VIBRATIONAL DISTRIBUTION OF MULTIATOM MOLECULES

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UDC 539.196.5

1. Introduction

A lot of attention has been devoted in recent years to the theory of quasi-steady-state vibrational distributions of diatomic molecules produced by vibrational V–V exchange [1-7]. Quasi-steady-state distributions are interesting in that their shape is determined to a significant extent by the anharmonicity of the vibrations of the molecules and depends far less on the cross sections of elementary processes. Under conditions in which V–V exchange dominates over a significantly large area, the vibrational distribution consists of a more rapidly decreasing Treanor section and a slowly decaying plateau. The theory of the distribution from the plateau is given in [4]. The formation of the plateau in a vibrational distribution leads, in particular, to the possibility of generation in a CO-laser [7]. Relaxation of the distribution from the plateau, which is associated with quenching in the area in which V–V processes are not already dominant, was discussed in [6].

A model of isolated modes in which the distributions are established independently as a result of V–V exchange within modes [2] has been adopted in the vibrational kinetics of multiatom molecules. It is necessary that V–V exchange within modes be much more probable than intermodal V–V' exchange (the exchange of a quantum of one mode for quanta of another mode). One has Boltzmann distributions in the harmonic approximation, and the temperatures may be different due to a difference in the pumping and quenching rates of the modes.

However, if sufficiently high levels are excited, then the harmonic approximation becomes inadequate (the Treanor effect). The model of isolated modes becomes inadequate along with the harmonic approximation. Actually, the rigorous division of the vibrations of molecules into modes is possible only in the harmonic approximation. Terms proportional to the products of the vibrational numbers of different modes arise upon taking account of anharmonicity in the energy equation of vibrational levels. This anharmonic relation of modes leads to a coupling of the vibrational distributions. Therefore, the topic of discussion for multiatom molecules should be the spatial distribution of the vibrational mode numbers.

The distribution from the plateau and its relaxation in multiatom molecules are discussed in this paper. The concept of a flux of vibrational quanta, which permits, in particular, deriving a general formula describing the relaxation rate (applicable to diatomic molecules as well), lies at the basis of the analysis. There is no necessity to calculate distributions in an area in which quenching is significant.

Let us consider a bimodal anharmonic oscillator as a model of a multiatom molecule. For definiteness, we will speak of a symmetrical and an asymmetrical mode. The excitation energy of the levels of the oscillator is described by the formula

$$E_{vu} = \omega_1 v + \omega_2 u - x_1 v^2 - x_{12} vu - x_2 u^2, \tag{1.1}$$

where v and u are the vibrational numbers of symmetrical (1) and asymmetrical (2) modes, respectively, ω_i are vibrational quanta, and x_i are anharmonicity constants. The vibrational levels of a bimodal oscillator can be conveniently represented in the plane of the vibrational numbers vu, where they form a square grid (Fig. 1).

Let us suppose that V–V exchange within each mode is far more probable in a rather large region than intermodal and vibrational–translational V–T exchange and other processes which do not conserve the number of quanta. Then one can neglect all processes except V–V exchange. Applying Boltzmann's H-theorem, one can show that a Treanor-type distribution [1] is obtained in this approximation which corresponds to equality of direct and inverse processes in all transitions [8]. The Treanor distribution for a bimodal oscillator is of the form

Moscow. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 4, pp. 3-10, July-August, 1976. Original article submitted August 25, 1975.

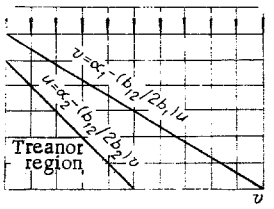

Fig. 1

$$n_{vu} = \exp[-2b_1\alpha_1 v - 2b_2\alpha_2 u + b_1 v^2 + b_{12}vu + b_2 u^2], \quad (1.2)$$

where $b_i = x_i/T$, T is the temperature, and α_i are constants associated with the vibrational temperatures of the modes; $n_{00} = 1$ is assumed here and below. The role of the anharmonic terms of (1.2) becomes significant if the constants α_i are small in comparison with the number of levels being considered in the corresponding mode. Due to the term $b_{12}vu$ in the exponent of the exponential, the Treanor distribution is not represented by the product of functions which depend (each of them) on the vibrational number of a single mode.

The values of the vibrational quanta of symmetrical and asymmetrical modes are constant along straight lines (isoquantum lines):

$$2b_1 v + b_{12}u = \text{const} \quad (1.3)$$

and

$$2b_2 u + b_{12}v = \text{const} \quad (1.4)$$

respectively. The families (1.3) and (1.4) contain lines on which partial derivatives of the Treanor distribution vanish. These lines bound a certain area around the origin of coordinates which we will call the Treanor region (see Fig. 1).

However, it is impossible to restrict oneself to the Treanor distribution. The point is that the distribution (1.2) increases rapidly outside the Treanor region. This increase is nonphysical, since there is always strong quenching on the upper levels, which limits their population. The nonphysical behavior of the distribution for large vibrational numbers is the result of the rather strong assumptions made in the derivation. If one weakens these assumptions somewhat, it is possible to derive a distribution caused by V–V exchange but which also satisfies the necessary boundary conditions.

2. Formulation of the Kinetic Model

The population distribution in the grid of levels is described by the balance equations

$$\frac{dn_{vu}}{dt} = j^{vu}_{v-1,u} - j^{v+1,u}_{vu} + j^{vu}_{v,u-1} - j^{v,u+1}_{vu}, \quad (2.1)$$

where $j^{vu}_{v-1,u}$, for example, is the difference between the number of direct and inverse transitions from the point v–1, u to the point vu, which we call the particle current. (We reserve the term "flux," which is used commonly in this situation, for another quantity.) The presence of just currents between adjacent levels is associated with the assumption of single-quantum V–V exchange. The currents flowing along the v and u axes are proportional to the significantly different V–V exchange constants in symmetrical and asymmetrical modes, respectively. Obviously, the V–V exchange constant in an asymmetrical mode is usually much larger than that in a symmetrical mode. This situation is associated with the fact that V–V exchange in an infrared-active asymmetrical mode occurs on account of the long-range dipole–dipole interaction of the molecules [9].

In order to obtain a distribution which satisfies the boundary conditions, it proves necessary to restrain the excitation and quenching processes in certain boundary transitions. Equation (2.1) is preserved in the remaining part of the plane. We note that a distribution which is not dependent on the ratio of the V–V exchange constants in asymmetrical and symmetrical modes should have been obtained (similarly to the Treanor distribution) upon setting the V–V currents (in transitions without pumping and quenching) to zero. However, the number of equations would exceed by a factor of two the number of points, i.e., the number of unknown populations. As one can show, these equations are consistent only in the pure Treanor case. Therefore, the distribution will depend on the ratio of the V–V exchange constants in the modes in the presence of pumping and quenching in some transitions.

Let us consider the case in which this ratio is small. Then one can neglect the currents in the symmetrical mode, assuming that V–V relaxation occurs for such a short time in the asymmetrical mode that there is no time for relaxation to occur in the symmetrical mode. When the currents in the symmetrical mode are included, an analogy arises with the problem of the vibrational distribution in a mixture of diatomic molecules. One can consider V–V processes as the transfer of excitation quanta from one transition to another. When the V–V currents in each transition are zero, the arrival rate of quanta is equal to the departure rate. Therefore, the equation for zero V–V current can be considered to be the continuity equation for the flux of quanta. We will write the equation for the V–V current in the form

$$\sum_{r,m} S_{vurm} = 0,$$

where

$$S_{vurm} = Q_{vurm}\left(n_{vu}n_{v-r,u-m+1} - e^{-(b_{12}r+2b_2m)}n_{v,u+1}n_{v-r,u-m}\right).$$

The rate constant of the corresponding process has the form

$$Q_{vurm} = Q(u+1)\ (u-m+1)\exp\left[-|b_{12}r + 2b_2m|^z/(2b_2)^z\Delta\right],$$
$$(b_{12}r + 2b_2m \geqslant 0),$$

where Q is the rate constant of the no-defect exchange 01 + 00 → 00 + 01 and z is equal to one for close and to two for long-range interaction [2, 5, 9]. The flux of quanta is different from zero in the presence of sources in transitions where the boundary conditions are specified. The sources and sinks of quanta are shown as arrows in Fig. 1. Satisfaction of the boundary conditions is associated with the choice of the strength of the boundary sources.

Since the energy defect does not depend on the distance of a V–V exchange along an isoquantum line, the effective mean free path of quanta along isoquantum lines is limited only by the dimensions of the area of vibrational numbers. The probability of large mean free paths in the transverse direction is small, so that the transfer is of a diffuse nature. The more effective transfer along isoquantum lines is quasi-steady-state with respect to transverse transfer. This fact indicates that it is possible to set the transfer along isoquantum lines to zero, i.e., $n_{vu}n_{v-r,\,n-m+1} - n_{v,\,u+1}n_{v-r,u-m} = 0$ when $b_{12}r + 2b_2m = 0$. Hence it follows that the derivative $\partial \ln n/\partial u$ is constant along an isoquantum line, i.e.,

$$\partial^2 \ln n/\partial l \partial u = 0. \tag{2.2}$$

From (2.2) we obtain

$$n = V(v)\eta(\tilde{u}), \tag{2.3}$$

where $\tilde{u}$ is the coordinate orthogonal to the isoquantum line. Transforming to the coordinates

$$\tilde{u} = u + v\,\mathrm{tg}\,\alpha,\ \mathrm{tg}\,\varphi = b_{12}/2b_2,\ \tilde{v} = v,$$

we find the representation (2.3) for the Treanor distribution

$$V(v) = \exp\left[(-2b_1\alpha_1 + 2b_2\alpha_2\,\mathrm{tg}\,\varphi)v + (b_1 - (b_{12}/2)\,\mathrm{tg}\,\varphi)v^2\right],$$
$$\eta(\tilde{u}) = \exp\left[-2b_2\alpha_2\tilde{u} + b_2\tilde{u}^2\right],$$

where the normalization $V(0) = \eta(0) = 1$ is chosen. Representation of the population in the form (2.3) indicates that distributions with respect to u in $v_k u$ layers differ from each other by a common multiplier and a shift by the amount $v_k \tan\varphi$.

The number of quanta transferred from transitions between the isoquantum lines $\tilde{u}-\tilde{m}$ and $\tilde{u}-\tilde{m}+1$ to transitions between the isoquantum lines $\tilde{u}$ and $\tilde{u}+1$ is equal to

$$\Pi_{\tilde{u}\tilde{m}} = \int_0^{\tilde{u}/\sin\varphi} dv \int_0^{(\tilde{u}-\tilde{m})/\sin\varphi} dv' Q_{\tilde{u}\tilde{m}}(v, v')\left[n(v, \tilde{u})\,n(v', \tilde{u}-\tilde{m}+1) - e^{-2b_2\tilde{m}}n(v, \tilde{u}+1)\,n(v', \tilde{u}-\tilde{m})\right],$$

where

$$\tilde{m} = m + r \operatorname{tg} \varphi;$$

$$Q_{\tilde{n}\tilde{m}}(v, v') = Q e^{-\tilde{m}^2/\Delta} (\tilde{u} + 1 - v \operatorname{tg} \varphi)(\tilde{u} - \tilde{m} + 1 - v' \operatorname{tg} \varphi).$$

Using the representation (2.3) for the population, we obtain

$$\Pi_{\tilde{u}\tilde{m}} = Q e^{-\tilde{m}^2/\Delta} \langle u + 1 \rangle \langle u - m + 1 \rangle g(\tilde{u}) g(\tilde{u} - \tilde{m}) [\eta(\tilde{u}) \eta(\tilde{u} - \tilde{m} + 1) - e^{-2b_2 \tilde{m}} \eta(\tilde{u} + 1) \eta(\tilde{u} - \tilde{m})],$$

where

$$\langle u + 1 \rangle = \frac{1}{g(\tilde{u})} \int_0^{\tilde{u}/\sin\varphi} (\tilde{u} + 1 - v \operatorname{tg} \varphi) V(v)\, dv,$$

and the quantity

$$g(\tilde{u}) = \int_0^{\tilde{u}/\sin\varphi} V(v)\, dv$$

plays the role of the statistical weight of the isoquantum line.

The total flux through the isoquantum line $\tilde{u}_k$ is equal to

$$\Pi = \int_1^{\infty} d\tilde{m} \int_{\tilde{u}_k}^{\tilde{u}_k + \tilde{m}} \Pi_{\tilde{u}\tilde{m}} d\tilde{u}. \tag{2.4}$$

Since small $\tilde{m}$ make the main contribution to the integral (only if the population does not decrease too rapidly), the integrand can be represented in differential form

$$\Pi = Q \int_1^{\infty} \tilde{m}^2 e^{-\tilde{m}^2/\Delta} d\tilde{m} \cdot \langle u \rangle^2 g^2 \eta^3 [2b_2 - d^2 \ln \eta / d\tilde{u}^2]. \tag{2.5}$$

Equation (2.5) changes into the one-dimensional case when g = 1.

3. Investigation of the Kinetic Model

Equating the flux through an isoquantum line to a constant, we obtain a differential equation for the function $\eta(\tilde{u})$. Initially, we neglect the dependence of $\langle u \rangle$ and g on $\tilde{u}$. Then

$$\eta^2 [2b_2 - d^2 \ln \eta / d\tilde{u}^2] = P = \text{const}.$$

Introducing the scale transformation

$$\eta = C\sqrt{P}, \tag{3.1}$$

we obtain the equation

$$C d^2C/d\tilde{u}^2 - (dC/d\tilde{u})^2 - 2b_2C^2 + 1 = 0. \tag{3.2}$$

Lowering the order with the help of the substitution $dC/d\tilde{u} = \tau$, we obtain an equation which reduces to a homogeneous one. Its general integral gives a first-order equation for C:

$$dC/d\tilde{u} = \pm\sqrt{f(C^2)}, \tag{3.3}$$

where

$$f(C^2) = 2b_2C^2 \ln (C^2/A^2) + 1;$$

and A^2 is an integration constant. Equation (3.3) in its final form is not integrable. Due to the fact that C^2 ln (C^2/A^2) has a minimum, which is equal to $-(A^2/e)$, three cases are distinguished in the investigation of the equation:

1. $A^2 < e/2b_2$. In this case $f(C^2)$ is everywhere positive. Therefore, the integral curves are monotonic. The descending curves, starting from the point $C_0^2 > A^2/e$, have points of inflection at $C^2 = A^2/e < 1/2b_2$, associated with the minimum of the function $f(C^2)$.

2. $A^2 > e/2b_2$. In this case $f(C^2)$ has two zeroes, between which it is negative. Therefore, the descending curves, starting from the point $C_0^2 > 1/2b_2$, have a minimum (above $1/2b_2$) at which the descending branch changes into the ascending branch.

3. $A^2 = e/2b_2$. In this case $f(C^2)$ has one zero at $C^2 = 1/2b_2$, which is the point of tangency. The descending curves, starting from the point $C_0^2 > 1/2b_2$, behave as

$$C = (1/\sqrt{2b_2})\,\mathrm{cth}[\sqrt{b_2}(\tilde{u} + \alpha)], \tag{3.4}$$

near the straight line $C = 1/\sqrt{2b_2}$, asymptotically approaching a constant. Here α is an integration constant.

When $C^2 \gg 1/2b_2$, integration of (3.3) gives

$$C = C_0 \exp(-2b_2\alpha_2\tilde{u} + b_2\tilde{u}^2), \tag{3.5}$$

where

$$C_0 = (1/\sqrt{2b_2}) \exp(b_2\alpha_2^2 + 1/2);$$

and α_2 is an integration constant.

Equation (3.5) satisfies the Treanor distribution. Curves which have a Treanor section start from large C_0, i.e., they correspond to small fluxes, as follows from (3.1).

If we restrict ourselves to curves which have a Treanor section, only the descending curves in case 1 (which have a point of inflection to the right of which they are convex upward) can satisfy the condition of rapid decline at large $\tilde{u}$ (corresponding to a Boltzmann distribution at the gas temperature). The choice of the constant A^2 is restricted also by the condition that C be positive when $\tilde{u} < N$, where N determines the size of the area in which V–V exchange dominates. Since N is large and the functions which are the solutions of (3.2) change rapidly (the behavior of the Treanor type of increase), only a curve which is close to a constant (to the solution of case 3) over a rather large area can satisfy both conditions (positiveness and rapid decline when $\tilde{u} \sim N$). The solution over almost the entire area depends very weakly on the specific form of the boundary conditions at $\tilde{u} \sim N$. In this case a solution can be obtained over the entire area by the matching of (3.4) and (3.5). Returning to the function η, we obtain

$$\eta = \exp(-2b_2\alpha_2\tilde{u} + b_2\tilde{u}^2)$$

in the Treanor region and

$$\eta = \exp(-b_2\alpha_2^2 - 1/2).$$

in the plateau region. The selected solution is associated with the specific quantity

$$P = 1/C_0^2 = 2b_2 \exp(-2b_2\alpha_2^2 - 1),$$

and hence with the specific value of the flux of quanta.

If we take account in (2.5) of the fact that

$$\langle u \rangle\, {}^2g^2 \sim \tilde{u}^k,$$

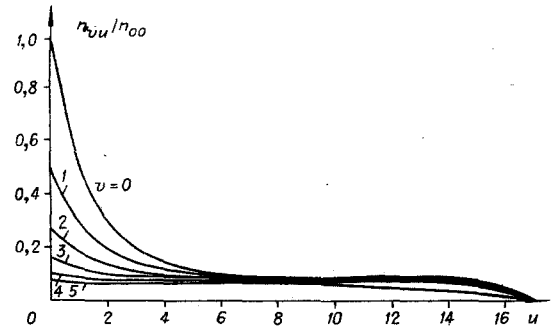

Fig. 2

where k varies from two in the case of weak excitation of a symmetrical mode to four when V(v) = const, then in view of the smallness of the derivative $d^2 \ln \eta / d\tilde{u}^2$ in the plateau region, we find

$$\eta \sim 1/\tilde{u}^{k/2}.$$

The variation of the function η does not extend into the Treanor region when factors dependent on $\tilde{u}$ are taken into account. Therefore, the level of the plateau which is matched to the Treanor region in the neighborhood of the Treanor minimum does not vary significantly. Since the value of the quantum flux is associated with the level of the plateau, we have

$$\Pi = n_{00}^2 Q \frac{\Delta^{3/z}}{z} \Gamma(3/z, 1/\Delta) \langle u(\alpha_2)\rangle^2 g^2(\alpha_2) \cdot 2b_2 \exp\left(-2b_2\alpha_2^2 - 1\right), \tag{3.6}$$

where $\Gamma(3/z, 1/\Delta)$ is the incomplete gamma function and the quantities $\langle u(\alpha_2)\rangle$ and $g(\alpha_2)$ are related to the line of the Treanor minimum. The population of the ground level is introduced explicitly in (3.6).

The possibility of changing to the differential expression in (2.4) is tied to the requirement of a small probability of V–V exchange between the plateau region and the Treanor section. The corresponding criterion of "strong excitation" is of the form

$$\exp\left[\alpha_2^2/\Delta - b_2\alpha_2^2 - 1/2\right] \alpha_2 g(\alpha_2) \cdot 2b_2 \gg 1.$$

Equation (3.6) determines the relaxation rate of the distribution from the plateau, which is related to quenching on the upper levels. There is no need for specific definition of the quenching processes and the calculation of the distribution in the region of strong quenching. The energy equation of the asymmetrical mode is of the form

$$dE_2/dt = -\omega_2\Pi, \tag{3.7}$$

where E_2 is the energy of the asymmetrical mode. In the case of a constant flux of quanta across an isoquantum line, the energy flux decreases along with the value of a quantum. The decrease in the energy flux is necessary due to V–V dissipation. Thus, the energy equation in the form (3.7) takes into account not only quenching on the upper levels, but also V–V dissipation over the entire region.

Let us now discuss the vibrational distribution in CO_2 molecules. In CO_2 Fermi-resonance exerts a strong effect on the vibrational distribution in the symmetrical and flexural modes, because of which it is necessary to consider all three modes. One can represent the excitation energy of the vibrational levels approximately in the form (1.1), where it is now necessary to understand v as being the vibrational number of a multiplet $v = 2v_1 + v_2$ ($v_{1,2}$ are the vibrational numbers of the symmetrical and flexural modes), plus a term which describes the Fermi division. The Fermi division does not depend on u; therefore, it does not have any effect on V–V exchange in the asymmetrical mode. Thus it follows that the results derived above in the absence of the Fermi division are preserved for the combined populations of multiplets.

The population distribution within multiplets is a Boltzmann distribution at the gas temperature. When the vibrational temperature of the Fermi-resonance modes is high (and the gas temperature is low), the distribution in them can have a sawtoothed shape [8]. The possibility of obtaining laser generation [10] is based on this fact. The sawtoothed shape is expressed more in layers of the asymmetrical mode with high vibrational numbers (in the plateau region with respect to u).

Quenching is associated mainly with the lower levels when the temperature of the asymmetrical mode is low. Upon excitation of the distribution from the plateau, quenching described by Eqs. (3.6) and (3.7) is also added. The flux of quanta increases rapidly as the vibrational temperature goes up, which results in a restriction on the latter.

The distribution in the plane of the vibrational numbers ($0 \leq v \leq 5$, $0 \leq u \leq 17$) is illustrated by the example of NO_2 ($T = 300°K$, $n_{01}/n_{00} = n_{10}/n_{00} = 1/2$) in Fig. 2. The NO_2 molecule has three nondegenerate vibrational modes: symmetrical, flexural, and asymmetrical. The flexural mode has the lowest quanta; therefore, it is quenched more strongly than the others and is considered to be unexcited.

The author expresses his gratitude to S. Ya. Bronin, M. B. Zheleznyak, and G. V. Naidis for valuable discussions.

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