

II 态双原子分子 Λ 分裂引起的量子干涉*

李永庆^a, 孙萌涛^b, 马凤才^{a**}

(a. 辽宁大学物理系, 沈阳 110036 ;

b. 中国科学院大连化学物理研究所分子反应动力学国家重点实验室, 大连 116023)

摘要: 为了从理论上解释 Sun 等在 $\text{CO}(\text{A}^1\Pi, v=3)$ 和 He 碰撞实验中转动传能截面的反常现象, 考虑一级含时波恩近似、长程相互作用势和直线轨道近似, 建立了 II 态双原子分子由于 Λ 分裂引起量子干涉的理论模型. 运用这一理论模型, 成功地解释了实验中碰撞伴为 He 时转动传能截面的反常现象: $\sigma_{\Delta J=0}^{\varepsilon \rightarrow \varepsilon'} < \sigma_{\Delta J=\pm 1}^{\varepsilon \rightarrow \varepsilon'}$. 首先介绍了碰撞诱导转动传能中量子干涉效应的研究进展, 然后建立了 II 态双原子分子由于 Λ 分裂引起量子干涉的理论模型, 最后对所得结果进行了讨论.

关键词: 碰撞诱导转动传能; 量子干涉; 传能截面; 跃迁几率

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Quantum Interference Induced from the Λ Split of II State Diatom*

Li Yongqing^a, Sun Mengtao^b, Ma Fengcai^{a**}

(a. Department of Physics, Liaoning University, Shenyang 110036 ;

b. State Key Lab of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023)

Abstract To interpret theoretically the abnormal phenomenon in the experiment of collision-induced rotational energy transfer of $\text{CO}(\text{A}^1\Pi, v=3)$ with He by Sun *et al.*, the time dependent first order Born approximation, and the long-range interaction potentials and "straight-line" trajectory approximation are taken into account. A theoretical model of quantum interference of II-state diatomic molecules, which originates from the difference between the two Λ -related collision potential energy surfaces, is presented. The abnormal phenomenon of $\sigma_{\Delta J=0}^{\varepsilon \rightarrow \varepsilon'} < \sigma_{\Delta J=\pm 1}^{\varepsilon \rightarrow \varepsilon'}$ for He is also interpreted successfully. At first the theoretical development of collision-induced quantum interference on rotational energy transfer is reported; then a theoretical model of quantum interference of II-state diatomic molecules, which originates from the difference between the two Λ -related collision potential energy surfaces, is presented; in the end the results have been discussed and concluded.

Keywords Collision-induced rotational energy transfer, Quantum interference, Cross section of energy transfer, Transition probability

1 引言

Sha 等在 $\text{CO}(\text{A}^1\Pi(v=0) \sim e^3\Sigma^-(v=1))$ 体系与 He、Ne、Ar 及其它碰撞伴的碰撞中, 首先观察到

了碰撞诱导转动传能中的量子干涉效应^[1,2]. 随后这种量子干涉被 Chen 等在 $\text{Na}_2(\text{A}^+\Sigma_u^+(v=8) \sim b^3\Pi_{0u}(v=14))$ 体系与 $\text{Na}(3s)$ 的碰撞中发现^[3]. 考虑一级含时波恩近似, 直线轨道近似, Sun 等建立了

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** Corresponding author, E-mail: fcma@lnu.edu.cn Received 8 May 2003; in final form 21 July 2003.

原子-分子体系碰撞诱导转动传能中的量子干涉模型,并成功的解释了实验^[4-6]. 同时又将理论扩展到极性分子-分子体系^[7]. Sun 等在 CO(A¹Π_{v=3})和 He、Ne、Ar 碰撞实验中,观察到 Π 态双原子分子由于 Λ 分裂引起的量子干涉^[8],同时发现碰撞伴为 He 时,转动传能截面的反常现象, $\sigma_{\Delta J=0}^{\epsilon \rightarrow \epsilon'} < \sigma_{\Delta J=\pm 1}^{\epsilon \rightarrow \epsilon'}$. 本工作考虑一级含时波恩近似、长程相互作用势和直线轨道近似,建立了 Π 态双原子分子由于 Λ 分裂引起量子干涉的理论模型,并成功解释了实验中的反常现象.

2 原子与 Π 态双原子分子体系的相互作用势

原子与 Π 态双原子分子体系电子态的哈密顿作用量可以写成^[4]:

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

其中, H_A 、 H_B 分别为原子 A 和分子 B 的哈密顿; V 为原子-分子体系的相互作用势. 本工作只考虑长程相互作用势^[9]:

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

其中 ξ 为纯几何系数,与原子 A 和分子 B 多极矩的耦合相关,

$$\xi_{l_A l_A' l_B l_B'}^{L_A L_B L} = (-1)^{l_A+l_A'} \times \left[\frac{(2l_A+2l_B+1)(2l_A'+2l_B'+1)!}{(2l_A)(2l_B)(2l_A')(2l_B')!} \right]^{1/2} \times [(2l_A+1)(2l_B+1)(2L+1)]^{1/2} \times (|l_A+l_B, 0, l_A'+l_B', \rho | L, \rho) \times \begin{Bmatrix} l_A & l_A' & L_A \\ l_B & l_B' & L_B \\ l_A+l_B & l_A'+l_B' & L \end{Bmatrix} \quad (3)$$

其中, R 为原子 A 和分子 B 质心间的距离; ψ 和 E 为本征函数和本征值; Q^l 为第 l 级张量算符; D_{MK}^L 为 Wigner D 转动矩阵; $C_M^L(\Omega)$ 为 Racah 球谐函数. 本工作只考虑 $l_A = l_B = l_A' = l_B' = 1$ 的情况,在原子与 Π 态双原子分子体系中, $L_A = K_A = 0$, $L_B = K_B = 0$, $L_B = 2$, $K_B = 0$, ± 2 ^[10-12]. 当 $m=0$ 时,式(2)简化

为诱导势^[4]:

$$V_{\text{ind}} = -\frac{1}{2} \xi_{1,1,1,1}^{0,1,1,1} \alpha_A \mu_B^2 R^{-6} \times \sum_{M_L} \begin{pmatrix} 0 & L_B & L \\ 0 & M_B & M_L \end{pmatrix} D_{M_B K_B}^{L_B} * (\Omega_2) C_{M_L}^L(\Omega_l) \quad (4)$$

其中 α 是不可约多级极化率^[13],

$$\alpha = 2 \sum_{n \neq 0} \frac{[\psi_0 | Q^l | \psi_n \otimes \psi_n | Q^{l'} | \psi_0]_{K}^L}{E_n - E_0} \quad (5)$$

μ^2 为偶极距^[9],

$$\mu^2 = [\psi_0 | Q^l | \psi_0 \otimes \psi_0 | Q^{l'} | \psi_0]_{K}^L \quad (6)$$

当 $m \neq 0$ 时,式(2)为色散势^[4],

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

其中 $I_1 = \sum_n E_n^A - E_0^A$ 、 $I_2 = \sum_m E_m^B - E_0^B$ 分别为原子和分子的第一电离能. 式(5)、(6)中的不可约张量积可以写成^[14]:

$$[T^l \otimes T^{l'}]_K^L = \sum_m 1m, 1K-m \parallel LK \quad \mathcal{T}(1, m) \mathcal{T}'(1, K-m) \quad (9)$$

其中 $1m, 1K-m \parallel LK$ 为 Clebsch-Gordan 系数. 考虑原子与分子 Π 态双原子分子体系 $L=0$ 或 $L=2$, $K=0$ 或 $K=\pm 2$ ^[10-12], 等关系:

$$[T^1 \otimes T^{1'}]_0^0 = -3^{1/2} T \cdot T' \quad (10)$$

$$[T^1 \otimes T^{1'}]_0^2 = \frac{3T_Z T_Z' - T \cdot T'}{6^{1/2}} \quad (11)$$

$$[T^1 \otimes T^{1'}]_{\pm 2}^2 = \frac{1}{2} [(T_X T_X' - T_Y T_Y') \pm \mathcal{X}(T_X T_Y' - T_Y T_X')] \quad (12)$$

由式(2)~(12),可以得原子与分子 Π 态双原子分子体系的长程相互作用势,

$$V = V_{\text{ind}} + V_{\text{dis}} = -B_0^0 R^{-6}(t) - B_0^2 R^{-6}(t) \times \sum_{M_L} (-1)^{2-M_L} D_{M_L, 0}^2 * (\Omega_2) C_{M_L}^2(\Omega_l) - B_{\pm 2}^2 R^{-6}(t) \sum_{M_L} (-1)^{-M_L} D_{M_L, \pm 2}^2 * (\Omega_2) C_{M_L}^2(\Omega_l) \quad (13)$$

$$B_0^0 = \frac{1}{3} \xi_{1,1,1,1}^{0,0,0,0} [\alpha_{XX} + \alpha_{YY} + \alpha_{ZZ}]_A \times \left[\frac{1}{2} (\mu_X^2 + \mu_Y^2 + \mu_Z^2) + \right]$$

$$\frac{1}{4} \frac{I_1 I_2}{I_1 + I_2} (\alpha_{XX} + \alpha_{YY} + \alpha_{ZZ}) \Big|_B \quad (14)$$

$$B_0^2 = -\frac{1}{3\sqrt{10}} \xi_{1,1,1,1}^{0,2,2} [\alpha_{XX} + \alpha_{YY} + \alpha_{ZZ}]_A \times$$

$$\left[\frac{1}{2} (2\mu_Z^2 - \mu_X^2 - \mu_Y^2) + \frac{1}{4} \frac{I_1 I_2}{I_1 + I_2} (2\alpha_{ZZ} - \alpha_{XX} - \alpha_{YY}) \right]_B \quad (15)$$

$$B_{\pm 2}^2 = -\frac{1}{2\sqrt{5}} \xi_{1,1,1,1}^{0,2,2} [\alpha_{XX} + \alpha_{YY} + \alpha_{ZZ}]_A \times$$

$$\left\{ \frac{1}{2} [(\mu_X^2 - \mu_Y^2) \pm \kappa(\mu_X \mu_Y - \mu_Y \mu_X)] + \frac{1}{4} \frac{I_1 I_2}{I_1 + I_2} [(\alpha_{XX} - \alpha_{YY}) \pm \kappa(\alpha_{XY} - \alpha_{YX})] \right\}_B$$

$$= -\frac{1}{2\sqrt{5}} \xi_{1,1,1,1}^{0,2,2} [\alpha_{XX} + \alpha_{YY} + \alpha_{ZZ}]_A \times$$

$$\left[\frac{1}{2} (\mu_X^2 - \mu_Y^2) + \frac{1}{4} \frac{I_1 I_2}{I_1 + I_2} (\alpha_{XX} - \alpha_{YY}) \right]_B \quad (16)$$

在海森堡绘景 相互作用势随时间的演化为^[15]:

$$V(t) = U^\dagger(t, \rho) V U(t, \rho) \quad (17)$$

其中 $U(t, \rho)$ 是时间演化算符

$$U(t, \rho) = \exp(-iH_0 t/\hbar) \quad (18)$$

把(18)式代入(17)式得

$$V(t) = \exp(-iH_0 t/\hbar) V \exp(-iH_0 t/\hbar) \quad (19)$$

如果只考虑转动能的变化,

$$H_0 = 2\pi h c B [J(J+1) - K(K+1)]$$

这里 B 是转动常数. 当 $\Delta J=0$ 时, 考虑 Λ 分裂, 则

$$H_0 = 2\pi h c q K(J+1)$$

这里 q 是能级分裂常数, $q \approx 10^{-3} B$ ^[16].

为了简化标识, 我们把原子 A 看做无结构的粒子, 并且电子激发能量远高于分子 B 的激发能, 所以原子的能量转移过程被忽略. 对于 $^1\Pi$ 态双原子分子的转动传能波函数有确定的宇称, 波函数为^[17]:

$$|JM_\varepsilon\rangle = \frac{1}{\sqrt{2}} [|JM|\Omega\rangle + \varepsilon |JM|\Omega\rangle] \quad (20)$$

其中, J 为总角动量子数; M 为总角动量 J 沿空间坐标系 Z -轴的投影; $\Omega = \Lambda = \pm 1$ 为总角动量 J 沿分子坐标系的投影; $\varepsilon = \pm 1$ 为宇称态, 在 $^1\Pi$ 态空间反演算符 I 的本征值为^[18]:

$$I |JM_\varepsilon\rangle = \varepsilon (-1)^J |JM_\varepsilon\rangle \quad (21)$$

这样, 对于特定的 J 存在 Λ 二重项, 一个能级具有偶宇称, 另外一个能级具有奇宇称, 量子数 ε 描述宇称指标, 在分子光谱中 $\varepsilon = +1$ 标识为 e , $\varepsilon = -1$ 标

识为 f ^[19]. 式(20)中的转动波函数 $|JM_\Omega\rangle$ 可以写成转动矩阵元的形式^[18],

$$|JM_\Omega\rangle = \left(\frac{2J+1}{8\pi^2} \right)^{1/2} D_{M\Omega}^{J*}(\alpha, \beta, \gamma) \quad (22)$$

根据一级含时 Born 近似微扰理论, 初态 $|i\rangle$ 和末态 $|f\rangle$ 的跃迁振幅为:

$$\int f |V(t)|i\rangle dt = \int J'M'\varepsilon' |V(t)|JM_\varepsilon\rangle dt \quad (23)$$

把(13)式代入(19)式后再代入(23)式得

$$\int f |V(t)|i\rangle dt$$

$$= -B_0^2 \sum_{M_L} (-1)^{2-M_L} J'M'\Omega' |D_{M_L, \Omega'}^{2*}|JM_\Omega\rangle \times$$

$$\int_{-\infty}^{\infty} \exp(i\tilde{\omega}_{JJ'}^{\varepsilon \rightarrow \varepsilon'} t) R^{-6}(t) C_{M_L}^2(\Omega_t) dt -$$

$$B_{\pm 2}^2 \sum_{M_L} (-1)^{2-M_L} J'M'\Omega' |D_{M_L, 2}^{2*}|JM_\Omega\rangle \times$$

$$\int_{-\infty}^{\infty} \exp(i\tilde{\omega}_{JJ'}^{\varepsilon \rightarrow \varepsilon'} t) R^{-6}(t) C_{M_L}^2(\Omega_t) dt \quad (24)$$

式(24)中的转动矩阵元可以写成,

$$J'M'\Omega' |D_{M_L, \Omega'}^{2*}|JM_\Omega\rangle = [(2J+1)(2J'+1)]^{1/2} \times$$

$$\begin{pmatrix} J' & 2 & J \\ M' & -M_L & M \end{pmatrix} \begin{pmatrix} J' & 2 & J \\ \Omega' & K & \Omega \end{pmatrix} \quad (25)$$

Gray 和 Kranendonk 考虑直线轨迹近似^[20], 得到

$$I_{M_L}^L = \int_{-\infty}^{\infty} \exp(i\tilde{\omega}_{JJ'} t) R^{-6}(t) C_{M_L}^L(\Omega_t) dt \quad (26)$$

的解析表达式, 结果列于附录中. 将附录中的计算结果代入式(24),

$$\int f |V(t)|i\rangle dt$$

$$= -B_0^2 \sum_{M_L} (-1)^{2-M_L} [(2J+1)(2J'+1)]^{1/2} \times$$

$$\begin{pmatrix} J' & 2 & J \\ M' & -M_L & M \end{pmatrix} \begin{pmatrix} J' & 2 & J \\ \Omega & 0 & \Omega \end{pmatrix} b^{-5} v^{-1} J_{M_L}^2(x^0) -$$

$$B_{\pm 2}^2 \sum_{M_L} (-1)^{2-M_L} [(2J+1)(2J'+1)]^{1/2} \times$$

$$\begin{pmatrix} J' & 2 & J \\ M' & -M_L & M \end{pmatrix} \begin{pmatrix} J' & 2 & J \\ \Omega' & 2 & \Omega \end{pmatrix} b^{-5} v^{-1} J_{M_L}^2(x^{\pm 2}) \quad (27)$$

通过对初末态磁量子数求和, 并对初态转动量子数求平均, 跃迁几率可以写为^[5]:

$$P_{J'J} = \frac{1}{2J+1} \sum_{MM'} \left| \frac{1}{i\hbar} \int_{-\infty}^{\infty} f |V(t)|i\rangle dt \right|^2 \quad (28)$$

把跃迁振幅(27)式代入跃迁几率(28)式中, 并且考虑 $3j$ 符号的正交关系和 Clebsch-Gordan 系数,

$$\sum_{m'} \begin{pmatrix} J' & l' & J \\ M' & m' & M \end{pmatrix} \begin{pmatrix} J' & l & J \\ M' & m & M \end{pmatrix} = \frac{\delta_{l'l'} \delta_{m,m'}}{2l+1} \quad (29)$$

我们可以得到 $J \rightarrow J'$ 的跃迁几率,

$$P_{JJ'} = P_{JJ'}^{\varepsilon \rightarrow \varepsilon'} + P_{JJ'}^{\varepsilon' \rightarrow \varepsilon} + 2 \sum_{M_L} [(P_{JJ'}^{\varepsilon \rightarrow \varepsilon})_{M_L} (P_{JJ'}^{\varepsilon' \rightarrow \varepsilon})_{M_L}]^{1/2} \quad (30)$$

其中宇称守恒跃迁为:

$$P_{JJ'}^{\varepsilon \rightarrow \varepsilon} = \frac{B_0^2 (2J' + 1)}{5\hbar^2 v^2 b^{10}} F^K \begin{pmatrix} J' & 2 & J \\ \Omega & 0 & \Omega \end{pmatrix}^2 \times \sum_{M_L} |J_{M_L}^2(x_{\varepsilon \rightarrow \varepsilon})|^2 \quad (31)$$

其中宇称变化跃迁为:

$$P_{JJ'}^{\varepsilon \rightarrow \varepsilon'} = \frac{B_{\pm 2}^2 (2J' + 1)}{5\hbar^2 v^2 b^{10}} F^K \begin{pmatrix} J' & 2 & J \\ \Omega' & K & \Omega \end{pmatrix}^2 \times \sum_{M_L} |J_{M_L}^2(x_{\varepsilon \rightarrow \varepsilon'})|^2 \quad (32)$$

对于 Π 态双原子分子 $K=0, \pm 2$, 守恒跃迁和宇称变化跃迁的量子干涉项^[12, 21-25]为:

$$\sum_{M_L} [(P_{JJ'}^{\varepsilon \rightarrow \varepsilon})_{M_L} (P_{JJ'}^{\varepsilon' \rightarrow \varepsilon})_{M_L}]^{1/2} = \frac{B_0^2 B_{\pm 2}^2 (2J' + 1)}{5\hbar^2 v^2 b^{10}} F^K \times \begin{pmatrix} J' & 2 & J \\ \Omega & 0 & \Omega \end{pmatrix} \begin{pmatrix} J' & 2 & J \\ \Omega' & K & \Omega \end{pmatrix} \sum_{M_L} |J_{M_L}^2(x_{\varepsilon \rightarrow \varepsilon}) J_{M_L}^2(x_{\varepsilon \rightarrow \varepsilon'})| \quad (33)$$

这里 F 就是众所周知的选择规则^[26]:

$$F^K = 1 + \varepsilon \varepsilon' (-1)^{J'+J+K} \quad (34)$$

将式(30)带入积分散射截面公式^[27]:

$$\sigma_{JJ'} = 2\pi \int_0^\infty P_{JJ'}(b) b db \quad (35)$$

可以得到

$$\sigma_{JJ'} = \sigma_{JJ'}^{\varepsilon \rightarrow \varepsilon} + \sigma_{JJ'}^{\varepsilon' \rightarrow \varepsilon} + 2(\sigma_{JJ'}^{\varepsilon \rightarrow \varepsilon} \sigma_{JJ'}^{\varepsilon' \rightarrow \varepsilon})^{1/2} \cos\theta_{\varepsilon\varepsilon'} \quad (36)$$

其中宇称守恒时的转动传能散射截面为:

$$\sigma_{JJ'}^{\varepsilon \rightarrow \varepsilon} = \frac{B_0^2 (2J' + 1)}{5\hbar^2 v^2} F^K \begin{pmatrix} J' & 2 & J \\ \Omega & 0 & \Omega \end{pmatrix}^2 \times \int \sum_{M_L} |J_{M_L}^2(x_{\varepsilon \rightarrow \varepsilon})|^2 b^{-9} db \quad (37)$$

守称变化的转动传能散射截面为:

$$\sigma_{JJ'}^{\varepsilon \rightarrow \varepsilon'} = \frac{B_{\pm 2}^2 (2J' + 1)}{5\hbar^2 v^2} F^K \begin{pmatrix} J' & 2 & J \\ \Omega' & K & \Omega \end{pmatrix}^2 \times \int \sum_{M_L} |J_{M_L}^2(x_{\varepsilon \rightarrow \varepsilon'})|^2 b^{-9} db \quad (38)$$

$$\cos\theta_{\varepsilon\varepsilon'} = \frac{\int \sum_{M_L} [(P_{JJ'}^{\varepsilon \rightarrow \varepsilon})_{M_L} (P_{JJ'}^{\varepsilon' \rightarrow \varepsilon})_{M_L}]^{1/2} v^3 b \exp\left(\frac{-\mu v^2}{2kT}\right) db dv}{\left[\int \int P_{JJ'}^{\varepsilon \rightarrow \varepsilon} v^3 b \exp\left(\frac{-\mu v^2}{2kT}\right) db dv \right]^{1/2} \left[\int \int P_{JJ'}^{\varepsilon' \rightarrow \varepsilon} v^3 b \exp\left(\frac{-\mu v^2}{2kT}\right) db dv \right]^{1/2}} \quad (44)$$

式(36)中的干涉角为:

$$\cos\theta_{\varepsilon\varepsilon'} = \frac{\int \sum_{M_L} [(P_{JJ'}^{\varepsilon \rightarrow \varepsilon})_{M_L} (P_{JJ'}^{\varepsilon' \rightarrow \varepsilon})_{M_L}]^{1/2} b db}{\left(\int P_{JJ'}^{\varepsilon \rightarrow \varepsilon} b db \right)^{1/2} \left(\int P_{JJ'}^{\varepsilon' \rightarrow \varepsilon} b db \right)^{1/2}} \quad (39)$$

表示 Λ 分裂引起的量子干涉程度.

3 结果与讨论

3.1 静态池实验下 Λ 分裂引起的量子干涉及干涉角

Sun 等在 CO ($A^1\Pi, \nu=3$) 和 He、Ne、Ar 碰撞的静态池实验中^[8], 观察到 Π 态双原子分子由于 Λ 分裂引起的量子干涉, 同时发现碰撞伴为 He 时, 转动传能截面的反常现象, $\sigma_{\Delta J=0}^{\varepsilon \rightarrow \varepsilon'} < \sigma_{\Delta J=\pm 1}^{\varepsilon \rightarrow \varepsilon'}$. 式(36)中要求碰撞对具有单一的速度, 而实验中相对速度是符合 Maxwell-Boltzmann 速度分布的, 在这种情况下, Braithwaite 给出平均速度下几率的公式^[28],

$$P = \frac{\int_0^\infty P(v) v^3 \exp\left(\frac{-\mu v^2}{2kT}\right) dv}{\int_0^\infty v^3 \exp\left(\frac{-\mu v^2}{2kT}\right) dv} = \frac{1}{2} \left(\frac{\mu}{kT}\right)^2 \int_0^\infty P(v) v^3 \exp\left(\frac{-\mu v^2}{2kT}\right) dv \quad (40)$$

其中 $\mu = \frac{m_1 m_2}{m_1 + m_2}$ 是碰撞系的折合质量; T 为静态池的实验温度. 先把(30)式代入(40)式得到 $P_{JJ'}$ (AV) 再代入(35)式得:

$$\sigma_{JJ'} = \sigma_{JJ'}^{\varepsilon \rightarrow \varepsilon} + \sigma_{JJ'}^{\varepsilon' \rightarrow \varepsilon} + 2[\sigma_{JJ'}^{\varepsilon \rightarrow \varepsilon} \sigma_{JJ'}^{\varepsilon' \rightarrow \varepsilon}]^{1/2} \cos\theta_{\varepsilon\varepsilon'} \quad (41)$$

其中,

$$\sigma_{JJ'}^{\varepsilon \rightarrow \varepsilon} = \frac{2B_0^2 \mu^2 (2J' + 1)}{5\hbar^2 (kT)^2} F^K \begin{pmatrix} J' & 2 & J \\ \Omega & 0 & \Omega \end{pmatrix}^2 \times \int \frac{v}{b^9} \sum_{M_L} |J_{M_L}^2(x_{\varepsilon \rightarrow \varepsilon})|^2 \exp\left(\frac{-\mu v^2}{2kT}\right) db dv \quad (42)$$

$$\sigma_{JJ'}^{\varepsilon \rightarrow \varepsilon'} = \frac{2B_{\pm 2}^2 \mu^2 (2J' + 1)}{5\hbar^2 (kT)^2} F^K \begin{pmatrix} J' & 2 & J \\ \Omega' & K & \Omega \end{pmatrix}^2 \times \int \frac{v}{b^9} \sum_{M_L} |J_{M_L}^2(x_{\varepsilon \rightarrow \varepsilon'})|^2 \exp\left(\frac{-\mu v^2}{2kT}\right) db dv \quad (43)$$

3.2 实验中反常现象的解释

Sun 等在 CO ($A^1\Pi, v=3$) 和 He、Ne、Ar 碰撞的静态池实验中,发现碰撞伴为 He 时,转动传能截面的反常现象, $\sigma_{\Delta J=0}^{\varepsilon \rightarrow \varepsilon'} < \sigma_{\Delta J=\pm 1}^{\varepsilon \rightarrow \varepsilon'}$. 因为根据能隙规则,应该 $\sigma_{\Delta J=0}^{\varepsilon \rightarrow \varepsilon'} > \sigma_{\Delta J=\pm 1}^{\varepsilon \rightarrow \varepsilon'}$,而且对于碰撞伴为 Ne 和

$$\frac{\sigma_{\Delta J=0}^{\varepsilon \rightarrow \varepsilon'}}{\sigma_{\Delta J=\pm 1}^{\varepsilon \rightarrow \varepsilon'}} \approx \frac{(2J+1) \left(\frac{J}{\Omega'} \frac{2}{K} \frac{J}{\Omega} \right)^2 \int \frac{v}{b^9} \sum_{M_L} |J_{M_L}^2(x_{\Delta J=0})|^2 \exp\left(\frac{-\mu v^2}{2kT}\right) db dv}{[2(J+1)+1] \left(\frac{J+1}{\Omega'} \frac{2}{K} \frac{J}{\Omega} \right)^2 \int \frac{v}{b^9} \sum_{M_L} |J_{M_L}^2(x_{\Delta J=1})|^2 \exp\left(\frac{-\mu v^2}{2kT}\right) db dv} \quad (45)$$

其中 $x_{\Delta J=0}/x_{\Delta J=\pm 1} \approx 10^{-3}$, 因为 $\Delta J=0$ 时的能量劈裂常数 $q \approx 10^{-3} B^{[16]}$. 可以计算出最可几速率和发生最可几跃迁时的速率 $\frac{\partial \mathcal{K}(v, T)}{\partial v}$, $\frac{\partial P_{\Delta J=\pm 1}(v, b_{\min})}{\partial v}$, $\frac{\partial P_{\Delta J=0}(v, b_{\min})}{\partial v}$ (见表 1). 从计算结果可以看出,当速度较小时易发生 $\Delta J=0$ 的跃迁, $P_{\Delta J=0}(v, b)$ 的最

Ar 的实验结果满足能隙规则^[8]. 这是因为,对于碰撞伴为 He 时,相互作用势以长程相互作用势为主^[4],而碰撞伴为 Ne 和 Ar 时短程势则不可忽略^[4-7]. 对于碰撞伴为 He 的宇称改变的实验, $\Delta J=0$ 与 $\Delta J=1$ 时积分截面之比为:

可几跃迁速率要远远小于 $P_{\Delta J=1}(v, b)$ 的最可几跃迁速率, $\sigma_{\Delta J=0}^{\varepsilon \rightarrow \varepsilon'} < \sigma_{\Delta J=\pm 1}^{\varepsilon \rightarrow \varepsilon'}$ 是速度分布与跃迁几率分布叠加的结果.

图 1 是 CO-He 在 $T=253$ K 时的速度分布函数,图 2 是 $\Delta J=1$ 时相对跃迁几率与速度的关系. 图 3 是 $\Delta J=0$ 时相对跃迁几率与速度的关系.

表 1 CO-He 碰撞系最可几速率和发生最可几跃迁时的速率的计算结果

Table 1 The most probable speed of CO system collision with He and its calculated values at most probable transition

| $v/(m/s)$ | | | $\sigma_{\Delta J=0}/\sigma_{\Delta J=1}$ | | $\sigma_{\Delta J=0}/\sigma_{\Delta J=-1}$ | |
|---|---|---|---|-------|--|-------|
| $\frac{\partial \mathcal{K}(v, T)}{\partial v} = 0$ | $\frac{\partial P_{\Delta J=\pm 1}(v, b_{\min})}{\partial v} = 0$ | $\frac{\partial P_{\Delta J=0}(v, b_{\min})}{\partial v} = 0$ | Exp. [8] | Thero | Exp. [8] | Thero |
| 1093.01 | 440.40 | 1.54 | 0.65 | 0.244 | 0.69 | 0.269 |

$v_{\min} = 100$ m/s, $v_{\max} = 3000$ m/s, $b_{\min} = 2.9 \text{ \AA}$, $b_{\max} = 20 \text{ \AA}$, $\mu = 3.5$ a. m. u. [4], $B = 1.5346 \text{ cm}^{-1}$ [30], $q = 10^{-3} B \text{ cm}^{-1}$ [16], $T = 253$ K.

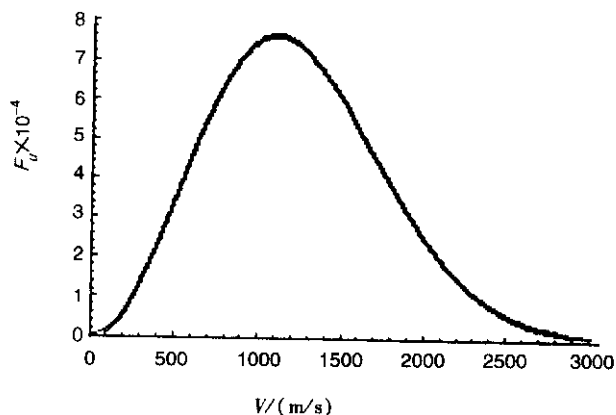


图 1 CO-He 在 $T=253$ K 时归一化的 Maxwell-Boltzmann 速度分布函数

Fig. 1 Unitary Maxwell-Boltzmann velocity distribution function via velocity for CO-He at $T=253$ K

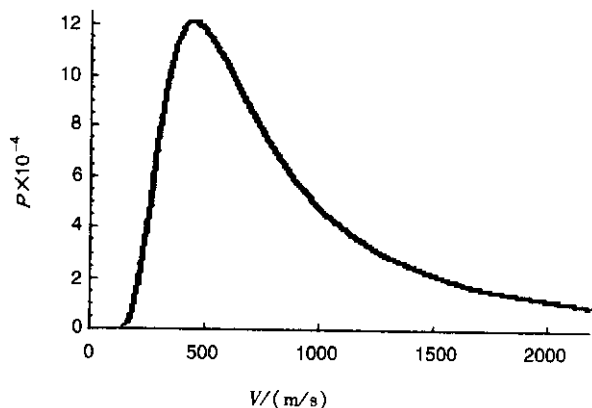


图 2 CO-He 在 $\Delta J=1$ 时相对跃迁几率与速度的关系
Fig. 2 Relative transition probability distribution via velocity for CO-He at $\Delta J=1$

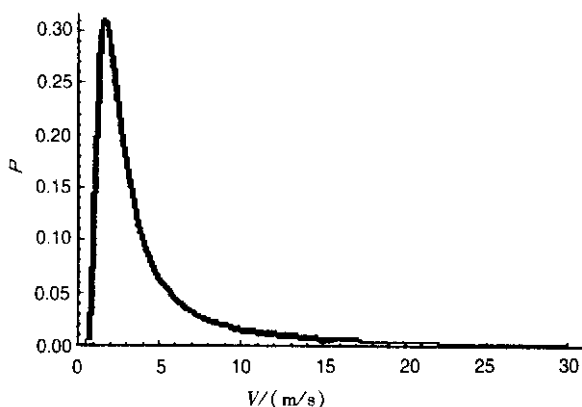


图 3 CO-He 在 $\Delta J=0$ 时相对跃迁几率与速度的关系

Fig. 3 Relative transition probability distribution via velocity for CO-He at $\Delta J=0$

4 结 论

考虑一级含时波恩近似,长程相互作用势和直线轨道近似,建立了 Π 态双原子分子由于 Λ 分裂引起量子干涉的理论模型,并成功解释了实验中的反常现象。

附 录

式(26)的积分方法被 Gray 和 Kranendonk 通过使用直线轨道近似方法得出^[20]。

$$I_m^L(n) = \int_{-\infty}^{\infty} \exp(i \varpi_{JJ} t) R^{-n}(t) C_m^L(\Omega_t) dt \quad (a)$$

$$R(t) = (v^2 t^2 + b^2)^{1/2} \quad (b)$$

为了方便计算,引进无量纲的量

$$x = \varpi_{JJ} b/v, \quad z = vt/b \quad (c)$$

其中 b 和 v 是碰撞常数和质心坐标系的相对速度。按照上面的方法,积分 $I_0^L(6)$ 、 $I_1^L(6)$ 、 $I_2^L(6)$ 是可积的结果如下:

$$I_M^L(6) = b^{-5} v^{-1} J_M^L(6) = b^{-5} v^{-1} i^{L-M} A_M^L(6) \quad (d)$$

$$A_0^2(6) = (3/2)F_4(x) - F_3(x), \quad (e)$$

$$A_1^2(6) = \sqrt{3/2}G_4(x), \quad A_2^2(6) = \sqrt{3/8}F_4(x)$$

$$F_n(x) = \frac{\pi e^{-x}}{(n-1)! 2^{2n-2}} \sum_{k=0}^{n-1} \frac{(2n-2-k)!}{k!(n-1-k)!} (2x)^k \quad (f)$$

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

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