When diffraction rules the stereodynamics of rotationally inelastic collisions

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1. Why is stereodynamics important?

2. Two words about the model

3. Ar – NO collisions: model vs. experiment and exact computations

4. Other systems: fingerprints of diffraction

5. First results on Ne – NO($A^2\Sigma$) collisions

6. Conclusions and outlook
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Why is stereodynamics important?

Usual scattering experiments furnish:
- integral cross sections (overall probability for collision to happen), and
- differential cross sections (probability of scattering into a particular angle)
Why is stereodynamics important?

Integral and differential cross sections miss important features
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Integral and differential cross sections miss important features

For instance, how will an NO molecule be rotating after colliding with an Ar atom?

Unpolarized $j$

\[ \text{Unpolarized } j \]

\[ \text{O} \quad \text{N} \quad \text{Ar} \]

\[ k \]
Why is stereodynamics important?

Integral and differential cross sections miss important features

For instance, how will an NO molecule be rotating after colliding with an Ar atom?

Unpolarized $j$

Polarized, $j' \perp k$

within the collision plane...
Why is stereodynamics important?

Integral and differential cross sections miss important features

For instance, how will an NO molecule be rotating after colliding with an Ar atom?

...or perpendicular to the collision plane?
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Integral and differential cross sections miss important features

For instance, how will an NO molecule be rotating after colliding with an Ar atom?

...or perpendicular to the collision plane?

The only way to obtain complete information about the potential is to measure the angular momentum disposal
We describe molecular rotation using two alignment moments, $a_{0}^2$ and $a_{2+}^2$. 
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$$a_0^2 = 1 \quad \rightarrow \quad j' \parallel k$$
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$$a_{0}^{2} = -\frac{1}{2} \rightarrow j' \perp k$$
Alignment moments

We describe molecular rotation using two alignment moments, $a_0^2$ and $a_{2+}^2$

\[ a_{2+}^2 = -\frac{\sqrt{3}}{2} \ldots \frac{\sqrt{3}}{2} \]

describes the alignment of \( j' \) within the plane perpendicular to \( k \).
Alignment moments

We describe molecular rotation using two alignment moments, $a_{0}^{2}$ and $a_{2+}^{2}$

$$a_{2+}^{2} = -\frac{\sqrt{3}}{2} \ldots \frac{\sqrt{3}}{2} \quad \text{describes the alignment of } j' \text{ within the plane perpendicular to } k$$

$$a_{2+}^{2} = \frac{\sqrt{3}}{2} \quad \rightarrow \quad j' \perp k; \quad \text{within the collision plane}$$
Alignment moments

We describe molecular rotation using two alignment moments, $a_0^2$ and $a_2^2$:

$$a_{2+}^2 = -\frac{\sqrt{3}}{2} \ldots \frac{\sqrt{3}}{2}$$

describes the alignment of $j'$ within the plane perpendicular to $k$:

$$a_{2+}^2 = -\frac{\sqrt{3}}{2} \rightarrow j' \perp k; \text{ perpendicular to the collision plane}$$

The figure illustrates the alignment of the molecular axes in the collision plane, with $j'$ perpendicular to $k$.
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The Fraunhofer model of molecular collisions

J.S. Blair, in Nucl. Str. Phys. VII C, 343 (1966); M. Faubel, JCP 81, 5559 (1984)

1. **Sudden approximation**: the collision is much faster than molecular rotation.
   
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\[ E_{\text{coll}} \]

\[ J=0 \quad J=1 \quad J=2 \]
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- The inelastic scattering amplitude can be expressed in terms of the elastic amplitude:

\[
fi \rightarrow f(\vartheta) = \langle f | f_{el}(\vartheta, \xi) | i \rangle
\]
2. We consider the molecule to be a perfectly absorptive target with sharp boundaries, and replace the true elastic scattering amplitude $f_{el}(\vartheta)$ by the amplitude for *Fraunhofer diffraction*
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3. The collision energy is high compared with any potential well

⇒ we consider only the “repulsive core” of the potential, neglecting the attractive part
The scattering amplitudes

\[ f_{i ightarrow f}(\vartheta) = \frac{ikR_0}{4\pi} \sqrt{\frac{2j + 1}{2j' + 1}} J_{|\Delta m|}(kR_0 \vartheta) \sum_{\kappa \neq 0, \kappa + \Delta m \text{ even}} \Xi_{\kappa 0} F_{\kappa, \Delta m} C(j \kappa j'; m \Delta mm') \]

\[ \times C(j \kappa j'; \Omega \Omega) \left[ (-1)^\kappa + (-1)^{\Delta j} \right] \]
The scattering amplitudes

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No way to study quantum stereodynamics without the scattering amplitudes
The scattering amplitudes

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No way to study quantum stereodynamics without the scattering amplitudes

Analytic expressions allow getting insight into the stereodynamics
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Results for Ar–NO ($X^2\Pi, j = \frac{1}{2} = \Omega \rightarrow j', \Omega = \frac{1}{2}$) collisions

Experiment and exact theory from Wade et al., Chem. Phys. 301, 261 (2004)
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Note the form factor

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Diffraction rules stereodynamics

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All the stereodynamics comes out of the diffraction by a two-dimensional egg!

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These correspond to the following distribution of angular momenta:
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Distribution of molecular axes:
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Other systems: He – NO \((j = \frac{1}{2} = \Omega \rightarrow j', \Omega = \frac{1}{2})\) at 520 cm\(^{-1}\)

Different scattering channels for fixed collision energy:
Other systems: He – NO ($j = \frac{1}{2} = \Omega \rightarrow j', \Omega = \frac{1}{2}$) at 520 cm$^{-1}$

Different scattering channels for fixed collision energy:

![Graph showing diffraction patterns for different scattering channels.](image-url)

The diffraction patterns have the same fingerprints.
Other systems: He – NO \((j = \frac{1}{2} = \Omega \rightarrow j', \Omega = \frac{1}{2})\) at 520 cm\(^{-1}\)

Different scattering channels for fixed collision energy:

![Graph](image.png)
Other systems: He – NO \((j = \frac{1}{2} = \Omega \rightarrow j', \Omega = \frac{1}{2})\) at 520 cm\(^{-1}\)

Different scattering channels for fixed collision energy:

![Graphs showing scattering angles and angular distributions for different channels.](image-url)
Other systems: He – NO ($j = \frac{1}{2} = \Omega \rightarrow j', \Omega = \frac{1}{2}$) at 520 cm$^{-1}$

Different scattering channels for fixed collision energy:

The diffraction patterns have the same fingerprints
Other systems: He – NO ($j = \frac{1}{2} = \Omega \rightarrow j' = \frac{9}{2}, \Omega = \frac{1}{2}$)

Let’s try it at different collision energies:

![Graph showing diffraction patterns at different collision energies.](image-url)
Other systems: He – NO ($j = \frac{1}{2} = \Omega \rightarrow j' = \frac{9}{2}, \Omega = \frac{1}{2}$)

Let’s try it at different collision energies:

![Graph showing variation of $a^2(j')$ with angle $\theta$.]

The form factors are the same: these are the fingerprints of diffraction.

Diffraction: oscillations scale with the (size of the molecule)/(de Broglie wavelength)!

Differences between scaled exact results are due to non-diffractive contributions.
Other systems: He – NO \((j = \frac{1}{2} = \Omega \rightarrow j' = \frac{9}{2}, \Omega = \frac{1}{2})\)

Let’s try it at different collision energies:

![Graph showing the form factors at different collision energies for He – NO system.](image-url)
Other systems: He – NO \((j = \frac{1}{2} = \Omega \rightarrow j' = \frac{9}{2}, \Omega = \frac{1}{2})\)

Let’s try it at different collision energies:

The form factors are the same: these are the fingerprints of diffraction

Fraunhofer 150, 520, 1000 cm\(^{-1}\) Exact 150 cm\(^{-1}\) Exact 520 cm\(^{-1}\) Exact 1000 cm\(^{-1}\)
Other systems: He – NO \( (j = \frac{1}{2} = \Omega \rightarrow j' = \frac{9}{2}, \Omega = \frac{1}{2}) \)

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Let’s try it at different collision energies:

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Diffraction: oscillations scale with the (size of the molecule)/(de Broglie wavelength)!

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Other systems: He – NO, O₂, OH, and CaH at 520 cm⁻¹

Let’s try different molecules:

Moments are scaled with the (size of the molecule)/(de Broglie wavelength)
Other systems: He – NO, O$_2$, OH, and CaH at 520 cm$^{-1}$

Let’s try different molecules:

Moments are scaled with the (size of the molecule)/(de Broglie wavelength)
We see the same fingerprints again!
The fingerprints of diffraction

If you observe such a behaviour of the alignment moments:

![Graph showing alignment moments vs. angle (θ)](image)

you know immediately that it comes from diffraction.
The fingerprints of diffraction

Well, probably not always...
A bit of speculation:
alignment moments for He – NO \((j = \frac{1}{2} = \Omega \rightarrow j' = \frac{3}{2}, \Omega = \frac{1}{2})\) at 10 cm\(^{-1}\)
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Ne – NO($A^2\Sigma, N = 0, J = 1/2 \rightarrow N'$) collisions at 470 cm$^{-1}$
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**Fraunhofer model**

**Exact calculations**

$N' = 1$

$N' = 2$

$N' = 3$

$N' = 4$

Breakdown of the sudden approximation?

$N' = 5$

$N' = 6$

$N' = 7$

$N' = 8$
Let’s try a higher collision energy of 1000 cm$^{-1}$:
Ne – NO($A^2\Sigma$, $N = 0$, $J = 1/2 \rightarrow N'$) collisions at 470 cm$^{-1}$

**Effect of a magnetic field:** weak for alignment moments, but substantial for differential cross sections
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We developed an analytic model to study the stereodynamics of rotationally inelastic atom-diatom collisions. The model results for Ar – NO and He – NO are in excellent agreement with experiment and exact calculations, which attests to the predominant role of diffraction in shaping the stereodynamics of these systems. We identified the fingerprints of diffraction, which can be used to interpret future experimental results. Alignment moments for Ne – NO (A\(_{2}\)\(\Sigma\)) are in good agreement with exact calculations for \(N' = 1\) ... 4, while for higher rotational transfer the sudden approximation breaks down. DCS's for Ne – NO (A\(_{2}\)\(\Sigma\)) are substantially affected by a magnetic field, while alignment moments are not.
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4. Alignment moments for Ne – NO ($A^2\Sigma$) are in good agreement with exact calculations for $N' = 1 \ldots 4$, while for higher rotational transfer the sudden approximation breaks down.
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5. DCS’s for Ne – NO ($A^2\Sigma$) are substantially affected by a magnetic field, while alignment moments are not.
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