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Abstract

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Toward the Study of the Phenomena of Vibrational Excitation and Dissociation of Oxygen Molecules at High Temperatures

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As is shown by consideration of the results of studies of vibrational relaxation (^1), the process of vibrational excitation of such molecules as O_2, N_2, Cl_2, CO at temperatures of the order of the characteristic vibrational temperature (and lower) is adiabatic in character. Under these conditions the possibility of multiquantum excitation of a molecule in a single collision is practically absent, and only vibrationally excited molecules can dissociate; moreover, according to existing ideas (^{2}-5), the transition to the continuous spectrum of energy values occurs with greatest probability from the upper vibrational levels, for which the condition $\omega\tau_{\text{st}} \sim 1$ is satisfied (ω is the angular frequency of vibrations, τ_{st} is the duration of the collision). In this case the characteristic time τ_{dis}, required for dissociation*, is much greater than the relaxation time of the vibrational energy of the molecule τ_{vib} ($\tau_{\text{dis}} \gg \tau_{\text{vib}}$), since the dissociation of molecules begins only after excitation of the upper vibrational levels.

However, it is clear that with a further increase in temperature the probability of dissociation from less excited levels must become appreciable; in principle, one may imagine the possibility of molecular dissociation in a very strong collision without vibrational excitation. Therefore, with increasing temperature one may expect convergence of the values of τ_{dis} and τ_{vib}, which may serve as an indication of a change in the picture of the processes occurring in molecular collisions (an increase in the role of multiquantum transitions, the possibility of nonadiabatic processes, etc.). Under these conditions, upon sudden heating of a gas in a shock wave, the usually applied method of dividing the region behind the wave front into separate "zones" of vibrational excitation and dissociation may prove untenable; the simultaneous occurrence of the indicated processes may substantially affect the characteristics of the gas state (temperature, density, etc.). Relying on the experiments we have carried out, which concern the propagation of strong shock waves in oxygen, we shall consider the question of separating the phenomena under consideration at $T < 7000 \div 8000°$. Let us note that Dorrance (^6), referring to James' s calculations, believes that in oxygen the relation $\tau_{\text{dis}} \sim \tau_{\text{vib}}$ is realized (at atmospheric pressure) already at 6500° K;

Camac and Vaughan (⁀7) consider that in a mixture of 21.5% O_2 + 78.5% Ar, $\tau_{\text{dis}} \sim \tau_{\text{vib}}$ at $T \sim 8000^\circ$ K.

In contrast to (⁀8), we shall assume that molecular dissociation occurs in transitions not from any vibrational level, but only from some the k-th "effective" level, lying below the dissociation limit by an amount γkT (k is Boltzmann' s constant, γ is a certain constant parameter), i.e., the probability of transition into the continuous spectrum will be assumed equal to unity for this level and to zero for all the others.

This assumption is supported by the dependence of τ_{col} on temperature obtained in experiments*. The values of τ_{col} were obtained from an analysis of the distribution of the vibrational energy E_{k} of unit mass in the gas behind the shock-wave front in accordance with the relaxation equation

$$\frac{dE_{\text{k}}}{dt} = \frac{E(T) - E_{\text{k}}}{\tau_{\text{col}}}, \tag{1}$$

where $E(T)$ is the equilibrium value of the vibrational energy of unit mass of gas at temperature T. It was assumed here that, in the process of vibrational relaxation, the population of sufficiently low ($v'' \leq 5$) vibrational levels changes while preserving a Boltzmann distribution over the levels (10). To reduce the possible influence of the onset of dissociation, only the initial portions of the relaxation zone were processed. In this way it was possible to obtain values of τ_{col} up to $T \sim 10\,000^\circ$. Relating the obtained values of τ_{col} to the mean time interval between two collisions, for the number of collisions Z_{col} required for deactivation of the first vibrational level we obtain

$$Z_{\text{col}} = \tau_{\text{col}} Z \left(1 - e^{-\Delta E/kT}\right), \tag{2}$$

where Z is the collision frequency of an O_2 molecule in 1 sec; ΔE is the first vibrational quantum. For adiabatic processes of energy transfer in molecular collisions (11,12), $Z_{\text{col}} \sim \exp(\omega\tau^*_{\text{ct}})$, where $\omega\tau^*_{\text{ct}}$ is the adiabatic factor

$$\omega\tau^*_{\text{ct}} = \frac{2\pi\Delta E}{v^*\alpha h}; \qquad v^* \simeq \left(\frac{4\pi^2 kT\Delta E}{\alpha h\mu}\right)^{1/3} \tag{3}$$

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* It may be defined as the time required to reduce the difference between the initial and final concentration of molecules by a factor of e (at constant temperature). τ_{dis} does not, of course, have the universal meaning possessed by the vibrational relaxation time τ_{vib}, since the dependence of τ_{dis} on molecular concentration is complex, whereas τ_{vib} is inversely proportional to concentration. The introduction of τ_{dis} is determined here solely by considerations of clarity.

Fig. 1

Figure 1: Fig. 1

(μ is the reduced mass of the O_2 molecule; α^{-1} is the radius of action of intermolecular forces for the potential $V = V_0 \exp(-\alpha r)$; v^* is the relative velocity $O_2 - O_2$ at which vibrational excitation is most probable (12)). Presenting the results obtained for oxygen in the form of the dependence $\lg Z_{\text{col}} = f(\omega\tau^*_{\text{ct}})$, and taking, in accordance with (13), $\alpha = 3.355$ Å^{-1}, we find that the resulting dependence in the region of $\omega\tau^*_{\text{ct}}$ corresponding to $T \sim 2000 \div 10\,000$°K is indeed sufficiently rectilinear** (Fig. 1). This indicates that in the region $6000 \div 8000$° it is difficult, while remaining within the framework of an adiabatic treatment, to expect any noticeable influence of multiquantum transitions, and still less of direct dissociation of molecules from the lower levels.

Fig. 1. Number of collisions Z_{col} required for deactivation of the first vibrational level of O_2, as a function of the adiabatic factor $\omega\tau^*_{\text{ct}}$. Black points are the data of (14).

* The method developed by us earlier for measuring the absorption capacity A ($\lambda = 2275$ Å) behind the shock-wave front in a shock tube (9) made it possible to obtain oscillograms of the distribution of vibrationally excited oxygen ($v'' \sim 4.5$) behind the wave front with high time resolution (down to 0.025 μsec).

** The results for $T < 2000$°K, obtained by Blackman (14), have a somewhat different slope, which may be connected with the influence of impurities, most effective at low T. It is interesting to note that the bend in the curve falls in the region of values of $\omega\tau^*_{\text{ct}}$ corresponding to the characteristic vibrational temperature of oxygen ($\theta = 2240$°).

Thus, in accordance with the assumption adopted above, the dissociation rate will be determined by the population of the k-th level N_k; the exact value of N_k can be found by solving a sufficiently complicated system of kinetic equations (4,5) under the conditions occurring behind the front of the shock wave. For an estimate, certainly considerably overestimating the magnitude of the dissociation rate, N_k may be related to the vibrational temperature T_k, if one assumes the distribution over the levels to be Boltzmannian (10). Then, for the dissociation rate constant under conditions of absence of vibrational equilibrium,

$$K(T) = \overline{K}(T)\frac{N_k(T_k)}{N_k(T)} = \overline{K}(T)\frac{1\{-\exp(-\theta/T_k)\}}{1-\exp\{-\theta/T\}} \exp\left\{\gamma\left(\frac{T}{T_k}-1\right) - \frac{D}{k}\left(\frac{1}{T_k}-\frac{1}{T}\right)\right\}, \tag{4}$$

where $\overline{K}(T)$ is the dissociation rate constant at vibrational equilibrium; D is the dissociation energy; θ is the characteristic vibrational temperature. Assuming that for states sufficiently far from complete equilibrium recombination may be neglected, for the change in n_{O2}—the number of O_2 molecules per unit volume —we shall, as usual, have

$$\frac{dn_{\mathrm{O2}}}{dt} = -K'(T)n_{\mathrm{O2}}^2 - K''(T)n_{\mathrm{O2}}n_{\mathrm{O}}, \tag{5}$$

where n_{O} is the number of oxygen atoms per unit volume; $K'(T)$ and $K''(T)$ are the dissociation rate constants in $\mathrm{O}_2 - \mathrm{O}_2$ and $\mathrm{O}_2 - \mathrm{O}$ collisions, respectively.

Fig. 2. Population N_i of the vibrational levels of the O_2 molecule isolated by the instrument as a function of time: 1—experiment, 2—calculation, 3—calculated values of the mole fraction $\xi_{\mathrm{O2}} = n_{\mathrm{O2}}/n$ (n is the total number of particles per unit volume). Equilibrium value $\xi_{\mathrm{O2}} = 0.55$.

Solving the system of two differential equations (1) and (5) and several algebraic equations following from the laws of conservation of mass, momentum, energy, and the equation of state, one can obtain the distribution of all thermodynamic and gasdynamic characteristics of the gas behind the front of the shock wave in the presence of simultaneous vibrational excitation and dissociation.

The solution of this problem, under the assumption of constancy of the pressure behind the wave front, was carried out numerically by the Runge–Kutta method for the case of propagation of a shock wave in oxygen at a velocity of 4 km/sec under conditions corresponding to one of the experiments (Fig. 2). In doing so, as a first approximation for τ_{col} and $\overline{K}(\overline{T})$, we took the values obtained by us under the assumption of separation of the processes of vibrational excitation and dissociation: the procedure for calculating τ_{col} was indicated above; for $\overline{K}(T)$ we used relation (4) of work (^{15}). It turned out that, despite the overestimate of $K(T)$, in the case under consideration dissociation does not begin immediately behind the shock-wave front: the mole fraction of O_2 decreases by 1% only after the difference between the vibrational-energy reserve and the equilibrium value $E_k - E(T)$ has decreased by a factor of 3. On the other hand, the dissociation of molecules begins before the complete end of vibrational-energy relaxation, which indicates a partial overlap of the processes under study. In this case the gas temperature in the overlap region is lower than that calculated under the assumption of complete separation of vibrational relaxation and dissociation. Comparison of the calculated values of the populations of the vibrational levels $(N_i)_{\mathrm{calc}}$ ($v'' \sim 4.5$), isolated by the spectral instrument used in the experiments, with the experimentally measured values $(N_i)_{\mathrm{exp}}$ (Fig. 2) indicates, however, that the estimates carried out

overlap are considerably overestimated: $(N_i)_{\mathrm{exp}}$ in this region noticeably exceeds $(N_i)_{\mathrm{calc}}$, which indicates a substantial violation of the Boltzmann distribution on those levels from which dissociation occurs. Thus, it may be assumed that at $T \leq 7000 \div 8000°$ no significant overlap of the "zones" of vibrational relaxation and dissociation yet occurs. Nevertheless, with a further increase in T (the shock-wave velocity), one should expect an expansion of the region in which the phenomena under consideration proceed simultaneously.

For illustration, one may carry out a direct comparison of the measured quantities τ_{dis} and τ_{vib}, if τ_{dis} is determined by the relation that follows directly from the definition given above and from equation (5) (on whose right-hand side, when considering only $O_2 - O_2$ collisions, only the first term was retained):

$$\tau_{\text{dis}} = \frac{1}{K'(T)n}\left(\frac{e}{\beta(e-1)+1} - 1\right), \tag{6}$$

where n is the initial concentration of O_2 molecules per unit volume; β is the ratio of the final (equilibrium) concentration of O_2 molecules to n; e is the base of natural logarithms. The results obtained, reduced to atmospheric pressure, are presented in Fig. 3, from which it is seen that with increasing temperature the ratio $\tau_{\text{dis}}/\tau_{\text{vib}}$ does indeed decrease: at $T \sim 6000$°K this difference is somewhat more than one order of magnitude, and at higher T it becomes still smaller. Taking into account $O_2 - O$ collisions (the dashed line in Fig. 3)* leads to a reduction of τ_{dis}, since $K''(T)$ exceeds $K'(T)$ by several times, which is associated with differences in the character of the interaction between $O_2 - O_2$ and $O_2 - O$. It follows from Fig. 3 that at temperatures above 8000°, the application of theories of thermal decomposition of molecules based on the assumption that the process of vibrational relaxation is completed before dissociation begins ($\tau_{\text{dis}} \gg \tau_{\text{vib}}$) requires a certain caution, since at such high temperatures molecular decomposition may begin long before relaxation of the vibrational energy is completed.

Fig. 3. Values of the vibrational relaxation time τ_{vib} (1) and of the characteristic decomposition time τ_{dis} (2) for $O_2 - O_2$ collisions at atmospheric pressure. The dashed curve gives the mean values of τ_{dis} allowing for $O_2 - O$ collisions.

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* The calculation of τ_{dis} allowing for $O_2 - O$ collisions was carried out under the assumption that the total number of O atoms per unit volume remains constant. The value $K''(T)$ was taken from work (7).