E_i, 0\right)\rangle\rangle$ value merits particular attention. This is the bulk average over $N(E, t)$, i.e., a macroscopic property. If the initial energy distribution is $\delta(E - E_i)$, then $\langle\langle\Delta E\left(E_i, 0\right)\rangle\rangle = \langle\Delta E(E_i)\rangle$. The latter is a per collision average, i.e., a microscopic property.

Equations (25) and (29), in conjunction with (26), are equivalent to

$$\frac{d}{dt}\langle\langle E\left(E_i, t\right)\rangle\rangle \;=\; v\,\langle\langle\Delta E\left(E_i, t\right)\rangle\rangle \tag{30}$$

This is a general result independent of any particular form of $P(E \rightarrow E')$ and well known in the theory of stochastic processes [25]. It is obvious that the internal energy relaxation is the measure of $\langle\langle\Delta E\rangle\rangle$ rather than of $\langle\Delta E\rangle$.

4 Conclusions

Relaxation in which the first moment of the transition probability depends linearly on initial energy (Eq. (19)), and therefore bulk observables decay via one-exponential term have received much attention [24–28]. In this connection, it should be noted that the statistical transition probability leads to the one-exponential relaxation of molecules of any complexity. This probability, in the version that permits an analytical solution of the population distribution, is used here to calculate a number of macroscopic (bulk) observables in an analytic form also.

Within the general scope of statistical considerations, the transition probability physically represents the strongest possible coupling between an active molecule and a heat bath and yields an upper limit to the energy transferred in a single collision. Due to dynamical constraints and the short duration of collisions, this upper limit is so large as to be of little predictive value for experiments on low excitation energies [14–17,29]. On the other hand, in supercollisions, the unusually large amounts of energy are transferred just near the upper limit. We hope that the theory developed will be suited for describing energy transfer in these collisions that are not the usual case but still of specialized interest.

References

1. S. Hassoon, I. Oref, C. Steel, J. Chem. Phys. **89**, 1743 (1988)
2. J.M. Morgulis, S.S. Sapers, C. Steel, I. Oref, J. Chem. Phys. **90**, 923 (1989)
3. J. Park, L. Shum, A.S. Lemoff, K. Werner, A.S. Mullin, J. Chem. Phys. **117**, 5221 (2002)
4. E.M. Miller, L. Murat, N. Bennette, M. Hayes, A.S. Mullin, J. Phys. Chem. A **110**, 3266 (2006)
5. J.A. Johnson, A.M. Duffin, B.J. Hom, K.E. Jackson, E.T. Sevy, J. Chem. Phys. **128**, 054304 (2008)

6. L. Yuan, J. Du, A.S. Mullin, J. Chem. Phys. **129**, 014303 (2008)
7. D.L. Clarke, K.C. Thompson, R.G. Gilbert, Chem. Phys. Lett. **182**, 357 (1991)
8. V. Bernshtein, I. Oref, J. Chem. Phys. **125**, 133105 (2006)
9. Z. Li, R. Sansom, S. Bonella, D.F. Coker, A.S. Mullin, J. Phys. Chem. A **109**, 7657 (2005)
10. R.G. Gilbert, S.C. Smith, *Theory of Unimolecular and Recombination Reactions* (Blackwell Scientific, Oxford, 1990)
11. D.C. Tardy, B.S. Rabinovitch, Chem. Rev. **77**, 369 (1977)
12. B. Widom, Adv. Chem. Phys. **5**, 353 (1963)
13. I. Oref, D.C. Tardy, Chem. Rev. **90**, 1407 (1990)
14. D. Nilsson, S. Nordholm, J. Chem. Phys. **119**, 11212 (2003)
15. S. Nordholm, B.C. Freasier, D.L. Jolly, Chem. Phys. **25**, 433 (1977)
16. R.C. Bhattacharjee, W. Forst, Chem. Phys. **30**, 217 (1978)
17. H. von Weyssenhoff, E.W. Schlag, J. Chem. Phys. **59**, 729 (1973)
18. M.L. Strekalov, Chem. Phys. Lett. **506**, 139 (2011)
19. L.S. Kassel, J. Chem. Phys. **32**, 1065 (1928)
20. L. Ming, T.D. Sewell, S. Nordholm, Chem. Phys. **199**, 83 (1995)
21. O. Szasz, N. Yeardley, Pac. J. Math. **8**, 621 (1958)
22. I.S. Gradshteyn, I.M. Ryzhik, *Tables of Integrals, Series and Products* (Academic, New York, 1965)
23. A.P. Prudnikov, Yu. A. Brychkov, O.I. Marichev. *Integrals and Series*, vol 2 (Gordon and Breach, New York, 1986)
24. K.E. Shuler, G.H. Weiss, K. Andersen, J. Math. Phys. **3**, 550 (1962)
25. C.W. Gardiner, *Handbook of Stochastic Methods for Physics, Chemistry, and the Natural Sciences* (Springer, Berlin, 1985)
26. M. Tabor, R.D. Levine, A. Ben-Shaul, J.I. Steinfeld, Mol. Phys. **37**, 141 (1979)
27. M.L. Strekalov, Chem. Phys. **373**, 289 (2010)
28. M.L. Strekalov, Chem. Phys. **389**, 47 (2011)
29. L.E.B. Börjesson, S. Nordholm, J. Phys. Chem. **99**, 938 (1995)