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Vibrational relaxation processes in a diatomic gas coupled to translational and radiational heat baths

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The relaxation of vibrationally excited diatomic molecules of one kind is studied by second-quantization methods. The relaxation processes are described by interactions of the vibrational degree of freedom with translational and radiational heat baths. General quantum-mechanical expressions are developed for transition rates in vibration-translation, vibration-vibration, and vibration-radiation processes. These expressions include the broadening of spectral lines in a nonequilibrium gas. The line broadening is affected by the correlation function of both the dipole moment and the density matrix. In the interaction of the vibrational degree of freedom with a radiational heat bath, cooperative effects are studied. Cooperative molecular effects do not influence the induced emission and absorption, but lead to changes in the process of spontaneous emission.

I. INTRODUCTION

In the present work we study the relaxation of the vibrational degree of freedom in a diatomic gas of one kind. At room temperatures (or higher), the thermal equilibrium of the gas is described by the Boltzmann vibrational, translational, and rotational distributions. We assume that an external perturbation is applied to the gas for a short time, leaving it in a vibrational nonequilibrium distribution, whereas the rotational and the translational degrees of freedom return to the Boltzmann equilibrium distribution immediately (in a very short time). We may describe our system as being composed of anharmonic oscillators prepared initially in a nonequilibrium vibrational distribution. After the external perturbation has been removed the system of oscillators relaxes to its final vibrational equilibrium distribution by collisions and by radiative transitions. These processes represent energy exchanges between the nonequilibrium vibrational degree of freedom and either the rotational-translational degrees of freedom or the radiational field. The rotational-translational degrees of freedom and the radiational field, which are assumed to be in thermal equilibrium, are represented by a very large number of closely spaced energy levels, and their interactions with the relaxing vibrational degree of freedom practically do not change their equilibrium temperature. In view of these considerations, the rotational-translational degrees of freedom and the radiational field, act as heat baths[1,2] for the relaxation processes of the vibrational levels. Such relaxation phenomena have recently become of practical interest in relation to the problem of population inversion in diatomic gas lasers.

The transfer of vibrational energy to or from the translational kinetic modes is made by two kinds of binary collisions. In a binary vibration-translation collision (VT process) only one molecule is vibrationally deexcited or excited. In a binary vibration-vibration collision (VV process) one molecule is vibrationally excited, and the other deexcited. The exchange between two molecules of a single quantum of vibration is the dominant process and occurs more frequently than do exchanges of multiple quanta of vibrational energy. Therefore we neglect vibrational multiple quanta transitions. In this approximation we use the energy levels of an anharmonic oscillator with the selection rules of a harmonic oscillator. The mathematical methods which will be developed here may be easily applied also to multiple quanta transitions, but this would complicate the calculations without significantly affecting our physical conclusions. Because we use energy levels of an anharmonic oscillator, VV processes introduce energy defects. These defects in energy are balanced by changes in the translational and rotational energies, so that the total energy of the colliding molecules is conserved. After VV and VT collisions the system is restored very rapidly by elastic collisions to a translational and rotational equilibrium.

While studying the vibrational relaxation of a diatomic gas many authors[3-5] started their research from the master equation

$$\begin{aligned}\frac{dn_r}{dt} &= P_{r+1,r}\left[n_{r+1}n - \exp\left(-\frac{E_{r+1}-E_r}{kT}\right)n_r n\right] - P_{r,r-1}\left[n_r n - \exp\left(-\frac{E_r - E_{r-1}}{kT}\right)n_{r-1}n\right]\\ &+\sum_s P_{s-1,r+1;\,s,r}\left[n_{r+1}n_{s-1} - \exp\left(-\frac{E_{r+1}+E_{s-1}-E_r-E_s}{kT}\right)n_r n_s\right]\\ &-\sum_s P_{s,r;\,s+1,r-1}\left[n_r n_s - \exp\left(-\frac{E_r+E_s-E_{s+1}-E_{r-1}}{kT}\right)n_{s+1}n_{r-1}\right]. \end{aligned} \tag{1}$$

Here n_r and n are, respectively, the population density of the vibrational quantum level r and the total number density. E_r is the vibrational energy of the r state. $P_{r+1,r}\,n_{r+1}n$ is the rate of production of r state molecules from $r+1$ state molecules, owing to VT energy exchanges. $P_{s-1,r+1;\,s,r}\times n_{r+1}n_{s-1}$ is the rate of production of r and s state molecules from $r+1$ and $s-1$ state molecules. The difference due to anharmonicity between the two quanta $(E_{r+1}-E_r)-(E_s-E_{s-1})$ is exchanged with the translational modes. In Eq. (1) the principle of detailed balance has been used, viz.,

$$\begin{aligned}&P_{r,r+1} = P_{r+1,r}\exp[-(E_{r+1}-E_r)/kT],\\ &P_{m,r;\,l,s} = P_{l,s;\,m,r}\exp[-(E_s+E_l-E_r-E_m)/kT)].\end{aligned} \tag{2}$$

Relaxation dissipation and fluctuation of the present system are discussed in the present work, using second-quantization methods. The master equation for vibrational relaxation is studied, using a quantum-mechanical description of the translational heat bath. The quantum-mechanical derivation of Eq. (1) shows its validity conditions and gives quantum-mechanical expressions for the rate coefficients $n_{r+1}nP_{r+1,r}$ and $n_{r+1}n_{s-1}\times P_{s-1,r+1;\,s,r}$. In the special case where the binary collision is isolated from other perturbing processes, and assuming that the "memory" of the heat bath is shorter than all other time constants of the system, we obtain the common expressions for transition rates.[6-12] The present methods enable us to derive new results for broadening and shifts of levels which are especially important in a dense gas. The expressions for the broadening take into account the time dependence of the density matrix. In the equilibrium condition of the gas our expressions are reduced to results similar to those obtained by other authors.

In the present work we also discuss the relaxation of the vibrational degree of freedom by a radiational heat bath (nonlasing modes). There are fundamental differences between the quantum-mechanical description of the translational heat bath and the radiational heat bath. In a radiational heat bath the operator B_ω or $B_\omega^\dagger$ destroys or creates a photon with frequency ω, while the corresponding translational heat-bath operators B_ν and $B_\nu^\dagger$ change the relative energy of a colliding pair of molecules and therefore act as shift operators. In a translational heat bath the collisions represent random processes, and cooperative effects are neglected. The many-body formalism is reduced to a treatment of bimolecular processes by using a mathematical method of contraction.[1] For a radiational heat bath we show that cooperative effects in the gas lead to coherent spontaneous emission.[13,14] Within the general assumptions about the radiational heat bath, the induced emission and absorption are not changed by cooperative effects of the gas. Neglecting the cooperation effects among the molecules, and using (in the mathematical formalism) the method of contraction, we get the usual expression for noncoherent spontaneous emission. In conclusion, cooperative effects might influence significantly the vibration-radiation relaxation rates of the diatomic gas.

II. HAMILTONIAN FOR VT RELAXATION

Our system consists of N diatomic molecules confined to a volume, V, and we are interested in the limit N, $V\to\infty$, with the density $n=N/V$ remaining constant. The translational wave functions are assumed to be periodic in the normalization box of volume V. According to our assumptions the translational and rotational degrees of freedom are in a thermodynamic equilibrium. Therefore from now on, when we refer to translation we take into account (without mentioning it explicitly) also the rotational degree of freedom.

In a binary collision the forces between the molecules depend only on the internal and relative coordinates of the particles. The center of mass of the two molecules moves like a free particle, and the internal energy is coupled by the interaction only to the relative motion of the molecules.[15] In a VT binary collision only one molecule loses or gains vibrational energy, and this amount of energy is added to or subtracted from the relative energy of motion of the two molecules. The kinetic energy gained or lost by the reduced mass of the molecular pair is "smeared" by many elastic collisions on the Boltzmann distribution of the heat bath. The "smearing" process is very rapid in comparison with all other characteristic time constants of the system. The exchange of energy between the vibrational and translational degrees of freedom depends mainly on matrix elements for strong collisions. The effect of rapid elastic collisions is expressed in our Hamiltonian by the assumption of the heat bath's short memory.

We assume that all the diatomic molecules are in the electronic ground state. The total wave function of one molecule is described by the quantum numbers of vibration, rotation, and translation. According to quantum mechanics two molecules in the gas with the same quantum numbers are indistinguishable. Since, in our system the gas is at a translational room temperature (or higher), we may assume that Boltzmann, Fermi, and Bose-Einstein statistics would give equivalent results. Using this assumption the gas is represented in our model by an ensemble of bosons characterized by the quantum numbers of vibration and translation (including rotation).

The Hamiltonian operator H_{tot} for the whole gas may be written

$$H_{\text{tot}} = H_{0M} + H_{0B} + H_{\text{VTB}} + H_{\text{VVB}}, \tag{3}$$

where H_{0M} is the unperturbed vibrational Hamiltonian for the N molecules and H_{0B} is the unperturbed Hamiltonian for the heat bath. H_{VTB} and H_{VVB} represent, respectively, the interactions with the heat bath by VT and VV collisions. In the present section we take into account only VT interactions and postpone the treatment of the VV interactions to Sec. VI.

The vibrational free part of the Hamiltonian can be written in the second-quantization formalism as

$$H_{0M} = \sum_i E_i\, b^\dagger(i) b(i) = \sum_i \hbar\omega_i b^\dagger(i) b(i) \ , \tag{4}$$

where i refers to the i vibrational level, $b^\dagger(i)$ and $b(i)$ are, respectively, the creation and annihilation operators for the vibrational state i. E_i represents the energy levels of the diatomic anharmonic oscillator.

In the description of the heat bath for VT interactions we consider colliding pairs of molecules. In our model we divide the gas into pairs of molecules so that the VT interactions take place only between the two molecules of each colliding pair. The VT energy exchanges occur only in a small part of the pairs, namely, in the pairs in which the collisions are very strong. The translational Hamiltonian of the gas can be separated into the Hamiltonian of free particles moving with the center-of-mass velocities of each pair, and into quasiparticles with the reduced mass of each pair moving relative to fixed scattering centers.[16,17] The translational Hamiltonian of the free particles is not coupled to the vibrational degree of freedom and can be written

$$H_{0B} = \sum_{\omega, k} \hbar\omega B^\dagger(\omega, k) B(\omega, k). \tag{5}$$

Here $B^\dagger(\omega, k)$ and $B(\omega, k)$ are, respectively, the creation and annihilation operators of the boson quasiparticles which have translational energies $\hbar\omega$ and are characterized also by a set of other quantum numbers k (including rotation, orientation of the bimolecular quasiparticle, etc.). In the following discussion we shall use the commutation relations:

$$[B(\omega, k),\ B^\dagger(\omega', k')] = \delta_{\omega, \omega'} \delta_{k, k'}, \tag{6}$$

$$[B(\omega, k), B(\omega', k')] = [B^\dagger(\omega, k), B^\dagger(\omega', k')] = 0, \tag{7}$$

$$[b(i), b^\dagger(j)] = \delta_{ij}, \tag{8}$$

$$[b(i), b(j)] = [b^\dagger(i), b^\dagger(j)] = 0 . \tag{9}$$

$B(\omega, k)$ and $B^\dagger(\omega, k)$ operate on the basis state vectors of the translational quasiparticles in the Fock space which have the form $|n(\omega_1, k_1), n(\omega_2, k_1), \ldots, n(\omega_i, k_j)\ldots\rangle$. Here $\omega_1, \omega_2, \ldots$ refer to the quantized translational energies in the normalization box, and $k_1, k_2, \ldots$ are all the other quantum numbers characterizing the bimolecular quasiparticles. $n(\omega_1, k_1)\, n(\omega_2, k_1)\ldots$ are the corresponding occupation numbers. According to second-quantization definitions

$$B(\omega_i, k_j)\,|n(\omega_1, k_1), n(\omega_1, k_2), \ldots, n(\omega_i, k_j), \ldots\rangle = [n(\omega_i, k_j)]^{1/2}\,|n(\omega_1, k_1), n(\omega_1, k_2), \ldots, n(\omega_i, k_j) - 1, \ldots\rangle , \tag{10}$$

$$B^\dagger(\omega_i, k_j)\,|n(\omega_1, k_1), n(\omega_1, k_2), \ldots, n(\omega_i, k_j), \ldots\rangle = [n(\omega_i, k_j) + 1]^{1/2}\,|n(\omega_1, k_1), n(\omega_1, k_2), \ldots, n(\omega_i, k_j) + 1, \ldots\rangle . \tag{11}$$

In a similar way we have

$$b(i)\,|n(1), n(2), \ldots, n(i), \ldots\rangle = [n(i)]^{1/2}\,|n(1), n(2), \ldots, n(i) - 1, \ldots\rangle , \tag{12}$$

$$b^\dagger(i)\,|n(1), n(2), \ldots, n(i), \ldots\rangle = [n(i) + 1]^{1/2}\,|n(1), n(2), \ldots, n(i) + 1, \ldots\rangle , \tag{13}$$

where $n(i)$ is the occupation number in Fock space for the molecules in the ith vibrational state.

The VT coupling between the translational heat bath and the vibrational degree of freedom is given by the Hamiltonian of interaction:

$$\begin{aligned} H_{\mathrm{VTB}} = \hbar \sum_i b^\dagger(i-1)b(i)M_{i,i-1} \\ \times \sum_{\omega,\omega'} \sum_{k,k'} B^\dagger(\omega,k)B(\omega',k')K_{\omega',k';\,\omega,k} \\ +\hbar \sum_i b^\dagger(i)b(i-1)M_{i-1,i} \\ \times \sum_{\omega,\omega'} \sum_{k,k'} B^\dagger(\omega',k')B(\omega,k)K_{\omega,k;\,\omega',k'} \,. \end{aligned} \tag{14}$$

As was explained in the introduction, we take into account only single-quantum transitions. The first and second terms of H_{VTB} represent, respectively, excitation and deexcitation of molecular pairs by one vibrational quantum. The matrix elements of interaction are separated into products of vibrational and translational parts. $M_{i,i-1}$ represents the vibrational matrix element of the molecular pair, where one molecule is deexcited by one vibrational quantum. $K_{\omega,k;\,\omega',k'}$ is the translational matrix element for the translational quasiparticle which is excited from the state ω, k to a new state ω', k'. The second part of H_{VTB} is the Hermitian conjugate of the first part, and we have the relations

$$M_{i-1,i} = M^*_{i,i-1}, \tag{15}$$

$$K_{\omega',k';\,\omega,k} = K^*_{\omega,k;\,\omega',k'} \,. \tag{16}$$

The complex conjugate is denoted in the present work by an asterisk. The operators b and B belong to different quantum-mechanical systems and are commuting operators:

$$[b, B^\dagger] = [b^\dagger, B] = [b^\dagger, B^\dagger] = [b, B] = 0 \tag{17}$$

for any operator $b(i)$ and $B(\omega, k)$.

In the rotating-wave approximation we assume $\omega - \omega' = \nu > 0$ and neglect in the Hamiltonian of interaction terms for which $\omega - \omega' < 0$. Using this approximation we define new operators of the translational heat bath

$$B_\nu^\dagger = \sum_{\omega'} \sum_{k,k'} B^\dagger(\omega'+\nu, k)B(\omega', k')K_{\omega'k';\,\omega'+\nu,k} \,, \tag{18a}$$

$$B_\nu = \sum_{\omega'} \sum_{k,k'} B^\dagger(\omega', k')B(\omega'+\nu, k)K_{\omega'+\nu,k;\,\omega',k'} \tag{18b}$$

and, then, we get the VT interaction Hamiltonian in a shorter notation:

$$\begin{aligned} H_{\mathrm{VTB}} = \hbar \sum_i b^\dagger(i-1)b(i)M_{i,i-1} \sum_\nu B_\nu^\dagger \\ +\hbar \sum_i b^\dagger(i)b(i-1)M_{i-1,i} \sum_\nu B_\nu \,. \end{aligned} \tag{19}$$

Here again the operators B_ν and $b(i)$ belong to different quantum-mechanical systems and therefore are commuting operators:

$$[b(i), B_\nu^\dagger] = [b^\dagger(i), B_\nu] = [b^\dagger(i), B_\nu^\dagger] = [b(i), B_\nu] = 0. \tag{20}$$

III. EQUATIONS OF MOTION FOR VIBRATIONAL OPERATORS $b(i)$ IN VT RELAXATION

The general Hamiltonian of the present system (neglecting H_{VVB} interactions) can be written

$$H = H_{0m} + H_{0B} + H_{\mathrm{VTB}} \,, \tag{21}$$

where H_{0m}, H_{0B}, and H_{VTB} are defined by Eqs. (4), (5), (18), and (19). Using the Heisenberg picture the equation of motion for the operator $b(r)$ can be written

$$\begin{aligned} i\hbar \frac{db(r)}{dt} = [b(r), H] = [b(r), H_{0m}] + [b(r), H_{0B}] \\ + [b(r), H_{\mathrm{VTB}}] \,. \end{aligned} \tag{22}$$

The first term on the right-hand side of Eq. (22) gives

$$\begin{aligned} [b(r), H_{0m}] &= [b(r), \sum_i \hbar\omega_i b^\dagger(i)b(i)] \\ &= \hbar\omega_r \{b(r)b^\dagger(r)b(r) - b^\dagger(r)b(r)b(r)\} \\ &= \hbar\omega_r b(r) \,. \end{aligned} \tag{23}$$

According to Eq. (17) we have

$$[b(r), H_{0B}] = 0 \,. \tag{24}$$

The third term on the right-hand side of Eq. (22) is calculated by using the following commutation relations for the b operators:

$$\begin{aligned} &[b(r), \sum_i b^\dagger(i-1)b(i)] = b(r+1) \quad \text{(since the contribution is only from } i-1=r\text{)}, \\ &[b(r), \sum_i b^\dagger(i)b(i-1)] = b(r-1) \quad \text{(since the contribution is only from } i=r\text{)}. \end{aligned} \tag{25}$$

As $b(r)$ and $B_\nu^\dagger$ (or B_ν) are commuting operators [Eq. (20)] we get according to Eqs. (19) and (25):

$$[b(r), H_{\mathbf{VTB}}] = \left(b(r), \hbar \sum_i b^\dagger(i-1)b(i)M_{i,i-1} \sum_\nu B_\nu^\dagger\right) + \left(b(r), \hbar \sum_i b^\dagger(i)b(i-1)M_{i-1,i} \sum_\nu B_\nu\right)$$

$$= \hbar b(r+1)M_{r+1,r} \sum_\nu B_\nu^\dagger + \hbar b(r-1)M_{r-1,r} \sum_\nu B_\nu \,. \qquad (26)$$

Using Eqs. (22)–(26) we get

$$i\hbar \frac{db(r)}{dt} = \hbar\omega_r b(r) + \hbar b(r+1)M_{r+1,r} \sum_\nu B_\nu^\dagger + \hbar b(r-1)M_{r-1,r} \sum_\nu B_\nu \,. \qquad (27)$$

A similar equation of motion is obtained for $b^\dagger(r)$:

$$i\hbar \frac{db^\dagger(r)}{dt} = -\hbar\omega_r b^\dagger(r) - \hbar b^\dagger(r+1)M_{r,r+1} \times \sum_\nu B_\nu - \hbar b^\dagger(r-1)M_{r,r-1} \sum_\nu B_\nu^\dagger \,. \qquad (28)$$

Formal solutions for Eqs. (27) and (28) can be given as

$$b(r,t) = b(r,0)e^{-i\omega_r t} - i \int_0^t dt' e^{-i\omega_r(t-t')} b(r+1,t')M_{r+1,r}(t') \sum_\nu B_\nu^\dagger(t')$$

$$-i \int_0^t dt'\, e^{-i\omega_r(t-t')} b(r-1,t')M_{r-1,r}(t') \sum_\nu B_\nu(t') \,, \qquad (29)$$

$$b^\dagger(r,t) = b^\dagger(r,0)e^{i\omega_r t} + i \int_0^t dt'\, e^{i\omega_r(t-t')} b^\dagger(r+1,t')M_{r,r+1}(t') \sum_\nu B_\nu(t')$$

$$+i \int_0^t dt'\, e^{i\omega_r(t-t')} b^\dagger(r-1,t')M_{r,r-1}(t') \sum_\nu B_\nu^\dagger(t') \,. \qquad (30)$$

Here we inserted matrix elements which may depend on time due to external perturbations on the binary VT interaction (like elastic collisions with distant molecules). We shall use later the formal solutions to discuss the vibrational relaxation phenomena.

IV. EQUATIONS OF MOTION FOR OCCUPATION NUMBER OPERATORS OF VIBRATIONAL STATES

The occupation-number operators of the vibrational states change during the relaxation process according to Eqs. (27) and (28) by the rate

$$i\hbar \frac{d}{dt}[b^\dagger(r)b(r)] = i\hbar \frac{db^\dagger(r)}{dt} b(r) + i\hbar b^\dagger(r) \frac{db(r)}{dt}$$

$$= -\hbar b^\dagger(r+1)b(r)M_{r,r+1} \sum_\nu B_\nu - \hbar b^\dagger(r-1)b(r)M_{r,r-1} \sum_\nu B_\nu^\dagger + \hbar b^\dagger(r)b(r+1)M_{r+1,r} \sum_\nu B_\nu^\dagger$$

$$+ \hbar b^\dagger(r)b(r-1)M_{r-1,r} \sum_\nu B_\nu \,. \qquad (31)$$

We shall assume that B_ν and $B_\nu^\dagger$ are Markoffian so that ensemble averages of products of either B_ν's alone, $B_\nu^\dagger$'s alone, or of odd products in which B_ν and $B_\nu^\dagger$ appear alternatively, vanish. Using this assumption, we shall take into account only the products $B_\nu B_\nu^\dagger$ and $B_\nu^\dagger B_\nu$ and ignore all other products of B_ν's and $B_\nu^\dagger$'s according to their appearance in the calculations.[1] For the operator B_ν defined in Eq. (18b) we have the equation of motion

$$i\hbar \frac{dB_\nu}{dt} = [B_\nu, H_{0m}] + [B_\nu, H_{0B}] + [B_\nu, H_{\mathbf{VTB}}] \,. \qquad (32)$$

Since the operators of the heat bath B_ν commute with the vibrational operators, the first term on the right-hand side of Eq. (32) vanishes. The third term gives, according to Eq. (19), the result

$$[B_\nu, H_{\mathbf{VTB}}] = \hbar \sum_i b^\dagger(i-1)b(i)M_{i,i-1}\left(\sum_{\nu'} [B_\nu, B_{\nu'}^\dagger]\right)$$

$$+ \hbar \sum_i b^\dagger(i)b(i-1)M_{i-1,i}\left(\sum_{\nu'} [B_\nu, B_{\nu'}]\right)$$

$$= \hbar \sum_i b^\dagger(i-1)b(i)M_{i,i-1} f_\nu(B)$$

$$+ \hbar \sum_i b^\dagger(i)b(i)M_{i-1,i}\, g_\nu(B). \qquad (33)$$

$f_\nu(B)$ and $g_\nu(B)$ denote in short notation the terms in the large parentheses which are functions only of the heat bath and their evaluation will not be needed here.

The second term on the right-hand side of Eq. (32) gives

$$[B_\nu, H_{0B}]$$

$$=\Big[\sum_{\omega'}\sum_{k'k''}B^\dagger(\omega',k'')B(\omega'+\nu,k')K_{\omega'+\nu,k';\omega',k''},$$

$$\times\sum_{\omega,k}\hbar\,\omega B^\dagger(\omega,k)B(\omega,k)\Big]=\hbar\nu B_\nu\,. \qquad (34)$$

Here we used the commutation relations according to Eqs. (6) and (7).

We finally get the equation of motion for B_ν as

$$i\hbar\frac{dB_\nu}{dt}=\hbar\nu B_\nu+\hbar\sum_i b^\dagger(i-1)b(i)M_{i,i-1}f_\nu(B)$$

$$+\hbar\sum_i b^\dagger(i)b(i-1)M_{i-1,i}\,g_\nu(B) \qquad (35)$$

and, in a similar way, we have

$$i\hbar\frac{dB_\nu^\dagger}{dt}=-\hbar\nu B_\nu^\dagger-\hbar\sum_i b^\dagger(i)b(i-1)M_{i-1,i}\,f_\nu^\dagger(B)$$

$$-\hbar\sum_i b^\dagger(i-1)b(i)M_{i,i-1}\,g_\nu^\dagger(B). \qquad (36)$$

The formal solutions of Eqs. (35) and (36) are

$$B_\nu(t)=B_\nu(0)e^{-i\nu t}-\int_0^t dt'\,e^{-i\nu(t-t')}$$

$$\times\Big(\sum_i b^\dagger(i-1)b(i)M_{i,i-1}f_\nu(B)$$

$$+\sum_i b^\dagger(i)b(i-1)M_{i-1,i}\,g_\nu(B)\Big), \qquad (37)$$

$$B_\nu^\dagger(t)=B_\nu^\dagger(0)e^{i\nu t}+i\int_0^t dt'\,e^{i\nu(t-t')}$$

$$\times\Big(\sum_i b^\dagger(i)b(i-1)M_{i-1,i}\,f_\nu^\dagger(B)$$

$$+\sum_i b^\dagger(i-1)b(i)M_{i,i-1}\,g_\nu^\dagger(B)\Big), \qquad (38)$$

where the terms in the large parentheses are functions of the time t'.

Let us substitute the formal solutions of B_ν and $B_\nu^\dagger$ into Eq. (31) and order these operators (to the left of the nearby operator b) so that they will always appear between the two vibrational operators b. This procedure is allowed (as the operators b and B commute) and appears to have computational advantages. One gets

$$i\hbar\frac{d}{dt}[b^\dagger(r)b(r)]=-\hbar b^\dagger(r+1)\Big(\sum_\nu B_\nu(0)e^{-i\nu t}\Big)b(r)M_{r,r+1}-\hbar b^\dagger(r-1)\Big(\sum_\nu B_\nu^\dagger(0)e^{i\nu t}\Big)b(r)M_{r,r-1}$$

$$+\hbar b^\dagger(r)\Big(\sum_\nu B_\nu^\dagger(0)e^{i\nu t}\Big)b(r+1)M_{r+1,r}+\hbar b^\dagger(r)\Big(\sum_\nu B_\nu(0)e^{-i\nu t}\Big)b(r-1)M_{r-1,r}$$

$$-\hbar b^\dagger(r+1)\Big[-i\int_0^t dt'\sum_\nu e^{-i\nu(t-t')}\Big(\sum_i b^\dagger(i-1)b(i)M_{i,i-1}f_\nu(B)$$

$$+\sum_i b^\dagger(i)b(i-1)M_{i-1,i}\,g_\nu(B)\Big)\Big]b(r)M_{r,r+1}$$

$$-\hbar b^\dagger(r-1)\Big[i\int_0^t dt'\sum_\nu e^{i\nu(t-t')}\Big(\sum_i b^\dagger(i)b(i-1)M_{i-1,i}\,f_\nu^\dagger(B)$$

$$+\sum_i b^\dagger(i-1)b(i)M_{i,i-1}\,g_\nu^\dagger(B)\Big)\Big]b(r)M_{r,r-1}$$

$$+\hbar b^\dagger(r)\Big[i\int_0^t dt'\sum_\nu e^{i\nu(t-t')}\Big(\sum_i b^\dagger(i)b(i-1)M_{i-1,i}\,f_\nu^\dagger(B)$$

$$+\sum_i b^\dagger(i-1)b(i)M_{i,i-1}\,g_\nu^\dagger(B)\Big)\Big]b(r+1)M_{r+1,r}$$

$$+\hbar b^\dagger(r)\Big[-i\int_0^t dt'\sum_\nu e^{-i\nu(t-t')}\Big(\sum_i b^\dagger(i-1)b(i)M_{i,i-1}f_\nu(B)$$

$$+\sum_i b^\dagger(i)b(i-1)M_{i-1,i}\,g_\nu(B)\Big)\Big]b(r-1)M_{r-1,r}\,. \qquad (39)$$

Here we shall use the idea of contraction as formulated by Haken.[1] The collisions are random processes and, by neglecting cooperative effects between the molecules products of the four operators, b should satisfy the general relation

$$\langle b^{\dagger}(i)b(j)b^{\dagger}(k)b(l)\rangle = \langle b^{\dagger}(i)b(l)\rangle\delta_{jk} \,. \tag{40}$$

This property of the algebraic ring of operators b can be verified directly by using a one-molecule wave function: $|n(1)=0, n(2)=0, \ldots, n(m-1)=0, n(m)=1, n(m+1)=0, \ldots\rangle$. The use of contraction might be incorrect for molecular interactions with radiational heat bath (see Sec. VII).

In the last four terms of Eq. (39), the functions $f_{\nu}(B)$ and $g_{\nu}(B)$ contain summation of pairs such as $B_{\nu}(t')B^{\dagger}_{\nu'}(t')$. We assume that the ensemble average of such products of heat-bath operators cannot contain a rapid phase factor. Therefore the ensemble average of $f_{\nu}(B)$ or $g_{\nu}(B)$ is a slow-varying function of ν. The summation over closely spaced values of ν may be exchanged by integration over ν, and we use the relation[1]

$$\int d\nu e^{-i\nu(t-t')}\langle f_{\nu}(B)\rangle = \langle f_{\overline{\nu}}(B)\rangle \int d\nu e^{-i\nu(t-t')}$$
$$= 2\pi\langle f_{\overline{\nu}}(B)\rangle\,\delta(t-t')\,,$$

where $\langle f_{\overline{\nu}}(B)\rangle$ is a mean value of $\langle f_{\nu}(B)\rangle$. After integration over time, and using the well-known properties of the function $\delta(t-t')$, the products of the vibrational operators $b^{\dagger}(i-1,t')b(i,t')$ and $b^{\dagger}(i,t')b(i-1,t')$ tend, respectively, to the values $b^{\dagger}(i-1,t)b(i,t)$ and $b^{\dagger}(i,t)b(i-1,t)$. A more detailed discussion of this procedure will be given later, in our treatment of the radiational heat bath. The mathematical formalism there is simpler, but the conclusions are of general validity to heat baths. We obtain therefore in the last four terms of Eq. (39) the products:

$$b^{\dagger}(r+1)b^{\dagger}(i-1)b(i)b(r);$$

$$b^{\dagger}(r+1)b^{\dagger}(i)b(i-1)b(r);$$

$$-b^{\dagger}(r-1)b^{\dagger}(i)b(i-1)b(r);$$

$$-b^{\dagger}(r-1)b^{\dagger}(i-1)b(i)b(r);$$

$$b^{\dagger}(r)b^{\dagger}(i)b(i-1)b(r+1);$$

$$b^{\dagger}(r)b^{\dagger}(i-1)b(i)b(r+1);$$

$$-b^{\dagger}(r)b^{\dagger}(i-1)b(i)b(r-1);$$

$$-b^{\dagger}(r)b^{\dagger}(i)b(i-1)b(r-1)$$

(all operators at time t). All the terms of this kind vanish according to Eq. (40) (after they have been put in the order of Eq. (40). Finally we obtain that the four last terms in Eq. (39) are equal to zero. One should take note of the fact that although $b(t)$ commutes with $B_{\nu}(t)$, $b(t)$ does not commute with $B_{\nu}(0)$.

Since the last four terms of Eq. (39) vanished we continue with the first four terms by using the following procedure: We substitute the operators b and $b^{\dagger}$ by their formal solutions [Eqs. (29) and (30)] and order the operators $B_{\nu}(t')$ or $B^{\dagger}_{\nu}(t')$ which appear in these formal solutions (to the right or the left of the nearby vibrational operator) so that the translational operators will appear always between the vibrational operators. Then we substitute the formal solutions of B_{ν} and $B^{\dagger}_{\nu}$ [Eqs. (37) and (38)] and assume that the heat bath has a short memory. The operators B_{ν} are Markoffian, and therefore ensemble averages of one operator B_{ν} or odd products of operators B_{ν} vanish. Only even products of $B^{\dagger}_{\nu}$ and B_{ν} contribute to the ensemble average. Using these properties we proceed in our calculations, excluding the terms which contain the functions $f_{\nu}(B)$ or $g_{\nu}(B)$ [which enter by the substitution of the formal solutions of $B_{\nu}(t')$ and $B^{\dagger}_{\nu}(t')$]. If these terms were included, the calculations would be more complicated and tedious, but would lead to the same result [Eq. (43)]. Part of the terms containing the functions $f_{\nu}(B)$ or $g_{\nu}(B)$ would vanish on ensemble averaging, and part would be included in the operators $b^{\dagger}(r+1,t)$ and $b(r,t)$ which appear in Eq. (43). It is emphasized that we do not use in the present work the approximation $B_{\nu}(t)=B_{\nu}(0)e^{-i\nu t}$ (although it might seem so from the final results). The complete equations of motion for B_{ν} and $B^{\dagger}_{\nu}$ are used, and only by certain ordering of the operators and by using Markoffian properties, second and third terms in the expressions for B_{ν} and $B^{\dagger}_{\nu}$ [Eqs. (37) and (38)] are excluded. By the present method we therefore obtain a certain ordering of the operators $B_{\nu}(0)$ and $B^{\dagger}_{\nu}(0)$, which is very important in evaluating the correct results. Without this ordering of operators the results would be the same, but the mathematical development would be much more complicated. In order to illustrate the methods of the calculation mentioned above, we show in great detail the treatment of the first term in Eq. (39). The second, third, and fourth terms are treated in a similar way. Using Eqs. (29) and (30 we get

$$\begin{aligned}
&b^\dagger(r+1,t)\biggl(\sum_\nu B_\nu(0)e^{-i\nu t}\biggr)b(r,t)M_{r,r+1}\\
&\qquad=\biggl(b^\dagger(r+1,0)e^{i\omega_{r+1}t}+i\int_0^t dt' e^{i\omega_{r+1}(t-t')}b^\dagger(r+2,t')M_{r+1,r+2}(t')\sum_\nu B_\nu(0)e^{-i\nu t'}\\
&\qquad\quad+i\int_0^t dt' e^{i\omega_{r+1}(t-t')}b^\dagger(r,t')M_{r+1,r}(t')\sum_\nu B_\nu^\dagger(0)e^{i\nu t'}\biggr)\biggl(\sum_\nu B_\nu(0)e^{-i\nu t}\biggr)\\
&\qquad\quad\times\biggl(b(r,0)e^{i\omega_r t}-i\int_0^t dt' e^{-i\omega_r(t-t')}\sum_\nu B_\nu^\dagger(0)e^{i\nu t'}b(r+1,t')M_{r+1,r}(t')\\
&\qquad\quad-i\int_0^t dt' e^{-i\omega_r(t-t')}\sum_\nu B_\nu(0)e^{-i\nu t'}b(r-1,t')M_{r-1,r}(t')\biggr)M_{r,r+1}(t)\,. \qquad (41)
\end{aligned}$$

Averaging and taking into account only the double products of the operators B_ν and $B_\nu^\dagger$, we get

$$\begin{aligned}
&\biggl\langle b^\dagger(r+1,t)\biggl(\sum_\nu B_\nu(0)e^{-i\nu t}\biggr)b(r,t)M_{r,r+1}\biggr\rangle=\biggl\langle b^\dagger(r+1,0)e^{i\omega_{r+1}t}M_{r,r+1}(t)\biggl(\sum_\nu B_\nu(0)e^{-i\nu t}\biggr)\\
&\qquad\times\biggl(-i\int_0^t dt' e^{-i\omega_r(t-t')}\sum_\nu B_\nu^\dagger(0)e^{i\nu t'}b(r+1,t')M_{r+1,r}(t')\biggr)\\
&\qquad+\biggl(i\int_0^t dt' e^{i\omega_{r+1}(t-t')}b^\dagger(r,t')M_{r+1,r}(t')\sum_\nu B_\nu^\dagger(0)e^{i\nu t'}\biggr)\\
&\qquad\times M_{r,r+1}(t)\biggl(\sum_\nu B_\nu(0)e^{-i\nu t}\biggr)b(r,0)e^{-i\omega_r t}\biggr\rangle\,. \qquad (42)
\end{aligned}$$

We can exchange in Eq. (42) the terms $b^\dagger(r+1,0)e^{i\omega_{r+1}t}$ and $b(r,0)e^{-i\omega_r t}$, respectively, by $b^\dagger(r+1,t)$ and $b(r,t)$ (as we add by these substitutions vanishing terms of triple products of B_ν). Using these properties of Markovian processes we finally get

$$\begin{aligned}
&\biggl\langle b^\dagger(r+1,t)\biggl(\sum_\nu B_\nu(0)e^{-i\nu t}\biggr)b(r,t)M_{r,r+1}\biggr\rangle=\biggl\langle b^\dagger(r+1,t)M_{r,r+1}(t)\biggl(\sum_\nu B_\nu(0)e^{-i\nu t}\biggr)\\
&\qquad\times\biggl(-i\int_0^t dt'\, e^{-i\omega_r(t-t')}\sum_\nu B_\nu^\dagger(0)e^{i\nu t'}\,b(r+1,t')M_{r+1,r}(t')\biggr)\\
&\qquad+\biggl(i\int_0^t dt'\, e^{i\omega_{r+1}(t-t')}b^\dagger(r,t')M_{r+1,r}(t')\sum_\nu B_\nu^\dagger(0)e^{i\nu t'}\biggr)\\
&\qquad\times M_{r,r+1}(t)\biggl(\sum_\nu B_\nu(0)e^{-i\nu t}\biggr)b(r,t)\biggr\rangle\,. \qquad (43)
\end{aligned}$$

In deriving Eq. (43) we have not so far used the perturbation theory, and the result is based only on the assumption that the heat bath has a short memory (Markoffian process) and on contraction (vibrational interaction with one representative molecule). By continuing the calculations in the second, third, and fourth term of Eq. (39) we get the complete results.

$$
\begin{aligned}
&\left\langle i\hbar\frac{d}{dt}[b^\dagger(r,t)b(r,t)]\right\rangle \\
&\quad=\Big\langle -i\hbar\Big(\int_0^t dt'\, e^{i\omega_{r-1}(t-t')}b^\dagger(r,t')M_{r-1,r}(t')\sum_\nu B_\nu(0)e^{-i\nu t'}\Big)M_{r,r-1}(t)\Big(\sum_\nu B_\nu^\dagger(0)e^{i\nu t}\Big)b(r,t) \\
&\qquad+i\hbar b^\dagger(r-1,t)M_{r,r-1}(t)\Big[\sum_\nu B_\nu^\dagger(0)e^{i\nu t}\Big]\Big(\int_0^t dt'\, e^{-i\omega_r(t-t')}\sum_\nu B_\nu(0)e^{-i\nu t'}b(r-1,t')M_{r-1,r}(t')\Big) \\
&\qquad-i\hbar\Big(\int_0^t dt'\, e^{i\omega_{r+1}(t-t')}b^\dagger(r,t')M_{r+1,r}(t')\sum_\nu B_\nu^\dagger(0)e^{i\nu t'}\Big)M_{r,r+1}(t)\Big(\sum_\nu B_\nu(0)e^{-i\nu t}\Big)b(r,t) \\
&\qquad+i\hbar b^\dagger(r+1,t)M_{r,r+1}(t)\Big(\sum_\nu B_\nu(0)e^{-i\nu t}\Big)\Big(\int_0^t dt'\, e^{-\omega_r(t-t')}\sum_\nu B_\nu^\dagger(0)e^{i\nu t'}b(r+1,t')M_{r+1,r}(t')\Big) \\
&\qquad+i\hbar\Big(\int_0^t dt'\, e^{i\omega_r(t-t')}b^\dagger(r+1,t')M_{r,r+1}(t')\sum_\nu B_\nu(0)e^{-i\nu t}\Big)M_{r+1,r}(t)\Big(\sum_\nu B_\nu^\dagger(0)e^{i\nu t}\Big)b(r+1,t) \\
&\qquad-i\hbar b^\dagger(r,t)M_{r+1,r}(t)\Big(\sum_\nu B_\nu^\dagger(0)e^{i\nu t}\Big)\Big(\int_0^t dt'\, e^{-i\omega_{r+1}(t-t')}\sum_\nu B_\nu(0)e^{-i\nu t'}b(r,t')M_{r,r+1}(t')\Big) \\
&\qquad+i\hbar\Big(\int_0^t dt'\, e^{i\omega_r(t-t')}b^\dagger(r-1,t')M_{r,r-1}(t')\sum_\nu B_\nu^\dagger(0)e^{i\nu t'}\Big)M_{r-1,r}(t)\Big(\sum_\nu B_\nu(0)e^{-i\nu t}\Big)b(r-1,t) \\
&\qquad-i\hbar b^\dagger(r,t)M_{r-1,r}(t)\Big(\sum_\nu B_\nu(0)e^{-i\nu t}\Big)\Big(\int_0^t dt'\, e^{-i\omega_{r-1}(t-t')}\sum_\nu B_\nu^\dagger(0)e^{i\nu t'}b(r,t')M_{r,r-1}(t')\Big)\Big\rangle\,.
\end{aligned}
\tag{44}
$$

V. FUNDAMENTAL EQUATIONS FOR VT RELAXATION OF DIATOMIC GAS

We can get from Eq. (44) higher-order terms by repeating the substitution of the b operators according to Eqs. (29) and (30). To get the second-order perturbation theory, we cut off this iteration procedure. We shall use the relation

$$
b(r,t)=b_0(r,t)e^{-i\omega_r t}\,.
\tag{45}
$$

Here $b_0(r,t)$ is a slowly varying function of time, and the rapid changes with time are included only in $e^{-i\omega_r t}$. In the products of summations over ν, in Eq. (44), we take into account only resonant terms (with the same ν). In the first stage of the calculation we take an average value of $B_\nu^\dagger(0)B_\nu(0)$ near the resonance frequency and leave the rapid fluctuating term $e^{i\nu(t-t')}$ of the phase unchanged. Equation (44) is then reduced to the fundamental equation of VT relaxation in a diatomic gas

$$
\begin{aligned}
&\left\langle i\hbar\frac{d}{dt}[b^\dagger(r,t)b(r,t)]\right\rangle \\
&\quad=\Big\langle -i\hbar\sum_\nu\int_0^t dt'\,\exp[i(\omega_{r-1}-\omega_r+\nu)(t-t')]\,b_0^\dagger(r,t')b_0(r,t)M_{r-1,r}(t')M_{r,r-1}(t)\langle B_\nu(0)B_\nu^\dagger(0)\rangle \\
&\qquad+i\hbar\sum_\nu\int_0^t dt'\,\exp[-i(\omega_r-\omega_{r-1}-\nu)(t-t')]\,b_0^\dagger(r-1,t)b_0(r-1,t')M_{r-1,r}(t')M_{r,r-1}(t)\langle B_\nu^\dagger(0)B_\nu(0)\rangle \\
&\qquad-i\hbar\sum_\nu\int_0^t dt'\,\exp[i(\omega_{r+1}-\omega_r-\nu)(t-t')]\,b_0^\dagger(r,t')b_0(r,t)M_{r+1,r}(t')M_{r,r+1}(t)\langle B_\nu^\dagger(0)B_\nu(0)\rangle \\
&\qquad+i\hbar\sum_\nu\int_0^t dt'\,\exp[-i(\omega_r-\omega_{r+1}+\nu)(t-t')]\,b_0^\dagger(r+1,t)b_0(r+1,t')M_{r+1,r}(t')M_{r,r+1}(t)\langle B_\nu(0)B_\nu^\dagger(0)\rangle \\
&\qquad+i\hbar\sum_\nu\int_0^t dt'\,\exp[i(\omega_r-\omega_{r+1}+\nu)(t-t')]\,b_0(r+1,t)M_{r,r+1}(t')M_{r+1,r}(t)\langle B_\nu(0)B_\nu^\dagger(0)\rangle \\
&\qquad-i\hbar\sum_\nu\int_0^t dt'\,\exp[-i(\omega_{r+1}-\omega_r-\nu)(t-t')]\,b_0^\dagger(r,t)b_0(r,t')M_{r,r+1}(t')M_{r+1,r}(t)\langle B_\nu^\dagger(0)B_\nu(0)\rangle \\
&\qquad+i\hbar\sum_\nu\int_0^t dt'\,\exp[i(\omega_r-\omega_{r-1}-\nu)(t-t')]\,b_0^\dagger(r-1,t')b_0(r-1,t)M_{r,r-1}(t')M_{r-1,r}(t)\langle B_\nu^\dagger(0)B_\nu(0)\rangle \\
&\qquad-i\hbar\sum_\nu\int_0^t dt'\,\exp[-i(\omega_{r-1}-\omega_r+\nu)(t-t')]\,b_0^\dagger(r,t)b_0(r,t')M_{r,r-1}(t')M_{r-1,r}(t)\langle B_\nu(0)B_\nu^\dagger(0)\rangle\Big\rangle\,.
\end{aligned}
\tag{46}
$$

In Eq. (46) the terms $\langle B_\nu(0)B_\nu^\dagger(0)\rangle$ and $\langle B_\nu^\dagger(0)B_\nu(0)\rangle$ are average values of the translational part of the interaction, which has a very slow dependence on energy. (We shall develop later the translational part of the interaction.) The vibrational part shows line-broadening effects near the resonance frequencies of the various vibrational transitions. In each term we have the correlation in time of the dipole $M(t')M(t)$ and another correlation of the form $b_0^\dagger(t')b_0(t)$. This result for the line shape describes general behavior which in cases of equilibrium reduces to the known expressions from other works on spectral line broadening.[18,19] Our general result is valid for nonequilibrium as well as for equilibrium conditions. For nonequilibrium conditions the line-shape expression contains correlation in time of parts of the density matrix $b_0^\dagger(t')b_0(t)$. The dependence of the matrix elements on time can result from external perturbations in the gas to the VT binary collision.[19]

Neglecting also memory effects of the vibrational part of the interaction, the summation over ν in Eq. (46) introduces the function $\delta(t-t')$, and Eq. (46) is reduced to

$$\begin{aligned}\left\langle\frac{d}{dt}[b^\dagger(r,t)b(r,t)]\right\rangle = \pi\,\langle & -2b_0^\dagger(r,t)b_0(r,t)|M_{r,r-1}(t)|^2\langle B_\nu(0)B_\nu^\dagger(0)\rangle_{\nu=\omega_r-\omega r-1} \\ & +2b_0^\dagger(r-1,t)b_0(r-1,t)|M_{r,r-1}(t)|^2\langle B_\nu^\dagger(0)B_\nu(0)\rangle_{\nu=\omega_r-\omega_{r-1}} \\ & -2b_0^\dagger(r,t)b_0(r,t)|M_{r,r+1}(t)|^2\langle B_\nu^\dagger(0)B_\nu(0)\rangle_{\nu=\omega_{r+1}-\omega_r} \\ & 2b_0^\dagger(r+1,t)b_0(r+1,t)|M_{r,r+1}(t)|^2\langle B_\nu(0)B_\nu^\dagger(0)\rangle_{\nu=\omega_{r+1}-\omega_r}\rangle\,. \end{aligned} \tag{47}$$

Using the relation $b_0^\dagger(r,t)b_0(r,t)=b^\dagger(r,t)b(r,t)$. The comparison between Eq. (47) and the VT transition rates in Eq. (1) is straightforward. We substitute for $\langle b_0^\dagger(r,t)b_0(r,t)\rangle$ the number of molecules in the vibrational state r at time t. The translational parts of the interaction can be developed as follows:

$$\langle B_\nu(0)B_\nu^\dagger(0)\rangle_{\nu=\omega_r-\omega_{r-1}} = n\sum_\beta \rho_{\beta\beta}\langle\beta|B_\nu(0)|\alpha\rangle\langle\alpha|B_\nu^\dagger(0)|\beta\rangle\,. \tag{48}$$

Here $B_\nu(0)$ is an energy-shift operator. α and β are the many-body quasiparticle bimolecular states. The translational energy of the state β is lower in energy $\hbar(\omega_r-\omega_{r-1})$ relative to α. Since the translational degree of freedom is in thermodynamic equilibrium at temperature T we have

$$\rho_{\beta\beta}=(1/z)e^{-E_\beta/kT}\,, \tag{49}$$

where z is the translational partition function. The transition probability of the translational interaction in Eq. (48) is given by

$$|K_{\beta,\alpha}|^2=\langle\beta|B_\nu(0)|\alpha\rangle\langle\alpha|B_\nu^\dagger(0)|\beta\rangle\,. \tag{50}$$

We get the final result

$$\langle B_\nu(0)B_\nu^\dagger(0)\rangle=\frac{n}{z}\sum_\beta e^{-E_\beta/kT}|K_{\beta,\alpha}|^2\,. \tag{51}$$

In a similar way we get

$$\langle B_\nu^\dagger(0)B_\nu(0)\rangle_{\nu=\omega_r-\omega_{r-1}} = n\sum_\alpha \rho_{\alpha\alpha}\langle\alpha|B_\nu^\dagger(0)|\beta\rangle\langle\beta|B_\nu(0)|\alpha\rangle\,, \tag{52}$$

where, here again, the translational energy state β is lower in energy $\hbar(\omega_r-\omega_{r-1})$ relative to α. For this term we have

$$\langle B_\nu^\dagger(0)B_\nu(0)\rangle_{\nu=\omega_r-\omega_{r-1}}=\frac{n}{z}\sum_\alpha e^{-E_\alpha/kT}|K_{\beta,\alpha}|^2\,. \tag{53}$$

Each term in $\langle B_\nu(0)B_\nu^\dagger(0)\rangle$ is larger by a factor $e^{(E_r-E_{r-1})/kT}$ than the corresponding term in $\langle B_\nu^\dagger(0)B_\nu(0)\rangle$, and therefore

$$\langle B_\nu^\dagger(0)B_\nu(0)\rangle_{\nu=\omega_r-\omega_{r-1}} = \langle B_\nu(0)B_\nu^\dagger(0)\rangle_{\nu=\omega_r-\omega_{r-1}}e^{-(E_r-E_{r-1})/kT}\,. \tag{54}$$

Let us use the following definitions:

$$\langle B_\nu^\dagger(0)B_\nu(0)\rangle_{\nu=\omega_r-\omega_{r-1}} = \frac{n}{z}\sum_\alpha e^{-E_\alpha/kT}|K_{\alpha,\beta}|^2\equiv nK_{r-1,r}\,, \tag{55}$$

$$\langle B_\nu(0)B_\nu^\dagger(0)\rangle_{\nu=\omega_r-\omega_{r-1}} = \frac{n}{z}\sum_\beta e^{-E_\beta/kT}|K_{\beta,\alpha}|^2\equiv nK_{r,r-1}\,. \tag{56}$$

From these relations we get the detailed-balance ratio

$$K_{r-1,r}=K_{r,r-1}e^{-(E_r-E_{r-1})/kT}\,. \tag{57}$$

By similar definitions and considerations for the spectral transitions $r\rightarrow r+1$ we have

$$K_{r,r+1}=K_{r+1,r}e^{-(E_{r+1}-E_r)/kT}\,. \tag{58}$$

Substituting Eqs. (54)–(58) for the transitions $r+1 \rightarrow r$ and $r \rightarrow r-1$ into Eq. (47), we get

$$\begin{aligned}\frac{dn(r)}{dt}&\\ &=2\pi|M_{r+1,r}|^2K_{r+1,r}[n(r+1)n-e^{-(E_{r+1}-E_r/kT}n(r)n]\\ &\quad-2\pi|M_{r,r-1}|^2K_{r,r-1}[n(r)n-e^{-(E_r-E_{r-1})/kT}n(r-1)n]\,.\end{aligned}\tag{59}$$

All the terms in Eq. (59) are defined for the same time t, and this equation is equivalent to the VT part in Eq. (1).

Vibration-translation transition probabilities have been calculated in great detail, by many authors for various molecules. Usually in practical calculations of the matrix elements (mostly for the squared absolute values) one cannot take into account a full description of the interactions in the gas, and various approximations are used. The term which is equivalent to $|M_{r,r+1}|^2$ (in our work) is often taken to be equal to the squared absolute value of the harmonic oscillator matrix element. The term $K_{r,r-1}$, defined in our work by Eqs. (55) and (50), turns out to be very complicated, and it was evaluated by other researchers only in simplified cases. The fundamental equation of VT relaxation of diatomic gas given in our work [Eq. (46)] is more general than usual expressions [equivalent to Eqs. (59)]. Although usually Eq. (59) is a good approximation for Eq. (46), the effects of broadening and the external perturbations to the VT relaxation might be important in studying the fine details of population inversion in diatomic gas lasers. These effects must also be important in dense gas systems far from thermal equilibrium (e.g., high-pressure lasers).

VI. VV RELAXATION IN DIATOMIC GAS

The theory of vibration-vibration relaxation coupled to a translational heat bath can be presented by the same methods given for the VT relaxation. Here we outline only the main results and the quantum-mechanical analogs for the VV expressions of Eq. (1). The quantum-mechanical expression for the rate coefficients $n_{r+1}n_{s-1}P_{s-1,r+1;s,r}$ is given by

$$\begin{aligned}\Big\langle \sum_\nu \int_0^t dt'\{&\exp[-i(\omega_r+\omega_s-\omega_{r+1}-\omega_{s-1}+\nu)(t-t')]b_0^\dagger(r+1,s-1;t)b_0(r+1,s-1;t')M_{r+1,s-1;r,s}(t')M_{r,s;r+1,s-1}(t)\}\\ &\times\sum_\beta\frac{e^{-E_\beta/kT}|K_{\beta,\alpha}|^2}{z}\\ &+\sum_\nu\int_0^t dt'\{\exp[i(\omega_r+\omega_s-\omega_{r+1}-\omega_{s-1}+\nu)(t-t')]b_0^\dagger(r+1,s-1;t')b_0(r+1,s-1;t)M_{r,s;r+1,s-1}(t')M_{r+1,s-1;r,s}(t)\}\\ &\times\sum_\beta\frac{e^{-E_\beta/kT}|K_{\beta,\alpha}|^2}{z}\Big\rangle\\ &\approx\langle b_0^\dagger(r+1,s-1;t)b_0(r+1,s-1;t)\rangle|M_{r+1,s-1;r,s}(t)|^2\sum_\beta\frac{e^{-E_\beta/kT}|K_{\beta,\alpha}|^2}{z}\,.\end{aligned}\tag{60}$$

One can verify that this expression is the analogous expression for the fourth and fifth terms on the right-hand side of Eq. (46). Here the vibrational transition is characterized by the vibrational quantum numbers of the two molecules. The summation over ν shows the distribution of the radiative transition near the resonance frequency $\nu_0=(\omega_s-\omega_{s-1})-(\omega_{r+1}-\omega_r)$. (According to the rotating-wave approximation ν_0 will always be positive.) $M_{s-1,r+1;s,r}$ is the dipole moment for the vibrational transition of two molecules. The translational part of the interaction is equal to that presented in VT relaxation. $|K_{\beta,\alpha}|^2$ is defined by Eq. (50) and z is the translational partition function. The right-hand side of Eq. (60) is obtained by neglecting memory effects also for the vibrational part of the interaction. The expectation values of the operators b on the right-hand side of Eq. (60) are given as

$$\langle b_0^\dagger(r+1,s-1;t)b_0(r+1,s-1;t)\rangle=n_{r+1}n_{s-1}\,.\tag{61}$$

The complete treatment of VV relaxation can be made by exchanging all rate coefficients of Eq. (1) [as illustrated for one term in Eq. (60)] by quantum-mechanical expressions. The full treatment of VV relaxation is similar to that of VT relaxation, and one can easily deduce the complete expressions. In the present work we do not treat resonant VV interactions $(r-1,r\rightarrow r,r-1)$ which do not change the vibrational population of the gas.

We can use the present methods only for cases in which the VV interaction is coupled (due to the anharmonicity of the diatomic molecule) to a translational heat bath.

VII. VIBRATIONAL RELAXATION BY RADIATIONAL HEAT BATH

The Hamiltonian operator H_{tot} for the whole gas may be written in the present case as

$$H_{\text{tot}} = H_{0m} + H_{0\text{RB}} + H_{m\text{RB}}, \tag{62}$$

where H_{0m} is defined by Eq. (4). $H_{0\text{RB}}$ is defined by

$$H_{0\text{RB}} = \sum_{\omega} \hbar\omega B_\omega^\dagger B_\omega, \tag{63}$$

where the summation is over all frequencies of the radiational heat bath.[20] $B_\omega^\dagger$ and B_ω are the creation and annihilation operators of a photon with frequency ω. $H_{m\text{RB}}$ can be written

$$H_{m\text{RB}} = \hbar \sum_{i} b^\dagger(i-1)b(i)M_{i,i-1} \sum_{\omega} g_\omega^* B_\omega^\dagger + \hbar \sum_{i} b^\dagger(i)b(i-1)M_{i-1,i} \sum_{\omega} g_\omega B_\omega, \tag{64}$$

where g_ω is a slowly varying function of the energy $\hbar\omega$. $M_{i,i-1}$ is the dipole matrix element for radiative transition (we neglect in the present work the Doppler broadening); g_ω includes constants which appear in the usual theory of matter-radiation interactions. The radiational heat bath represents an equilibrium state of the radiation with a constant frequency distribution. For example, this distribution might be equal to that of a blackbody radiation or to that of nonlasing modes in a cw laser. Equation (64) describes the matter-radiation heat-bath interaction, which is analogous to the vibration-translation heat-bath interaction described in Eq. (19).

Using the Heisenberg picture the equation of motion for the operator $b(r)$ can be written in the present case as

$$i\hbar \frac{db(r)}{dt} = [b(r), H_{0m}] + [b(r), H_{0\text{RB}}] + [b(r), H_{m\text{RB}}], \tag{65}$$

where

$[b(r), H_{0\text{RB}}] = 0, \quad [b(r), H_{0m}] = \hbar\omega_r b(r), \quad [b(r), H_{m\text{RB}}]$

is evaluated according to Eqs. (25) and (64). We get

$$i\hbar \frac{db(r)}{dt} = \hbar\omega_r b(r) + \hbar b(r+1)M_{r+1,r} \sum_{\omega} g_\omega^* B_\omega^\dagger + \hbar b(r-1)M_{r-1,r} \sum_{\omega} g_\omega B_\omega. \tag{66}$$

Equation (66) is analogous to Eq. (27), where the radiational term $\sum_\omega g_\omega B_\omega$ exchanges the translational term $\sum_\nu B_\nu$. The equation of motion for B_ω is given by

$$i\hbar \frac{dB_\omega}{dt} = [B_\omega, H_{\text{tot}}] = [B_\omega, H_{0m}] + [B_\omega, H_{0\text{RB}}] + [B_\omega, H_{m\text{RB}}], \tag{67}$$

where $[B_\omega, H_{0m}] = 0$ and $[B_\omega, H_{0\text{RB}}] = \hbar\omega B_\omega$. Here we use the commutation relations

$$[B_\omega, B_{\omega'}^\dagger] = \delta_{\omega,\omega'}. \tag{68}$$

Our treatment of the radiational heat bath is different from that of the translational heat bath in two fundamental points. The use of Eq. (68) simplifies the treatment of the radiational heat bath, but, on the other hand, we shall avoid using here the contraction and shall consider the possibility of cooperative effects between molecules (while in the treatment of the translational heat bath such effects were excluded).

Using Eqs. (64) and (68) we evaluate the expression $[B_\omega, H_{m\text{RB}}]$ and get

$$i\hbar \frac{dB_\omega}{dt} = \hbar\omega B_\omega + \hbar g_\omega^* \sum_{i} b^\dagger(i-1)b(i)M_{i,i-1}. \tag{69}$$

The formal solutions of B_ω and $B_\omega^\dagger$ can be written

$$B_\omega(t) = B_\omega(0)e^{-i\omega t} - i \int_0^t dt' e^{-i\omega(t-t')} g_\omega^* \sum_{i} b^\dagger(i-1)b(i)M_{i,i-1}, \tag{70}$$

$$B_\omega^\dagger(t) = B_\omega^\dagger(0)e^{i\omega t} + i \int_0^t dt' e^{i\omega(t-t')} g_\omega \sum_{i} b^\dagger(i)b(i-1)M_{i-1,i}. \tag{71}$$

Equations (70) and (71) for radiational heat-bath operators are analogous, respectively, to Eqs. (37) and (38) for the translational heat-bath operators, but here the expressions are simplified due to Eq. (68). We insert the formal solutions of B_ω and $B_\omega^\dagger$ into Eq. (66) (ordering the operators B_ω to the left of operators b), and then we get

$$\begin{aligned} i\hbar \frac{db(r)}{dt} = {} & \hbar\omega_r b(r) + i\hbar \int_0^t dt' \sum_{\omega} e^{i\omega(t-t')} |g_\omega|^2 \sum_{i} b^\dagger(i,t')b(i-1,t')b(r+1,t)M_{i-1,i}M_{r+1,r} \\ & - i\hbar \int_0^t dt' \sum_{\omega} e^{-i\omega(t-t')} |g_\omega|^2 \sum_{i} b^\dagger(i-1,t')b(i,t)b(r-1,t)M_{i,i-1}M_{r-1,r} \\ & + \hbar \left(\sum_{\omega} g_\omega^* B_\omega^\dagger(0)e^{i\omega t} \right) b(r+1)M_{r+1,r} + \hbar \left(\sum_{\omega} g_\omega B_\omega(0)e^{-i\omega t} \right) b(r-1)M_{r-1,r}. \end{aligned} \tag{72}$$

Equation (72) is simplified by using the relation

$$\sum_{\omega} |g_{\omega}|^2 e^{i\omega(t-t')} = \sum_{\omega} |g_{\omega}|^2 e^{-i\omega(t-t')} = 2\kappa\delta(t-t'), \tag{73}$$

where $\kappa = \pi |g_{\omega}|^2_{\text{av}}$. We obtain

$$\begin{aligned} i\hbar \frac{db(r)}{dt} &= \hbar\omega_r b(r) + i\hbar\kappa \sum_i b^{\dagger}(i) b(i-1) b(r+1) M_{i-1,i} M_{r+1,r} - i\hbar\kappa \sum_i b^{\dagger}(i-1) b(i) b(r-1) M_{i,i-1} M_{r-1,r} \\ &\quad + \hbar\left(\sum_{\omega} g^*_{\omega} B^{\dagger}_{\omega}(0) e^{i\omega t}\right) b(r+1) M_{r+1,r} + \hbar\left(\sum_{\omega} g_{\omega} B_{\omega}(0) e^{-i\omega t}\right) b(r-1) M_{r-1,r} . \end{aligned} \tag{74}$$

All operators in Eq. (73) are at time t, and memory effects are neglected by this approximation. In a similar way,

$$\begin{aligned} i\hbar \frac{db^{\dagger}(r)}{dt} &= -\hbar\omega_r b^{\dagger}(r) - i\hbar\kappa \sum_i b^{\dagger}(r-1) b^{\dagger}(i) b(i-1) M_{i-1,i} M_{r,r-1} + i\hbar\kappa \sum_i b^{\dagger}(r+1) b^{\dagger}(i-1) b(i) M_{i,i-1} M_{r,r+1} \\ &\quad - \hbar b^{\dagger}(r-1) M_{r,r-1} \left(\sum_{\omega} g^*_{\omega} B^{\dagger}_{\omega}(0) e^{i\omega t}\right) - \hbar b^{\dagger}(r+1) M_{r,r+1} \left(\sum_{\omega} g_{\omega} B_{\omega}(0) e^{-i\omega t}\right) . \end{aligned} \tag{75}$$

The formal solutions of Eqs. (74) and (75) are

$$\begin{aligned} b(r,t) &= b(r,0) e^{-i\omega_r t} + \kappa \int_0^t dt' e^{-i\omega_r(t-t')} \sum_i b^{\dagger}(i,t') b(i-1,t') b(r+1,t') M_{i-1,i}(t') M_{r+1,r}(t') \\ &\quad - \kappa \int_0^t dt' e^{-i\omega_r(t-t')} \sum_i b^{\dagger}(i-1,t') b(i,t') b(r-1,t') M_{i,i-1}(t') M_{r-1,r}(t') \\ &\quad - i \int_0^t dt' e^{-i\omega_r(t-t')} \left(\sum_{\omega} g^*_{\omega} B^{\dagger}_{\omega}(0) e^{i\omega t'}\right) b(r+1,t') M_{r+1,r}(t') \\ &\quad - i \int_0^t dt' e^{-i\omega_r(t-t')} \left(\sum_{\omega} g_{\omega} B_{\omega}(0) e^{-i\omega t'}\right) b(r-1,t') M_{r-1,r}(t') \end{aligned} \tag{76}$$

and

$$\begin{aligned} b^{\dagger}(r,t) &= b^{\dagger}(r,0) e^{i\omega_r t} - \kappa \int_0^t dt' e^{i\omega_r(t-t')} \sum_i b^{\dagger}(r-1,t') b^{\dagger}(i,t') b(i-1,t') M_{i-1,i}(t') M_{r,r-1}(t') \\ &\quad + \kappa \int_0^t dt' e^{i\omega_r(t-t')} \sum_i b^{\dagger}(r+1,t') b^{\dagger}(i-1,t') b(i,t') M_{i,i-1}(t') M_{r,r+1}(t') \\ &\quad + i \int_0^t dt' e^{i\omega_r(t-t')} b^{\dagger}(r-1,t') M_{r,r-1}(t') \sum_{\omega} g^*_{\omega} B^{\dagger}_{\omega}(0) e^{i\omega t'} \\ &\quad + i \int_0^t dt' e^{i\omega_r(t-t')} b^{\dagger}(r+1,t') M_{r,r+1}(t') \sum_{\omega} g_{\omega} B_{\omega}(0) e^{-i\omega t'} . \end{aligned} \tag{77}$$

The rate of change of the occupation-number operators of the vibrational states during the vibration-radiation interaction process is given by

$$\begin{aligned} i\hbar \frac{d}{dt} [b^{\dagger}(r) b(r)] &= i\hbar \frac{db^{\dagger}(r)}{dt} b(r) + i\hbar b^{\dagger}(r) \frac{db(r)}{dt} \\ &= -i\hbar\kappa \sum_i b^{\dagger}(r-1) b^{\dagger}(i) b(i-1) b(r) M_{i-1,i} M_{r,r-1} + i\hbar\kappa \sum_i b^{\dagger}(r+1) b^{\dagger}(i-1) b(i) b(r) M_{i,i-1} M_{r,r+1} \\ &\quad + i\hbar\kappa \sum_i b^{\dagger}(r) b^{\dagger}(i) b(i-1) b(r+1) M_{i-1,i} M_{r+1,r} - i\hbar\kappa \sum_i b^{\dagger}(r) b^{\dagger}(i-1) b(i) b(r-1) M_{i,i-1} M_{r-1,r} \\ &\quad - \hbar b^{\dagger}(r-1) M_{r,r-1} \left[\sum_{\omega} g^*_{\omega} B^{\dagger}_{\omega}(0) e^{i\omega t}\right] b(r) - \hbar b^{\dagger}(r+1) M_{r,r+1} \left(\sum_{\omega} g_{\omega} B_{\omega}(0) e^{-i\omega t}\right) b(r) \\ &\quad + \hbar b^{\dagger}(r) \left(\sum_{\omega} g^*_{\omega} B^{\dagger}_{\omega}(0) e^{i\omega t}\right) b(r+1) M_{r+1,r} + \hbar b^{\dagger}(r) \left[\sum_{\omega} g_{\omega} B_{\omega}(0) e^{-i\omega t}\right] b(r-1) M_{r-1,r} . \end{aligned} \tag{78}$$

In deriving Eq. (78) we used Eqs. (74) and (75), where all the operators b of this equation are at time t. Substituting Eqs. (76) and (77) in Eq. (78), and using the Markoffian properties of the radiational heat-bath operators B_ω in an analogous way to that which has been used in developing the translational heat-bath equations, we get

$$
\begin{aligned}
&\left\langle i\hbar \frac{d}{dt}\left[b^\dagger(r,t)b(r,t)\right]\right\rangle \\
&\quad=\Big\langle i\hbar\kappa\sum_i b^\dagger(r,t)b^\dagger(i,t)b(i-1,t)b(r+1,t)M_{i-1,i}(t)M_{r+1,r}(t) \\
&\qquad -i\hbar\kappa\sum_i b^\dagger(r-1,t)b^\dagger(i,t)b(i-1,t)b(r,t)M_{i-1,i}(t)M_{r,r-1}(t) \\
&\qquad -i\hbar\kappa\sum_i b^\dagger(r,t)b^\dagger(i-1,t)b(i,t)b(r-1,t)M_{i,i-1}(t)M_{r-1,r}(t) \\
&\qquad +i\hbar\kappa\sum_i b^\dagger(r+1,t)b^\dagger(i-1,t)b(i,t)b(r,t)M_{i,i-1}(t)M_{r,r+1}(t) \\
&\qquad -i\hbar\left(\int_0^t dt' e^{i\omega_{r-1}(t-t')}b^\dagger(r,t')M_{r-1,r}(t')\sum_\omega g_\omega B_\omega(0)e^{-i\omega t'}\right)M_{r,r-1}(t)\left(\sum_\omega g_\omega^* B_\omega^\dagger(0)e^{i\omega t}\right)b(r,t) \\
&\qquad +i\hbar b^\dagger(r-1,t)M_{r,r-1}(t)\left(\sum_\omega g_\omega^* B_\omega^\dagger(0)e^{i\omega t}\right)\left(\int_0^t dt' e^{-i\omega_r(t-t')}\sum_\omega g_\omega B_\omega(0)e^{-i\omega t'}b(r-1,t')M_{r-1,r}(t')\right) \\
&\qquad -i\hbar\left(\int_0^t dt' e^{i\omega_{r+1}(t-t')}b^\dagger(r,t')M_{r+1,r}(t')\sum_\omega g_\omega^* B_\omega^\dagger(0)e^{i\omega t'}\right)M_{r,r+1}(t)\left(\sum_\omega g_\omega B_\omega(0)e^{-i\omega t}\right)b(r,t) \\
&\qquad +i\hbar b^\dagger(r+1,t)M_{r,r+1}(t)\left(\sum_\omega g_\omega B_\omega(0)e^{-i\omega t}\right)\left(\int_0^t dt' e^{-i\omega_r(t-t')}\sum_\omega g_\omega^* B_\omega^\dagger(0)e^{i\omega t'}b(r+1,t')M_{r+1,r}(t')\right) \\
&\qquad +i\hbar\left(\int_0^t dt' e^{i\omega_r(t-t')}b^\dagger(r+1,t')M_{r,r+1}(t')\sum_\omega g_\omega B_\omega(0)e^{-i\omega t'}\right)\left(\sum_\omega g_\omega^* B_\omega^\dagger(0)e^{i\omega t}\right)b(r+1,t)M_{r+1,r}(t) \\
&\qquad -i\hbar b^\dagger(r,t)\left(\sum_\omega g_\omega^* B_\omega^\dagger(0)e^{i\omega t}\right)\left(\int_0^t dt' e^{-i\omega_{r+1}(t-t')}\sum_\omega g_\omega B_\omega(0)e^{-i\omega t'}b(r,t')M_{r,r+1}(t')\right)M_{r+1,r}(t) \\
&\qquad +i\hbar\left(\int_0^t dt' e^{i\omega_r(t-t')}b^\dagger(r-1,t')M_{r,r-1}(t')\sum_\omega g_\omega^* B_\omega^\dagger(0)e^{i\omega t'}\right)\left(\sum_\omega g_\omega B_\omega(0)e^{i\omega t}\right)b(r-1,t)M_{r-1,r}(t) \\
&\qquad -i\hbar b^\dagger(r,t)M_{r-1,r}(t)\left(\sum_\omega g_\omega B_\omega(0)e^{-i\omega t}\right)\left(\int_0^t dt' e^{i\omega_{r-1}(t-t')}\sum_\omega g_\omega^* B_\omega^\dagger(0)e^{i\omega t'}b(r,t')M_{r,r-1}(t')\right)\Big\rangle\,. \qquad (79)
\end{aligned}
$$

The use of the Markoffian properties in deriving Eq. (79) is made in the same way as was illustrated in Eq. (41). Equation (79) is analogous to Eq. (44), but here we get additional terms [the first four terms of Eq. (79)] since we do not use contraction [Eq. (40)]. One can proceed in the same way as was described in Sec. V and derive formal results for the broadening. The memory effect (i.e., the broadening) has already been neglected in the first four terms of Eq. (79) by using Eq. (73). Neglecting the memory effects in other terms in Eq. (79) we can proceed in a way similar, although not equivalent, to that which has been described in the translational heat-bath treatment.

In the products of summation over ω [in Eq. (79)] we consider only resonant terms with the same ω. We take the averages $\langle B_\omega(0)B_\omega^\dagger(0)\rangle$ $\langle B_\omega^\dagger(0)B_\omega(0)\rangle$ out of the integral signs evaluated near the resonance frequencies and then introduce the δ function using Eq. (73). These calculations give the results

$$
\begin{aligned}
i\hbar\frac{dn(r)}{dt} &= i\hbar\left\langle\frac{d}{dt}[b^\dagger(r)b(r)]\right\rangle \\
&= \Big\langle i\hbar\kappa\sum_i b^\dagger(r)b^\dagger(i)b(i-1)b(r+1)M_{i-1,i}M_{r+1,r} - i\hbar\kappa\sum_i b^\dagger(r-1)b^\dagger(i)b(i-1)b(r)M_{i-1,i}M_{r,r-1} \\
&\quad - i\hbar\kappa\sum_i b^\dagger(r)b^\dagger(i-1)b(i)b(r-1)M_{i,i-1}M_{r-1,r} + i\hbar\kappa\sum_i b^\dagger(r+1)b^\dagger(i-1)b(i)b(r)M_{i,i-1}M_{r,r+1}\Big\rangle \\
&\quad + 2i\hbar\kappa n(r-1)|M_{r,r-1}|^2\langle\!\langle B_\omega^\dagger(0)B_\omega(0)\rangle\!\rangle_{\omega=\omega_r-\omega_{r-1}} - 2i\hbar\kappa n(r)|M_{r,r-1}|^2\langle\!\langle B_\omega(0)B_\omega^\dagger(0)\rangle\!\rangle_{\omega=\omega_r-\omega_{r-1}} \\
&\quad + 2i\hbar\kappa n(r+1)|M_{r,r+1}|^2\langle\!\langle B_\omega(0)B_\omega^\dagger(0)\rangle\!\rangle_{\omega=\omega_{r+1}-\omega_r} - 2i\hbar\kappa n(r)|M_{r,r+1}|^2\langle\!\langle B_\omega^\dagger(0)B_\omega(0)\rangle\!\rangle_{\omega=\omega_{r+1}-\omega_r}\,. \qquad (80)
\end{aligned}
$$

In Eq. (80) all operators b are at time t, and we again substitute $\langle\!\langle b^\dagger(r)b(r)\rangle\!\rangle = n(r)$. The first four terms of Eq. (80) describe coherent spontaneous emission,[13,14] as will be shown later. We shall now show that the last four terms of Eq. (80) describe the induced absorption and emission and the usual spontaneous emission. The averaged nonvanishing products of the radiational heat-bath operators can be developed as follows

$$
\begin{aligned}
\langle\!\langle B_\omega^\dagger(0)B_\omega(0)\rangle\!\rangle_{\omega=\omega_r-\omega_{r-1}}
&= n\sum_\alpha \rho_{\alpha\alpha}\langle\alpha|B_\omega^\dagger(0)|0\rangle\langle 0|B_\omega(0)|\alpha\rangle \\
&= nf(\omega_r-\omega_{r-1})_1\,, \qquad (81)
\end{aligned}
$$

where $|\alpha\rangle$ are all the photon states with energy $\omega=\omega_r-\omega_{r-1}$. $|0\rangle$ is the radiational vacuum state, and n is the total density of the photons in our system. $f(\omega_r-\omega_{r-1})$ describes the result of the summation over one-photon states with energy $\omega=\omega_r-\omega_{r-1}$. According to its definition $nf(\omega_r-\omega_{r-1})$ is proportional to the density of the photons at the resonance frequency $\omega_r-\omega_{r-1}$.

Using the commutation relations of B_ω and $B_\omega^\dagger$ we have

$$
\langle\!\langle B_\omega(0)B_\omega^\dagger(0)\rangle\!\rangle_{\omega=\omega_r-\omega_{r-1}} = \langle\!\langle B_\omega^\dagger(0)B_\omega(0)\rangle\!\rangle_{\omega=\omega_r-\omega_{r-1}} + 1\,. \qquad (82)
$$

Other products of radiational heat bath operators are calculated in a similar way. Substituting these results [Eqs. (81) and (82) into Eq. (80), and ordering the operators b in a different way [Eqs. (8) and (9)] we get

$$
\begin{aligned}
\frac{dn(r)}{dt} &= \Big\langle \kappa\sum_i b^\dagger(r)b(i-1)b^\dagger(i)b(r+1)M_{i-1,i}M_{r+1,r} - \kappa\sum_i b^\dagger(r-1)b(i-1)b^\dagger(i)b(r)M_{i-1,i}M_{r,r-1} \\
&\quad - \kappa\sum_i b^\dagger(r)b(i)b^\dagger(i-1)b(r-1)M_{i,i-1}M_{r-1,r} \\
&\quad + \kappa\sum_i b^\dagger(r+1)b(i)b^\dagger(i-1)b(r)\,M_{i,i-1}M_{r,r+1}\Big\rangle \\
&\quad + 2\kappa nf(\omega_r-\omega_{r-1})|M_{r,r-1}|^2[n(r-1)-n(r)] + 2\kappa|M_{r,r+1}|^2n(r+1) - 2\kappa|M_{r,r-1}|^2n(r)\,. \\
&\quad - 2\kappa|M_{r,r+1}|^2nf(\omega_{r+1}-\omega_r)[n(r)-n(r+1)] \qquad (83)
\end{aligned}
$$

The last two terms in Eq. (83) describe the usual spontaneous emission from levels $r+1$ and r, respectively, to r (a positive term) and $r-1$ (a negative term). The induced emission and absorption have opposite signs for certain radiative transitions and are described in Eq. (83) by the terms which are proportional to the total photon density n. For a blackbody radiation heat bath we have the relation $nf(\omega_r-\omega_{r-1}) = [e^{\hbar\omega/kT}-1]^{-1}$.

On ensemble averaging, the first four terms of Eq. (83) will contribute only diagonal expressions in the vibrational quantum numbers. By the present approximation of a diagonalized form for the statistical density matrix, we neglect cooperative effects between radiative transitions and take into account only products of matrix elements which belong to the same radiative transitions. Using this approximation we get for the first four terms of Eq. (83) the result

$$
\begin{aligned}
\left(\frac{dn(r)}{dt}\right)_{\text{SCE}} &= 2\langle\!\langle\kappa b^\dagger(r)b(r)b^\dagger(r+1)b(r+1)\rangle\!\rangle|M_{r+1,r}|^2 \\
&\quad - 2\langle\!\langle\kappa b^\dagger(r-1)b(r-1)b^\dagger(r)b(r)\rangle\!\rangle|M_{r,r-1}|^2\,. \qquad (84)
\end{aligned}
$$

The index SCE refers to spontaneous coherent emission. We can evaluate Eq. (84) by various approximations. By using contraction and assuming one-molecule states [Eq. (40)], the expressions for spontaneous coherent emission in Eq. (84) vanish. By using many-body states and assuming maximum coherence between molecules, we get

$$\left(\frac{dn(r)}{dt}\right)_{\text{SCE}} = 2\kappa n(r)n(r+1)|M_{r+1,r}|^2 - 2\kappa n(r)n(r-1)|M_{r,r-1}|^2 . \qquad (85)$$

This result is interesting as it shows the possibility of cooperative spontaneous emission which depends on the population density of both the upper and lower levels of the radiative transitions. Cooperative radiation effects (which are proportional to the squared values of population numbers) are well known from descriptions of super-radiance, Bloch-type equations, etc.[13,14] The amount of spontaneous coherent emission in a real case should be much smaller than in the idealized many-body case expressed in Eq. (85). The many-body formalism has a physical meaning if we take into account the number of molecules that "build" the photon cooperatively. In our system the wavelength λ is much larger than the mean distance between molecules, and cooperative effects are important. However, collisions between molecules, including resonant effects (which are possible among identical molecules) tend to destroy the cooperative effects. In passing from Eq. (79) to Eq. (80) we assume short memory approximation and neglect the effect of collisions. Practically, collisions may decrease the volume in which cooperative effects are important.

VIII. SUMMARY AND CONCLUSIONS

The vibrational relaxation of a diatomic gas by vibrational and translational heat baths has been studied by second-quantization methods. General methods have been developed for treating the various heat baths that have a short memory. New expressions are developed for the broadening of a gas which is in a nonequilibrium state [Eqs. (46) and (79)].

The fundamental equations for VT relaxation of a diatomic gas are presented in Eq. (44) and are much more general than previous semiclassical expressions. The methods developed here for treating a translational heat bath are useful also for treating nonresonant VV relaxation. The rate of production of molecules in one state from molecules of other states is described in the present work by quantum-mechanical expressions.

A many-body formalism is developed for treating the relaxation of the diatomic gas by radiation. The cooperative effects in the gas do not change the rate of induced emission or absorption, but can change the rate of spontaneous emission. In addition to the usual spontaneous emission we get a spontaneous coherent emission. [Eqs. (80) and (85)]. The authors hope that experimental studies will be made on the broadening of a nonequilibrium gas, and on the possibility for a coherent spontaneous emission in a diatomic gas.

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$$H_{0\mathbf{RB}} = \sum_{\sigma=1}^{2} \sum_{\omega} \hbar\omega B^{+}_{\omega,\sigma} B_{\omega,\sigma},$$

where σ denotes the polarization of the photon. The summation over σ could be carried through all the calculations without affecting the final result. A possible coupling between the two polarizations vanishes in the ensemble averaging [in passing from Eq. (79) to Eq. (80)].

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