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Abstract

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ROTATIONAL RELAXATION OF DIATOMIC MOLECULES

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The calculation of the rate of energy exchange between the rotational and translational degrees of freedom in a nonequilibrium gas is of interest for a number of problems in kinetics (⌒1). A consistent theoretical calculation of rotational-excitation cross sections encounters the difficulty that the various versions of perturbation theory are usually inapplicable because of the strong interaction responsible for rotational transitions. The only exception is the case of adiabatic collisions, when the rotational frequency ω_j substantially exceeds the inverse collision time $1/\tau$ (rotational transitions in hydrogen at comparatively low temperatures (⌒2)).

In the present work a derivation is given of relaxation equations for the rotational distribution function of diatomic molecules colliding with a particle C (atom or electron) under the condition $\omega_j\tau \lesssim 1$. Taking $\omega_j \sim (B/\beta)^{1/2}$, $\tau \sim (\mu\beta)^{1/2}/\alpha$, where $B = \hbar^2/Mr_e^2$ is the rotational constant of the molecule, $\beta = 1/kT$, μ is the reduced mass of AB and C, and $1/\alpha$ is the radius of action of the potential (all parameters of the dimension of energy are expressed in frequency units), we find $\bar{\omega}\tau \sim \mu^{1/2}/M^{1/2}\alpha r_e$. Thus the condition $\bar{\omega}\tau \lesssim 1$ is fulfilled either when the radius of action of the potential is considerably smaller than the equilibrium interatomic distance AB, or when the mass ratio μ/M is small.

To take account of the strong coupling between the rotational states of the molecule during collision, Bernstein, Dalgarno, Massey, and Percival (⌒3) long ago proposed a statistical theory whose idea is analogous to the random-phase approximation in the calculation of elastic-scattering cross sections. It is assumed that the elements of the scattering matrix $S(j, l; j', l')$ from the channel j, l (j is the angular momentum of the molecule, l is the angular momentum of the relative motion) into the channel j', l' are, on the average in modulus (after averaging over a small energy interval), equal, provided only that l and l' do not exceed a certain value l_0. The quantity l_0 is determined from the condition that the total probability of transition from the channel j, l_0, calculated in the distorted-wave approximation, should be of order unity. Thus, for the change of angular momenta one obtains the condition $|j' - j| \leq 2l_0$. Assuming the rotation to be quasiclassical ($j, j' \gg 1$), we shall consider cases corresponding to different relations among the quantities j, j', and l_0.

1. The angular momentum of the relative motion l_0 is considerably larger

than the angular momenta j, j' that make the main contribution to the mean rotational energy $(1 \ll j, j' \ll l_0)$. First of all, we note that the statistical character of the distribution over the levels j' means an equiprobable distribution over rotational energies: this follows from the fact that the phase volume $(2j+1)dj$ coincides, to within a constant, with $d\varepsilon$. Then the partial rates of transitions between the states $\varepsilon \to \varepsilon'$ of a diatomic molecule in a heat reservoir can be found on the basis of the following considerations. Deactivation to any level is equiprobable (the condition $j' \ll l_0$); the probability of activation is determined through the probability of deactivation by the principle

detailed equilibrium, and the total cross section for inelastic collision is equal to $\pi l_0^2/k^2$ (3) $(k = \mu v/\hbar)$. The integral equation for the distribution function $x(\varepsilon)$ corresponding to a probability of this type was discussed by Hoare (4). For the case under consideration it has the form

$$\frac{dx(\varepsilon)}{dt} = Z_1 \int \left[K(\varepsilon' \to \varepsilon)x(\varepsilon')\,d\varepsilon' - K(\varepsilon \to \varepsilon')x(\varepsilon)\,d\varepsilon'\right], \tag{1}$$

$$K(\varepsilon' \to \varepsilon) = \beta \exp(\beta\varepsilon') \int_{\max(\varepsilon,\varepsilon')}^{\infty} \frac{1}{s} \exp(-\beta s)\,ds,$$

where

$$Z_1 = \left\langle v\pi \frac{l_0^2}{k^2} \right\rangle n_c.$$

Multiplying (1) by ε and integrating, we find the following equation for the relaxation of the mean rotational energy $\bar{\varepsilon}$:

$$\frac{d\bar{\varepsilon}}{dt} = -k_1(\bar{\varepsilon} - kT), \qquad k_1 = \frac{1}{2} Z_1. \tag{2}$$

Thus, $\bar{\varepsilon}$ relaxes according to a simple exponential law. Relation (2) makes it possible to connect the experimentally observed rotational relaxation time τ_1 (for example, from the thickness of the shock-wave front) and the quantity l_0, which characterizes the anisotropy of the intermolecular potential. In this case l_0 has no direct relation to the probability of a one-quantum rotational transition (see on this point the note on p. 303 in the book (1)). Setting $l_0 = \mu v R_0/\hbar$, we find $\tau_1 = 2/\pi R_0^2 \bar{v}$, with the condition $j \ll l_0$ imposing a lower bound on R_0:

$$\sqrt{\frac{M}{\mu}}\, r_e \ll R_0. \tag{3}$$

2. The angular momentum of the relative motion l_0 is substantially smaller than $\bar{j}$ and j' ($\bar{j}, j' \gg l_0 \gg 1$). The relaxation can be described as diffusion in energies, with the distribution function obeying the Fokker–Planck equation (see, for example, (^{5}))

$$\frac{\partial x(\varepsilon)}{\partial t} = \frac{1}{2}\frac{\partial}{\partial\varepsilon}\left[Z_2\langle\Delta\varepsilon^2\rangle\beta\left(1+\frac{1}{\beta}\frac{\partial}{\partial\varepsilon}\right)\right]x(\varepsilon). \tag{4}$$

The factor $Z_2\langle\Delta\varepsilon^2\rangle$ is equal to the mean square of the energy transferred to the molecule per unit time. Defining the number of collisions Z_2 as $v\pi R_0^2 n_c$, the quantity $\langle\Delta\varepsilon^2\rangle$ can be calculated with a U-shaped distribution function over the transferred energies, whose limits are determined by the relation $\Delta j_{\max} = 2l_0$, or $\Delta\varepsilon^{\pm} = 4\sqrt{B}\,l_0\sqrt{\varepsilon}$. In this way we obtain

$$\frac{1}{2}Z_2\langle\Delta\varepsilon^2\rangle = \left\langle v\pi R_0^2\frac{8}{3}Bl_0^2\right\rangle n_c\varepsilon, \tag{5}$$

where the averaging on the right-hand side has been performed with the equilibrium velocity distribution function. The solution of equation (4) for the case in which the mean square transferred energy is proportional to the energy is well known (^{5,6}).

The principal feature of the relaxing system is that, first, the mean energy (the first moment of the distribution function) relaxes independently of the higher moments, analogously to equation (2), and the corresponding rate constant k_2 is equal to $\beta Z_2\langle\Delta\varepsilon^2\rangle/\varepsilon$. Assuming, for simplicity, R_0 independent of v, we find

$$k_2 = \frac{1}{\tau_2} = \bar{v}\pi R_0^2\frac{16}{3}\frac{R_0^2}{r_e^2}\frac{\mu}{M}. \tag{6}$$

Second, the initial Boltzmann distribution relaxes to the final one through a sequence of distributions of the same type. Although the form of the relaxation equations for ε, obtained from (1) and (6), is the same,

nevertheless, the latter conclusion is not valid for the distribution function of equation (1). The conditions of quasiclassicality of the collision and the condition $j \gg l_0$ take the form

$$\lambda \ll R_0 \ll r_e\sqrt{\frac{M}{\mu}}, \tag{7}$$

where λ is the wavelength of the relative motion of AB and C.

3. The angular momentum of relative motion l_0 is substantially smaller than j, and the relative motion of AB and C is not quasiclassical ($\bar{j}$, $\bar{j}' \gg l_0 \sim 1$). Such a situation corresponds to the collision of a slow electron

with a diatomic molecule, where l_0 in this case denotes the maximum effective angular momentum contributing to the scattering. Under typical conditions the interaction is weak, and the cross section can be calculated in the Born approximation. For quasiclassical rotation of the molecule and far from threshold, the cross section is equal to (7)

$$\sigma(j',j) = \sum_m N_m \frac{2j'+1}{(2m+1)^2} C^2(j,j',m(000)),$$

$$N_m = \int d\omega \left| \int_0^\infty r^2 \frac{2\mu}{\hbar^2} V_m(r) J_m(\Delta kr)\, dr \right|^2, \tag{8}$$

where $V_m(r)$ are the coefficients in the expansion of the electron-molecule potential in Legendre polynomials $P_m(\cos\theta)$, and N_m does not depend on j under the condition $\hbar^2(k^2 - {k'}^2)/\mu \gg Bjl_0$. Then the calculation of $Z_3\langle\Delta\varepsilon^2\rangle$ can be carried out in closed form:

$$^1/_2\, Z_3\langle\Delta\varepsilon^2\rangle = \left[B \sum_m \langle vN_m(v)\rangle\, P'_m(1)/(2m+1) \right] \varepsilon. \tag{9}$$

Thus, in case 3 the relaxation kinetics is analogous to the relaxation kinetics for case 2, and the rate constant of relaxation of the mean energy is equal to

$$k_3 = \beta B \sum_m \langle vN_m\rangle \frac{P'_m(1)}{2m+1}. \tag{10}$$

The condition of applicability of the first approximation of perturbation theory for slow electrons can formally be expressed in terms of the collision radius $R_0 \sim \sqrt{\sigma}$ as

$$R_0 \lesssim \lambda. \tag{11}$$

The three limiting cases (3), (7), and (11) make it possible to trace qualitatively the influence of changes in the reduced mass on the rate of rotational relaxation. As the ratio μ/M decreases, the relaxation rate falls. However, the relative contribution of inelastic processes to the rate of energy relaxation of light partners increases (relative to elastic ones) by the factor $16R_0^2/3r_e^2$ under condition (7), and by the factor $\sim \dfrac{M}{\mu}\dfrac{B}{kT}$ under condition (11). Conditions are quite probable in which these factors are quantities of the order of 10 and 100, respectively.

Let us now dwell on one application of relations (4) and (10). In accordance with them, the rotational relaxation of molecules in a heat reservoir of light particles (electrons) can be described by an equation in which conservation of the Boltzmann distribution is taken into account:

$$\frac{dT_{\mathrm{vr}}}{dt} = -k_3(T_{\mathrm{el}})\,[T_{\mathrm{vr}} - T_{\mathrm{el}}], \tag{12}$$

where T_{rot} is the rotational temperature of the molecular gas, and T_{el} is the electron temperature. Suppose that the system of rotating molecules and electrons is isolated, and that the Maxwellian distribution of the electrons is maintained by collisions between them. Then, evidently, the relaxation equation for the electron temperature must have the form

$$\frac{dT_{\mathrm{el}}}{dt} = -k_3(T_{\mathrm{el}})[T_{\mathrm{el}} - T_{\mathrm{rot}}]. \tag{13}$$

This equation is nonlinear; it is valid, in particular, also in the case where $T_{\mathrm{rot}} =$ const. Then (13) describes the change in the electron temperature in the process most effective for slow electrons—inelastic excitation of molecular rotation. In the linear approximation $k_3(T_{\mathrm{el}})$ should be replaced by $k_3(T_{\mathrm{rot}})$. The limits of applicability of the linear approximation are easy to find, since the temperature dependence of k_3 is known in principle. Thus, for the quadrupole-monopole interaction, which is most effective in the case of molecules with identical nuclei, k_3 is equal to

$$k_3 = {}^{16}/_{15}\sqrt{\pi}\, a_0^2 q^2 B\beta \sim T^{-1/2}, \tag{14}$$

where q is the quadrupole moment of A_2 (in atomic units). Comparison of (14) with the result of a direct numerical calculation k_3' (7), as the limit of the ratio

$$k_3' = \lim_{T_{\mathrm{el}} \to T} (dT_{\mathrm{el}}/dt)/(T - T_{\mathrm{el}}) \tag{15}$$

for the case of N_2 leads to agreement between them. A discrepancy of about 10% is obtained only in the region of low temperatures ($T = 100$°K), which is connected with the insufficient accuracy of the quasiclassical approximation (for this case $\bar{j} \sim 6$). Hence it follows, for example, that the linear relaxation equation at $T_{\mathrm{rot}} = 300$°K and $T_{\mathrm{el}} = 700$°K overestimates the rate of the initial stage of relaxation by $\sqrt{7/3} \sim 1.5$ times, which is in agreement with the numerical results of work (7).

In atom-molecule collisions, equation (4) is applicable for describing the rotational relaxation of molecules of the J_2 type in an atmosphere of a light gas (He) under conditions, for example, of photoexcitation (see (1), p. 305). As for equations (1) and (2), when applied to experimental data on the rotational relaxation of oxygen and nitrogen, they give a reasonable estimate for R_0: the value of R_0 turns out to be 2–3 times smaller than the van der Waals radius of the colliding molecules.

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