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Multipolar model for collisional quantum interference on rotational energy transfer *

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Abstract A theoretical model of collisional quantum interference (CQI) is developed in a diatom-diatom system based on the first-order Born approximation of time-dependent perturbation theory and the multipolar interaction potential. The transition cross section is obtained. The relations between the differential and integral interference angles are discussed. The key factors on the determination of the differential and integral interference angles are obtained. The changing tendency of the interference angles with the experimental temperatures is obtained.

Keywords: multipolar, collisional quantum interference (CQI), rotational energy transfer.

The first evidence of collisional quantum interference (CQI) in intramolecular rotational energy transfer was obtained by Sha et al. in the CO $A^1\Pi(v=0) \sim e^3\Sigma^-(v=1)$ system in collision with He, Ne and other partners^[1,2]. CQI was also observed by Chen et al. in Na₂ $A^1\Sigma_u^+(v=8) \sim b^3\Pi_{0u}(v=14)$ system in collision with Na (3s)^[3]. The model of CQI on rotational energy transfer was derived in an atom-diatom system (with the atom being a partner), and the experiment in CO $A^1\Pi(v=0) \sim e^3\Sigma^-(v=1)$ system in collision with He was simulated successfully^[4]. To further study CQI, the experiment of CO $A^1\Pi(v=0) \sim e^3\Sigma^-(v=1)$ system in collision with a polar molecule as the partner is prepared. In this paper, a theoretical model of CQI in intramolecular energy transfer is derived in a diatom-diatom system, being in line with the model in an atom-diatom system^[4], based on the first-order Born approximation of time-dependent perturbation theory and the multipolar interaction potential. This model can be used to predict and simulate such an experiment.

1 Collisional quantum interference in a diatom-diatom system

The Born-Oppenheimer electronic Hamiltonian is written in the form

$$H_e = H_A + H_B + V, \quad (1)$$

where H_A and H_B are the electronic Hamiltonians of molecules A and B, and V is the electrostatic interaction potential. The interaction potential between two diatomic molecules is expanded in the standard multipolar series^[5],

$$V = \sum_{l_A, l_B} (-1)^{l_B} [(2l)! / (2l_A)! (2l_B)!]^{1/2} \cdot T_{lm}(\mathbf{r}_A \mathbf{r}_B) \cdot U_{lm}(\mathbf{R}), \quad (2)$$

where $l = l_A + l_B$, l_A and l_B are the order of the multiple, \mathbf{r}_A and \mathbf{r}_B denote the coordinates of all the electrons and nuclei in molecules A and B, \mathbf{R} is the vector joining the mass centers of the two molecules and is a function of time $\mathbf{R} = \mathbf{R}(t)$, and $U_{lm}(\mathbf{R})$ is a spherical tensor with components^[6],

$$U_{lm}(\mathbf{R}) = [4\pi / (2l + 1)]^{1/2} R^{-l-1} Y_{lm}(\mathbf{R}), \quad (3)$$

where $Y_{lm}(\mathbf{R})$ is the spherical function. Also, $T_l(\mathbf{r}_A \mathbf{r}_B)$ denotes a tensor product of two spherical tensors with components,

$$T_l(\mathbf{r}_A \mathbf{r}_B) = \sum_{m_A m_B} (l_A m_A l_B m_B | l_A l_B lm) Q_{l_A m_A}(\mathbf{r}_A) Q_{l_B m_B}(\mathbf{r}_B), \quad (4)$$

where $(l_A m_A l_B m_B | l_A l_B lm)$ is the Clebsch-Gordon coefficient and the spherical tensor operator Q_{lm} is an operator for the l th electric multipole, defined in

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general as^[7]

$$Q_{lm}(\mathbf{r}) = e[4\pi/(2l+1)]^{1/2} \sum_i r_i^l Y_{lm}(\mathbf{r}). \quad (5)$$

We further recall that the scalar product of two tensor operators is given by the expression^[6]

$$T_l \cdot U_l = \sum_m (-1)^m T_{lm} U_{l-m}. \quad (6)$$

It is necessary to convert the multipolar operator $Q_{l,\Lambda'-\Lambda}$ in molecule fixed frame into a space-fixed frame

$$Q_{lm} = D_{m,\Lambda'-\Lambda}^{l*} Q_{l,\Lambda'-\Lambda}, \quad (7)$$

where D_m^{l*} is a rotation matrix element, and the definition of Euler angle was given by Brink and Satchler^[8]. Note that there is no summation on the right-hand side of Eq. (7), because there is only one non-vanishing molecular frame component. Molecule A is a polar partner in this paper.

The evolution of the interaction potential^[9] is

$$V(t) = U^+(t,0) V U(t,0), \quad (8)$$

where $U(t,0)$ is a time evolution operator,

$$U(t,0) = \exp(-iH_0 t/\hbar). \quad (9)$$

Introducing Eq. (9) into Eq. (8), one can get

$$\begin{aligned} V(t) &= U^+(t,0) V U(t,0) \\ &= \exp(iH_0 t/\hbar) V \exp(-iH_0 t/\hbar). \end{aligned} \quad (10)$$

The unperturbed wave functions are

$$\begin{pmatrix} \varphi_J^S \\ \varphi_J^T \end{pmatrix} = \begin{pmatrix} |\psi JKM\rangle^S \\ |\psi JKM\rangle^T \end{pmatrix}, \quad (11)$$

where φ are the wave functions of electronic state and vibration state, and $|JKM\rangle$ represent rotation wave function^[10],

$$|JKM\rangle = [(2J+1)/8\pi^2] D_M^{J*}. \quad (12)$$

The zeroth order unperturbed energies are defined as $E(\varphi_J^S)$ and $E(\varphi_J^T)$. If v_{ST} is the coupling between these zeroth order states, the perturbed states have energies^[11],

$$\begin{aligned} E_{\pm}(JKM) &= \frac{1}{2} [E(\varphi_J^S) + E(\varphi_J^T)] \\ &\pm \frac{1}{2} \{ [E(\varphi_J^S) - E(\varphi_J^T)]^2 + 4v_{ST}^2 \}^{1/2}. \end{aligned} \quad (13)$$

The perturbed wave functions are

$$\begin{pmatrix} \Psi_J^S \\ \Psi_J^T \end{pmatrix} = \begin{pmatrix} \cos\phi_J & \sin\phi_J \\ -\sin\phi_J & \cos\phi_J \end{pmatrix} \begin{pmatrix} \varphi_J^S \\ \varphi_J^T \end{pmatrix}. \quad (14)$$

Eq. (13) shows that the mutual perturbing states are repulsive to each other. The energy level shifts Δ_{\pm} are

$$\Delta_{\pm} \equiv E_{\pm}(JKM) - E(\varphi_J), \quad (15)$$

where Δ_+ denotes an upward shift and Δ_- a downward shift. The argument ϕ , characterizing the mixing effects, is given by

$$\phi = \arcsin |v_{ST}/[E(\Psi_J^S) - E(\varphi_J^T)]|. \quad (16)$$

In the later derivation, according to Eq. (14), we set the mixing coefficients at $c_J \equiv \cos\phi_J$ and $d_J \equiv \sin\phi_J$, or $c_J \equiv -\sin\phi_J$ and $d_J \equiv \cos\phi_J$ depending on whether the perturbed state is a singlet or a triplet state. From Eqs. (13) ~ (16), the values and the signs of c_J and d_J can be obtained. c_J and d_J will have the same sign if energy level J is shifted upwards by perturbation; otherwise, c_J and d_J will have the opposite signs. If both the initial state $|i\rangle$ and final state $|f\rangle$ of a collision-induced transition are singlet-triplet mixed states, then

$$|i\rangle = |\psi JKM\rangle_A [c_J |\psi JKM\rangle^S + d_J |\psi JKM\rangle^T]_B \quad (17)$$

and

$$|f\rangle = |\psi J'K'M'\rangle_A [c_{J'} |\psi J'K'M'\rangle^S + d_{J'} |\psi J'K'M'\rangle^T]_B. \quad (18)$$

The matrix elements $\langle J'M'\psi | Q^l | JM\psi \rangle$ can be expressed as

$$\begin{aligned} &\langle J'M'\psi | Q_{lm} | JM\psi \rangle \\ &= (-1)^{J'-M'} \begin{pmatrix} J' & l & J \\ -M' & m & M \end{pmatrix} \langle J'\psi || Q_{lm} || J\psi \rangle \\ &= (-1)^{J'-M'} (-1)^{J'-\Omega'} \delta(J', l, J) \\ &\quad \times [(2J'+1)(2J+1)]^{1/2} \\ &\quad \times \begin{pmatrix} J' & l & J \\ -M' & m & M \end{pmatrix} \begin{pmatrix} J' & l & J \\ -\Omega' & \Lambda' - \Lambda & \Omega \end{pmatrix} \\ &\quad \times \langle \psi || Q_{l,\Lambda'-\Lambda} || \psi \rangle. \end{aligned} \quad (19)$$

The amplitude of the transition in the first-order Born approximation can be written as

$$\begin{aligned} &\frac{1}{i\hbar} \int_{-\infty}^{\infty} \langle f | \exp(iH_0 t/\hbar) V \exp(-iH_0 t/\hbar) | i \rangle dt \\ &= \frac{1}{i\hbar} \sum_{l_A l_B} (-1)^{l_B} [(2l)!/(2l_A)!(2l_B)!]^{1/2} \\ &\quad \times (-1)^{J'_A+J'_B-M'_A-M'_B} \langle J'_A\psi_A || Q_{l_m}^A || J_A\psi_A \rangle \\ &\quad \times \sum_{M'_A M'_B} (l_A m_A l_B m_B | l_A l_B l m) (-1)^m \\ &\quad \times \begin{pmatrix} J'_A & l_A & J \\ -M'_A & m & M \end{pmatrix} \begin{pmatrix} J'_B & l_B & J \\ -M'_B & m & M \end{pmatrix} \\ &\quad \times [c_{J'} c_J \langle J'_B\psi_B || Q_{l_m}^B || J_B\psi_B \rangle^S I_{l_m}^A(\varpi_{J'}^S, b) \\ &\quad + d_{J'} d_J \langle J'_B\psi_B || Q_{l_m}^B || J_B\psi_B \rangle^T I_{l_m}^B(\varpi_{J'}^T, b)], \end{aligned} \quad (20)$$

where

$$I_{lm}(\varpi_{JJ}, b) = \int_{-\infty}^{\infty} \exp(i\varpi_{JJ} t) R^{-l-1} C_{lm} dt, \quad (21)$$

and C_{lm} is a Racah spherical harmonic,

$$C_{lm} = [4\pi/(2l + 1)]^{1/2} Y_{lm}. \quad (22)$$

It is convenient, following Gray and Van Kranendonk^[12], to define the dimensionless variables as

$$x = \varpi b/v, \quad z = vt/b. \quad (23)$$

In terms of these variables, the integral I_{lm} can be written as

$$I_{lm}(x) = (1/vb^{2l})J_{lm}(x), \quad (24)$$

where $J_{lm}(\varpi J_J, b)$ is dimensionless, given by

$$J_{lm}(x) = \frac{2^{l-m}}{(l-m)!(l+m)!} x^l K_m(x). \quad (25)$$

The expression of transition probability in the first order Born approximation is

$$P_{JJ} = \frac{1}{(2J_A + 1)(2J_B + 1)} \sum_{MM} \left| \frac{1}{i\hbar} \int_{-\infty}^{\infty} \langle f | V(t) | i \rangle dt \right|^2. \quad (26)$$

Introducing Eq. (20) into Eq. (26) and considering the orthogonal relations involving the 3 j symbols and Clebsch-Gordan coefficients, we obtain an explicit formula for the $J \rightarrow J'$ transition probability:

$$P = c_J^2 c_{J'}^2 P_{JJ'}^S + d_J^2 d_{J'}^2 P_{JJ'}^T + 2c_J c_{J'} d_J d_{J'} \sum_m [(P_{JJ'}^S)_m (P_{JJ'}^T)_m]^{1/2}. \quad (27)$$

$P_{JJ'}^S$ and $P_{JJ'}^T$ in Eq. (27) can be expressed as

$$P_{JJ'}^H(b) = \sum_m [(P_{JJ'}^H)_m] = \sum_{A', B} \frac{(2l)! \langle J_A \psi_A || Q_{lm}^A || J \psi_A \rangle^2 \langle J_B \psi_B || Q_{lm}^B || J_B \psi_B \rangle^H}{(2l_A)!(2l_B)!(2J_A + 1)(2J_B + 1) \hbar^2 b^{2l} v^2} \cdot \sum_m |J_{lm}(\varpi J_J, b)|^2, \quad (28)$$

where H is S or T. Eq. (27) can be rewritten in the form of Eq. (4a) in Ref. [1],

$$P = c_J^2 c_{J'}^2 P_{JJ'}^S + d_J^2 d_{J'}^2 P_{JJ'}^T + 2c_J c_{J'} d_J d_{J'} (P_{JJ'}^S P_{JJ'}^T)^{1/2} \cos\theta_{ST}^D, \quad (29)$$

with the differential interference angle

$$\cos\theta_{ST}^D = \frac{\sum_m [(P_{JJ'}^S)_m (P_{JJ'}^T)_m]^{1/2}}{[P_{JJ'}^S P_{JJ'}^T]^{1/2}}. \quad (30)$$

The energy transfer cross section can be expressed as^[13]

$$\sigma_{JJ'} = 2\pi(b) \int_0^\infty P_{JJ'} b db. \quad (31)$$

$$\cos\theta_{ST}^I = \frac{\iint \frac{\nu}{b^3} |J_{20}(x_T)| |J_{20}(x_S)| \exp\left(\frac{-\mu\nu^2}{2kT}\right) db d\nu}{\left(\iint \frac{\nu}{b^3} \sum_{m=0, \pm 2} |J_{2m}(x_S)|^2 \exp\left(\frac{-\mu\nu^2}{2kT}\right) db d\nu\right)^{1/2} \left(\iint \frac{\nu}{b^3} |J_{20}(x_T)|^2 \exp\left(\frac{-\mu\nu^2}{2kT}\right) db d\nu\right)^{1/2}} \quad (37)$$

if we only consider the dipolar interaction. In the cal-

By introducing Eq. (27) into Eq. (31), the integral cross section can be obtained,

$$\sigma_{JJ'} = c_J^2 c_{J'}^2 \sigma_{JJ'}^S + d_J^2 d_{J'}^2 \sigma_{JJ'}^T + 2c_J c_{J'} d_J d_{J'} (\sigma_{JJ'}^S \sigma_{JJ'}^T)^{1/2} \cos\theta_{ST}^I, \quad (32)$$

with cosine of the integral interference angle

$$\cos\theta_{ST}^I = \frac{\int \sum_m [(P_{JJ'}^S)_m (P_{JJ'}^T)_m]^{1/2} b db}{\left(\int (P_{JJ'}^S(b) b db)\right)^{1/2} \left(\int (P_{JJ'}^T(b) b db)\right)^{1/2}}. \quad (33)$$

$\cos\theta_{ST}^I$ can also be obtained by substituting Eq. (29) into Eq. (31),

$$\cos\theta_{ST}^I = \frac{\int (P_{JJ'}^S(b) P_{JJ'}^T(b))^{1/2} \cos\theta(b) b db}{\left(\int (P_{JJ'}^S(b) b db)\right)^{1/2} \left(\int (P_{JJ'}^T(b) b db)\right)^{1/2}}. \quad (34)$$

Eq. (34) gives out the relation between the differential and integral interference angle. If we only consider the dipolar interaction, by substituting Eq. (28) into Eq. (33), an explicit formula for $\cos\theta_{ST}^I$ is obtained,

$$\cos\theta_{ST}^I = \frac{\int \sum_m \frac{1}{b^3} |J_m^2(x_T)| |J_m^2(x_S)| db}{\left(\int \frac{1}{b^3} \sum_m |J_m^2(x_S)|^2 db\right)^{1/2} \left(\int \frac{1}{b^3} \sum_m |J_m^2(x_T)|^2 db\right)^{1/2}}. \quad (35)$$

However, Eq. (35) for the integral interference angle, which has been derived for the partners with uniform collision velocity, is not fit to deal with the cell experiments in which the gas species have the Maxwell-Boltzmann velocity distribution. In this case, Braithwaite et al. have derived a formula to get velocity-averaged probability^[14],

$$P_{AV} = \int_{-\infty}^{\infty} P(\nu) \nu^3 \exp\left(\frac{-\mu\nu^2}{2kT}\right) d\nu / \int_{-\infty}^{\infty} \nu^3 \exp\left(\frac{-\mu\nu^2}{2kT}\right) d\nu = 2\left(\frac{\mu}{kT}\right)^2 \int_0^\infty P(\nu) \nu^3 \exp\left(\frac{-\mu\nu^2}{2kT}\right) d\nu. \quad (36)$$

Now, the velocity-averaged integral interference angle can be obtained by first substituting Eq. (28) into Eq. (36) to get $P_{JJ'}(AV)$ and then the $P_{JJ'}(AV)$ into Eq. (33),

calculation of $\text{COA}^1\Pi/e^3\Sigma^-$ with a polar diatom colli-

sion interference angle, the first summation in the denominator is for the $^1\Pi$ channel, so $m = 0$ and $m = \pm 2$ ^[15]; the second summation in the denominator is for the $^3\Sigma^-$ channel, $m = 0$ only.

2 Discussion

The integral interference angle, θ_{ST}^I , represents the average effect of the differential interference angle, $\theta_{S,T}^D$ (see Eq. (34)). The key factors on which the integral interference angle depends (see Eq. (37)) are: (i) the molecular rotation constant, B ; (ii) the initial and final angle quantum numbers J , J' ($x = \varpi b/\nu$ and $\omega = 2\pi cB [J'(J'+1) - J(J+1)]$); (iii) reduced mass μ ($\mu = \frac{m_{CO}m_{partner}}{m_{CO} + m_{partner}}$) and impact parameter b ($b_{min} = r(CO) + r(partner)$); (iv) experiment temperature, T ; and (v) the relative velocity between colliders.

If the experiments of CO $A^1\Pi(v=0) \sim e^3\Sigma^-(v=1)$ system in collision with HCl (partner) are carried out at 200, 250, 300, 350 and 400 K, we can obtain the changing tendency between the interference angles and the experimental temperatures. In the calculations, the initial and final rotational quantum numbers are $J = 9$ and $J' = 10$, respectively. The other parameters in the calculations are shown in Table 1. From the calculated values shown in Fig. 1, with the increase of the experimental temperature, the interference angle will increase, i. e. the degree of the interference decreases. It is interpreted by Sha et al. that with the increase of experimental temperature (the kinetic energy increases), the collision becomes stronger, and the singlet-triplet mixed states may de-

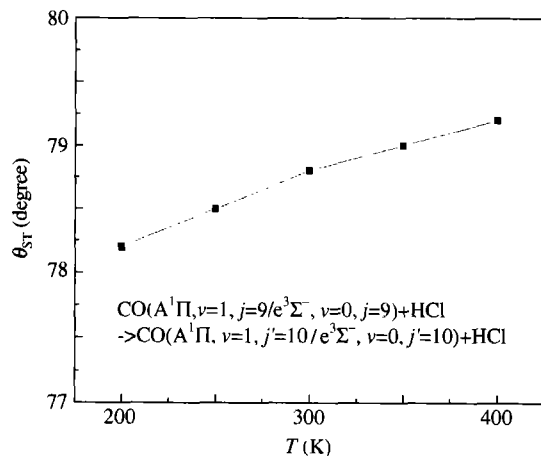


Fig.1. The relation between the interference angles and the experimental temperatures.

couple due to the different energy level shifts of the singlet and triplet states induced by the collision perturbation. As the results of decoupling, the mixing degree of corresponding wave functions would become smaller than that of the isolated-molecule and the interference will become weaker as well^[4].

Table 1. Parameters for the theoretical calculation of the integral interference angle θ_{ST}^I

Collision system	Reduced mass (a. u.)	$b_{min}(\text{\AA})$	Rotational constants B (cm^{-1}) ^{a)}	
			CO($A^1\Pi$)	CO($e^3\Sigma^-$)
CO-HCl	15.85	4	1.6105	1.2836

a) From Ref. [16].

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