DEPENDENCE OF THE PROBABILITY OF DEACTIVATION OF VIBRATIONS OF IODINE MOLECULES ON THE RATIO BETWEEN THE COLLISION TIME AND THE VIBRATION PERIOD

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DEPENDENCE OF THE PROBABILITY OF DEACTIVATION OF VIBRATIONS OF IODINE MOLECULES ON THE RATIO BETWEEN THE COLLISION TIME AND THE VIBRATION PERIOD

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Recently, progress has been achieved in the theoretical and experimental study of energy exchange between the vibrational and translational degrees of freedom of gas molecules. However, the experimental results obtained pertain only to the case of adiabatic collisions, when the time of collision of the particles is greater than the period of vibration of the molecule ($\omega\tau_{\mathrm{st}} > 1$). For these same conditions the theory has been developed most fully and comprehensively (^{1}). In the region $\omega\tau_{\mathrm{st}} \leqslant 1$, experimental data are completely lacking, while theoretical treatments of collision processes are limited mainly to the very special case $\omega\tau_{\mathrm{st}} \ll 1$ for particles whose masses differ greatly ($^{2-4}$).

In the present work an experimental study has been undertaken of the dependence of the probability of deactivation of the first vibrational level of the iodine molecule on the magnitude of $\omega\tau_{\mathrm{st}}$ over wide limits of its variation. Iodine vapor proved to be a very convenient system for carrying out this type of study, since the vibrational frequency ω of the molecule J_2 is small. As a result, even at room temperatures the gas contains vibrationally excited molecules. In addition, iodine has an intense absorption and emission spectrum in the visible region, which makes it possible to use a rather simple optical method for recording the number of vibrationally excited molecules in several spectral regions simultaneously. The experimental studies were carried out in a shock tube over a wide temperature interval $T = 800 \div 3500°$ K. Variation of the collision time was achieved not only by varying the gas temperature, but also by changing the composition of the gas system. Therefore the processes of vibrational relaxation were studied both in pure iodine and in mixtures with helium, argon, and nitrogen. The method for obtaining the vibrational relaxation time from the distribution of the absorptivity of J_2 behind the shock-wave front will be published in the journal *Fizika goreniya i vzryva.* Here we merely note that from two oscillograms the distribution of density and of the vibrational energy of the

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

gas behind the shock-wave front was found. This made it possible to determine the vibrational relaxation time τ of the system at a specified temperature T.

In the case of a harmonic oscillator, the vibrational relaxation time of the system τ and the probability of deactivation of the first vibrational level are connected by the known relation

$$\tau = \frac{1}{P_{10} Z \left(1 - e^{-h\omega/kT}\right)},$$

where Z is the collision frequency of the molecule, and $h\omega$ is the magnitude of the vibrational quantum.

The results of calculating P_{10} for the $\mathrm{J_2 - N_2}$ system are presented in Fig. 1 as a function of the gas temperature. It is interesting to note that for the systems $\mathrm{J_2}$—Ar and $\mathrm{J_2}$—$\mathrm{N_2}$ a decrease in the value of P_{10} with increasing temperature is observed,

for J_2—He the probability of deactivation of J_2 molecules remains unchanged within the limits of measurement error, while in pure iodine in the region $T \sim 2500^\circ$ K there is a clearly pronounced maximum of the value P_{10}.

Let us plot all the data on one common graph as a function of a parameter characterizing the general properties of particle collisions in the gas systems considered above. The quantity $\omega\tau_{\mathrm{ct}}$ may serve as such a parameter (Fig. 2). It turns out that all the results fall on one common curve

Fig. 1. Dependence of the probability of deactivation of the first vibrational level of J_2 molecules on temperature in collisions with nitrogen

Fig. 2. Dependence of the probability of deactivation of the first vibrational level of J_2 molecules on the quantity $\omega\tau_{\mathrm{ct}}$ in collisions with iodine, helium, argon, and nitrogen.
a—J_2—J_2; *b*—J_2—J_2 ultraactive; *v*—J_2—He; *g*—J_2—Ar; *d*—J_2—N_2

with a characteristic maximum, and this maximum occurs at $\omega\tau_{\mathrm{ct}} \sim 1$. Thus, when the collision time coincides with the period of oscillation of the J_2 molecule, the probability of deactivation of the first vibrational level P_{10} reaches its maximum value. The values of the probability P_{10} obtained for pure iodine pass through the maximum. For the mixtures J_2—N_2, J_2—Ar, and J_2—He the value of $\omega\tau_{\mathrm{ct}}$ is less than 1, and for the system J_2—He it is much smaller than for the other two. In connection with this, the probability P_{10} in the system J_2—He is smaller than in J_2—N_2 and J_2—Ar, if the temperature interval is the same for all mixtures. In these mixtures, under fixed conditions, the collision time of the particles will be determined mainly by their reduced mass.

Fig. 3. Dependence of the probability of deactivation of the first vibrational level of O_2 molecules on the value of $\omega\tau_{\text{st}}$ for the O_2—O_2 system

Figure 2: Fig. 3. Dependence of the probability of deactivation of the first vibrational level of O_2 molecules on the value of $\omega\tau_{\text{st}}$ for the O_2—O_2 system

The results presented in Fig. 2 make it possible to draw certain conclusions about the processes of deactivation of vibrational levels in some molecular systems. As an example, let us consider a gas whose molecules possess different modes of vibration. It is possible to select such conditions in the gas (temperature, impurity, etc.) that the addition of an impurity will lead to an acceleration of the deactivation of the vibrational levels of one of the modes in comparison with the others. This result can be used in laser technology.

The Landau—Teller theory describes the experimental data for pure iodine fairly well under the condition $\omega\tau_{\text{ct}} > 1$ ($T \leq 1000°$ K). However, in the region of higher temperatures a deviation of the theory from experiment is observed; it turns out that the experimental values of the probability P_{10} increase considerably more slowly than the theoretical ones. In the region $\omega\tau_{\text{ct}} \sim 1$, their growth first ceases, and then a decrease in the value P_{10} is observed. None of the above-mentioned theories of vibrational relaxation explains such behavior of the deactivation probability as a function of $\omega\tau_{\text{ct}}$.

Since in the region $\omega\tau_{\text{st}} < 1$ all the experimental data fall on a single curve, under these conditions the process of collision of particles may be regarded as the collision of hard spheres.

In the range $\omega\tau_{\text{st}} < 1$, the dependence of the deactivation probability on the reduced mass of the colliding particles is opposite to the dependence that occurs for $\omega\tau_{\text{st}} > 1$. It should be noted that, for the dissociation rate, the same picture is observed as for vibrational relaxation at high collision velocities. This is also understandable, since in both cases the inequality $\omega\tau_{\text{st}} < 1$ is satisfied (in dissociation it is always satisfied, since decomposition occurs from the upper vibrational levels).

It may be expected that the form of the curve shown in Fig. 2 for iodine will also be reproduced for other gases, for example for oxygen. As an illustration, let us construct an analogous graph for O_2 (Fig. 3). We shall use the data for the probability P_{10} of oxygen up to $T = 10500°$ K, which corresponds to $\omega\tau_{\text{st}} \sim 1.2$. Just as in the case of iodine, in oxygen, as $\omega\tau_{\text{st}}$ approaches unity, the growth of the probability P_{10} almost ceases. As a result, in this region of $\omega\tau_{\text{st}}$ a deviation of the experimental data from the Landau-Teller theory is observed.

Fig. 3. Dependence of the probability of deactivation of the first vibrational level of O_2 molecules on the value of $\omega\tau_{\text{st}}$ for the O_2—O_2 system

The curve in Fig. 2 apparently has a certain analogy with the excitation function of atoms and molecules when the latter collide with electrons.

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REFERENCES

1. K. Herzfeld, T. A. Litovitz, *Absorption and Dispersion of Ultrasonic Waves*, N. Y., 1959.
2. M. N. Safaryan, E. V. Stupochenko, *Zhurn. prikl. mekh. i tekhn. fiz.*, No. 1, 93 (1965).
3. A. I. Osipov, *DAN*, **143**, 1392 (1962).
4. G. K. Ivanov, Yu. S. Sayasov, *DAN*, **154**, No. 6 (1964).

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