ARTICLE

# Differential Interference Angle of Collision-induced Rotational Energy Transfer in Na$_2$(A$^1\Sigma_\mathrm{u}^+$, $v$=8$\sim$ b$^3\Pi_\mathrm{0u}$, $v$=14)-Na System

Jian Li[a], Yong-qing Li[a], Wei-li Wang[b], Feng-cai Ma[a]*

a. Department of Physics, Liaoning University, Shenyang 110036, China; b. School of Science, Liaoning Technical University, Fuxin 12300, China

Here we report calculation of the differential interference angles (including $b \leq \rho$ and $b \geq \rho$ ) for singlet-triplet mixed states of Na$_2$(A$^1\Sigma_\mathrm{u}^+$, $v$=8$\sim$b$^3\Pi_\mathrm{0u}$, $v$=14) system in collision with Na, in order to study the collision-induced quantum interference on rotational energy transfer in an atom-diatom system. The calculation is based on the first-order Born approximation of time-dependent perturbation theory, and the anisotropic Lennard-Jones interaction potentials are also employed. The relationships between differential interference angle and impact parameter, including collision diameter and velocity, are obtained.

**Key words:** Rotational energy transfer, Collision-induced quantum interference, Interference angle

## I. INTRODUCTION

Interference effect in the rotational energy transfer has been a hot topic in last couple of decades both in experimental and theoretical studies. The evidence of collisional quantum interference (CQI) on rotational energy transfer was observed 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 impact parameter [1,2]. CQI was also observed by Chen *et al.* in Na$_2$A$^1\Sigma_\mathrm{u}^+$($v$=8)$\sim$b$^3\Pi_\mathrm{0u}$($v$=14) system in collision with Na(3s) [3]. In Sha's experiment, the two mutually perturbed states are the singlet state CO A$^1\Pi$($v$=0) and the triplet state CO e$^3\Sigma^-$($v$=1). While in Chen's experiment, they are the singlet state Na$_2$ A$^1\Sigma_\mathrm{u}^+$($v$=8) and the triplet state Na$_2$ b$^3\Pi_\mathrm{0u}$($v$=14). In these experiments mentioned above, intramolecular rotational energy transfer was observed.

In this work, our purpose is to compute the differential interference angles ($\theta_\mathrm{ST}^D$ ) for the singlet-triplet mixed states of Na$_2$(A$^1\Sigma_\mathrm{u}^+$, $v$=8$\sim$b$^3\Pi_\mathrm{0u}$, $v$=14) system in collision with Na. It is meaningful and necessary to calculate the values of $\theta_\mathrm{ST}^D$, since the magnitude of $\theta_\mathrm{ST}^D$ can give us a quantitative and accurate description of CQI. Chen *et al.* predicted that the interference angle of Na$_2$-Na system should be comparable to that of CO [3], i.e. CQI should be significant or act itself as a complete enhancement state.

The first-order Born approximation of time-dependent perturbation theory has been used in our theoretical approach. The translational motion is treated classically, whereas vibrational and rotational motions are treated quantum mechanically. Binary collision and the semiclassical impact parameter ap-

proximation have also been employed in the theoretical treatment. We have also employed the anisotropic Lennard-Jones interaction potentials.

## II. THEORETICAL TREATMENT

The evolution of the interaction potential $V$ is [4],

$$V(t) = \exp\left(\frac{iH_0t}{\hbar}\right)V\exp\left(-\frac{iH_0t}{\hbar}\right) \tag{1}$$

$$H_0 = -\frac{1}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}R^2} - \frac{L^2}{2\mu R^2} + H_\mathrm{at} + H_\mathrm{e} + H_\mathrm{vib} + H_\mathrm{rot} \tag{2}$$

in which $\mu$ is the collision reduced mass, $R$ is the distance from the atom to the ma-ss center of the molecule, $L$ is the operator for the orbital angular momentum of the atom-molecule pair, $H_\mathrm{at}$ is the atom electronic state Hamiltonian, $H_\mathrm{e}$, $H_\mathrm{vib}$ and $H_\mathrm{rot}$ are the electronic, vibrational, and rotational Hamiltonian of diatom, respectively. In this work, because we only consider the rotational energy transfer, $H_0$ can be simplified approximately to the form as follows [5]:

$$H_0 = \hbar\omega = \hbar\overline{B}J(J+1) \tag{3}$$

where $\overline{B}$ is the rotation constant of molecule, $J$ is the rotation quantum number.

The anisotropic Lennard-Jones potential [4] is as following.

$$V = 4\varepsilon\left[\left(\frac{\rho}{R}\right)^{12} - \left(\frac{\rho}{R}\right)^6\right]$$
$$\cdot\left[1 + a_2\sum_m(-1)^{2-m}D_{m,0}^2{}^*(\alpha,\beta,\gamma)\,C_m{}^2(\theta,\varphi)\right] \tag{4}$$

in which $R$ is the distance between the atom and the mass center of the molecule. The parameters $\varepsilon$ and

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*Author to whom correspondence should be addressed. E-mail: fcma@lnu.edu.cn

$\rho$ represent the potential-well depth and the collision diameter, respectively. $a_2$ is the anisotropic parameters. $C_m{}^l(\theta,\varphi)$ is the Racah harmonic function, i.e.,

$$C_m{}^l(\theta,\varphi) = \sqrt{\frac{4\pi}{2l+1}} Y_m{}^l(\theta,\varphi) \tag{5}$$

$Y_m{}^l(\theta,\varphi)$ is the spherical harmonics function. The angles $\theta$ and $\varphi$ represent the direction of $R$ in a space-fixed coordinate. $D_{K_l M}^J(\alpha,\beta,\gamma)$ [6] is the Wigner rotational matrix. Euler angles $\alpha$, $\beta$ and $\gamma$ are the rotational coordinates of the diatomic molecule. $V$ includes not only the long range attractive but also the short range repulsive interactions.

The unperturbed singlet and triplet wave functions are

$$\begin{pmatrix} \varphi_J^{\mathrm{S}} \\ \varphi_J^{\mathrm{T}} \end{pmatrix} = \begin{pmatrix} |v\rangle^{\mathrm{S}} |JKM\rangle^{\mathrm{S}} \\ |v\rangle^{\mathrm{T}} |JKM\rangle^{\mathrm{T}} \end{pmatrix} \tag{6}$$

where $|v\rangle$ and $|JKM\rangle$ represent the vibration and rotation wave functions, respectively. S and T represent singlet and triplet states respectively. Here,

$$|JKM\rangle^H = \sqrt{\frac{2J+1}{8\pi^2}} D_{KM}^{J\,*}(\alpha,\beta,\gamma) \tag{7}$$

in which $H$ is either $S$ or $T$.

The zeroth order unperturbed energies are defined as $E(\varphi_J^{\mathrm{S}})$ and $E(\varphi_J^{\mathrm{T}})$. If $\nu_{\mathrm{ST}}$ is the coupling between these zeorth order states, the perturbed states energies are [7,8]

$$\begin{aligned} E_{\pm}(JKM) = &\frac{1}{2}\left[E(\varphi_J^{\mathrm{S}}) + E(\varphi_J^{\mathrm{T}})\right] \\ &\pm \frac{1}{2}\left\{\left[E(\varphi_J^{\mathrm{S}}) - E(\varphi_J^{\mathrm{T}})\right]^2 + 4\nu_{\mathrm{ST}}^2\right\}^{1/2} \end{aligned} \tag{8}$$

and the perturbed wave functions are

$$\begin{pmatrix} \psi_J^{\mathrm{S}} \\ \psi_J^{\mathrm{T}} \end{pmatrix} = \begin{pmatrix} \cos\phi_J & \sin\phi_J \\ -\sin\phi_J & \cos\phi_J \end{pmatrix} \begin{pmatrix} \varphi_J^{\mathrm{S}} \\ \varphi_J^{\mathrm{T}} \end{pmatrix} \tag{9}$$

Eq.(8) shows that the mutually perturbing states are repulsive to each other. The energy level shifts $\Delta_{\pm}$ is defined as

$$\Delta_{\pm} \equiv E_{\pm}(JKM) - E(\varphi_J) \tag{10}$$

here $\Delta_+$ denotes the upward shift and $\Delta_-$ the downward shift. The phase angle $\phi$, characterizing the mixing effects, is given by,

$$\phi = \arcsin\left\{\frac{\nu_{\mathrm{ST}}}{\left[E(\psi_J^{\mathrm{S}}) - E(\psi_J^{\mathrm{T}})\right]}\right\} \tag{11}$$

According to Eq.(9), 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.(8)-(11), 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

$$|i\rangle = c_J |v\rangle^{\mathrm{S}} |JKM\rangle^{\mathrm{S}} + d_J |v\rangle^{\mathrm{T}} |JKM\rangle^{\mathrm{T}} \tag{12}$$

$$|f\rangle = c_{J'} |v'\rangle^{\mathrm{S}} |J'K'M'\rangle^{\mathrm{S}} + d_{J'} |v'\rangle^{\mathrm{T}} |J'K'M'\rangle^{\mathrm{T}} \tag{13}$$

Because the potentials include only electrostatic interactions with no magnetic coupling, they can not change the spin of the states. So a transition between singlet and triplet states is prohibited. According to the first-Born approximation of time dependent perturbation theory, the amplitude for a transition between $|i\rangle$ and $|f\rangle$ is,

$$\begin{aligned} A_{i\to f} = &\frac{1}{i\hbar} \int \langle f|\, V(t)\, |i\rangle \,\mathrm{d}t \\ = &\frac{1}{i\hbar} c_J c_{J'} \int \langle J'K'M'|\, \langle v'|\, V_{\mathrm{S}}(t)\, |v\rangle\, |JKM\rangle \,\mathrm{d}t \\ &+ \frac{1}{i\hbar} d_J d_{J'} \int \langle J'K'M'|\, \langle v'|\, V_{\mathrm{T}}(t)\, |v\rangle\, |JKM\rangle \,\mathrm{d}t \end{aligned} \tag{14}$$

in Eq.(14), the vibration factor $\langle v'|\, v\rangle = 1$, because in atom-diatom rotational energy transfer, the atom can be treated as a particle with its inner freedoms frozen and only rotational wave function of the molecule changes during the collision process, i.e., $|v'\rangle^{\mathrm{S,T}} = |v\rangle^{\mathrm{S,T}}$.

Introducing Eq.(1) into Eq.(14), one has,

$$\begin{aligned} A_{i\to f}^H = &\frac{4\varepsilon^H a_2}{i\hbar} c_J c_{J'} \\ &\cdot \sum_{M_L} (-1)^{2-M_L} \langle J'K'M'|\, D_{M_L,0}^{2\,*}\, |JKM\rangle \\ &\cdot \int_{-\infty}^{\infty} \exp(i\varpi_{J'J}^H t)\left(\frac{\sigma^{12}}{R^{12}} - \frac{\sigma^6}{R^6}\right) C_{M_L}^2(\Omega_t)\,\mathrm{d}t \end{aligned} \tag{15}$$

with $\omega_{J'J} = 2\pi c B \left[J'(J'+1) - J(J+1)\right]$ being the energy difference of the $J \to J'$ transition.

The integral in Eq.(15) is defined as

$$I_m^l(n) = \int_{-\infty}^{\infty} \exp(i\omega_{J'J}t) R(t)^{-n} C_m^l(\Omega_t)\,\mathrm{d}t \tag{16}$$

considering the fact that the rotational matrix element in Eq.(14) is [6]

$$\begin{aligned} \langle J'K'M'|\, D_{m,0}^{l\,*}\, |JKM\rangle = &\left[(2J+1)(2J'+1)\right]^{1/2} \\ &\cdot \begin{pmatrix} J' & l & J \\ M' & -m & M \end{pmatrix} \begin{pmatrix} J' & l & J \\ K' & 0 & K \end{pmatrix} \end{aligned} \tag{17}$$

Introducing Eq.(16) and Eq.(17) into Eq.(15) and using the orthogonal relations involving the 3$j$ symbols [5],

$$\sum_{M,M'} \begin{pmatrix} J' & l' & J \\ M' & m' & M \end{pmatrix} \begin{pmatrix} J' & l & J \\ M' & m & M \end{pmatrix} = \frac{1}{(2l+1)} \delta_{l,l'} \delta_{m,m'}$$

(18)

one has,

$$A_{i \to f}^H = \frac{4\varepsilon^H a_2^H}{i\hbar} \sqrt{(2J+1)(2J'+1)} \begin{pmatrix} J' & 2 & J \\ K' & 0 & K \end{pmatrix}$$
$$\cdot \sum_m (-1)^{2-m} \begin{pmatrix} J' & 2 & J \\ M' & -m & M \end{pmatrix}$$
$$\cdot \left[ \sigma^{12} I_m^{2H}(12) - \sigma^6 I_m^{2H}(6) \right]$$

(19)

Because the $C_{2v}$ symmetry of the electron charge distribution should also present in the symmetry of the potential function, for the singlet state A$^1\Sigma_u^+$, one has $m=0$; while for the triplet state b$^3\Pi_{0u}$, one has both $m=0$ and $\pm 2$ [9].

The transition probability between the initial and the final states can be written as [4],

$$P_{JJ'} = \frac{1}{(2J+1)} \sum_{MM'} |A_{i \to f}|^2$$

(20)

Introducing Eq.(19) into Eq.(20), one has

$$P_{JJ'} = c_J^2 c_{J'}^2 P_{JJ'}^S + d_J^2 d_{J'}^2 P_{JJ'}^T$$
$$+ 2c_J c_{J'} d_J d_{J'} \sum_{M_L} [(P_{JJ'}^S)_{M_L} (P_{JJ'}^T)_{M_L}]^{1/2}$$

(21)

where $P_{JJ'}^S$ and $P_{JJ'}^T$ are transition probability for the pure singlet and triplet channels with

$$P_{JJ'}^H = \frac{(4a_2^H \varepsilon^H)^2 (2J'+1)}{5\hbar^2} \begin{pmatrix} J' & 2 & J \\ K' & 0 & K \end{pmatrix}^2$$
$$\cdot \sum_m \left| \sigma^{12} I_m^{2H}(12) - \sigma^6 I_m^{2H}(6) \right|^2$$

(22)

here $H$ stands for S or T.

For $b \geq \rho$, the integration in Eq.(16) can be carried out with a "straight-line" trajectory approximation [10-15], i.e., $R(t) = v^2 t^2 + b^2$. This requires that the rotational energy transferred is much less than the energies relative to the translational motion. For the experiment of Na$_2$-Na collision, the rotational energy transferred ($\Delta J = |J' - J| = 2$) is $\Delta E_{\rm rot} = B(4J + 6) \approx 5.7$ cm$^{-1}$ at $J=10$ (the rotational constants B of Na$_2$(A$^1\Sigma_u^+$, $v=8$) and Na$_2$(b$^3\Pi_{0u}$, $v=14$) are 0.106203 [16] and 0.142501 cm$^{-1}$ [17] respectively), which is indeed much less than the energies relative to the translational motion $E_{\rm tra} = (3/2)KT \approx 782$ cm$^{-1}$ at 750 K. So the "straight-line" trajectory approximation for $b \geq \rho$ is valid.

For $b \leq \rho$, the transition probability between the initial and the final states can be calculated by interpolation between $P_{J,J'}(b=0)$ and $P_{J,J'}(b=\rho)$. $P_{J,J'}(b)$ is smooth at $b=0$, so the simplest form of interpolation function can be written as [18,19]

$$P_{J,J'}(b \leq \rho) = P_{J,J'}(b=0) + b^2/\rho^2$$
$$\cdot [P_{J,J'}(b=\rho) - P_{J,J'}(b=0)]$$

(23)

The integral in Eq.(16) can be solved by applying the following reference frame: an atom, which moves along the coordinate axis with the speed $v$ and the impact parameter $b=0$, is in collision with the diatom, and is rebounded at the same speed. The integrals for $b=0$ and $b \geq \rho$ are listed in Appendix of Ref.[19]. Eq.(21) can also be rewritten as [1]

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

(24)

$$\cos\theta_{\rm ST}^D = \frac{\sum_{M_L} [(P_{JJ'}^S)_{M_L} (P_{JJ'}^T)_{M_L}]^{1/2}}{(P_{JJ'}^S P_{JJ'}^T)^{1/2}}$$

(25)

### III. CALCULATION AND DISCUSSION

In the molecular beam experiment, the relative velocity of the gases is uniform and can be controlled, so the differential interference angle can be measured. Using Eq.(24) we can obtain the relationship of the differential interference angle for the Na$_2$(A$^1\Sigma_u^+$,$v=8$ b$^3\Pi_{0u}$,$v=14$) -Na system with the impact parameter $b$ and the relative velocity $v$ at 750 K. It is clear that the following two situations for the Na$_2$-Na collision are different, namely, the interference-neglected extreme situation of gateway model ($\theta=90°$, $\cos\theta = 0$) and the complete interference extreme situation of infinite order sudden approximation ($\theta=0°$, $\cos\theta=1$). The sign of the product $c_J c_{J'} d_J d_{J'} \cos\theta_{\rm ST}^D$ determines whether a constructive or a destructive interference effect occurs, and the magnitude of the product depends on the degree of the interference effect.

The rotational quantum numbers involved in this study are the initial rotational state $J=10$ and the final rotational state $J'=12$. The rotational constants $B$ for the Na$_2$(A$^1\Sigma_u^+$, $v = 8$) state and Na$_2$(b$^3\Pi_{0u}$, $v = 14$) state are 0.106203 and 0.142501 cm$^{-1}$, respectively [20]. The reduced mass $m$ of the collision system and the collision diameter $\rho$ used in our calculation are 15.327 atomic units [4] and 4.41Å [7], respectively. The interaction between molecules almost disappears when $b > 10$ Å, so the discussion below is in the condition of the maximum $b$ value is 10 Å. The relationships of interference angle with impact parameter have been calculated and the results are shown in Fig.1.
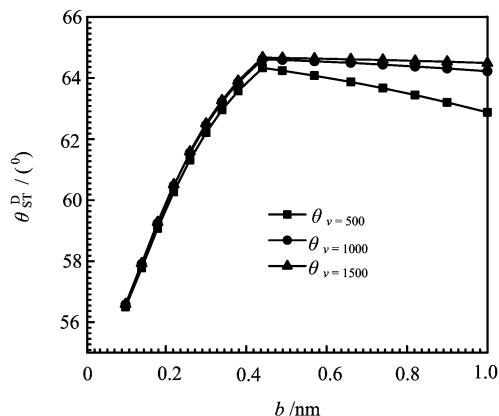
FIG. 1 The tendency of the differential interference angle with the impact parameter $b$ and $v$.

With the increase of the impact parameter, the differential interference angle increases for $b<\rho$, so the quantum interference effect of rotational energy transfer decreases. But for $b>\rho$, the changing tendency of differential interference angle with the impact parameter is reverse. The nonmonotone changing tendencies are illustrated in Fig.1.

Two main aspects, we think, contribute to it: (i) The probability of rotational energy transfer and interference will increase with the elongation of the duration of collision, and the impact parameter just play a key role in affecting the duration. (ii) The energy interval has a large connection with the impact parameter, and larger impact parameter will bring an opposite effect to the interference when contrasted to aspect (i).

The curve given in Fig.1 also exhibits the changing tendency of the differential interference angles which are consistent with the velocity. It not only affects the duration of collision but also the ability of the impact parameter to overcome interactive potential barrier. The higher the relative velocity is, the shorter the duration of collision is, which will be favorable to the enhancement of interference. And the higher the energy is, the easier the access to each other is, which will decrease the interference. And the competition between them are supposed to determine the final velocity-dependent relationships.

## IV. CONCLUSION

In this report we studied the collisional quantum interference of $Na_2(A^1\Sigma_u^+, v=8\sim b^3\Pi_{0u}, v=14)$ system in collision with $Na(3s)$. The treatments are based on the time-dependent first-order Born approximation,

and the anisotropic Lennard-Jones interaction potentials are used. The factors that the differential interference angle depends on are obtained, and the changing tendency of the differential interference angle with them is discussed: (i) With the increase of velocity, the differential interference angles increase. (ii) When $b>\rho$, the differential interference angles decrease monotonously with the increase of the impact parameter, when $b<\rho$, with the increase of $b$, the differential interference angles increase, so the degree of the interference decreases.

## V. ACKNOWLEDGMENT

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