VIBRATIONAL RELAXATION OF J_2 IN A J_2–He MIXTURE

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Abstract

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VIBRATIONAL RELAXATION OF J_2 IN A J_2–He MIXTURE

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The study of vibrational relaxation, as is known, makes it possible to obtain information on the probabilities of transfer of vibrational energy into translational energy in molecular collisions. In the most studied cases of vibrational relaxation (relaxation in a pure gas or in a mixture whose components do not differ greatly in mass), this information pertains mainly to the probabilities of transition in almost adiabatic collisions, i.e., under conditions when $\omega\tau \gg 1$ ([1]), $\omega = \Delta E/\hbar$, where ΔE is the transferred energy and τ is the duration of the collision. The study of vibrational relaxation of J_2 in a J_2–He mixture is of special interest in this respect, since the process of transfer of vibrational energy into translational energy in collisions of J_2 and He molecules, even at room temperatures, takes place under conditions of strong nonadiabaticity ($\omega\tau \ll 1$).

The probability of transfer of vibrational energy into translational energy in a collision of molecules under conditions of strong nonadiabaticity was calculated in ([2]). In particular, the probability of transition of a diatomic molecule from the n-th vibrational state to the m-th in a collision with some atom has the form*

$$p_{nm}(v) = \left| \int_{-\infty}^{\infty} \psi_m^*(x) \exp(-2i\lambda k_n x) \psi_n(x)\, dx \right|^2, \tag{1}$$

where $\psi_p(x)$ are the wave functions of the molecule, which in what follows will be approximated by the harmonic-oscillator model; $k_n = Mv/\hbar$ is the wave number of the incident atom; M is the reduced mass of the colliding particles; $\lambda = 1/2$ for molecules with identical atoms. From formula (1) it is seen that, in molecular collisions under conditions of strong nonadiabaticity, multiquantum energy transitions occur. In this case the scheme for calculating the time of vibrational relaxation developed in the work of Landau and Teller ([3]) is inapplicable, since it is based on the assumption of one-quantum transitions. However, in the case of a J_2–He collision the situation is substantially simplified.

Let us consider the quantity $k_n x_{\text{cp}}$, where $x_{\text{cp}} \sim \sqrt{\hbar/2\mu\omega}$ is the mean amplitude of oscillations of the atoms in the molecule, and μ is the reduced mass of the molecule:

$$k_n x_{\text{cp}} \sim \sqrt{\frac{M}{\mu}\frac{Mv^2}{2\hbar\omega}} \sim \sqrt{\frac{M}{\mu}\frac{T}{\theta}},$$

where $\theta = \hbar\omega/k$ is the characteristic temperature. For $T/\theta \ll \mu/M \sim 16$, the condition $k_n x_{\text{cp}} \ll 1$ will always be satisfied. In this case the exponential in (1) may be expanded in a series in powers of $k_n x_{\text{cp}}$ and one may restrict oneself to the first nonvanishing term. In this way we obtain

$$p_{nm} = \left|k_n(\psi_m^*|x|\psi_n)\right|^2. \tag{2}$$

It follows from formula (2) that, for the molecular model under consideration, p_{nm} differs from zero only for $m = n \pm 1$. Thus, in a collision

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* Formula (1) is valid for $\Delta E \ll Mv^2/2$.

molecules J_2 with He in a certain range of relative-motion energies only single-quantum transitions take place. The probability of these transitions, averaged over the Maxwellian distribution, has the form

$$P_{n+1,n} = (n+1)P_{10},$$

where

$$P_{10} = 2\left(\frac{M}{2kT}\right)^2 \int_0^\infty v^3 p_{10}(v) \exp\left(-\frac{Mv^2}{2kT}\right) dv = \frac{2kT}{\hbar\omega}\frac{M}{\mu}. \tag{3}$$

In accordance with the preceding,

$$\frac{2kT}{\hbar\omega}\frac{M}{\mu} \ll 1.$$

In calculating P_{10} it was assumed that $T > \theta$. In all other cases the values of P_{10} will be smaller than (3).

For relaxation processes effected by means of single-quantum transitions, the Landau–Teller scheme is valid, as already indicated. Therefore, for the vibrational relaxation time one may write

$$\tau = \left[ZP_{10}\left(1 - e^{-\hbar\omega/kT}\right)\right]^{-1}, \tag{4}$$

where Z is the number of collisions of a J_2 molecule with He atoms per second. For $\hbar\omega/kT \ll 1$,

$$\tau = \left[ZP_{10}\frac{\hbar\omega}{kT}\right]^{-1} = \left[Z \cdot 2\frac{M}{\mu}\right]^{-1}. \tag{5}$$

The vibrational relaxation time, as is evident from formula (5), corresponds to several tens of collisions, i.e., to the order of the time for establishment of the Maxwellian distribution in a heavy gas [4], present as a small admixture in a light one. This latter circumstance, however, does not affect the calculation of P_{10}. Indeed, even under equilibrium conditions the mean thermal velocities of J_2 molecules are an order of magnitude smaller than the mean thermal velocities of He molecules; therefore, in averaging over relative-motion velocities the J_2 molecules may be regarded as at rest, and the Maxwellian distribution may be used for the incident He molecules.

Expression (4) is valid approximately up to 1000° K. Under these conditions the quantity $P_{10}(1 - e^{-\hbar\omega/kT})$ should depend only weakly on temperature. The result obtained can be checked experimentally by studying vibrational relaxation in a J_2–He mixture by the ultrasonic method or by means of a shock tube. In doing so, one should bear in mind that under the conditions considered $P_{10}(J_2—J_2) \ll P_{10}(J_2—\text{He})$ [5,6], and therefore practically no restrictions are imposed on the ratio of the concentrations of J_2 and He. At the same time, it is most desirable to study vibrational relaxation under "isothermal" conditions, when the J_2 molecules constitute a small admixture in He. If He is replaced by hydrogen, the upper limit of applicability of (4) is shifted toward higher temperatures. In the latter case, however, the picture is somewhat complicated by the appearance of HJ molecules.

On passing to higher temperatures in a J_2–He mixture, the condition $k_n x_{\text{cp}} \ll 1$ is violated and the energy transitions become multiquantum. In this case the process of vibrational relaxation will proceed faster than follows from formula (4).

On passing to heavier inert gases, first of all the condition $\omega\tau \gg 1$ is violated. For $\omega\tau \sim 1$ there are no data on the transition probability; therefore, at present it is not possible to make any quantitative judgments about the vibrational relaxation time in this case. Qualitatively, one may point to two opposite tendencies that appear on passing to heavier inert gases. On the one hand, the difference in the masses of the components decreases, and this facilitates exchange

energies. On the other hand, there is an increase in $\omega\tau$, and this makes energy exchange more difficult.

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