DIFFERENTIAL CROSS SECTIONS FOR $\Delta m$ TRANSITIONS
IN SUDDEN ATOM–MOLECULE COLLISIONS *

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Differential $(j m_j) \to (j' m_{j'})$ cross sections in repulsive He–Na$_2$ collisions are calculated within the IOS approximation probing various choices for the effective angular momentum quantum number $l$. Oscillatory structures in $\Delta m$ distributions almost independent of the collisional dynamics are explained by a classical hard-shell model.

1. Introduction

Rotational rainbow structures in rotationally inelastic differential cross sections for atom–diatom collisions predicted in several theoretical studies [1–5] and partly observed in recent experiments [6–11] provide valuable information on the collisional dynamics and the interaction potential. Within the IOS approximation these structures were qualitatively explained by semi-classical arguments as interference between contributions belonging to different orientation angles $\gamma$ [1,2]. A recently developed semiclassical version of the IOS scattering amplitude based on a uniform stationary-phase approximation for a two-dimensional integral gives cross sections in close agreement with numerically exact IOS results [12]. Rotational rainbow structures are expected to be dominant whenever many states are energetically accessible and the rotational coupling is strong. The latter is fulfilled for repulsive collisions (large scattering angles, high energies, small potential wells) sampling the inner part of the interaction potential surface.

In view of the rapid development of new experimental techniques state-to-state differential cross sections for detailed $(j m_j) \to (j' m_{j'})$ transitions soon may become available. The present work is considered as a first step in a theoretical investigation and because of the IOS approximation applied here it is restricted to the strong coupling regime governed by rotational rainbow structures.

2. Theory

Because of its simplicity the IOS approximation has received considerable attention [13]. Here we list only the basic equations in the notation of ref. [14]. The IOS cross section for a $(j m_j) \to (j' m_{j'})$ transition into solid angle $\hat{R}$ is given by

$$d\sigma(j m_j \to j' m_{j'} \hat{R})/d\Omega = (k_{j'}/k_j)f_j(j m_j \to j' m_{j'} \hat{R})^2.$$ (1)

In the space fixed coordinate system with the scattering axis chosen as quantization axis the scattering amplitude reads

$$f_j(j m_j \to j' m_{j'} \hat{R}) = (\pi/k_j k_{j'})^{1/2} \sum_{Jm_J} (-1)^{j+j'+l-l'}$$
$$\times (2l'+1)^{1/2}[(2l+1)(2J+1)] C(j,lJ;m_j 0 m_j)$$
$$\times C(j' l' J; m_{j'} m_j - m_{j'} m_{j'}) C(j,lJ; 0 0 )$$
$$\times C(j' l' J; 0 0 ) Y_n^* (j' m_{j'}) Y_l m_{j'} - m_{j'} (\hat{R}).$$ (2)
In eqs. (1) and (2) the subscript \( I \) refers to the particular choice for the effective orbital angular momentum quantum number. The \( T \)-matrix is defined as

\[
T_{\bar{I}}(j | j') = 2\pi \int_0^\pi d\gamma \sin \gamma Y_{\mu I} (\gamma, 0) 
\times \{ \delta_{J' I} \delta_{J' I'} - \exp [2i\eta(\gamma)] \} Y_{\mu' I'} (\gamma, 0). \tag{3}
\]

Here, \( \eta(\gamma) \) is the elastic phase-shift for the potential \( V(R, \gamma) \) and depends parametrically on the electron angle \( \gamma \).

The most crucial point is a proper \( \bar{I} \)-labelling on the scattering amplitude. Natural choices are \( I, I' \), \( J, J' \) or \( (I+I')/2 \), which have been discussed extensively in the literature [13]. It has been shown analytically [14,15] that the choices \( I = I \) and \( I = I' \) lead to identical degeneracy averaged cross sections, e.g.

\[
\frac{d\sigma(I | I'; \bar{R})}{d\Omega} = (2j + 1)^{-1} \sum_{m_I m_I'} \frac{d\sigma(I m_I j m_I' | \bar{R})}{d\Omega} . \tag{4}
\]

However, the \( \Delta m \) distributions depend strongly on the specific choice of \( \bar{I} \). While \( I = I' \) leads to cross sections, which are diagonal in \( m_I \), the other choices allow for the computation of \( \Delta m \) cross sections for magnetic transitions. The question of \( \bar{I} \)-labelling with respect to magnetic transitions is discussed by Khare et al. [16].

Recently Fritz [17,18] has studied \( m_I \)-dependent IOS integral cross sections for \( Ar + N_2 \) at 25 8 meV collision energy and \( j = 0 \to 2 \) and \( j = 2 \to 4 \) rotational transitions. From comparison with close-coupling calculations of Alexander [19] he concluded that \( \bar{I} = (1/2)(I + I') \) is more appropriate than the choice \( \bar{I} = I \), for example.

3. Results and discussion

Rigid-rotor calculations for the He–Na\(_2\) system are reported for collision energies of \( E = 0.1 \) and 0.15 eV utilizing the analytic potential surface of ref. [12] which is a fit to preliminary ab initio CI energies [20]. Degeneracy-averaged IOS cross sections involving rotational transitions up to \( \Delta j = 12 \) using a slightly improved ab initio surface [21] are in very good accord with detailed state-to-state experimental data [10] and prove the applicability of the IOS approximation for this system. In the following we restrict ourselves to scattering out of the rotational ground state \( j = 0 \), for which the cross sections are symmetric in \( m_I \) and only the results for \( m_I \geq 0 \) are given.

Table 1 lists degeneracy-averaged differential cross sections for \( \theta = 50^\circ \) and 100° and various definitions for \( \bar{I} \). The choices \( I = I \) and \( I = I' \) (in the special case with \( j = 0 \) [14]) give identical cross sections, which differ from those obtained with \( \bar{I} = (1/2)(I + I') \) or \( \bar{I} = (I')^{1/2} \). However, the deviations are generally small with the tendency to increase with \( \Delta j \). As a special result we note that the rotational rainbow oscillations in the \( j' \)-distributions in table 1 are almost independent of the \( \bar{I} \)-labelling. Otherwise one could speculate, whether they are a real physical effect or an artifact of the IOS approximation.

The influence of various labelings on \( \Delta m \) cross sections is studied in detail for \( \bar{I} = (1/2)(I + I') \) and \( \bar{I} = I \) in figs. 1 and 2 for \( j = 4, 8 \) and 12 at three scattering angles. All cross sections show the same typical behaviour: oscillations for low magnetic transitions, a

| Table 1 | Degeneracy-averaged IOS differential cross sections \( d\sigma(0 \to j')/d\Omega \) in A\(^2\) at \( \theta = 50^\circ \) and 100° using various choices \( \bar{I} \) as effective orbital angular momentum quantum number \( m_I \) \( a) \)
<table>
<thead>
<tr>
<th>( \theta )</th>
<th>( j' )</th>
<th>( \bar{I} = I ) ( b) )</th>
<th>( \bar{I} = (1/2)(I + I') )</th>
<th>( \bar{I} = (I')^{1/2} )</th>
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<td>0.7671</td>
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<tr>
<td>4</td>
<td>0.4524</td>
<td>0.4630</td>
<td>0.4650</td>
<td></td>
</tr>
<tr>
<td>6</td>
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<td>2.2474</td>
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</tr>
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<td>8</td>
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a) The collision energy is \( E = 0.1 \) eV.

b) \( I = I \) and \( I' \) give identical degeneracy-averaged cross sections.
Fig. 1. IOS differential cross sections $d\sigma(00 \rightarrow j'/m_j')/d\Omega$ versus final magnetic quantum number $m_j'$ for selected $0 \rightarrow j'$ rotational transitions at three scattering angles. The collision energy is 0.1 eV and $l = \frac{1}{2}(l + 1')$ is chosen as effective orbital angular momentum. The largest cross section for each curve is normalized to one. The arrows mark the maximal classical projection $M_{\text{max}}^j$ as predicted by eq. (7).

relatively broad maximum at intermediate values and rapid fall-off beyond it. The similarity with rotational rainbow structures is striking. We note that this qualitative behaviour is independent on whether the rotational transition $0 \rightarrow j'$ is classically allowed or forbidden. In table 1 we find the rotational rainbow maxima at $j' = 6$ and 12 for $\theta = 50^\circ$ and $100^\circ$, respectively.

Thus in fig. 1 with $\theta = 50^\circ$ only $j' = 4$ is classically accessible. The results of figs. 1 and 2 differ only in the angle dependence of $M_{\text{max}}^j(j', \theta)$, the magnetic transition for which the maximum occurs. While $M_{\text{max}}$ becomes maximal ($\approx j'$) at $\theta \approx 100^\circ$ for $l = l$ (independent of $j'$) this occurs at $\theta \approx 20^\circ$ for $l = \frac{1}{2}(l + 1')$, an angular region not shown in figs. 1 and 2. With respect to eq. (2) we note, that the IOS amplitude just as the exact amplitude [22] fulfils the selection rule $\Delta m = 0$ for $\theta = 0^\circ$ or $180^\circ$ independent for the $l$-choice.

In order to give a simple explanation of these findings we discuss the model of classical hard-shell scattering for rotational excitation as studied by Beck et al. [8]. Though obviously simplistic, it provides useful insight into the mechanism of rotational excitation in the strong coupling regime. In this model the excitation occurs momentarily at point $R$ on the surface of the hard-shell (measured from the molecular center-of-mass) depending on the initial conditions, e.g., impact parameter and orientation angles of the molecule with respect to the scattering axis. For a given point of contact $R$, the change of the molecular angular momentum vector $j$ is immediately obtained by conservation of the total angular momentum [8]

$$j + R \times P = j' + R \times P',$$  

where $P$ is the incoming momentum of relative motion. With $j = 0$ and $\Delta P = P' - P$ we obtain

$$j' = \Delta P \times R.$$  

For a given rotational transition into scattering angle $\theta$ all possible final vectors $j'$ are therefore constrained to lie on a circle of radius $|j'|$ orthogonal to $\Delta P$ as illustrated in fig. 3. The distribution of $j'$ on this circle depends on the dynamics, because eq. (6) requires $j'$ to be orthogonal to $R$, too. Classically, the maximal projection of $j'$ onto the scattering axis is

$$M_{\text{max}}^j = |j'| \sin \alpha,$$  

Fig. 3. Classical vector model for hard-shell scattering. For definitions see the text.
with the angle \( \alpha \) related to the scattering angle \( \theta \) by

\[
\cos \alpha = \frac{P - P' \cos \theta}{[P^2 + (P')^2 - 2PP' \cos \theta]^{1/2}}. \tag{8}
\]

The location of \( M_{\text{max}}^{\text{cl}} \) obtained with \( P = P' \) (valid under sudden conditions) and \( |j'\rangle = |j'\rangle \) are indicated in figs. 1 and 2. In all cases this simple classical formula, eq. (7) determines precisely the onset of the exponential fall-off in the quantum distributions in fig. 1.

This close agreement supports the choice \( I = \frac{1}{2}(l + l') \) as effective angular momentum quantum number as used in the IOS calculations displayed in fig. 1.

Under sudden conditions \((P \approx P') M_{\text{max}}^{\text{cl}} \) is independent of the collisional dynamics, e.g. the potential surface, energy of masses. The energy dependence of the IOS \( m_j \)-distributions obtained with \( I = \frac{1}{2}(l + l') \) is investigated in fig. 4 comparing the results for \( E = 0.1 \text{ eV} \) and \( E = 0.15 \text{ eV} \). Surprisingly, only small changes are observed. Especially the location of the maximum remains almost unchanged as predicted by eq. (7). The same result is found for other transitions and scattering angles and for \( m_j \)-distributions using \( I = l \). We note, that the rotational rainbow structures are very sensitive to changes of the collision energy [3,12]. For example, the location of the rotational rainbow maximum at fixed scattering angle is found to be approximately proportional to the square root of the energy.

We further assume that for fixed \( 0 \rightarrow j' \) transition and scattering angle the vector of final molecular angular momentum \( j' \) precesses uniformly about the \( \Delta P \) axis. According to the vector model of angular momentum [23] the probability of finding a value \( m_j \) in a measurement of the projection of \( j' \) onto the \( P \) axis is given by

\[
P_{m_j'} = |d_m^{m_j'}(\alpha)|^2, \tag{9}
\]

where the rotation angle \( \alpha \) is defined in fig. 3 and eq. (8), respectively, and \( \mu \) is the projection quantum number with respect to the \( \Delta P \) axis. In the present case \( j' \) is assumed to be orthogonal to \( \Delta P (\mu = 0) \) and eq. (9) simplifies to

\[
P_{m_j'} = |(j' - m_j \cdot \mu)/(j' + m_j \cdot \mu)| |P_{j,m_j'}^{m_j'}(\cos \alpha)|^2. \tag{10}
\]

where \( P_{j,m_j'}^{m_j'} \) is an associated Legendre polynomial. The same probabilities have been derived in an approximate spectator model by Eckelt and Korsch [24].

Results obtained with eq. (10) are compared in fig. 4 to the IOS probabilities with \( I = \frac{1}{2}(l + l') \) and remarkable agreement is observed. The classical limit of eq. (9) is [23]

\[
P_{j,m_j}(\theta) = \pi^{-1} [\langle j' \rangle^2 (1 - \cos^2 \theta) - (\mu^2 + (m_j)^2 - 2\mu m_j \cdot \cos \theta)]^{-1/2}. \tag{11}
\]

For \( \mu = 0 \) and using eq. (7) it reduces to

\[
P_{j,m_j}^{\text{cl}} = \pi^{-1} [(M_{\text{max}}^{\text{cl}})^2 - (m_j)^2]^{-1/2} \tag{12}
\]

The continuous classical probabilities for \( j' = 10 \) and \( \theta = 100^\circ \) are also shown in fig. 4. They average out the quantum oscillations for low magnetic transitions, have a singularity at \( M_{\text{max}}^{\text{cl}} \) and are zero in the classically forbidden region, \( m_j \geq M_{\text{max}}^{\text{cl}} \).

4. Conclusions

The degeneracy-averaged differential cross sections for rotationally inelastic collisions depend only slightly on the choice of the effective orbital angular momentum quantum number \( I \). The choices \( I = l \) and \( I = \frac{1}{2}(l + l') \) investigated in more detail predict \( \Delta m \) distributions for fixed rotational transition and fixed
scattering angle, which are similar to rotational rainbow features: Oscillations for low magnetic transitions and a broad maximum at intermediate values followed by a rapid fall-off to higher transitions. The two choices give distributions which differ only in the respective angle dependence of the maxima for a given rotational excitation process. The $\Delta m$ distributions are only slightly energy dependent. The magnetic transition probabilities obtained with $I = \frac{1}{2}(I + I')$ are in good accord with a simple formula derived from a classical hard-shell scattering model. Within this model the predicted structures are referred to the behaviour of rotation matrices and, in contrast to rotational rainbow structures, contain only little information on the potential surface. Obviously, this strong conclusion must be proven by future exact calculations, because the determination of $\Delta m$ dependent cross sections within the IOS approximation remains questionable, even though agreement with other models is achieved. Finally, we like to stress once again, that the present conclusions are expected to be valid only in the strong coupling regime, when the sudden conditions are fulfilled.

References