

## ARTICLE

## Collision-induced Rotational Energy Transfer in an Atom-Diatom System

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(Dated: Received on March 13, 2008; Accepted on August 4, 2008)

As a further theoretical study of the collision-induced quantum interference on rotational energy transfer in an atom-diatom system, based on the first-Born approximation of time-dependent perturbation theory, taking into account the anisotropic Lennard-Jones interaction potential and the long-range interaction potential, the differential interference angles in singlet-triplet mixed states of CO  $A^1\Pi(v=0)-e^3\Sigma^-(v=1)$  system in collision with He, Ne, Ar, and other partners were calculated theoretically. The relationships of differential interference angle versus impact parameters, including collision parameter  $b$  and velocity, are obtained.

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

## I. INTRODUCTION

Due to the ultrasensitive optical-optical double resonance multiphoton ionization technique, state-to-state cross sections have now become measurable to an accuracy of 10%. The evidence of collisional quantum interference (CQI) on rotational energy transfer 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 [1,2]. CQI was also observed by Chen *et al.* in Na<sub>2</sub>  $A^1\Sigma_u^+(v=8)-b^3\Pi_{0u}(v=14)$  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  $e^3\Sigma^-(v=1)$  [1,2]. In Chen's experiment, they are the singlet state Na<sub>2</sub>  $A^1\Sigma_u^+(v=8)$  and the triplet state Na<sub>2</sub>  $b^3\Pi_{0u}(v=14)$  [3]. In the experiments of Sha *et al.* and Chen *et al.*, only intramolecular rotational energy transfer happened [1-3]. The collisional partners are atoms, and all the interference angles are less than 90°. However, with HCl as the collisional partner [4], the interference angles are larger than 90°, which is a significant complementarity. Such angles also have been interpreted theoretically [5,6]. In addition, because the experiment was done in a static sample cell, only the integral cross sections and the integral interference angles have been measured. If experiments can be conducted in molecular beams to measure the differential cross section and the differential interference angle, it might be possible to observe the collisional quantum more precisely, because the integral interference angle is the average effect of the differential interference angle.

The theory of rotational energy transfer can be developed along the lines of Cross and Gordon's calculation of dipole-dipole rotationally inelastic scattering [7], Gray and van Kranendonk's theory of pressure broaden-

ing (only the long range interaction was considered) [8], and Alexander's calculation (or rotational energy transfer) using the time-dependent Born approximation and assuming a dipole-dipole interaction potential [9].

In this work, we compute the differential interference angles for the singlet-triplet mixed states of CO  $A^1\Pi(v=0)-e^3\Sigma^-(v=1)$  system in collision with He, Ne, and other partners under the conditions of the anisotropic Lennard-Jones interaction potential and the long-range interaction potential. It is necessary to calculate the values of  $\theta_{ST}^D$  since the magnitude of  $\theta_{ST}^D$  can give us a quantitative and accurate description of CQI.

We have employed the anisotropic Lennard-Jones interaction potential and the long-range interaction potential to simulate the interference angle. The first-order Born approximation of time-dependent perturbation theory is also used in the theoretical approach. The translational motion is treated classically, whereas vibrational and rotational motions are handled quantum mechanically. Binary collision and the semiclassical impact parameter approximation are also taken into account in the theoretical treatment. The relationships of interference angle versus impact parameter are plotted and the physical meanings are discussed.

## II. DIFFERENTIAL INTERFERENCE ANGLE OF CQI IN AN ATOM-DIATOM SYSTEM

The Born-Oppenheimer electronic Hamiltonian is written in the form,

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

where  $H_A$  and  $H_B$  are the electronic Hamiltonians of atom A and molecule B, and  $V$  represents the electrostatic interaction potentials.

In the computation, we employ two different expressions for the interaction potential. The first is the long-

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range interaction potential,

$$V_1 = -B_1 R^{-6}(t) - B_2 R^{-6}(t) \cdot \sum_m (-1)^m D_{m,0}^{2*}(\alpha, \beta, \gamma) C_m^2(\theta, \varphi) \quad (2)$$

The second is the anisotropic Lennard-Jones potential

$$V_2 = 4\varepsilon \left[ \left( \frac{\rho}{R} \right)^{12} - \left( \frac{\rho}{R} \right)^6 \right] \left[ 1 + a_2 \sum_m (-1)^{2-m} D_{m,0}^{2*}(\alpha, \beta, \gamma) C_m^2(\theta, \varphi) \right] \quad (3)$$

where  $R$  is the distance between the atom and the mass center of the molecule. The parameters  $\varepsilon$  and  $\rho$  represent the potential-well depth and the collision diameter, respectively.  $B_1$ ,  $B_2$ , and  $a_2$  are the anisotropic parameters.  $C_m^l(\theta, \varphi)$  is a Racah harmonic function.

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

$Y_m^l(\theta, \varphi)$  is the usual spherical harmonics. The arguments  $\theta$  and  $\varphi$  represent the direction of  $R$  in a space-fixed coordinate.  $D_{K'M}^J(\alpha, \beta, \gamma)$  [11] is the Wigner rotational matrix. Euler angles  $\alpha$ ,  $\beta$ , and  $\gamma$  are rotational coordinates of the diatom.  $V$  considers not only long range attractive but also short range repulsive interactions.

The evolution of the interaction potential  $V$  is [12],

$$V(t) = \exp\left(\frac{iH_0 t}{\hbar}\right) V \exp\left(-\frac{iH_0 t}{\hbar}\right) \quad (5)$$

In this work, because we consider the rotational energy transfer only,  $H_0$  can be simplified approximately to the form as follows [13]:

$$H_0 = \hbar\omega = \hbar\bar{B}J(J+1) \quad (6)$$

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

The unperturbed wave functions are

$$\begin{pmatrix} \varphi_J^S \\ \varphi_J^T \end{pmatrix} = \begin{pmatrix} |v\rangle^S |JKM\rangle^S \\ |v\rangle^T |JKM\rangle^T \end{pmatrix} \quad (7)$$

where  $|v\rangle$  and  $|JKM\rangle$  represent the vibration and rotation wave function respectively. The 0th order unperturbed energies are defined as  $E(\varphi_J^S)$  and  $E(\varphi_J^T)$ . If  $v_{ST}$  is the coupling between these 0th order states, the perturbed states have energies,

$$E_{\pm}(JKM) = \frac{1}{2} [E(\varphi_J^S) + E(\varphi_J^T)] \pm \frac{1}{2} \left\{ [E(\varphi_J^S) - E(\varphi_J^T)]^2 + 4v_{ST}^2 \right\}^{1/2} \quad (8)$$

The perturbed wave functions are

$$\begin{pmatrix} \psi_J^S \\ \psi_J^T \end{pmatrix} = \begin{pmatrix} \cos \phi_J & \sin \phi_J \\ -\sin \phi_J & \cos \phi_J \end{pmatrix} \begin{pmatrix} \varphi_J^S \\ \varphi_J^T \end{pmatrix} \quad (9)$$

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

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

where  $\Delta_+$  denotes an upward shift and  $\Delta_-$  a downward shift. The argument  $\phi$ , characterizing the mixing effects, is given by,

$$\phi = \arcsin \frac{v_{ST}}{E(\psi_J^S) - E(\psi_J^T)} \quad (11)$$

In the later derivation, according to Eq.(8), 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 Eq.(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  $J$  is shift 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

$$|i\rangle = c_J |v\rangle^S |JKM\rangle^S + d_J |v\rangle^T |JKM\rangle^T \quad (12)$$

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

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

$$\begin{aligned} A_{i \rightarrow f} &= \frac{1}{i\hbar} \int \langle f | V(t) | i \rangle dt \\ &= \frac{1}{i\hbar} c_J c_{J'} \int \langle J'K'M' | \langle v' | V_S(t) | v \rangle |JKM\rangle dt + \\ &\quad \frac{1}{i\hbar} d_J d_{J'} \int \langle J'K'M' | \langle v' | V_T(t) | v \rangle |JKM\rangle dt \end{aligned} \quad (14)$$

In Eq.(14), the vibration factor  $\langle v' | v \rangle = 1$  can be omitted, because in atom-diatom rotational energy transfer, the atomic collision partner can be seen as structureless with its inner freedoms frozen and only the rotational wave function of the molecule changes during the collision process.

Introducing Eq.(5) into Eq.(14) when  $V=V_1$ , one can

obtain,

$$A_{i \rightarrow f}^H = -\frac{B_2^H}{i\hbar} c_J c_{J'} \cdot \sum_{M_L} (-1)^{2-M_L} \langle J' K' M' | D_{M_L,0}^{2*} | J K M \rangle \cdot \int_{-\infty}^{\infty} \exp(i\varpi_{J',J}^H t) \frac{1}{R^6} C_{M_L}^2(\Omega_t) dt \quad (15)$$

When  $V=V_2$ , we obtain

$$A_{i \rightarrow f}^H = \frac{4\varepsilon^H a_2}{i\hbar} c_J c_{J'} \cdot \sum_{M_L} (-1)^{2-M_L} \langle J' K' M' | D_{M_L,0}^{2*} | J K M \rangle \cdot \int_{-\infty}^{\infty} \exp(i\varpi_{J',J}^H t) \left( \frac{\sigma^{12}}{R^{12}} - \frac{\sigma^6}{R^6} \right) C_{M_L}^2(\Omega_t) dt \quad (16)$$

with  $\omega_{J',J} = 2\pi cB [J'(J'+1) - J(J+1)]$  being the energy difference of  $J \rightarrow J'$  transition.

The integral in Eq.(15) is defined as

$$I_m^l(n) = \int_{-\infty}^{\infty} \exp(i\omega_{J',J} t) R(t)^{-n} C_m^l(\Omega_t) dt \quad (17)$$

We can obtain for the case  $V=V_1$

$$A_{i \rightarrow f}^H = -\frac{B_2^H}{i\hbar} \sqrt{(2J+1)(2J'+1)} \begin{pmatrix} J' & 2 & J \\ K' & 0 & K \end{pmatrix} \cdot \sum_m (-1)^{2-m} \begin{pmatrix} J' & 2 & J \\ M' & -m & M \end{pmatrix} (I_m^H)^2(6) \quad (18)$$

while for the case  $V=V_2$ ,

$$A_{i \rightarrow f}^H = \frac{4\varepsilon^H a_2^H}{i\hbar} \sqrt{(2J+1)(2J'+1)} \begin{pmatrix} J' & 2 & J \\ K' & 0 & K \end{pmatrix} \cdot \sum_m (-1)^{2-m} \begin{pmatrix} J' & 2 & J \\ M' & -m & M \end{pmatrix} \cdot [\sigma^{12}(I_m^H)^2(12) - \sigma^6(I_m^H)^2(6)] \quad (19)$$

Because the  $C_{2v}$  symmetry of the electron charge distribution should be reflected by the symmetry of the potential function, it should be noted that for singlet state  $A^1\Sigma_u^+$ ,  $m=0$  only; whereas for triplet state  $b^3\Pi_{0u}$ ,  $m=0$  and  $\pm 2$  [14,15].

The transition probability between the initial and the final states can be written as [16]

$$P_{JJ'} = \frac{1}{2J+1} \sum_{MM'} |A_{i \rightarrow f}|^2 \quad (20)$$

When  $V=V_1$ ,

$$P_{JJ'}^H = \frac{(B_2^H)^2(2J'+1)}{5\hbar^2} \begin{pmatrix} J' & 2 & J \\ K' & 0 & K \end{pmatrix}^2 \cdot \sum_m |(I_m^H)^2(6)|^2 \quad (21)$$

but when  $V=V_2$ ,

$$P_{JJ'}^H = \frac{(4a_2^H \varepsilon^H)^2(2J'+1)}{5\hbar^2} \begin{pmatrix} J' & 2 & J \\ K' & 0 & K \end{pmatrix}^2 \cdot \sum_m |\sigma^{12}(I_m^H)^2(12) - \sigma^6(I_m^H)^2(6)|^2 \quad (22)$$

H stands for S or T.

For  $b > \rho$ , the integral in Eq.(17) can be done as by Gray and Kranendonk in a "straight-line" trajectory approximation [14-25], i.e.,  $R(t) = v^2 t^2 + b^2$ .

For  $b \leq \rho$ , the transition probability between the initial and the final states can be calculated by interpolation between  $P_{JJ'}(b=0)$  and  $P_{JJ'}(b=\rho)$ .  $P_{JJ'}(b)$  is a smooth curve at  $b=0$ , so the simplest form of the interpolation function can be written as [17,18],

$$P_{JJ'}(b \leq \rho) = P_{JJ'}(b=0) + \frac{b^2}{\rho^2} [P_{JJ'}(b=\rho) - P_{JJ'}(b=0)] \quad (23)$$

The integral in Eq.(17) can be solved by applying such a reference frame: an atom moves along the coordinate axis at the speed of  $v$  (impact parameter  $b=0$ ), and when the atom collides with the diatom, it rebounds at the same speed.

Eq.(20) can also be rewritten as [1],

$$P_{JJ'} = c_J^2 c_{J'}^2 P_{JJ'}^S + d_J^2 d_{J'}^2 P_{JJ'}^T + 2c_J c_{J'} d_J d_{J'} (P_{JJ'}^S P_{JJ'}^T)^{1/2} \cos \theta_{ST}^D \quad (24)$$

with Eq.(20), we can obtain

$$\cos \theta_{ST}^D = \frac{\sum_{M_L} [(P_{JJ'}^S)_{M_L} (P_{JJ'}^T)_{M_L}]^{1/2}}{(P_{JJ'}^S P_{JJ'}^T)^{1/2}} \quad (25)$$

### III. CALCULATION

We have calculated the differential interference and other partners phase angles for CO  $A^1\Pi(v=0)$ - $e^3\Sigma^-(v=1)$  system in collision with He and Ne, at temperature 253 K for  $b \geq \rho$ . The rotational quantum numbers are from the initial rotational state  $J=9$  to the final rotational state  $J'=10$ . The reduced mass  $m$  and the collision diameter  $\rho$  used in our calculation for CO system in collision with He, Ne, Ar are 3.5 atomic units [26] and 2.56 Å [28], 11.75 atomic units [27] and 2.75 Å [28], 17.5 atomic units [27] and 3.41 Å [28], respectively. The rotational constants  $B$  for the CO  $A^1\Pi(v=0)$ - $e^3\Sigma^-(v=1)$  system in collision with He, Ne, and other partners are 1.6105 and 1.2836  $\text{cm}^{-1}$  for CO  $A^1\Pi(v=0)$  and CO  $e^3\Sigma^-(v=1)$ , respectively [29]. The relationships of interference angle with impact parameter have been calculated and the results are shown in Table I.

TABLE I The tendency of the deferential interference angle with the impact parameter  $b$ .

$b/\text{\AA}$	$\theta/(\text{\textcircled{C}})$ (long range interaction)			$\theta/(\text{\textcircled{C}})$ (Lennard-Jones potential)		
	CO-He	CO-Ne	CO-Ar	CO-He	CO-Ne	CO-Ar
3	58.4187			55.9113		
4	54.1215	54.1215	54.1215	53.6038	53.2869	49.3084
5	50.7182	50.7182	50.7108	50.5400	50.4408	49.5999
6	48.0408	48.0408	48.0408	47.9667	47.9264	47.6092
7	45.9152	45.9152	45.9152	45.8802	45.8613	45.7157
8	44.2036	44.2036	44.2036	44.1853	44.1754	44.1004
9	42.8042	42.8042	42.8042	42.7939	42.7883	42.7463
10	41.6434	41.6434	41.6434	41.6372	41.6339	41.6087

TABLE II The tendency of the deferential interference angle with the velocity.

Velocity/(m/s)	$\theta/(\text{\textcircled{C}})$ (long range interaction)			$\theta/(\text{\textcircled{C}})$ (Lennard-Jones potential)		
	CO-He	CO-Ne	CO-Ar	CO-He	CO-Ne	CO-Ar
500	51.1966	51.1965	51.1965	50.5884	50.2181	45.6915
700	56.2007	56.2007	56.2007	55.8688	55.6710	53.4855
900	59.7112	59.7112	59.7112	59.5475	59.4508	58.4215
1100	62.1931	62.1931	62.1931	62.1427	62.1130	61.8033
1300	63.9800	63.9800	63.9800	64.0097	64.0271	64.2068
1500	65.2942	65.2942	65.2942	65.3823	65.4339	65.9636
1700	66.2815	66.2815	66.2815	66.4134	66.4905	67.2789
1900	67.0380	67.0380	67.0380	67.2034	67.3001	68.2847

As presented in Table I, for the static cell experiment ( $T=253$  K), under the experimental temperature, the most probable collision velocity is 593 m/s, so we assume the collision velocity is 593 m/s. We can see that when  $b > \rho$ , the differential interference angles decrease monotonically with the increase of impact parameter, the reason being that when  $b$  is chosen to have larger values, the interaction between partners will be much weaker, the degree of the interference will be increased, and the differential interference angles will be decreased. In addition, differential interference angles calculated with the anisotropic Lennard-Jones interaction potential and the long-range interaction potential are almost equal. This indicates that the influence of the short range repulsive interaction potential on the interference angle is slight and the long range interaction between diatom and atom is the dominant factor. Even so, the difference does exist. The long range interaction potential gives larger value for  $\theta_{ST}^l$  while the Lennard-Jones interaction potential gives a smaller value for it. This shows the former potential leads to smaller interference extent than the latter one.

Table II show that for the straight-line trajectory approximation  $b > \rho$ , when  $b=4$  \AA, the collision is stronger. Consider the changing tendency of the interference angles with velocity when  $V$  is long range interaction and Lennard-Jones potential. It indicates that the increase of velocity, on one hand, leads to the shortening of the time duration of collision which makes the collision be

closer to the infinite-order-sudden approximation and is favorable to the enhancement of interference; on the other hand, higher velocity makes the impact parameter have more energy to overcome the interactive potential barrier, access to the impact parameter and the potential barrier more easily, and suffer more violent interaction which will be unfavorable to the enhancement of interference. The competition between them determines the final velocity-dependent relationships, and obviously, the effect of the former has surpassed that of the latter.

#### IV. CONCLUSION

Under the conditions of the anisotropic Lennard-Jones interaction potential and the long-range interaction potential, we consider binary collisions and adopt the semiclassical or impact parameter approximation, based on the time-dependent first-order Born approximation. The collision quantum interference of CO  $A^1\Pi(v=0)-e^3\Sigma^-(v=1)$  system in collision with He is studied theoretically. The factors that the differential interference angle depends on are obtained, and the changing tendency of the differential interference angle with them is discussed.

#### V. DISCUSSION

$\theta_{ST} \equiv |\theta_S - \theta_T|$  is formally defined as an interference phase angle in Ref.[1]. However, we must note that

unlike the phase shift  $\Delta\varphi$  in the Yang's optic double-slit experiment, here the physical interpretation for  $\theta_{ST}$  does not represent unambiguously the phase angle shift between the rotation wave of singlet and triplet transition channels. This is because in CQI, instead of monochromatic plane waves, two transient wave-packets on the molecular excited potential surfaces of singlet and triplet states are involved in the interference. Actually, from Eq.(24), it is not  $\theta_{ST}$  but only its cosine that is calculated directly from the transition probability  $P_{JJ'}$ . The values of  $\cos\theta_{ST}^I$  must be in the range of  $0 \rightarrow 1$  with a clear physical significance that it characterizes the degree of coherence of the mutually coherent wave-packets during the collision time interval.  $\cos\theta_{ST}^I=0$  (or  $\theta_{ST}^I=90^\circ$ ) and  $\cos\theta_{ST}^I=1$  (or  $\theta_{ST}^I=0^\circ$ ) represent the two extreme cases of complete incoherence and complete coherence respectively.

In this work, the long-range dipole-induced dipole and dispersion interactions are considered, but the short-range interaction potential has been neglected. The good consistency between the theoretical and experimental  $\theta_{ST}$  for CO ( $A/e$ )-He collision as shown in the above section may mean that in this case the rotational energy transfer for  $\Delta J=\pm 1$  is dominated by the long-range forces. However, when the collision partners are Ne or Ar atoms, the calculations have shown that with the increase of atom diameter,  $\theta_{ST}$  decreases. That is in contradiction with our experimental results [2]. This may be explained by the idea that with the increase of atom diameter, the short-range repulsive force and the electron orbital overlap will play a bigger role in the collision. It is easy to understand that for a rather strong collision, 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 the result of decoupling, the mixing degree of corresponding wave functions would become much smaller than that of isolated-molecule and the interference effect will become weaker as well.

Under the long-range interaction potential, the changing tendency of the differential interference angle with the parameters of experiments in a molecular beam is roughly the same, including the impact parameters  $b$  and  $v$ . The method of computing the differential interference angle is limited.

## VI. ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (No.10374040) and the Educational Department of Liaoning Province (No.20060347).

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## APPENDIX A:

$$\begin{aligned}
V = & \sum_{l_A, l'_A, l_B, l'_B} -\xi_{l_A, l'_A, l_B, l'_B}^{L_A, L_B, L} R^{-l_A - l'_A - l_B - l'_B - 2} \cdot \\
& \sum_{m, n} (E_n^A - E_0^A + E_m^B - E_0^B)^{-1} \cdot \\
& \left[ \langle \psi_0^A | Q^{l_A} | \psi_n^A \rangle \otimes \langle \psi_n^A | Q^{l'_A} | \psi_0^A \rangle \right]_{K_A}^{L_A} \cdot \\
& \left[ \langle \psi_0^B | Q^{l_B} | \psi_m^B \rangle \otimes \langle \psi_m^B | Q^{l'_B} | \psi_0^B \rangle \right]_{K_B}^{L_B} \cdot \\
& \sum_{M_A, M_B, M_L} \begin{pmatrix} L_A & L_B & L \\ M_A & M_B & M_L \end{pmatrix} \cdot \\
& D_{M_A, K_A}^{L_A} * D_{M_B, K_B}^{L_B} * C_{M_L}^L(\Omega_t) \quad (A1)
\end{aligned}$$

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

$$\begin{aligned}
\xi_{l_A, l'_A, l_B, l'_B}^{L_A, L_B, L} = & \left[ \frac{(2l_A + 2l_B + 1)!(2l'_A + 2l'_B + 1)!}{(2l_A)!(2l_B)!(2l'_A)!(2l'_B)!} \right]^{1/2} \cdot \\
& (-1)^{l_A + l'_A} (2L_A + 1)^{1/2} (2L_B + 1)^{1/2} (2L + 1)^{1/2} \\
& (l_A + l_B, 0, l'_A + l'_B, 0 | L, 0) \cdot \\
& \left\{ \begin{matrix} l_A & l'_A & L_A \\ l_B & l'_B & L_B \\ l_A + l_B & l'_A + l'_B & L \end{matrix} \right\} \quad (A2)
\end{aligned}$$

and  $R$  is the distance between atom A and the mass center of molecule B,  $\psi$  and  $E$  stand for the eigenfunctions and the eigenvalues respectively,  $Q^l$  is the multipole tensor operator of order  $l$ ,  $D_{M, K}^L$  is the Wigner  $D$  rotation matrix, and  $C_M^L(\Omega)$  is a Racah harmonic function.

As the first approximation in this model, we only consider the dipole-induced dipole and the induced dipole-induced dipole interaction, i.e.  $l_A = l_B = 1$ . In an atom-diatom system,  $D_{M_A, K_A}^{L_A} = 1$ ,  $D_{M_B, K_B}^{L_B} = 1$  or  $D_{M_B, K_B}^{L_B} = D_{M_B, D}^2$ , because  $L_A = K_A = 0$  and  $L_B = K_B = 0$  or  $L_B = 2$  [11].

When  $m \neq 0$ , Eq.(A2) is reduced to the induction potential  $V_{\text{ind}}$ ,

$$\begin{aligned}
V_{\text{ind}} = & -\frac{1}{2} \xi_{1,1,1,1}^{0, L_B, L} \alpha_A \mu_B^2 R^{-6} \cdot \\
& \sum_{M_L} \begin{pmatrix} 0 & L_B & L \\ 0 & M_B & M_L \end{pmatrix} D_{M_B, 0}^{L_B} * (\Omega_2) C_{M_L}^L(\Omega_t) \quad (A3)
\end{aligned}$$

where  $\alpha$  is the irreducible multipolar polarizability,

$$\begin{aligned}
\alpha = & 2 \sum_{n \neq 0} (E_n - E_0)^{-1} \cdot \\
& \left[ \langle \psi_0 | Q^l | \psi_n \rangle \otimes \langle \psi_n | Q^{l'} | \psi_0 \rangle \right]_K^L \quad (A4)
\end{aligned}$$

and  $\mu$  is the multipole [14],

$$\mu^2 = \left[ \langle \psi_0 | Q^l | \psi_0 \rangle \otimes \langle \psi_0 | Q^{l'} | \psi_0 \rangle \right]_K^L \quad (A5)$$

When  $m \neq 0$ , Eq.(A2) is the dispersion potential  $V_{\text{dis}}$ ,

$$\begin{aligned}
V_{\text{dis}} = & -\frac{1}{4} \xi_{1,1,1,1}^{0, L_B, L} \frac{I_1 I_2}{I_1 + I_2} \alpha_A \alpha_B R^{-6} \cdot \\
& \sum_{M_L} \begin{pmatrix} 0 & L_B & L \\ 0 & M_B & M_L \end{pmatrix} D_{M_B, 0}^{L_B} * (\Omega_2) C_{M_L}^L(\Omega_t) \quad (A6)
\end{aligned}$$

$$I_1 = \sum_n (E_n^A - E_0^A) \quad (A7)$$

$$I_2 = \sum_n (E_n^B - E_0^B) \quad (A8)$$

The irreducible tensor product between two sets of tensors in Eq.(A4) and Eq.(A7-A8) can be written as,

$$\begin{aligned}
[T^1 \otimes T'^1]_K^L = & \\
& \sum_m \langle 1m, 1K - m | LK \rangle T(1, m) T'(1, K - m) \quad (A9)
\end{aligned}$$

with  $\langle 1m, 1K - m | LK \rangle$  being a Clebsch-Gordan coefficient. In our cases, with  $L=0$  or  $L=2$  and  $K=0$ , Eq.(A9) is reduced to

$$[T^1 \otimes T'^1]_0^0 = -3^{1/2} T \cdot T' \quad (A10)$$

$$[T^1 \otimes T'^1]_0^2 = \frac{3T_Z T'_Z - T \cdot T'}{\sqrt{6}} \quad (A11)$$

Using Eqs.(A3)-(A10), the long-range interaction potential in atom-diatom system can be derived:

$$\begin{aligned}
V = & V_{\text{ind}} + V_{\text{dis}} \\
= & -B_1 - B_2 \sum_{M_L} (-1)^{2-M_L} D_{M_L, 0}^2 * (\Omega_2) C_{M_L}^2(\Omega_t) \quad (A12)
\end{aligned}$$

$$\begin{aligned}
B_1 = & \frac{1}{3\sqrt{3}} \xi_{1,1,1,1}^{0,0,0} R^{-6}(t) [\alpha_{XX} + \alpha_{YY} + \alpha_{ZZ}]_A \cdot \\
& \left[ \frac{1}{2} (\mu_X^2 + \mu_Y^2 + \mu_Z^2) + \right. \\
& \left. \frac{1}{4} \frac{I_1 I_2}{I_1 + I_2} (\alpha_{XX} + \alpha_{YY} + \alpha_{ZZ}) \right]_B \quad (A13)
\end{aligned}$$

$$\begin{aligned}
B_2 = & \frac{1}{3\sqrt{10}} \xi_{1,1,1,1}^{0,2,2} R^{-6}(t) [\alpha_{XX} + \alpha_{YY} + \alpha_{ZZ}]_A \cdot \\
& \left[ \frac{1}{2} (\mu_X^2 + \mu_Y^2 + \mu_Z^2) + \right. \\
& \left. \frac{1}{4} \frac{I_1 I_2}{I_1 + I_2} (\alpha_{XX} + \alpha_{YY} - 2\alpha_{ZZ}) \right]_B \quad (A14)
\end{aligned}$$

$B$  can be  $B^S$  or  $B^T$  depending on the molecule is in a singlet state or a triplet state.