DISTRIBUTION OF RATE OF VIBRATIONAL RELAXATION RELATIVE TO VIBRATIONAL LEVELS AND DISSOCIATION OF DIATOMIC MOLECULES UNDER UNBALANCED CONDITIONS

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INTRODUCTION

The influence of vibrational anharmonicity on the distribution of molecules under unbalanced conditions has been studied in a number of papers [1, 2-4]. Nonequilibrium conditions are due to an increase in the vibrational energy resources of the molecules beyond the equilibrium value corresponding to the gas temperature. The basic details of the distribution have been clarified [5, 6] for steady-state conditions. A Treanor [7] distribution is realized in the lower group of levels. A group of levels whose concentration varies quite slowly is next and the distribution has the form of a plateau. Quantum exchange processes predominate in this group of levels as well as in the region of the Treanor distribution. Vibrational−translational exchange becomes substantial in the upper part of the vibrational levels. This induces a drop in the populations and, in the end, leads to a Boltzmann distribution. All three characteristic regions of the distribution are realized only under highly nonequilibrium conditions (a criterion under which the three regions exist was obtained in [3, 4]). Distribution relative to levels in the Treanor region and on a plateau has been analytically described in [2], in which a diffusion approximation was used to obtain the corresponding equation. A plateau region coinciding with previous results [2] also in passing from a plateau to a Boltzmann distribution has been found [3, 4] using this approximation. However, the approximation and the use of a number of assumptions in [3, 4] do not allow a sufficiently precise description of the entire transition region. In this work, using a system of balance equations for particles on the vibrational levels, an approximate analytic equation for the distribution in the transition region is obtained for steady-state conditions. The case of strong nonequilibrium conditions in a single-component gas of diatomic nonradiating molecules is considered. The distribution corresponding to the analytic equation agrees with results of a numerical calculation. A relaxation equation for the number of vibrational quanta and the rate constant for nonequilibrium dissociation are also obtained.

§ 1. A Morse oscillator (energy of k-th level, $E_k = \omega k - \lambda k^2$) will be taken as the model of a molecule. Vibrational relaxation of nonradiating molecules is described by the system of balance equations

$$\begin{gathered}\frac{dN_n}{dt} = j_{n+1} - j_n,\\ j_{n+1} = P^*_{n+1,n} N_{n+1} - P^*_{n,n+1} N_n,\end{gathered} \tag{1.1}$$

where N_n is the concentration of molecules on the n-th vibrational level, $P^*_{n+1,\,n}$ is the probability of the transition n + 1 → n within a unit of time and is determined by vibrational−translational and vibrational−vibrational exchanges (V−T and V−V processes, respectively):

$$P^*_{n+1,n} = P_{n+1,n} + \frac{1}{N_{\text{м}}} \sum_m Q^{m,m+1}_{n+1,n} N_m, \tag{1.2}$$

where $N_{\text{м}} = \sum\limits_n N_n$ is the concentration of molecules. The probabilities of V−T and V−V processes can be given in the form [1]

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$$P_{n+1,n} = (n+1) P_{10}\, e^{\delta n},\; Q_{n+1,n}^{m,m+1} = (n+1)(m+1) Q_{10}^{01} e^{-\delta|n-m| - \frac{\lambda}{T}\{n-m+|n-m|\}}, \tag{1.3}$$

where δ depends on gas temperature T and the parameters of the molecule.

The time derivatives in Eqs. (1.1) vanish under the steady-state conditions and Eqs. (1.1) can be rewritten, without taking into account dissociation ($j_n = 0$), in the form [1]

$$N_n = N_k \prod_{i=k}^{n-1} \varphi_i,\; \varphi_i = \frac{P^*_{i,i+1}}{P^*_{i+1,i}}. \tag{1.4}$$

The system of equations (1.4) for populations is nonlinear and a method of iterations can be one possible method for its solution. We will take the distribution, obtained without explicitly taking into account V–T processes in [2], as the zero-order approximation,

$$N_n^{(0)} = \begin{cases} N_0^{(0)} \exp\left\{-n\left(\frac{E_1}{T_1} - \frac{\lambda(n-1)}{T}\right)\right\}, & n \leqslant n^*, \\ N_{n^*}^{(0)} \frac{n^*}{n} e^{-1/2}, & n > n^*. \end{cases} \tag{1.5}$$

Here $n^* = (E_1 T/2\lambda T_1) + 1/2$ is the number of the level corresponding to the minimum Treanor distribution with population temperature of the first level T_1. The distribution (1.5) describes correctly only the Treanor distribution and plateau regions.

In the case of a strong deviation from equilibrium V–V exchange in the upper group of levels ($n > n^*$) occurs preferably with neighbors and the contribution of V–T processes to $P^*_{n+1,n}$ becomes significant only when $n - n^* \gg 1$. These two conditions lead to the fact that V–T processes will not vary the distribution when $n \leq n^*$, so that the Treanor distribution will remain invariant in the iterations. On the other hand, these conditions make it possible to approximate the exchange sums in Eq. (1.2),

$$P^*_{n,n+1} = P_{n,n+1} + (n+1) S,\; P^*_{n+1,n} = P_{n+1,n} + \frac{(n+1)^2}{n} S, \tag{1.6}$$

$$S = Q_{01}^{10} \frac{n^* N_{n^*}^{(0)} e^{-1/2}}{N_{\text{м}}} F,\; F = (e^{\alpha} - 1)^{-1} + (e^{\delta} - 1)^{-1},\; \alpha = \delta + \frac{2\lambda}{T}.$$

Using these probabilities, we calculate the ratio φ_n of populations of the two next levels to a first approximation,

$$\varphi_n = \frac{R e^{\alpha n} + CF}{e^{\delta n} + CF \frac{n+1}{n}},\; R = e^{-\frac{E_1}{T}},\; C = \frac{Q_{01}^{10} n^* N_{n^*}^{(0)} e^{-1/2}}{P_{10} N_{\text{м}}}. \tag{1.7}$$

Let us note that we obtain a distribution coinciding with Eq. (1.5) if we disregard the contribution of V–T processes in Eqs. (1.6) and if we substitute Eqs. (1.7) in (1.4).

Equation (1.7) is rather complex for calculations, so that we will simplify it. According to Eqs. (1.5), there exists a drop in population in the region of the plateau proportional to 1/n. Moreover, a decrease in the populations of the higher vibrational levels occurs as a consequence of an increase in the role of V–T processes. We may find using Eqs. (1.7) the level r above which the drop due to V–T processes is most substantial. This level is determined by the equation

$$e^{\delta r} = \frac{1}{r} CF, \tag{1.8}$$

where in the region in which the slope is determined by V–T processes ($n > r$), $(n+1)/n \simeq 1$.

Since $r \gg 1$, the role of V–T processes is insignificant when $n < r$ as follows from Eq. (1.8), and the distribution practically coincides with Eqs. (1.5) to a first approximation. When $n > r$, we have

$$N_n^{(1)} = N_r^{(0)} \prod_{i=r}^{n-1} \varphi_i = N_r^{(0)} \exp\left\{\sum_{i=r}^{n-1} \ln \varphi_i\right\} \simeq N_r^{(0)} \exp\left\{\int_r^{n-1} di \ln \varphi_i + \frac{1}{2}(\ln \varphi_r + \ln \varphi_{n-1})\right\}. \tag{1.9}$$

We note that the replacement of the sum in Eq. (1.8) by the integral is permitted, since $\ln \varphi_i$ slowly varies from level to level. The integral in Eq. (1.9) is calculated approximately by expanding the logarithm into a series and retaining two terms in the decomposition (the error is insignificant). We then obtain when $r \leq n \leq p$

$$N_n^{(1)} = N_r^{(0)} \exp\left\{-\left(\frac{1}{\delta}+\frac{1}{2}\right)\left[e^{(n-1-p)\delta} - e^{(r-1-p)\delta}\right]\right\}, \tag{1.10}$$

$$p = \frac{\ln(CF)}{\delta} = r + \frac{1}{\delta}\ln r$$

(p is a parameter that arises upon integration). We may obtain the distribution to a first approximation also when $n > p$, but it will not be subsequently required and is therefore not presented. Obviously, the distribution to a first approximation is an upper bound, since the exchange sums used in calculating Eq. (1.9) are overstated [they are calculated using the slowly decreasing (for large n) distribution (1.5)].

It is difficult to calculate the populations at all vibrational levels using subsequent iteration in an analytic form. We will therefore use an approximation that allows us to satisfactorily describe the distribution with respect to levels. We note that vibrational exchange on the plateau chiefly occurs between neighboring levels. A drop in the distribution (1.10) occurs in the transition region. This leads (unlike the case of the plateau) to the fact that the contribution of neighboring levels is small and that exchange occurs preferably with distant levels having greater population at sufficiently high level numbers. We may prove, using the probability (1.3), that a transition from short-range exchange to long-range exchange occurs in the region of the level s satisfying the condition

$$\frac{N_{s+1}}{N_s} = e^{-\alpha}. \tag{1.11}$$

We find, proceeding on the basis of the distribution (1.10), that

$$s = p + \frac{1}{\delta}\ln\left[\frac{2\alpha\delta}{(2+\delta)(1-e^{-\delta})}\right].$$

We find that s is less than p in most cases of interest, which corresponds to the inequality $2\alpha\delta < (2+\delta)(1-e^{-\delta})$. This condition leads to constraints on gas temperature with the given parameters (for N_2, for example, $s < p$ when $T > 0.02$ eV).

Direct calculation of the distribution to a second approximation is difficult to carry out when $n < s$. However, we may expect that even the first iteration in this region satisfactorily describes the distribution. This is due to the fact that when $n < s$, the contribution of V–T processes to $P^*_{n+1,\,n}$ is not great, so that some decrease in the exchange sums in this region will not noticeably influence the distribution as we pass from the zero-order approximation to the first approximation. Therefore, the populations in the second approximation will be found only when $n > s$. The contribution of levels with numbers less than s will be taken into account in the exchange sums of Eqs. (1.2). We find that

$$\varphi_i = \frac{Re^{\alpha i} + Ae^{-\delta i}}{e^{\delta i} + Be^{-\alpha i}},$$

$$A = Ce^{\delta p}\frac{2}{2+\delta}\left[1 - \exp\left(-\frac{\alpha}{e^{\delta}-1}\right)\right],$$

$$B = Ce^{\alpha(p+1)}\frac{1}{\delta}\left(\frac{2\delta}{2+\delta}\right)^{\alpha/\delta}\gamma\left(\frac{\alpha}{\delta}, \frac{\alpha e^{-\delta}}{e^{\delta}-1}\right),$$

where $\gamma(a, t)$ is an incomplete gamma function,† by replacing the exchange sums with distribution (1.10) by integrals and taking into account the fact that $s - r \ll s$. We find the populations in the second approximation using Eq. (1.4).

As before, replacing the sum by an integral, which is calculated approximately, we obtain

$$N_{n+1}^{(2)} = N_s^{(1)}\frac{N_{n+1}^{B}}{N_s^{B}}\exp\left\{-\frac{1}{\theta}e^{\theta(s-q_2)} + \chi_{n+1}\right\}, \tag{1.12}$$

$$\chi_{n+1} = \frac{\theta}{2}(z-s+1)(2q_2-s-z) + \frac{1}{\theta}\left[1 - e^{\theta(q_1-s)} + e^{\theta(q_2-n)} + \frac{n-q_2}{|n-q_2|}\left(1-e^{-\theta|n-q_2|}\right)\right], \quad q_1 < s,$$

$$\chi_{n+1} = \frac{\theta}{2}[(q_2-q_1)(q_1+q_2+1-2s) + (q_2-x)(1+n+y-q_1-q_2)]$$
$$+ \frac{1}{\theta}\left[e^{\theta(s-q_1)} + \frac{n-q_2}{|n-q_2|}\left(1-e^{-\theta|n-q_2|}\right) - \frac{n-q_1}{|n-q_1|}\left(1-e^{-\theta(n-q_1)}\right)\right],$$
$$q_1 > s,$$

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†The curve $\gamma(a, x)$ is presented in [8].

$$y = \min\{n, q_1\},\ z = \min\{n, q_2\},\ \theta = \alpha + \delta,$$

$$q_1 = \frac{1}{\theta}\ln B,\ q_2 = \frac{1}{\theta}\ln\left(\frac{A}{R}\right),\ N_k^{\mathrm{B}} = N_{M}e^{-E_k/T},\ x = \begin{cases} q_1, & n \leqslant q_1, \\ n, & q_1 < n \leqslant q_2. \\ q_2, & n > q_2, \end{cases}$$

The distribution is given by Eq. (1.5) in the region $0 \le n \le r$ and by Eq. (1.10) in the region $r \le n \le s$. Thus our distribution describes all three characteristic regions and becomes a Boltzmann distribution at levels with numbers n, such that $n - q_2 \gg 1$.

A number of assumptions were made in calculating the distribution, since it is quite difficult to estimate the accuracy of our calculations. A comparison of the distribution found above to results of numerical calculations can thus be a fundamental criterion. Unfortunately, no numerical calculations of a stationary distribution under strong nonequilibrium conditions exist in the literature for nonradiating molecules.

Thus numerical calculations of stationary distributions were carried out for the system of equations (1.1)-(1.3). The parameters determining the probabilities (1.3) correspond to a molecule of N_2. The magnitudes λ and δ were found from the equations $\lambda = \omega^2/4D$ (D is the dissociation energy of N_2) and $\delta = 0.0765\ T^{-1/2}$ (T, eV) [1]. Figure 1 depicts calculations of the distributions for the two variants: curves 1, T = 0.03 eV and $T_1 = 0.252$ eV; curves 2, T = 0.1 eV and $T_1 = 0.406$ eV (curves 2 are shifted for convenience three orders of magnitude below the y axis). The unbroken curves correspond to an exact numerical calculation, while the dashed-dot curves correspond to a calculation using the equations presented in this work.† Satisfactory agreement is obtained.

A calculation of the distribution using previously obtained [3, 4] equations is depicted here for the first variant of the dashed-dot curve. It is evident by comparing the numerical calculations and the previous [3, 4] results that the transition region in the latter case is shifted towards highly excited levels. This divergence is possibly due to the calculation of the constant, on which the distribution depended in [3, 4] and which was selected by comparing exact numerical calculations carried out for carbon monoxide and a carbon monoxide–helium mixture.

§ 2. We will obtain a relaxation equation for the quantum number $Q = \sum\limits_k kN_k/N_M$. using the distribution with respect to vibrational levels (1.5), (1.10), and (1.12). Neglecting excitation processes under these conditions, we find that

$$\frac{dQ}{dt} = -\frac{1}{N_M}\sum_n P_{n+1,n}N_{n+1}, \tag{2.1}$$

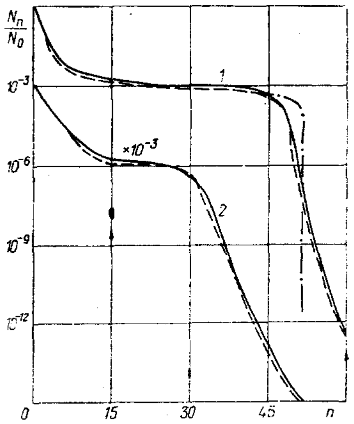

Fig. 1

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† Results presented in Fig. 1 of analytic calculations in the region $n \le n^*$ were obtained by multiplying Eq. (1.5) by $\exp\{-n/2n^*\}$ in order to match the distribution when $n > n^*$.

while we may limit ourselves in summing with respect to n as a consequence of Eq. (1.11), to levels with number $n = s - 1$. The influence of the Treanor region on relaxation can be ignored under strong nonequilibrium conditions. We then write the rate of variation of the quantum number in the form

$$\frac{dQ}{dt} = -\frac{n^* N_{n^*}^{(0)} e^{-1/2}}{N_M} P_{10} e^{r\delta} \left\{ \frac{1 - e^{-\delta(r - n^*)}}{\delta e^{\delta}} + \frac{2r}{2+\delta} \exp\left(\frac{e^{-\delta}}{r} \frac{2+\delta}{2\delta}\right) \left[1 - \exp\left(-\frac{\alpha}{e^{\delta} - 1}\right)\right] \right\}, \tag{2.2}$$

by substituting the plateau distribution (1.5) in Eq. (2.1) and using Eq. (1.10) for the transition region up to the level $s - 1$.

An analogous equation was obtained in [3, 4]. We note that dQ/dt calculated in accordance with [3, 4] increases the corresponding value given by Eq. (2.2) by roughly a factor of 10 under the conditions of the first variant.

§ 3. Let us obtain an equation for the nonequilibrium dissociation constant for diatomic molecules. The distribution in the case of equilibrium and nonequilibrium dissociations is identical in a sufficiently large group of upper levels, i.e., it is a Boltzmann distribution distorted only near the continuum. We may therefore assume, in analogy with [3], that the rate constant of nonequilibrium and equilibrium dissociations are related in the same way as the corresponding populations near the dissociation threshold, i.e.,

$$K_d(T, T_1) = K_d(T) \frac{N_n}{N_n^B}, \quad n - q_2 \gg 1. \tag{3.1}$$

Substituting the value of N_n when $n - q_2 \gg 1$, in Eq. (3.1), we obtain the nonequilibrium dissociation constant,

$$K_d(T, T_1) = K_d(T) \frac{n^*}{r} \left(1 - e^{-E_1/T_1}\right) \exp\left\{ \frac{E_s}{T} - \frac{\lambda}{T} (n^*)^2 - \frac{1}{2} - \frac{\alpha}{e^{\delta} - 1} + \frac{2+\delta}{2\delta r} e^{-\delta} \right.$$

$$\left. + \frac{\theta}{2} (q_2 - v)(q_2 + v - 2s + 1) + \frac{1}{\theta} \left[1 - e^{-\theta(q_2 - s)} + \frac{s - q_1}{|s - q_1|} \left(1 - e^{-\theta|s - q_1|}\right) \right] \right\}, \quad v = \max\{s, q_1\}.$$

In conclusion, we note that the results of this work refer only to the case of a single-component gas of diatomic molecules lacking a dipole moment. An investigation of the vibrational distribution of molecules having a dipole moment or constituting an addition to a neutral gas leads to a dependence of transition probabilities that differs from Eq. (1.3). This leads to substantial difficulties in considering the problem by the method set forth.

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