VIBRATIONAL RELAXATION OF DIATOMIC MOLECULES IN A NON-BOLTZMANN THERMOSTAT

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The action of resonance IR laser radiation on a molecular gas leads, at high-power absorption intensity, to a breakdown in the equilibrium (Boltzmann) energy distribution in the internal degrees of freedom [1]. Under realistic conditions, molecular gases usually are (due to small amounts of impurities or isotopic components) multicomponent systems. In this case resonance IR laser radiation (or other methods of selective action), disturbing the distribution function of the primary gas, does not interact directly with impurities. The problem thus arises of determining the distribution function of the impurity gas interacting with the nonequilibrium (non-Boltzmann) thermostat. The present paper, devoted to the solution of this problem, treats the distribution function of harmonic oscillators A, consisting of a small amount of impurities in a system of harmonic oscillators B with given nonequilibrium distribution functions of vibrational energy. The behavior of a system in a nonequilibrium thermostat was first considered in [2, 3] where, as well as in [4, 5], it was shown that in a non-Maxwellian thermostat with a small amount of harmonic oscillator impurities, a Boltzmann distribution in harmonic oscillator vibrational energies is established under stationary conditions, with a temperature differing from the gas-kinetic temperature of the thermostat, defined in terms of the mean-square velocity. The behavior of a small amount of impurities (heavy monoatomic particles and harmonic oscillators) in a non-Maxwellian thermostat of a light gas was further investigated in [6-8]. Unlike the papers mentioned, the present one considers the behavior of a small amount of harmonic oscillator impurities in a thermostat with a Maxwellian velocity distribution and with a nonequilibrium (non-Boltzmann) distribution in vibrational energies.

1. Basic Equations. Stationary Solution. The kinetic equations describing the process of vibrational relaxation of a small amount of diatomic molecule impurities A in a thermostat of diatomic molecules B are [1]

$$\frac{dx_n}{dt} = Z_{AB} \sum_{l,m,s,} \left(Q_{mn}^{sl} x_m y_s - Q_{nm}^{ls} x_n y_l \right), \tag{1.1}$$

where x_n is the number of molecules A at the n-th vibrational level per unit volume $\left(\sum\limits_{n=0} x_n = N_A\right)$ and y_n is the number of molecules B at the n-th vibrational level $\left(\sum\limits_{n=0} y_n = N_B\right)$. The functions y_n are assumed known, Z_{AB} is the number of collisions of one A molecule with B molecules per unit time for $N_B = 1$, and Q_{mn}^{sl} is the vibrational exchange probability for one collision of A and B molecules, as a result of which the A and B molecules pass from states m and s into states n and l, respectively.

Only collisions of A and B molecules are taken into account in Eq. (1.1), while collisions of A molecules with each other are neglected.

Assuming that in collisions of A and B molecules q B quanta are converted into p A quanta, for the harmonic oscillator model, system (1.1) decomposes into a system of p uncoupled equations

$$\frac{dx_{r+pl}}{dt} = Z_{AB} \frac{Q_{p0}}{p!} \left\{ \frac{[r+p(l+1)]!}{(r+pl)!} x_{r+p(l+1)} - \right.$$
$$\left. - \left[\frac{[r+p(l+1)]!}{(r+pl)!} \frac{Q_{0p}}{Q_{p0}} + \frac{(r+pl)!}{[r+p(l-1)]!} \right] x_{r+pl} + \frac{(r+pl)!}{[r+p(l-1)]!} \frac{Q_{0p}}{Q_{p0}} x_{r+p(l-1)} \right\}, \tag{1.2}$$
$$r = 0, 1, 2, \ldots, p-1, \quad l = 0, 1, 2, \ldots$$

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In deriving (1.2) from (1.1), it was assumed that

$$Q_{n+p,n}^{s,s+q} \equiv \frac{Q_{n+p,n}^{s,s+q}}{Q_{p0}^{0q}} Q_{p0}^{0q} = \frac{\langle \psi_s^B | y^q | \psi_{s+q}^B \rangle^2 \langle \psi_{n+p}^A | x^p | \psi_n^A \rangle^2}{\langle \psi_0^B | y^q | \psi_q^B \rangle^2 \langle \psi_p^A | x^p | \psi_0^A \rangle^2} Q_{p0}^{0q}, \tag{1.3}$$

where $\psi_s^B(y)$ and $\psi_n^A(x)$ are wave functions of harmonic oscillators B and A in states s and n, respectively.

Substituting in (1.3) the well-known values of the matrix elements [9], we obtain

$$Q_{n+p,n}^{s,s+q} = \frac{(s+q)!}{s!\,q!} \frac{(n+p)!}{n!\,p!} Q_{p0}^{0q}. \tag{1.4}$$

In Eqs. (1.2)

$$Q_{p0} = \frac{Q_{p0}^{0q}}{q!} \sum_{s=0} \frac{(s+q)!}{s!} y_s; \tag{1.5}$$

$$Q_{0p} = \frac{Q_{0p}^{q0}}{q!} \sum_{s=q} \frac{s!}{(s-q)!} y_s. \tag{1.6}$$

The decoupling of system (1.1) and its transformation to the system of p independent equations (1.2) for multiquantum (p-quantum) transitions correspond to the physically obvious circumstance that p-quantum transitions do not mix the states m and n, whose difference $|m-n|$ is not a multiple of p. Multiquantum transitions by p quanta occur between levels m and n satisfying the condition $|m-n| = p$, i.e., they couple states with subscripts $r + lp$, where r is fixed ($r = 0, 1, 2, \ldots, p-1$), and $l = 0, 1, 2, \ldots$.

The system of equations (1.2) has an interesting feature consisting in the fact that under stationary conditions its solutions are the Boltzmann distribution functions

$$x_{r+lp} = C_r e^{-\frac{\varepsilon_{r+lp}^A}{kT_v^A}}$$

with a temperature determined by the relation

$$p \frac{\hbar\omega_A}{kT_v^A} = \ln \frac{Q_{p0}}{Q_{0p}} \tag{1.7}$$

where ω_A is the frequency of oscillator A.

The normalization constants C_r are determined from the conservation conditions of the number of particles

$$\sum_{l=0} x_{r+lp} = \sum_{l=0} x_{r+lp}(0).$$

For $p = 1$ (single-quantum transitions in component A) the natural normalization coefficient is $C_0 = N_A[1 - \exp(-\hbar\omega_A/kT_v^A)]$. Besides, for $p = 1$ system (1.2) possesses the property of canonical invariance, i.e., in the relaxation process it retains the Boltzmann shape of the distribution function [1]. If in Eq. (1.1) one takes into account single-quantum exchange of vibrational energy in collisions of A molecules with each other, this leads to all C_r being equal to each other.

Thus, in a harmonic oscillator system being a small impurity in a non-Boltzmann thermostat of harmonic oscillators of a different kind, a Boltzmann distribution is established for all levels (in case of single-quantum transitions $p = 1$) or for a group of levels (in case of multiquantum transitions $p \neq 1$) with a vibrational temperature T_v^A, determined by relation (1.7).

In the case of a Maxwellian velocity distribution, the energy exchange probabilities are related by the principle of detailed balance:

$$Q_{0p}^{q0} e^{-q\frac{\hbar\omega_B}{kT}} = Q_{p0}^{0q} e^{-p\frac{\hbar\omega_A}{kT}}, \tag{1.8}$$

where T is the temperature of the translational degrees of freedom (the gas temperature) and ω_B is the frequency of a B oscillator.

Taking into account (1.8), relation (1.7) acquires the form

$$p\frac{\hbar\omega_A}{kT_v^A} - q\frac{\hbar\omega_B}{kT_v^{B*}} = \frac{p\hbar\omega_A - q\hbar\omega_B}{kT}, \tag{1.9}$$

where the effective vibrational temperature T_V^{B*} is determined as follows:

$$q\frac{\hbar\omega_B}{kT_v^{B*}} = \ln\frac{\sum\limits_{n=0}\frac{(n+q)!}{n!}y_n}{\sum\limits_{n=q}\frac{n!}{(n-q)!}y_n}. \tag{1.10}$$

For a Boltzmann thermostat with vibrational temperature $T_V^B(y_n = y_0\exp(-\varepsilon_n^B/kT_V^B))$, the following obvious equality is satisfied

$$T_v^{B*} = T_v^B,$$

and Eq. (1.9) reduces to the well-known Treanor relation [1], relating T_V^A, T_V^B, and T. Thus, equality (1.9) can be considered as a generalization of the Treanor relation to the case of a non-Boltzmann thermostat.

For nearly resonance vibrational exchange

$$q\hbar\omega_B = (1+\gamma)p\hbar\omega_A, \quad |\gamma| < 1 \tag{1.11}$$

relation (1.9) can be written in the form

$$T_v^A = \frac{1}{1+\gamma-\gamma T_v^{B*}/T}T_v^{B*}. \tag{1.12}$$

A peculiar feature of (1.12) is that for $\gamma > 0$ and $T_V^{B*} \sim T/\gamma$ the vibrational temperature of a small impurity increases without bound. In reality this effect is restricted by vibrational–translational energy exchange and by molecular anharmonicity.

The existence of a Boltzmann distribution of a small impurity in a nonequilibrium thermostat makes it possible to determine experimentally the characteristics of a nonequilibrium thermostat by measuring only the impurity vibrational temperature.

2. Effective Vibrational Temperature of a Non-Boltzmann Thermostat. As seen from relation (1.10), the effective vibrational temperature of a nonequilibrium thermostat depends not only on the nonequilibrium distribution function of the thermostat, but also on the specific shape of the resonance energy exchange, as determined from (1.11). For q = 1 the temperature T_V^{B*} is determined by the average supply of vibrational quanta per molecule by the equation

$$\frac{\hbar\omega_B}{kT_v^{B*}} = \ln\frac{1+\alpha}{\alpha},$$

where $\alpha = \frac{1}{N_B}\sum\limits_{n=0} ny_n$.

For q > 1 the temperature T_V^{B*} is no longer expressed in terms of α, which makes it possible, in principle, to change T_V^{B*} without essentially changing the average vibrational energy.

We investigate now how the specific shape of the nonequilibrium distribution over vibrational levels in the thermostat y_n affects the temperature T_V^{B*}. The temperature T_V^{B*} is determined by relation (1.10), having two peculiar features. First, the thermostat molecules in the first q levels do not participate in the activation of A molecules, since their energy is insufficient. These molecules, however, do participate in the deactivation process of A molecules (formally, this is expressed by the fact that the summation in Eqs. (1.5), (1.6), and consequently (1.10), starts with different values of vibrational levels).

The second important feature of (1.10) (see also Eq. (1.8)) is that the exchange probability $Q_{n\pm p,n}^{s,s\pm q}$ defined by (1.4) increases with s approximately as s^q, which enhances the active role of vibrationally excited molecules of the thermostat having a large reserve of vibrational energy in thermal exchange with the system under investigation. These two features cause two opposite effects: lowering and enhancement of T_V^{B*} with respect to the kinetic vibrational temperature of the nonequilibrium thermostat $\bar{T}_n^B$, defined by the relation

$$\frac{\hbar\omega_B}{k\bar{T}_v^B} = \ln\frac{1+\alpha}{\alpha}, \tag{2.1}$$

for a gradual enhancement of the average vibrational energy reserve of the thermostat α.

We illustrate this discussion on examples. We assume that there exists a Boltzmann distribution in the nonequilibrium thermostat, enriched by a small amount of vibrationally excited molecules:

$$y_n = (1-x)\,(1-e^{-\vartheta})\,e^{-\vartheta n} + x\delta_{nn_0}, \tag{2.2}$$

where $\vartheta = \frac{\hbar\omega_B}{kT_v^B}$, and $x \ll 1$. In this case we have for $n_0 \geq q$

$$q\frac{\hbar\omega_B}{kT_x^{B*}} = \ln\frac{q!\,(1-x)\,(1+\alpha_0)^q + x\frac{(n_0+q)!}{n_0!}}{q!\,(1-x)\,\alpha_0^q + x\frac{n_0!}{(n_0-q)!}},$$

where $\alpha_0 = (e^{\vartheta}-1)^{-1}$, and the summation in (1.10) for y_n of form (2.2) is carried out by means of the obvious relation

$$\sum_{n=0}^{\infty}\frac{(n+q)!}{n!}(1-e^{-\vartheta})\,e^{-\vartheta n} = (1-e^{-\vartheta})\frac{d^q}{dz^q}\sum_{n=0}^{\infty} z^{n+q}\Bigg|_{z=e^{-\vartheta}},$$

where $\sum_{n=0}^{\infty} z^{n+q} = z^q\frac{1}{1-z}$. If one chooses x and n_0 in the manner

$$(1-x)\,(1+\alpha_0)^q \ll x(n_0+q)!/n_0!,$$

$$(1-x)\,\alpha_0^q \ll xn_0!\,/\,(n_0-q)!,$$

T_v^{B*} is completely determined by the small impurity of vibrationally excited molecules

$$q\frac{\hbar\omega_B}{kT_v^{B*}} = \ln\frac{(n_0+q)!}{n_0!}\,\frac{(n_0-q)!}{n_0!},$$

and $\overline{T}_v^B$ differs little from the vibrational temperature of the unperturbed thermostat T_v^B, while T_v^{B*} can exceed $\overline{T}_v^B$ significantly.

Consider now an example in which the second case is realized, lowering of T_v^{B*} with respect to $\overline{T}_v^B$ during heating of the thermostat.

In equilibrium let almost all molecules be at the zeroth level, i.e., $\alpha \ll 1$. If we now transform them to level $q-1$, the energy flow from system A to the thermostat B is enhanced, since the transition probabilities increase with the level subscript. In this case, however, the opposite energy flow from the thermostat B into system A does not change, since there is no change in the population of levels participating in energy transfer by system A. This leads to lowering of T_v^{B*}, though the reserve of quanta and consequently the kinetic vibrational temperature $\overline{T}_v^B$ increase.

We estimate this effect. Under equilibrium conditions

$$T_v^{B*} = T_v^B,$$

where $q\frac{\hbar\omega_B}{kT_v^B} = \ln\frac{(1+\alpha_0)^q}{\alpha_0^q}$. After transforming the molecules of B from the zeroth level to level $q-1$, the effective temperature T_v^{B*} is approximately determined by the equation

$$q\frac{\hbar\omega_B}{kT_v^{B*}} = \ln\frac{(2q-1)!}{(q-1)!\,q!\,\alpha_0^q},$$

with

$$T_v^B - T_v^{B*} = \frac{\hbar\omega_B}{k}\,\frac{\ln\frac{(2q-1)!}{q!\,(q-1)!\,(1+\alpha_0)^q}}{\ln\frac{1+\alpha_0}{\alpha_0}\,\ln\frac{(2q-1)!}{q!\,(q-1)!\,\alpha_0^q}}.$$

The kinetic vibrational temperature $\overline{T}_v^B$ after molecular excitation to level $q-1$ is determined by relation (2.1) with $\alpha = q-1$, i.e.,

$$\frac{\hbar\omega_B}{k\overline{T}_v^B} = \ln\frac{q}{q-1},$$

where

$$\frac{\overline{T_v^B}}{T_v^B}=\frac{\ln\dfrac{1+\alpha_0}{\alpha_0}}{\ln\dfrac{q}{q-1}}\geqq 1.$$

Numerical estimates for $\alpha_0 \sim 10^{-1}$, $T_V^B \approx 420$, and $q=3$ give $T_V^B-T_V^{B*} \sim 90K$, $\overline{T}_V^B/T_V^B \sim 6$. Thus, the significant increase in the average vibrational energy ($\alpha/\alpha_0 \sim 20$) is accompanied in the given case by a decrease in T_V^{B*}.

The nonequilibrium distributions considered so far are mostly of an illustrative nature, since they cannot be easily realized in the stationary regime. Realistic distributions formed under the action of electron and laser pumping have more complicated shapes. It can be assumed, however, that in the simplest case of sufficiently intense laser pumping, occurring by the scheme of successive single-step excitations $0 \rightarrow 1 \rightarrow 2 \rightarrow \ldots \rightarrow l$, the first $l+1$ levels are almost identically populated, with exponential decay at the higher levels, starting with level l [1]. In this connection, we consider a distribution of the form

$$y_n=\begin{cases}A, & n\leqslant l,\\ A\exp[-\vartheta(n-l)], & n\geqslant l\end{cases}\tag{2.3}$$

$$A=\frac{1-\exp(-\vartheta)}{1+[1-\exp(-\vartheta)]\,l}.$$

At sufficiently low temperatures ($\vartheta \gg 1$) the exponential tail in the distribution (2.3) can be neglected. In this approximation the distribution (2.3) corresponds to the kinetic vibrational temperature

$$\overline{T_v^B}=\frac{\hbar\omega_B}{k}\left[\ln\left(1+\frac{2}{l}\right)\right]^{-1}.\tag{2.4}$$

Expression (2.4) is obtained from (2.1) by substituting $\alpha = l/2$.

According to (1.10) the effective vibrational temperature of the thermostat equals

$$T_v^{B*}=\frac{\hbar\omega_B}{k}\left[\frac{1}{q}\ln\frac{\sum\limits_{n=0}^{l}\dfrac{(n+q)!}{n!}}{\sum\limits_{n=0}^{l-q}\dfrac{(n+q)!}{n!}}\right]^{-1}.\tag{2.5}$$

Direct comparison of (2.4) and (2.5) shows that for $q=2$ and 3

$$T_v^{B*}<\overline{T_v^B}.\tag{2.6}$$

Obviously, (2.6) is valid at any q ($q \leq l$) for distributions differing little from (2.3), i.e., for distributions formed by laser or electron pumping.

A noticeable deviation from T_V^{B*} to $\overline{T}_V^B$ can be expected for distributions of type (2.2), which are characteristic of systems with vibrationally excited molecular sources [1].

Analysis of the stationary states in a system of harmonic oscillators placed in a non-Boltzmann thermostat of harmonic oscillators of a different kind leads to the following basic results:

1. A Boltzmann distribution with temperature T_V^A, determined by relation (1.11), is established in the harmonic oscillator system. This is a generalization of the well-known Treanor relation to the case of a nonequilibrium thermostat.

2. The temperature T_V^A depends on integral characteristics of the thermostat T_V^{B*}, called the effective vibrational temperature of the thermostat. The latter differs from the kinetic vibrational temperature of the thermostat $\overline{T}_V^B$, which is determined in terms of the average reserve of thermostat vibrational energy.

3. The temperature T_V^{B*} is sensitively dependent on the nature of the vibrational energy distribution in the thermostat and on the method of vibrational energy exchange between the thermostat molecules, and can differ appreciably from the kinetic temperature $\overline{T}_V^B$. This opens up the possibility of significantly changing T_V^A by a small perturbation of the distribution function of the thermostat vibrational energy, which enables one, e.g., to control chemical or other processes in the system.

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