Semiclassical Analysis of the Anisotropic Total Cross Section in Thermal Energy Collisions between a Non-Spherical and a Spherical Atom

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Thermal energy atomic collisions of the type $A(^2P_{3/2}) + B(^1S_o)$ are discussed to clarify the dependence of the orientational anisotropy $\Delta\sigma$ in the total cross section $\sigma$ on the relative velocity $v$. Simple expressions for $\Delta\sigma/\sigma$ are derived by semiclassical treatments designed to be appropriate for large spin-orbit interactions. The $\Delta\sigma/\sigma$ oscillates with $v$ around its average value. The velocities giving the extrema in the oscillating curve are almost solely determined by the isotropic part $\bar{V}(R)$ in the interaction potential, while the amplitude of the oscillation depends sensitively on the anisotropic interaction near $R_{mi}$, where $R_{mi}$ is the location of the minimum in $\bar{V}(R)$. The oscillation-averaged $\Delta\sigma/\sigma$ is independent of the relative velocity and proportional to the anisotropy in the van der Waals interaction.

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1. Introduction

The orientational anisotropy in the interatomic interaction always occurs if interacting atoms are not in S-state, and modifies the familiar scattering by the isotropic interaction usually in a complicated manner. Recent scattering experiments of oriented Ga($^2P_{3/2}$) and In($^2P_{3/2}$) atomic beams colliding with rare-gas($^1S_o$) atoms made it clear that the anisotropic part in the total cross section is large enough to permit an accurate measurement, and oscillating as a function of the relative collision velocity $v$ [1, 2]. The total cross section for the $F(^2P) + \text{rare-gas}(^1S_o)$ collision has been also reported to show a complex velocity-dependence ascribable to the anisotropic interaction [3]. This paper discusses thermal-energy atomic collisions of the type $A(^2P_{3/2}) + B(^1S_o)$, where $A$ and $B$ mean atoms in the ground state (including its higher spin-orbit state).

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The orientation dependent total cross section $\sigma_{j,m_j}$ for the $^2P_j$ atom is defined by

$$\sigma_{j,m_j} = \sum_{j',m'_j} \sigma(j|m_j \rightarrow j'|m'_j)$$

with the quantization axis directed along the initial direction of $v$. Because $\sigma_{j,m_j}$ depends only on $j$ and $|m_j|$, there are three different cross sections $\sigma_{3/2,3/2}$, $\sigma_{3/2,1/2}$, and $\sigma_{1/2,1/2}$. We assume, as usual, that the doublet splitting $\Delta W$ is independent of the internuclear distance $R$ [4], then we may describe the low-energy $A(^2P) + B(^1S_o)$ collision in terms of the two interatomic potentials $V_a(R)$ and $V_b(R)$ corresponding respectively to the $A=0$ and $A=\pm 1$ molecular states, where $A$ represents the projection of the electron orbital angular momentum on the internuclear axis. The scattering process is more closely related with the average $\bar{V}(R) = (V_a(R) + 2V_b(R))/3$ over the $A$ states and the difference $\Delta V(R) = V_a(R) - V_b(R)$: the former plays the part of the isotropic potential,
while the latter is responsible for the anisotropy effect [5].

The information on $\tilde{V}(R)$ and $\Delta V(R)$ is obtained by measuring any two of the above three $\sigma_{j'm_j}$, however from an experimental point of view [1, 2], a reliable measurement is most easily carried out for $\Delta \sigma/\sigma_{av}$ defined by

$$\Delta \sigma = \sigma_{3/2,3/2} - \sigma_{3/2,1/2},$$

$$\sigma_{av} = (\sigma_{3/2,3/2} + \sigma_{3/2,1/2})/2.$$  

The aim of this paper is to clarify what information on $\tilde{V}(R)$ and $\Delta V(R)$ can be obtained from the measurement of $\Delta \sigma/\sigma_{av}$. The semiclassical treatment is introduced for the analysis with the aid of the assumption that the anisotropy $\Delta V(R)$ is much smaller than the doublet splitting $\Delta W$ in an important $R$-region for the scattering. This assumed situation applies to the anisotropic glory phenomena in the scattering of heavy IIIb atoms (Ga, In, Ta) and halogen atoms except, probably, fluorine. The semiclassical treatment is generally useful for the non-glory part of the anisotropy effect and gives a simple interpretation of it.

The notation used for the quantum numbers in this paper is as follows: $j$ is the total electron angular momentum, $m_j$ is the projection of $j$ on a space-fixed axis, $\Omega$ is the projection of $j$ on the internuclear axis, $I$ is the orbital angular momentum of the relative motion, and $J$ is the total angular momentum of the colliding system.

2. Mathematical Formulation

2.1. Basic Formula

The cross section $\sigma_{j'm_j}$ is most conveniently obtained by using the optical theorem,

$$\sigma_{j'm_j} = \frac{4\pi}{k} \text{Im} f(jm_j \rightarrow jm_j)/\theta = 0$$

with the forward elastic scattering-amplitude determined from

$$f(jm_j \rightarrow jm_j)/\theta = 0 = \frac{i}{2k} \sum_{l' \neq l} \sum_{m_{l'}} (2l + 1)(2l' + 1)^2 \times$$

$$
\langle jl'm_j | 0(JM) \rangle \langle jm_j | 0(JM) \rangle \{ \delta_{j',j} - S^l(jlj), \delta_{m_{j'},m_{j}}, \delta_{m_{l'},m_{l}} \},$$  

(2)

where $k$ denotes the wave number. The $S$-matrix $S^l(jlj)$ is obtained by solving a set of coupled radial Schrödinger equations for each eigenfunction of $J$, which can be written as

$$[d^2/dR^2 - (l + 1/2)^2/R^2 + k^2] F_j^l(R) = \frac{2m}{\hbar^2} \sum_{l'} V_{j,l',l}(R) F_{l'}^j(R),$$

where $m$ is the reduced mass and $(l + 1/2)^2$ is used in place of $l(l + 1)$. The potential matrix in the space-fixed frame, $V^l_{j,l',l}(R)$, can be evaluated from that in the molecule-fixed frame, $V_{j,a,l',a}$ by the relation [4]

$$V^l_{j,l',l}(R) = \sum_{a} (-1)^{a+a'} \langle Jl - \Omega l | 0 \rangle$$

$$\times \langle Jl' - \Omega l' | 0 \rangle V_{j,a,l',a}.$$  

(4)

Thus, writing down the matrix $V_{j,a,l',a}$ in terms of $\tilde{V}(R)$, $\Delta V(R)$, and $\Delta W$ [4, 5], we get a complete set of equations for our purpose. To make these equations more transparent, we first replace the vector coupling coefficients in (2) and (4) by the rotation matrices. Because the important region of $l$ is normally $l \geq 100 \gg j$ for the collision we have in mind, we can use the asymptotic relations [6]

$$[(2l + 1)/(2J + 1)]^l \langle jm_j | 0(JM) \rangle = \delta_{l,l} \delta_{m_{l},m_{j}},$$

$$\delta_{l,l} \delta_{m_{l},m_{j}} = \delta_{m_{l},m_{j}}$$

(5)

with $\mu$ defined by

$$\mu = J - l.$$

(6)

Then, denoting the $j = j' = 3/2$ part of the $S$-matrix by $S^l_{3/2}(\mu', \mu)$, we can rewrite (2) as

$$f(3/2m_j \rightarrow 3/2m_j)/\theta = 0 = \frac{i}{2k} \sum_{l} (2J + 1)$$

$$\{ 1 - \sum_{\mu'} d^l_{m_{l},m_{j}}(\pi/2) S^l_{3/2}(\mu', \mu) d^l_{m_{l},m_{j}}(\pi/2) \},$$

(7)

and reduce (4) to

$$V^l_{j,l',l} = \sum_{a} d^l_{m_{l},m_{j}}(\pi/2) d^l_{m_{l},m_{j}}(\pi/2) V_{j,a,l',a}.$$  

(8)

The matrix element $S^l_{3/2}(\mu', \mu)$ is non-zero only if $\mu = \mu'$ is even, according to the law of parity conservation. Thus, the difference $\Delta \sigma$ and the average $\sigma_{av}$ are expressed to be

$$\Delta \sigma = \frac{2\pi}{k^2} \sum_{J} (2J + 1) \text{Re} \left\{ \frac{1}{4} \left[ S^l_{3/2}(\mu, \mu) + S^l_{3/2}(-\mu, -\mu) \right] \right\},$$

(9)

$$\sigma_{av} = \frac{2\pi}{k^2} \sum_{J} (2J + 1) \text{Re} \left\{ -\frac{1}{4} \left[ S^l_{3/2}(\mu, \mu) + S^l_{3/2}(-\mu, -\mu) \right] \right\},$$

(10)

It should be noted that simple expressions like (7), (9), and (10) can be obtained by taking the z axis to be parallel to the initial v.