

Building transition probabilities per collision from transition rates per unit time for finding the mean observable quantities in the gas phase

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Abstract A new method of finding transition probabilities per collision from a set of transition rates per unit time is proposed. The problem is solved by introducing a normalization function that is easily derived from a recursion equation. The solution of recursion equation is obtained in the analytical form for the case of separable kernels. The Morse oscillator in a thermal bath is considered as an example.

Keywords Vibrational relaxation · Energy transfer · Rate coefficients · Transition probabilities · Recursion equations

1 Introduction

A study of energy transfer upon collisions of highly excited molecules in a thermal bath provides significant information for the prediction and interpretation of relaxation rates per unit time. This input information serves as the basis for obtaining the transition probabilities per collision [1–8]. Given these probabilities, one can calculate the mean observables per collision. Considerable progress has been made in the development of the techniques of finding the transition probabilities per collision in vibrational relaxation of highly excited polyatomic molecules [4–6]. The analysis is substantially simplified when vibrational energy of a quasicontinuum of internal states can be treated as a continuous variable.

In this paper, we present a new method of finding the transition probabilities per collision from the rate coefficients per unit time in a discrete case. These normalized probabilities satisfy the constraint of detailed balance even in the case of the

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rate coefficients obeying the detailed balance just approximately, for example, those calculated in a semiclassical approximation. The problem is solved by introducing a normalization function that can be determined in a step-by-step fashion from the recursion equation without any approximations, and for any dependence of rate coefficients on quantum numbers specifying the energy levels of a system. The representative example is considered that shows the ability of the theory to build the transition probabilities necessary for the calculation of the mean observables per collision.

2 Statement of the problem

A highly excited molecule loses the stored energy upon collisions with the surrounding particles of a thermal bath, thus its internal state varies with time. This variation is described by the master equation where the transition rate, $n_B K_{v \rightarrow v'}$, plays a central role. Here $K_{v \rightarrow v'}$ is the rate coefficient for energy transfer from the state v to the state v' , and n_B is the number density of a buffer gas. Collisional energy transfer between a highly excited molecule (quantum system) and a buffer gas gradually forms the thermal or Boltzmann distribution. The time evolution of the population $N_v(t)$ of the v -th quantum state of the system is given by the master equation [7–9]

$$\frac{d}{dt} N_v(t) = n_B \sum_{v'=0}^{\infty} [K_{v' \rightarrow v} N_{v'}(t) - K_{v \rightarrow v'} N_v(t)], \quad (1)$$

For definiteness, of interest is the case where no chemical reactions are involved in the system. At $t \rightarrow \infty$, the solution $N_v(t)$ tends to the definite limit, N_v^{eq} , corresponding to the equilibrium state of the system, which is of the form

$$N_v^{eq} = Q^{-1} \rho(v) \exp\left(-\frac{E_v}{k_B T}\right), \quad (2)$$

where Q and $\rho(v)$ are the partition function and the density of states, respectively. With $t \rightarrow \infty$ Eq. 1 provides the constraint of detailed balance

$$N_v^{eq} K_{v \rightarrow v'} = N_{v'}^{eq} K_{v' \rightarrow v}, \quad (3)$$

The scattering theory makes it possible to calculate cross sections and rate coefficients based on the rigorous formalism or its various approximations. These quantities may also be measured experimentally.

Transition probabilities appear in the theory owing to the conventional (although artificial) factorization of $K_{v \rightarrow v'}$ into $Z P_{v \rightarrow v'}$, where Z is the number of collisions. The mean moments of energy transfer are of great importance in both the qualitative understanding of the nature of the energy transfer process and the quantitative estimation of the strength of collisions

$$\langle \Delta E^k(v) \rangle = \sum_{v'=0}^{\infty} (E_{v'} - E_v)^k P_{v \rightarrow v'} \quad (4)$$

Here the transition probabilities satisfy the condition of detailed balance

$$N_v^{eq} P_{v \rightarrow v'} = N_{v'}^{eq} P_{v' \rightarrow v} \tag{5}$$

and are normalized to unity for any initial quantum state v

$$\sum_{v'=0}^{\infty} P_{v \rightarrow v'} = 1 \tag{6}$$

Unfortunately, the number of collisions $Z = \omega/n_B$, or the collision frequency $\omega = 1/\tau_0$, where τ_0 is the mean time between collisions, is not a rigorously defined quantity. The collision frequency is often defined as the Lennard-Jones collision frequency [2]. Obviously, the energy transfer moments will depend on the chosen Z value [2–5]. Again, the transition probabilities are frequently defined by [1,8]

$$P_{v \rightarrow v'} = \frac{K_{v \rightarrow v'}}{\sum_{v'=0}^{\infty} K_{v \rightarrow v'}} \tag{7}$$

This definition is also unsatisfactory. The transition probabilities from Eq. 7 are normalized to unity but do not satisfy the detailed balance. The sum over the final v' of all rate coefficients depends on the initial quantum number v , i.e., the number of collisions is the function of v , which follows from the quantum scattering theory [10,11]. This means that the substitution of the transition probabilities in the master equation yields the solution that is not equal to the thermal distribution function N_v^{eq} at $t \rightarrow \infty$. Thus the normalized distribution satisfying the detailed balance should be found.

3 The method

Assume that there is the necessary set of rate coefficients obtained from experiments or theory. For energy loss (down) collisions, the transition probability may be represented as

$$P_{v \rightarrow v'} = A(v') \frac{K_{v \rightarrow v'}}{(K_{v \rightarrow v} K_{v' \rightarrow v'})^{\frac{1}{2}}}, \quad v \geq v' \tag{8}$$

The principle of detailed balance enables one to write the transition probability for energy gain (up) collisions in the form

$$P_{v \rightarrow v'} = A(v) \frac{N_{v'}^{eq} K_{v' \rightarrow v}}{N_v^{eq} (K_{v' \rightarrow v'} K_{v \rightarrow v})^{\frac{1}{2}}}, \quad v' > v \tag{9}$$

The unknown function $A(v)$, appearing in Eqs. 8 and 9, should be found from the normalization condition of the entire $P_{v \rightarrow v'}$. Note that the transition probabilities are expressed in terms of the rate coefficients solely for downward collisions, which is convenient when the rate coefficients are either calculated by a semiclassical

approximation or given as fitting laws. We have specified the factor in the denominators of both of the expressions from physical considerations to bound the normalization function for large v . The diagonal elements $K_{v \rightarrow v'}$, appearing in the equations, are noteworthy. There is no way to introduce the conservation of probability into theory without these elements.

In view of Eq. 6, the normalization function is determined from the integral equation in the finite-difference form

$$\sum_{v'=0}^v A(v') \frac{K_{v \rightarrow v'}}{(K_{v \rightarrow v} K_{v' \rightarrow v'})^{\frac{1}{2}}} + A(v) \sum_{v'=v+1}^{\infty} \frac{N_{v'}^{eq} K_{v' \rightarrow v}}{N_v^{eq} (K_{v' \rightarrow v'} K_{v \rightarrow v})^{\frac{1}{2}}} = 1 \quad (10)$$

It is convenient throughout this paper to define a function

$$f(v) = \sum_{v'=v+1}^{\infty} \frac{N_{v'}^{eq} K_{v' \rightarrow v}}{N_v^{eq} (K_{v' \rightarrow v'} K_{v \rightarrow v})^{\frac{1}{2}}} \quad (11)$$

Then Eq. 10 may be recast as

$$A(v) = \frac{1}{1 + f(v)} \left[1 - \sum_{v'=0}^{v-1} A(v') \frac{K_{v \rightarrow v'}}{(K_{v \rightarrow v} K_{v' \rightarrow v'})^{\frac{1}{2}}} \right], \quad v = 1, 2, \dots \quad (12)$$

In addition, at $v = 0$ Eq. 10 can be written in the form

$$A(0) = \frac{1}{1 + f(0)} \quad (13)$$

Using Eq. 12 one can find $A(1), A(2), \dots, A(V)$ in a step-by-step fashion, where V is some arbitrarily high value sufficient for the convergence of all computations with $P_{v \rightarrow v'}$. So recursive relation (12) provides an exact, non-perturbation solution to integral Eq. 10 for the arbitrary dependence of the rate coefficients on quantum numbers v and v' . Consequently, formulae (8)–(13) yield the solution of the problem formulated making it possible to determine the normalized transition probabilities obeying the detailed balance by the known rate coefficients.

4 Separable kernel approximation

Let us consider the special case of separable kernels that is of considerable importance in applications. Assume that the rate coefficient may be represented as the product of two functions $K_1(v)K_2(v')$ at $v \geq v'$. Then instead of (8) and (9) we get, respectively,

$$P_{v \rightarrow v'} = A(v') \left[\frac{K_1(v)K_2(v')}{K_1(v')K_2(v)} \right]^{\frac{1}{2}}, \quad v \geq v' \quad (14)$$

and

$$P_{v \rightarrow v'} = A(v) \frac{N_{v'}^{eq}}{N_v^{eq}} \left[\frac{K_1(v')K_2(v)}{K_1(v)K_2(v')} \right]^{\frac{1}{2}}, \quad v' > v \tag{15}$$

Equation for the function $f(v)$ becomes

$$f(v) = \sum_{v'=v+1}^{\infty} \frac{N_{v'}^{eq}}{N_v^{eq}} \left[\frac{K_1(v')K_2(v)}{K_1(v)K_2(v')} \right]^{\frac{1}{2}} \tag{16}$$

In this case recursive relation (12) is considerably simplified. At $v = 1, 2, \dots$ we have

$$A(v) = \frac{1}{1 + f(v)} \{1 - \kappa(v) [1 - f(v - 1)A(v - 1)]\}, \tag{17}$$

where

$$\kappa(v) = \left[\frac{K_1(v)K_2(v - 1)}{K_1(v - 1)K_2(v)} \right]^{\frac{1}{2}} \tag{18}$$

As in the general case, the value of $A(0)$ is given by Eq. 13.

An interesting distinction of the recursive relation is that $A(v)$ is expressed solely in terms of $A(v - 1)$. Then the solution of Eq. 17 may be found in the analytical form. For this purpose, we define the two functions:

$$B(v) = \frac{1 - \kappa(v) (1 - \delta_{v0})}{1 + f(v)}, \quad v = 0, 1, \dots \tag{19}$$

and

$$C(v) = \frac{\kappa(v)f(v - 1)}{1 + f(v)}, \quad v = 1, 2, \dots \tag{20}$$

We now write Eq. 17 in more detail beginning with $v = 0$

$$\begin{aligned} A(0) &= B(0), \\ A(1) &= B(1) + C(1)B(0), \\ A(2) &= B(2) + C(2)B(1) + C(2)C(1)B(0), \end{aligned} \tag{21}$$

etc. For the more general case, one finds

$$\begin{aligned} A(v) &= B(v) + C(v)B(v - 1) + C(v)C(v - 1)B(v - 2) + \dots \\ &+ C(v)C(v - 1) \dots C(1)B(0) \end{aligned} \tag{22}$$

Therefore, the $A(v)$ is obtained by

$$A(v) = \sum_{k=0}^v D_k(v) B(v-k), \quad (23)$$

where the expansion coefficients are given by the expression

$$D_k(v) = \begin{cases} 1, & k = 0 \\ \prod_{m=1}^k C(v-m+1), & k = 1, 2, \dots, v \end{cases} \quad (24)$$

Thus, formulae (23) and (24) give the analytical solution of recursion Eq. 17 in the form of a finite sum.

5 The exponential energy-gap law

There are two essentially different approaches to the theoretical study of inelastic collisions in gases. In the first approach, the cross-sections and rate coefficients are calculated based on the quantum scattering theory or its various approximations. In the second approach, the moments of energy transfer and the characteristic relaxation rates are expressed in terms of the rate coefficients whose functional form is assumed to be known. Therefore, such rate coefficients are usually specified from physical considerations in the form of the functional dependence on v and v' with few adjustable parameters. Expressions of this type are known as fitting or scaling laws [12–14] (and references therein). The exponential energy-gap law (EGL) is the simplest model in which the rate coefficient decreases exponentially with the amount of energy transferred at collision. The EGL was first proposed empirically [15] and then derived from the entropy maximization principle of information theory [16]. In accordance with the EGL, we have

$$\frac{K_1(v)}{K_1(v')} = \frac{K_2(v')}{K_2(v)} = \exp \left[-\frac{E_v - E_{v'}}{a} \right], \quad (25)$$

where a is the model parameter characterizing the energy transfer efficiency. Now, the transition probability is the completely defined function

$$P_{v \rightarrow v'} = A(v') \exp \left[-\frac{E_v - E_{v'}}{a} \right], \quad v \geq v' \quad (26)$$

and

$$P_{v \rightarrow v'} = A(v) \frac{\rho(v')}{\rho(v)} \exp \left[-\frac{E_{v'} - E_v}{b} \right], \quad v' > v, \quad (27)$$

where

$$\frac{1}{b} = \frac{1}{a} + \frac{1}{k_B T} \quad (28)$$

It is seen from the foregoing that the theory can be applied to the systems with the energy levels enumerated by a single quantum number v . These are harmonic and anharmonic oscillators including the case of degeneracy. Rotational relaxation of diatomic and spherical molecules can serve as an example of the developed formalism. Below we shall consider two simple examples to demonstrate the ability of the EGL model to build the normalized transition probabilities obeying the detailed balance.

5.1 The Morse oscillator

The case of the Morse oscillator is taken as a familiar example. The energy levels of the Morse oscillator are given by the expression

$$E_v = \hbar\omega \left(v + \frac{1}{2} \right) - x\hbar\omega \left(v + \frac{1}{2} \right)^2, \quad (29)$$

where ω is the harmonic frequency of vibrations, x is the anharmonicity constant related to the maximal number V of the bound states by $x = 1/(2V + 1)$. The energy levels are not degenerate, i.e., $\rho(v) = 1$. Now the function $f(v)$ is of the form

$$f(v) = \sum_{v'=v+1}^{V+1} \exp \left\{ -\frac{\hbar\omega}{b}(v' - v) [1 - x(v + v' + 1)] \right\} \quad (30)$$

It immediately follows from the definition that

$$\kappa(v) = \exp \left[-\frac{\hbar\omega}{a}(1 - 2xv) \right] \quad (31)$$

Therefore, we are in position to calculate the normalization function, the transition probabilities, and the mean energy transferred per collision.

The Morse oscillator was used for modeling the vibrations of the I_2 molecule with $\omega = 133.47 \text{ cm}^{-1}$ and $x\omega = 1.039 \text{ cm}^{-1}$ ($V = 63$) to compare theoretical [17] and experimental [18] vibrational energy transfer rates for the collisional system $I_2(v = 35) + \text{He} \rightarrow I_2(v') + \text{He}$. Experimental data was represented by the EGL model with the parameter a equal to 100 cm^{-1} [19]. Figure 1 shows the calculated normalization function depending on vibrational quantum number v . As is seen, the $A(v)$ is a bounded function, and decreases non-monotonically with v . For such a behavior to be more clear, the functions $\kappa(v)$ and $f(v)$ are shown in the figure. The normalized transition probability from the initial level $v = 35$ is presented in Fig. 2 as a function of $\Delta v = v' - v$. It is evident that up ($\Delta v > 0$) and down ($\Delta v < 0$) transition probabilities are not equal to one another obeying the detailed balance. Finally, the mean energy transferred per collision is depicted in Fig. 3 as a function of initial quantum

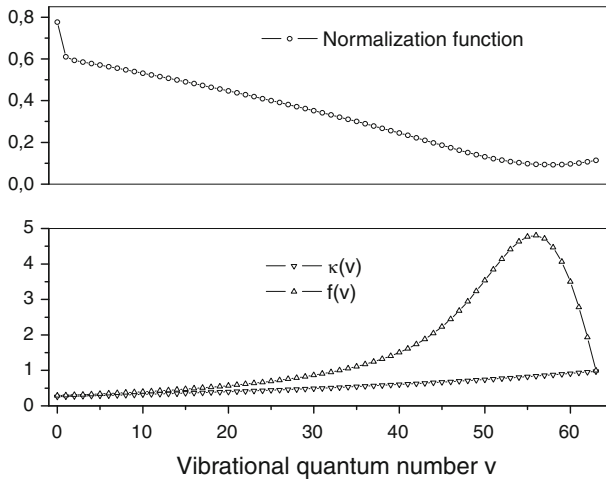


Fig. 1 The normalization function $A(v)$ plotted against v . The functions $\kappa(v)$ and $f(v)$ are shown for comparison

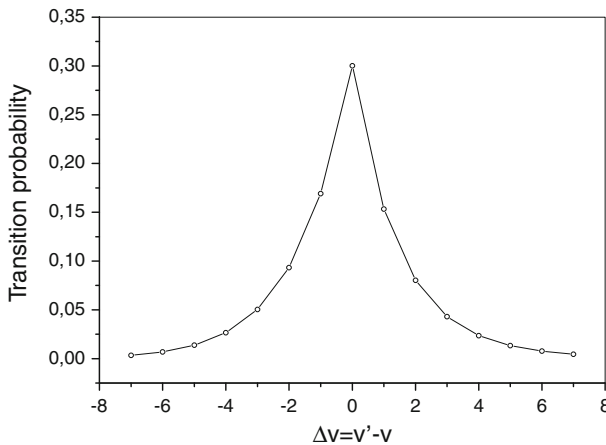


Fig. 2 The transition probability $P_{35 \rightarrow 35 + \Delta v}$ for the collisional system $I_2 + He$ as a function of the quantum number difference $\Delta v = v' - v$

number v . In particular, at $v = 35$ the calculated value $\langle \Delta E(v = 35) \rangle = -6.3 \text{ cm}^{-1}$ is in excellent agreement with the experimental value -6.5 cm^{-1} [19].

5.2 Harmonic oscillator

By definition, $x = 0$ for a harmonic oscillator. The function $f(v)$ takes the form

$$f(v) = \frac{1}{\exp(\omega/b) - 1} \quad (32)$$

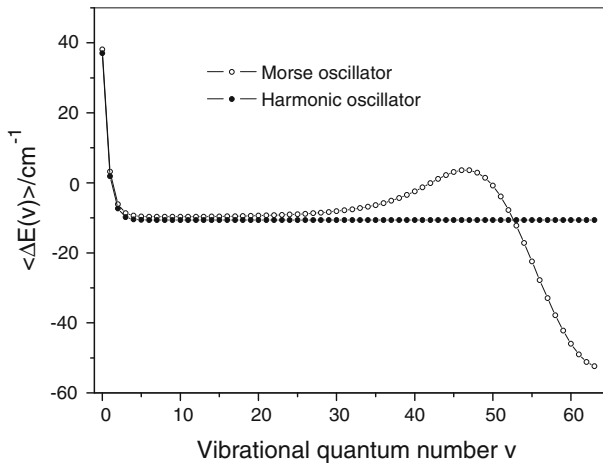


Fig. 3 The mean energy transfer of the Morse and harmonic oscillators characterized by the initial quantum number

In this situation both functions $f(v)$ and $\kappa(v)$ are independent of vibrational quantum number v ; this considerably simplifies the subsequent calculations. After tedious and lengthy algebra, we get from Eqs. 23 and 24 a simple relation

$$A(v) = \alpha + \beta \exp\left(-\frac{\omega v}{c}\right), \tag{33}$$

Note that the solution in this form can be substituted directly in Eq. 17 to find the unknown parameters α , β and c . We determine in any fashion

$$\alpha = \frac{1 - e^{-\omega/a} - e^{-\omega/b} + e^{-\omega/c}}{1 - e^{-\omega/c}}, \tag{34}$$

$$\beta = 1 - e^{-\omega/b} - \alpha, \tag{35}$$

and

$$\frac{1}{c} = \frac{1}{a} + \frac{1}{b} = \frac{2}{a} + \frac{1}{k_B T} \tag{36}$$

Thus, the above formulae (26), (27) and (33)–(36) define completely the transition probabilities of harmonic oscillator under the action of collisions in a thermal bath within the EGL approximation. As is seen from Fig. 3, the mean energy transfer does not depend on vibrational quantum number in the range of large v . For the forced harmonic oscillator this is true for all v [20]. In this case $\langle \Delta E \rangle$ is equal to the value given by classical mechanics. In the framework of the EGL model, this approximation is partially revised.

6 Summary

The study of collisional energy transfer allows one to find the mean energy transferred per collision from direct experiments [5,21]. Comparison with experimental data calls for the knowledge of the energy transfer moments calculated with the normalized transition probabilities that satisfy the detailed balance. These quantities are obtained from the set of rate coefficients. In this paper, we propose the method that gives such transition probabilities using the normalization function from recursion Eq. 12 without any approximations. These calculations require only trivial computer time at arbitrary dependence of the rate coefficients $K_{v \rightarrow v'}$ on quantum numbers v and v' . The recursion equation is essentially simplified for separable kernels (Eq. 17). In this case, we have the exact analytical solution in the form of a finite sum. The particularly simple dependence of the normalization function on v takes place for the harmonic oscillator.

In conclusion, it must be mentioned that comparison between the energy transfer rate computed from another theory and the mean energy transfer per collision deduced from experiment is made by a simple scaling with the collision number Z . In our approach, there is no necessity of determining the collision number Z at all. However, a more complicated procedure is required for the systems where energy levels are given by a set of quantum numbers.

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