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Abstract

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On the Violation of the Boltzmann Distribution in the Process of Thermal Dissociation of Molecules

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The process of thermal dissociation of molecules leads, as was shown in ([1]), to an appreciable violation of the Boltzmann distribution on the upper vibrational levels. The reason is that thermal dissociation occurs as a result of the transition of molecules from the upper vibrational levels into the continuous spectrum; moreover, the rate of transition of a molecule into the continuous spectrum is greater than the rate of excitation of molecules to the upper levels. In ([1]) a system was considered consisting of a monatomic gas with a small admixture of dissociating diatomic molecules. Of practical interest is also the distribution of vibrational energy in an isolated system of dissociating diatomic molecules. In calculating the distribution function of vibrational energy in this case, it is necessary, along with the transition of translational energy into vibrational energy upon collision of molecules, to take into account also the processes of transfer of ready vibrational quanta. The present work is devoted to clarifying the role of the latter processes in the formation of a quasi-stationary distribution of vibrational energy in the process of dissociation.

The influence of processes of transfer of vibrational quanta on the distribution of the vibrational energy of molecules is most conveniently traced on the model of a truncated harmonic oscillator. This model has repeatedly been used in calculations of the rate of dissociation of molecules constituting a small admixture in a monatomic gas ([2]-[4]).

The process of dissociation in an isolated system of such oscillators is described by the equations

$$\frac{dx_n}{dt} = ZP_{10}\{(n+1)x_{n+1} - [(n+1)e^{-\theta} + n]x_n + ne^{-\theta}x_{n-1}\} +$$

$$+ZQ_{10}\{(n+1)(1+\alpha)x_{n+1} - [(n+1)\alpha + n(1+\alpha)]x_n + n\alpha x_{n-1}\}, \qquad (1)$$

$$n = 0, 1, 2, \ldots, n_0 - 1;$$

$$\frac{dx_{n_0}}{dt} = ZP_{10}\{n_0 e^{-\theta} x_{n_0-1} - n_0 x_{n_0}\} + ZQ_{10}\{n_0 \alpha x_{n_0-1} - n_0(1+\alpha)x_{n_0}\} - ZP_{n_0} x_{n_0},$$

where $x_n(t)$ is the number of oscillators on the n-th vibrational level, Z is the number of collisions of an oscillator per second; P_{10} is the probability of transition of the oscillator from the first excited state to the ground state; Q_{10} is the probability of transfer of a vibrational quantum upon collision of oscillators in the first excited and ground states; P_{n_0} is the probability of transition of a molecule into the continuous energy spectrum; $\alpha = \frac{1}{N}\sum_{n=0}^{n_0} n x_n(t)$; $N(t)$ is the total number of oscillators.

The system of equations (1) is analogous to the system of equations describing the process of vibrational relaxation in an isolated system of harmonic

oscillators, and differs from the latter by a finite number of equations and by the last equation, which describes the process of transition of molecules into the dissociated state. As in ([1,2]), we assume that dissociation of molecules occurs as the result of the transition of molecules from some level n_0 into a continuous spectrum. We consider only the initial stage of dissociation, and therefore neglect recombination processes.

Solving the nonlinear system (1) in the general case is associated with considerable difficulties. In the present problem, however, the quasistationary distribution, which determines the rate of dissociation, is of interest. This distribution is meaningful, since the time of vibrational relaxation is considerably less than the relaxation time associated with dissociation ([1]). Obtaining the quasistationary solution is a much easier problem, since it is determined by the value of the reaction rate at each given instant of time. The quasistationary distribution, as shown in ([1]), differs noticeably from the Boltzmann distribution only at the upper vibrational levels. This assertion is valid when only the processes of conversion of translational energy into vibrational energy are taken into account; therefore it will be all the more valid if processes of transfer of vibrational quanta are also taken into account. On the basis of this result, the system of equations (1) can be simplified. The quantity a in (1) is determined mainly by molecules occupying the first vibrational levels. These molecules, with a high degree of accuracy, have a Boltzmann distribution; therefore

$$a = \frac{1}{N}\sum_{n=0}^{n_0} n x_n(t) = (1 - e^{-\theta}) \sum n e^{-n\theta} = \frac{1}{e^{\theta} - 1}. \tag{2}$$

Taking (2) into account, the system (1) can be written in the form

$$\frac{dx_n}{dt} = ZP^*_{10}\{(n+1)x_{n+1} - [(n+1)e^{-\theta} + n]x_n + ne^{-\theta}x_{n-1}\},$$

$$n = 0, 1, 2, \dots, n_0 - 1; \tag{3}$$

$$\frac{dx_{n_0}}{dt} = ZP^*_{10}\{n_0 e^{-\theta} x_{n_0-1} - n_0 x_{n_0}\} - ZP_{n_0} x_{n_0},$$

where

$$P^*_{10} = P_{10}\left[1 + (1 - e^{-\theta})^{-1}\frac{Q_{10}}{P_{10}}\right] \equiv \beta P_{10}.$$

We emphasize that the system of equations (3) is suitable only for determining the quasistationary distribution. It is precisely under this condition that the nonlinear system (1) reduces to the linear system (3).

The system of equations (3) has the same form as the analogous system derived in considering the process of dissociation of molecules constituting a small impurity in a monatomic gas ([1,2]). The only difference is that instead of P_{10}, which appears in ([2]), in the present case there stands P^*_{10}, differing from P_{10} by the factor β. The system of equations (3) was solved in ([1]). The solution has the form

$$x_n = x_0 e^{-\varepsilon_n}(1 + \varphi_n), \qquad \varepsilon_n = \frac{E_n}{kT}.$$

For the molecular model under consideration, in the temperature range less than or of the order of the characteristic temperatures, φ_n differs noticeably from zero only for $n = n_0$. In particular,

$$x_{n_0} = x_0 e^{-\varepsilon_{n_0}}\left[P_{n_0} e^{-\varepsilon_{n_0}} \sum_{n=1}^{n_0} \frac{e^{\varepsilon_n - 1}}{nP_{10}}\right]^{-1}.$$

Replacing P_{10} by P^*_{10} leads to an increase in x_{n_0} by a factor of β. At temperatures below the characteristic ones, $Q_{10} \gg P_{10}$ ([5]), and therefore $\beta \gg 1$; at temperatures of the order of the characteristic ones, $Q_{10} \sim P_{10}$ and $\beta - 1$.

Thus, the process of transfer of vibrational quanta in molecular collisions during dissociation increases the quasi-stationary population of molecules in the upper vibrational levels, bringing it closer to the equilibrium one. This increase is substantial at temperatures below the characteristic ones and does not play a noticeable role at temperatures above, or of the order of, the characteristic ones.

The physical reason for the increase in the population of molecules in the upper vibrational levels is evident. At low temperatures the process of energy transfer to highly excited molecules through exchange of vibrational quanta occurs more rapidly than the process of energy transfer associated with the conversion of translational energy into vibrational energy. An increase in the rate of supply of molecules to the upper vibrational levels, with the probability of transition into the continuous spectrum unchanged ($P_{n_0} \sim 1$), leads to an increase in the quasi-stationary population.

When comparing the results obtained with experimental data, one should bear in mind that the model considered does not take anharmonicity into account; therefore, as applied to diatomic molecules, the present results are qualitative in character. However, in the case of polyatomic molecules whose thermal dissociation occurs with a change in multiplicity, the interaction potential along the bond being broken is approximated rather well by the model of a truncated harmonic oscillator. This applies, in particular, to N_2O upon dissociation into N_2 and O. In this case the results obtained in this work claim to provide a quantitative description.

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