

Formula for the Transition Probability Induced by Long-range Potential Terms Varying as R^{-8} and R^{-10} for Atom-dimer Collisions

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An explicit formula is derived for the transition probability between two different states of the atom-dimer collisional system governed by second-order long-range interaction potential terms varying as R^{-8} and R^{-10} .

1. Introduction

Atom-dimer collision systems have been the subject of a number of studies [1–7]. These systems offer attractive possibilities for the study of many fundamental phenomena such as pre-dissociation, perturbation and dynamic aspects of collisions.

In previous work, we have investigated energy transfers between rovibrational levels in Li_2 and Na_2 molecules [6, 7]. An explicit theoretical study has been developed for the first order, semi-classical rotationally inelastic transition probabilities with an electric multipole long-range potential [6] and for a second-order long-range interaction potential varying as R^{-6} [7] in the atom-dimer collision, where R is the distance between the two partners.

This paper completes the previous theoretical work [7] by establishing the formula for the transition probability for each channel between an initial and a final states for the colliding system with the dispersion-induction interaction potential terms varying as R^{-8} and R^{-10} .

2. Theoretical Model

The main difficulty in studying atom-dimer collisions arises from the choice of interaction potentials governing these atom-diatomic molecule collisions. It seems reasonable to describe this interaction potential

in terms of the electrostatic multipoles of the isolated partners at long-range distance because the transfer cross sections are to be larger [6]. The second-order dispersion-induction interaction potential, for atom-dimer system, may be written in space-fixed coordinates [7]:

$$V = \sum_{lm'} V_l^{m'} \sum_m D_{mm'}^l Y_l^m, \quad (1)$$

where D is the usual rotation matrix and $V_l^{m'}$ are the electronic multipolar parts of the potential. Thus, the rotational matrix element of V between the initial i and the final f states is given by [7]:

$$\begin{aligned} \langle f | V | i \rangle_{\text{rot}} &= (-1)^M [(2J+1)(2J'+1)]^{1/2} \\ &\cdot \sum_l \sum_{m'=-l}^l V_l^{m'} \begin{pmatrix} J' & l & J \\ -\Omega' & m' & \Omega \end{pmatrix} \\ &\cdot \sum_{m=-l}^l Y_l^m \begin{pmatrix} J' & l & J \\ M' & m & -M \end{pmatrix}, \end{aligned} \quad (2)$$

where Ω is the projection of the total angular momentum J on the internuclear axis while M is its projection on the OZ axis of the fixed system. $\begin{pmatrix} J' & l & J \\ -\Omega' & m' & \Omega \end{pmatrix}$ are Wigner $3J$ coefficients. We have considered elsewhere [7] the first two terms $l=0$ and $l=2$ in the sum (2), giving the dispersion and induction interaction term varying as R^{-6} . Now, if we consider the two further terms $l=3$ and $l=4$ in the sum, we can study the part of the transition probability due to the second-order potential including the two terms varying as R^{-8} and R^{-10} in the interaction potential between the collisional partners.

Using the known expression for the integral over the three rotation matrix elements, we can write (2) in

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the factorized form

$$\begin{aligned}\langle f|V|i\rangle_{\text{rot}} &= \sum_l \langle f|V|i\rangle_{\text{rot}}^{(l)} \\ &= (-1)^M [(2J+1)(2J'+1)]^{1/2} \\ &\cdot \sum_{m'=-l}^l V_l^{m'} \begin{pmatrix} J' & l & J \\ -\Omega' & m' & \Omega \end{pmatrix} \sum_{m=-l}^l Y_l^m \begin{pmatrix} J' & l & J \\ M' & m & -M \end{pmatrix}.\end{aligned}\quad (3)$$

Consideration of the two terms $l=3$ and $l=4$ in (3) yields

$$\begin{aligned}\langle f|V|i\rangle_{\text{rot}}^{(3)} + \langle f|V|i\rangle_{\text{rot}}^{(4)} &= (-1)^M [(2J+1)(2J'+1)]^{1/2} \\ &\cdot \left[\sum_{m'} V_3^{m'} \begin{pmatrix} J' & 3 & J \\ -\Omega' & m' & \Omega \end{pmatrix} \sum_{m=-3}^3 Y_3^m \begin{pmatrix} J' & 3 & J \\ M' & m & -M \end{pmatrix} \right. \\ &\left. + \sum_{m'} V_4^{m'} \begin{pmatrix} J' & 4 & J \\ -\Omega' & m' & \Omega \end{pmatrix} \sum_{m=-4}^4 Y_4^m \begin{pmatrix} J' & 4 & J \\ M' & m & -M \end{pmatrix} \right].\end{aligned}\quad (4)$$

Using (4) for $\langle f|V|i\rangle_{\text{rot}}^{(l)}$, and after an integration over the vibrational part in the Franck-Condon approximation the transition probability between the levels i and f becomes

$$\begin{aligned}P_{\text{if}} &= (2J'+1) \hbar^{-2} \langle v'|v''\rangle^2 \left[1/7 \begin{pmatrix} J' & 3 & J \\ -\Omega' & \Omega'-\Omega & \Omega \end{pmatrix}^2 \right. \\ &\cdot \sum_{m=-3}^3 \left| \int_{-\infty}^{+\infty} \exp(i w_{\text{if}} t) Y_3^m V_3^{\Omega'-\Omega} dt \right|^2 \\ &+ 1/9 \begin{pmatrix} J' & 4 & J \\ -\Omega' & \Omega'-\Omega & \Omega \end{pmatrix}^2 \\ &\cdot \sum_{m=-4}^4 \left| \int_{-\infty}^{+\infty} \exp(i w_{\text{if}} t) V_4^{\Omega'-\Omega} Y_4^m dt \right|^2 \Big] \quad (5)\end{aligned}$$

with $\hbar w_{\text{if}} = |E_f - E_i|$, where E_i is the energy of the colliding system in the initial state, and E_f is the similar quantity for the final state in the (1BA) first-order Born approximation [6]. v' , v'' are the vibrational quantum numbers for the initial and final states, respectively. $V_3^{\Omega'-\Omega}$ and $V_4^{\Omega'-\Omega}$ are the electronic parts of the matrix element. Equation (5) has been obtained using orthogonality properties of the $3J$ Wigner coefficients which imply that the interference term between $V_3^{\Omega'-\Omega}$ and $V_4^{\Omega'-\Omega}$ vanishes. The two terms of the dispersion-induction energy considered here are

$$V_3^{\Omega'-\Omega} = C_8 R^{-8} \quad \text{and} \quad V_4^{\Omega'-\Omega} = C_{10} R^{-10}, \quad (6)$$

where R is the distance between the two partners. C_8 and C_{10} are higher order long-range coefficients

neglected elsewhere [7] in the second-order interaction potential between the atom and the molecule.

The determination of the two integrals over the time variable involved in (5) is performed in the framework of the impact parameter b method [8–10] with constant velocity v . In the general case, the transition probability corresponding to the two terms for the potential (6) becomes

$$\begin{aligned}P_{\text{if}}(b) &= \hbar^{-2} v^{-2} (2J'+1) \langle v'|v''\rangle^2 \\ &\cdot \left[C_8^2/7 b^{14} \begin{pmatrix} J' & 3 & J \\ -\Omega' & \Omega'-\Omega & \Omega \end{pmatrix}^2 R_3(x) \right. \\ &\left. + C_{10}^2/9 b^{18} \begin{pmatrix} J' & 4 & J \\ -\Omega' & \Omega'-\Omega & \Omega \end{pmatrix}^2 R_4(x) \right],\end{aligned}\quad (7)$$

where

$$R_3(x) = (1.2439 + 2.4633x + 2.7139x^2 + \dots) \exp(-2x) \quad \text{and} \quad (8)$$

$$R_4(x) = (1.0287 + 2.0538x + 2.1267x^2 + \dots) \exp(-2x).$$

$R_i(x)$ (for $i=3, 4$) are the resonance functions with $x = w_{\text{if}} b/\hbar v$ [11, 12].

From the non zero conditions for any Wigner $3J$ coefficient the mechanism of energy obeys to the following selection rules:

$$\begin{aligned}|J-3| &\leq J' \leq J+3 \quad \text{for } C_8 R^{-8} \text{ term,} \\ |J-4| &\leq J' \leq J+4 \quad \text{for } C_{10} R^{-10} \text{ term.}\end{aligned}\quad (9)$$

3. Conclusion

In this paper, a formula has been derived for the transition probability of the collisions between an atom and a diatomic molecule. This model is based on the approximation of a multipolar second-order interaction potential (dispersion and induction terms varying as R^{-8} and R^{-10}) at large distance between the two collisional partners. For a colliding system, once the long-range coefficients C_8 and C_{10} are known, transition probabilities and then cross sections may be obtained through the proposed formula.

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