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Abstract

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THEORY OF VIBRATIONAL EXCITATION OF MOLECULES IN THE IMPULSE APPROXIMATION

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The general theory of scattering in the impulse approximation, developed in ([2]) and representing a new formulation of the method first proposed in ([1]), can be used, in particular, to calculate the probabilities of vibrational transitions in molecules characterized by sufficiently small frequencies. In this special case the method of ([2]) can be formulated as follows. Let the interaction potential V of the incident atom with the molecule be represented as a sum of pair potentials $V_\nu(\mathbf{r}-\mathbf{r}_\nu)$, i.e.

$$V=\sum_{\nu=1}^{N} V_\nu(\mathbf{r}-\mathbf{r}_\nu);$$

$\mathbf{r}$ are the coordinates of the incident particle; $\mathbf{r}_\nu$ are the coordinates of the atoms making up the molecule; N is the number of atoms in the molecule. Suppose further that, at least for one of the atoms in the molecule, the condition

$$\frac{\bar{\omega}_\nu A_\nu}{v_{n-\nu}} \ll 1, \qquad \bar{\omega}_\nu=\sum_{i=1}^{s} m_\nu \overline{(\mathbf{n}\mathbf{c}_\nu^i)^2}\,\omega_i; \tag{1}$$

is fulfilled. Here $\mathbf{n}$ is a unit vector; $A_\nu, v_{n-\nu}$ are the effective interaction radius and the relative velocity of the ν-th atom in the molecule and the incident particle; $\mathbf{c}_\nu^i$ are amplitude vectors (i.e.

$$\mathbf{r}_\nu^{\text{vib}}=\sum_{i=1}^{s}\mathbf{c}_\nu^i Q_i,$$

Q_i are generalized coordinates of the molecule); $\omega_1,\ldots,\omega_s$ are the vibrational frequencies of the molecule. Then the cross section for the transition of the molecule $d\sigma_{if}$ from one vibrational-rotational state ψ_i to another ψ_f due to collision of the incident atom with the ν-th atom in the molecule is given by a formula that is a certain generalization of the Fermi pseudopotential method:

$$d\sigma_{if}^{(\nu)} = \frac{k}{k_0}\left|\frac{m}{2\pi\hbar^2}\int \psi_i e^{-i(\mathbf{k}-\mathbf{k}_0)\mathbf{r}}\hat{V}_\nu(\mathbf{r}-\mathbf{r}_\nu)\psi_f^*\,d\mathbf{r}\prod_{\nu'}(d\mathbf{r}_{\nu'})\right|^2 do, \qquad (2)$$

where k_0, k are the wave numbers of the incident particle before and after scattering, do is the element of solid angle into which the incident particle is scattered, and $\hat{V}_\nu$ is a certain effective potential, different from V_ν and connected with the amplitude of pair scattering $F_\nu(\mathbf{k}_{\nu 0}, \mathbf{k}'_{\nu 0})$ in the collision of the incident particle with the ν-th atom in the following way:

$$F(\mathbf{k}_{\nu 0}, \mathbf{k}'_{\nu 0}) = \frac{\mu_\nu}{2\pi\hbar^2}\int \hat{V}_\nu(\vec{\rho})e^{i\vec{\chi}\vec{\rho}}\,d\vec{\rho}, \qquad \mathbf{k}_{\nu 0} = \mathbf{k}'_{\nu 0} + \vec{\chi} = \frac{m_\nu \mathbf{k}_0}{m_\nu + m}; \qquad (3)$$

μ_ν are the reduced masses of the colliding particles with masses m and m_ν.

If rotational transitions are treated classically (this is possible, since we shall henceforth assume everywhere the energy of the colliding particles to be much greater than the distances between vibrational, and still more rotational, levels), while the vibrational states i, f are described by the wave functions of a harmonic oscillator, then from (2) there follows the following expression for the cross section of scattering accompanied by transfer to the molecule of vibrational energy $\sum_{i=1}^{s} n_i\hbar\omega_i$ and rotational energy E:

$$d\sigma_\nu = \frac{k}{k_0}|F_\nu|^2\left(\frac{m_\nu + m}{m_\nu}\right)^2 \times \qquad (4)$$

$$\times\left\langle \delta\left(E - \frac{\hbar^2}{2}\vec{\chi}\mathbf{R}_\nu\vec{\chi} - \frac{\hbar^2\chi^2}{2M}\right)\exp\left(-\sum_{i=1}^{s}\frac{\hbar(\vec{\chi}\mathbf{c}_\nu^i)^2}{2\omega_i}\right)\prod_{i=1}^{s}\frac{1}{n_i!}\left[\frac{\hbar(\vec{\chi}\mathbf{c}_\nu^i)^2}{2\omega_i}\right]^{n_i}\right\rangle dE\,do;$$

M is the mass of the molecule; $\vec{\chi} = \mathbf{k}_0 - \mathbf{k}$; m_ν are the masses of the atoms in the molecule; m is the mass of the incident particle; R_ν is the molecular mass tensor (see (3)); in the case of a diatomic molecule, the only nonzero components of the tensor R are $R_{1,2}^{11} = R_{1,2}^{22} = m_{2,1}/(m_1 + m_2)$; the sign $\langle\ \rangle$ denotes averaging over the orientations of the molecule. Expression (4) should be summed over all atoms of the molecule for which condition (1) is satisfied, which gives, generally speaking, the total cross section for vibrational excitation of the molecule. Indeed, one should expect that if condition (1) is not satisfied, but the opposite condition $\bar{\omega}\sqrt{A_\nu}/v_{n-\nu} > 1$ holds, then the contribution from the corresponding atoms may be neglected, since collisions with them will occur adiabatically and be characterized by exponentially small probabilities.

Let us first consider, on the basis of (4), the vibrational excitation of diatomic molecules. In this case formula (4), after averaging over the orientations of the molecule, is simplified as follows:

$$d\sigma^{(1),(2)} = \frac{k}{k_0}\left(\frac{m_{1,2}+m}{m_{1,2}}\right)^2\left[\frac{(m_1+m_2)m_{1,2}}{2m_{2,1}}\right]^{-1/2}|F_{1,2}|^2\frac{1}{\hbar\chi\sqrt{\hbar^2\chi^2/2m_{1,2}-E}}\times$$

$$\times\frac{1}{n!}\left[\frac{1}{\hbar\omega}\left(\frac{\hbar^2\chi^2}{2m_{1,2}}-E\right)\right]^n\exp\left[-\frac{1}{\hbar\omega}\left(\frac{\hbar^2\chi^2}{2m_{1,2}}-E\right)\right]dE\,do. \qquad (5)$$

To find the total cross section for vibrational excitation it is necessary to integrate (5) over the angles and rotational energies E. We shall carry out this integration, assuming that $|F_{1,2}|^2 = \frac{1}{4\pi}\sigma_0^{(1),(2)} = \text{const}$. Strictly speaking, this corresponds to the interaction between the incident particle and an atom in the molecule according to the hard-sphere model; in fact, however, the result will be valid for any short-range potential corresponding to $|F_\nu|^2$ that varies only weakly over an angular interval of order $\sqrt{\hbar\omega/E_0}$ (E_0 is the energy of the incident particle in the center-of-inertia system particle–molecule), over which the exponent $(\hbar^2\chi^2/2m - E)/\hbar\omega$ in (5) changes substantially. Thus we find for the cross section $\sigma_{0n} = \sigma_{0n}^{(1)} + \sigma_{0n}^{(2)}$ of the transition from the ground vibrational state to a state with vibrational energy $n\hbar\omega$ the formula ($E_0 \gg n\hbar\omega$):

$$\sigma_{0n}^{(1),(2)} = \frac{1}{2}\sigma_0^{(1),(2)}\frac{1}{n!}\left[x_{1,2}^{-1/2}\Gamma\left(n+\frac{1}{2},x_{1,2}\right) - x_{1,2}^{-1}\Gamma\left(n+1,x_{1,2}\right)\right]; \qquad (6)$$

$$\sigma_{01}^{(1),(2)} = \frac{1}{2}\sigma_0^{(1),(2)}\left[x_{1,2}^{-1/2}\int_0^{x_{1,2}^{1/2}} e^{-t^2}\,dt - x_{1,2}^{-1}\left(1-e^{-x_{1,2}}\right) + e^{-x_{1,2}}\right], \qquad (6a)$$

where $x_{1,2} = E_{\max}^{(1),(2)}/\hbar\omega$; $\Gamma(p,x) = \int_0^x e^{-t}t^{p-1}\,dt$ is the incomplete gamma function;

$$E_{\max}^{(1),(2)} = \frac{4m_{1,2}m}{(m_{1,2}+m)^2}\frac{m_{2,1}}{m_1+m_2}\frac{m+m_1+m_2}{m_1+m_2}E_0$$

has the meaning of the maximum energy transferred to the first or second atom in the center-of-inertia system incident particle–molecule.

In the case $E_{\max} \ll \hbar\omega$, it follows from (6) that

$$\sigma_{0n}^{(1),(2)} = \frac{1}{2}\sigma_0^{(1),(2)}\frac{1}{(n+1)!(2n+1)}\left(\frac{E_{\max}^{(1),(2)}}{\hbar\omega}\right)^n. \qquad (7)$$

Thus, in this case σ_{0n} decreases rapidly with the number n, i.e. with the vibrational excitation energy $n\hbar\omega$.

Fig. 1

Figure 1: Fig. 1

In the other limiting case $E_{\max} \gg \hbar\omega$, we have

$$\sigma_{0n}^{(1),(2)} = \frac{1}{2}\sigma_0^{(1),(2)}\frac{\Gamma(n+1/2)}{n!}\sqrt{\frac{\hbar\omega}{E_{\max}^{(1),(2)}}}, \tag{8}$$

i.e. σ_{0n} decreases inversely proportionally to the velocity of the incident particle and depends only very weakly on n (as $n^{-1/2}$ for $n \gg 1$).

Formula (6) can be used to find the quantity $\overline{\sigma_{01}v}$, averaged over the Maxwell distribution of the colliding particles, which determines the rate of excitation of the first vibrational level under gas-kinetic conditions and, in particular, the vibrational relaxation time τ according to the Landau-Teller scheme $1/\tau = \overline{\sigma_{01}v}\,N(1-e^{-\hbar\omega/kT})$ (N is the particle density). The result of the integration can be represented by a simple formula, which we give for the case $m_{1,2} \gg m$:

$$\overline{\sigma_{01}^{(1),(2)}v} = \frac{1}{\sqrt{\pi}}\,\sigma_0^{(1),(2)}\left(\frac{2\hbar\omega}{m}\right)^{1/2}\gamma_{1,2}^{1/2}\frac{\hbar\omega}{kT}\Phi(q_{1,2}); \tag{9}$$

$$\Phi(q) = \frac{1}{2q}\left[\frac{\pi}{2} - \operatorname{arc\,tg}\frac{1}{\sqrt{q}}\right] - \frac{1}{2}\,\frac{1}{\sqrt{q}\,(q+1)}; \qquad q_{1,2} = \gamma_{1,2}\frac{kT}{\hbar\omega};$$

$$\gamma_{1,2} = 4\,\frac{m}{m_{1,2}}\,\frac{m_{2,1}}{m_1+m_2} \ll 1.$$

Fig. 1

Figure 1 gives the plot of the function $1/\Phi(q)$, which has a minimum $\Phi_{\min} \simeq 7$ at $q_{\min} \simeq 0.5$. For $q \ll 1$, it follows from (9) that

$$\overline{\sigma_{01}v} = \frac{\sigma_0}{3\sqrt{\pi}}\left(\frac{2kT}{m}\right)^{1/2}\gamma\,\frac{kT}{\hbar\omega},$$

whereas for $q \gg 1$ we have

$$\overline{\sigma_{01}v} = \frac{\sqrt{\pi}}{4}\,\sigma_0\left(\frac{2\hbar\omega}{m}\right)^{1/2}\gamma^{-1/2} = \text{const}.$$

As can be shown, in the region $q \lesssim 1$ the quantities $\overline{\sigma_{0n}v}$ characterizing multiquantum transitions turn out to be considerably smaller than $\overline{\sigma_{01}v}$. This makes it possible, in calculating the vibrational relaxation time, to apply for $q \lesssim 1$,

i.e., in the most interesting region of the minimum of $\tau(T)$, the Landau-Teller scheme, which in the case under consideration leads to the formula

$$\frac{1}{\tau} = \frac{1}{\sqrt{\pi}} \left(\frac{2\hbar\omega}{m}\right)^{1/2} N \left[\sigma_0^{(1)} \gamma_1^{1/2} \Phi(q_1) + \sigma_0^{(2)} \gamma_2^{1/2} \Phi(q_2)\right], \tag{10}$$

or, for $m_1 = m_2 = m_0,\ \gamma_1 = \gamma_2 = \gamma$:

$$\frac{1}{\tau} = \frac{2}{\sqrt{\pi}} \left(\frac{2\hbar\omega}{m}\right)^{1/2} \sigma_0 N \gamma\, \Phi(q). \tag{10a}$$

According to (10a), the temperature dependence of τ has a minimum at

$$T_{\min} = \frac{1}{4} \frac{m_0}{m} \frac{\hbar\omega}{k}$$

and

$$\tau_{\min} = \left(11\, \gamma \sigma_0 N \sqrt{\frac{2kT}{m}}\right)^{-1}.$$

For $q \ll 1$, it follows from (10a) that

$$\frac{1}{\tau} = \frac{2}{3\sqrt{\pi}} \left(\frac{2kT}{m}\right)^{1/2} \frac{2m}{m_0}\, \sigma_0 N. \tag{11}$$

For the case of the mixture $J_2 + He$, to which the theory under consideration is applicable already at room temperatures, the minimum of $\tau(T)$ lies at $T_{\min} \simeq 2100^{\circ}$K (we take, for the ground electronic state of J_2, $\omega = 214$ cm^{-1} and $\gamma = 1/10$). The existence of a minimum of $\tau(T)$ can apparently be observed in experiments measuring the vibrational relaxation time behind a direct shock wave in the mixture $J_2 + He$.

The regularities set forth above, calculated for the example of diatomic molecules, are in principle also valid for polyatomic molecules, although a rigorous calculation of vibrational-excitation cross sections for them is difficult because the averaging over orientation in (4) generally leads to very complicated expressions. It is possible, however, to give approximate formulas based on replacing the rigorous averaging over orientation in (4) by the introduction of certain orientation-averaged quantities $\overline{\vec{\varkappa} R_\nu \vec{\varkappa}}$, $\overline{(\vec{\varkappa} c_i^\nu)^2}$. Thus, the total cross section for vibrational excitation of a polyatomic molecule $\sigma_{0n}^{(\nu)}$ as a result of its collision with the ν-th atom

can be represented (under the assumption $|F_\nu|^2 = \frac{1}{4\pi}\sigma_0^{(\nu)} = \text{const}$) by the simple formula

$$\sigma_{0n}^{(\nu)} = \sigma_0^{(\nu)} \prod_{i=1}^{s} \frac{1}{n_i!} \left(\frac{\overline{\omega_{i\nu}^{-1}}}{\overline{\omega_\nu^{-1}}} \right)^{n_i} \frac{1}{x} \Gamma \left(\sum_{i=1}^{s} n_i + 1, x \right), \tag{12}$$

where

$$\overline{\omega_{i\nu}^{-1}} = m_\nu (n c_\nu^i)^2 / \omega_i, \qquad \overline{\omega_\nu^{-1}} = \sum_{i=1}^{s} \overline{\omega_{i\nu}^{-1}}, \qquad x = 4 \frac{m m_\nu}{(m+m_\nu)^2} \frac{m + \sum m_\nu}{\sum m_\nu} E_0 \overline{\omega_\nu^{-1}}.$$

For $x \ll 1$, (12) gives the formula

$$\sigma_{0n}^{(\nu)} = \sigma_0^{(\nu)} \prod \frac{1}{n_i!} \left(\frac{\overline{\omega_{i\nu}^{-1}}}{\overline{\omega_\nu^{-1}}} \right)^{n_i} \frac{1}{\sum_{i=1}^{s} n_i} x^{\sum_{i=1}^{s} n_i}, \tag{13}$$

analogous to (7). Application of formula (12) to diatomic molecules leads to an expression for $\sigma_{01}\nu$ that is in approximate quantitative agreement with (9). Formulas (12), (13) can be used to calculate the cross sections of vibrational excitation of polyatomic molecules for which either all fundamental frequencies are small (for example JCN), or the effective frequencies $\overline{\omega}_\nu$ of vibrations of individual atoms are small (the latter may occur, in particular, when hydrogen bonds are present in the molecule).

In conclusion, let us compare the results of the present work with the results of some authors who calculated the probabilities of vibrational excitation of diatomic molecules under conditions analogous to our condition (1). In work ([4]), an idealized model was used of a one-dimensional collision of an incident atom with one of the atoms in the molecule, under an additional condition analogous to $q = \gamma kT/\hbar\omega \ll 1$. The formula found in ([4]) for τ coincides, up to a constant factor, with our formula (11), which is the limiting case of the more general formula (10), covering a broad region $q \lesssim 1$. Let us note that, according to ([4]), only transitions between neighboring levels are allowed, whereas our formula (6) leads to the conclusion that transitions between any two vibrational levels are allowed, and moreover with appreciable probabilities. In work ([5]), three-dimensional collisions of an incident atom with a molecule were considered, the molecule being approximated by the model of a "harmonically oscillating hard sphere." As the authors themselves note ([5]), this model is very far from reality and does not claim quantitative results ([5], p. 178). It is therefore not surprising that formula (6) found in our work, whose derivation was made without the use of any arbitrary assumptions, leads to results that differ noticeably from the results of the numerical calculations of ([5]). In particular, according to ([5]), the

maximum of $\sigma_{01}(E_0)$ lies at $E_0/\hbar\omega \sim 2.5$, whereas from our formula (6a) it follows that this maximum lies at $E_{\max}/\hbar\omega \sim 3$, i.e. at $E_0/\hbar\omega \sim m_{1,2}/m$ (if $m \ll m_{1,2}$). For a large or small mass ratio $m/m_{1,2}$, the difference in the positions of the maxima of $\sigma_{01}(E_0)$ may be very large.

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CITED LITERATURE

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