VIBRATIONAL RELAXATION

PHYSICS

1968

SovietRxiv

Abstract

Full Text

UDC 539.196.5

PHYSICS

B. V. KUKSENKO, S. A. LOSEV

VIBRATIONAL RELAXATION IN ATOM-MOLECULE COLLISIONS

(Presented by Academician G. I. Petrov on March 30, 1967)

The theory of vibrational excitation of diatomic molecules in collisions with atoms aims to establish a connection between the parameters of the potential of the intermolecular interaction of the colliding particles and the vibrational relaxation time, i.e., between the results of experiments on elastic scattering and experiments on excitation of molecules in shock and acoustic waves, etc. (1). The difficulties encountered along this path indicate the need to clarify the role of particle orientation during collision, vibrational anharmonicity, initial rotation of the molecules, and other factors.

Let us consider the problem of excitation of molecular vibrations upon collision with an atom in the formulation described by us in (1), i.e., within the framework of classical mechanics under the assumption that the relative-velocity vector lies in the plane containing all three atoms. The Hamilton equations were solved on an electronic computer for a large number of variants of the O_2—Ar collision. In the solution, the magnitude of the excited vibrational energy of the molecule, ΔE_k, was obtained as a function of the state of the molecule before collision: the magnitude of the angular momentum P, the impact parameter b, the energy of relative motion E_R, and also the type of intramolecular potential (harmonic oscillator and anharmonic Morse oscillator). Calculations were performed for various values of the angle ψ, which specifies the initial orientation of the molecular axis relative to the relative-velocity vector, in steps of 10°. It is assumed that before the collision the molecule is not vibrating. The parameters of the intermolecular potential were also varied in the calculations.

In the particular case of a collinear collision ($\psi = 0,\ b = 0,\ P = 0$), the calculation results admit a good approximation of the dependence of ΔE_k on E_R for $0.15D < E_R < 2D$ (D is the dissociation energy of the molecule) in the form

$$\Delta E_k = c_1^0 \exp\left[-a_1^0/\sqrt{E_R}\right], \qquad (1)$$

Fig. 1

Figure 1: Fig. 1

where c_1^0, a_1^0 are numerical quantities depending (for selected values of the masses of the colliding particles) only on the form of the potentials of the intra- and intermolecular forces. The analogy with the results obtained in the adiabatic approximation in the Landau–Teller theory is not merely qualitative. The coefficient a_1^0 obtained by the least-squares method for the harmonic-oscillator model coincides with the analogous quantity obtained in the known approximate analytical solutions (^{2}, ^{3}) (i.e., $a_1^0/\sqrt{E_R} = 2\pi\omega/\alpha v_R$, where ω is the frequency of harmonic vibrations, v_R is the velocity of relative motion, and α is the inverse value of the radius of the intermolecular forces). Taking anharmonicity into account leads to a significant (more than tenfold) decrease in the pre-exponential factor c_1^0, whereas the magnitude a_1^0 practically does not change.

In studying the dependence of ΔE_k on the initial angle ψ, it was established that collinear ($\psi = 0$) and normal ($\psi = 90^\circ$) collisions belong

belong to the least effective ones (Fig. 1). The values of ΔE_k obtained after averaging over the angles ψ can be approximated by dependences of the form

$$\Delta E_k = c_1 \exp\left[-\frac{a_1}{\sqrt{E_R}} + \gamma_1 \frac{P}{E_R} - \frac{b^2}{q}\right] \quad \text{for } 0.15D < E_R < 2D; \tag{2a}$$

$$\Delta E_k = c_2 \exp\left[-\frac{a_2}{\sqrt{E_R} + \gamma_2 P} - \frac{b^2}{q}\right] \quad \text{for } E_R \ll 0.15D, \tag{2b}$$

where, as above, $c_1, c_2, a_1, a_2, \gamma_1, \gamma_2, q$ depend only on the type of potentials (q also depends weakly on E_R). A small difference between a_1^0 and a_1 is noted; for example, for $\alpha = 4.12\,\text{Å}^{-1}$, for the harmonic oscillator $a_1^0 = 6.037$ and $a_1 = 5.78$, and for the Morse oscillator $a_1^0 = 6.191$ and $a_1 = 6.15$ (if E_R is expressed in fractions of D).

Fig. 1. Epure of the values of the amount of excited vibrational energy ΔE_k in an O_2-Ar collision as a function of the initial orientation angle of the molecule for $E_R/D = 0.285$, at $b = 0$, $P = 0$. Solid line–Morse oscillator; dashed line–harmonic oscillator.

With initial rotation, the internal energy of the molecule is divided into vibrational and rotational energy at the point of minimum potential energy; the energy expenditure on shifting the equilibrium position owing to the centrifugal effect, according to (4), is assigned to the rotational energy. A significant increase of ΔE_k was found for a rotating molecule at small values of E_R (Fig. 2).* This phenomenon may be connected with the transfer of the molecule' s rotational energy into vibration under the retarding action of a comparatively slowly

Fig. 2

Figure 2: Fig. 2

flying atom. At large E_R, the influence of the initial rotation is insignificant—the molecule does not have time to turn appreciably during the collision. The results for the harmonic oscillator and the Morse oscillator differ only slightly.

The solution (2a), (2b) obtained was used to calculate $d\varepsilon_k/dt$—the mean value of the change in vibrational energy per unit time, calculated per one molecule, for a specified concentration of atoms per unit volume, in the presence of a Maxwellian distribution for the energy of relative motion and a Boltzmann distribution for the angular momentum in the absence of initial vibrations of the molecule. In passing to three-dimensional averaging it is assumed that: 1) ΔE_k does not depend on the angle ε in the plane perpendicular to the relative-velocity vector, and 2) the rotation of the molecule occurs only in the plane under consideration. Then, according to (5):

Fig. 2. Dependence of $\Delta E_k/D$ for the Morse oscillator on the energy of relative motion for different values of the initial rotational energy of the molecule. The numbers $0, 2, 1, \ldots$ indicate the value of the angular momentum divided by $h/2\pi$ (h is Planck' s constant).

$$\frac{d\varepsilon_k}{dt} = cn \iiiint \Delta E_k \exp\left[-\frac{E_R}{kT} - \frac{P^2}{2IkT}\right] E_R \, dE_R \, b \, db \, dP \, d\varepsilon \tag{3}$$

where c is a normalization factor; n is the number of atoms per unit volume; I is the moment of inertia of the molecule. The integration over P for small values of the relative-motion energy was carried out by the saddle-point method near the point P^*, corresponding to the region of the maximum contribution of rotation to vibrational excitation. The integration over the Maxwellian distribution was carried out numerically; moreover, as in the analytical solution, one can single out the quantity E_R^*, the most effective in exciting vibrations. Calculations for $T = 1000$–$20\,000$°K show that the effect of rotation on vibrational excitation is noticeable only for $T < 1500°$: at $T = 1000°$ allowance for rotation increases the result by a factor of 4-5, while at $T = 1500°$ by a few percent. Integration over b and ε gives the excitation cross section $\bar{Q} = \pi q$ reduced to the value at $b = 0$; the dependence of $\bar{Q}$ on E_R^* is given in Fig. 3 for different values of α and V_0—parameters of the intermolecular-interaction potential. Let us note that decreasing the pre-exponential factor V_0 by a factor of 27 leads to a decrease in the cross section only by a factor of 1.5-2; simultaneously ΔE_k increases for $b = 0$, so that overall the quantity $d\varepsilon_k/dt$ decreases only by 20-30%. Thus, changing V_0 has little effect on the result. A correction for the influence of spherically symmetric attractive forces has been introduced into the results by

---

[*] In (1), the quantity E_R denoted the energy of the incident atom.

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

the method described in (^{6}); at $T = 2000°$ this correction increases the result by a factor of 2, and at $T = 1000°$ by a factor of 3.

Fig. 3. Dependence of the reduced excitation cross section $\bar{Q}$ on the value of the most effective relative-motion energy E_R^* for $\alpha = 3.296$ $\mathring{A}^{-1}$ (1); 4.12 $\mathring{A}^{-1}$ (2 and 4); 4.944 $\mathring{A}^{-1}$ (3). The dashed line refers to the result of the calculation for the value V_0 reduced by a factor of 27 relative to the result indicated by the solid line.

The value of the vibrational-relaxation time τ of O_2 in a mixture with Ar can be obtained by postulating a relaxation equation for the vibrational energy*

$$d\varepsilon_k/dt = [\varepsilon_k(T) - \varepsilon_k]/\tau, \tag{4}$$

so that

$$\tau = \frac{\varepsilon_k(T)}{(d\varepsilon_k/dt)_{\varepsilon_k=0}},$$

Fig. 4. Dependence of the vibrational-relaxation time τ of O_2 molecules in an Ar mixture on $T^{-1/3}$ at normal density. The solid line is a calculation using data for the parameters of the intermolecular potential obtained in (^{7}). The dashed lines are the results of calculations for exponential potentials with $\alpha = 3.296$ $\mathring{A}^{-1}$ (1), 4.12 $\mathring{A}^{-1}$ (2), and 4.944 $\mathring{A}^{-1}$ (3). Experimental points: *a*—for mixtures containing $O_2 \leqslant 1\%$ (^{8}); *b*—obtained by recalculation from the results for mixtures 21% O_2+79% Ar (^{9}); *v*—the same for mixtures 21.5% O_2+78.5% Ar (^{10}).

* Strictly speaking, the relaxation equation in the form (4) is valid only for a system of harmonic oscillators.

where $\varepsilon_k(T)$ is the equilibrium value of the vibrational energy, calculated per molecule. The values of τ for various values of a are given in Fig. 4 as functions of $T^{-1/3}$. For comparison, this figure also shows the results of calculations that take into account the potential parameters obtained in elastic-scattering experiments[7], and the experimental results of measurements of τ in O_2—Ar mixtures in shock tubes[8–10]. On the whole, one may note satisfactory agreement between the results of the calculations performed on the basis of elastic-scattering data and direct measurements of τ, which allows one to hope that the assumptions adopted here are basically justified. The discrepancy of the results at $T \sim 1000^\circ$K may be associated with the inaccuracy of taking into account the influence of attractive forces (deviations from spherical symmetry of the potential of the attractive forces), the need to consider molecular rotation in a three-dimensional representation, and the influence of quantization of the oscillator energy. We note that the experimental data at $T \sim 1000^\circ$K are too few in number. Thus, the question of vibrational relaxation of diatomic molecules at comparatively low temperatures apparently requires special consideration.

The somewhat higher calculated values than the experimental ones observed in the remaining temperature range (on average by a factor of 2) can be explained primarily by the inaccuracy of the adopted model of the intermolecular-force potential, since, as is seen from Fig. 4, the calculation results are very sensitive to the magnitude of the range radius of these forces.

Scientific Research Institute of Mechanics
Moscow State University
named after M. V. Lomonosov

Received

References

1. B. V. Kuksenko, V. B. Leonas et al., DAN, **167**, No. 6, 1280 (1966).
2. D. Karp, J. Chem. Phys., **40**, 2813 (1964).
3. J. G. Parker, Phys. Fluids, **2**, 449 (1959).
4. G. Herzberg, *Spectra of Diatomic Molecules*, N. Y., 1950.
5. S. Ch' en, T. K. Uhlenbeck, *Mathematical Theory of Nonequilibrium Gases*, IL, 1960.
6. E. E. Nikitin, *Optics and Spectroscopy*, **6**, 141 (1959).
7. Yu. N. Belyaev, V. B. Leonas, ZhTF, **36**, 353 (1966).
8. M. Camac, J. Chem. Phys., **34**, 448 (1961).
9. N. A. Generalov, S. A. Lossev, Izv. AN SSSR, ser. fiz., **27**, 1110 (1963).
10. D. R. White, R. C. Millikan, J. Chem. Phys., **39**, No. 7, 1807 (1963).

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

original.