THERMAL EFFECTS ACCOMPANYING NONRESONANT VIBRATIONAL EXCHANGE

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Calculation has been made of the thermal effects attending nonresonant vibrational exchange in a molecular gas in a nonequilibrium state. Study has been made of the binary mixture, modeled as a set of harmonic oscillators of various frequencies. Vibrational exchange, the most rapid relaxation process occurring in the system, was assumed to completely determine the distribution of vibrational energy. It is shown that nonresonant vibrational exchange can lead to either heating or cooling in nonequilibrium states of the gaseous mixture. Calculation has been made of the amount of thermal energy liberated or absorbed in these processes.

The heating or cooling of a gas as the result of relaxation processes such as nonresonant vibrational exchange can be of considerable importance for various aspects of relaxation kinetics. These processes are particularly significant in the transfer of thermal energy between nonequilibrium system and translational degrees of freedom in low-temperature gases where vibrational–translational relaxation proceeds very slowly. There [1] rapid (V−V') nonresonant vibrational exchange leads to an appreciable redistribution of energy over the vibrating system. This can result in either an absorption or liberation of thermal energy by the system. An analysis of these effects is given in the present paper.

Let us consider the thermal effects accompanying nonresonant vibrational exchange in a binary mixture modeled as a system of A, B harmonic oscillators of different frequencies, $\omega_a \neq \omega_b$. Let it be supposed that $\tau_{VV'}$, the time of vibrational exchange, is much less than τ_{VT}, the characteristic time for vibrational–translational relaxation ($\tau_{VV'} \ll \tau_{VT}$) in an A+B system which permits quasiequilibrium energy distributions with oscillator temperatures, T_a and T_b, different from the gas temperature T. For the quasiequilibrium distribution resulting from multiquanta vibrational exchange through a channel in which P_a A-oscillator quanta undergo nonresonant exchange with P_b B-oscillator quanta, the relation between the vibrational temperatures T_a and T_b takes the form [2, 3]

$$P_a\omega_a/T_a - P_b\omega_b/T_b = (P_a\omega_a - P_b\omega_b)/T. \tag{1}$$

It is essential here that the total number of quasiparticles involved in $P_a \rightleftarrows P_b$ vibrational exchange in the A+B system (i.e., the A-oscillator P_a quanta or the P_b B-oscillator quanta) be conserved [3];

$$n_a\varepsilon_a/P_a + n_b\varepsilon_b/P_b = \text{const}, \tag{2}$$

where $n_i (i = a, b)$; $\varepsilon_i = [\exp(\hbar\omega_i/kT_i) - 1]^{-1}$ are, respectively, the concentration ($n_a + n_b = 1$) and mean number of i-oscillator quanta.

Let us now estimate the value of E, the thermal energy liberated or absorbed (per molecule) when a quasiequilibrium energy distribution (1) is established in a nonequilibrated vibrating system. The expression for E can be obtained directly from the equation for total energy (vibrational and thermal) conservation in the molecular system:

$$E + \hbar\omega_a n_a\varepsilon_a + \hbar\omega_b n_b\varepsilon_b = \hbar\omega_a n_a\varepsilon_a^0 + \hbar\omega_b n_b\varepsilon_b^0$$

and Eq. (2) for conservation of the number of quasiparticles;

$$E = -(\Delta\omega_{a,b}/P_b)\, n_b\, (\varepsilon_b^0 - \varepsilon_b), \tag{3}$$

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where $\Delta\omega_{a,b} = (\hbar/k)(\omega_a P_a - \omega_b P_b)$ is the resonance defect for vibrational exchange at °K, and ε^0_i, ε_i are the mean numbers of quanta in the A + B system before and after establishment of the quasiequilibrium. For the quasiequilibrium energy distribution of (1), the value of ε_b is fixed by K_0, the number of quasiparticles present in the system, and T, the gas temperature, through the equation $K_0 = n_a\varepsilon_a/P_a + n_b\varepsilon_b/P_b$. Equation (1) can be rewritten as $\varepsilon_a = f_{a,b}(T, \varepsilon_b)\varepsilon_b$, with

$$f_{a,b}(T, \varepsilon_b) = \varphi_{a,b}^{1/P_a} x_b^{P_b/P_a} \varepsilon_b^{-1}\left[1 - \varphi_{a,b}^{1/P_a} x_b^{P_b/P_a}\right]^{-1}; \tag{4}$$
$$\varphi_{a,b} = \exp(-\Delta\omega_{a,b}/T); \quad x_b = \varepsilon_b/(\varepsilon_b + 1),$$

and Eq. (2) then drawn to obtain the relation

$$\varepsilon_b = K_0(n_b/P_b + n_a/P_a f_{a,b}(T, \varepsilon_b))^{-1}. \tag{5}$$

The expression for the thermal energy effect accompanying nonresonant vibrational exchange follows from (5) as

$$E = \frac{n_b n_a}{P_a n_b + P_b n_a f_{a,b}} \Delta\omega_{a,b}\left[\varepsilon_a^0 - f_{a,b}\varepsilon_b^0\right]. \tag{6}$$

So far we have been concerned with the thermal effects accompanying establishment of a quasiequilibrium energy distribution in the A + B system over a time of the order of $\tau_{VV'}$, the gas temperature T and the total number of quasiparticles K_0 being assumed constant. We will now consider thermal exchange in a nonequilibrium system with translational degrees of freedom, variation in the gas temperature and the number of quanta in oscillators A and B being allowed. Let us suppose that T, ε_a, and ε_b each change under the effect of external factors, but so slowly that the energy distribution in the A + B system is at each instant essentially the quasiequilibrium distribution corresponding to T(t) and $K_0(t)$. The magnitude of the thermal effect in the gaseous mixture then proves to be independent of the rate of nonresonant vibrational exchange and can be calculated from Eqs. (3)-(6). With constant k_0 and varying gas temperature T(t), the fraction of the energy of the A + B system evolved in the brief time span (K_0 = const) as a result of nonresonant (V−V') exchange is, according to Eq. (6), equal to

$$\Delta E = -\Delta\omega_{a,b}\delta(t_*)[f_{a,b}(t+\Delta t) - f_{a,b}(t)]\varepsilon_b(t), \tag{7}$$

where

$$\delta = n_b n_a/(P_a n_b + P_b n_a f_{a,b}), \quad t < t_* < (t + \Delta t).$$

Here account has been taken of the fact that values of ε_a and ε_b satisfying the quasistationary distribution condition $\varepsilon_a(t) = f_{a,b}(t)\varepsilon_b(t)$, at time t, are initial values for time t + Δt, i.e., $\varepsilon_b(t) = \varepsilon_b^0(t + \Delta t)$; $\varepsilon_a(t) = \varepsilon_a^0(t + \Delta t)$.

It follows from (7) that the magnitude of the thermal effect $Q = \Delta E/\Delta t$ will be given by

$$Q = -C_V dT/dt, \quad C_V = +\delta\Delta\omega_{a,b}\varepsilon_b df_{a,b}/dT, \tag{8}$$

C_V being the heat capacity of the quasiequilibrium vibrational system.

The thermal effect Q accompanying nonresonant (V−V') vibrational exchange in a quasiequilibrium vibrational system with energy pumping into the A and B oscillators can be calculated in the same way:

$$Q = \delta\Delta\omega_{a,b}(R_a - f_{a,b}R_b), \tag{9}$$

$R_a = d\varepsilon_a/dt$, and $R_b = d\varepsilon_b/dt$ representing the respective rates of A and B oscillator excitation.

The expressions for ε_b and $f_{a,b}$ substituted into (8) and (9) from (4) and (5) contain T and K_0, the parameters of the quasiequilibrium distribution which may, themselves, be functions of the time. It is to be noted that $R_i \neq 0$ and $\sum_i R_i/P_i = 0$, under pumping, so that K_0, the number of quasiparticles in the A + B system, remains constant. An analytical solution for Eq. (5) has been obtained, but only for the simplest case of single-quantum exchange. In the low temperature region, where $T < \Delta\omega_{a,b}$, this solution leads to the following expressions for ε_b and $f_{a,b}$:

$$\varepsilon_b(K_0, T) \approx K_0/n_b[1 - \varphi_{a,b}n_a/(n_b + K_0(1 - \varphi_{a,b}))];$$
$$f_{a,b}(K_0, T) \approx \varphi_{a,b}n_b/(n_b + K_0(1 - \varphi_{a,b}) - \varphi_{a,b}n_a);$$
$$\varphi_{a,b} = \exp(-\Delta\omega_{a,b}/T) \ll 1, \quad \Delta\omega_{a,b} > 0.$$

Thermal energy transfer between the quasiequilibrium vibrational system and the translational degrees of freedom of the molecule resulting from single-quantum nonresonant (V−V') exchange leads to a heat capacity, C_V, equal to

$$C_V \approx \frac{K_0 n_a (n_b + K_0)}{[n_b + K_0 (1 - \varphi_{a,b})]^2} \left(\frac{\Delta\omega_{a,b}}{T}\right)^2 \varphi_{a,b}. \tag{10}$$

It is to be noted that the heat capacity of the quasiequilibrium system has a low-temperature maximum ($T \sim \Delta\omega_{a,b}/2$) the value of C_V at this point being fixed by K_0 and the mixture composition as given by n_a, n_b.

Let us briefly discuss the above equations and illustrate their significance by calculations on the thermal effects in certain typical systems. As is seen from Eq. (6), the nonresonant vibrational transfer $P_a \rightleftarrows P_b$ will be accompanied by an evolution or absorption of thermal energy only if there is a nonequilibrium amount of vibrational energy in the A + B system. The sign of the heat effect (E, Q are negative for cooling, and positive for heating) is determined by the predominating direction of vibrational energy pumping in the A + B oscillator system. If, as a result of nonresonant exchange, energy is pumped into the oscillator with the greater number of quasiparticle quanta, say, from B to A ($P_a\omega_a > P_b\omega_b$), which is possible only if $\varepsilon_a^0 < f_{a,b}\varepsilon_b^0$, the system will be forced to absorb thermal energy and $E < 0$. Thus cooling is assured when nonresonant vibrational exchange occurs in a nonequilibrium gas. On the other hand, if energy is pumped from the oscillator with the higher number of quasiparticle quanta, i.e., from A to B ($\varepsilon_a^0 > f_{a,b}\varepsilon_b^0$), a part of the vibrational energy will be converted into heat, the gas will be warmed, and $E > 0$.

Let us consider in detail the thermal effects resulting from nonresonant vibrational exchange under steady-pumping, a situation of practical importance in connection with the study of stationary, nonequilibrium vibrational systems. Let it be supposed that energy enters the A oscillators from below at a rate $R_a > 0$, that the B oscillators, nonresonantly bound to A, lose energy [through radiation, (V−T) processes] at a rate $R_b < 0$, and that a stationary energy balance is maintained in the system. Let it be further assumed that nonresonant vibrational exchange is rapid in comparison with excitation ($\tau_{VV} \cdot R_i/\varepsilon_i \ll 1$), and the vibrational energy distribution close to quasiequilibrium $\varepsilon_a \approx f_{a,b}(K_0, T)\,\varepsilon_b$. Here the magnitude of the thermal energy liberation or absorption in nonresonant exchange can be calculated through the Eq. (9). If the oscillator with the lower number of quanta is excited, while that with the higher number is quenched, the system will absorb thermal energy and $Q < 0$. In the opposite case, the system will liberate thermal energy and $Q > 0$.

Let us now carry out some calculations. By way of illustration, we will consider the heat effects associated with nonresonant vibrational exchange leading to the establishment of a quasiequilibrium energy distribution in the vibrational system $N_2(A)-CO(B)$, $\Delta\omega_{a,b} = 270$°K. If the N_2 molecule was initially excited, $\varepsilon_a^0 = 1$ ($\varepsilon_B^0 \ll 1$), then for a gaseous mixture with parameters $n_a = 0.9$, $n_b = 0.1$ at $T = 270$°K, $E \approx 120$°K. On the other hand, if the CO molecule was initially excited, $\varepsilon_B^0 = 1$, ($\varepsilon_a^0 \ll 1$), and (V−V') relaxation in a gaseous N_2-CO mixture with parameters $n_a = 0.5$, $n_b = 0.5$, should lead to cooling with $E \approx -30$°K. At a total pressure of 1 atm, the rate of thermal energy evolution or absorption due to nonresonant vibrational exchange, $E/\tau_{VV'}$, would in each respective case be

$$E/\tau_{VV'} \approx 1 \cdot 10^7 \text{ deg/sec}, \quad \tau_{VV'} \approx 1.2 \cdot 10^{-5} \text{ sec [4]};$$
$$E/\tau_{VV'} \approx -0.6 \cdot 10^7 \text{ deg/sec}, \quad \tau_{VV'} \approx 5 \cdot 10^{-6} \text{ sec [4]}.$$

It is also possible to estimate the heat capacity of the quasiequilibrium gaseous mixture of N_2 and CO with the parameters $n_a = 0.9$, $n_b = 0.1$. The value given by Eq. (10) is $C_V = 0.6$, at $k_0 = 1$ and $T = 200$°K.

It should be pointed out that these estimates apply only to systems in which the molecules can be modeled as harmonic oscillators. A more detailed analysis would be required if it were a matter of calculating the heat effects accompanying nonresonant (V−V') exchange in a system of anharmonic oscillators.

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