Chapter IV

Section IV: Semiclassical Close-coupling Calculations
for the Rotational Transitions of HCN
Molecule by Collision with Hydrogen
Molecule
Abstract

The rotational transitions of the linear triatomic molecule H\textsubscript{2}CN by collision with H\textsubscript{2} molecule has been treated by the semi-classical exponential approximation of the strong coupling method suggested by Takayanagi. The interaction potential between H\textsubscript{2} and H\textsubscript{2}CN has been carefully constructed by taking into account the various types of intermolecular forces, including the short-range repulsive forces. H\textsubscript{2}CN has been taken to be in the initial rotational states \( j^0_1 = 0, 1 \) and H\textsubscript{2} in the states \( j^0_2 = 0, 1, 2 \). The rotational excitation of H\textsubscript{2} molecule has not been considered. For \( j^0_2 = 0 \), the electrostatic forces do not influence the transitions of H\textsubscript{2}CN. The transition probabilities and inelastic cross sections have been evaluated for different combinations of \( j^0_1 \) and \( j^0_2 \). The results of calculations have brought out the effects of coupling between states and also the different factors influencing the rotational excitation process in molecule-molecule collisions.

Introduction

The theoretical study of rotational excitations of molecules by collision with an atom or another molecule in the thermal energy range is one of the difficult and interesting problems in collision physics. This is particularly true for the strongly interacting systems for which the coupling between a number of states has to be considered. This problem can be tackled, in principle, satisfactorily by the close coupling method. For a
rigid rotator in collision with an atom or structureless particle a rigorous close coupling formulation has been given by Arthurs and Dalgarno. For atom-diatomic collisions with this formulation a number of theoretical works have been done on rotational transitions in light molecules as well as in rather heavier ones. This rigorous method requires the solution of sets of coupled second-order differential equations, the number of which may be very large making the computation unwieldy and expensive.

For the molecule-molecule collisions further complications arise due to the presence of electrostatic forces and the possibility of simultaneous excitations of both the molecules. Inclusion of the first factor results in much stronger interaction so that many more states become involved in rotational excitation process. Due to these difficulties close-coupling calculations for the molecule-molecule collisions have till now been confined only to the simplest case like H₂-H₂ collisions. For the polar molecules rotational transitions in collision between like molecules HCN-HCN, ICN-ICN have been studied by using second order perturbation theory and straight line trajectory due to which the cross-sections obtained are not likely to be quantitatively correct. For the unlike interactions the only study has been performed for H₂-CO system for which H₂ has been taken to be in the $j_z = 0$ state and to be an effectively structureless particle.

It is thus necessary to study theoretically the rotational transitions in molecule-molecule systems so that some features
of these processes may be understood. For this purpose, in this section we have studied the purely rotational excitations of HCN molecule in collision with H₂ molecule. We have considered H₂ molecule to be in the states \( j^\|= 0 \) and \( j^\|= 1, 2 \) so that the role played by the electrostatic forces can be brought out. The interaction potential has been carefully constructed by taking into account the interactions for the short-range forces also.

The rotational excitation cross sections for HCN have been calculated by a semiclassical method suggested and developed by Takayanagi\(^1,11,12\) which deals with an approximate solution of the strong coupling problem. This method belongs to the class of semiclassical approximations in that the classical trajectory is used while the rotational transition is treated quantum mechanically. A further advantage of this method is that it brings out certain features of the close-coupling between many rotational channels. This so called exponential approximation method has been used to study rotational transitions in atom-diatom collisions by Saha et al.\(^{107,108}\). The HCN-H₂ system is of special importance in astrophysics as both the molecules are important constituents of the interstellar medium.

**Intermolecular Potential and Formulation**

For molecule-molecule collision the rotational motion of the molecules in a perturbing field \( V'(\hat{r}, \hat{r}_1, \hat{r}_2) \) is governed by
the time dependent Schrödinger equation

\[
\left[ H^{(1)}_{\text{rot}} + H^{(2)}_{\text{rot}} + V'(\vec{r}(t), \hat{\rho}_1, \hat{\rho}_2) \right] \Psi(t) = i\hbar \frac{\partial \Psi(t)}{\partial t}, \ldots (1)
\]

where \( H^{(1)}_{\text{rot}} \) and \( H^{(2)}_{\text{rot}} \) are the Hamiltonian operators for free rotation of the molecules, \( \vec{r}(t) \) the vector distance between the centres of mass of the molecules at time \( t \) and \( \hat{\rho}_1, \hat{\rho}_2 \) represent the angular coordinates of the molecular axes. The wave function \( \Psi(t) \) may be expanded in terms of the unperturbed rotational eigenstates \( Y_{j_1 m_1} (\hat{\rho}_1) \) and \( Y_{j_2 m_2} (\hat{\rho}_2) \) of the diatomic molecules and the energies of rotation \( E_{j_1} \) and \( E_{j_2} \) in the \( j_1 \) and \( j_2 \) states respectively, as

\[
\Psi(t) = \sum_{j_1 j_2 m_1 m_2} C_{j_1 j_2 m_1 m_2}(t) Y_{j_1 m_1} (\hat{\rho}_1) Y_{j_2 m_2} (\hat{\rho}_2) \exp \left( -\frac{i}{\hbar} E_{j_1} t \right) \exp \left( -\frac{i}{\hbar} E_{j_2} t \right), \ldots (2)
\]

where the expansion coefficients \( C_{j_1 j_2 m_1 m_2}(t) \) are bounded by the initial condition

\[
C_{j_1 j_2 m_1 m_2} (-\infty) = \delta_{j_1 j_1^0} \delta_{j_2 j_2^0} \delta_{m_1 m_1^0} \delta_{m_2 m_2^0},
\]

\( j_1^0, j_2^0, m_1^0, m_2^0 \) being the initial quantum numbers (at \( t = -\infty \)).

From eqns (1) and (2) it follows that

\[
\begin{align*}
\text{i} \hbar \frac{\partial}{\partial t} C_{j_1 j_2 m_1 m_2}(t) &= \sum_{j_1' j_2' m_1' m_2'} \langle j_1' m_1' j_2' m_2' | V'(\vec{r}(t), \hat{\rho}_1, \hat{\rho}_2) | j_1 m_1 j_2 m_2 \rangle C_{j_1 j_2 m_1 m_2}(t) e^{\frac{i}{\hbar} \left( (E_{j_1'} - E_{j_1} + E_{j_2'} - E_{j_2}) t \right)} \ldots (3)
\end{align*}
\]
The matrix representation of eqn. (3) is

$$i \hbar \frac{\partial \vec{\varphi}(t)}{\partial t} = \vec{A}(t) \vec{\varphi}(t), \quad \ldots \quad (4)$$

where $\vec{\varphi}$ is a column matrix and $\vec{A}$ is a Hermitian matrix with diagonal elements put to zero and off-diagonal elements given by

$$A_{j_1m_1j_2m_2; j_1'm_1'j_2'm_2'}(t) = \langle j_1'm_1'; j_2'm_2' | V' \left( \vec{r} \left( t \right), \vec{p}_1, \vec{p}_2 \right) | j_1m_1j_2m_2 \rangle \quad \ldots \quad (5)$$

where $\omega_{j_1j_1'} = (E_{j_1'} - E_{j_1})/\hbar$ is the angular frequency for the transition $j_1 \rightarrow j_1'$ of the molecule $i$. The approximate solution of the matrix equation (4) is

$$\vec{\varphi}(t) = \exp \left\{ - \frac{i}{\hbar} \int_{-\infty}^{t} \vec{A}(t') dt' \right\} \vec{\varphi}(-\infty), \quad \ldots \quad (6)$$

which becomes exact when $\exp \left\{ i \omega_{j_1j_1'} t \right\}$ is replaced by 1, and when the time dependence of the potential matrix elements may be separated out as

$$\langle j_1'm_1'; j_2'm_2' | V' \left( \vec{r} \left( t \right), \vec{p}_1, \vec{p}_2 \right) | j_1m_1j_2m_2 \rangle = \langle j_1'm_1'; j_2'm_2' | V' \left( \vec{r}_1, \vec{p}_1, \vec{p}_2 \right) | j_1m_1j_2m_2 \rangle \quad \ldots \quad (7)$$

where

$$V_{j_1m_1j_2m_2; j_1'm_1'j_2'm_2'} = \langle j_1'm_1'; j_2'm_2' | V' \left( \vec{r}_1, \vec{p}_1, \vec{p}_2 \right) | j_1m_1j_2m_2 \rangle$$

are independent of time.

Then we can write

$$\vec{\varphi}(\infty) = \left[ I + K + \frac{K^2}{2!} + \ldots \right] \vec{\varphi}(-\infty), \quad \ldots \quad (8)$$
The approximate solution (8) may be used when the condition
\[ \omega_{ji} t \ll \tau_{\text{coll}} / \tau_{\text{rot}} \ll 1 \]
is satisfied. \( \tau_{\text{coll}} \) is the time taken for a collision and \( \tau_{\text{rot}} \) is the time taken for the transition. The solution is valid when \( \overline{A}(t) \) and \( \int_{-\infty}^{t} \overline{A}(t') dt' \) commute i.e., when the condition (7) holds. The transition probabilities may be calculated from eqn. (8). The matrix multiplication in higher order terms in eqn. (8) brings out clearly the coupling between intermediate rotational levels.

For molecule-molecule collision the interaction potential may be written as sum of long range and short range interaction potentials:

\[ V\left(\vec{r}, \hat{r}_1, \hat{r}_2\right) = V_{\text{disp}} + V_{\text{ind}} + V_{\text{elec}} + V_{\text{SR}} \]

where \( V_{\text{disp}}, V_{\text{ind}} \) and \( V_{\text{elec}} \) are long range interaction potentials due to dispersion, induction and electrostatic forces, respectively and \( V_{\text{SR}} \) is that due to short range forces. \( V_{\text{disp}} \) can be written as

\[ V_{\text{disp}}\left(\vec{r}, \hat{r}_1, \hat{r}_2\right) = -C_{\text{disp}}^{(6)}\vec{r}^{-6} \left[ 1 + q_{\text{disp}}^{(1)} P_2 \left(\vec{r}, \hat{r}_1\right) \right. \\
+ q_{\text{disp}}^{(2)} P_2 \left(\vec{r}, \hat{r}_2\right) \right] \]

\[ \ldots (11) \]

with

\[ K_{j_1 m_1 j_2 m_2; j_1' m_1' j_2' m_2'} = -\frac{i}{\hbar} \int_{-\infty}^{\infty} A_{j_1 m_1 j_2 m_2; j_1' m_1' j_2' m_2'}(t) dt \]

\[ \ldots (9) \]
where
\[ C_{\text{disp}}^{(6)} = \frac{3}{2} \alpha_1 \alpha_2 \frac{I_1 I_2}{I_1 + I_2}, \quad Q_{\text{disp}}^{(i)} = \frac{\alpha_i - \alpha_i^\perp}{\alpha_i^\perp + 2 \alpha_i^\parallel}. \]

\( \alpha_i^\parallel \) and \( \alpha_i^\perp \) are the polarizabilities parallel to and perpendicular to the molecular axis. \( \alpha_1, \alpha_2 \) are the average polarizabilities and \( I_1, I_2 \) are ionization potentials of the two molecules.

In addition to the dispersion force, various induction forces arise from the interaction of induced moments of one molecule with the multipole moments of the other molecule:

\[ V_{\text{ind}} \left( \vec{r}, \hat{\mu}_1, \hat{\mu}_2 \right) = -r^{-6} \left[ \frac{C_1^{(6)}}{r} \right] + \frac{C_2^{(6)}}{r^2} \left[ 1 + P_2 (\hat{\mu}_1, \hat{\mu}_2) \right] - r^{-7} \left[ \frac{C_1^{(7)}}{r^2} \left\{ \frac{3}{5} P_1 (\hat{\mu}_1, \hat{\mu}_2) + \frac{3}{5} P_3 (\hat{\mu}_1, \hat{\mu}_2) \right\} \right] + \frac{C_2^{(7)}}{r^3} \left\{ \frac{3}{7} P_2 (\hat{\mu}_1, \hat{\mu}_2) + \frac{6}{7} P_4 (\hat{\mu}_1, \hat{\mu}_2) \right\} \right] - r^{-8} \left[ \frac{C_1^{(8)}}{r^4} \left\{ 1 + \frac{3}{7} P_2 (\hat{\mu}_1, \hat{\mu}_2) + \frac{6}{7} P_4 (\hat{\mu}_1, \hat{\mu}_2) \right\} \right]. \]

where
\[ C_1^{(6)} = \alpha_2 D_1^2; \quad C_2^{(6)} = \alpha_1 D_2^2; \quad C_1^{(7)} = \alpha_2 D_1 Q_1; \quad C_2^{(7)} = \alpha_1 D_2 Q_2; \quad C_1^{(8)} = \frac{3}{2} \alpha_2 Q_1^2; \quad C_2^{(8)} = \frac{3}{2} \alpha_1 Q_2^2. \]

\( D_1, D_2 \) being dipole moments and \( Q_1, Q_2 \) being quadrupole moments of molecules 1 and 2.
Thus the angle-dependent part of the interaction potential due to dispersion and induction forces may be written in the form

\[
V_{\text{dis} + \text{ind}} (\mathbf{r}, \hat{p}_1, \hat{p}_2) = \sum_{i,n,\lambda} \frac{4\pi}{(2\lambda + 1)} \frac{c_i^{(n,\lambda)}}{r} \sum_{m_{\lambda} = -\lambda}^{\lambda} Y_{\lambda m_{\lambda}}(\hat{p}_1) Y_{\lambda m_{\lambda}}(\hat{r})
\]

where \( c_i^{(n,\lambda)} \) is the coefficient for \((n,\lambda)\) term in the potential for \(i\)-th molecule.

The electrostatic interaction potential may be written with reference to the space-fixed axes as

\[
V_{\text{elec}} (\mathbf{r}, \hat{p}_1, \hat{p}_2) = V'_{\lambda_1,\lambda_2} = C_{\lambda_1,\lambda_2} \sum_{m_{\lambda_1},m_{\lambda_2}} c (\lambda_1,\lambda_2,\lambda; m_{\lambda_1},m_{\lambda_2},m_{\lambda})
\]

\[
\times Y_{\lambda_1 m_{\lambda_1}}(\hat{p}_1) Y_{\lambda_2 m_{\lambda_2}}(\hat{p}_2) Y_{\lambda m_{\lambda}}^*(\hat{r}) / r^{\lambda+1}
\]

where

\[
C_{\lambda_1,\lambda_2} = 4\pi (-1)^{\lambda_2} \frac{Q_{\lambda_1} Q_{\lambda_2}}{(2\lambda + 1)} \left[ \frac{4\pi \left( \frac{(2\lambda+1)!}{(2\lambda+1)!(2\lambda_1+1)!(2\lambda_2+1)!} \right)}{\frac{\lambda}{2}} \right]^{1/2}
\]

where \(\lambda_1 + \lambda_2 = \lambda\) and \(Q_{\lambda_i}\) is the \(\lambda_i\) th multipole moment of \(i\)-th molecule.

Very little is known about the anisotropy of the repulsive part of the molecule-molecule interaction. To estimate the short-range potential it is necessary to assume additivity of the
Fig. 1. Schematic diagram for HCN - H$_2$ interaction. $O_1$, $O_2$ are the centres of masses of HCN and H$_2$ molecule respectively and $\rho_i$ ($= \rho_H + \rho_N$), $2\xi$ are the corresponding internuclear distances.
repulsive forces between the individual atoms making up the molecules. For atom-atom repulsive interaction potentials, some theoretical calculations have been made and the potentials thus obtained may be best described by exponential terms. Let \( O_1 \) and \( O_2 \) be the centres of mass of the two molecules HCN and \( H_2 \) (Fig. 1). The short range potential may be written as

\[
V_{SR} = 2 \left\{ \psi_{HH}(r_{HH}) + \psi_{HC}(r_{HC}) + \psi_{HN}(r_{HN}) \right\}
\]

\[
= 2 \left\{ A_{HH} e^{-\alpha_{HH} r_{HH}} + A_{HC} e^{-\alpha_{HC} r_{HC}} + A_{HN} e^{-\alpha_{HN} r_{HN}} \right\} \ldots \ldots (15)
\]

where \( A_{pq} \) and \( \alpha_{pq} \) are potential parameters for interaction between \( p \) and \( q \) atoms. \( r_{pq} \) is the distance between \( p \)-th and \( q \)-th atoms. Writing the interatomic distance in terms of distance between centres of mass of the molecules \( r \), the first term on the right hand side of eqn (15) can be written as a series expansion in Legendre functions.

\[
\psi_{HH}(r) = A_{HH} e^{-\alpha_{HH} |\vec{r} - \vec{p}_H + \vec{p}'_H|}
\]

\[
= A_{HH} e^{-\alpha_{HH} r} \left[ b^{(0)}_H + b^{(1)}_H P_1 (\hat{r} \cdot \hat{p}_1) + b^{(2)}_H P_2 (\hat{r} \cdot \hat{p}_1) \right.

\[+ \left. \beta^{(2)}_H P_2 (\hat{r} \cdot \hat{p}_2) \right]\]

\ldots \ldots (16)
where $\vec{r}_H = \vec{a}_1 H$ and $\vec{r} = \vec{a}_2 H$ (fig 1).

$$b_H^{(c)} = 1 + \frac{\alpha_{HH}^2 \rho_H^2}{6} \left(1 - \frac{2}{\alpha_{HH} r}\right) + \frac{\alpha_{HH}^2 \xi^2}{6} \left(1 - \frac{2}{\alpha_{HH} r}\right).$$

$$b_H^{(1)} = \alpha_{HH} \rho_H.$$

$$b_H^{(2)} = \frac{\alpha_{HH}^2 \rho_H^2}{3} \left(1 + \frac{1}{\alpha_{HH} r}\right).$$

$$\beta_H^{(2)} = \frac{\alpha_{HH}^2 \xi^2}{3} \left(1 + \frac{1}{\alpha_{HH} r}\right).$$

The expression in eqn (16) is obtained assuming $\xi$ and $\rho_H$ both small compared to the intermolecular distance $r$ and hence neglecting third and higher order terms of $\rho_H / r$ and $\xi / r$.

The interaction potential given by eqn. (16) is now a function of intermolecular distance $r$. The second and third terms on the right hand side of eqn. (15) may be written by similar expressions.

The expression for short-range potential obtained by us is similar to that obtained by Takayanagi\textsuperscript{1} using more general series expansion. The angle-dependent part of the short-range repulsive force may be written as

$$V'_{rep} (\vec{r}_1, \vec{p}_1, \vec{p}_2) = \sum_{i \phi, \lambda} \frac{4\pi}{(2\lambda+1)} \left(\phi_{\lambda} \lambda \right) A_i \left(\rho\right) \sum_{m_{\lambda} = -\lambda}^{\lambda} Y_{\lambda m_{\lambda}} (\vec{p}_1) Y_{\lambda m_{\lambda}} (\vec{p}_2) \cdots (17)$$

where $A_i \left(\rho\right)$ is coefficient for interaction of $\phi$ atom of $H_2$. 

molecule with p-atom of HCN molecule and for $A_i$ term of the potential for $i$th molecule.

The spherical part of the total interaction potential is

$$V_0(r) = 2 \left( b_c^{(s)} A_{HH} e^{-\alpha_{HH} r} + b_e^{(s)} A_{HC} e^{-\alpha_{HC} r} + b_N^{(s)} A_{HN} e^{-\alpha_{HN} r} \right)$$

$$- \left( c_{dis}^{(s)} + c_1^{(s)} \right) r^{-6} - \left( c_1^{(g)} + c_2^{(g)} \right) r^{-8} \quad \cdots \quad (18)$$

$\beta_c$ and $\beta_N$ are coefficients for H-C and H-N interactions.

The trajectory is assumed to be governed by $V_0(r)$ and therefore planar. The radial and angular equations of the trajectory for the impact parameter $b_0$ are

$$\dot{r} = \frac{v_0}{Bo} \left[ 1 - \frac{V_0(r)/E_0 - b_0^2/r^2}{\mu} \right]^{1/2} \quad \cdots \quad (19)$$

$$\dot{\theta} = \frac{b_0 v_0}{r^2} \quad \cdots \quad (20)$$

in the centre of mass system. $r$ and $\theta$ are the plane polar coordinates of the trajectory. $E_0$ and $v_0$ are the initial relative kinetic energy and velocity respectively. In the semiclassical limit $b_0 = (l_0 + 1/2)/k_0$, $l_0$ being the initial orbital quantum number and $k_0 = (2 \mu E_0/\hbar^2)^{1/2}$ the initial wave number for relative motion. $\mu$ is the reduced mass of the colliding pair. Many rotational levels may be involved in the intermediate stages of the collision process and any of these may be the final state with comparable probability. Thus in each step,
E and \( \ell \) change, the effects of which may be considerable on the trajectory. Therefore in the calculation of the matrix elements \( K_{j_1, m_1, j_2, m_2; j'_1, m'_1, j'_2, m'_2} \) we have used the weighted mean values\(^\text{12}\).

\[
E = E_0 + E_{j_1} + E_{j_2} - \frac{1}{\hbar} \left( E_{j_1} + E_{j_1'} + E_{j_2} + E_{j_2'} \right) \quad \ldots (21)
\]

and

\[
\ell = l_0 + j_1^0 + j_2^0 - \frac{1}{\hbar} \left( j_1 + j_1' + j_2 + j_2' \right) \quad \ldots (22)
\]

\( j_1^0, j_2^0 \) and \( l_0 \) being the values of \( j_1, j_2 \) and \( \ell \) before the collision (\( t = -\infty \)).

We have taken the reference axis along the direction of the classical distance of closest approach \( \vec{r}_0 \) about which the trajectory is symmetrical. This simplifies the calculations to a large extent.

From eqns. (5), (9) and (13) the matrix element for the transition from \( j, m, j_2, m_2 \) to \( j', m', j'_2, m'_2 \) for dispersion and induction forces for impact parameter \( b \) is given by

\[
K_{j, m, j_2, m_2; j', m', j'_2, m'_2}^{(b)} = -\frac{2i}{\hbar \nu} \sum_{i, k=1}^{2} \sum_{n, \lambda} \left[ \frac{4\pi (2j_1 + 1)}{(2\lambda + 1)(2j_1' + 1)} \right] \mathcal{C}_i^{(n, \lambda)} C(j, \lambda; i, 000).
\]
\[ x \sum_{m^\lambda} c \left( j_1, j'_1, m_i, m_\lambda m_i' \right) \left\{ \int_0^{y_0} Y_{\lambda m_\lambda} (\theta', y, 0) \right. \]

\[ \times \cos \left\{ \left( \omega_{i,j_i} + \omega_{j,j_i'} \right) t(y) \right\} \frac{y^{n-2} dy}{[F(y)]^{1/2}} + i \int_0^{y_0} Y_{\lambda m_\lambda} (\theta', y, 0) \]

\[ \times \sin \left\{ \left( \omega_{i,j_i} + \omega_{j,j_i'} \right) t(y) \right\} \frac{y^{n-2} dy}{[F(y)]^{1/2}} \delta_{j,j_i'} \delta_{m,m_i'} \]

\[ \cdots (23) \]

where

\[ t(y) = \pm \frac{1}{y} \int_0^{y_0} \frac{dy}{y^2 [F(y)]^{1/2}} \]

\[ \theta'(y) = \pm b \int_0^{y_0} \frac{dy}{[F(y)]^{1/2}} \]

\[ \cdots (24) \]

\[ \cdots (25) \]

and

\[ F(y) = 1 - V_\delta(y)/E - b^2 y^2 \]

\[ \cdots (26) \]

\[ y_0 = 1/r \] and the positive and negative signs refer to the outgoing and incoming branches of the trajectory respectively. The superscript (even) or (odd) indicates that the integral exists only when the function \( Y_{\lambda m_\lambda} (\theta', y, 0) \) is even or odd depending on the value of \( m_\lambda \). Since the trajectory is confined to \( xz \)-plane the azimuthal angle has been put equal to zero. The summation over \( m_\lambda \) in eqn. (23) is formal as\( m_\lambda = m_i' - m_i \).
The matrix element for transition \( j, m, j_2 m_2 \rightarrow j', m', j_2' m_2' \)
for repulsive potential is obtained from eqns. (5), (9) and (17) as

\[
K_{j, m, j_2 m_2 ; j', m', j_2' m_2'}^{(rep)} (b) = - \frac{2i}{\hbar \nu} \sum_{i, k = 1}^{2} \sum_{\phi, \lambda \neq k} \left[ \frac{4\pi i (2j_i + 1)}{(2\lambda_1 + 1) (2\lambda_2 + 1)} \right] \frac{1}{2} 
\times A_i \cos (j_1 \lambda j_1' ; 0 0 0) \sum_{m_\lambda} \sum_{m_\lambda'} c (j_1 \lambda j_1' ; m_1 m_\lambda m_1')
\times \left\{ \int \int_{y_0} Y_{\lambda m_\lambda} (\theta' (y), 0) \cos \left\{ (\omega_{j_1 j_1'} + \omega_{j_1 j_2}) t(y) \right\} \frac{e^{-\alpha_p y}}{y^2 [F(y)]^{1/2}} dy \right. 
\left. + i \int \int_{y_0} Y_{\lambda m_\lambda} (\theta' (y), 0) \sin \left\{ (\omega_{j_1 j_1'} + \omega_{j_1 j_2}) t(y) \right\} \frac{e^{-\alpha_p y}}{y^2 [F(y)]^{1/2}} dy \right\} 
\times \delta_{j_1 j_1'} \delta_{m_1 m_1'} \ldots \ldots (27)
\]

The matrix element for \( j, m, j_2 m_2 \rightarrow j', m', j_2' m_2' \)
transition for electrostatic forces may be obtained from eqns. (5), (9) and (14) as

\[
K_{j, m, j_2 m_2 ; j', m', j_2' m_2'}^{(elec)} (b) = - \frac{2i}{\hbar \nu} \frac{[(2\lambda_1 + 1) (2\lambda_2 + 1)]^{1/2}}{4\pi} e^{\lambda_1 \lambda_2}
\]
Takayanagi\textsuperscript{11} found by actual calculation that the contribution of the integrals in eqns (23), (27) and (28) which involve \( m \) transitions are negligible compared to those for which \( \Delta m_1 = 0 \). The reference axis was taken along the symmetry axis for an in-plane trajectory. For other choices of reference axis this selection rule may not hold. Since we have taken the reference axis to coincide with the symmetry axis, we have made \( m_\lambda = 0 \) throughout the collision and so the integrals involving 'Sine' function in eqns. (23), (27) and (28) are to be ignored from the 'ab initio' parity consideration.
The scattering amplitude associated with the transition
\[ J_1^o m_1^o j_2^o m_2^o \rightarrow J_1 m_1 j_2 m_2 \] is obtained from eqn. (8) using
total matrix element due to dispersion, induction, electrostatic
and short-range forces as
\[ C_{J_1^o m_1^o j_2^o m_2^o ; J_1 m_1 j_2 m_2} (\infty \mid b_0) \]
\[ = \sum_{j' = 0}^{\infty} \frac{1}{\gamma_j} \left( \frac{K_j}{j'} \right) C_{J_1^o m_1^o j_2^o m_2^o ; J_1 m_1 j_2 m_2} (\infty \mid b_0) \] \hspace{1cm} (29)
The corresponding transition probability is
\[ T_{J_1^o m_1^o j_2^o m_2^o ; J_1 m_1 j_2 m_2} (b_0) = \left| C_{J_1^o m_1^o j_2^o m_2^o ; J_1 m_1 j_2 m_2} (\infty \mid b_0) \right|^2 \] \hspace{1cm} (30)
The probability for the transition \( J_1^o j_2^o \rightarrow J_1 j_2 \) is
\[ T_{J_1^o j_2^o ; J_1 j_2} (b_0) = \frac{1}{(2j_1^o + 1)(2j_2^o + 1)} \sum_{m_1^o m_2^o m_1 m_2} T_{J_1^o m_1^o j_2^o m_2^o ; J_1 m_1 j_2 m_2} (b_0) \] \hspace{1cm} (31)
The degeneracy averaged transition probability \( T_{J_1^o j_2^o ; J_1 j_2} \) is
independent of the choice of the coordinate system. The cross
section for the transition \( J_1^o j_2^o \rightarrow J_1 j_2 \) is given by
\[ \sigma_{J_1^o j_2^o ; J_1 j_2} = 2\pi \int_0^\infty T_{J_1^o j_2^o ; J_1 j_2} (b_0) b_0 \, db_0 \]
\[ = \frac{\pi}{k^2} \sum_{\ell_0 = 0}^\infty (2\ell_0 + 1) T_{J_1^o j_2^o ; J_1 j_2} (\ell_0) \] \hspace{1cm} (32)
where \( k = \left( \frac{2\mu E}{\hbar^2} \right)^{1/2} \) is the mean wave number for relative
motion.
The higher order matrix terms in eqn. (29) are cut off at \( \gamma = N \) for which the condition

\[
\langle N \rangle
\sum_{j_1, m_1, j_2, m_2} c_{j_1, m_1, j_2, m_2} (b_0) \right|^2 \sim 1
\]

is satisfied. \( K \) is a \((J \times J)\) matrix. For a particular energy \( E_0 \), \( J \) is determined by the highest permissible values of \( j_1, j_1', j_2, j_2' \).

**Calculation and Results**

It is clear from the expressions (23) and (27) of the transition matrix elements that simultaneous excitations of both the molecules \( i \) and \( k \) cannot occur in a single collision for the form of dispersion, induction and repulsive potential we have taken. Only the electrostatic forces can excite both the molecules simultaneously. But for simplicity, for the HCN-\( \text{H}_2 \) system we have considered the rotational excitation of the HCN molecule only (indicated as 1) with the \( \text{H}_2 \) molecule (indicated as 2) remaining in its initial state throughout the collision.

The internuclear distance of \( \text{H}_2 \) molecule \( (0.7416 \text{ \AA}) \) and the distance between \( \text{HC} \) \( (1.064 \text{ \AA}) \) and \( \text{CN} \) \( (1.156 \text{ \AA}) \) atoms of HCN molecule have been taken from Herzberg. From these the position of centre of mass of HCN and the distances \( 0_1C, 0_1N, 0_1H \) (Fig.1) have been calculated. The dipole moment of \( \text{H}_2 \)
and the dipole and quadrupole moments of HCN are taken from Stogryn and Stogryn\textsuperscript{82} and their polarizabilities are taken as given by Hirschfelder et al.\textsuperscript{114} For short-range forces potential parameters $A$ and $\alpha$ for C - C and N - N interactions are taken from Abrahamson\textsuperscript{111} and that for H - H from Hirschfelder.\textsuperscript{114} From these, the parameters corresponding to H - C, H - N interactions have been obtained by combination rules.\textsuperscript{114} Numerical values of all these potential parameters are given in Table I. The electrostatic forces considered by us are due to dipole-quadrupole and quadrupole-quadrupole interactions. For dipole-quadrupole interaction in eqn. (14) we have to put $\lambda_1 = 1$, $\lambda_2 = 2$ and $\lambda = 3$ and for quadrupole-quadrupole interaction $\lambda_1 = 2$, $\lambda_2 = 2$, $\lambda = 4$.

Then with all these interaction terms, matrix elements for different transitions have been calculated from expressions (23), (27) and (28) and then the transition probability from eqn. (30). The order of matrix $(J)$ and the number of higher order terms $(N)$ have been increased till the condition (33) is satisfied. The transition probabilities and the inelastic cross sections have been calculated for the following combinations of the initial rotational states of HCN and $H_2$. The rotational states of HCN and $H_2$ are indicated by the subscripts 1 and 2 respectively,
In our calculations we have taken \( J = 15 \) (for \( E_0 = 0.041 \text{ ev} \), \( J \) was taken to be 11).

For \( j_2^0 = 0 \), \( N = 16 \) was sufficient for convergence of the series (29), but for \( j_2^0 = 1, 2 \), \( N \) was increased to 24 to get the convergence. This is due to the strong electrostatic forces playing part in the latter case.

The energy range covered in our calculation is from 0.041 ev to 0.073 ev. The transition probabilities corresponding to different combinations of the rotational states have been shown in Figs. 2-6. The cross sections \( \sigma_{j_1^0 j_2^0 ; j_1 j_2} \) for the excitation of HCN have been given in Tables II and III. The total inelastic cross sections \( \sum_j \sigma_{j_1^0 j_2^0 ; j_1 j_2} \) \( (j_1 \neq j_2^0) \) have been shown in Table IV. The cross sections for the important transitions for \( j_1^0 = 0 \) and \( j_2^0 = 0 \) as function of energy have been plotted in Fig. 7.
Table I. Potential parameters for HCN-H\(_2\) and other relevant physical quantities for HCN and H\(_2\)

<table>
<thead>
<tr>
<th>Parameters for short range forces</th>
<th>(A_{HH} \times 10^{12})</th>
<th>(A_{HC} \times 10^{12})</th>
<th>(A_{HN} \times 10^{12})</th>
<th>(\alpha_{HH})</th>
<th>(\alpha_{HC})</th>
<th>(\alpha_{HN})</th>
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</thead>
<tbody>
<tr>
<td></td>
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<td>erg</td>
<td>erg</td>
<td>(\AA^{-1})</td>
<td>(\AA^{-1})</td>
<td>(\AA^{-1})</td>
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<table>
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<th>Parameters for long range forces</th>
<th>(D_1 \times 10^{18})</th>
<th>(Q_1 \times 10^{26})</th>
<th>(Q_2 \times 10^{26})</th>
<th>(\alpha_1 \times 10^{25})</th>
<th>(\alpha_2 \times 10^{25})</th>
<th>(I_1 \times 10^{12})</th>
<th>(I_2 \times 10^{12})</th>
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<tr>
<td></td>
<td>esu.cm</td>
<td>esu.cm(^2)</td>
<td>esu.cm(^2)</td>
<td>cm(^3)</td>
<td>cm(^3)</td>
<td>erg</td>
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<tr>
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<td>7.9</td>
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Table II. Inelastic cross sections $\sigma_{j_1^0,j_2^0;j_1,j_2}$ (Å$^2$) for HCN-H$_2$ collision for different combinations of initial states $j_1^0$ and $j_2^0$ at different energies $E_0 (\Delta j_1 = -1$ to $+6)$.

<table>
<thead>
<tr>
<th>$j_1^0$</th>
<th>$j_2^0$</th>
<th>$E_0$ (ev)</th>
<th>$\Delta j_1$</th>
<th>-1</th>
<th>0</th>
<th>+1</th>
<th>+2</th>
<th>+3</th>
<th>+4</th>
<th>+5</th>
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<td>-</td>
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<td></td>
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<td>-</td>
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<td></td>
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<td>-</td>
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Table III. Inelastic cross sections $\sigma_{j_1 j_2; j'_1 j'_2}$ (A$^2$) for HCN-H$_2$ collision for different combinations of initial states $j_1^0$ and $j_2^0$ at different energies $E_0$ ($\Delta j_1 = +7$ to +14).

<table>
<thead>
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<th>$j_1^0$</th>
<th>$j_2^0$</th>
<th>$E_0$ (ev)</th>
<th>$\Delta j_1$</th>
<th>+7</th>
<th>+8</th>
<th>+9</th>
<th>+10</th>
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<tr>
<td></td>
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Table IV. The total inelastic cross section $\sum_{j_1,j_2} \sigma_{j_1;j_2}^* : j_1,j_2^*$ for different combinations of the initial values of $j_1^o$ and $j_2^o$ and energy $E_0$.

<table>
<thead>
<tr>
<th>$j_1^o$</th>
<th>$j_2^o$</th>
<th>$E_0$ (ev)</th>
<th>$\sum_{j_1} \sigma_{j_1;j_2}^* : j_1,j_2^*$ ($\AA^2$)</th>
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Fig. 2. Transition probabilities $T_{00; j_0} \text{ vs. } l_0$ plots for different values of $\Delta j$ at $E_0 = 0.062$ ev.
Fig. 3. Transition probabilities $T_{01; j_1 l}$ vs. $l_0$ plots for different values of $\Delta j_1$ at $E_0 = .065$ ev.
Fig. 4. Transition probabilities $T_{02; j_1j_2}$ vs. $l_0$ plots for different values of $\Delta j_1$ at $E_0 = 0.065$ ev.
Fig. 5. Transition probabilities $T_{10; j_1 0}$ vs. $\ell_0$ plots for different values of $\Delta j_1$ at $E_0 = .065$ ev.
Fig. 6. Transition probabilities $T_{H_j,j'}$ vs. $l_o$ plots for different values of $\Delta j_1$ at $E_0 = .065$ ev.
Fig. 7. Inelastic cross sections $\sigma_{00; j_1 0}$ vs. $E_0$ plots for different $\Delta j_1$ values.
Discussion of Results

Fig. 2 shows a plot of the transition probability $T_{0\rightarrow j_0}$ as a function of $l_0$ for the different values of $\Delta j$. Since $j_2^z = 0$, in this case the electrostatic forces (dipole - quadrupole and quadrupole - quadrupole) do not influence the excitation process. For the transition $0 \rightarrow 1$, the maximum in the $T_{0\rightarrow j_0}$ vs $l_0$ plot is due to the interference between the short-range and the long-range forces. The nature of the curve for $0 \rightarrow 2$ transition is similar to that for $0 \rightarrow 1$ transition. For the higher order transitions, the main contributions come from the lower values of $l_0$ showing thereby that these transitions are mainly due to short-range forces which are strong enough to make the order of magnitude of these transition probabilities same as those for the lower order transitions. In fact, due to the strong interactions the transition probability for $\Delta j = 4$ is higher than even that for $\Delta j = 1$ transition at very small values of $l_0$. Such behaviour of the transition probability with $l_0$ in the dominant coupling region has also been observed by Bernstein and Kramer\textsuperscript{117} and Saha et al\textsuperscript{107} for atom-diatom collisions. The humps in the curves are totally absent for $\Delta j = 4$ and $+ 5$ transitions showing further the comparatively small role played by the long-range forces for the higher order transitions. Hence we may conclude that the transitions involving a number of step-wise jumps predominate at small $l_0$ while the first order is most important in the region of large $l_0$. 


Fig. 3 shows the plots of $T_{01; j1}^{0}$ for the different transitions as function of $\ell_0$ for $E_0 = .065$ ev. In this case since $j_2^0 = 1$, the electrostatic forces also affect the transitions. For figs 2 and 3, the $E_0$ values are close enough so that they may be taken as the same for our discussions. For $j_2^0 = 1$, the probabilities for $0 \rightarrow 1$ transition are in general higher than the corresponding values for $j_2^0 = 0$. The position of the maximum in the curve is shifted to the right in the former case. The most significant effect of the electrostatic forces is the contributions to the transition probabilities from values of $\ell_0$ which are higher than those for $j_2^0 = 0$ (Fig.2). This is due to the longer range of the electrostatic forces. For the $0 \rightarrow 2$ transition, $T_{01; j1}^{0}$ values are however, lower than those for $T_{01; j0}^{0}$ values. The hump in the curve as that for $0 \rightarrow 1$ transition is shifted to the right compared to that of the corresponding curve for $j_2^0 = 0$ and higher values of $\ell_0$ contribute. For the higher order transitions almost the same range of $\ell_0$ values contribute to the transition probability for $j_2^0 = 0$ and 1 showing that the electrostatic forces in the longer range are not strong enough to induce higher order transitions. For these transitions, the effects of electrostatic forces seems to be lowering of the transition probabilities and the appearance of the humps in the curves even for $\Delta j_1 = 5$ transition. In Fig. 4 the $T_{0j; j1}^{0}$ values have been plotted as function of $\ell_0$ for $E_0 = .065$ ev. A comparison of the curves in Figs. 3 and 4 shows that the change in the rotational state
of H₂ affects the transition probabilities in a complicated way which does not follow a regular pattern. The general features are that the humps in the curves are shifted further towards right in Fig. 4 and slightly higher values of ℓ₂ than those in Fig. 3 contribute to Δj₁=1,2 transitions.

Fig. 5 gives plots of T₁₀;j₁₀ as function of ℓ₀ i.e., when HCN is in the initial state j₁₀ = 1 and H₂ in j₂₀ = 0. In this case, the nature of the curves is similar to that for T₀₀; j₁₀ shown in Fig. 2. The transition probability for 1 → 2 transition is higher than that for 0 → 1 transition and for other values of Δj₁, the transition probabilities in Fig. 5 are lower. Thus the change in the initial rotational state of HCN affects the transitions to some extent. The result may be interpreted in the following way. For j₁₀ = 1, the ΔE values (the energy gap between rotational levels of HCN) for same Δj₁ are higher than those for j₁₀ = 0. Thus the interactions being the same, the step-wise jumps become less probable in the first case resulting in higher transition probabilities for the first order transition and lower values for the higher order transitions. In Fig. 6, T₁₁; j₁₁ values are plotted against ℓ₀. The effects of the electrostatic forces are similar to those for which j₁₀ = 0 (Fig. 3). However the transition probabilities are affected in a complicated way.

In Fig. 7, the cross sections σ₁₂₁; j₁₂ have been plotted as function of energy for j₁₀ = 0 and j₂₀ = 0. The
cross sections show a decrease with the increase of energy, the only special feature being the higher values of cross sections for $0 \rightarrow 4$ transition than for $0 \rightarrow 3$ transition which is due to the coupling of intermediate states.

Thus from the above discussions it is seen that for molecule-molecule collisions the transition probabilities are strongly influenced by the initial rotational states of the molecules. Further complications arise due to the existence of electrostatic forces. The nature of variation of the transition probabilities with these various factors is rather unpredictable. Further studies both theoretical and experimental on carefully chosen systems are therefore necessary.
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