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Abstract

Full Text

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PHYSICS

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EXCITATION OF VIBRATIONS AND DISSOCIATION OF DIATOMIC MOLECULES IN ATOM-MOLECULE COLLISIONS IN A HIGH-TEMPERATURE GAS

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To elucidate the mechanism of excitation of vibrations and dissociation of diatomic molecules at high temperatures, it is first necessary to determine the results of an individual collision, i.e., to solve the dynamical problem for various initial states of the colliding particles, and then to consider the kinetic problem of determining the macroscopic characteristics of the gas system.

We shall solve the dynamical problem using as an example collisions of O_2—Ar within classical mechanics, in a formulation analogous to (^{1}). For the intramolecular potential we take an oscillator model of the form

$$U = D\left\{1 - \frac{1+r^4}{2r}\exp\left[-\beta(r^2-1)\right]\right\}^2, \tag{1}$$

which is a good approximation to the real potential calculated by the Rydberg–Klein–Rees method (D is the dissociation energy; r is the distance between the nuclei relative to the equilibrium distance; β is a constant determined from spectroscopic data; for O_2, $\beta = 2.1015$).

Fig. 1. Probability of deactivation by one quantum (solid lines) and by two quanta (dashed lines) as a function of the number of the initial vibrational level

For each prescribed pair of values of the relative collision energy E_R and the initial vibrational energy of the molecule E_k, the system of Hamilton' s equations

Figure 2: graph

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was solved for various initial values of the angle of orientation of the molecular axis relative to the vector of the relative velocity of the colliding particles (with a step of 10°) and various initial values of the phase of vibration of the molecule (with a step of 1/11 of the vibration period). This made it possible to obtain distribution functions of the molecules $f(E'_k, E_k, E_R)$ in the space of vibrational energy E'_k after the collision. If the space E'_k is divided into cells corresponding to known vibrational levels of the molecule, and Bohr’ s correspondence principle is used, then from this one can arrive at the probabilities of transition of molecules $P^0_{jm}(E_R)$ between levels j, m (performing the calculations for various initial values of E_k corresponding to state j). In the same way, the probability of dissociation of the molecule P^0_{jd} was established.

(entry of the molecule into the region $E'_k > D$)*. Next, averaging over the Maxwell distribution for the energy of relative motion and an analytical approximation of the results were carried out. For one- and two-quantum transitions, the obtained values of the probabilities as functions of the initial level number are shown in Fig. 1.

Fig. 2. Ratio of the probability of dissociation to the probability of excitation of the next level

Let us note several features of these results. For $j \geqslant 20$, over the entire temperature range considered ($3000° < T < 20\,000°$K), the transition probability is practically independent of temperature and decreases with increasing level number; in this region the probability of multiquantum transitions is large. At a temperature of $\sim 12\,000°$K, the probability is practically independent of the initial vibrational energy of the molecule. All this indicates a significant difference from the known results of the Landau–Teller theory for the harmonic oscillator (see (^{2})). Only for $T \leqslant 8000°$K and for low-lying levels does the dependence $P^0_{jm}(T)$ approach the Landau–Teller dependence.

The probability of dissociation of an oxygen molecule possessing a reserve of vibrational energy E_j is approximated by the simple expression $P^0_{jd} = 0.5 \exp[-1.705(D - E_j)/kT]$. Let us draw attention to the fact that under certain conditions the probability of dissociation may exceed the probability of transition of the molecule to the next level (Fig. 2). The region of values of the vibrational energy E^*_k, corresponding to $P_{jd}/P_{j,j+1} = 1$, recedes from the dissociation limit with increasing temperature in such a way that $D - E^*_k = 1.19\,kT + 0.23$ eV, i.e., the difference $D - E^*_k$ is close to the mean thermal energy of the gas.

Fig. 3. Change in the population of levels, expressed through the conditional temperature ϑ_m, for different instants of time (the numbers near the curves are the numbers of collisions) as a function of the vibrational energy. To the left

Figure 3: graphs

Figure 3: Figure 3: graphs

of the dashed line 90% of the molecules are concentrated; a–$T = 6000$°K, b–$T = 12\,000$°K

The macroscopic characteristics of the gas mixture were determined as a result of the numerical solution of a system of kinetic equations describing the change in the population x_m of the molecular levels and in the concentration of dis—

of dissociated atoms x_d with time:

$$\frac{dx_m}{dt} = Z\sum_{j\neq m}^{d-1} P_{jm}(T)x_j - Z\sum_{j\neq m}^{d} P_{mj}(T)x_m + ZP_{dm}(T)x_d^2, \qquad m = 0, 1, 2, \ldots, d-1; \tag{2}$$

$$\frac{1}{2}\frac{dx_d}{dt} = Z\sum_{j=0}^{d-1} P_{jd}(T)x_j - Z\sum_{j=0}^{d-1} P_{dj}(T)x_d^2, \tag{3}$$

where Z is the collision frequency. It was assumed that initially the molecules are distributed over the levels according to the Boltzmann law at a temperature $T_0 = 300$°K, and then the temperature T suddenly takes the values indicated above.

The results of solving (2), (3) are conveniently represented in the form of a certain conditional "temperature" ϑ_m for each level, characterizing the population of the given level relative to the population of the zero level in such a way that

$$x_m/x_0 = g_{E_m}\exp(-E_m/k\vartheta_m), \tag{4}$$

where g_{E_m} is the statistical weight of the level corresponding to the vibrational energy E_m. An example of the solution is given in Fig. 3. After the very first collisions, in all cases the level population is such that ϑ_m increases as the number m increases. This result is closely connected with the allowance for multiquantum transitions, which accelerate the process of populating the upper levels (^{3}); at the same time, the reverse flux of molecules downward is still small because of the considerable difference between the actual and equilibrium populations. A very important fact is that a substantial deviation from

* Because of the laboriousness, the calculations for $E_k \neq 0$ were carried out for the limiting parameter $b = 0$ (the right upper index in the notation of the probability). The dependence P_{jm} on b was taken to be that which follows from the calculations for $E_k = 0$ (see (^{1})).

the Boltzmann distribution occurs only at those levels where the number of molecules is relatively small (to the right of the dotted line in Fig. 3). This indicates definite possibilities for using the relaxation equation for the vibrational energy of a gas in its usual form (see, for example, relations 17.91 and 18.30 ([2])) even at $T \sim 20\,000$°K. After some time the character of the population distribution of the levels changes: the "temperature" of the upper levels drops because of the dissociation that has begun, while for the lower levels it tends toward the temperature of the surrounding gas. The establishment of such a distribution, which does not change over a certain interval of time, indicates a transition to the quasi-stationary period of the process. In this case the losses of vibrational energy associated with the breakup of molecules are compensated by vibrational excitation. Finally, after a sufficiently large number of collisions, the role of recombination of atoms increases and the population of all levels comes to equilibrium (this moment is not indicated in Fig. 3).

Fig. 4. Comparison of measured values (points ([4])) and calculated values of the rate constant for dissociation of oxygen molecules in a mixture with argon (quasi-stationary period). Calculated curves: 1 –result of calculations without taking into account initial rotation and the influence of excited electronic terms, 2 –the same with allowance only for initial rotation, 3 –the same with allowance for initial rotation and the influence of electronic terms

Let us calculate the dissociation rate constant k in the form

$$k = \sum P_{md} x_m(t) \Big/ \sum x_m(t). \tag{5}$$

The quantity k here depends on time and increases from zero to k^* (in the quasi-stationary stage) and then to k^0 (in the state of complete equilibrium). We note that for all T, k^*/k^0 in the O_2–Ar mixture considered proved to be close to 0.5.

A comparison of the value of the constant k with the results of measurements in shock tubes (4) is given in Fig. 4. We note that taking into account the initial rotation of the molecules and the excited electronic terms of O_2, according to the estimates in (5), leads to agreement between the calculation results and experiment. Apparently, the significant negative temperature dependence of the pre-exponential factor A observed in the experiments in the expression for k, taken in the form $k = A(T)\sqrt{T}\exp(-D/kT)$, is associated with the different participation of the upper electronic terms in the process of molecular dissociation.

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