

Laguerre polynomial solutions to master equation for vibrational energy relaxation in gases

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Abstract Collisional energy transfer between highly vibrationally excited molecules and a bath gas is considered as a stochastic process occurring in energy space. An exact solution to master equation for the conditional probability is given in terms of simple analytical formulas for weak and strong collisions. The strong collisions are shown to manifest themselves in the distribution pattern composed of maxima and minima in the energy dependence of conditional probability. This effect is explained in detail on physical grounds.

Keywords Vibrational relaxation · Energy transfer · Transition probability · Stochastic processes

1 Introduction

Most theoretical studies on vibrational energy relaxation in gases are based on a Markov approximation in which collisions are considered as a sequence of almost entirely uncorrelated events due to the substantial difference in the time of collision and the time between collisions. Over the course of many collisions, E can acquire many values, and the resulting trajectory is a random walk among the allowed values in the energy space. The Markov process is known to be entirely defined by two probability density functions used to obtain the averages per collision with the transition probability $P(E \rightarrow E')$ and the bulk averages with the conditional probability $G(E, t|E', t')$ [1–5]. Theoretically, the probability $P(E \rightarrow E')$ is of the utmost significance since

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it contains exhaustive information on the energy-transfer processes, which can be extracted from the solution of master equation. The problem is that until recently, the $P(E \rightarrow E')$ probability could not be measured experimentally except for its first and second moments.

Usually, the transition probability is modeled by simple analytical functions that depend on the adjustable parameters, which are closely related to the first and, in some cases, to the second moments of $P(E \rightarrow E')$ [3–9]. Recently, the exact relationship has been determined between the $P(E \rightarrow E')$ distribution and the quantum transition probabilities $P_{i \rightarrow f}$ of an active molecule under the action of collisions in a thermal bath [10]. Considering the active molecule as a system of harmonic oscillators, we have derived an analytical expression for $P(E \rightarrow E')$ from the “first principles” using the first-order perturbation theory for the $P_{i \rightarrow f}$ probability of transition between vibrational states i and f . The only parameter of the model is expressed in terms of the mean number of collisions Z_V that may be either calculated numerically or taken from experiments. In this case, the Laguerre polynomials are the eigenfunctions of the $P(E \rightarrow E')$ kernel and, therefore, the solution of master equation is found as an eigenfunction expansion in terms of these polynomials.

For polyatomic gases, the mean number of collisions Z_V changes within wide limits from 10^0 to 10^5 [11]. With a great number of steps, the process, during which the equilibrium is reached, shows up as diffusion. Unfortunately, the solution to the master equation, found as a series, appears to be of no use for the most interesting case where the diffusion approximation holds, because at $Z_V \gg 1$, the series converges very slowly. In this Letter, we are going to clear up the trouble (a limitation of this solution method) and to derive a compact expression in the form of a simple analytical formula. For strong collisions ($Z_V \approx 1$), a numerical solution to the master equation also involves certain problems. In this case, it is necessary to rewrite the input series as a double series in which the finite one is given in terms of the effectively computable functions. This solution is of interest because of the structure, consisting of maxima and minima in the energy dependence of conditional probability. We will interpret this phenomenon physically.

2 Transition probabilities

Consider the system of vibrationally excited molecules that are highly dispersed in a constant-temperature heat bath. We assume then that an active molecule consists of s harmonic oscillators whose internal energy varies at collisions in a heat bath. The collisions cause transitions only between the neighboring vibrational levels. In the specified conditions, the probability of transition from the state with the initial energy E to that with the final energy E' near $E' + dE'$ is given by the expression [10]

$$P(E \rightarrow E'; \gamma) = N^{eq}(E') \sum_{k=0}^{\infty} \gamma^k \Phi_k(E) \Phi_k(E') \quad (1)$$

In this case, $N^{eq}(E)$ is the equilibrium or thermal internal energy distribution, and $\Phi_k(E)$ is the system of orthonormalized polynomials, generated by the weight function

$N^{eq}(E)$ over the interval $(0, \infty)$. Obviously, $\Phi_k(E)$ are the eigenfunctions of the $P(E \rightarrow E')$ kernel. Parameter γ is related to the mean number of collisions via the equation

$$\gamma = 1 - \frac{1}{Z_V} \quad (2)$$

The collisions are weak at $Z_V \gg 1$. In each collision, the internal energy varies negligibly and the energy-transfer process shows up as diffusion in energy space. In the absence of relaxation, we get $P(E \rightarrow E') = \delta(E - E')$, which corresponds to the limit $Z_V = \infty$. The collisions are strong at $Z_V \approx 1$. In particular, the limiting case $Z_V = 1$ corresponds to the model of strong collisions. The collisions, considered in the model, are so strong that, in the mean, the equilibrium state is reached in one collision $P(E \rightarrow E') = N^{eq}(E')$.

Thus, in the case of strong collisions, the thermal distribution of internal energy is of great importance for the problem under study. The simplifying condition, implicit in Eq. (1), is that $N^{eq}(E)$ is the classical thermal distribution. With this distribution, the mean thermal energy becomes equal to $sk_B T$. For the molecules with a great number of vibrational degrees of freedom, this limiting value is inaccessible at all temperatures with the molecule observed as a bound system. We believe that the model, involving a realistic vibrational density of states, can be used to remove this assumption in evaluating $P(E \rightarrow E')$. Recently, the simple relations between the thermodynamic properties and the molecular density of states have been applied to formulate an accurate method for determining the vibrational state density, taking into account both the quantum and anharmonic effects [12–14]. The energy dependence of the state density is of the form

$$\rho(E) \propto (E - E_*)^{a-1} \quad (3)$$

With regard to the density of states, $\rho(E)$, the normalized thermal distribution obeys the equation

$$N^{eq}(E) = \frac{1}{\Gamma(a)k_B T} \left(\frac{E - E_*}{k_B T} \right)^{a-1} \exp\left(-\frac{E - E_*}{k_B T}\right), \quad E \geq E_* \quad (4)$$

Note that $N^{eq}(E) = 0$ at $E < E_*$. The unknown parameters are determined from this distribution by calculating the mean thermal energy $\langle E \rangle_T$ and the total vibrational heat capacity of the gas, C_{vib} , namely:

$$\langle E \rangle_T = E_* + ak_B T \quad (5)$$

and

$$a = \left\langle \left(\frac{E - \langle E \rangle_T}{k_B T} \right)^2 \right\rangle_T = \frac{C_{vib}}{k_B} \quad (6)$$

To gain greater insight into the physical meaning of these parameters, we give the limiting form of relations (5) and (6) at low and high temperatures

$$a = \begin{cases} 0, & T = 0 \\ s, & T \rightarrow \infty \end{cases} \quad \text{and} \quad E_* = \begin{cases} E_0, & T = 0 \\ 0, & T \rightarrow \infty \end{cases}, \quad (7)$$

where s is the number of vibrational degrees of freedom, and E_0 is the zero-point energy. Thus, the parameter a is the effective number of oscillators and E_* is taken as the zero of energy. At high temperatures, Eq. (4) gives the classical distribution of vibrational energy. The $\Phi_k(E)$ polynomials are related directly to the Laguerre polynomials

$$\Phi_k(E) = \left[\frac{\Gamma(a)k!}{\Gamma(a+k)} \right]^{\frac{1}{2}} L_k^{(a-1)} \left(\frac{E - E_*}{k_B T} \right) \quad (8)$$

Now we use the generating function of Laguerre polynomials [15]

$$\sum_{k=0}^{\infty} \frac{k! \gamma^k}{\Gamma(a+k)} L_k^{(a-1)}(x) L_k^{(a-1)}(y) = \frac{(\gamma xy)^{-(a-1)/2}}{1-\gamma} \exp\left(-\gamma \frac{x+y}{1-\gamma}\right) \times I_{a-1}\left(\frac{2\sqrt{\gamma xy}}{1-\gamma}\right), \quad (9)$$

where I_{a-1} is the modified Bessel function. Taking into account Eq. (9), which implies Eq. (8), we can rewrite Eq. (1) in the compact form

$$P(E \rightarrow E'; \gamma) = \frac{1}{k_B T (1-\gamma)} \left(\frac{y}{\gamma x} \right)^{(a-1)/2} \exp\left[-\frac{y+\gamma x}{k_B T (1-\gamma)}\right] \times I_{a-1}\left[\frac{2\sqrt{\gamma xy}}{k_B T (1-\gamma)}\right], \quad (10)$$

where x , y are the dimensionless variables

$$x = \frac{E - E_*}{k_B T}, \quad y = \frac{E' - E_*}{k_B T} \quad (11)$$

The limiting cases of strong and weak collisions follow from this distribution at $\gamma = 0$ and 1, respectively.

3 Analytical solutions to the master equation

The master equation is the starting point of many investigations of time-dependent phenomena in the statistical description of relaxation processes. Specifically, the time

evolution of the population, $N(E, t)$, where E is the internal energy of the system, taken as a continuous variable, is given by the master equation [1, 2]

$$\frac{\partial}{\partial t} N(E, t) = \nu \int_0^\infty [P(E' \rightarrow E) N(E', t) - P(E \rightarrow E') N(E, t)] dE', \quad (12)$$

where ν is the collision frequency. The general solution can be expressed in terms of a series of the $\Phi_k(E)$ polynomials

$$N(E, t) = N^{eq}(E) \sum_{k=0}^\infty c_k g_k(t) \Phi_k(E), \quad (13)$$

where the coefficients c_k are determined by initial conditions with $c_0 = 1$ and $g_k(0) = 1$. From Eq. (1), it is concluded that the transition probability is the kernel of the integral equation with the $\Phi_k(E)$ eigenfunctions and the γ^k eigenvalues. Since the population is also expressed in terms of these eigenfunctions, the solution is found quite readily. In this case, we get a simple solution to the $g_k(t)$ functions

$$g_k(t) = \exp\left[-(1 - \gamma^k) \nu t\right] \quad (14)$$

Of special interest is the so-called fundamental solution (or the Green function), $G(E_i, t_i|E, t)$, which at $t = t_i$ is reduced to $\delta(E - E_i)$. If the Green function is known, the population, corresponding to the arbitrary initial condition, $N(E_i, 0)$, is given by the integral

$$N(E, t) = \int_0^\infty N(E_i, 0) G(E_i, 0|E, t) dE_i \quad (15)$$

Physically, $G(E_i, t_i|E, t)$ is the conditional probability that the random variable $E(t)$ takes the value E at time t provided it was E_i at previous time t_i . At fixed t , it represents the fractional population of hot molecules as a function of their internal energy E . According to the completeness property for the $\Phi_k(E)$ polynomials, we use $c_k = \Phi_k(E_i)$ to obtain

$$G(E_i, t_i|E, t) = N^{eq}(E) \sum_{k=0}^\infty \exp\left[-(1 - \gamma^k) \nu(t - t_i)\right] \Phi_k(E_i) \Phi_k(E) \quad (16)$$

It is readily seen that this solution describes the Markov process where the probability of transition to a new state of the system depends on the current state only (see for details [1]).

Let us consider the two limiting cases following from Eq. (16) for weak and strong collisions. For the weak collisions ($Z_V \gg 1$), we approximately get $1 - \gamma^k \approx k/Z_V$.

In this case, the expression for $G(E_i, t_i|E, t)$ can be rewritten in a more compact form using the generating function of Laguerre polynomials (see Eq. 9). Finally, we get the analytical representation for the conditional probability

$$G(E_i, t_i|E, t) = \frac{1}{(1 - e^{-\tau}) k_B T} \left(\frac{y}{x e^{-\tau}} \right)^{(a-1)/2} \exp \left(-\frac{y + x e^{-\tau}}{1 - e^{-\tau}} \right) \times I_{a-1} \left(\frac{2\sqrt{xy e^{-\tau}}}{1 - e^{-\tau}} \right), \quad (17)$$

where the variables x and y are defined by Eq. (11) and τ is given by

$$\tau = \frac{\nu(t - t_i)}{Z_V} \quad (18)$$

Equation (17) makes it clear that the initial distribution of the $\delta(E - E_i)$ form gradually spreads and at long times, tends to thermal distribution.

For comparison, we give the expression, which follows from Eq. (16) in the limit of strong collisions ($Z_V = 1$)

$$G(E_i, t_i|E, t) = \delta(E - E_i) e^{-\tau} + N^{eq}(E) (1 - e^{-\tau}) \quad (19)$$

Now, the conditional probability (as a function of energy) demonstrates the structure, consisting of two components that do not mix. As the probability of finding molecules with initial energy decreases exponentially, the probability of molecule occurrence in thermal equilibrium increases. The initial conditions are “forgotten” in a time between two collisions, $t_0 = 1/\nu$, which, in this limit, is the relaxation time of internal energy.

Finally, the general solution can be written as a double series obtained by expanding the time-dependent exponent into a power series

$$G(E_i, t_i|E, t) = \sum_{m=0}^{\infty} (-1)^m \frac{[\nu(t - t_i)]^m}{m!} \sum_{n=0}^m (-1)^n \binom{m}{n} [\delta_{n0} \delta(E - E_i) + (1 - \delta_{n0}) P(E_i \rightarrow E; \gamma^n)] \quad (20)$$

For the strong collisions, equilibrium is reached during a relatively short time νt . Therefore, the infinite series converges rather rapidly. On the other hand, the finite series is expressed in terms of the effectively computable functions given by Eq. (10).

4 Weak and strong collisions

To demonstrate the actual numerical results for a concrete collisional system, we shall use, for illustrative purposes, the parameters applicable to azulene ($C_{10}H_8$) which is highly diluted in argon at 300 K. It is usual practice to use E as the vibrational energy above the zero-point energy. In other words, E should be substituted by $E + E_0$ in (11). At $E_i - \langle E \rangle_T = 27,916 \text{ cm}^{-1}$ and $E_i = 28,895 \text{ cm}^{-1}$, the average energy

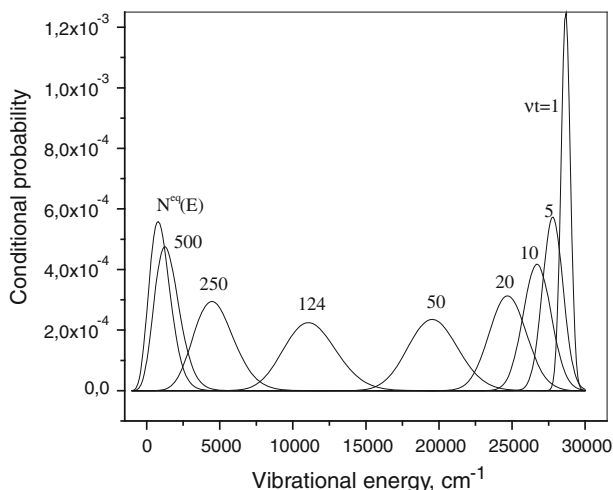


Fig. 1 Relaxation of the initial δ -function distribution with $Z_V = 124$ (weak collisions) to the final thermal distribution with $\langle E \rangle_T = 979 \text{ cm}^{-1}$

transferred per collision is 226 cm^{-1} , i.e., on the average, 124 collisions are required to reach equilibrium [16]. These data are suffice to calculate the conditional probability with $E_0 = 30,892 \text{ cm}^{-1}$, $E_* = 29,267 \text{ cm}^{-1}$, and $a = 12.49$ (vibrational frequencies are taken from [17]). Figure 1 shows the conditional probability for weak collisions as a function of energy for different values of the reduced time vt . As vt increases, the peak displaces along axis E from its initial position to the final one. At short times, a very narrow distribution located at $E_i \exp(-vt/Z_V)$ displaces towards low energies with a peak shift of $[1 - \exp(-vt/Z_V)] E_i$. With a further increase in vt , the distribution gradually broadens, but within the limit $vt \rightarrow \infty$, leads to the narrow thermal distribution with $\langle E \rangle_T = 979 \text{ cm}^{-1}$. Remember that the conditional probability is normalized to unity.

The classical trajectory calculations have confirmed the existence of “supercollisions” at which the abnormally large amount of energy is transferred in a single collision [18–20]. The large polyatomic molecules undergo just few (less than 1%) supercollisions during which an energy of about $10^3 - 10^4 \text{ cm}^{-1}$ is transferred to the surrounding cold molecules, whereas the average energy transfer per collision is weak (of order of 10^2 cm^{-1}). We consider here the supercollisions with $Z_V = 3$ using the highly excited azulene in argon, as an example. In this case, the rare events take place in which an energy of $9,305 \text{ cm}^{-1}$ is transferred per collision. The time evolution of the conditional probability for a sub-ensemble of strong collisions is shown in Fig. 2. At long times ($vt \gg Z_V$), the distribution approaches the thermal distribution, representing an asymmetric curve with a tail directed towards high energies. Quite a different pattern is observed at short times. There are both a very narrow peak located at the initial energy and a long tail of probability distribution with a structure of several maxima and minima at lower energies. This distribution pattern is demonstrated in detail in Fig. 3. The hot molecules lose their energy which, on the average, is equal to $\langle \Delta E \rangle$, given by $P(E \rightarrow E')$ as

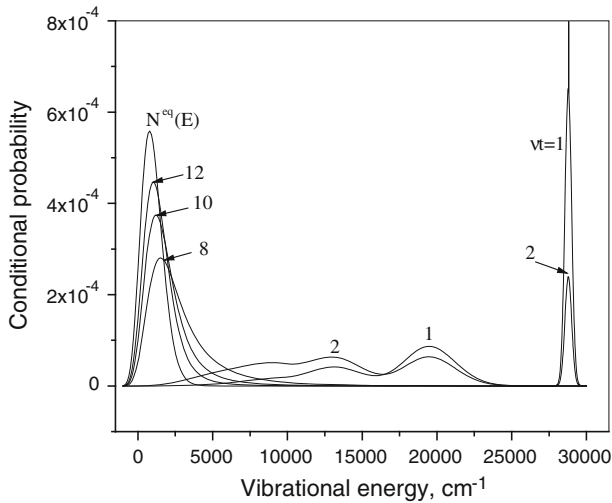


Fig. 2 Change of conditional probability as a function of energy (and reduced time νt) for strong collisions with $Z_V = 3$

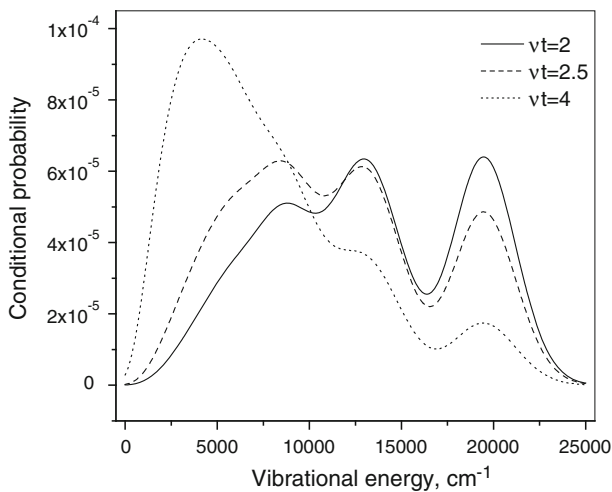


Fig. 3 The energy dependence of conditional probability at fixed νt for strong collisions with $Z_V = 3$. For $\nu t = 2$, the maxima are localized at 19,600, 13,140, and 9,040 cm^{-1} , respectively. The predicted values are 19,600, 13,400, and 9,300 cm^{-1} , correspondingly

$$\langle E_i - E \rangle = \frac{E_i - \langle E \rangle_T}{Z_V} \quad (21)$$

Therefore, the cooled molecules arise with the energy $E_i - \langle \Delta E \rangle$. The portion of these molecules in the distribution is indicated by the peak centered at the energy

$$E_{\max}(1) = E_i - \frac{E_i - \langle E \rangle_T}{Z_V} \quad (22)$$

The molecules continue to lose their energy due to collisions, but now the initial energy is $E_i - \langle \Delta E \rangle$. It is readily calculated that the second peak of the cooled molecules will be localized at the energy

$$E_{\max}(2) = E_i - \left(2 - \frac{1}{Z_V}\right) \frac{E_i - \langle E \rangle_T}{Z_V} \quad (23)$$

The third peak is localized at the energy

$$E_{\max}(3) = E_i - \left(3 - \frac{3}{Z_V} + \frac{1}{Z_V^2}\right) \frac{E_i - \langle E \rangle_T}{Z_V} \quad (24)$$

The cooled molecules, losing all their energy, give rise to thermal distribution. It is clear that the probability to find hot molecules (at high energies) vanishes with time and the probability to find molecules in thermal equilibrium (with energy $\langle E \rangle_T$) increases with time, as shown in Fig. 3.

5 Conclusions

The master equation for collisional deactivation of the highly vibrationally excited molecules has been solved for the model of harmonic oscillators with the real density of vibrational states. The results are represented by analytical solutions to the strong- and weak-collision-type energy transfer. Thus, the present approach reduces the solution of the master equation to the much simpler estimation of $G(E_i, t_i | E, t)$ from Eqs. (17) and (20). The careful considerations indicate that the case of weak collisions is realized for Z_V exceeding $Z_V \approx 10$. In this case, the conditional probability is calculated from analytical formula (17). For strong collisions, we recommend to use Eq. (20) instead of (16). The latter should take into account very many terms at short time νt to derive a smooth solution. As compared with the well-studied weak collisions [21], the energy dependence of the conditional probability is unusual (but physically clear) for the strong collisions. The observed manifestations of this effect are of particular interest and deserve further studying, in particular, in rotational relaxation, where the strong collisions are quite common.

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