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## Abstract

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# RESONANT VIBRATIONAL RELAXATION OF A SYSTEM OF HARMONIC OSCILLATORS

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Vibrational relaxation of a closed system of harmonic oscillators, which is a model for a number of physical and chemical nonequilibrium processes in gases, was considered by A. I. Osipov ($^1$) and Shuler ($^2$). These authors solved the relaxation equations, the transition probabilities in which were calculated in the first order of perturbation theory with respect to the interaction $W = U(R)x_1x_2/\rho^2$. Here $\rho$ is the characteristic radius of interaction between the oscillators; $x_1$ and $x_2$ are their vibrational coordinates, $U$ is the energy of their interaction at distance $R$. Under the condition of adiabatic collisions, when the collision time $\tau$ is large compared with the vibrational time $1/\omega$, the interaction $W$ leads only to resonant transitions $n_1 \to n_1 \pm 1$ and $n_2 \to n_2 \mp 1$, whose probability in the first order of perturbation theory is equal to

$$\mathcal{P}(n_1 \to n_1 + 1;\, n_2 \to n_2 - 1) = (n_1 + 1)n_2(\overline{U}\tau/\hbar)^2(x_{01}/\rho)^4, \tag{1}$$

where $x_{01}$ is the matrix element of the vibrational transition $0 \to 1$, and the quantity $\overline{U}$ is defined as the average energy over the entire time of interaction. Remaining within the framework of the oscillator approximation, the ratio $x/\rho$ (as well as its matrix elements) should be regarded as a small parameter; however, since the quantity $\overline{U}\tau$, in principle, is not restricted in any way, in a number of cases the conditions of applicability of the first approximation of perturbation theory prove to be violated, so that calculation by formula (1) gives $\mathcal{P} > 1$. Under these conditions the transition probabilities must be calculated more accurately. The solution of the problem in the adiabatic approximation ($\omega\tau \gg 1$) can be obtained easily, since the Hamiltonian of two oscillators, with the interaction taken into account, permits separation of variables. General expressions in integral form for the transition probabilities $\mathcal{P}(n_1 \to n_1';\, n_2 \to n_2')$ were obtained by A. I. Osipov ($^3$). They, however, can be substantially simplified if the maximum rate of change of the amplitudes of the transition probabilities in the system of interacting oscillators beats is small in comparison with $\omega$. The classical variant of this problem corresponds to slow beats of two coupled identical harmonic oscillators. In this case the time dependence of their amplitudes can be represented by the $z$-component of a vector of constant length rotating in the $xz$-plane with an angular velocity equal to the beat frequency. It is not difficult to show that this analogy is preserved also in the quantum-mechanical treatment, so that the amplitude of the probability of the transition $n_1 \to n_1'$ is expressed through the matrix elements of the rotation matrix of the angular-momentum operator. Omitting the calculations, we give only the final result:

$$\mathcal{P}(n_1 \to n_1';\, n_2 \to n_2') = \left| P^{n_1+n_2}_{(n_1-n_2)/2,\,(n_1'-n_2')/2}(\cos\theta) \right|^2 \delta(n_1+n_2-n_1'-n_2'), \quad (2)$$

where $\theta = 2(\overline{U}\tau/\rho)(x_{01}/\rho)^2$, and $P^l_{mk}(\mu)$ are generalized spherical functions, defined in accordance with (4).

We note that the adiabaticity condition makes it possible to single out from the infinite system of equations for the amplitudes of probabilities a finite system $n_1 + n_2$

equations, which turn out to be strongly coupled as a result of the absence in it of a rapidly oscillating factor $\exp(i\omega t)$, while the condition of slow beats makes it possible to neglect the change in the frequency $\omega$ as a result of the interaction. The kinetic equation for the population of oscillators at level $n$ has the form

$$\frac{d}{dt} x_n = 2Z \sum_{n' n_1 n_1'} \langle \mathcal{P}(n' \to n;\, n_1' \to n_1) \rangle\, x_{n'} x_{n_1'} - 2Z \sum_{n' n_1} \langle \mathcal{P}(n \to n';\, n_1 \to n_1') \rangle\, x_n x_{n_1}, \quad (3)$$

where $\langle \mathcal{P} \rangle$ is the transition probability averaged over unit flux; $Z$ is the number of binary collisions, and the factor 2 on the right-hand side of (3) takes into account the possibility of a change in the vibrational state of either of the colliding partners.

In the limiting case $\theta \ll 1$, the equations with index $n \ll (1/\theta)^2$ coincide with the equations of Refs. (1,2).

The general character of relaxation can be traced from the time dependence of the moments of the distribution function. These equations can be obtained from (3), using the orthogonality property of the functions

$$\sum_k P^l_{mk} P^l_{km'} = \delta_{mm'} \quad (4)$$

and the recurrence relation (4)

$$2\,\frac{m - k\mu}{\sqrt{1-\mu^2}}\, P^l_{mk}(\mu) =$$

$$= i\sqrt{(l+k)(l-k+1)}\, P^l_{m,k-1} - i\sqrt{(l+k+1)(l-k)}\, P^l_{m,k+1}. \quad (5)$$

In this way we obtain

$$\frac{d}{dt}\sum x_n = 0, \qquad \frac{d}{dt}\langle n\rangle = \frac{d}{dt}\sum n x_n = 0,$$

$$\frac{d}{dt}\langle n^2\rangle = 2Z\left\langle \frac{\sin^2\theta}{4}\right\rangle \left[-2\langle n^2\rangle + 4\langle n\rangle^2 + 2\langle n\rangle\right]. \tag{6}$$

The first two equations mean conservation of the normalization of the distribution function and of the total energy of the system, while the third describes the relaxation of the mean square of the vibrational energy. Thus, it follows from (6) that the second moment relaxes to its equilibrium value according to a simple exponential law.

Comparison with the result of Ref. (2) shows that for $\theta \ll 1$ equation (6) coincides exactly with the relaxation equation derived under the assumption that the first approximation of perturbation theory is valid. Thus it turns out that the range of applicability of (6) for $\theta \ll 1$ is limited by the smallness of the interaction of the oscillators only in the resonant transfer of the first vibrational quantum, and not by the smallness of the interaction in all those states that make an essential contribution to the mean energy. Without going into the details of estimating $\theta$ for real cases, we note that at $T \sim 300^\circ$ and for molecules such as $N_2$, $\theta$ proves to be of order $10^{-1}$, while for ion-molecular collisions with a strong polarization interaction it is of order 1 (an example of the latter may be the vibrational relaxation of $O_2^-$ in $O_2$, which determines the rate of attachment of slow electrons in oxygen (6)).

Equation (6) makes it possible to trace the influence of triple collisions on the vibrational relaxation of diatomic molecules. Suppose that the diatomic molecules AB are a small admixture in an inert gas M, so that the number of binary collisions AB—AB is much smaller than the number of collisions AB—M; however, the rate of resonant exchange of quanta in an AB—AB collision is much greater than the rate of nonresonant vibrational deactivation in a collision of AB and M.

If, as a result of triple collisions AB + AB + M, a molecular complex $(\mathrm{AB})_2$ with a sufficiently long lifetime can be formed, then the efficiency of vibrational-energy exchange must be greatly increased. Then the rates of the bimolecular and trimolecular relaxation mechanisms are obtained, respectively, as

$$k_2 = \frac{1}{4}Z(\mathrm{AB}+\mathrm{AB})\langle\sin^2\theta\rangle_2 \sim Z(\mathrm{AB}+\mathrm{AB})\langle\theta^2/4\rangle, \tag{7a}$$

$$k_3 = Z(\mathrm{AB}+\mathrm{AB}+\mathrm{M})\langle\sin^2\theta/4\rangle_3. \tag{7b}$$

For the complex $(\mathrm{AB})_2$, in accordance with the definition of $\theta$, one should set $\theta = \Omega t$, where $t$ is its lifetime and $\Omega = (x_{01}/\rho)^2 D/\hbar$ is the beat frequency, proportional to the interaction energy $D$ of the molecules AB. Averaging over the random distribution of collision times of $(\mathrm{AB})_2$ and M, we obtain

$$\langle \sin^2\theta \rangle = z\int_0^\infty \sin^2 \Omega t \, \exp(-zt)\, dt, \tag{8}$$

where $z$ is the number of double collisions of $(\mathrm{AB})_2$ with M leading to dissociation of the complex. Taking into account that the dissociation $(\mathrm{AB})_2 \to 2\mathrm{AB}$ requires the expenditure of energy $D$, one may set $z = z_0 p \exp(-D/kT)$, where $T$ is the temperature of the translational motion of the molecules; $z_0$ is the gas-kinetic number of collisions of $(\mathrm{AB})_2$ with M; $p$ is the probability of association $2\mathrm{AB} \to (\mathrm{AB})_2$ in a triple collision. Substituting (8) into (7b), we obtain

$$k_2 = \frac{1}{4} Z(\mathrm{AB}+\mathrm{AB})\,\Omega^2\tau^2, \tag{9a}$$

$$k_3 = \frac{1}{8} Z(\mathrm{AB}+\mathrm{AB}+\mathrm{M})\, 4\Omega^2/(z^2+4\Omega^2). \tag{9b}$$

Putting $Z(\mathrm{AB}+\mathrm{AB}+\mathrm{M}) \sim Z(\mathrm{AB}+\mathrm{AB}) z_0 \tau p$ and expressing the parameters in (9) in terms of the probability $\mathcal{P}(0\to 1;\, 1\to 0)$, we find the condition under which relaxation through triple collisions with formation of the complex $(\mathrm{AB})_2$ proceeds faster than in double collisions:

$$\mathcal{P}(0\to 1;\, 1\to 0)/p \ll z_0\rho \ll [\mathcal{P}(0\to 1;\, 1\to 0)]^{1/2} \exp(D/kT). \tag{10}$$

For typical values $\mathcal{P} \sim 10^{-3} - 10^{-4}$, $\tau \sim 10^{-13}$ sec., $p \sim 1$, and $D/kT \sim 5$, triple collisions prove to be significant at partial pressures of the order of several atmospheres.

These qualitative conclusions will apparently remain unchanged also for relaxation in a pure diatomic gas (in (7) and (9), M should then be replaced by AB).

An important special case is the resonant relaxation of a small number of strongly vibrationally excited molecules in a heat reservoir consisting of the same molecules. In this case one may take into account only collisions between the excited molecules and the reservoir molecules, the distribution of the latter being regarded as equilibrium. Then system (3) becomes linear:

$$\frac{d}{dt}x_n = Z\sum_{n'} \Pi(n,n')x_{n'} - X\sum_{n'} \Pi(n',n)x_n, \tag{11}$$

where

$$\Pi(n, n') = \sum_{n_1' n_1} \langle \mathcal{P}(n' \to n,\ n_1' \to n_1) \rangle (x^0_{n_1'}). \tag{12}$$

From this the following equation for relaxation of the mean vibrational energy is easily obtained:

$$\frac{d\bar{E}}{dt} = -Z \left\langle \sin^2 \frac{\theta}{2} \right\rangle [\bar{E} - E^0], \tag{13}$$

where $E^0$ is the mean vibrational energy of a reservoir molecule. Although for small $\theta$ this equation coincides with the equation for energy relaxation under weak interaction of the oscillators, the time dependence of the distribution function in the case of one-quantum and multiquantum transitions proves to be different. For example, an exponential decrease in the population of the $n$-th level for an initial $\delta_{mn}$-distribution under conditions of a low vibrational temperature of the reservoir ($E^0 \ll \hbar\omega$) corresponds to the rate constant

$$k_n = Z \langle 1 - \exp(-n\theta^2/4) \rangle. \tag{14}$$

For one-quantum transitions (first order of perturbation theory) one should set $n\theta^2/4 \ll 1$.

For an approximate study of the relaxation process in the classical approximation ($E^0 \gg \hbar\omega$) under strong interaction, when the averaging interval over beats is considerably greater than one period, the sinusoidal beats of two oscillators may be approximately replaced by a sequence of rectangular pulses. Physically this means that transitions from any level of each of the colliding oscillators to any of the lower ones are regarded as equiprobable, while the probability of "upward" transitions is determined by the principle of detailed balance. The relaxation of such a system with a statistical energy distribution was studied by Hoare ($^5$). The relaxation equation for the mean energy, which can readily be obtained from the kinetic equations of that work, is

$$\frac{d\overline{E}}{dt} = -\frac{Z}{2} [\overline{E} - E^0]. \tag{15}$$

This equation is obtained as a special case of (13), when the averaged rapidly oscillating factor $\sin^2 \dfrac{\theta}{2}$ may be replaced by 1/2.

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*Note: Figure translations are in progress. See original paper for figures.*