Vibrational relaxation of anharmonic oscillators with a distributed excited-particle sink

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The diffusion approximation is used to analyze the vibrational distribution function of a system of anharmonic oscillators which are excited by external sources and deexcited by interactions with a trace gas. Analytic expressions are derived for the time derivatives of the vibrational populations and for the interaction pumping efficiency as functions of the external source power and relaxation times.

INTRODUCTION

In recent years workers in various areas of physics have become interested in nonlinear vibrational relaxation of highly excited molecules. For example, Zel'dovich and Ovchinnikov[1] studied the vibrational energy distribution in molecular crystals excited by infrared radiation; vibrational populations for molecules excited by an electrodischarge CO laser were analyzed in Ref. 2; the vibrational relaxation dynamics for diatomic molecules excited by radiation pulses was considered in Ref. 3; the influence of nonlinear relaxation processes on the molecular disssociation rate well away from equilibrium was investigated in Ref. 4; nonlinear vibrational relaxation was examined in Ref. 5 for molecular gases expanding adiabatically in a supersonic nozzle. The list of papers dealing wth vibrational relaxation in highly excited molecules could be extended to include work on gas discharge physics, quantum electronics, plasma chemistry, and atmospheric physics in which applied aspects of this problem have been considered.

Landau and Teller[6] developed the first theory of vibrational relaxation, which was based on the harmonic oscillator model. This theory has proven to be very successful in describing vibrational relaxation for systems not too far from equilibrium. For highly excited systems, in which the average stored vibrational energy is much greater than the translational and rotational energy of the molecules, the anharmonic nature of the molecular vibrations greatly alters the relaxation process and the Landau-Teller theory breaks down.[7,8] An anharmonic relaxation theory based on the "diffusion" approximation was developed to treat this case.[9] In this paper we generalize the theory in Ref. 9 to cover the situation when vibrational excitation in a system of anharmonic oscillators is accompanied by quenching (loss of energy from the excited particles). In practice such quenching may be due to dissociation processes[4] or to chemical reactions involving excited molecules.[10]

1. KINETIC MODEL

We considr a gas of diatomic molecules A excited by an external source; the gas also contains molecules B which interact with and quench the excited molecules A. The vibrational distribution function for the A molecules obeys the kinetic equation

$$\frac{d}{dt}f_v=-[\Pi_{v+1}-\Pi_v]+i_v-K_vf_v[B]-\frac{f_v}{[A]}\frac{d[A]}{dt},\qquad v=0,1,2,\ldots, \tag{1}$$

where v is the vibrational quantum number, Π_v is the population flux in "vibrational quantum number space," i_v is the vibrational excitation frequency of A molecules due to the external source, K_v is the quenching rate constant for A molecules in the v-th vibrational level, and $[M]$ is the number density of molecules of species M. The gas can be maintained in a nonequilibrium state by vibrationally exciting the molecules either by infrared radiation or by electron impact in a gas-discharge plasma. In the latter case, if we neglect the collisions between the electrons and the excited molecules we can write i_v as $i_v=n_eK_{0v}f_v$, where n_e is the electron density and K_{0v} is the rate constant for excitation of the vth level of the A molecules. If we assume single-quantum transitions, we have the expression[9]

$$\Pi_{v+1}=\Pi_{v+1}^{V-V}+\Pi_{v+1}^{V-T}+\Pi_{v+1}^{A} \tag{2}$$

for Π_{v+1}, where

$$\Pi_{v+1}^{V-V}=\sum_{v'}Q_{v+1,v}^{v',v'+1}\left[f_vf_{v'+1}\exp\left(\frac{E_v+E_{v'+1}-E_{v+1}-E_{v'}}{kT}\right)-f_{v+1}f_{v'}\right], \tag{3}$$

$$\Pi_{v+1}^{V-T}=P_{v+1,v}\left[f_v\exp\left(\frac{E_v-E_{v+1}}{kT}\right)-f_{v+1}\right], \tag{4}$$

$$\Pi_{v+1}^{A}=-A_{v+1,v}f_{v+1}. \tag{5}$$

Here Π_{v+1}^{A}, Π_{v+1}^{V-V}, Π_{v+1}^{V-T} are the components of the population flux due to spontaneous emission (A), vibrational-vibrational ($V-V$), and vibrational-translational ($V-T$) exchange processes, respectively; $A_{v+1,v}$, $Q_{v+1,v}^{v',v'+1}$, and $P_{v+1,v}$ are the corresponding frequencies; E_v is the energy of an A molecule in vibrational level v; T is the gas temperature, and k is Boltzmann's constant. We account for the anharmonic nature of the vibrations by writing $E_v=[E_1-\Delta E(v-1)]v$, where ΔE is the anharmonic energy correction. One usually calculates Q and P in the anharmonic case by using the approximations[9]

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$$Q_{v+1,v}^{v',v'+1}=Q_{1,0}^{0,1}(v+1)(v'+1)\exp(-\delta_{V-V}|v-v'|),\quad v>v',$$
$$P_{v+1,v}=P_{1,0}(v+1)\exp(\delta_{V-T}v),\tag{6}$$

where δ_{V-V} and δ_{V-T} depend on the temperature and nature of the molecules involved in the exchange processes.

We will analyze system (1) in the steady-state case, i.e., when the A molecules are excited by a constant external source. Assume that the source delivers B_0 photons per unit time to the system. If the vibrations are excited by electron impact in an electric discharge, we have $B_0 = WE_1^{-1}[A]^{-1}\eta_V$, where W is the power input to the discharge per unit volume and η_V is the fraction of the energy expended in vibrationally exciting the A molecules. The relation

$$B_0=\sum_v i_v v.$$

is obvious. We will henceforth assume that the quenching rate constant has a step-function dependence:

$$K_v[B]=K_v\theta(v-v_0),\tag{7}$$

where $\theta(x)$ is the Heaviside function and v_0 is the vibrational quantum number for which the vibrational energy is comparable to the energy barrier for the process. In most nonequilibrium systems the external source excites only a few low-lying vibrational levels (this is true for a gas discharge, e.g., because the rate constant K_{0v} decreases exponentially as v increases). Moreover, the external source generally does not change the total number of particles in the system but rather merely redistributes them over the vibrational levels. With these remarks system (1) readily yields

$$\Pi_v=\Pi_{v_0}=\sum_{v=v_0}^{v_\Gamma}K_v f_v,\quad v_i<v<v_0,$$
$$\Pi_{v+1}-\Pi_v=-K_v f_v,\quad v_0\leqslant v,\tag{8}$$

in the steady-state case. Here v_i is the upper limit for excitation by the source ($i_{v>v_i}=0$), and the vibrational quantum number v_Γ corresponds to the dissociation energy of the A molecules. According to (8), Π_{v_0} is related to the quenching rate of the A molecules by the simple formula

$$d[A]/dt=-[A][B]\sum_{v=v_0}^{v_\Gamma}K_v f_v=-\Pi_{v_0}[A].\tag{9}$$

If the quenching rate is low enough so that the distribution f_v is not changed significantly, we can solve the system (1) by successive approximations. We choose the solution of (1) for noninteracting A and B molecules ($K_v\equiv 0$) as the lowest-order approximation $f_v^{(0)}$. We then find from (8) that

$$\Pi_{v_0}^{(0)}=\sum_{v=v_0}^{v_\Gamma}K_v f_v^{(0)}.\tag{10}$$

We can also derive an estimate for Π_{v_0} in the other extreme case when the quenching perturbs f_v significantly. Indeed, if the constant $K(v_0)$ is large enough then every excited A molecule at level v_0 will be quenched immediately; we may therefore take $f(v_0)$ as $K_{v_0}\to\infty$, and

$$\Pi_{v_0}=\lim_{K_{v_0}\to\infty}K_{v_0}f_{v_0}.\tag{11}$$

We use an energy estimate to evaluate the limit (11). Let Φ_v be the net flux of vibrational quanta through the vth vibrational level for the A molecules. Defining the "vibrational quantum density" $\varepsilon_v = vf_v$, we then find from (1) that

$$\frac{d\varepsilon_v}{dt}=-[\Phi_{v+1}-\Phi_v]+i_v v-\frac{vf_v}{[A]}\frac{d[A]}{dt}-K_v vf_v,$$
$$v=0,1,2,\ldots,\tag{12}$$

where Φ_v is given by

$$\Phi_v=v\Pi_v+\sum_{v'=v+1}^{v_\Gamma}\Pi_{v'}.\tag{13}$$

Setting $v_i<v_0$ and using (2), we find from (12) and (13) for a steady-state system that

$$\Pi_{v_0}\approx\frac{1}{v_0}\Big[B_0-\sum_{v=1}^{v_0}(\Pi_v^{V-T}+\Pi_v{}^A)\Big].\tag{14}$$

If there are no dissipative processes, Eq. (14) simplifies to

$$\Pi_{v_0}\approx B_0/v_0,\tag{15}$$

which maximizes the external pumping efficiency of the interaction between the A and B molecules. The conditions for (15) and (10) to be valid will be found below; however, we note here that in the two extreme cases considered above only the absolute value of the rate constant K_v is important—its dependence on v plays no significant role. In order to solve the equations in the intermediate case, one must specify how K_v depends on the vibrational quantum number v. As noted in Refs. 11 and 12, the dependence of K_v on v is roughly the same for a large class of endothermal reactions involving vibrationally excited diatomic molecules—specifically, K_v drops abruptly (exponentially) with decreasing v for $v<v_0$ and increases as a power of v for $v>v_0$. Figure 1 plots K_v versus v for the oxidation reaction $N_2^*(v)+O\to NO+N$ (Ref. 12). Figure 1 shows that the depen-

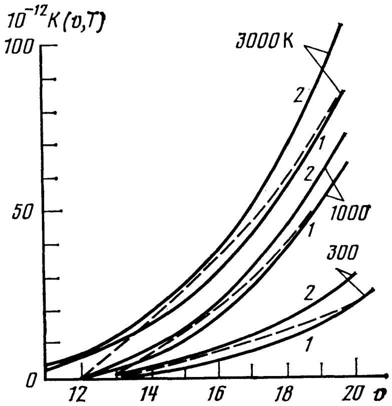

FIG. 1. Plot of $K(v,T)$ [cm^3/s] versus v for three different temperatures. The dashed curves were calculated using Eq. (16); the solid curves show data from Ref. 12; curves 1 and 2 indicate the minimum and maximum rate constants found from the data in Ref. 12.

dence is accurately approximated by

$$K_v \approx K_{v_0+1} v (v_0+1)^{-1} (v-v_0) \theta (v-v_0), \qquad (16)$$

where $v_0 \approx 11$. Below we will analyze the system (1) for K_v given by (16). As we have noted, this assumption involves no loss of generality because (16) holds quite generally for endothermal reactions involving vibrationally excited molecules.[11]

2. DIFFUSION APPROXIMATION

In order to systematically analyze physico-chemical processes involving vibrationally excited molecules, one must solve the kinetic equations (1) numerically for multilevel vibrational systems. Since accurate experimental data on the rate constants are not available, a numerical solution of (1) will be meaningful only if the values of the rate constants are varied, which greatly complicates the problem even in the simplest cases. In this paper we employ an analytic approach[9] which is based on the diffusion approximation and reduces the kinetic equations (1) to a single Fokker-Planck differential equation. Expressions (2)–(5) were analyzed in Ref. 9 for steady excitation without particle sinks, and three characteristic intervals were found for the quantum numbers v: 1) $0 < v < v^*$, for which "nonresonant" $V-V$ exchange between the lower and upper vibrational levels gives the principal contribution to Π_v; 2) $v^* < v < v^{**}$, for which "resonant" $V-V$ exchange between close-lying levels contributes significantly; 3) $v^{**} < v$, for which $V-T$ exchange give the dominant contribution to Π_v. The distribution function f_v for $0 < v < v^*$ is closely approximated by

$$f_v{}^{\mathrm{T}} = f_0 \exp\left\{ -v \left[\frac{E_1}{T_V} - \frac{\Delta E}{T} (v-1) \right] \right\}, \qquad (17)$$

where f_v^T is the Treanor distribution[13] and the "vibrational temperature" T_v is defined by $f_1 = f_0 \exp(-E_1/T_v)$. For $v^* < v < v^{**}$ the *DF* is a gently sloping "plateau" on which f_v decays by a power law. Finally, the *DF* for $v^{**} < v$ approaches a Boltzmann distribution $f_v^B \sim \exp(-E_v/T)$. The vibrational quantum numbers v^* and v^{**} bounding these intervals must be found by considering the balance equation for the nonresonant, resonant $V-V$ exchange, and $V-T$ relaxation processes. Resonant and nonresonant $V-V$ exchange processes were compared in Refs. 9 and 14, and v^* for steady excitation was found to be close to the Treanor value $v^T = E_1 T/2\Delta E T_v + 1/2$, for which the *DF* in (17) is a minimum. The number v^{**} is found by requiring that the flux Φ_v^{V-V} of quanta toward higher v in $V-V$ exchange processes should be equal to the total rate L_v at which quanta are consumed in dissipative processes when $v = v^{**}$. According to (13) and (14),

$$\Phi_v^{V-V} = v \Pi_v^{V-V} + \sum_{v'=v+1}^{v_\Gamma} \Pi_{v'}^{V-V}, \qquad (18)$$

$$L_v = L_v^{V-T} + L_v{}^A = \sum_{v'=1}^{v} (\Pi_{v'}^{V-\mathrm{T}} + \Pi_{v'}{}^A).$$

In this paper we consider the case $v^* < v_0 < v^{**}$ (recall that v_0 determines the characteristic scale of the quantum numbers v corresponding to vibrational energy levels whose populations are perturbed due to quenching). As noted above, resonant $V-V$ exchange gives the dominant contribution to the flux Π_v. According to Refs. 9, 14, and 15, the diffusion approximation in this case leads to the expressions

$$\Pi_v^{V-V} = -\nu \frac{d}{dv} (f^2 v^2), \qquad (19)$$

$$\Phi_v^{V-V} = -\nu \left[v \frac{d}{dv} (f^2 v^2) - f^2 v^2 \right], \qquad (20)$$

$$L_v^{V-T} = \int_1^v P_{1,0} v f \exp(\delta_{V-T} v)\, dv \approx \delta_{V-T}^{-1} P_{1,0} v f_v \exp(\delta_{V-T} v), \qquad (21)$$

$$\nu = \frac{4\Delta E}{T} \delta_{V-V}^{-3} Q_{1,0}^{0,1},$$

where ν is the effective frequency of $V-V$ exchange. The derivation of Eqs. (19)–(21) in Refs. 9, 14, and 15 requires that f_v be sufficiently smooth (which is certainly the case on the plateau) and that the vibrational levels not be excited thermally (this is true for sufficiently low gas temperatures). Approximation $\Pi_{v+1} - \Pi_v$ in (1) by $d\Pi/dv \cdot \Delta v$, neglecting spontaneous emission, and using (16) and (19), we easily get the equation

$$\nu \frac{d^2}{dv^2} (f^2 v^2) = K_0 v (v - v_0) f \theta (v-v_0), \quad v^* < v \leqslant v^{**}, \qquad (22)$$

for the distribution function $f \equiv f(v)$, where

$$K_0 = K_{v_0+1} [B] (v_0+1)^{-1}.$$

Since dissipation does not occur on the plateau, the boundary conditions for (22) should correspond to quantum flux conservation for $v \leqslant v_0$ (the flux is determined by the external source):

$$-\nu \left[v \frac{d}{dv} (f^2 v^2) - f^2 v^2 \right] = B_0, \quad v^* < v \leqslant v_0. \qquad (23)$$

We can take (23) with $v = v_0$ as a boundary condition for Eq. (22). A second boundary condition follows from the vanishing of the net population flux at $v = v^{**}$ (this is because $V-T$ exchange processes consume vibrational quanta but conserve the total number of particles). The second condition for Eq. (22) can thus be written as

$$-\nu \frac{d}{dv} (f^2 v^2) \big|_{v=v^{**}} = 0. \qquad (24)$$

The quantum number v^{**} in (23) is not known *a priori* but must be found (as noted above) by equating Φ_v^{V-V} and L_v^{V-T} at $v = v^{**}$:

$$-\nu \left[v \frac{d}{dv} (f^2 v^2) - f^2 v^2 \right] \Big|_{v=v^{**}} = \delta_{V-T}^{-1} P_{1,0} f v \exp(\delta_{V-T} v) \big|_{v=v^{**}}. \qquad (25)$$

Defining the new variables $y = (\nu/K_0)^2 f^2 v^2$ and $x = v - v_0$, we can recast Eq. (22) and conditions (23)–(25) in the form

$$y'' = x y^{1/2} \theta (x), \qquad (26)$$

$$v_0 y'(0) - y(0) = -b, \qquad (27)$$

$$y'(x_1) = 0, \qquad (28)$$

$$y(x_1) = b_n \exp(2\delta_{V-T} x_1), \qquad (29)$$

TABLE I. The coefficients a_n.

n	a_n	n	a_n	n	a_n
1	$-8{,}57143\cdot10^{-1}$	5	$9{,}52728\cdot10^{-5}$	9	$1{,}27663\cdot10^{-6}$
2	$1{,}68367\cdot10^{-1}$	6	$2{,}94772\cdot10^{-5}$	10	$4{,}86437\cdot10^{-7}$
3	$1{,}45773\cdot10^{-3}$	7	$9{,}83213\cdot10^{-6}$	20	$8{,}74632\cdot10^{-11}$
4	$3{,}42826\cdot10^{-4}$	8	$3{,}46743\cdot10^{-6}$	30	$3{,}69102\cdot10^{-14}$

where

$$b=\nu B_0K_0^{-2},\quad b_n=\left(\frac{P_{1,0}}{K_0\delta_{V-T}}\right)^2\exp(2\delta_{V-T}v_0),\quad x_1=v^{**}-v_0.$$

The derivative $y'(0)$ in (27) is important because it characterizes the interaction between the A and B molecules under nonequilibrium conditions. Indeed, (9) and (19) imply that the quenching rate of the A molecules is given by

$$d[A]/dt=K_c^2\nu^{-1}y'(0)[A][B]. \qquad (30)$$

Using (15) and dividing (30) by the rate for which the $A-B$ interaction is pumped most effectively by the external source, we readily get the expression

$$\eta=-v_0b^{-1}y'(0) \qquad (31)$$

for the pumping efficiency. The quantities $d[A]/dt$ and η are the ones of greatest practical interest for processes such as nonequilibrium dissociation or nonequilibrium chemical reactions involving excited molecules.

The quantity $y'(0)$ also determines the behavior of $y(x)$ for $x<0$:

$$y=b+y'(0)v,\quad x\leqslant0. \qquad (32)$$

According to the mathematical formulation of the problem (26)–(29), $y'(0)$ depends only on specific combinations of the relaxation parameters $P_{1,0}$, δ_{V-T}, ν, the $A-B$ interaction rate constant K_0, and the intensity B_0 of the external source:

$$y'(0)=F(b,\ b_n,\ \delta_{V-T},\ v_0). \qquad (33)$$

Equations (30–(32) provide a criterion for assessing the similarity of vibrationally excited systems in which excited A molecules interact with B molecules.

3. RELAXATION WITHOUT V – T EXCHANGE

If $V-T$ exchange is unimportant ($P_{1,0}=0$), the boundary condition (29) for Eq. (26) simplifies to

$$y(x_1)=0. \qquad (34)$$

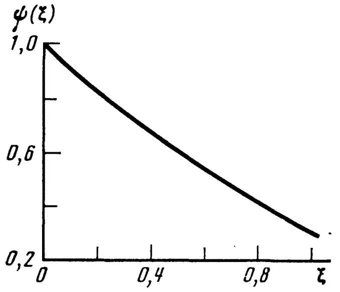

FIG. 2. The function $\psi(\xi)$.

This says that the vibrational quantum flux must vanish for the same $v=v^{**}$ at which the population flux vanishes. Equation (26) and boundary conditions (28), (34) imply that $y(x)$ is given in the limit $x\to x_1$ by

$$y(x\to x_1)\sim x_1^2(x-x_1)^4/144. \qquad (35)$$

We seek a solution of (26) of the form

$$y(x)=\frac{x_1^2(x_1-x)^4}{144}\psi\left(1-\frac{x}{x_1}\right),\quad \psi(\xi)=\sum_{n=0}^{\infty}a_n\xi^n,\ a_0=1. \qquad (36)$$

Substituting (36) into (26), we get the recursion formula[16] for the coefficients a_η:

$$a_n=\frac{12}{(n+3)(n+4)-6}\left[\frac{1}{n}\sum_{k=1}^{n-1}\left(\frac{3}{2}k-n\right)a_kA_{n-k}-A_{n-1}\right],$$

$$A_m=\frac{1}{m}\sum_{i=1}^{m}\left(\frac{3}{2}i-m\right)a_iA_{m-i},\quad A_0=1. \qquad (37)$$

Numerical calculations show that $|a_n/a_{n-1}|<0.5$, at least for n up to 10^3. This suggests that the expansion (36) describes the solution of (26) for all x of interest ($0\leqslant x\leqslant x_1$; $0\leqslant\xi\leqslant1$). Table I gives the first few coefficients a_n, while Fig. 2 plots the function $\psi(\xi)$ needed to find $y(x)$ for a given value of x_1. In general, the latter depends on the parameter b; the dependence $x_1=x_1(b)$ can be found by using boundary condition (27). Indeed, by (36)

$$y(0)=\alpha x_1^6,\quad y'(0)=-\beta x_1^5, \qquad (38)$$

with α and β given by

$$\alpha=\frac{1}{144}\sum_{n=0}^{\infty}a_n,\quad \beta=\frac{1}{144}\sum_{n=0}^{\infty}(n+4)a_n. \qquad (39)$$

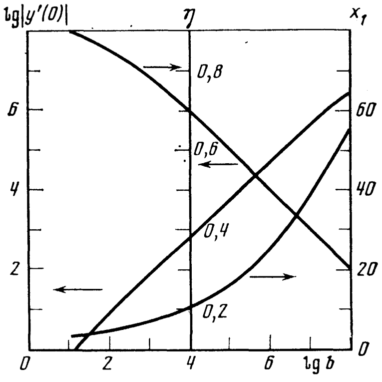

FIG. 3. Plot of log $|y'(0)|$, η, and x_1 as functions of log b for $b_n=0$ and $v_0=11$.

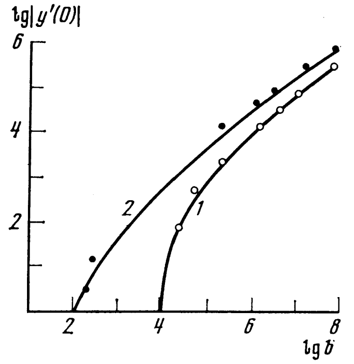

FIG. 4. Plot of log $|y'(0)|$ versus log b; $b_n = 10^2$ and 10^4 for curves 1 and 2, respectively; ○ and ● show values calculated by Eq. (50) with $\delta_{V-T} = 0.5$.

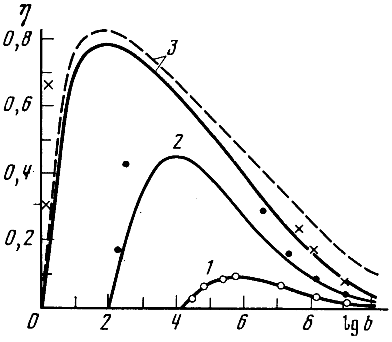

FIG. 5. The function η (b);$b_n = 10^4$, 10^2, and 10^0 for curves 1-3, respectively. The solid and dashed curves are for $\delta_{V-T} = 0.5$ and 0.25, respectively; ×, ●, and ○ give values calculated by Eq. (52) for $b_n = 10°$, 10^2, and 10^4, respectively, for $\delta_{V-T} = 0.5$. In all cases $v_0 = 10$.

If we substittue (38) into (27) we easily find the algebraic equation

$$\alpha x_1^6+\beta v_0 x_1^5=b \tag{40}$$

for $x_1(b)$ which can be solved for x_1 (and hence also $y'(0)$ and $y(0)$) as a function of b. We calculated α and β in (40) by summing the series (39) up to $n = 1000$; this gave the values

$$\alpha=2.1747\cdot 10^{-3};\quad \beta=5.1303\cdot 10^{-3}. \tag{41}$$

Figure 3 plots $y'(0)$, x_1, and the pumping efficiency η as functions of b calculated using Eqs. (38)–(41), (31). It is interesting that according to Fig. 3, if b is increased solely by increasing the pump power (keeping v and K_0 fixed), the efficiency η drops even though (30) implies that the quenching rate increases. In the limits $b\to 0$ and $b\to\infty$, (38) and (40) yield the explicit dependences

$$y'(0)\approx\begin{cases} -\dfrac{b}{v_0}\left[1-\dfrac{\alpha}{\beta v_0}\left(\dfrac{b}{v_0\beta}\right)^{1/5}\right], & \dfrac{v_0\beta}{\alpha}\left(\dfrac{v_0\beta}{b}\right)^{1/5}\gg 1\\ -\beta\left(\dfrac{b}{\alpha}\right)^{5/6}\left[1-\dfrac{v_0\beta}{\alpha}\left(\dfrac{\alpha}{b}\right)^{1/6}\right], & \dfrac{v_0\beta}{\alpha}\left(\dfrac{\alpha}{b}\right)^{1/6}\ll 1\end{cases}. \tag{42}$$

Formulas (42) and the definition of y imply that

$$\lim_{K_0\to 0} f_{v_0}=\frac{1}{v_0}\left(\frac{B_0}{v}\right)^{1/2}, \tag{43}$$

which corresponds to the solution of (26) when the $A-B$ interaction does not quench any particles[9]; in addition, $\Pi_{v_0}\to 0$. In the opposite limit we have

$$\lim_{K_0\to\infty}\Pi_{v_0}=\frac{B_0}{v},\quad \lim_{K_0\to\infty} f v_0=0, \tag{44}$$

which corresponds to maximum pumping efficiency.

We verified the above analytic formulas by solving (26) numerically with the boundary conditions (27), (28), (34). The easiest way to do the calculation was to choose an arbitrary value x_1 and solve (26) by the Runge-Kutta method down to $x = 0$ to obtain $y(0)$ and $y'(0)$, whereupon (27) yields the corresponding value of b. The calculated values $y(0)$ and $y'(0)$ agree with the results from Eqs. (38)–(40) to within the 10^{-7} relative error in solving Eq. (26).

4. RELAXATION WITH *V* – *T* EXCHANGE

$V-T$ exchange greatly alters the relaxation of reacting excited anharmonic molecules. For instance, (26) and conditions (17)–(29) imply that for $b_n\neq 0$, all the characteristic relaxation parameters have a threshold dependence on b:

$$y'(0)\,|_{b\leqslant b_n}=0,\quad y(0)\,|_{b\leqslant b_n}=y(x_1)\,|_{b\leqslant b_n}=b,$$

$$v^{**}=\delta_{V-T}^{-1}\ln\left[\frac{(B_0 v)^{1/2}}{P_{1,0}}\delta_{V-T}\right]\Bigg|_{b\leqslant b_n}. \tag{45}$$

Equations (45) describe relaxation for noninteracting A and B molecules ($v_0\leqslant v^{**}$) and coincide with the results in Refs. 9, 14, and 15. Unfortunately, it is not possible to derive simple analytic expressions for $y'(0), y(0), y(x)$, and x_1 from an expansion of the type (36) when $b > b_n$, because the expansion coeffcients depend on x_1. We therefore solved (26)–(29) numerically for several values of the parameters b, b_n, δ_{V-T}, and v_0; the results are shown in Figs. 4 and 5. We note that as in the case $b_n = 0$ considered previously, Eq. (26) was solved by the Runge-Kutta method down to $x = 0$, and the value b corresponding to x_1, δ_{V-T}, V_0, and b_n was then found from (27). Figure 5 shows that $\eta(b)$ has a peak, i.e., there is an optimum external source power at which the pump energy is utilized most effectively in the interaction between the A and B molecules. The peak is present because for large b, rapid $V-V$ exchange transfers energy to the level v^{**} above which rapid $V-T$ relaxation occurs. We note that acording to Fig. 4, $|y'(0)|$ increases with b.

We can solve (26) approximately if $y(0)$ and $y(x_1)$ are nearly equal, i.e., if the $A-B$ interaction perturbs the $DF f_v$ only slightly. Indeed, if we make the Ansatz

$$y(x)=y(x_1)\sum_{n=0}^{\infty}a_n\left(1-\frac{x}{x_1}\right)^n,\quad a_0=1, \tag{46}$$

and substitute into (26), we readily find a recursion formula for the a_n which is similar to Eqs. (37). However, because the a_n now depend on x_1 there is little point in calculating the a_n out to large n; instead, ti is preferable to calculate only the first few a_n so as to preserve an analytic dependence on x_1. The first seven coefficients yield the approximations

$$y(0)\approx y(x_1)\left[1+\frac{1}{3}\Delta+\frac{1}{144}\Delta^2+\frac{1}{180\cdot 156}\Delta^3\right], \tag{47}$$

$$y'(0) \approx -\frac{y(x_1)}{x_1}\left[\frac{1}{2}\Delta + \frac{1}{60}\Delta^2 + \frac{1}{720}\Delta^3\right], \tag{48}$$

where $\Delta = x_1^3 \bar{b}_n^{1/2} \exp(-\delta_{V-T} x_1)$. If

$$\frac{1}{8\delta^3_{V-T}} b^{-1/2} \ln^3\left(\frac{b}{b_n}\right) \ll 3$$

$$\left(\frac{8\delta^2_{V-T}}{v_0 b}\right)^{1/2} \ln^2\left(\frac{b}{b_n}\right) \ll 1, \tag{49}$$

the boundary conditions (27)–(29) and (48) imply that

$$y(0) \approx b, \quad y(x_1) \approx b, \quad x_1 \approx (2\delta_{V-T})^{-1} \ln\left(\frac{b}{b_n}\right),$$

$$y'(0) \approx -\frac{1}{8\delta^2_{V-T}} b^{1/2} \ln^2\left(\frac{b}{b_n}\right). \tag{50}$$

We note that (50) is the diffusion analog of Eq. (10).

It is noteworthy that if b_n satisifes

$$b_n^{1/2} \gg 2v_0/e^2\delta^2_{V-T}, \quad b_n^{1/2} \gg 9/e^3\delta^3_{V-T} \tag{51}$$

(where $e = 2.71828\cdots$), (49) holds for all values of b and Eqs. (50) are valid for $b \geqslant b_n$. By the definition of η (31) and Eq. (50), the pumping efficiency reduces to the simple form

$$\eta = \frac{v_0 b^{-1/2}}{8\delta^2_{V-T}} \ln^2\left(\frac{b}{b_n}\right) \tag{52}$$

when conditions (49) are satisfied. If b_n satisifes (51) then Eq. (52) is valid for all $b \geqslant b_n$, so that we can calculate the value $\tilde{b}$ which is energetically most favorable from the relaxation standpoint:

$$\tilde{b} = b_n e^4, \quad \eta(\tilde{b}) = 2v_0/e^2\delta^2_{V-T} b_n^{1/2}. \tag{53}$$

Figures 4 and 5 compare the numerical calculations for (26)–(29) with results calculated using Eqs. (50) and (52). We see that the agreement is close for large b_n. Comparison of the values $y(0)$ and $y'(0)$ found by (48) with the results of the numerical calculations revealed that Eqs. (48) are valid for Δ as large as ≈ 4. The error in $y'(0)$ was less than 5%, while that in $y(0)$ was an order of magnitude smaller.

As we noted earlier, the fundamental constraint here on the validity of the diffusion approximation[9] is the requirment that the vibrational *DF* of the *A* molecules must have a plateau. Since $v^* \approx v_T$, we can express this as the inequality $v_T < v_0 < v^{**}$. Because the vibrational temperature T_v in the definition of ther Treanor number must be found by piecing the distributions (17) and (43) together at $v = v_T$ (Refs. 9, 14, 15), the "plateau condition" constrains the external source power:

$$\frac{1}{v_0}\left(\frac{B_0}{v}\right)^{1/2} > f_0 \exp\left(-\frac{\Delta E}{T} v_0^2\right), \quad b \geqslant b_n. \tag{54}$$

These inequalities define the limits within which our results are valid.

CONCLUSIONS

The present method for solving vibrational kinetic problems for anharmonic oscillators can be used to analyze diverse physical processes involving excited molecules. For example, it will be of interest to use the techniques and results discussed above to design and optimize plasmachemical systems and to determine how the interaction of the vibrationally excited molecules alters the physical and chemical processes in gas laser-plasmas, in the ionosphere, and in nonequilibrium gasdynamics.

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