

振動的遷移確率의計算, $N_2 + Ar^*$

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Calculation of Vibrational Transition Probabilities in
 $N_2 + Ar$ by Use of Crossed Beam Scattering Data*

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Some of the potentials frequently used in the theory of molecular energy transfer are described in terms of powers of the separation r between the centers of mass of the colliding particles; of these the Lennard-Jones (12-6) function is most commonly used¹⁻⁶. The quantitative knowledge that is available on the Lennard-Jones(LJ) potential has been derived from a knowledge of macroscopic properties of the gas, such as the viscosity and the second virial coefficient; i. e., the knowledge obtained from the properties depend on the behavior of a gas in near-equilibrium⁷. Therefore, use of such knowledge to calculate transition probabilities or collision cross sections is unsatisfactory since we are now interested in the properties of a gas in short range which is far removed from equilibrium. In recent years, important progress, however, has been made in determining intermolecular potentials from molecular beam experiments⁸⁻¹⁰. Tully and Lee⁹ have deter-

mined the potential parameters for the LJ (20-6), (12-6), and (8-6) functions from crossed beam experiments for $N_2 + Ar$, $N_2 + Kr$, $O_2 + Ar$, and $O_2 + Kr$ systems; they have found that the LJ (12-6) and (20-6) potentials give best agreement to the angular distribution of the rainbow extrema.

The purpose of this Letter is to derive an analytic expression for the vibrational transition probability of atom+diatomic system, by use of the LJ (12-6) potential for which potential parameters are available from crossed beam experiments⁹, which provides a framework for discussing the dependences of vibrational transitions on collision velocity, orientation angle, and impact parameter. For this purpose we shall construct the overall interaction potential, which contains the perturbing force, in a general form based on the information on the relative motion determined from beam experiments.

The experimental data by Tully and Lee provides information only on the spherically symmetric portion of the overall interaction

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potential. This potential can be used to determine the collision time and/or the collision trajectory of the relative motion. In studying molecular energy transfer problems, in addition to the r dependence, we also need to know the dependence of the interaction energy on the vibrational and orientation coordinates. However, from the knowledge of interaction potential obtained from scattering experiments, with some reasonably reliable procedures, we construct a form of the overall potential, which is appropriate for the study of vibrational transitions. For this purpose, we take the LJ(12-6) potential, $U(r) = 4D[(\sigma/r)^{12} - (\sigma/r)^6]$, to represent the spherically symmetric portion of the overall interaction.

For the atom+diatomic system, we express the overall interaction potential as

$$U(r_1, r_2) = 2D \sum_{i=1}^2 [(\sigma/r_i)^{12} - (\sigma/r_i)^6], \quad (1)$$

where r_1 and r_2 represent the distances between the incident atom and two atoms of the homonuclear diatomic molecule. This form is chosen because it can produce $U(r)$ as the leading term. The interatomic distances are $r_{1,2} = (r^2 + 2S_{2,1}(d+x)r \cos \theta + S_{2,1}^2(d+x)^2)^{1/2}$, where d is the equilibrium bond distance of the diatomic molecules, x is the displacement of the bond distance from the equilibrium value, θ is the angle between the r and the internuclear axis of the molecule, and $S_{1,2} = m_{1,2}/(m_1+m_2)$, m 's being the atomic masses of the molecule. Equation (1) contains the generating functions r_1^{-12} , r_2^{-12} , r_1^{-6} , and r_2^{-6} , which are functions of r , x , and θ . These generating functions can be developed in terms of the Tschebysheff polynomials of the second kind^{11,12}. The explicit expressions for these functions including terms up to the fourth-order in $(d+x)/r$ are

$$r_{1,2}^{-12} = \frac{1}{r^{12}} \left[1 \pm 6 \left(\frac{d+x}{r} \right) \cos \theta + \left(21 \cos^2 \theta - \frac{3}{2} \right) \right]$$

$$\left(\frac{d+x}{r} \right)^2 \pm \left(56 \cos^3 \theta - \frac{21}{2} \cos \theta \right) \left(\frac{d+x}{r} \right)^3 + \left(126 \cos^4 \theta - \frac{81}{2} \cos^2 \theta + \frac{21}{16} \right) \left(\frac{d+x}{r} \right)^4 \quad (2)$$

$$r_{1,2}^{-6} = \frac{1}{r^6} \left[1 \pm 3 \left(\frac{d+x}{r} \right) \cos \theta + \left(6 \cos^2 \theta - \frac{3}{4} \right) \left(\frac{d+x}{r} \right)^2 \pm \left(10 \cos^3 \theta - 3 \cos \theta \right) \left(\frac{d+x}{r} \right)^3 + \left(15 \cos^4 \theta - \frac{15}{2} \cos^2 \theta + \frac{3}{8} \right) \left(\frac{d+x}{r} \right)^4 \right] \quad (3)$$

Substitution of these equations in eq. (1) gives the overall interaction energy as a function of r , x , and θ ; we shall denote it by $U(r, \theta, x)$:

$$U(r, \theta, x) = 4D \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + 4D \left(\frac{\sigma}{r} \right)^{12} \left[\left(21 \cos^2 \theta - \frac{3}{2} \right) \left(\frac{d+x}{r} \right)^2 + \left(126 \cos^4 \theta - \frac{81}{2} \cos^2 \theta + \frac{21}{16} \right) \left(\frac{d+x}{r} \right)^4 \right] - \left(\frac{\sigma}{r} \right)^6 \left[\left(6 \cos^2 \theta - \frac{3}{4} \right) \left(\frac{d+x}{r} \right)^2 + \left(15 \cos^4 \theta - \frac{15}{2} \cos^2 \theta + \frac{3}{8} \right) \left(\frac{d+x}{r} \right)^4 \right] \equiv U(r) + V(r, \theta, x), \quad (4)$$

in which the second term $V(r, \theta, x)$ represents the perturbation energy that is responsible for vibrational transitions.

To derive the perturbing force in a form which can facilitate the explicit formulation of vibrational transition probabilities, we transform the perturbation energy $V(r, \theta, x)$ into the form $-F(r, \theta)x$, where $F(r, \theta)$ is the orientation-dependent perturbing force which acts on the molecule to cause vibrational transitions. The force can be derived by expanding $V(r, \theta, x)$ in a power series of x/d and taking the terms that are linear in x/d . The resulting expression for $F(r, \theta)$ is

$$F(r, \theta) = 4D \left[\left(\frac{2d}{\sigma^2} \right) \left(21 \cos^2 \theta - \frac{3}{2} \right) \left(\frac{\sigma}{r} \right)^{14} + \left(\frac{4d^3}{\sigma^4} \right) \left(126 \cos^4 \theta - \frac{81}{2} \cos^2 \theta + \frac{21}{16} \right) \left(\frac{\sigma}{r} \right)^{16} - \left(\frac{2d}{\sigma^2} \right) \left(6 \cos^2 \theta - \frac{3}{4} \right) \left(\frac{\sigma}{r} \right)^8 - \left(\frac{4d^3}{\sigma^4} \right) \right]$$

$$\begin{aligned} & \left(15 \cos^4 \theta - \frac{15}{2} \cos^2 \theta + \frac{3}{8}\right) \left(\frac{\sigma}{r}\right)^{10} \\ & \equiv -4D \left[f_1(\theta) \left(\frac{\sigma}{r}\right)^{14} + f_2(\theta) \left(\frac{\sigma}{r}\right)^{16} \right. \\ & \quad \left. - g_1(\theta) \left(\frac{\sigma}{r}\right)^8 - g_2(\theta) \left(\frac{\sigma}{r}\right)^{10} \right] \quad (5) \end{aligned}$$

Then, the amount of vibrational energy transfer derived above is a function of v , θ , and b , and takes the form

$$\Delta E = \frac{1}{2M} \left| \int_{-\infty}^{\infty} F(r(t), \theta) \exp(i\omega t) dt \right|^2 \quad (6)$$

in which the time-dependent perturbing force obtained by parameterizing r in time t . Substitution of eq. (5) in this expression gives

$$\begin{aligned} \Delta E = & \frac{8D^2}{M} \left| f_1(\theta) \int_{-\infty}^{\infty} \left[\frac{\sigma}{r(t)} \right]^{14} \exp(i\omega t) dt \right. \\ & + f_2(\theta) \int_{-\infty}^{\infty} \left[\frac{\sigma}{r(t)} \right]^{16} \exp(i\omega t) dt - g_1(\theta) \\ & \int_{-\infty}^{\infty} \left[\frac{\sigma}{r(t)} \right]^8 \exp(i\omega t) dt - g_2(\theta) \\ & \left. \int_{-\infty}^{\infty} \left[\frac{\sigma}{r(t)} \right]^{10} \exp(i\omega t) dt \right|^2 \quad (7) \end{aligned}$$

For the evaluation of the integrals in this equation, the trajectory can be determined from the equation of motion¹³

$$\begin{aligned} t = & \left(\frac{\mu}{2}\right)^{\frac{1}{2}} \int_{r^*}^r \frac{dr}{[E - E(b/r)^2 - U(r)]^{\frac{1}{2}}} \\ = & i\tau - i \left(\frac{\mu}{2D}\right)^{\frac{1}{2}} \left(\frac{\sigma}{14}\right) \left(\frac{r}{\sigma}\right)^7, \quad (8) \end{aligned}$$

where E is the relative collision energy $\left(\frac{1}{2}\mu v^2\right)$, b is the impact parameter, and t is the collision time defined as $t = (\mu/2)^{1/2} \int_0^{r^*} (U(r) + E(b/r)^2 - E)^{-1/2} dr$, r^* being the distance of closest approach. With eq. (8), the integrals can be evaluated as^{4,13}

$$\int_{-\infty}^{\infty} \frac{\exp(i\omega t)}{(t-i\tau)^n} dt = \frac{2\pi(i\omega)^n}{\omega \Gamma(\omega)} \exp(-\omega\tau); \quad (9)$$

$$n=2, \frac{16}{7}, \frac{8}{7}, \frac{10}{7}$$

We can thus obtain the expression for the magnitude of vibrational energy transfer as

$$\Delta E = \frac{18}{49} \frac{(\pi\mu\omega d)^2}{M} \left\{ \left(\cos^2 \theta - \frac{1}{14}\right) + \frac{2}{\Gamma\left(\frac{6}{7}\right)} \left(\frac{d}{\sigma}\right)^2 \right\}$$

$$\begin{aligned} & \left[\left(\frac{\mu}{2D}\right)^{\frac{1}{2}} \frac{\sigma\omega}{14} \right]^{\frac{1}{2}} \left(6 \cos^4 \theta - \frac{27}{14} \cos^2 \theta + \frac{1}{16}\right) - \frac{1}{\Gamma\left(\frac{8}{7}\right)} \\ & \left[\left(\frac{\mu}{2D}\right)^{\frac{1}{2}} \frac{\sigma\omega}{14} \right]^{\frac{1}{2}} \left(\frac{2}{7} \cos^2 \theta - \frac{1}{28} - \frac{2}{\Gamma\left(\frac{10}{7}\right)} \left(\frac{d}{\sigma}\right)^2 \right) \\ & \left[\left(\frac{\mu}{2D}\right)^{\frac{1}{2}} \frac{\sigma\omega}{14} \right]^{\frac{1}{2}} \left(\frac{5}{7} \cos^4 \theta - \frac{5}{14} \cos^2 \theta + \frac{1}{56}\right) \Bigg\}^2 \\ & \exp(-2\omega\tau) \\ & \equiv \frac{18}{49} \frac{(\pi\mu\omega d)^2}{M} G(\theta) \exp(-2\omega\tau), \quad (10) \end{aligned}$$

where the collision time is¹³

$$\begin{aligned} \tau = & \frac{\Gamma\left(\frac{7}{12}\right)}{\Gamma\left(\frac{1}{12}\right)} \left(\frac{\pi\mu}{2}\right)^{1/2} \frac{\sigma(4D)^{1/12}}{E^{7/12}} \\ & - \frac{\Gamma\left(\frac{13}{12}\right)}{12\Gamma\left(\frac{7}{12}\right)} \left(\frac{\pi\mu}{2}\right)^{\frac{1}{2}} \frac{\sigma(4D)^{7/12}}{E^{13/12}} \\ & + \frac{\Gamma\left(\frac{7}{12}\right)}{12\Gamma\left(\frac{11}{12}\right)} \left(\frac{\pi\mu}{2}\right)^{\frac{1}{2}} \frac{b^2}{(4D)^{1/12} \sigma E^{5/12}} \\ & + \frac{7}{288} \frac{\Gamma\left(\frac{7}{12}\right)}{\Gamma\left(\frac{1}{12}\right)} \left(\frac{\pi\mu}{2}\right)^{1/2} \frac{(4D)^{13/12} \sigma}{E^{19/12}} \\ & + \dots \quad (11) \end{aligned}$$

In eq. (10) the energy and impact-parameter dependences appear in the exponential part determining the duration of collision, and the angle dependence in the pre-exponential parts. By use of this expression we can therefore calculate the amount of vibrational energy transfer at any initial angle (or its orientation-averaged quantity) as a function of energy. The orientation-averaged amount of vibrational energy transfer contains the factor $\bar{G} = \frac{1}{2} \int_0^{\pi} G(\theta) \sin \theta d\theta$.

According to the forced harmonic oscillator model, the vibrational transition probability for $k \rightarrow n$ is^{14,15}

$$P_{kn} = k!n! \varepsilon^{(n-k)} \exp(-\varepsilon) \left| \sum_{l=0}^{\frac{1}{2}} \frac{(-)^l E^l}{l! (k-l)! (n-k+l)!} \right|^2 \quad (12)$$

where $\varepsilon = \Delta E/\hbar\omega$. The first several probabilities take the forms

$$P_{01} = \varepsilon \exp(-\varepsilon), \quad P_{02} = \frac{1}{2} \varepsilon^2 \exp(-\varepsilon),$$

$$P_{03} = \frac{1}{6} \varepsilon^3 \exp(-\varepsilon), \quad P_{12} = 2\varepsilon \left(1 - \frac{1}{2}\varepsilon\right)^2 \exp(\varepsilon),$$

We now present results for the transition probabilities using the expressions given above. The potential parameters determined by Tully and Lee are $\sigma = r_m/2^{1/6} = 3.47 \text{ \AA}$ and $D = 1.88 \times 10^{-4} \text{ erg}$; other well-known molecular constants are¹⁶ $\omega_e = 2359.61 \text{ cm}^{-1}$, $\omega_e x_e = 14.456 \text{ cm}^{-1}$, and $d = 1.094 \text{ \AA}$. Note that when the constants of the angle dependent part $G(\theta)$ are calculated, we have $G(\theta) = 7.20 (\cos^4 \theta + 0.0465 \cos^2 \theta - 0.155)^2$, which becomes zero at 71.2° . The transition probabilities are complicated functions of the angle θ , $G(\theta)$ appearing in both the exponential and pre-exponential parts, but the integration can be readily carried out numerically. We performed the integration on an XDS Sigma-7 computer by Simpson's 1/3 rule. Three different spacings and Richardson's extrapolations are used to improve the results¹⁷.

In Fig. 1, we plot the values of the orientation-averaged transition probabilities \bar{P}_{kn} for $b=0$ as a function of collision velocity. For nonzero impact parameters, the amount of vibrational energy transfer decreases from the

collinear case at a given velocity so the curves shown in Fig. 1 will shift towards high velocity ranges but the general shapes should remain unchanged. Below $v = 3 \times 10^5 \text{ cm/sec}$, as shown in the figure, the probabilities are very small; e. g., at 10^5 cm/sec , $\bar{P}_{01} = 7.48 \times 10^{-17}$ and $\bar{P}_{02} = 1.34 \times 10^{-32}$, while $\bar{P}_{12} = 1.49 \times 10^{-16}$. At $3 \times 10^5 \text{ cm/sec}$, $\bar{P}_{01} = 1.91 \times 10^{-3}$, $\bar{P}_{02} = 8.88 \times 10^{-6}$, $\bar{P}_{03} = 3.50 \times 10^{-8}$, $\bar{P}_{12} = 3.80 \times 10^{-3}$, and $\bar{P}_{13} = 2.63 \times 10^{-5}$, and $\bar{P}_{23} = 5.64 \times 10^{-3}$. As the collision velocity increases, \bar{P}_{kn} rapidly rises to a maximum value; it shows another broad maximum at still higher velocities. For $0 \rightarrow 1$, the first maximum value of 9.55×10^{-2} appears at $4.5 \times 10^5 \text{ cm/sec}$ and the second maximum value of 0.120 at $1.6 \times 10^6 \text{ cm/sec}$, indicating that the $0 \rightarrow 1$ transition is efficient over a wide velocity range above $4 \times 10^5 \text{ cm/sec}$. Other one-quantum transition probabilities vary similarly at lower velocities. However, at higher collision velocities, we find one or more very broad but low maximum values compared to the $0 \rightarrow 1$ case. The numbers of maxima are 2, 3, and 4, respectively, for $0 \rightarrow 1$, $1 \rightarrow 2$, and $2 \rightarrow 3$ transitions.

The first maximum is the sharpest; thereafter, the maxima become broader. The second maximum always takes the largest value. The $0 \rightarrow 2$ and $1 \rightarrow 3$ transitions take substantially smaller probabilities compared to one-quantum transitions below $1.4 \times 10^6 \text{ cm/sec}$, but at higher collision velocities the probabilities are comparable to those of the latter. The $0 \rightarrow 2$ and $1 \rightarrow 3$ transition probabilities take two and three maximum values, respectively. Finally, the $0 \rightarrow 3$ transition probability is the smallest of all of the transitions under considerations below $2 \times 10^6 \text{ cm/sec}$, but above $3 \times 10^6 \text{ cm/sec}$ it is as large

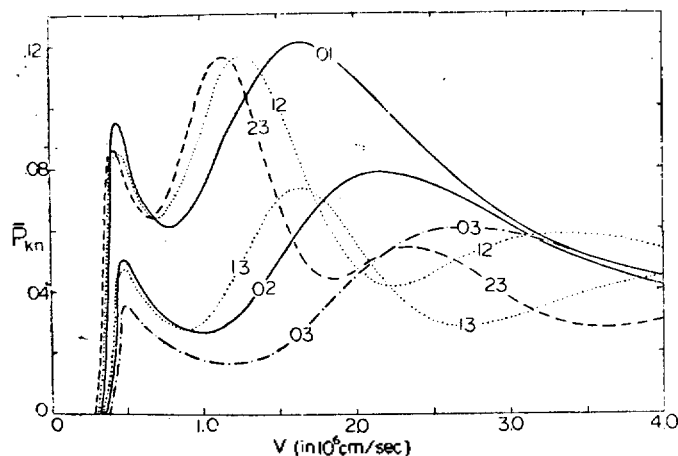


Fig. 1. Variation of the orientation-averaged transition probabilities \bar{P}_{kn} with v for $b=0$.

as the 0→1 probability; the 0→3 probability takes two maximum values, the second maximum being very broad. The figure clearly shows that as the collision velocity increases, many channels are open for vibrational transitions and many of them become important.

The orientation-dependent probability P_{kn} has a much simpler velocity dependence. For example, P_{0n} takes a single maximum value of $n^n \exp(-n)/n!$ at $\epsilon=n$. For the collinear collision (i. e., $\theta=0^\circ$), the maximum values of 0.367, 0.270, and 0.224 then appear for 0→1, 0→2, and 0→3, respectively, in the velocity range 4.5×10^5 – 5×10^5 cm/sec. As shown in Fig. 1, this is the range where the first peaks of the orientation-averaged probabilities \bar{P}_{01} , \bar{P}_{02} , and \bar{P}_{03} appear with the values 9.55×10^{-2} , 5.03×10^{-2} , and 3.54×10^{-2} , respectively, which are significantly smaller than the corresponding collinear probabilities. However, beyond this velocity range, the collinear probabilities rapidly decrease with rising velocity.

From the above results we make the following concluding statements. (1) We have developed a procedure to construct the perturbation energy in an appropriate form for the study of vibrational transitions in atom+diatomic systems on the basis of the knowledge obtained from crossed beam experiments. (2) Application of the vibrational transition probabilities derived from the perturbation energy to N_2+Ar shows that the 0→1, 0→2, 0→3, 1→2, 1→3, and 2→3 probabilities have a complicated structured dependence on collision velocity in the range of 4×10^5 to 4×10^6 cm/sec. In this velocity range, all these transitions are found to be important. (3) In the present collision system, the anisotropy of the interaction potential is not severe. Even so the comparison of \bar{P}_{kn} with \bar{P}_{kn} indicates that the angle dependence can seriously

affect the transition probabilities.

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