

# An exact analytical solution to the master equation for the vibration–dissociation process of Morse oscillators

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**Abstract** The coupled vibration–dissociation process for Morse oscillators and structureless particles has been examined. A method to solve the appropriate master equation is developed. The case has been studied carefully where the dissociation process starts mainly from the bound level nearest to the dissociation limit. The master equation has an exact analytical solution in this case upon many-quantum transitions and for an arbitrary amount of energy transferred per collision. Simple expressions for the steady-state dissociation rate and for the incubation time are obtained.

**Keywords** Vibration–dissociation processes · Master equation · Transition probability · Shock-heated molecules · Orthogonalization procedure

## 1 Introduction

Vibrational relaxation of diatomic molecules, accompanied by dissociation, has long been the subject of theoretical investigations [1–5]. Due to the progress in computers, a numerical treatment of complicated models for the rotation–vibration–dissociation coupling has become feasible. Nevertheless, analytical approaches shed light on the nature of the process; allow general conclusions and a correct statement of the problem for further numerical modeling. This approach holds for the case where dissociation proceeds from the topmost bound level only. In the framework of this model, account may be taken of multi-quantum transitions for any amount of internal energy transferred per collision.

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The Morse oscillator is a practical model of vibrational relaxation. It can reproduce the vibrational spectrum of diatomic molecules in a semi-quantitative manner. The matrix elements of vibrational coordinate are also known for discrete-discrete and discrete-continuum transitions [6]. Numerous calculations are available for collisional cross-sections and for the rate constants of these transitions [7–11]. A knowledge of the vibration–dissociation process involved in a system of oscillators makes it possible to calculate the time-dependent populations of oscillators in the available energy levels. Conversely, measuring these populations can yield the values for the parameters of energy transfer accompanied by dissociation. The system of relaxing Morse oscillators is further called the molecules diluted in inert gas.

Let us assume that the molecules are distributed in a large excess of chemically inert gas that acts as a heat bath throughout the reaction. The requirement of a constant temperature  $T$  of the heat bath implies that the concentration of reactant molecules is small compared to that of inert atoms. The vibrational degrees of freedom are initially characterized by the equilibrium thermal distribution at temperature  $T_i$  such that  $T_i \ll T$ . A shock wave serves as a source of nonequilibrium. Due to collisions with atoms, the molecules are excited into higher vibrational energy levels until they reach the  $N$ th level where they dissociate irreversibly and remove from the reaction system. In the framework of this approach, we are going to offer an analytical model with an exact solution.

## 2 Model of the vibration–dissociation process

The Morse oscillator is commonly used to model vibrations of a diatomic molecule. In the discrete spectrum there are  $N + 1$  bound energy levels

$$E_n = \hbar\omega_e \left( n + \frac{1}{2} \right) - \hbar x_e \omega_e \left( n + \frac{1}{2} \right)^2, \quad (1)$$

where the anharmonicity constant  $x_e$  relates to the topmost level  $N$  via the equation  $x_e = 1/(2N + 1)$  and equals  $\hbar\omega_e/4D$ , where  $D$  is the dissociation energy. The equilibrium thermal distribution is of the form

$$\rho_n(\theta) = Q^{-1} \exp \left\{ -\theta \left( n + \frac{1}{2} \right) \left[ 1 - \frac{2n + 1}{2(2N + 1)} \right] \right\}, \quad (2)$$

where  $\theta = \hbar\omega_e/k_B T$  and  $Q$  is the partition function of the Morse oscillator.

A conventional method to calculate the master equation involves the expansion of populations in terms of a proper set of eigenfunctions. We are going to apply the orthonormalized polynomials  $\Phi_k(n, \theta)$ , generated by the weight function  $\rho_n(\theta)$ , in the range  $n = 0, 1, \dots, N$ , namely:

$$\sum_{n=0}^N \rho_n(\theta) \Phi_k(n, \theta) \Phi_{k'}(n, \theta) = \delta_{kk'}, \quad (3)$$

where  $\Phi_0(n, \theta) = 1$  and the other polynomials are determined using orthogonalization procedure (“Appendix”). These polynomials satisfy the completeness property

$$\rho_n(\theta) \sum_{k=0}^N \Phi_k(n, \theta)\Phi_k(n', \theta) = \delta_{nn'} \tag{4}$$

Collisions result in the  $X_n(t)$  fraction of excited molecules in the vibrational level  $n$  at the time  $t$ . On the way up the energy ladder, the molecules reach the dissociation threshold and decompose. This process is described by a system of linear differential equations with constant coefficients (the so-called master equation) [1–5]

$$\frac{d}{dt} X_n(t) = \sum_{n'=0}^N [k_{n' \rightarrow n} X_{n'}(t) - k_{n \rightarrow n'} X_n(t)] - k_{n \rightarrow c} X_n(t), \tag{5}$$

where  $k_{n \rightarrow n'}$  is the level-to-level rate coefficient proportional to the number density of inert gas, and  $c$  denotes the continuum.

At present, there are a lot of interpolation formulas or fitting laws to reproduce rate constants, calculated for VT energy transfer [7–11]. In particular, the studies on vibrational relaxation [12–14] indicate that expanding in terms of a complete set of orthonormalized polynomials is a good approximation for rate coefficients

$$k_{n \rightarrow n'} = \nu \rho_{n'}(\theta) \sum_{k=0}^N \left(1 - \frac{1}{Z_V}\right)^k \Phi_k(n, \theta)\Phi_k(n', \theta) \tag{6}$$

Here  $\nu$  is the frequency of collisions in the large excess of inert gas,  $Z_V$  is the mean number of collisions necessary to attain the equilibrium state. The  $Z_V$  values are determined experimentally by various methods [15]. The limit of strong collisions implies that  $Z_V = 1$  and the weak collisions are realized at  $Z_V \gg 1$ . The rates  $k_{n \rightarrow n'}$  satisfy the principle of detailed balance.

For the discrete-continuum transitions, the rate  $k_{n \rightarrow c}$  decreases exponentially with the difference between the energy in the continuum spectrum and the discrete level energy [8, 9]. Approximately, the dissociation follows mainly from the last bound level (the ladder climbing model). The dependence of dissociation rate coefficients on the vibrational quantum number is taken into account in the simplest way in the framework of this model

$$k_{n \rightarrow c} = \delta_{nN} k_N \tag{7}$$

Solution to the master equation for populations is sought as the expansion in terms of the orthonormalized polynomials

$$X_n(t) = \rho_n(\theta) \sum_{k=0}^N C_k(t)\Phi_k(n, \theta) \tag{8}$$

The temporal evolution of the populations is determined by the time-dependent expansion coefficients  $C_k(t)$ . The completeness property of the  $\Phi_k(n, \theta)$  polynomials is used to express these coefficients through the populations

$$C_k(t) = \sum_{n=0}^N X_n(t) \Phi_k(n, \theta) \quad (9)$$

Thus, the coefficients  $C_k(0)$ , taken at  $t = 0$ , are given in terms of the initial condition for the populations. Note that the concentration of molecules (the sum of all populations) is provided by  $C_0(t)$ .

We solve now the master equation in which all the populations are expressed in terms of the population of the topmost level. Substituting Eq. (8) into (5) and taking account of the orthogonality condition, we get

$$\frac{d}{dt} C_k(t) = - \left( 1 - \gamma^k \right) \nu C_k(t) - k_N \Phi_k(N, \theta) X_N(t) \quad (10)$$

To avoid cumbersome formulas, we introduce the notation

$$\gamma = 1 - \frac{1}{Z_V} \quad (11)$$

Solution to this equation is of the form

$$C_k(t) = C_k(0) \exp \left[ - (1 - \gamma^k) \nu t \right] - k_N \Phi_k(N, \theta) \int_0^t X_N(t') \exp \left[ - (1 - \gamma^k) \nu (t - t') \right] dt' \quad (12)$$

The calculated coefficients  $C_k(t)$  are used to obtain the solution to Eq. (5)

$$X_n(t) = \rho_n(\theta) \sum_{k=0}^N C_k(0) \Phi_k(n, \theta) \exp \left[ - (1 - \gamma^k) \nu t \right] - k_N \rho_n(\theta) \sum_{k=0}^N \Phi_k(n, \theta) \Phi_k(N, \theta) \int_0^t X_N(t') \exp \left[ - (1 - \gamma^k) \nu (t - t') \right] dt' \quad (13)$$

The first term describes the relaxation process with the VT energy transfer and depends on the initial condition. The second term is proportional to the outgoing rate and contributes to dissociation. Vibrational relaxation exerts some action on its change with time. Thus, all the populations are given in terms of the unstable level population to be determined.

### 3 Time-dependent population of the unstable level

As follows, Eq. (13) at  $n = N$  is the integral equation of the Volterra type for the desired  $X_N(t)$  population. In other words, at time  $t$  the unstable level population depends on the complete previous history of  $X_N(t')$ . Since the kernel of this equation depends on the argument difference, the Laplace transform is a standard method of solution. We use the notation

$$\widehat{X}_n(z) = \int_0^\infty e^{-zt} X_n(t) dt \tag{14}$$

Applying the Laplace transform to both of the sides of Eq. (13), we get

$$\widehat{X}_n(z) = \rho_n(\theta) \sum_{k=0}^N \frac{\Phi_k(n, \theta)}{z + (1 - \gamma^k)\nu} \left[ C_k(0) - k_N \Phi_k(N, \theta) \widehat{X}_N(z) \right] \tag{15}$$

From this equation, we find the desired relation for  $\widehat{X}_N(z)$

$$\widehat{X}_N(z) = \rho_N(\theta) \left[ 1 + k_N \rho_N(\theta) \sum_{k=0}^N \frac{\Phi_k(N, \theta)^2}{z + (1 - \gamma^k)\nu} \right]^{-1} \sum_{k=0}^N \frac{C_k(0) \Phi_k(N, \theta)}{z + (1 - \gamma^k)\nu} \tag{16}$$

Now Eq. (15) may be used to determine all the other  $\widehat{X}_n(z)$ . For calculations it is more convenient to restore the inverse transform  $X_N(t)$ , and to find the time-dependent populations from Eq. (13). Then, we are going to calculate the unstable level population as a function of time without any approximations.

To this end, the  $\widehat{X}_N(z)$  function is presented as the ratio of two polynomials

$$\widehat{X}_N(z) = \frac{a(z)}{b(z)}, \tag{17}$$

where

$$a(z) = \rho_N(\theta) \sum_{k=0}^N C_k(0) \Phi_k(N, \theta) d_k(z) \tag{18}$$

and

$$b(z) = c(z) + k_N \rho_N(\theta) \sum_{k=0}^N \Phi_k(N, \theta)^2 d_k(z) \tag{19}$$

We have introduced the following notations

$$c(z) = \prod_{k=0}^N \left[ z + (1 - \gamma^k)\nu \right] \tag{20}$$

and

$$d_k(z) = \frac{c(z)}{z + (1 - \gamma^k)v} = \prod_{j=0}^N \text{if} \left[ j = k, 1, z + (1 - \gamma^j)v \right] \tag{21}$$

The function under the product sign is 1 with  $j = k$ , otherwise  $z + (1 - \gamma^j)v$ .

As the  $\widehat{X}_N(z)$  function is the ratio of two polynomials, its singular points are only zeroes of the  $b(z)$  denominator. In this case, all of these are the poles. Hence the inverse transform  $X_N(t)$  has the form

$$X_N(t) = \sum_{k=0}^N \text{res} \left[ e^{zt} \frac{a(z)}{b(z)}, z_k \right] \tag{22}$$

where  $b(z_k) = 0$ . Let all of the zeroes be simple. Then, using the formula for calculating residues of function in simple poles, we obtain

$$X_N(t) = \sum_{k=0}^N \frac{a(z_k)}{b'(z_k)} e^{z_k t} \tag{23}$$

The  $b(z)$  polynomial may be represented as the product  $(z - z_0) \cdots (z - z_N)$ . In this case, the  $b'(z_k)$  derivative is readily calculated to be

$$b'(z_k) = \prod_{j=0}^N \text{if} (j = k, 1, z_k - z_j) \tag{24}$$

In general, the solution is of the form

$$X_N(t) = \sum_{k=0}^N f_k(t) e^{z_k t} \tag{25}$$

When the multiplicity of root is  $s$ , then  $f_k(t)$  is written as the expansion in terms of  $t$

$$f_k(t) = f_{0k} + f_{1k}t + \cdots + f_{s-1,k}t^{s-1} \tag{26}$$

The expansion coefficients are determined from the formula for calculating the residue of the  $s$ th power. We have calculated these coefficients numerically.

Now, we obtain a few analytical results following from the general theory. The numerical calculations indicate that the minimal root  $z_0$  is negligibly small. Thus, this root is determined from Eq. (19) in the limit where  $z$  tends to zero. The simple calculations give

$$z_0 \approx -k_N \rho_N(\theta) \left[ 1 + \frac{k_N \rho_N(\theta)}{v} \sum_{k=1}^N \frac{\Phi_k(N, \theta)^2}{1 - \gamma^k} \right]^{-1} \tag{27}$$

When there is no decomposition of molecules, the minimal root is rigorously zero. By order of magnitude it equals  $k_N \rho_N(\theta)$ . Since the denominator contains a positive value,  $|z_0|$  is always smaller than  $k_N \rho_N(\theta)$ . Usually, the  $|z_0|$  value is identified with the steady-state dissociation rate  $k_d$ . This notation will be used in what follows.

Of particular interest is the general character of the expression derived without both using the explicit dependence of energy levels on the vibrational quantum number and concretizing the form of transition probabilities. Therefore, we may indicate the interval within which the  $k_d$  value varies. For strong collisions, we have  $\gamma^k = \delta_{k0}$ , and the outgoing rate is approximately equal to the collision frequency. In this case,  $k_d$  reaches its maximal value  $\nu \rho_N(\theta)/2$  which actually holds for “supercollisions”, where an inordinate amount of energy is transferred in a single event [16–18]. For weak collisions,  $1 - \gamma^k$  is equal to  $k/Z_V$ , where the mean number of collisions is large. This is the most interesting case of vibrational relaxation where the main contribution is made by transitions between the neighboring levels. For a harmonic oscillator this dependence is the exact result [1, 19]. Then Eq. (27) takes on the form

$$k_d = \frac{k_N \rho_N(\theta)}{1 + k_N Z_V / \nu N_*}, \quad (28)$$

where

$$\frac{1}{N_*} = \rho_N(\theta) \sum_{k=1}^N \frac{\Phi_k(N, \theta)^2}{k} \quad (29)$$

Using the completeness property of the  $\Phi_k(N, \theta)$  polynomials, it is concluded that the number  $N_*$  is limited and varies between unity and  $N$ . Taking into account these considerations, we conclude that

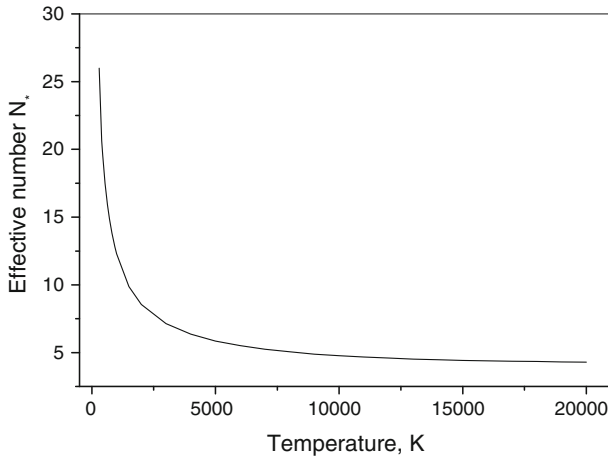
$$\frac{N_*}{Z_V} < \frac{k_d}{\nu \rho_N(\theta)} < \frac{1}{2} \quad (30)$$

It is instructively to compare the results of the general theory with those obtained for the truncated harmonic oscillator [1, 19, 20]. The main shortcoming of the model is that it neglects the anharmonicity of vibrations. Although the steady-state dissociation rate takes on the form of Eq. (28), the effective number  $N_*$  is equal to the number of the bound levels in this model [1]. Figure 1 shows the real temperature dependence of  $N_*$  for oxygen. Only at low temperature  $N_*$  tends to the number of bound levels.

The asymptotic behavior of  $X_N(t)$  is determined by the first term in the infinite series (23). For the  $\exp(-k_d t)$  term, the coefficient of proportionality may be written in the explicit form by tending  $z_0$  to zero in the  $a(z_0)/b'(z_0)$  ratio. It is easy to see that

$$X_N(t) \approx X(0) \rho_N(\theta) \frac{(1 - \gamma) \cdots (1 - \gamma^N)}{(-z_1/\nu) \cdots (-z_N/\nu)} e^{-k_d t} \quad (31)$$

where  $X(0) = C_0(0)$  is the initial concentration of molecules. The ratio of the roots is always less than unity. This simple fact implies that the concentration of molecules differs from the initial one when an exponential decay is reached. Let us rewrite



**Fig. 1** The effective number  $N_*$  as a function of temperature for oxygen with  $N = 52$

Eq. (31), taking into account the condition at  $t = \tau$ , where  $\tau$  is the time from which the exponential decay is valid with the rate  $|z_0| = k_d$

$$X_N(t) = X_N(\tau) \exp[-k_d(t - \tau)], \quad t \geq \tau \quad (32)$$

Equation for evaluating this time is

$$\frac{(1 - \gamma) \cdots (1 - \gamma^N) X(0) \rho_N(\theta)}{(-z_1/\nu) \cdots (-z_N/\nu) X_N(\tau)} e^{-k_d \tau} \approx 1 \quad (33)$$

This fraction is the ratio between the approximate and the exact solutions. Beginning from the time  $\tau$  this ratio reaches unity and stops to depend on  $\tau$  with further increase in this time. This delay at the beginning of the dissociation process corresponds to the incubation time.

#### 4 Relaxation of the mean vibrational energy

It is interesting to determine how the mean energy of a system relaxes to the steady state. To this end we apply the  $X_n(t)/X(t)$  distribution. The time-dependent mean vibrational energy is defined as

$$\langle\langle E(t) \rangle\rangle = \frac{1}{X(t)} \sum_{n=0}^N E_n X_n(t) \quad (34)$$

All the calculations are performed quite easily if the dependence of energy levels on the vibrational quantum number is represented as the expansion in terms of the  $\Phi_k(n, \theta)$  polynomials, namely:



$$\begin{aligned} \frac{E_n}{\hbar\omega_e} &= (1 - x_e) \left[ \langle n \rangle_T + \sqrt{d_2} \Phi_1(n, \theta) \right] \\ &- x_e \left[ \langle n^2 \rangle_T + \frac{d_3}{\sqrt{d_2}} \Phi_1(n, \theta) + \left( d_4 - \frac{d_3^2}{d_2} \right)^{\frac{1}{2}} \Phi_2(n, \theta) \right] \end{aligned} \tag{35}$$

The zero-point energy is taken, as is the convention, as the energy zero. Formulas for the  $d_k$  coefficients, the first and the second polynomials are presented in the ‘‘Appendix’’. The mean energy is expressed in the obvious way through the first and second moments of the time-dependent distribution

$$\frac{\langle \langle E(t) \rangle \rangle}{\hbar\omega_e} = (1 - x_e) \langle \langle n(t) \rangle \rangle - x_e \langle \langle n^2(t) \rangle \rangle \tag{36}$$

Equation (8) and the orthogonality condition allow these moments to be given in terms of the  $C_k(t)$  coefficients:

$$\langle \langle n(t) \rangle \rangle = \langle n \rangle_T + \sqrt{d_2} \frac{C_1(t)}{C_0(t)} \tag{37}$$

and

$$\langle \langle n^2(t) \rangle \rangle = \langle n^2 \rangle_T + \frac{d_3}{\sqrt{d_2}} \frac{C_1(t)}{C_0(t)} + \left( d_4 - \frac{d_3^2}{d_2} \right)^{\frac{1}{2}} \frac{C_2(t)}{C_0(t)} \tag{38}$$

Remember that  $X(t) = C_0(t)$ . As is seen each moment is expressed via the finite sum of the  $C_k(t)$  coefficients. Conversely, each coefficient is provided by the finite sum of the moments. Thus, Eq. (36) together with Eqs. (12) and (25) solve the problem stated. Besides, the time-dependent coefficients take a remarkably simple form when in the equation  $b(z_k) = 0$  all  $z_k$  are the simple roots

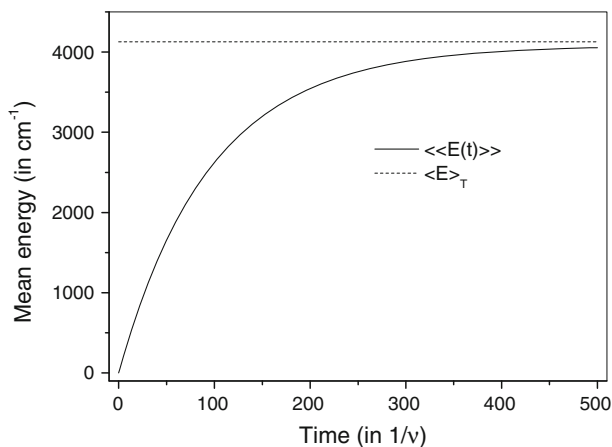
$$C_k(t) = C_k(0)e^{-(1-\gamma^k)\nu t} - k_N \Phi_k(N, \theta) \sum_{m=0}^N \frac{a(z_m) \left( e^{-(1-\gamma^k)\nu t} - e^{-|z_m|t} \right)}{b'(z_m) \left[ |z_m| - (1 - \gamma^k)\nu \right]} \tag{39}$$

The concentration of molecules is given by the equation

$$X(t) = X(0) - k_N \sum_{m=0}^N \frac{a(z_m) \left( 1 - e^{-|z_m|t} \right)}{b'(z_m) |z_m|} \tag{40}$$

At short times, for  $k_d t \ll 1$ , all the  $C_k(t)$  coefficients relax at the rates of vibrational relaxation,  $(1 - \gamma^k)\nu$ . At long times, on order of  $1/k_d$ , the system tends to the steady state. In this case, the time dependence of the coefficients with  $k \neq 0$  changes due to dissociation and depends on the term of the  $\exp(-k_d t)$  type. The concentration of the molecules tends to the steady-state limit  $X(\infty)$ .

The time-dependent moments approach the steady-state values from below if the temperature of inert gas exceeds that of the vibrational system (after shock heating). In



**Fig. 2** The mean vibrational energy of HCl in argon at 7,000 K and  $Z_V = 110$  as a function of the number of collisions  $\nu t$

the course of time, the mean vibrational energy also manifests such a behavior. Figure 2 shows the mean vibrational energy of HCl in argon as a function of the number of collisions. In other words, the time is given in  $1/\nu$  units, where  $\nu = 3.7 \times 10^8 \text{ s}^{-1}$  for an argon density of  $1.05 \times 10^{18} \text{ cm}^{-3}$ . The mean number of collisions was estimated as  $Z_V = \nu \tau_V$ , where the vibrational relaxation time is  $0.3 \mu\text{s}$  [21]. Thus, we get  $Z_V = 110$  at 7000 K. The dissociation rate constant ( $k_d/n_{Ar}$  where  $n_{Ar}$  is the number density of argon) is equal to  $4.6 \times 10^{-15} \text{ cm}^3/\text{s}$ . From formula (28) we get  $4.8 \times 10^{-15} \text{ cm}^3/\text{s}$ . The coincidence of these values indicates that the main contribution is made by the one-quantum transitions. The incubation time is  $2 \mu\text{s}$ , i.e., the quasi-stationary phase is attained after about 700 collisions. At these times, the mean energy is almost equal to a steady-state value of  $4,127 \text{ cm}^{-1}$ .

## 5 Conclusions

The coupled vibration–dissociation process has been thoroughly discussed in the literature. Nevertheless, we have presented a physically meaningful example where the master equation has an exact, analytical solution. The populations are represented as the expansion in terms of the orthonormalized polynomials and the time-dependent expansion coefficients are given by the simple expression. These equations allow one to present clearly the temporal evolution of the mean occupation number and the higher moments for the coupled vibration–dissociation process. This is the main achievement of the analytical approach because a numerical solution to the system of equations from (5) may be obtained without any difficulty at least for not too large number of bound states.

The orthonormalized polynomials are constructed so that their orthogonalization may be verified at each step and the completeness property may be checked at the end. It is the condition which guarantees the ability to present solution as the expansion in

terms of these polynomials. Thereafter, the polynomials may be used in any relaxation process involving the Morse oscillators.

### 6 Appendix: Orthogonalization procedure

The general theory of orthogonal polynomials offers the following recurrent equation for three neighboring polynomials [22]

$$P_{k+1}(n) = \left( n - \frac{\langle n P_k(n)^2 \rangle_T}{\langle P_k(n)^2 \rangle_T} \right) P_k(n) - \frac{\langle n P_{k-1}(n) P_k(n) \rangle_T}{\langle P_{k-1}(n)^2 \rangle_T} P_{k-1}(n), \quad (41)$$

where  $P_{-1}(n) = 0$  and  $P_0(n) = 1$ . The angular brackets indicate the averaging with a weight function. In this case, this is the thermal distribution from Eq. (2). The orthonormalized polynomials are given by the equation

$$\Phi_k(n, \theta) = \frac{P_k(n)}{\sqrt{\langle P_k(n)^2 \rangle_T}} \quad (42)$$

The orthogonalization procedure allows one to sequentially find all the necessary polynomials beginning with  $\Phi_0(n, \theta) = 1$ . The following two polynomials are of the form

$$\Phi_1(n, \theta) = \frac{n - \langle n \rangle_T}{\sqrt{d_2}} \quad (43)$$

and

$$\Phi_2(n, \theta) = \left( \frac{d_2}{d_4 d_2 - d_3^2} \right)^{\frac{1}{2}} \left[ n^2 - \langle n^2 \rangle_T - \frac{d_3}{d_2} (n - \langle n \rangle_T) \right] \quad (44)$$

The coefficients  $d_k$  are defined as

$$d_2 = \langle (n - \langle n \rangle_T)^2 \rangle_T, \quad (45)$$

$$d_3 = \left\langle \left( n^2 - \langle n^2 \rangle_T \right) (n - \langle n \rangle_T) \right\rangle_T, \quad (46)$$

$$d_4 = \left\langle \left( n^2 - \langle n^2 \rangle_T \right)^2 \right\rangle_T \quad (47)$$

All the other polynomials were calculated numerically.

In the high-temperature limit, where  $\theta = \hbar\omega_e/k_B T$  is less than unity, the recurrent equation makes it possible to sequentially calculate all the necessary polynomials up to  $N \approx 100$ , which corresponds to the anharmonicity constant of bromine ( $x_e = 0.005$ ). Of particular interest is the case of high temperatures where the vibrational nonequilibrium is produced by a shock wave.

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