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 Λ -related Quantum Interference of ${}^2\Pi$ [Case(a)] Diatom on Rotational Energy TransferJian Li^a, Yan-qing Ni^b, Yong-qing Li^{b,c}, Wei-li Wang^d, Feng-cai Ma^{b*}*a. Department of Science, Shenyang Institute of Aeronautical Engineering, Shenyang 110036, China**b. Department of Physics, Liaoning University, Shenyang 110036, China**c. Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal**d. School of Science, Liaoning Technical University, Fuxin 123000, China*

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To study theoretically the relationship between the integral interference angle and the scattering angle in collisional quantum interference, the integral interference angle of atom- ${}^2\Pi$ [case(a)] diatomic molecules system is described. To simulate the experiment theoretically, the theoretical model on collision-induced rotational energy transfer in an atom- ${}^2\Pi$ [case(a)] diatom system is presented based on the first order Born approximation taking into account of the long-range interaction potential. For the ${}^2\Pi$ electronic state in the Hund's case(a) diatom, the degree of the interference is discussed. The interference angles of collision-induced rotational energy transfer of CN($A^2\Pi$) in Hund's case(a) with He, Ne, and Ar are calculated quantitatively. The key parameters in the determination of integral interference angles are obtained.

Key words: Collisional quantum interference, Rotational energy transfer, Interference angle

I. INTRODUCTION

The collisional quantum interference (CQI) effect on the rotational energy transfer has been a hot topic in the two decades both in experimental and theoretical studies. CQI is different from the other well-known quantum interference effects such as the quantum beat spectroscopy and the so-called rotational coherence spectroscopy in at least two aspects. First, CQI appears in radiationless transition processes e.g., molecular collision. In Sha's experiments, only intramolecular rotational energy transfer happened [1]. Second, CQI is the quantum interference between de Broglie waves while the above described well-known quantum interference is due to the interaction between electromagnetic waves and molecules. The evidence of CQI on rotational energy transfer was observed 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 impact parameters [1,2]. CQI was also observed by Chen *et al.* in Na₂ $A^1\Sigma_u^+$ ($v=8$)- $b^3\Pi_{0u}$ ($v=14$) system in collision with Na(3s) [3]. In Sha's experiment [1], the two mutually perturbed states are the singlet state CO $A^1\Pi$ ($v=0$) and the triplet state CO $e^3\Sigma^-$ ($v=1$). In contrast, in Chen's experiment [3], they are the singlet state Na₂ $A^1\Sigma_u^+$ ($v=8$) and the triplet state Na₂ $b^3\Pi_{0u}$ ($v=14$). In these experiments, intramolecular ro-

tational energy transfer was considered. 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 calculation of dipole-dipole rotationally inelastic scattering and Gray and van Kranendonk's theory of pressure broadening. Moreover, the theory of CQI on rotational energy transfer can be developed along the lines of Alexander's calculation by using the time-dependent Born approximation and assuming a dipole-dipole interaction potential. Sun *et al.* improved the theory of CQI further [4].

The CQI studied in previous experiments [1-4] and models [5-11] occurred in the mixed electronic states. In the same electronic states, the CQI which results from the Λ splits of open-shell ${}^1\Pi$ -states diatomic molecules was also observed experimentally [12-16] and interpreted theoretically [17,18].

Rotational inelastic collisions of diatomic molecules in electronic states have been extensively studied both experimentally and theoretically. This interest has been facilitated by the development of modern experimental molecular beam and laser techniques which have allowed the measurement of state-to-state cross sections for a number of systems. Collisions of the CN radical have been the subject of a large number of experimental investigations [19,20]. In part, this is due to favorable spectroscopy since CN in both its ground $X\Sigma^+$ and first excited $A^2\Pi$ electronic states can be sensitively and quantum state selectively detected by

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laser fluorescence excitation to the $B^2\Sigma^+$ state [21-24]. Theoretically, Alexander also discovered and discussed the interference effects on several collision systems such as $\text{NO}(X^2\Pi)+\text{Ar}$, $\text{OH}(X^2\Pi)+\text{Ar}$, $\text{CN}(A^2\Pi)+\text{Ar}$, and $\text{CN}(X^2\Sigma^+, A^2\Pi)+\text{Ar}$ [9]. Maricq presented his calculations on the oscillation distribution of cross sections within the systems Li_2 , Na_2 , N^{2+} , and CN in collision with rare gases [7]. Dagdigian *et al.* studied the interaction potential for the interaction of a closed-shell atom with a molecule in an electronic state of $^2\Pi$ -symmetry [25]. Moreover, the electronic quenching of $\text{CN}(A^2\Pi)$ by rare gases is a model system for the study of collision-induced state-to-state electronic transitions. Alexander and co-workers have carried out an extensive series of theoretical studies [25-27].

Similar to Eq.(1) in Ref.[1], the interference angle in the same electronic state, motivated by the experiments and theories [28-30], is presented in this work. It reflects the degree of quantum interference (resulting from the Λ splits). For the $^2\Pi$ electronic state in the Hund's case(a) diatomic, the factors (the experimental temperatures, different partners, and molecular nature) that the interference angle depends on are obtained. The tendency of interference angle in experiment of $\text{CN}(A^2\Pi)$ with He, Ne, and Ar is discussed.

II. THEORETICAL APPROACH

For the atom-diatom system, the interaction potential V can be written as [30],

$$V(R, \theta, \phi) = \sum_{l,m,k} V_{l,k}(R) D_{m,k}^l(\Omega) C_m^l(\theta, \phi) \quad (1)$$

where R is the orientation from the atom to the mass center of diatom, $D_{m,k}^l(\Omega)$ is the Wigner D rotational matrix, the Euler angles $\Omega=\alpha, \beta, \gamma$ refer to the space fixed by orientation of the diatom, $C_m^l(\theta, \phi)$ is a Racah harmonic function, i.e., $C_m^l(\theta, \phi) = \sqrt{\frac{4\pi}{2l+1}} Y_m^l(\theta, \phi)$, and $Y_m^l(\theta, \phi)$ is the spherical harmonics function. The angles θ and ϕ represent the direction of R in a space-fixed coordinate. In the atom and $^2\Pi$ -states diatomic molecules system, $k=0$ or $k=\pm 2$ [31,32]. The evolution of the interaction potential is,

$$V(t) = U^+(t, 0) V U(t, 0) \quad (2)$$

where t is the time, $U^+(t, 0)$ is the hermitian operator, $U(t, 0)$ is the time evolution operator,

$$U(t, 0) = \exp\left(-\frac{iH_0 t}{\hbar}\right) \quad (3)$$

here the Hamiltonian H_0 can be written as:

$$H_0 = -\frac{1}{2\mu} \frac{d^2}{dR^2} - \frac{\mathbf{L}^2}{2\mu R^2} + H_{\text{at}} + H_{\text{e}} + H_{\text{vib}} + H_{\text{rot}} \quad (4)$$

μ is the collision reduced mass, R is the distance from the atom to the mass center of the molecule, \mathbf{L} is the operator for the orbital angular momentum of the atom-molecule pair, H_{at} is the atom electronic state Hamiltonian, H_{e} , H_{vib} , and H_{rot} are the electronic, vibrational, and rotational Hamiltonian of diatom, respectively. In this work, without considering the translational, electronic and vibrational energy transfer, H_0 in Eq.(4) can be simplified to rotational energy and the rotational kinetic energy of the atom about the diatom,

$$H_0 = -\frac{\mathbf{L}^2}{2\mu R^2} + H_{\text{rot}} \quad (5)$$

For a $^2\Pi$ electronic state the case(a) wave functions are of definite parity, which may be written as [30],

$$|JM\varepsilon\rangle = \frac{1}{\sqrt{2}} [|JM\Omega\rangle |\Lambda = 1, \Sigma = \pm 1/2\rangle + \varepsilon |JM, -\Omega\rangle |\Lambda = -1, \Sigma = \mp 1/2\rangle] \quad (6)$$

where J is the total angular momentum quantum number, M is the projection of J along a space-fixed Z -axis, Ω is the projection of total angular momentum on the molecular frame, Λ is the total orbit angular momentum, Σ is the total spin angular momentum, and ε is the parity index, $\varepsilon=\pm 1$. Within the spectroscopic nomenclature, the $\varepsilon=+1$ are designated as e parity and the $\varepsilon=-1$ as f, with the upper sign corresponding to the $\Omega=3/2$ spin-orbit manifold and the lower sign to the $\Omega=1/2$ spin-orbit manifold. e and f are the even parity and odd parity respectively. The Hund's case(a) wave functions given in Eq.(6) are a correct description of a molecule in a $^2\Pi$ electronic state only when the magnitude of the spin-orbit constant A is only infinitely large compared of the product of the rotational constant B multiplied by the total angular momentum quantum number J . The rotational wave function $|JM\Omega\rangle$ which appears in Eq.(6) can be written as a rotational matrix element.

$$|JM\Omega\rangle = \left(\frac{2J+1}{8\pi^2}\right)^{1/2} D_{M\Omega}^{J*}(\alpha\beta\gamma) \quad (7)$$

Considering the interaction between a $^2\Pi$ [case(a)] diatom and a spherical atom in a singlet state, the total wave function is usually expanded in terms of eigenfunctions of the total angular momentum \mathfrak{S} , which is defined by [27]

$$|J\Omega\varepsilon\mathfrak{S}\zeta\rangle = \sum_{MM_L} \langle JMLM_L|\mathfrak{S}\zeta\rangle |LM_L\rangle |JM\varepsilon\rangle \quad (8)$$

where ζ is the space-frame projection of \mathfrak{S} , L is the orbital angular momentum of the atom-molecule pair and its space-frame projection is M_L , and $|LM_L\rangle$ is a spherical harmonic [30],

$$\begin{aligned} |LM_L\rangle &= Y_{M_L}^L(\theta, \phi) \\ &= \left(\frac{2L+1}{4\pi}\right)^{1/2} D_{M_L,0}^L(\theta, \phi, 0) \end{aligned} \quad (9)$$

According to the first order Born approximation, considering the product of three rotation matrix elements and spherical harmonics and the relationship between $3j$ symbol and $6j$ symbol, the transition matrix element is [6],

$$\begin{aligned} & \langle J' L' \varepsilon' \mathfrak{S} \zeta | V(t) | J L \varepsilon \mathfrak{S} \zeta \rangle \\ &= (-1)^{J+J'+\mathfrak{S}-\Omega} [(2J+1)(2J'+1)(2L+1) \cdot \\ & (2L'+1)]^{1/2} \sum_l \frac{1}{2} [1 - \varepsilon \varepsilon' (-1)^{J+J'+l}] \cdot \\ & \left(\begin{array}{ccc} L' & l & L \\ 0 & 0 & 0 \end{array} \right) \left\{ \begin{array}{ccc} J & L & \mathfrak{S} \\ L' & J' & l \end{array} \right\} \left\{ \delta_{\Omega\Omega'} \begin{pmatrix} J' & l & J \\ -\Omega' & 0 & \Omega \end{pmatrix} \cdot \right. \\ & \exp(i\varpi_{JJ'}^{\Delta\Omega=0} t) V_{l,0}[R(t)] + \varepsilon(1 - \delta_{\Omega\Omega'}) \cdot \\ & \left. \left(\begin{array}{ccc} J' & l & J \\ -\Omega' & 2 & -\Omega \end{array} \right) \exp(i\varpi_{JJ'}^{\Delta\Omega=1} t) V_{l,2}[R(t)] \right\} \quad (10) \end{aligned}$$

where $[R(t)]$ is the distance from the atom to the mass center of diatom, and ϖ is the energy difference of the $J \rightarrow J'$ transition, $\Delta\Omega = \Omega' - \Omega$.

The unpolarized transition probability $P_{JJ'}$ for $J \rightarrow J'$ transition can be written as [29],

$$\begin{aligned} P_{JJ'} &= \frac{1}{2J+1} \cdot \sum_{LL'} \left\{ \left| \frac{1}{i\hbar} \int_{-\infty}^{\infty} \langle J' \Omega' \varepsilon' \mathfrak{S} \zeta | \cdot \right. \right. \\ & \left. \left. V(t) | J \Omega \varepsilon \mathfrak{S} \zeta \rangle dt \right|^2 \right\} \quad (11) \end{aligned}$$

An explicit formula for the $J \rightarrow J'$ transition probability is obtained, involving quantum interference, which originates from the difference between the two Λ -related collision potential energy surfaces on ${}^2\Pi$ [case(a)] diatom [18],

$$\begin{aligned} P_{JJ'} &= P_{JJ'}^{\Delta\Omega=0} + P_{JJ'}^{\Delta\Omega=1} + \\ & 2\varepsilon \sum_l [(P_{JJ'}^{\Delta\Omega=0})_l]^{1/2} [(P_{JJ'}^{\Delta\Omega=1})_l]^{1/2} \quad (12) \end{aligned}$$

Similar to Eq.(1) in Ref.[1], Eq.(12) also can be written as:

$$\begin{aligned} P_{JJ'} &= P_{JJ'}^{\Delta\Omega=0} + P_{JJ'}^{\Delta\Omega=1} + \\ & 2\varepsilon (P_{JJ'}^{\Delta\Omega=0} P_{JJ'}^{\Delta\Omega=1})^{1/2} \cos \theta^D \quad (13) \end{aligned}$$

where θ^D refers to differential interference angle, the spin-orbit conserving transition, the spin-orbit changing transitions, and the interference between them are expressed in Eq.(14)-Eq.(16) [31-35], respectively,

$$\begin{aligned} P_{JJ'}^{\Delta\Omega=0} &= \frac{2J'+1}{\hbar^2} \sum_{L,L'} (2L+1)(2L'+1) \cdot \\ & \sum_l F^2 \delta_{\Omega\Omega'} \left(\begin{array}{ccc} L' & l & L \\ 0 & 0 & 0 \end{array} \right)^2 \left\{ \begin{array}{ccc} J & L & \mathfrak{S} \\ L' & J' & l \end{array} \right\}^2 \cdot \\ & \left(\begin{array}{ccc} J' & l & J \\ -\Omega' & 0 & \Omega \end{array} \right)^2 \left| \int_{-\infty}^{\infty} \exp(i\varpi_{JJ'}^{\Delta\Omega=0} t) V_{l,0}(R) dt \right|^2 \quad (14) \end{aligned}$$

$$\begin{aligned} P_{JJ'}^{\Delta\Omega=1} &= \frac{2J'+1}{\hbar^2} \sum_{L,L'} (2L+1)(2L'+1) \cdot \\ & \sum_l F^2 (1 - \delta_{\Omega\Omega'}) \left(\begin{array}{ccc} L' & l & L \\ 0 & 0 & 0 \end{array} \right)^2 \left\{ \begin{array}{ccc} J & L & \mathfrak{S} \\ L' & J' & l \end{array} \right\}^2 \cdot \\ & \left(\begin{array}{ccc} J' & l & J \\ -\Omega' & 2 & -\Omega \end{array} \right)^2 \left| \int_{-\infty}^{\infty} \exp(i\varpi_{JJ'}^{\Delta\Omega=1} t) V_{l,2}(R) dt \right|^2 \quad (15) \end{aligned}$$

$$\begin{aligned} & \sum_l [(P_{JJ'}^{\Delta\Omega=0})_l]^{1/2} [(P_{JJ'}^{\Delta\Omega=1})_l]^{1/2} \\ &= \frac{2J'+1}{\hbar^2} \sum_{L,L'} (2L+1)(2L'+1) \cdot \\ & \sum_l F^2 \left(\begin{array}{ccc} J' & l & J \\ -\Omega' & 0 & \Omega \end{array} \right) \left(\begin{array}{ccc} J' & l & J \\ -\Omega' & 2 & -\Omega \end{array} \right) \cdot \\ & \left(\begin{array}{ccc} L' & l & L \\ 0 & 0 & 0 \end{array} \right)^2 \left\{ \begin{array}{ccc} J & L & \mathfrak{S} \\ L' & J' & l \end{array} \right\}^2 \cdot \\ & \left\{ \int_{-\infty}^{\infty} \exp(i\varpi_{JJ'}^{\Delta\Omega=0} t) V_{l,0}(t) dt \cdot \right. \\ & \left. \left(\int_{-\infty}^{\infty} \exp(i\varpi_{JJ'}^{\Delta\Omega=1} t) V_{l,2}(t) dt \right)^* + \text{h.c.} \right\} \quad (16) \end{aligned}$$

where F is the well-known selection rule [31],

$$F = \frac{1}{2} [1 - \varepsilon \varepsilon' (-1)^{J+J'+l}] \quad (17)$$

if only the rotational energy transfer is considered [31], then

$$\begin{aligned} \varpi_{JJ'} &= 2\pi cB [J'(J'+1) - 2\Omega'\Omega + \Omega^2] - \\ & 2\pi cB [J(J+1) - 2\Omega\Omega + \Omega^2] \quad (18) \end{aligned}$$

here, B is the rotational constant, π and c are the constants. The velocity-averaged probability is,

$$\langle P \rangle = \frac{\int_0^{\infty} P(v) v f(v, T) dv}{\int_0^{\infty} v f(v, T) dv} \quad (19)$$

$$f(v, T) = v^2 \exp\left(\frac{-\mu v^2}{2kT}\right) \quad (20)$$

where $f(v, T)$ is the Maxwell-Boltzmann velocity distribution function, v is the velocity, μ is the reduced mass of the collision system, and T is the temperature of the static cell.

$$\sigma_{JJ'} = 2\pi \int_0^{\infty} \langle P_{JJ'}(b) \rangle b db \quad (21)$$

here, b is the impact parameter [7], $\sigma_{JJ'}$ is the cross sections can be obtained,

$$\begin{aligned} \sigma_{JJ'} &= \sigma_{JJ'}^{\Delta\Omega=0} + \sigma_{JJ'}^{\Delta\Omega=1} + \\ & 2\varepsilon (\sigma_{JJ'}^{\Delta\Omega=0} \sigma_{JJ'}^{\Delta\Omega=1})^{1/2} \cos \theta^I \quad (22) \end{aligned}$$

with the integral interference angle $\cos \theta^I$

$$\begin{aligned} \cos \theta^I = & \int \int \sum_l \left\{ [(P_{JJ'}^{\Delta\Omega=0})_l]^{1/2} \cdot \right. \\ & \left. [(P_{JJ'}^{\Delta\Omega=1})_l]^{1/2} v^3 \exp\left(\frac{-\mu v^2}{2kT}\right) \right\} bdbdv \cdot \\ & \left[\int \int P_{JJ'}^{\Delta\Omega=0} v^3 \exp\left(\frac{-\mu v^2}{2kT}\right) bdbdv \right]^{-1/2} \\ & \left[\int \int P_{JJ'}^{\Delta\Omega=1} v^3 \exp\left(\frac{-\mu v^2}{2kT}\right) bdbdv \right]^{-1/2} \quad (23) \end{aligned}$$

III. RESULTS AND DISCUSSION

In the following section, we detail the relationships of the differential interference angle versus the factors of the experiment in the molecular beam. The differential interference angle measures the degree of coherence, which originates from the difference between the two Λ -related collision potential energy surfaces. To simplify the discussion, we adopt the anisotropic Lennard-Jones interaction ($l \leq 2$) in the space frame,

$$\begin{aligned} V_{A'}(R, \theta, \phi) = & V_1(R) \sum_m [a_{1,0} D_{m,0}^1 * (\Omega) C_m^1(\theta, \phi)] + \\ & V_2(R) \sum_m [a_{2,0} D_{m,0}^2 * (\Omega) C_m^2(\theta, \phi) + \\ & a_{2,2} D_{m,2}^2 * (\Omega) C_m^2(\theta, \phi)] \quad (24) \end{aligned}$$

$a_{1,0}$, $a_{2,0}$, and $a_{2,2}$ are the anisotropic parameters. For ${}^2\Pi$ diatomic molecules, $\Lambda = \pm 1$ and $\Sigma = \pm 1/2$. Λ and Σ can be parallel. It will lead to a state with $|\Omega| = 3/2$. In contrast, Λ and Σ can be antiparallel. It will lead to a state with $|\Omega| = 1/2$. To simplify the discussion, we take $|\Omega| = 1/2$. For the experiments of $\text{CN}(A^2\Pi)$ with He, Ne, and Ar, one can obtain the interference angle for $J' = J \pm 1$, then the interference of Eq.(14) is [19]

$$\cos \theta^I = \frac{\langle A \rangle}{\langle B \rangle^{1/2} \langle C \rangle^{1/2}} \quad (25)$$

$$\langle A \rangle = \left| \frac{\sigma^6}{b^{11}} F_6(x^{\Delta\Omega=0}) - \frac{1}{b^5} F_3(x^{\Delta\Omega=0}) \right| \left[\frac{\sigma^6}{b^{11}} F_6(x^{\Delta\Omega=1}) - \frac{1}{b^5} F_3(x^{\Delta\Omega=1}) \right] \quad (26)$$

$$\langle B \rangle = \frac{(a_{1,0})^2 \sum_{L,L'} (2L'+1) \begin{pmatrix} L' & 1 & L \\ 0 & 0 & 0 \end{pmatrix}^2 \left\{ \begin{matrix} J & L & \mathfrak{S} \\ L' & J' & 1 \end{matrix} \right\}^2 \begin{pmatrix} J' & 1 & J \\ -1/2 & 0 & 1/2 \end{pmatrix}^2}{(a_{2,0})^2 \sum_{L,L'} (2L'+1) \begin{pmatrix} L' & 2 & L \\ 0 & 0 & 0 \end{pmatrix}^2 \left\{ \begin{matrix} J & L & \mathfrak{S} \\ L' & J' & 2 \end{matrix} \right\}^2 \begin{pmatrix} J' & 2 & J \\ -3/2 & 2 & -1/2 \end{pmatrix}^2}$$

$$\left| \frac{\sigma^6}{vb^{11}} F_6(x^{\Delta\Omega=0}) - \frac{1}{vb^5} F_{7/2}(x^{\Delta\Omega=0}) \right|^2 + \left| \frac{\sigma^6}{vb^{11}} F_6(x^{\Delta\Omega=0}) - \frac{1}{vb^5} F_3(x^{\Delta\Omega=0}) \right|^2 \quad (27)$$

$$\langle C \rangle = \left[\frac{\sigma^6}{b^{11}} F_6(x^{\Delta\Omega=1}) - \frac{1}{b^5} F_3(x^{\Delta\Omega=1}) \right]^2 \quad (28)$$

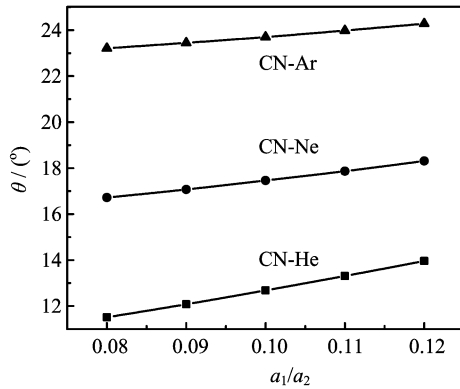
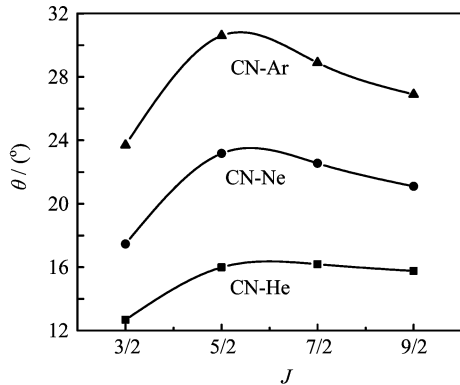
We suspect that $\cos \theta^I$ in Eq.(25) is closely related to the orbital angular momentum mentioned above. But the interference angle $\cos \theta^D$ given in Eq.(13) is a correct description of a molecule in a ${}^2\Pi$ electronic state only when the magnitude of the spin-orbit constant A is only infinitely large compared with the product of the rotational constant B multiplied by the total angular momentum quantum number J . When $B \times J > A$, ${}^2\Pi$ electronic state will result in Hund's case(b) limit [19]. Now the further theoretical study of the collision-induced Λ -related quantum interference on rotational energy transfer in an atom-diatom system and a dynamic model of atom- ${}^2\Pi$ [case(b)] diatomic molecules system is under way. The interference angle of experiment of collision-induced rotational energy transfer of $\text{CN}(A^2\Pi)$ in Hund's case(a) with He, Ne, and Ar can be calculated quantitatively. Some of the derivations are referenced in the Appendix. The needed parameters of the theoretical calculation are listed in Table I.

Four conclusions can be obtained: (i) As presented in Fig.1, with the increase of $a_{1,0}/a_{2,0}$, the interference angle increases, so the quantum interference effect of rotational energy transfer decreases. When $a_{1,0}/a_{2,0}=0$, the interference is the complete interference. (ii) Figure 2 exhibits the tendency of the interference angles, which is consistent with the experimental results qualitatively [1,2]. We give the interpretation of the interference angle values as: The changing tendency is not monotone with the increase of the rotational quantum number; due to the collision perturbation, there will be different energy level shifts on the spin-orbit conserving transition and the spin-orbit changing transition; and the level shifts will result in the decoupling of the spin-orbit mixed states. (iii) With the increase of orbit angular momentum (i.e., with the increase of mass of partner, impact parameter, or experimental temperature), the interference angle decreases. $L = \mu v b / \hbar = (ub/\hbar)(8kT/\pi\nu)^{1/2}$ is the orbital angular momentum of the atom-molecule pair, and $\mu = m_{\text{CN}} m_{\text{partner}} / (m_{\text{CN}} + m_{\text{partner}})$ is the collision reduced mass. Therefore, the quantum interference

TABLE I Parameters for the theoretical calculation of the integral interference angle θ_{ST}^I ($B^a=15346\text{cm}^{-1}$ [26]).

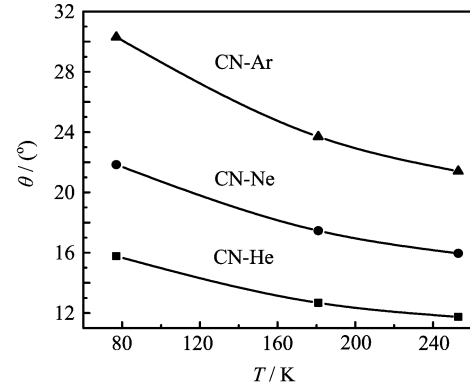
Collision system	Reduced mass/a.m.u	σ_{\min}/nm	b_{\min}/nm	L		
				$T=77\text{ K}$	$T=181\text{ K}$	$T=253\text{ K}$
CN-He	3.47 [5]	0.216 [12]	0.25 [25]	9	14	17
CN-Ne	11.3 [6]	0.235 [12]	0.27 [6]	18	28	33
CN-Ar	15.76 [6]	0.301 [12]	0.31 [6]	25	38	45

$${}^a L = \frac{\mu v b}{\hbar} = \frac{\mu b}{\hbar} \sqrt{\frac{8kT}{\pi\mu}}$$

FIG. 1 The changing tendency of the integral interference angles with the ratio of a_1/a_2 at $J=3/2$ and $T=181\text{ K}$.FIG. 2 The changing tendency of the integral interference angles with J at $a_1/a_2=0.1$ and $T=181\text{ K}$.

effect of rotational energy transfer increases, as shown in Fig.3.

We suggest that the orbit angular momentum and the relative velocity depend on the experimental temperature. The former influences the electrostatic interaction potential between the atom and diatom. The mixing degree of corresponding wave functions will become much bigger than that of the isolated molecule due to the increasing of the temperature, and the interference effect will become stronger as well. (iv) The interference angles will increase with the increase of reduced mass, so the quantum interference effect of rotational energy

FIG. 3 The changing tendency of the integral interference angles with T at $J=3/2$ and $a_1/a_2=0.1$.

transfer decreases.

IV. CONCLUSION

A theoretical model is presented for collision induced rotational energy transfer of polar diatomic molecule in the ${}^2\Pi$ state due to interaction with an inert gas atom.

Collisional quantum interference of the ${}^2\Pi$ electronic state, which is well described by Hund's case(a) on rotational energy transfer and originates from the difference between the two Λ -related collision potential energy surfaces, was studied theoretically. Based on the time dependent first order Born approximation, taking into account the anisotropic Lennard-Jones interaction potentials and "straight-line" trajectory approximation, the factors that the interference angle depends on are obtained, and the tendency of the interference with them is discussed.

V. ACKNOWLEDGMENTS

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APPENDIX A:

$$\begin{aligned} \begin{pmatrix} J' & l & J \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix}^2 &= -\frac{(-1)^{-J}\sqrt{2}\sqrt{J+1/2}\sqrt{3/2+J}}{\sqrt{1+2J}\sqrt{2+2J}\sqrt{3+2J}} \\ \begin{pmatrix} L' & l & L \\ 0 & 0 & 0 \end{pmatrix}^2 &= -\frac{(-1)^{-L}\sqrt{2}(1+L)}{\sqrt{1+2L}\sqrt{2+2L}\sqrt{3+2L}} \\ \left\{ \begin{matrix} J & L & \mathfrak{S} \\ L' & J' & l \end{matrix} \right\}^2 &= -\frac{(-1)^{-2J-2L}\sqrt{J}\sqrt{-2+2L}}{\sqrt{2+2J}\sqrt{3+2J}\sqrt{L}\sqrt{1+2L}} \\ &\text{for } \mathfrak{S}=J+L-1 \\ \begin{pmatrix} J' & 2 & J \\ -\frac{3}{2} & 2 & -\frac{1}{2} \end{pmatrix}^2 &= -\frac{(-1)^J\sqrt{3/2+J}\sqrt{5/2+J}\sqrt{1+2J}}{\sqrt{2}\sqrt{J}\sqrt{2+2J}\sqrt{3+2J}\sqrt{4+2J}} \\ \begin{pmatrix} L' & l & L \\ 0 & 0 & 0 \end{pmatrix}^2 &= \frac{(-1)^L\sqrt{3}(-1+L)\sqrt{L}}{\sqrt{3+2L}\sqrt{-2+2L}\sqrt{-1+2L}\sqrt{1+2L}} \\ \left\{ \begin{matrix} J & L & \mathfrak{S} \\ L' & J' & 2 \end{matrix} \right\}^2 &= -\frac{2(-1)^{-2J-2L}\sqrt{-1+2J}\sqrt{-4+2L}}{\sqrt{2+2J}\sqrt{3+2J}\sqrt{4+2J}\sqrt{L}} \\ &\frac{\sqrt{-1+2J+2L}}{\sqrt{-1+2L}\sqrt{1+2L}} \\ &\text{for } \mathfrak{S}=J+L-2 \end{aligned}$$