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Abstract

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Physics

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EXCITATION OF VIBRATIONAL DEGREES OF FREEDOM IN MOLECULAR COLLISIONS

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The modern theory of vibrational relaxation (in its dynamic aspect) is based on the following assumptions:

1. Molecules are approximated by harmonic oscillators.
2. The process of an inelastic collision, accompanied by excitation of vibrational degrees of freedom, is calculated within the framework of perturbation theory. In the zeroth approximation, only elastic scattering is taken into account.
3. Linear collisions (the one-dimensional case) of an incident particle (atom or molecule) with a molecule are considered.

Within these assumptions the existing relaxation theory satisfactorily describes the temperature dependence of the vibrational relaxation time. Quantitative agreement between experimental and theoretical values of the vibrational relaxation time can be achieved by an appropriate choice of the parameters of the intermolecular potential, which thus become empirical constants. However, the following difficulty then arises. The values of the parameters of the intermolecular interaction potential determined from data on vibrational relaxation do not coincide with analogous values found from experiments on elastic scattering of molecular beams (⌃1). This latter circumstance compels a more careful analysis of the basic premises of the theory of vibrational relaxation. Some results of such an analysis are presented in the present paper.

Fig. 1. Scheme of the collision of a molecule with an atom

To simplify the problem, we shall consider molecular collisions within the framework of classical mechanics. The results thus obtained can be used for a quantitative description of the phenomenon only at large relative velocities* and at large energies of the initial vibrational excitation (Bohr correspondence principle). For a harmonic oscillator, however, the latter condition is not obligatory.

1. Let us first consider the collision of an atom with a diatomic molecule, restricting ourselves to the planar case, in which the relative-velocity vector lies in the plane passing through the centers of gravity of the three atoms. The Hamiltonian of the entire system H has the form

$$H = P_\rho^2/2M + P_\theta^2/2M\rho^2 + P_r^2/2\mu + P_\psi^2/2\mu r^2 + U(r) + \\ + P_R^2/2m_3 + P_\varphi^2/2m_3R^2 + V(R_1, R_2), \tag{1}$$

* In most cases this will correspond to temperatures exceeding 1000°.

where $U(r)$ is the intramolecular potential; $V(R_1, R_2)$ is the potential of interaction between the atom and the molecule; $M = m_1 + m_2$, $\mu = m_1m_2/(m_1 + m_2)$; the remaining notation is clear from Fig. 1. The solution of Hamilton' s equations makes it possible to determine the energy transferred to the vibrational degrees of freedom in a collision. As is known (^{2}), for a head-on collision ($\psi = 0$) of an atom with an unexcited molecule (oscillator) and for an intermolecular interaction potential of the form $V(R_1) = V_0 \exp(-\alpha R_1)$, the energy of the excited vibrations is given by the expression

$$\Delta E_{\text{vib}} = \frac{2\pi^2\lambda^2\widetilde{m}^2\omega^2}{\mu\alpha^2}\frac{1}{\text{sh}^2(\pi\omega/\alpha v)}; \tag{2}$$

here $\omega = 2\pi\nu$ is the angular frequency of the oscillator; $\widetilde{m} = m_3(m_1+m_2)/(m_1+m_2+m_3)$, $\lambda = 1/2$.

In Fig. 2 the dependences of $\Delta E_{\text{vib}}/D$ (D is the dissociation energy) on the energy of relative motion $(E_R/D) = m_3v_0^2/2D$, calculated from formula (2) and numerically, are presented. The numerical calculation of ΔE_{vib} was carried out both for the model of a harmonic oscillator

$$\left(U(r) = \frac{1}{2}\mu\omega^2(r - r_e)^2 = \beta^2 D(r - r_e)^2\right),$$

and for a Morse oscillator

$$\left(U(r) = D\{1 - \exp[-\beta(r - r_e)]\}^2\right).$$

In the calculation, the intermolecular interaction potential $V(R_1, R_2)$ was taken to be

$$V(R_1, R_2) = V_0e^{-\alpha R_1} + V_0e^{-\alpha R_2}, \tag{3}$$

Fig. 2. Magnitude of the excited vibrational energy of an oxygen molecule $\Delta E_{\text{vib}}/D$ in a head-on collision with an argon atom as a function of the energy of relative motion E_R/D (D is the dissociation energy, equal to 5.1 eV). 1 – analytical solution by formula (2), 2 –numerical solution for a harmonic oscillator, 3 –numerical solution for a Morse oscillator

Figure 2: Fig. 2. Magnitude of the excited vibrational energy of an oxygen molecule $\Delta E_{\text{vib}}/D$ in a head-on collision with an argon atom as a function of the energy of relative motion E_R/D (D is the dissociation energy, equal to 5.1 eV). 1 –analytical solution by formula (2), 2 –numerical solution for a harmonic oscillator, 3 –numerical solution for a Morse oscillator

and the parameters had values corresponding to the collision $O_2 - Ar$:

$$\begin{aligned} m_3 &= 6.64 \cdot 10^{-23}\ \text{g}, & M &= 5.312 \cdot 10^{-23}\ \text{g}, \\ \mu &= 1.328 \cdot 10^{-23}\ \text{g}, & r_e &= 1.207 \cdot 10^{-8}\ \text{cm}, \\ D &= 8.3514 \cdot 10^{-12}\ \text{erg}, & \beta &= 2.6536 \cdot 10^{8}\ \text{cm}^{-1}, \\ \alpha &= 4.12 \cdot 10^{8}\ \text{cm}^{-1}, & V_0 &= 1.952 \cdot 10^{-9}\ \text{erg}. \end{aligned}$$

Fig. 2. Magnitude of the excited vibrational energy of an oxygen molecule $\Delta E_{\text{vib}}/D$ in a head-on collision with an argon atom as a function of the energy of relative motion E_R/D (D is the dissociation energy, equal to 5.1 eV). 1 –analytical solution by formula (2), 2 –numerical solution for a harmonic oscillator, 3 –numerical solution for a Morse oscillator.

In a head-on collision the role of the second term in expression (3) is insignificant and, thus, the potential (3) coincides with $V(R_1)$.

It follows from Fig. 2 that analytical calculations of ΔE_{vib} give somewhat overestimated values. More substantial differences, however, appear when the results of the numerical calculation are compared with each other. Allowance for anharmonicity, as is seen from Fig. 2, reduces the value of ΔE_{vib} (in the range $0.2 < E_R/D < 10$) by more than an order of magnitude. This effect had not been noted previously.

2. In analytical calculations of ΔE_{vib}, the specificity of the incident particle (atom or molecule, within perturbation theory) is determined only by its mass and by the intermolecular interaction potential. The results of numerical calculations* of ΔE_{vib} (per molecule) for head-on collisions ($\psi = 0$) of a Morse oscillator $U(r)$ (the values of the parameters are given above) with an atom and an unexcited molecule are presented in Fig. 3. It was assumed here that the intermolecular potential is also specified in the form of a Morse potential with the same parameters, except that $D_R = 6.2385 \cdot 10^{-14}$ erg; the mass of the incident atom was equal to the mass of the molecule. As is seen from Fig. 3, the efficiency of excitation of the vibrational degrees of freedom of the molecule, at equal masses

and values of the parameters of the intermolecular potential, is higher for collision with an atom,

* The numerical solution was carried out according to the scheme described in ([3]). This case differs from the preceding one in the character of the intermolecular potential (a Morse potential instead of an exponential repulsive potential).

than for collision with a molecule. This effect also had not previously been taken into account, although its origin may be regarded as quite obvious. Indeed, impacts of a molecule and an atom of equal mass have different efficiencies, since in a collision different masses come into direct contact (for the molecule, essentially only the mass of the outermost atom).

Fig. 3. Excitation of molecular vibrations in collision with an atom of twice the mass (1) and with a molecule (2)

3. In the theory of vibrational relaxation, head-on collisions are considered the most effective. In order to test this assumption, the quantity ΔE_{vib} transferred to a harmonic oscillator and to a Morse oscillator was calculated for a head-on collision with an atom ($\psi = 0$) and for a collision along the normal to the molecular axis ($\psi = \pi/2$).

The results obtained are presented in Fig. 4, from which it is seen that for a Morse oscillator at relative-motion energies $(E_R/D) > 0.2$, collisions along the normal are the most effective. For a harmonic oscillator this effect is much weaker; for energies $(E_R/D) < 1$, the efficiency of head-on collisions is somewhat (approximately by a factor of 4) higher than that of perpendicular collisions.

4. The effects found are characteristic of collisions with large relative-motion velocities ($E_R/D \geq 0.2$). One can establish an approximate temperature range in which these effects must be taken into account. As is known ([4]), the main role in vibrational relaxation is played by fast molecules whose velocities lie in the tail of the Maxwellian distribution in a rather narrow region near the value v^*, determined by the condition

$$\tilde{m} v^{*2}/2 = \chi k T, \tag{4}$$

where $\chi = (\pi^2 \tilde{m} \omega^2 / 2a^2 kT)^{1/3}$, $\tilde{m}$ is the reduced mass of the colliding particles. Usually χ is of order $5 \div 10$, and for O_2—Ar collisions at $E_R/D \geq 0.2$, according to (4), we obtain $T \geq 1000^\circ$K.

Fig. 4. Excitation of vibrations of an O_2 molecule by an Ar atom in a head-on collision (a) and in a collision along the normal (b). The designations 2 and 3 are the same as the caption to Fig. 2.

This temperature region is at present quite accessible to experimental study, and reliable experimental data are available here. The effects described above —the influence of anharmonicity, the different efficiency of atom-molecule and molecule-molecule collisions, and the predominant role of collisions along the normal—should be manifested in the practically interesting temperature region ($> 1000°$K). The observed features of vibrational excitation must be taken into account in further refinements of the theory of vibrational relaxation. However, it is already clear that a simple transfer of data obtained from the analysis of vibrational relaxation to another class of phenomena (for example, the calculation of transport properties) cannot at present be considered justified.

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