ROTATIONAL TRANSITION PROBABILITIES IN TWO DIMENSIONS. A STRONG-COUPLING APPROACH

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ABSTRACT

Rigid rotor collision transition probabilities are calculated for a two-dimensional model by a strong-coupling approach. N_2-Ar interactions are approximated by a sum of Lennard-Jones potentials, and the dependence of the transition probabilities on initial relative translational energy and on initial orbital angular momentum quantum number is investigated. Transitions involving a (*D*m) of the rotor of 4, 6, and even 8 are quite probable even at relatively low energies.

INTRODUCTION

The problem of calculating rotational transition probabilities is one of long standing, dating back to Zener's work in 1931.[1] The older literature is well reviewed by Takayanagi,[2] and by Gordon, Klemperer and Steinfeld.[3] A variety of approaches has been used, including the adiabatic[4] and sudden[5] approximations, and the method of distorted waves.[6,7,8,9,10] Arthurs and Delgarno[11] used Racah's formalism to couple the rigid rotor states with the colliding particle's orbital angular momentum states, with which they then considered several approximations. Takayanagi and Nishimura[12] used the modified wave number method,[2] and Allison and Dalgarno[13] did close-coupling calculations for the 0 *?* 2 rotational transitions of H_2 and D_2.

The major problems with the calculation of rotational transition probabilities are that (1) the interactions are sufficiently strong that some form of close coupling method is needed, and (2) the number of quantum states which must be coupled is large. These difficulties are similar to those which arise in computing molecular vibrational transition probabilities, and we here present an approach to the rotational problem very similar to ones used earlier by Gordon[14] and by ourselves[15] for computing vibrational transition probabilities. We consider the problem in two dimensions for reasons of economy.

ANALYSIS

We consider the model shown in Fig. 1, representing a planar collision of an atom of mass m_3 with a rigid diatomic rotor composed of masses m_1 and m_2 separated by a distance of r_0. Coordinates r, Θ and ϕ are as indicated; the origin is taken as the center of mass of the system, and r is measured from the center of mass of the rotor to m_3; a = $r_0 m_2 / 2 / (m_1 + m_2)$; b = $r_0 m_1 / (m_1 + m_2)$; u_1 and u_2 are the distances between m_3 and atoms 1 and 2, respectively, of the rotor, as given by Eq. (1).

$$u_1^2 = r^2 + a^2 - 2racos(\Theta-\phi)$$

$$u_2^2 = r^2 + b^2 + 2rbcos(\Theta-\phi) \tag{1}$$

The time-independent Schrödinger equation of the system is given by

$$\left[\frac{-\hbar^2}{2\mu r_0^2}\frac{\partial^2}{\partial\Theta^2} - \frac{\hbar^2}{2M}\left(\frac{1}{r}\frac{\partial}{\partial r}\frac{r\partial}{\partial r}\right) - \frac{\hbar^2\partial^2}{2Mr^2\partial\phi^2} + V(r,\Theta-\phi)\right]\psi = E\psi ,$$

$$\mu = m_1 m_2/(m_1+m_2), \quad M = (m_1+m_2)m_3/(m_1+m_2+m_3) . \tag{2}$$

We approximate the interaction potential by

$$V = V(r_j, \Theta-\phi), \quad \sigma_{j-1} < r \leq \sigma_j ;$$

$$r_j = (\sigma_{j-1} + \sigma_j)/2 , \tag{3}$$

and in the same annular region we approximate

$$\tag{4}$$

$$\frac{-\hbar^2}{2Mr^2} = \frac{-\hbar^2}{2Mr_j^2}$$

With the above approximations the Schrödinger equation is separable, yielding

$$\frac{-\hbar^2}{2\mu r_0^2}\frac{\partial^2 Y^{(j)}}{\partial\Theta^2}\frac{1}{Y^{(j)}} - \frac{\hbar^2}{2M}\left(\frac{1}{r}\frac{\partial}{\partial r}\frac{r\partial R^{(j)}}{\partial r}\right)\frac{1}{R^{(j)}} \tag{5}$$

$$\frac{-\hbar^2}{2Mr_j^2}\frac{\partial^2 Y^{(j)}}{\partial\phi^2}\frac{1}{Y^{(j)}} + V(r_j,\Theta-\phi) = E ,$$

$$\psi = R^{(j)}(r)Y^{(j)}(\Theta,\phi) .$$

We expand $V(r_j, \Theta - \Phi)$ in a Fourier series:

$$V(r_j, \Theta - \Phi) = d_0^{(j)}(r_j) + \sum_{n=\pm 1, \pm 2, \ldots}' d_n^{(j)}(r_j) \exp[in(\Theta - \Phi)] , \qquad (6)$$

where the prime indicates omission of the $n = 0$ term in the summation. On separating the variables in Eq. (5), we obtain

$$\frac{-\hbar^2}{2\mu r_0^2} \frac{\partial^2 Y^{(j)}}{\partial \Theta^2} - \frac{\hbar^2}{2Mr_j^2} \frac{\partial^2 Y^{(j)}}{\partial \phi^2} + \sum_m' d_m^{(j)} \exp[im(\Theta - \phi)] Y^{(j)} - \alpha_p^{(j)} Y^{(j)} = 0 \qquad (7)$$

and

$$\frac{-\hbar^2}{2M} \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} \right) R^{(j)} + (d_0^{(j)} - E + \alpha_p^{(j)}) R^{(j)} = 0 , \qquad (8)$$

where the $\alpha_p^{(j)}$ are separation constants. We define

$$(\eta_p^{(j)})^2 = (E - \alpha_p^{(j)} - d_0^{(j)}) 2M/\hbar^2 , \qquad (9)$$

and note that the general solution of Eq. (8) in the jth annular region can be written in terms of Hankel functions of order zero, as follows:

$$R_p^{(j)} = A_p^{(j)} H_0^{(1)}(\eta_p^{(j)} r) + B_p^{(j)} H_0^{(2)}(\eta_p^{(j)} r) , \qquad (10)$$

where the index p anticipates the existence of a set of separation constants $\alpha_p^{(j)}$.

We assume a trial solution for $Y_p^{(j)}(\Theta, \Phi)$ as follows:

$$Y_p^{(j)} = \sum_{n=n_0-N}^{n_0+N} a_n^{(j)} \exp(in\phi) \exp[i(m_0 + n_0 - n)\Theta] ; \qquad (11)$$

on substitution into Eq. (7) this yields

$$\sum_{n=n_0-N}^{n_0+N} \left[\frac{\hbar^2}{2\mu r_0^2} (m_0 + n_0 - n)^2 + \frac{\hbar^2}{2Mr_j^2} n^2 \right] a_n^{(j)} \exp\left\{ i[n\phi + (m_0 + n_0 - n)\Theta] \right\}$$

$$+ \sum_{n=n_0-N}^{n_0+N} \sum_m' a_n^{(j)} d_m^{(j)} \exp\left\{ i[(n-m)\phi + (m_0 + n_0 - n + m)\Theta] \right\}$$

$$= \alpha^{(j)} \sum_{n=n_0-N}^{n_0+N} a_n^{(j)} \exp\left\{ i[(n\phi + (m_0 + n_0 - n)\Theta] \right\} . \qquad (12)$$

This form of solution is suggested by the fact that the total angular momentum of the system is conserved during collision, so that, if our incident energy eigenstate is an eigenstate of the total angular momentum, the scattered eigenstates will have the same total angular momentum.

The orthogonality of the exponentials then requires that the coefficient of $\exp\{i[p\phi + (m_0 + n_0 - p)\Theta]\}$ in Eq. (12) vanish for all p, from which we obtain

$$\left[\frac{\hbar^2}{2\mu r_0^2} (m_0 + n_0 - p)^2 + \frac{\hbar^2}{2Mr_j^2} p^2 - \alpha^{(j)} \right] a_p^{(j)} + \sum_{m=-p-N}^{-p+N} d_m^{(j)} a_{p+m}^{(j)} = 0 . \qquad (13)$$

Equation (13) is an eigenvalue problem for the $\alpha^{(j)}$'s and the $a_k^{(j)}$; let the solutions be $\alpha_l^{(j)}$, $a_{kl}^{(j)}$, $l = -N, \ldots + N$.

The solution to the Schrödinger equation in region j is then given by

$$\psi^{(j)} = \sum_{p=-N}^{N} \left\{ \left[A_p^{(j)} H_0^{(1)}(\eta_p^{(j)} r) + B_p^{(j)} H_0^{(2)}(\eta_p^{(j)} r) \right] \right. \qquad (14)$$

$$\left. \cdot \sum_{k=n_0-N}^{n_0+N} a_{kp}^{(j)} \exp(ik\phi) \exp[i(m_0 + n_0 - k)\Theta] \right\} .$$

The wavefunction and its gradient must be continuous at the boundary $r = \sigma_j$ between regions j and $j+1$. This yields the following set of equations:

$$\sum_p \left[H_0^{(1)}(\eta_p^{(j)} \sigma_j) a_{kp}^{(j)} A_p^{(j)} + H_0^{(2)}(\eta_p^{(j)} \sigma_j) a_{kp}^{(j)} B_p^{(j)} \right] \qquad (15)$$

$$= \sum_p \left[H_0^{(1)}(\eta_p^{(j+1)} \sigma_j) a_{kp}^{(j+1)} A_p^{(j+1)} + H_0^{(2)}(\eta_p^{(j+1)} \sigma_j) a_{kp}^{(j+1)} B_p^{(j+1)} \right] ,$$

$$k = n_0 - N, \ldots n_0 + N;$$

and

$$\sum_p \left[\frac{dH_0^{(1)}}{dr} (\eta_p^{(j)} \sigma_j) a_{kp}^{(j)} A_p^{(j)} + \frac{dH_0^{(2)}}{dr} (\eta_p^{(j)} \sigma_j) a_{kp}^{(j)} B_p^{(j)} \right]$$

$$= \sum_p \left[\frac{dH_0^{(1)}}{dr} (\eta_p^{(j+1)} \sigma_j) a_{kp}^{(j+1)} A_p^{(j+1)} + \frac{dH_0^{(2)}}{dr} (\eta_p^{(j+1)} \sigma_j) a_{kp}^{(j+1)} B_p^{(j+1)} \right] . \qquad (15)$$

The A's are the amplitude factors for outgoing partial waves, and the B's are associated with incoming waves.

We write Eqs. (15) in matrix notation as

$$T_j \begin{pmatrix} A^{(j)} \\ B^{(j)} \end{pmatrix} = U_j \begin{pmatrix} A^{(j+1)} \\ B^{(j+1)} \end{pmatrix} . \qquad (15a)$$

At the inner boundary to the innermost annular region we require that the wavefunction vanish; this yields

$$
(16)
$$

$$
\sum_p H_0^{(1)}(\eta_p^{(1)}\sigma_0)a_{kp}^{(1)}A_p^{(1)'} + H^{(2)}(\eta_p^{(1)}\sigma_0)a_{kp}^{(1)}B_p^{(1)} = 0 \quad,
$$

or, in matrix notation,

$$
JA^{(1)} = KB^{(1)}
$$

or

$$
B^{(1)} = K^{-1}JA^{(1)} = GA^{(1)} \quad.
$$

We rewrite Eq. (15a) as

$$
(17)
$$

$$
\begin{pmatrix} A^{(j)} \\ B^{(j)} \end{pmatrix} = T_j^{-1}U_j \begin{pmatrix} A^{(j+1)} \\ B^{(j+1)} \end{pmatrix} \quad,
$$

and then by recursion obtain

$$
(18)
$$

$$
\begin{pmatrix} A^{(1)} \\ B^{(1)} \end{pmatrix} = T_1^{-1}U_1 T_2^{-1}U_2 \ \cdots \ T_{f-1}^{-1}U_{f-1} \begin{pmatrix} A^{(f)} \\ B^{(f)} \end{pmatrix} = \tau \begin{pmatrix} A^{(f)} \\ B^{(f)} \end{pmatrix} \quad.
$$

We use Eq. (16a) to rewrite Eq. (18) as

$$
(19)
$$

$$
\begin{pmatrix} A^{(1)} \\ GA^{(1)} \end{pmatrix} = \tau \begin{pmatrix} A^{(f)} \\ B^{(f)} \end{pmatrix} \quad,
$$

which we then partition as

$$
A^{(1)} = \tau_{11}A^{(f)} + \tau_{12}B^{(f)} \tag{20}
$$

$$
GA^{(1)} = \tau_{21}A^{(f)} + \tau_{22}B^{(f)} \quad. \tag{21}
$$

We eliminate $A^{(1)}$ between Eqs. (20) and (21), and solve for $A^{(f)}$ to obtain

$$
(22)
$$

$$
A_f = SB_f \quad,
$$

where

$$
(23)
$$

$$
S = (\tau_{11} - G^{-1}\tau_{21})^{-1}(-\tau_{12} + G^{-1}\tau_{22}) \quad.
$$

The transition probabilities for the rotor associated with the incident energy and angular momentum eigenstate (specified by a rotor quantum number m_0 and an orbital quantum number n_0) are then given by

$$
(24)
$$

$$
P_{m \leftarrow m_0} = |\, A_{m_0+n_0-m}^{(f)} \,|^2 \quad.
$$

No quotient of wave numbers is needed for normalization, as these are already included in the asymptotic forms of the Hankel functions.

The coefficients $d_n^{(j)}$ introduced in Eq. (6)—the Fourier coefficients of the interaction potential—are given as follows when the interaction potential is taken as

$$
(25)
$$

$$
V(r_1\theta-\phi) = \sum_{i=1}^{2} 4\epsilon_i \left[\left(\frac{\sigma_i}{u_i}\right)^{12} - \left(\frac{\sigma_i}{u_i}\right)^{6} \right]
$$

$$
(26)
$$

$$
d_k^{(j)} = 4\epsilon_1 \left[\sigma_1^{12}F(6,r_j,a,k) - \sigma_1^{6}F(3,r_j,a,k) \right]
$$
$$
+ 4\epsilon_2 \left[\sigma_2^{12}F(6,r_j,-b,k) - \sigma_2^{6}F(3,r_j,-b,k) \right]
$$

Here $F\left(n, r_j, a, k\right)$

$$
(27)
$$

$$
= \frac{(r_j a)^k}{(r_j^2 + a^2)^{n+k}} \sum_{p=0}^{\infty} \frac{(n+k+2p-1)!\,(k+2p)!}{(n-1)!\,(k+2p)!\,(2p)!\,k!} \left(\frac{r_j a}{r_j^2+a^2}\right)^{2p} \quad.
$$

RESULTS

Transition probabilities were computed on an XDS Sigma 7 computer using up to 21 channels. Calculations were made principally for argon-nitrogen collisions; Lennard-Jones parameters were estimated from data for argon and neon,[16] and r_0 was taken from Herzberg's tabulation.[17] The interaction potential was approximated in nine concentric annular regions, a compromise between accuracy and economics. Normalization was found to be quite satisfactory, an anticipated $\pm 2j$ selection rule ($j = 0, 1, 2...$) for the homonuclear rotor was observed, and it was observed that $P_{m \leftarrow 0} = P_{-m \leftarrow 0}$ for the case of an incident s-wave ($n_0 = 0$), as expected.

A frequent approximation in rotational scattering calculations is to expand the interaction potential in terms only through the second spherical harmonic, corresponding in our work to the terms in exp ($\pm 2i\Theta$). In Table 1 we list the Fourier coefficients, $d_0^{(j)}$, $d_{\pm 2}^{(j)}$, $d_{\pm 4}^{(j)}$, etc. for argon-nitrogen collisions. It is evident that the $d_{\pm 4}^{(j)}$ are very frequently of the order of a fifth as large as the $d_{\pm 2}^{(j)}$, and that the $d_{\pm 6}^{(j)}$ are often about a fiftieth as large as the $d_{\pm 2}^{(j)}$. The effect of neglecting these higher coefficients ($|n| > 2$) is indicated in Table 2. While the transition probabilities show similar trends, they do show some substantial differences.

Plots of transition probabilities at various relative translational energies are shown in Fig. 2. One can calculate an effective impact parameter by means of the formula $b = n_0/k_0$, where k_0 is the wave number of the incident wave; these are given in the figure, and are such that only one of the collisions corresponds to grazing incidence or a "near miss". We find that transitions involving Δm values of 4, 6, and even 8 are by no means of negligible importance except for the collision of lowest energy and largest impact parameter.

TABLE 1. *Fourier Coefficients of the Interaction Potential.*

r	3.175	3.375	3.675	4.250 Å
n				
0	.4498x10^{-13}	.4009x10^{-14}	-.5388x10^{-14}	-.4912x10^{-14}
± 2	.2884	.7576	.1814	-.0205
± 4	.0539	.1390	.0380	.0012
± 6	.0060	.0139	.0035	.0001
± 8	.0005	.0010	.0004	.0000

TABLE 2. *Effect of Higher Fourier Coefficients in the Interaction Potential.*

m	$P_{m \leftarrow 0}$ (complete)	$P_{m \leftarrow 0}$ (2-term approx.)
8	.0473	.0221
6	.0174	.0203
4	.3929	.3523
2	.0031	.0251
0	.0473	.1575
-2	.0690	.0104
-4	.3238	.3406
-6	.0558	.0528
-8	.0435	.0189

Ar-N$_2$ collision, $n_{init} = 10$, $m_{init} = 0$, $\varepsilon_1 = \varepsilon_2 = 4.416 \times 10^{-15}$ erg, $\sigma_1 = \sigma_2 = 3.12$ Å, $E_{init\ trans} = 3.5 \times 10^{-14}$ erg, r_0 1.094 Å.

The occurrence of multi-quantum transitions is again observed in Fig. 3, where the initial orbital quantum number, n_0, is varied at constant initial relative translational energy. Note that $P_{0 \to m} = P_{0 \to -m}$ for $n_0 = 0$, which one would anticipate from symmetry. These results also suggest that one would need to do calculations for $n_0 = 0, 5, 10...$ up to about 60 or 70 for this model at this particular incident relative translational energy if one wished to obtain plane wave scattering cross-sections. This would be a rather ambitious undertaking.

In Fig. 4 we see the effect of changing the initial orbital quantum number at lower energies. At grazing incidence (b = 4.28 Å), two-quantum transitions predominate, as one would expect. At a somewhat smaller impact parameter, transitions become most important even at these low energies.

The results of this analysis of a planar model for rotational transitions do not bode well for an extension to three dimensions. Although the three-dimensional calcaulation by this method is possible in principle, the enormous size of the set of basis functions which would be needed indicates that very large quantities of core and machine time would be needed for all but collisions of the lowest energy.

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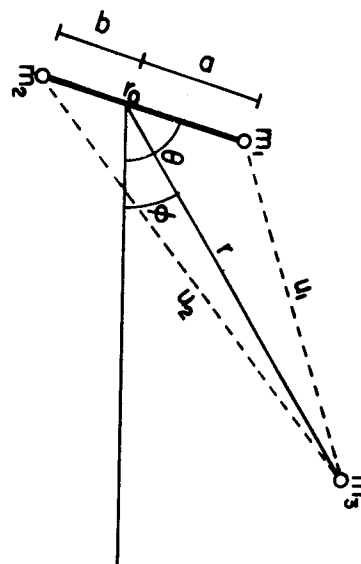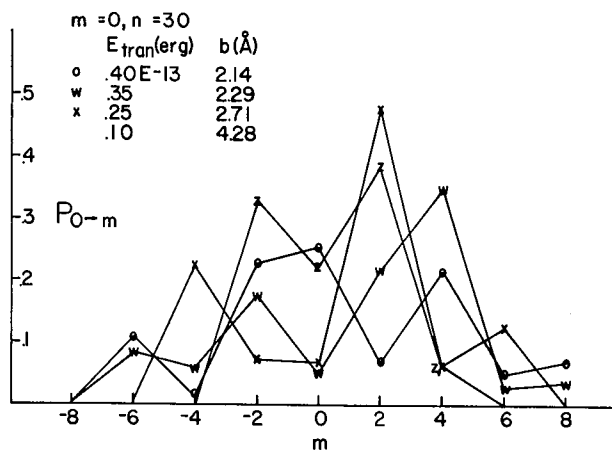
FIGURE 1. *The model and notation.*

FIGURE 2. *Rotational transition probabilities for N_2-Ar collisions at various initial translational energies. $\varepsilon_1 = \varepsilon_2 = 4.416 \chi 10^{-15}$ erg, $\sigma_1 = \sigma_2 = 3.12$ Å, $r_0 = 1.094$ Å*
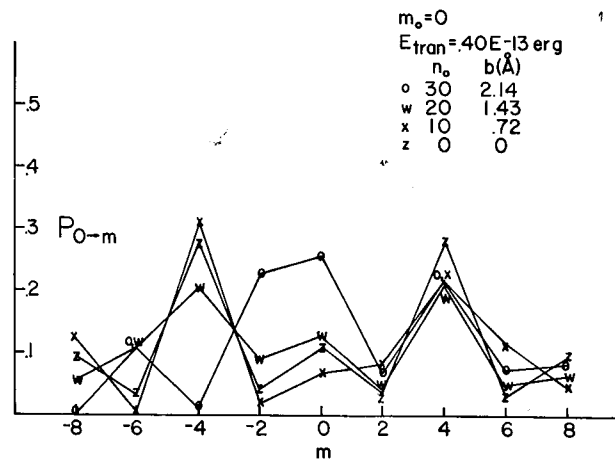
FIGURE 3. *Rotational transition probabilities for N_2-Ar collisions at various initial orbital angular momenta. Parameters as in Fig. 2.*
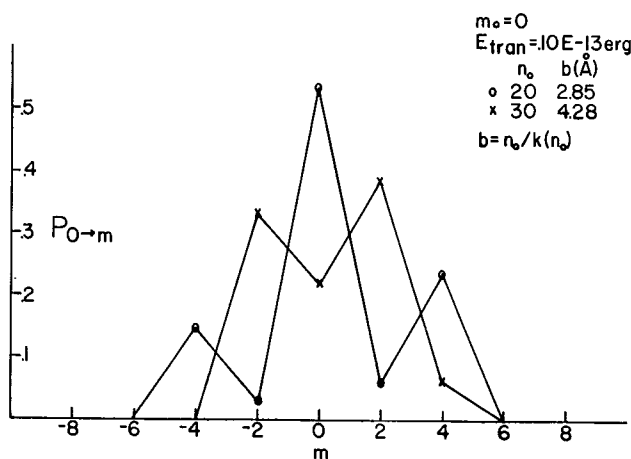

FIGURE 4. *Rotational transition probabilities for N_2-Ar collisions at grazing incidence. Parameters as in Fig. 2.*