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Collisional quantum interference on rotational energy transfer: physical interpretation of the differential interference angle*

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Collisional quantum interference (CQI) on the intramolecular rotational energy transfer is observed in an experiment with a static cell, and the integral interference angles are measured. To obtain more accurate information, an experiment with a molecular beam is carried out, and thereby the relationship between the differential interference angle and the scattering angle is obtained. Based on the first-Born approximation of time-dependent perturbation theory, the theoretical model of CQI is developed in an atom–diatom system in the condition of the molecular beam, with the long-range interaction potential taken into account. The method of measuring correctly the differential interference angle is presented. The tendencies of the differential interference angle changing with the impact parameter and relative velocity are discussed. The theoretical model presented here is important for understanding or performing the experiment in the molecular beam.

Keywords: collisional quantum interference, rotational energy transfer, interference angle, long-range interaction potential

PACC: 3400

1. Introduction

The evidence for collisional quantum interference (CQI) on rotational energy transfer was obtained by Sha *et al* in a CO $A^1\Pi(v=0)-e^3\Sigma^-(v=1)$ system in collision with He, Ne and other partners.[1−5] The CQI was also observed by Chen *et al* in a $Na_2 A^1\Sigma_u^+(v=8)-b^3\Pi_{0u}(v=14)$ system in collision with Na(3s).[6] The CQI mentioned here is different from some other quantum interferences in molecular dynamics and spectroscopy, such as quantum beat spectroscopy [7] and rotational coherence spectroscopy.[8,9] The CQI is a radiationless transition process, while the others result from the interaction of light with an atom or a molecule. The theory of rotational energy transfer by long-range forces was developed based on Cross and Gordon's [10] calculation of dipole–dipole rotationally inelastic scattering and Gray and van Kranendonk's [11] theory of pressure broadening. Moreover, the theory of CQI on rotational energy transfer can be developed along the lines of Alexander's [12] calculation by using the time-dependent Born approximation and assuming a dipole–dipole interaction potential. Sun *et al* improved the theory of CQI further.[13,14] In this article, we develop a model for CQI in atom–diatom systems, in which we obtain a method of calculating the interference angle proposed by Sha. In this model, we consider only binary collisions and adopt the semiclassical or impact parameter approximation, the first-order Born approximation of time-dependent perturbation theory, and consider the long-range interaction potential (neglecting the overlap force). The translational motion is treated classically, whereas vibrational and rotational motions are handled quantum mechanically. Treating translational motion classically is a good approximation if the wave packet for the relative translational motion is not broadened appreciably during the collision. Margenau and Lewis [15] have shown that this restriction, when applied to distant collisions, reduces to the criterion of the angular momentum, $l = Mbv/\hbar \gg 1$. For the experiment of CO–He, Ne or Ar collision system, $l = Mbv/\hbar \geq 15$, indicating that treating translational motion classically is a good approximation. In integrating with respect to the impact parameter, the 'straight-line' trajectory approximation for $b \geq d$ is used, which is proposed by Gray and van Kranen-

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donk [11] (b is the impact parameter and d is the hard-sphere collision diameter). This approximation requires that the energy transferred to/from the internal degrees of freedom is much less than the energy of relative translational motion. For the static cell experiments[1,2] of CO collision with He, Ne or Ar, the rotational energy transferred ($\Delta J = |J' - J| = 1$) is $\Delta E_{\rm rot} = 2B(J+1) \approx 25 - 30\,{\rm cm}^{-1}$ at $J = 9$ (the rotational constants B are shown in Section 4), which is much less than the energy of relative translational motion $E_{\rm tra} = \frac{3}{2}kT \approx 262\,{\rm cm}^{-1}$ at 253 K. So the 'straight-line' trajectory approximation for $b \geq d$ is a good approximation. This model can be used to simulate molecular beam experiments to calculate differential cross sections and differential interference angles.

2. Interaction potential in an atom-diatom system

The Born–Oppenheimer electronic Hamiltonian is written in the form

$$H_{\rm e} = H_A + H_B + V, \tag{1}$$

where $\rm H_A$ and $\rm H_B$ are the electronic Hamiltonians of atom A and molecule B respectively, and V represents the electrostatic interaction potential. In this paper, only long-range interaction is considered, and because atom A has no permanent multipole moment, V in Eq.(1) is restricted to the induction potential and the dispersion potential,[14,16,17]

$$\begin{aligned} V = & \sum_{l_A,l'_A,l_B,l'_B} -\xi^{L_A,L_B,L}_{l_A,l'_A,l_B,l'_B} R^{-l_A-l'_a-l_B-l'_B} \sum_{m,n} (E^A_n - E^A_0 + E^B_m - E^B_0)^{-1} \\ & \times \left[\langle \psi^A_0 \left| Q^{l_A} \right| \psi^A_n \rangle \otimes \langle \psi^A_n \left| Q^{l'_A} \right| \psi^A_0 \rangle \right]^{L_A}_{K_A} \left[\langle \psi^B_0 \left| Q^{l_B} \right| \psi^B_m \rangle \otimes \langle \psi^B_m \left| Q^{l'_B} \right| \psi^B_0 \rangle \right]^{L_B}_{K_B} \\ & \times \sum_{M_A,M_B,M_L} \begin{pmatrix} L_A & L_B & L \\ M_A & M_B & M_L \end{pmatrix} D^{L_A}_{M_A,K_A}{}^* D^{L_B}_{M_B,K_B}{}^* C^L_{M_L}(\Omega_t), \end{aligned} \tag{2}$$

where ξ is a purely algebraic coefficient, which depends on the coupling of the multipoles between atom A and molecule B,

$$\begin{aligned} \xi^{L_A,L_B,L}_{l_A,l'_A,l_B,l'_B} = & \ (-1)^{l_A+l'_A} \left[\frac{(2l_A+2l_B+1)!(2l'_a+2l'_B+1)!}{(2l_A)!(2l_B)!(2l'_A)!(2l_B)!} \right]^{1/2} (2L_A+1)^{1/2}(2L_B+1)^{1/2}(2L+1)^{1/2} \\ & \times (l_A+l_B, 0, l'_A+l'_B, 0|L,0) \begin{Bmatrix} l_A & l'_A & L_A \\ l_B & l'_B & L_B \\ l_A+l_B & l'_A+l'_B & L \end{Bmatrix}, \end{aligned} \tag{3}$$

and R is the distance between atom A and the mass centre of molecule B, ψ and E denote the eigenfunction and the eigenvalue respectively, Q^l is the multipole tensor operator of order l. $D^L_{M,K}$ is the Wigner D rotation matrix, and $C^L_M(\Omega)$ is a Racah harmonic function.

As the first approximation in this model, we consider only the dipole-induced dipole and the induced dipole-induced dipole interactions, i.e. $l_A = l_B = 1$. In an atom–diatom system, $D^{L_A}_{M_A,K_A} = 1$, $D^{L_B}_{M_B,K_B} = 1$ or $D^{L_B}_{M_B,K_B} = D^2_{M_B,0}$, because $L_A = K_A = 0$ and $L_B = K_B = 0$ or $L_B = 2$.[16]

When $m = 0$, Eq.(2) reduces to the induction potential $V_{\rm ind}$,

$$V_{\rm ind} = -\frac{1}{2}\xi^{0,L_B,L}_{1,1,1,1} \alpha_A \mu^2_B R^{-6} \sum_{M_L} \begin{pmatrix} 0 & L_B & L \\ 0 & M_B & M_L \end{pmatrix} D^{L_B}_{M_B,0}{}^*(\Omega_2) C^L_{M_L}(\Omega_t), \tag{4}$$

where α is the irreducible multipolar polarizability[18]

$$\alpha = 2\sum_{n\neq 0}(E_n - E_0)^{-1}\left[\langle\psi_0|Q^l|\psi_n\rangle \otimes \langle\psi_n|Q^{l'}|\psi_0\rangle\right]_K^L, \tag{5}$$

and μ is the multipole[19]

$$\mu^2 = \left[\langle\psi_0|Q^l|\psi_0\rangle \otimes \langle\psi_0|Q^{l'}|\psi_0\rangle\right]_K^L. \tag{6}$$

When $m \neq 0$, Eq.(2) is the dispersion potential

$$V_{\rm dis} = -\frac{1}{4}\xi_{1,1,1,1}^{0,L_B,L}\frac{I_1 I_2}{I_1+I_2}\alpha_A\alpha_B R^{-6}\sum_{M_L}\begin{pmatrix} 0 & L_B & L \\ 0 & M_B & M_L \end{pmatrix} D_{M_B,0}^{L_B\,*}(\Omega_2)C_{M_L}^L(\Omega_t), \tag{7}$$

where

$$I_1 = \sum_n E_n^A - E_0^A \quad \text{and} \quad I_2 = \sum_m E_m^B - E_0^B. \tag{8}$$

The irreducible tensor product between two sets of tensors in Eq.(5) and Eq.(6) can be written as[13]

$$\left[T^1 \otimes T'^1\right]_K^L = \sum_m \langle 1m, 1K-m||LK\rangle T(1,m)T'(1,K-m) \tag{9}$$

with $\langle 1m, 1K-m||LK\rangle$ being a Clebsch–Gordan coefficient. In our cases, $L = 0$ or $L = 2$, and $K = 0$, Eq.(9) reduces to

$$[T^1 \otimes T'^1]_0^0 = -3^{1/2}T\cdot T', \quad \text{and} \quad [T^1 \otimes T'^1]_0^2 = (3T_zT'_z - T\cdot T')/6^{1/2}. \tag{10}$$

Using Eqs.(2)–(10), the long-range interaction potential in an atom–diatom system can be derived as follows:

$$\begin{aligned} V = {} & V_{\rm ind} + V_{\rm dis} \\ = {} & -\frac{1}{3\sqrt{3}}\xi_{1,1,1,1,1}^{0,0,0}R^{-6}(t)[\alpha_{XX}+\alpha_{YY}+\alpha_{ZZ}]_A\left[\frac{1}{2}\left(\mu_X^2+\mu_Y^2+\mu_Z^2\right)+\frac{1}{4}\frac{I_1I_2}{I_1+I_2}(\alpha_{XX}+\alpha_{YY}+\alpha_{ZZ})\right]_B \\ & -\frac{1}{3\sqrt{10}}x_{1,1,1,1,1}^{0,2,2}R^{-6}(t)[\alpha_{XX}+\alpha_{YY}+\alpha_{ZZ}]_A\left[\frac{1}{2}\left(\mu_X^2+\mu_Y^2-2\mu_Z^2\right)+\frac{1}{4}\frac{I_1I_2}{I_1+I_2}(\alpha_{XX}+\alpha_{YY}-2\alpha_{ZZ})\right]_B \\ & \times\sum_M(-1)^{2-M_L}D_{M_L,0}^{2\,*}(\Omega_2)C_{M_L}^2(\Omega_t) \\ = {} & -B_1R^{-6}(t) - B_2R^{-6}(t)\sum_{M_L}(-1)^{2-M_L}D_{M_L,0}^{2\,*}(\Omega_2)C_{M_L}^2(\Omega_t), \end{aligned} \tag{11}$$

where

$$B_1 = \frac{1}{3\sqrt{3}}\xi_{1,1,1,1,1}^{0,0,0}R^{-6}(t)[\alpha_{XX}+\alpha_{YY}+\alpha_{ZZ}]_A\left[\frac{1}{2}\left(\mu_X^2+\mu_Y^2+\mu_Z^2\right)+\frac{1}{4}\frac{I_1I_2}{I_1+I_2}(\alpha_{XX}+\alpha_{YY}+\alpha_{ZZ})\right]_B$$

and

$$B_2 = \frac{1}{3\sqrt{10}}x_{1,1,1,1,1}^{0,2,2}[\alpha_{XX}+\alpha_{YY}+\alpha_{ZZ}]_A\left[\frac{1}{2}\left(\mu_X^2+\mu_Y^2-2\mu_Z^2\right)+\frac{1}{4}\frac{I_1I_2}{I_1+I_2}(\alpha_{XX}+\alpha_{YY}-2\alpha_{ZZ})\right]_B. \tag{12}$$

In Eq.(12), B can be $B^{\rm S}$ or $B^{\rm T}$, depending on whether the molecule is in a singlet state or a triplet state.

3. The differential interference angle of CQI in an atom–diatom system

The evolution of the interaction potential is[20]

$$V(t) = U^{+}(t,0)VU(t,0), \tag{13}$$

where $U(t,0)$ is the time evolution operator in the form

$$U(t,0) = \exp(-\mathrm{i}H_0 t/\hbar) \tag{14}$$

with

$$H_0 = \hbar\omega = \hbar\bar{B}J(J+1), \tag{15}$$

where $\bar{B}$ is the rotation constant of molecule B, and J is the rotation quantum number. Substituting Eq.(14) into Eq.(13), we obtain

$$V(t) = \exp(\mathrm{i}H_0 t/\hbar)V\exp(-\mathrm{i}H_0 t/\hbar). \tag{16}$$

The unperturbed wave functions are

$$\begin{pmatrix} \varphi_J^{\mathrm{S}} \\ \varphi_J^{\mathrm{T}} \end{pmatrix} = \begin{pmatrix} |v\rangle^{\mathrm{S}}|JKM\rangle^{\mathrm{S}} \\ |v\rangle^{\mathrm{T}}|JKM\rangle^{\mathrm{T}} \end{pmatrix}, \tag{17}$$

where $|v\rangle$ and $|JKM\rangle$ represent the vibration and rotation wave functions, respectively. The zeroth order unperturbed energies are defined as $E(\varphi_J^{\mathrm{S}})$ and $E(\varphi_J^{\mathrm{T}})$. If v_{ST} is the coupling between these zeroth order states, the perturbed states have energies as follows:[21]

$$E_{\pm}(JKM) = \frac{1}{2}\left[E(\varphi_J^{\mathrm{S}}) + E(\varphi_J^{\mathrm{T}})\right] \pm \frac{1}{2}\left\{\left[E(\varphi_J^{\mathrm{S}}) - E(\varphi_J^{\mathrm{T}})\right]^2 + 4v_{\mathrm{ST}}^2\right\}^{1/2}. \tag{18}$$

The perturbed wave functions are

$$\begin{pmatrix} \psi_J^{\mathrm{S}} \\ \psi_J^{\mathrm{T}} \end{pmatrix} = \begin{pmatrix} \cos\phi_J & \sin\phi_J \\ -\sin\phi_J & \cos\phi_J \end{pmatrix} \begin{pmatrix} \varphi_J^{\mathrm{S}} \\ \varphi_J^{\mathrm{T}} \end{pmatrix}. \tag{19}$$

Equation (18) shows that the mutual perturbing states are repulsive each other. The energy level shifts $\Delta_{\pm}$ are

$$\Delta_{\pm} \equiv E_{\pm}(JKM) - E(\varphi_J), \tag{20}$$

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

$$\phi = \arcsin\left\{v_{\mathrm{ST}}/\left[E\left(\psi_J^{\mathrm{S}}\right) - E(\psi_J^{\mathrm{T}})\right]\right\}. \tag{21}$$

In the derivation below, according to Eq.(19), 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 whether the perturbed state is a singlet or a triplet state. From Eqs.(18)–(21), the values and the signs of c_J and d_J can be obtained. c_J and d_J have the same sign if energy level J is shift 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

$$|i\rangle = c_J|v\rangle^{\mathrm{S}}|JKM\rangle^{\mathrm{S}} + d_J|v\rangle^{\mathrm{T}}|JKM\rangle^{\mathrm{T}} \tag{22}$$

and

$$|f\rangle = c_{J'}|v'\rangle^{\mathrm{S}}|J'K'M'\rangle^{\mathrm{S}} + d_{J'}|v'\rangle^{\mathrm{T}}|J'K'M'\rangle^{\mathrm{T}}. \tag{23}$$

According to the first-Born approximation of time-dependent perturbation theory, the amplitude for a transition between $|i\rangle$ and $|f\rangle$ is

$$\begin{aligned}\frac{1}{\mathrm{i}\hbar}\int\langle f|V(t)|i\rangle\mathrm{d}t = {} & \frac{1}{\mathrm{i}\hbar}c_J c_{j'}\int\langle J'K'M'|\langle v'|V_{\mathrm{S}}(t)|v\rangle|JKM\rangle\mathrm{d}t \\ & + \frac{1}{\mathrm{i}\hbar}d_J d_{J'}\int\langle J'K'M'|\langle v'|V_{\mathrm{T}}(t)|v\rangle|JKM\rangle\mathrm{d}t.\end{aligned} \tag{24}$$

Substituting Eq.(11) into Eq.(24), one can obtain

$$\frac{1}{\mathrm{i}\hbar}\int\langle f|V(t)|i\rangle \mathrm{d}t = -\frac{B_2^{\mathrm{S}}}{\mathrm{i}\hbar}c_J c_{J'}\sum_{M_L}(-1)^{2-M_L}\langle J'K'M'|D^2_{M_L,0}{}^*|JKM\rangle \int_{-\infty}^{\infty}\exp\left(\mathrm{i}\varpi^S_{J'J}t\right)R^{-6}(t)C^2_{M_L}(\Omega_t)\mathrm{d}t$$
$$-\frac{B_2^{\mathrm{T}}}{\mathrm{i}\hbar}d_J d_{J'}\sum_{M_L}(-1)^{2-M_L}\langle J'K'M'|D^2_{M_L,0}{}^*|JKM\rangle \int_{-\infty}^{\infty}\exp\left(\mathrm{i}\varpi^{\mathrm{T}}_{J'J}t\right)R^{-6}(t)C^2_{M_L}(\Omega_t)\mathrm{d}t. \quad (25)$$

In Eq.(25), the vibration factor $\langle v'|v\rangle = 1$ has been omitted, because only the rotational energy transfer is considered $\left(|v'\rangle^{\mathrm{S,T}} = |v\rangle^{\mathrm{S,T}}\right)$. The rotational matrix element in Eq.(25) is

$$\langle J'K'M'|D^2_{M_L,0}{}^*|JKM\rangle = [(2J+1)(2J'+1)]^{1/2}\begin{pmatrix} J' & 2 & J \\ M' & -M_L & M\end{pmatrix}\begin{pmatrix} J' & 2 & J \\ K' & 0 & K\end{pmatrix}. \quad (26)$$

The integral in Eq.(25)

$$I^L_{M_L} = \int_{-\infty}^{\infty}\exp(\mathrm{i}\varpi_{J'J}t)R^{-6}(t)C^2_{M_L}(\Omega_t)\mathrm{d}t \quad (27)$$

has been carried out in a "straight-line" trajectory approximation $[R(t) = (v^2t^2 + b^2)]$, by introducing the dimensionless variables[11]

$$x = \varpi b/v, \quad \text{and} \quad z = vt/b, \quad (28)$$

where b is the impact parameter and v the relative velocity in the centre of mass coordinate system. The result of the integral is

$$I^L_{M_L} = b^{-5}v^{-1}J^L_{M_L}(x) \quad (29)$$

and

$$J^L_{M_L} = \mathrm{i}^{L-M_L}A^L_{M_L}(x). \quad (30)$$

When $L = 2$ and $M_L = 0$, 1, 2, then $A^L_{M_L}(x)$ are

$$A^2_0(x) = (3/2)F_4(x) - F_3(x), \quad A^2_1(x) = (3/2)^{1/2}G_4(x), \quad \text{and} \quad A^2_2(x) = (3/8)^{1/2}F_4(x), \quad (31)$$

where

$$F_n(x) = \frac{\pi}{(n-1)!2^{2n-2}}\mathrm{e}^{-x}\sum_{k=0}^{n-1}\frac{(2n-2-k)!}{k!(n-1-k)!}(2x)^k,$$
$$G_n(x) = \frac{\pi}{(n-1)!2^{2n-3}}x\mathrm{e}^{-x}\sum_{k=0}^{n-2}\frac{(2n-4-k)!}{k!(n-2-k)!}(2x)^k. \quad (32)$$

Substituting Eqs.(26)–(29) into Eq.(25), we can obtain,

$$\frac{1}{\mathrm{i}\hbar}\int\langle f|V(t)|i\rangle \mathrm{d}t = -\frac{B_2^{\mathrm{S}}}{\mathrm{i}\hbar}c_J c_{J'}\sum_{M_L}(-1)^{2-M_L}[(2J+1)(2J'+1)]^{1/2}\begin{pmatrix} J' & 2 & J \\ M' & -M_L & M\end{pmatrix}\begin{pmatrix} J' & 2 & J \\ K' & 0 & K\end{pmatrix}$$
$$\times b^{-5}v^{-1}J^2_{M_L}(x^{\mathrm{S}})$$
$$-\frac{B_2^{\mathrm{T}}}{\mathrm{i}\hbar}d_J d_{J'}\sum_{M_L}(-1)^{2-M_L}[(2J+1)(2J'+1)]^{1/2}\begin{pmatrix} J' & 2 & J \\ M' & -M_L & M\end{pmatrix}\begin{pmatrix} J' & 2 & J \\ K' & 0 & K\end{pmatrix}$$
$$\times b^{-5}v^{-1}J^2_{M_L}(x^{\mathrm{T}}). \quad (33)$$

The transition probability can be written as [14]

$$P_{JJ'} = \frac{1}{(2J+1)}\sum_{M'M}\left|\frac{1}{\mathrm{i}\hbar}\int\langle f|V(t)|i\rangle\mathrm{d}t\right|^2. \quad (34)$$

Substituting Eq.(33) into Eq.(34) and considering the orthogonal relations involving the $3j$ symbols and Clebsch–Gordan coefficients, we obtain an explicit formula for the $J \to J'$ transition probability

$$P_{JJ'} = c_J^2 c_{J'}^2 P_{JJ'}^{\mathrm{S}} + d_J^2 d_{J'}^2 P_{JJ'}^{\mathrm{T}} + 2c_j c_{j'} d_j d_{j'} \sum_{M_L} \left[(P_{JJ'}^{\mathrm{S}})_{M_L} (P_{JJ'}^{\mathrm{T}})_{M_L} \right]^{1/2}, \tag{35}$$

where $P_{JJ'}^{H}$ is

$$P_{JJ'}^{H} = \frac{B_2^{H^2}(2J'+1)}{5\hbar^2 v^2 b^{10}} \begin{pmatrix} J' & 2 & J \\ K' & 0 & K \end{pmatrix} \sum_{M_L} \left| J_{M_L}^2(x_H) \right|^2. \tag{36}$$

In the above equation, H represents S or T. Equation (35) can be rewritten in the form of Eq.(4a) in Ref.[1], i.e.

$$P_{JJ'} = c_J^2 c_{J'}^2 P_{JJ'}^{\mathrm{S}} + d_J^2 d_{J'}^2 P_{JJ'}^{\mathrm{T}} + 2c_J c_{J'} d_J d_{J'} (P_{JJ'}^{\mathrm{S}} P_{JJ'}^{\mathrm{T}})^{1/2} \cos\theta \frac{D}{\mathrm{ST}} \tag{37}$$

with $\cos\theta_{\mathrm{ST}}^{\mathrm{D}}$ defined as

$$\cos\theta_{\mathrm{ST}}^{D} = \frac{\sum\limits_{M_L} \left[(P_{JJ'}^{\mathrm{S}})_{M_L} (P_{JJ'}^{\mathrm{T}})_{M_L} \right]^{1/2}}{(P_{JJ'}^{\mathrm{S}} P_{JJ'}^{\mathrm{T}})^{1/2}}. \tag{38}$$

By substituting Eq.(36) into Eq.(38) and reducing B_2^{S} and B_2^{T}, which are independent of v and b as can be seen from Eq.(12), an explicit formula for $\cos\theta_{\mathrm{ST}}^{\mathrm{D}}$ is obtained as follows:

$$\cos\theta_{\mathrm{ST}}^{D} = \frac{\sum\limits_{M_L} \frac{1}{b^{10}} \left| J_{M_L}^2(x_{\mathrm{T}}) \right| \left| J_{M_L}^2(x_{\mathrm{S}}) \right|}{\left(\sum\limits_{M_L} \frac{1}{b^{10}} \left| J_{M_L}^2(x_{\mathrm{T}}) \right|^2 \right)^{1/2} \left(\sum\limits_{M_L} \frac{1}{b^{10}} \left| J_{M_L}^2(x_{\mathrm{S}}) \right|^2 \right)^{1/2}}, \tag{39}$$

which will be used in the calculation of differential interference angle in the next section. However, Eq.(39) for the differential interference angle, which has been derived for the partners with uniform collision velocity, is not appropriate to deal with the cell experiments, in which the gas species have the Maxwell–Boltzmann velocity distribution. In this case, the velocity-averaged differential interference angle can be obtained as follows:

$$\cos\theta_{AV}^{D} = \frac{\int \sum\limits_{M_L} \frac{v}{b^{10}} \left| J_{M_L}^2(x_{\mathrm{T}}) \right| \left| J_{M_L}^2(x_{\mathrm{S}}) \right| \exp\left(\frac{-\mu v^2}{2kT} \right) \mathrm{d}v}{\left(\int \sum\limits_{M_L} \frac{v}{b^{10}} \left| J_{M_L}^2(x_{\mathrm{T}}) \right|^2 \exp\left(\frac{-\mu v^2}{2kT} \right) \mathrm{d}v \right)^{1/2} \left(\int \sum\limits_{M_L} \frac{v}{b^{10}} \left| J_{M_L}^2(x_{\mathrm{S}}) \right|^2 \exp\left(\frac{-\mu v^2}{2kT} \right) \mathrm{d}v \right)^{1/2}} \tag{40}$$

4. Calculation and discussion

4.1. Calculation of the differential interference angle in the condition of the molecular beam

In the molecular beam experiment, the relative velocity of the gases is uniform and can be controlled, so the differential interference angle may be measured, in which the scattering angle is sensitive to the impact parameter and the potential energy surface. Using Eq.(39) we can obtain the relationship of the differential interference angle with the impact parameter b and the relative velocity v (see Fig.1).

In the calculation of CO($\mathrm{A}^1\Pi$–$\mathrm{e}^3\Sigma^-$)–He collision differential interference angle, the first summation in the denominator is for the $^1\Pi$ channel, so $M_L = 0$ and $M_L = \pm 2$; the second summation in the denominator is for $^3\Sigma^-$ channel, so $M_L = 0$ only.[22] We have calculated the differential interference phase angles for the CO($\mathrm{A}^1\Pi$–$\mathrm{e}^3\Sigma^-$) system in collision with He from the initial rotational state $J = 9$ to the final rotational

state $J' = 10$. The rotational constants B for the $CO(A^1\Pi)$ state and $CO(e^3\Sigma^-)$ state are $1.6105\,cm^{-1}$ and $1.2836\,cm^{-1}$, respectively.[13] The collision diameter σ used in our calculation is 2.56 Å. The greatest value of b is chosen to be 10 Å, because when $b >$ 10 Å, the interaction between atom and diatom almost disappears. The calculated values are presented in Fig.1. From Fig.1, we can see that the differential interference angle decreases with the increase of the impact parameter, i.e. the degree of the interference increases. This is because the time duration of collision becomes larger with the increase of the impact parameter, so the degree of the interference also increases, i.e. the differential interference angles decrease correspondingly.

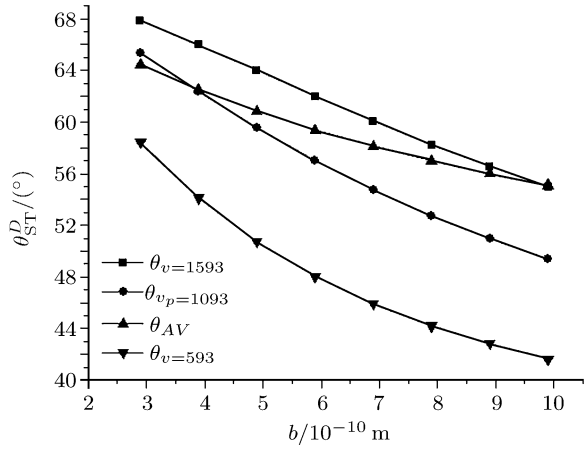


Fig.1. The tendency of the deferential interference angle varying with the impact parameter b. Here θ_{AV} refers to velocity-averaged differential interference angle at 253 K, $\theta_{v=1093}$ is the differential interference angle in the case of the most probable velocity of 1093 m/s at 253 K, $\theta_{v=593}$ and $\theta_{v=1593}$ denote differential interference angles for the larger and smaller values chosen of v, respectively.

From Fig.1, we also can see that with the increase of the relative velocity (i.e. with the increase of experimental temperature), the differential interference angle increases, i.e. the degree of the interference decreases. This tendency is consistent with the experimental results[1,2] and the calculated values of the integral interference angle, and can be explained as follows: with the increase of relative velocity (the kinetic energy increases), the collision becomes stronger, and the singlet–triplet mixed states may decouple due to the different energy level shifts of the singlet and triplet states induced by the collision perturbation. As a consequence of decoupling, the mixing degree of corresponding wave functions becomes smaller than that of isolated-molecule and the interference becomes weaker as well.

4.2. The relationship between the differential interference angle and the integral interference angle

The energy transfer cross section can be expressed as[23]

$$\sigma_{JJ'} = 2\pi \int_0^\infty P_{JJ'}(b) b \mathrm{d}b. \tag{41}$$

By substituting Eq.(35) into Eq.(41), the integral cross-section can be obtained

$$\sigma_{JJ'} = c_J^2 c_{J'}^2 \sigma^{\mathrm{S}}_{JJ'} + d_J^2 d_{J'}^2 \sigma^{\mathrm{T}}_{JJ'} + 2 c_J c_{J'} d_J d_{J'} \left(\sigma^{\mathrm{S}}_{JJ'} \sigma^{\mathrm{T}}_{JJ'}\right)^{1/2} \cos\theta^{\mathrm{I}}_{\mathrm{ST}} \tag{42}$$

with cosine of the integral interference angle being

$$\cos\theta^{\mathrm{I}}_{\mathrm{ST}} = \frac{\int \sum\limits_{M_L} \left[\left(P^{\mathrm{S}}_{JJ'}\right)_{M_L} \left(P^{\mathrm{T}}_{JJ'}\right)_{M_L}\right]^{1/2} b\mathrm{d}b}{\left(\int \left(P^{\mathrm{S}}_{JJ'}(b) b\mathrm{d}b\right)^{1/2} \left(\int P^{\mathrm{T}}_{JJ'}(b) b\mathrm{d}b\right)^{1/2}}, \tag{43}$$

where $\cos\theta^{\mathrm{I}}_{ST}$ can also be obtained by substituting Eq.(37) into Eq.(41)

$$\cos\theta^{\mathrm{I}}_{\mathrm{ST}} = \frac{\int \left(P^{\mathrm{S}}_{JJ'}(b) P^{\mathrm{T}}_{JJ'}(b)\right)^{1/2} \cos\theta(b)^D_{\mathrm{ST}} b\mathrm{d}b}{\left(\int \left(P^{\mathrm{S}}_{JJ'}(b) b\mathrm{d}b\right)^{1/2} \left(\int P^{\mathrm{T}}_{JJ'}(b) b\mathrm{d}b\right)^{1/2}}. \tag{44}$$

Equation (44) gives out the relation between the differential and integral interference angles. The experiment of CO($A^1\prod$–$e^3\sum^-$) in collision with He has been performed by Sha *et al* in a static sample cell at the bulk temperature 253 K, and Maxwell–Boltzmann velocity-averaged integral interference angle obtained is 61°. In this paper, the differential interference angles obtained are in the range from 65.34° to 49.38° with the impact parameter b ranging from 2.9 ($b_{\min}$) to 10Å at 1093 m/s, which explicitly shows that the integral interference angle result from the average effect of the differential interference angle. Theoretically this confirms that in the experiment of CO ($A^1\prod$–$e^3\sum^-$)–He system, most of the collision-induced rotational energy transfers between atom and molecule are nearly at $b_{\min} = 2.9$ Å.

5. Conclusion

As a further theoretical study of the collision-induced quantum interference on rotational energy transfer in an atom–diatom system, a dynamic model of differential interference angle is described in this paper. Based on the first order Born approximation of the time-dependent perturbation theory, the relation between the differential and the integral interference angle is obtained, with the long-range interaction potential taken into account. This model can be used for simulating molecular beam experiments to calculate differential cross sections and differential interference angles. The calculated value gives a quantitative description of CQI.

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