When diffraction governs the stereodynamics of rotationally inelastic collisions

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Outline

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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within the collision plane...
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...or perpendicular to the collision plane?
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...or perpendicular to the collision plane?

The only way to obtain complete information about the potential is to measure the angular momentum disposal
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$$a_0^2 = 1 \quad \rightarrow \quad j' \parallel k$$
Alignment moments

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

We describe molecular rotation using two alignment moments, $a_{20}^2$ and $a_{22}^2$.

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The Fraunhofer model of molecular collisions


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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:

$$f_{i \rightarrow f}(\vartheta) = \langle f | f_{\text{el}}(\vartheta, \xi) | i \rangle$$
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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

\[ f_{i \rightarrow f}(\vartheta) = \frac{ikR_0}{4\pi} \sqrt{\frac{2j + 1}{2j' + 1}} J_{|\Delta m|}(kR_0\vartheta) \sum_{\kappa \neq 0}^{\kappa + \Delta m \text{ even}} \Xi_{\kappa,\Delta m} F_{\kappa,\Delta m} C(j \kappa j'; m \Delta mm') \times C(j \kappa j'; \Omega_0 \Omega) \left[ (-1)^{\kappa} + (-1)^{\Delta j} \right] \]
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No way to study quantum stereodynamics without the scattering amplitudes

Analytic expressions allow getting insight into the stereodynamics
1. Why is stereodynamics important?

2. Two words about the model

3. \( \text{Ar} – \text{NO} \) collisions: model vs. experiment and exact computations

4. Other systems: fingerprints of diffraction

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

6. Conclusions and outlook
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!

![Graphs showing diffraction patterns for different j']
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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:

![Diagram showing diffraction patterns for different collision energies and angular positions.](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:

![Diffraction patterns](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:

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

The diffraction patterns have the same fingerprints.
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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 for different collision energies. The graph compares Fraunhofer and exact results for different values of \( \vartheta \) and \( \frac{R_0}{\lambda} \).]
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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, 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)
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:

\[ a_{0}^{2}(\theta') \]

\[ a_{2}^{2}(\theta') \]

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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$\text{Ne} - \text{NO}(A^{2}\Sigma, N = 0, J = 1/2 \rightarrow N')$ collisions at 470 cm$^{-1}$

Breakdown of the sudden approximation?
Ne – NO($A^2\Sigma\, N = 0, \ J = 1/2 \rightarrow N'$) collisions at 1000 cm$^{-1}$

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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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.

DCS’s for Ne – NO \((A_{2}^{\Sigma})\) are substantially affected by a magnetic field, while alignment moments are not.
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