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The differential interference angle in collisional quantum interference on rotational energy transfer*

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Collisional quantum interference (CQI) in the intramolecular rotational energy transfer was observed in experiment by Sha and co-workers.[1] The interference angle, which measuring the degree of the coherence, were measured in the experiment of the static cell. Based on the first Born approximation of time dependent perturbation theory, taking into accounts the anisotropic Lennard-Jones interaction potentials, this paper describes the theoretical model of CQI in intramolecular rotational energy transfer in an atom–diatom collision system. In the model, the differential interference angle for the experiment of the molecular beam is calculated, the changing tendencies of the differential interference angle with the impact parameter and collision partners are obtained. This theoretical model is important for understanding or performing this kind of experiments.

Keywords: rotational energy transfer, differential interference angle, collision parameter
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1. Introduction

In intramolecular rotational energy transfer, the evidence of collisional quantum interference (CQI) was obtained by Sha *et al* in the CO $A^1\Pi(v = 0) - e^3\Sigma^-(v = 1)$ system in collision with He, Ne and other partners.[1−4] CQI was also observed by Chen *et al* in $Na_2 A^1\Sigma_u^+(v = 8) - b^3\Pi_{0u}(v = 14)$ system in collision with Na (3s).[5] The CQI mentioned here is different from some other quantum interferences in molecular dynamics and spectroscopy, such as quantum beat spectroscopy[6] and rotational coherence spectroscopy.[7,8] The CQI is a radiationless transition process, while the others result from the interaction of an atom and a molecule system.

The experiments of CO $(A^1\Pi - e^3\Sigma^-)$- He, Ne and other partners were taken in a static cell, so only the integral cross sections and the integral interference angles have been measured.[1,2] The integral interference angle is the average effect of the differential interference angle.[9−11] If experiments can be conducted in molecular beams to measure the differential cross section and the differential interference angle, the CQI effect might be able to be observed more precisely. Differential cross sections for rotationally inelastic scattering of NO from He and D_2 have been measured by crossed molecular beam product imaging,[7] and rotational state-to-state differential cross sections for the HCL–Ar collision system have also been measured by using velocity-mapped ion imaging.[12,13] Similar to these experiments, experiments on the CO $(A^1\Pi - e^3\Sigma^-)$ system in collision with He, Ne and other partners may be performed in the molecular beams by using velocity-mapped ion imaging.

To study theoretically experiments of the CO $(A^1\Pi - e^3\Sigma^-)$ system in collision with He, Ne and other partners in the condition of molecular beams by using velocity-mapped ion imaging, we proposed a theoretical model in this paper, basing on the time dependent first order Born approximation, taking into account the anisotropic Lennard-Jones interaction potentials[14] and 'straight-line' trajectory approximation. The differential interference angle can be calculated, and the changing tendency of the differential interference angle with the impact parameter

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and collision partner is obtained.

2. Theoretical approach

2.1. Hamiltonian

For the atom–diatom system, the Born–Oppenheimer electronic Hamiltonian is given as

$$H = H_A + H_B + V. \tag{1}$$

Where H_A and H_B are the electronic Hamiltonians of the atom A and the diatom B respectively, V represents the electrostatic interaction potential between the atom and diatom in the space frame,

$$V(R,\theta,\phi) = \sum_{l,m,k} V_{l,k}(R) D^l_{m,k}(\Omega) C^l_m(\theta,\phi), \tag{2}$$

where R is the distance from the atom to the mass centre of diatom, $D^l_{m,k}(\Omega)$ is the Wigner D rotational matrix, the Euler angles $\Omega = \alpha, \beta, \gamma$ refer to the space fixed orientation of the diatomic molecule, $C^l_m(\theta,\phi)$ is a Racah spherical harmonic function, the angles θ, ϕ describe the orientation of R in the space frame. In the atom and $^1\Pi$-states diatomic molecules system, $k = 0$ or $k = \pm 2$,[15] which reflects the Π electronic cloud distribution of C_{2v} group. In the atom and $^3\Sigma$-states diatomic molecules system, $k = 0$.[16] The evolution of the interaction potential is

$$V(t) = U^+(t,0) V U(t,0). \tag{3}$$

Where $U(t,0)$ is the time evolution operator,

$$U(t,0) = \exp(-\mathrm{i} H_0 t/\hbar). \tag{4}$$

If only rotational energy transfer is considered,

$$H_0 = \omega\hbar = 2\pi h c B^{\mathrm{T}} J(J+1), \tag{5}$$

for the $^3\Sigma$-states diatomic molecules

$$H_0 = \omega\hbar = 2\pi h c [B^{\mathrm{S}} J(J+1) - 2\Omega'\Lambda + \Lambda^2] \tag{6}$$

for the $^1\Pi$-states diatomic molecules, where $\Lambda = 1$ and $\Omega' = \Omega = \pm 1$ or $\Omega' = -\Omega = \pm 1$.

2.2. Wavefunction for the $^1\Pi$-state diatomic molecule

For a $^1\Pi$-state diatomic molecule, the wavefunctions are of definite parity, which may be written as

$$|JM\varepsilon\rangle = \frac{1}{\sqrt{2}} \left[|JM\,|\Omega|\rangle + \varepsilon\,|JM,-|\Omega|\rangle \right], \tag{7}$$

where J is the total angular momentum quantum number, M is the projection of J along a space-fixed Z-axis, $\Omega = \Lambda = \pm 1$ are the projection of total angular momentum on the molecular frame, and $\varepsilon = \pm 1$. The quantity ε will be designated as the parity index. Within the spectroscopic nomenclature, the $\varepsilon = +1$ levels are designated as e and the $\varepsilon = -1$ levels as f.[17] The rotational wavefunction $|JM\Omega\rangle$ which appears in Eq.(7) can be written as a rotational matrix element

$$|JM\Omega\rangle = \left[(2J+1)/8\pi^2\right]^{1/2} D^{J*}_{M\Omega}(\alpha\beta\gamma). \tag{8}$$

Consider the interaction between a $^1\Pi$ diatomic molecule and a spherical atom in a singlet state, the total wavefunction is usually expanded in terms of the eigenfunction of the total angular momentum $\Im$, which are defined by

$$|J\Omega\varepsilon\Im\varsigma\rangle = \sum_{MM_L} \langle JMLM_L|\Im\varsigma\rangle\,|LM_L\rangle\,|JM\varepsilon\rangle, \tag{9}$$

where ς is the space-frame projection of $\Im$, L is the orbital angular momentum of the atom-molecule pair with space-frame projection M_L, and $|LM_L\rangle$ is a spherical harmonic[18]

$$\begin{aligned} |LM_L\rangle &= Y^L_{M_L}(\theta,\phi) \\ &= \left[(2L+1)/4\pi\right]^{1/2} D^L_{M_L,0}(\theta,\phi,0). \end{aligned} \tag{10}$$

2.3. Wavefunction for the $^3\Sigma$ state diatomic molecule

For a $^3\Sigma_\Omega$ state molecule, $\Omega = 0$ or ± 1, In the case of $|\Omega| = 1$, the wavefunction can be written as

$$\begin{aligned} &|NM1\varepsilon\rangle \\ &= \frac{1}{\sqrt{2}} \left[|NM,\Omega=1\rangle + \varepsilon\,|NM,\Omega=-1\rangle \right], \end{aligned} \tag{11}$$

where the parity index ε can take on the values ± 1. In contemporary spectroscopy notation, $\varepsilon = 1$ levels are labelled f for Σ^+ states and e for Σ^- states; $\varepsilon = -1$ levels are labelled e for Σ^+ states and f for Σ^- states. For the CO $e^3\Sigma^-$ state in the experiment, $\varepsilon = 1$ levels are labelled e parity (F_1 and F_3); $\varepsilon = -1$ levels are labelled f parity (F_2). $\Omega = 0$ and $\Omega = \pm 1$ levels are mixed by the nuclear rotation and spin-rotation terms in the molecular Hamiltonian.[19] The wave functions for F_1, F_2 and F_3 levels can be written as

$$|NMF_1\rangle = \cos\varsigma_J\,|NM0\rangle + \sin\varsigma_J\,|NM1\varepsilon\rangle, \tag{12}$$

$$|NMF_2\rangle = |NM1\varepsilon\rangle, \tag{13}$$

$$|NMF_3\rangle = -\sin\varsigma_J\,|NM0\rangle + \cos\varsigma_J\,|NM1\varepsilon\rangle, \tag{14}$$

where

$$\cos\varsigma_N = \left[\frac{F_2(N)-F_1(N)}{F_3(N)-F_1(N)}\right]^{1/2}, \quad (15)$$

$$\sin\varsigma_N = \left[\frac{F_3(N)-F_2(N)}{F_3(N)-F_1(N)}\right]^{1/2}. \quad (16)$$

For Hund's case (b),[20] the energy eigenvalues are well expressed, which leads to a narrowly paced triplet structure denoted by the terms of F_1 for $N = J-1$, F_2 for $N = J$, and F_3 for $N = J+1$,

$$\begin{aligned} F_1 &= BN(N+1) - (2N-1)B - \lambda \\ &\quad + \left[\lambda^2 - 2B\lambda + B^2(2N-1)^2\right]^{1/2} \\ &\quad -\gamma N + \frac{1}{2}\gamma, \end{aligned} \quad (17)$$

$$F_2 = BN(N+1), \quad \varepsilon = -1, \quad (18)$$

$$\begin{aligned} F_3 &= BN(N+1) + (2N+3)B - \lambda \\ &\quad - \left[\lambda^2 - 2B\lambda + B^2(2N+3)^2\right]^{1/2} \\ &\quad +\gamma(N+1) + \frac{1}{2}\gamma. \end{aligned} \quad (19)$$

Consider the interaction between a $^3\Sigma$ diatomic molecule and a spherical atom in a singlet state, the total wavefunction is usually expanded in terms of eigenfunctions of the total angular momentum $\Im$, which are defined by

$$\begin{aligned} &|NMF_i\Im\varsigma\rangle \\ &= \sum_{MM_L} \langle NMF_iLM_L|\Im\varsigma\rangle\,|NMF_i\rangle\,|LM_L\rangle\,. \end{aligned} \quad (20)$$

2.4. Perturbations between singlet and triplet states

The perturbed wavefunctions are

$$\begin{pmatrix} \varphi_J^{\rm S} \\ \varphi_J^{\rm T} \end{pmatrix} = \begin{pmatrix} |J\Omega\varepsilon\Im\varsigma\rangle^{\rm S} \\ |NMF_i\Im\varsigma\rangle^{\rm T} \end{pmatrix}. \quad (21)$$

The zero order perturbed energies are defined as $E(\varphi_J^{\rm S})$ and $E(\varphi_J^{\rm T})$. If $\nu_{\rm ST}$ is the coupling between these zero order states, the perturbed states have energies,

$$\begin{aligned} &E_\pm(JKM) \\ &= \frac{1}{2}\left[E(\varphi_J^S) + E(\varphi_J^T)\right] \\ &\quad \pm\frac{1}{2}\left\{\left[E(\varphi_J^S) - E(\varphi_J^T)\right]^2 + 4\nu_{ST}^2\right\}^{1/2}. \end{aligned} \quad (22)$$

The perturbed wave functions can be written as

$$\begin{pmatrix} \psi_J^{\rm S} \\ \psi_J^{\rm T} \end{pmatrix} = \begin{pmatrix} \cos\phi_J & \sin\phi_J \\ -\sin\phi_J & \cos\phi_J \end{pmatrix} \begin{pmatrix} \varphi_J^{\rm S} \\ \varphi_J^{\rm T} \end{pmatrix}. \quad (23)$$

Equation (23) shows that the mutual perturbing states are repulsive each other. The energy level shifts $\Delta_\pm$ are

$$\Delta_\pm \equiv E_\pm(JKM) - E(\varphi_J), \quad (24)$$

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

$$\phi = \arcsin\left\{\nu_{\rm ST}/\left[E(\psi_J^{\rm S}) - E(\psi_J^{\rm T})\right]\right\}. \quad (25)$$

In the later derivation, according to Eq.(23), we set that the mixing coefficients $c_J \equiv \cos\phi_J$ and $d_J \equiv \sin\phi_J$, or $c_J \equiv -\sin\phi_J$ and $d_J \equiv \cos\phi_J$ depending on the perturbed state which is a singlet or a triplet state. From Eqs.(22)–(25), the values and the sign of c_J and d_J can be obtained. c_J and d_J will have the same sign if energy level J shifts upwards by perturbation, otherwise, c_J and d_J will have the opposite sign. If both the initial state $|i\rangle$ and final state $|f\rangle$ of a collision-induced transition are singlet–triplet mixed states, then

$$|i\rangle = c_J\,|J\Omega\varepsilon\Im\varsigma\rangle^{\rm S} + d_J\,|NMF_i\Im\varsigma\rangle^{\rm T}, \quad (26)$$

and

$$|f\rangle = c_{J'}\,|J'\Omega'\varepsilon'\Im\varsigma\rangle^{\rm S} + d_{J'}\,|N'M'F_{i'}\Im\varsigma\rangle^{\rm T}. \quad (27)$$

2.5. The transition matrix element and the transition probability

According to the first order Born approximation of time dependent perturbation theory, the transition matrix element is

$$\begin{aligned} &\langle f|\,V(t)\,|i\rangle \\ &= c_Jc_{J'}\,\langle J'\Omega'\varepsilon'\Im\varsigma|\,V(t)\,|J\Omega\varepsilon\Im\varsigma\rangle \\ &\quad + d_Jd_{J'}\,\langle N'M'F_i\Im\varsigma|\,V(t)\,|NMF_i\Im\varsigma\rangle\,, \end{aligned} \quad (28)$$

where only electrostatic interaction is involved with no magnetic coupling, a transition between the two states is prohibited. In Eq.(28), according to the perturbation theory, $N = J$ and $N' = J'$. In Eq.(28), the transitional matrix for the singlet state is

$$\begin{aligned}
&\langle J'\Omega'\varepsilon'\Im_\varsigma|\,V(t)\,|J\Omega\varepsilon\Im_\varsigma\rangle \\
&= (-1)^{J+J'+\Im-\Omega}[(2J+1)(2J'+1)(2L+1)(2L'+1)]^{1/2}\sum_{\mathrm{l}}\frac{1}{2}\left[1+\varepsilon\varepsilon'(-1)^{J+J'+\mathrm{l}}\right]\begin{pmatrix} L' & l & L \\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix} J & L & \Im \\ L' & J' & l\end{Bmatrix} \\
&\times\left\{\begin{pmatrix} J' & l & J \\ 1 & 0 & -1\end{pmatrix}\exp\left(\mathrm{i}\varpi_{J'J}^{\Delta\Omega=0}t\right)V_{l,0}[R(t)]+\varepsilon\begin{pmatrix} J' & l & J \\ -1 & 2 & -1\end{pmatrix}\exp\left(\mathrm{i}\varpi_{J'J}^{\Delta\Omega=2}t\right)V_{l,2}[R(t)]\right\},
\end{aligned}\tag{29}$$

and the transitional matrix of the triplet state is

$$\begin{aligned}
&\langle N'M'F_i'\Im_\varsigma|\,V(t)\,|NMF_i\Im_\varsigma\rangle \\
&= \delta_{\Omega'\Omega}(-1)^{N+N'+l+2\Omega}\left[(2N+1)(2N'+1)(2L+1)(2L'+1)\right]^{1/2}\sum_{\mathrm{l}}\begin{pmatrix} L' & l & L \\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix} N & L & \Im \\ L' & N' & l\end{Bmatrix} \\
&\times\left\{\frac{1}{2}\left[1+\varepsilon\varepsilon'(-1)^{N+N'+\mathrm{l}}\right]\begin{pmatrix} N' & l & N \\ 1 & 0 & -1\end{pmatrix}D_{N'N}+\begin{pmatrix} N' & l & N \\ 0 & 0 & 0\end{pmatrix}E_{N'N}\right\}\exp(\mathrm{i}\varpi_{N'N}t)V_{l,0}[R(t)].
\end{aligned}\tag{30}$$

The unpolarized transition probability can be written as

$$P_{J'J}=\frac{1}{(2J+1)}\sum_{LL'}\left|\frac{1}{\mathrm{i}\hbar}\int_{-\infty}^{\infty}\langle f|\,V(t)\,|\mathrm{i}\rangle\,\mathrm{d}t\right|^2. \tag{31}$$

Substituting Eq.(28) into Eq.(31), considering the orthogonal relationship of the three J symbol,

$$\begin{aligned}
&\sum_{m_1m_2}\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3\end{pmatrix}\begin{pmatrix} j_1 & j_2 & j_3' \\ m_1 & m_2 & m_3'\end{pmatrix} \\
&= \frac{1}{2j_3+1}\delta_{j_3,j_3'}\delta_{m_3,m_3'},
\end{aligned}\tag{32}$$

$$\begin{aligned}
&\sum_{j_{31}m_3}(2j_3+1)\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3\end{pmatrix}\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1' & m_2' & m_3\end{pmatrix} \\
&= \delta_{m_1,m_1'}\delta_{m_2,m_2'},
\end{aligned}\tag{33}$$

one can obtain,

$$\begin{aligned}
P_{JJ'} &= c_J^2c_{J'}^2P_{JJ'}^S+d_J^2d_{J'}^2P_{JJ'}^{\mathrm{T}} \\
&\quad +2c_Jc_{J'}d_Jd_{J'}P_{\mathrm{ST}}^{\mathrm{Inter}}
\end{aligned}\tag{34}$$

where $P_{JJ'}^{\mathrm{S}}$, $P_{JJ'}^{\mathrm{T}}$ are the pure transition probability of the singlet and triplet states, the third term is the interference term. The transition probability for the singlet state is

$$P_{J'J}^{\mathrm{S}}=P_{JJ'}^{\Delta\Omega=0}+P_{JJ'}^{\Delta\Omega=2}+P_{\mathrm{S}}^{\mathrm{Inter}}, \tag{35}$$

where the spin-orbit conserving transition, the spin-orbit changing transitions and the interference between the spin-orbit conserving and the spin-orbit changing transitions are, respectively,

$$\begin{aligned}
P_{JJ'}^{\Delta\Omega=0} &= \frac{(2J'+1)}{\hbar^2}\sum_{L,L'}(2L+1)(2L'+1)\sum_l F^2\begin{pmatrix} L' & l & L \\ 0 & 0 & 0\end{pmatrix}^2\begin{Bmatrix} J & L & \Im \\ L' & J' & l\end{Bmatrix}^2\begin{pmatrix} J' & l & J \\ 1 & 0 & -1\end{pmatrix}^2 \\
&\quad\times\left|\int_{-\infty}^{\infty}\exp(\mathrm{i}\varpi_{J'J}^{\Delta\Omega=0}t)V_{l,0}(R)\mathrm{d}t\right|^2,
\end{aligned}\tag{36}$$

$$\begin{aligned}
P_{JJ'}^{\Delta\Omega=2} &= \frac{(2J'+1)}{\hbar^2}\sum_{L,L'}(2L+1)(2L'+1)\sum_l F^2\begin{pmatrix} L' & l & L \\ 0 & 0 & 0\end{pmatrix}^2\begin{Bmatrix} J & L & \Im \\ L' & J' & l\end{Bmatrix}^2\begin{pmatrix} J' & l & J \\ -1 & 2 & -1\end{pmatrix}^2 \\
&\quad\times\left|\int_{-\infty}^{\infty}\exp(\mathrm{i}\varpi_{J'J}^{\Delta\Omega=2}t)V_{l,2}(R)\mathrm{d}t\right|^2,
\end{aligned}\tag{37}$$

$$P_{\mathrm{S}}^{\mathrm{Inter}} = \frac{(2J'+1)}{\hbar^2}\sum_{L,L'}(2L+1)(2L'+1)\sum_l F^2\begin{pmatrix} J' & l & J \\ 1 & 0 & -1\end{pmatrix}\begin{pmatrix} J' & l & J \\ -1 & 2 & -1\end{pmatrix}\begin{pmatrix} L' & l & L \\ 0 & 0 & 0\end{pmatrix}^2$$

$$\times \left\{ \begin{array}{ccc} J & L & \Im \\ L' & J' & l \end{array} \right\}^2 \left\{ \int_{-\infty}^{\infty} \exp(\mathrm{i}\varpi_{J'J}^{\Delta\Omega=0} t) V_{l,0}(t) \mathrm{d}t \left(\int_{-\infty}^{\infty} \exp(\mathrm{i}\varpi_{J'J}^{\Delta\Omega=2} t) V_{l,2}(t) \mathrm{d}t \right)^* + \text{h.c.} \right\}. \quad (38)$$

The transition probability of the triplet state is

$$P_{J'J}^{\mathrm{T}} = \frac{(2J'+1)}{\hbar^2} \sum_l \sum_{L'L} [(2L+1)(2L'+1)] \left(\begin{array}{ccc} L' & l & L \\ 0 & 0 & 0 \end{array} \right)^2 \left\{ \begin{array}{ccc} J & L & \Im \\ L' & J' & l \end{array} \right\}^2 \left\{ F^2 \left(\begin{array}{ccc} J' & l & J \\ 1 & 0 & -1 \end{array} \right)^2 D_{N'N}^2 + \left(\begin{array}{ccc} J' & l & J \\ 0 & 0 & 0 \end{array} \right)^2 E_{N'N}^2 \right\} \left| \int \exp(\mathrm{i}\varpi_{J'J} t) V_{l,0}[R(t)] \right|^2. \quad (39)$$

The interference term in Eq.(34) is

$$P_{\mathrm{S,T}}^{\mathrm{Inter}} = \frac{1}{2} \frac{(2J'+1)}{\hbar^2} \sum_{L,L'} (2L+1)(2L'+1) \sum_l F^2 \left(\begin{array}{ccc} L' & l & L \\ 0 & 0 & 0 \end{array} \right)^2 \left\{ \begin{array}{ccc} J & L & \Im \\ L' & J' & l \end{array} \right\}^2 \left(\begin{array}{ccc} J' & l & J \\ 1 & 0 & -1 \end{array} \right)^2 D_{N'N}^2 \times \left| \int_{-\infty}^{\infty} \exp\left(\mathrm{i}\varpi_{J'J}^{S,\Delta\Omega=0} t\right) V_{l,0}(R) \mathrm{d}t \left(\int_{-\infty}^{\infty} \exp\left(\mathrm{i}\varpi_{J'J}^{T,\Delta\Omega=0} t\right) V_{l,0}(R) \mathrm{d}t \right) + \text{h.c.} \right|^2. \quad (40)$$

It should be noted that the interference terms of Eq.(38) and Eq.(40) are different. The interference term in Eq.(38) is the interference spin-orbit conserving and the spin-orbit changing transitions in the state of $\mathrm{CO}(\mathrm{A}^1\Pi, v=0)$; while the interference term in Eq.(40) is the interference between the state of $\mathrm{CO}(\mathrm{A}^1\Pi, v=0)$ and the $\mathrm{CO}(e^3\Sigma, v=1)$. The selection rules of the perturbation between $\mathrm{CO}(\mathrm{A}^1\Pi, v=0)$ and the $\mathrm{CO}(e^3\Sigma, v=1)$ are $\Delta\Omega = |\Omega_{\mathrm{S}} - \Omega_{\mathrm{T}}| = 0$, $\Delta J = |J_{\mathrm{S}} - J_{\mathrm{T}}| = 0$ and e/f parity conservation holds,[21] so there is no perturbation between $\mathrm{CO}(A^1\Pi_{\Omega=1}, v=0, J')$ with $\mathrm{CO}(e^3\Sigma_{\Omega=-1}, v=1, J')$ at the final state. So in Eq.(40), there is an interference term $\sum_l \left[\left(P_{JJ'}^{\mathrm{S},\Delta\Omega=0} \right)_l \left(P_{JJ'}^{T,\Delta\Omega=0} \right)_l \right]^{1/2}$, resulting from the perturbation.

2.6. The differential interference angle

Equation (32) can be written as

$$P_{JJ'} = c_J^2 c_{J'}^2 P_{JJ'}^{\mathrm{S}} + d_J^2 d_{J'}^2 P_{JJ'}^{\mathrm{T}} + 2 c_J c_{J'} d_J d_{J'} \left(P_{JJ'}^{\mathrm{S}} P_{JJ'}^{\mathrm{T}} \right)^{1/2} \cos\theta^D, \quad (41)$$

where the differential interference angle

$$\cos\theta^D = \frac{P^{\mathrm{Inter}}}{\left[P_{JJ'}^{\mathrm{T}} P_{JJ'}^{\mathrm{S}} \right]^{1/2}}. \quad (42)$$

The experiment of CO $\mathrm{A}^1\Pi(v=0) - e^3\Sigma^-(v=1)$ system in collision with He has been done by Sha *et al* in a static sample cell with the bulk temperature 77, 253 or 470 K.[1,2] However, Eq.(42) for the differential interference angle, which has been derived for the partners with uniform collision velocity, is not suitable 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[22]

$$P_{\mathrm{AV}} = \int_0^{\infty} P(v) v^3 \exp\left(\frac{-\mu v^2}{2kT} \right) \mathrm{d}v \Big/ \int_0^{\infty} v^3 \exp\left(\frac{-\mu v^2}{2kT} \right) \mathrm{d}v = 2 \left(\frac{\mu}{kT} \right)^2 \int_0^{\infty} P(v) v^3 \exp\left(\frac{-\mu v^2}{2kT} \right) \mathrm{d}v. \quad (43)$$

Now, the velocity-averaged differential interference angle can be obtained by first substituting Eq.(43) into Eq.(34) to get $P_{JJ'}(\mathrm{AV})$ and then the $P_{JJ'}(\mathrm{AV})$ into Eq.(41),

$$\cos\theta_{\mathrm{ST}}^D(\mathrm{AV}) = \frac{\iint P^{\mathrm{Inter}} v^3 \exp\left(\frac{-\mu v^2}{2kT} \right) \mathrm{d}v}{\left(\iint \left(P_{JJ'}^{\mathrm{S}} v^3 \exp\left(\frac{-\mu v^2}{2kT} \right) \mathrm{d}v \right)^{1/2} \left(\iint P_{JJ'}^{\mathrm{T}} v^3 \exp\left(\frac{-\mu v^2}{2kT} \right) \mathrm{d}v \right)^{1/2}}. \quad (44)$$

Considering the anisotropic Lennard-Jones interaction potentials, we can write Eq.(3) as

$$V(R,\theta,\phi) = 4\varepsilon\left[\left(\frac{\rho}{R}\right)^{12} - \left(\frac{\rho}{R}\right)^{7}\right]\sum_{m} a_{1,0} D^{1}_{m,0}{}^{*}(\alpha,\beta,\gamma)\, C^{1}_{m}(\theta,\varphi) + 4\varepsilon\left[\left(\frac{\rho}{R}\right)^{12} - \left(\frac{\rho}{R}\right)^{6}\right]\sum_{m,k} a_{2,k} D^{2}_{m,k}{}^{*}(\alpha,\beta,\gamma)\, C^{2}_{m}(\theta,\varphi) + \cdots . \quad (45)$$

In Eq.(45), $a_{l,k}$ is the anisotropic parameter. Because the ratio of $a_1, 0/a_2, 0$ for CO collision with He, Ne and Ar is $0.08 \le a_{1,0}/a_{2,0} \le 0.12$,[23] and the first term is R^{-7} for V_1 and V_3 for the long range interaction potential, while the second term is R^{-6} for the long range interaction potential, so for simple discussion in this paper, we only consider V_2. Equation (44) can be written as

$$\cos\theta^{D} = \frac{\iint \left|I_{\mathrm{S}}^{\Delta\Omega=0} \times I_{\mathrm{T}}^{\Delta\Omega=0}\right| v^{3} \exp\left(\frac{-\mu v^{2}}{2kT}\right) \mathrm{d}v}{\left(\iint \left|\left(I_{\mathrm{S}}^{\Delta\Omega=0} + a g I_{\mathrm{S}}^{\Delta\Omega=2}\right)\right|^{2} v^{3} \exp\left(\frac{-\mu v^{2}}{2kT}\right) \mathrm{d}v\right)^{1/2} \left(\iint \left|\left(I_{\mathrm{T}}^{\Delta\Omega=0}\right|^{2} v^{3} \exp\left(\frac{-\mu v^{2}}{2kT}\right) \mathrm{d}v\right)^{1/2}}, \quad (46)$$

where

$$I_{\mathrm{S,T}}^{\Delta\Omega} = \int \exp\left(\mathrm{i}\varpi_{N'N}^{\mathrm{S,T}} t\right)\left(\frac{\rho^{12}}{R^{12}} - \frac{\rho^{6}}{R^{6}}\right)\mathrm{d}t. \quad (47)$$

3. Discussion

3.1. The relation of the differential interference angle and impact parameter

In the static cell experiment, the distribution of velocity is from 0 to infinite, but, according to the Maxwell velocity distribution law, the most possible velocity should be in the middle of Maxwell velocity distribution curve. The Maxwell velocity curve is showed in Fig.1, so the differential interference angle was integrated with velocity from 400 to 1300.

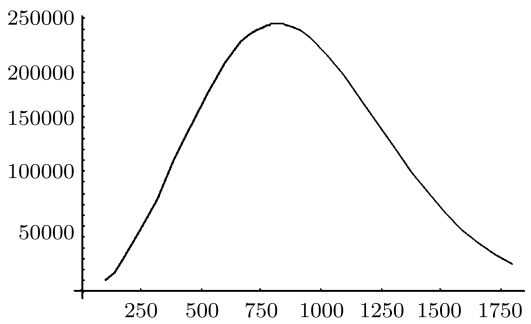


Fig.1. Maxwell velocity distribution curve in CO-Ne collision system.

We can calculate the differential interference angles for the CO $A^1\Pi(v=0) - e^3\Sigma^-(v=1)$ system in collision with Ne from the initial rotational state $J=9$ to the final rotational state $J'=10$. The rotational constants B for the CO $A^1\Pi(v=0)$ state and $e^3\Sigma^-(v=1)$ state are $1.6105\,\mathrm{cm}^{-1}$ and $1.2836\,\mathrm{cm}^{-1}$, respectively.[7] The collision diameter used in our calculation is $\rho = 2.75$A. The tendencies of the differential interference angles at $T = 253\,\mathrm{K}$ and $T = 470\,\mathrm{K}$ are presented in Figs.2 and 3.

From the Figs.2 and 3 we can get the conclusions:

(1) The change tendency of the differential interference angle is identical when $T = 253\,\mathrm{K}$ and $T = 470\,\mathrm{K}$, but the angles are different, the interference degree is bigger in high temperature than in low temperature.

(2) From the Fig.3, the differential interference angle increases with the increase of the impact parameter when $b > \sqrt{2}\rho$, so the interference degree decreases. When $b > 2\,\mathrm{nm}$, the interference angle is close to 90, it means that the distance ($b > 2\,\mathrm{nm}$) has overstepped the collision partners effective distance, and the interaction between atom and diatom is disappeared, so there is no more CQI.

(3) From the Fig.2, when $0 < b < \sqrt{2}\rho$, there is a bigger differential interference angle at $b = 2^{1/6}\rho$, the reason is that the repulsive potential energy equals to long-range potential in the distance, so the mixing degree of corresponding wavefunctions is weak, and the interference degree becomes weaker as well.

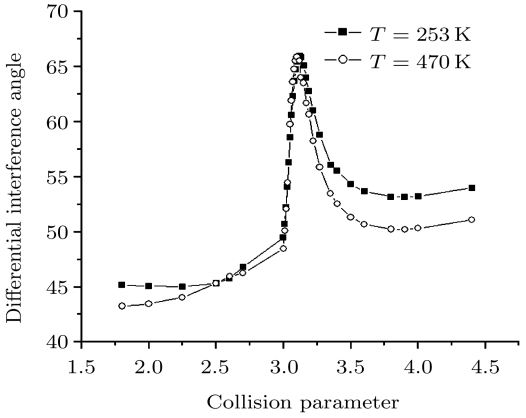


Fig.2. The relation of the differential interference $\theta^D_{\rm ST}$ and collision parameter $b(0 < b < \sqrt{2}\rho)$ in CO-Ne system.

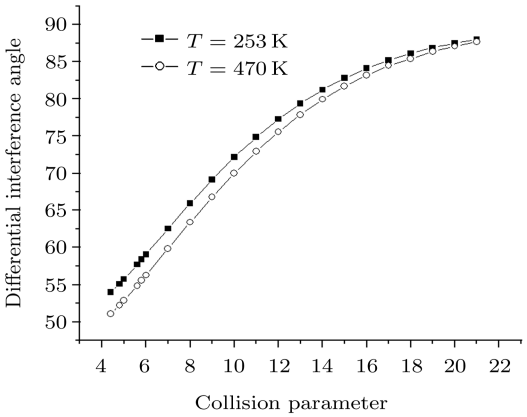


Fig.3. The relation of the differential interference $\theta^D_{\rm ST}$and collision parameter $b(\sqrt{2}\rho < b < 2.2\,\text{nm})$ in CO-Ne system.

4. Conclusion

As a further theoretical study of the collision-induced quantum interference on rotational energy transfer in atom–diatom system, a dynamic model of differential interference angle is described in this paper, basing on the time dependent first order Born approximation, and taking into account the anisotropic Lennard-Jones interaction potentials, we researched into the relation of differential interference angle and collision parameter in CO $A^1\Pi(v=0)-e^3\Sigma^-(v=1)$-Ne system. The calculated value gives a quantitative description of CQI.

References

[1] Sha G H, He J B, Jiang B and Zhang C H 1995 *J. Chem. Phys.* **102** 2772

[2] Chen X L, Sha G H, Jiang B, He J B and Zhang C H 1996 *J. Chem. Phys.* **105** 8661

[3] Sha G H and Zhang C H 2004 *Acta Phys. Chem. Sin.* **20** 1010

[4] Ma S H, Zhang X Z, Liang Y T and Sun J F 2000 *Acta Phys. Sin.* **49** 1517 (in Chinese)

[5] Chen X L, Chen H M, Li J, Liu Y M, Dai X C, Sha G H, Xie J C, Zhang C H and Li L 2000 *Chem. Phys. Lett.* **318** 107

[6] Bitto H and Hubber J R 1992 *Chem. Res.* **25** 65

[7] Shi D H, Liu Y F, Sun J F, Yang X D and Zhu Z L 2005 *Chin. Phys.* **14** 2208

[8] Felker P M 1992 *J. Phys. Chem.* **96** 7884

[9] Li Y Q, Li J and Ma F C 2006 *Chin. Phys.* **15** 2920

[10] Sun M T, Li J, Ma F C and Sha G H 2001 *Chem. Phys.* **274** 175

[11] Jiang Y H and Sun J F 2000 *Chin. Phys.* **9** 888

[12] Lorenz K T, Westley M S and Chandle D W 2000 *Phys. Chem. Chem. Phys.* **2** 481

[13] Lee S 1995 *J. Chem. Phys.* **103** 3501

[14] Alexander M H 1982 *J. Chem. Phys.* **76** 5974

[15] Alexander M H 1985 *Chem. Phys.* **92** 337

[16] Davis S and Alexander M H 1983 *J. Chem. Phys.* **78** 800

[17] Brown J M, Hougen J T, Huber K P, Johns J W C, Kopp I, Lefebvre B H, Merer A R, Ramsay D A, Rostas J and Zare R N 1975 *J. Mol. Spectrosc.* **55** 500

[18] Zare R N, Schmeltekopf A L, Harrop W J and Albritton D L 1973 *J. Mol. Spectrosc.* **46** 37

[19] Alexander M H and Dagdigian P J 1983 *J. Chem. Phys.* **79** 302

[20] Hougen J T 1970 *Journal of Research of the National Bureau of Standards (U.S.)* p115

[21] Herzberg G 1950 *Molecular Spectra and Molecular Structure* (New York: Van Nostrand-Reinhold) p55

[22] Sun M T, Ma F C and Sha G H 2003 *Chem. Phys. Lett.* **374** 20

[23] Wang W L, Song P, Shen Y and Ma F C 2005 *Commun. Theor. Phys.* **43** 879