Molecular Quantum Scattering

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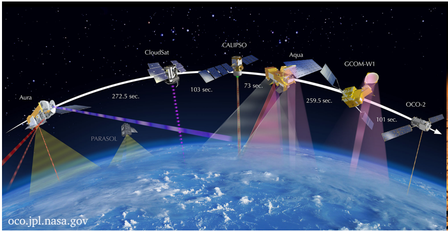
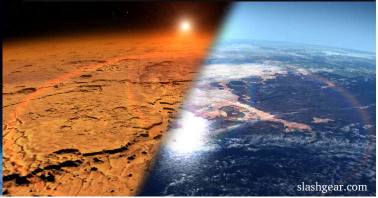
ISM & Atmosphere

Collisions for:

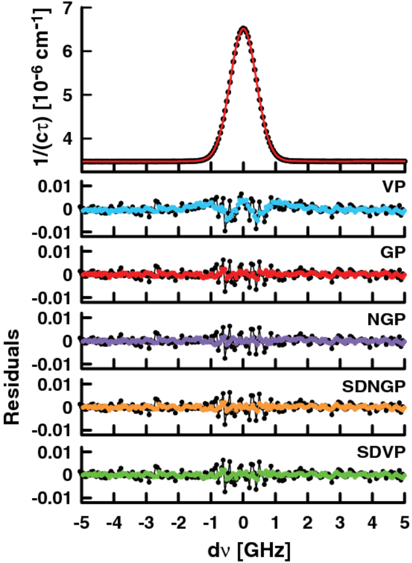
- Thermal equilibrium
- Non-thermal populations



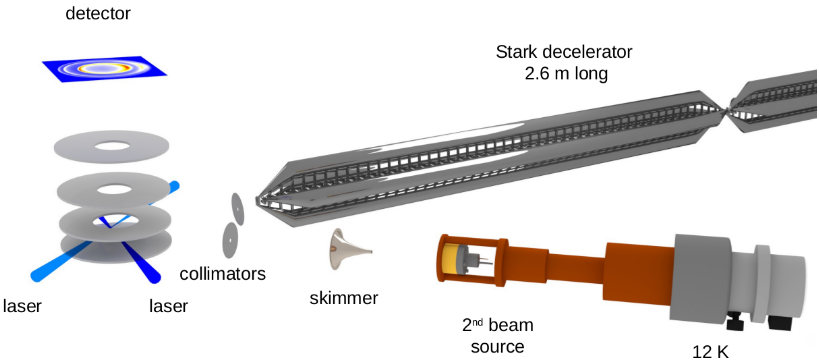


Spectroscopy

- Collisions perturb absorption lines
  - Accurate (atmospheric) retrievals
  - AMO tests of fundamental physics
- Additional collision-induced absorption



Molecular Beam Experiments



- Probe intermolecular interactions
- Chemistry and stereodynamics under controlled conditions

Types of collisions

- Elastic

$$A + B \rightarrow A + B \tag{1}$$

Momentum transfer, transport properties

- Inelastic

$$A + B \rightarrow A + B^* \tag{2}$$

Rates and non-thermal populations

- Reactive

$$A + B \rightarrow C + D \tag{3}$$

Gas-phase chemistry

Types of collisions

- Elastic

$$A + B \to A + B \tag{1}$$

Momentum transfer, transport properties

- Inelastic

$$A + B \to A + B^* \tag{2}$$

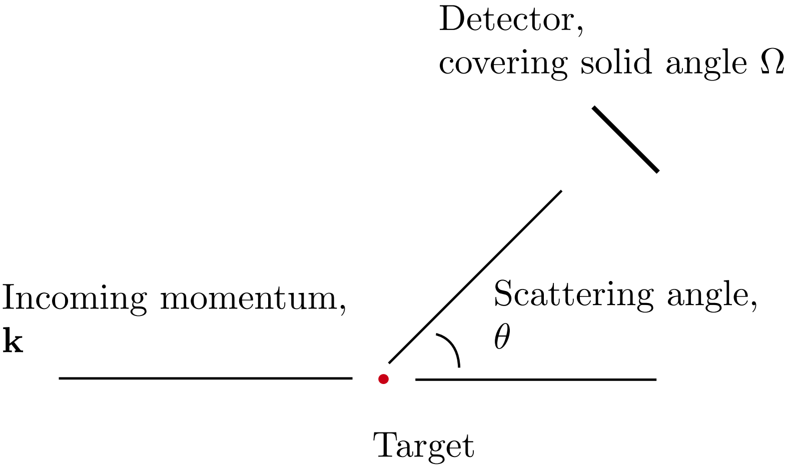
Rates and non-thermal populations

- Reactive

$$A + B \to C + D \tag{3}$$

Gas-phase chemistry

Main Question



Why scattering theory

- Aforementioned applications
  - Probing intermolecular interactions,
    Benchmarking electronic structure theory
  - Controlled state-to-state studies of chemical processes
  - Atmospheric science, astrophysics, combustion
  - Precision measurements and tests of fundamental physics

- Framework path-integral MD, quantum transition-state theories, ...
- Quantum mechanics exercise!

Outline

Basics: Plane waves

1D

$$\hat{H}_0 = -\frac{1}{2m}\frac{d^2}{dx^2} \tag{4}$$

eigenstate $\langle x|k\rangle = \exp(ikx)$

$$\hat{H}_0|k\rangle = \frac{k^2}{2m}|k\rangle \tag{5}$$

In 3D

$$\hat{H}_0 = -\frac{1}{2m}\nabla^2 \tag{6}$$

eigenstate $\langle \mathbf{r}|\mathbf{k}\rangle = \exp(i\mathbf{k}\cdot\mathbf{r}) = \exp(ikr\cos\theta)$

$$\hat{H}_0|\mathbf{k}\rangle = \frac{k^2}{2m}|\mathbf{k}\rangle \tag{7}$$

Basics: Spherical waves

Spherical coordinates

$$\hat{H}_0 = -\frac{1}{2m}\nabla^2 = -\frac{1}{2m}\frac{1}{r}\frac{d^2}{dr^2}r + \frac{L^2}{2mr^2} \tag{8}$$

Eigenstates of $\hat{L}^2$ are the spherical harmonics

$$\hat{L}^2|l, m\rangle = L(L+1)|l, m\rangle \tag{9}$$

At large r

$$\hat{H}_0 \approx -\frac{1}{2m}\frac{1}{r}\frac{d^2}{dr^2}r \tag{10}$$

the eigenstates at $k^2/2m$ will look like[1]

$$\psi(r) = \frac{\exp(ikr)}{r} \tag{11}$$

[1] And spherical Hankel functions at finite r

Basics: Completeness and normalization

$$\langle x|k\rangle = \exp(ikx) \tag{12}$$

$$\langle k|k'\rangle = \int dx \exp(-ikx)\exp(ik'x) = 2\pi\delta(k-k') \tag{13}$$

$$1 = \frac{1}{2\pi}\int dk|k\rangle\langle k| \tag{14}$$

- Momentum normalization

$$\langle x|k\rangle = \frac{1}{\sqrt{2\pi}}\exp(ikx) \tag{15}$$

- Energy normalization

$$\langle x|k\rangle = \sqrt{\frac{m}{k\pi}}\exp(ikx) \tag{16}$$

This results in $\langle k|k'\rangle = \delta(E-E')$

- Flux normalization

Flux

$$i\frac{\partial}{\partial t}|\psi\rangle = \hat{H}|\psi\rangle \tag{17}$$

Say $\hat{H}|\psi\rangle = E|\psi\rangle$

$$i\frac{\partial}{\partial t}|\psi\rangle = E|\psi\rangle \tag{18}$$

$$\rightarrow |\psi(t)\rangle = |\psi(t=0)\rangle \exp(-iEt) \tag{19}$$

Density $\rho(x,t) = |\psi(x,t)|^2$
Probability $P_{a,b}(t) = \int_a^b \rho(x,t)dx$
Flux $\frac{\partial}{\partial t}P_{a,b} = j(a) - j(b)$

$$\frac{\partial}{\partial t}P_{a,b} = \int_a^b \frac{\partial}{\partial t}\rho dx \tag{20}$$

$$\frac{\partial}{\partial t}\rho = \psi^*\frac{\partial\psi}{\partial t} + \frac{\partial\psi^*}{\partial t}\psi \tag{21}$$

Flux II

$$\frac{\partial}{\partial t}P_{a,b} = \int_a^b \psi^*(-i\hat{H}\psi)dx + \int_a^b (i\hat{H}\psi^*)\psi dx \tag{22}$$

$$= \frac{i}{2m}\int_a^b \psi^*\frac{d^2}{dx^2}\psi - \psi\frac{d^2}{dx^2}\psi^* dx \tag{23}$$

Using $fg'' - f''g = (fg' - f'g)'$, this gives

$$\frac{\partial}{\partial t}P_{a,b} = \frac{i}{2m}\left[\psi^*\frac{d}{dx}\psi - \psi\frac{d}{dx}\psi^*\right]_a^b \tag{24}$$

$$= \frac{i}{2m}2i\Im\left[\psi^*\frac{d}{dx}\psi\right]_a^b \tag{25}$$

For all a and b, so we must have

$$j_x = \frac{1}{m}\Im\left[\psi^*\frac{d}{dx}\psi\right]_x \tag{26}$$

Wronskian

Flux

$$j_x = \frac{1}{m}\Im\left[\psi^* \frac{d}{dx}\psi\right]_x \tag{27}$$

for the special case $\psi = f \pm ig$ with f, g real valued:

$$j_x = \frac{1}{m}\Im\left[(f \mp ig)\frac{d}{dx}(f \pm ig)\right] = \pm\frac{1}{m}\left[fg' - gf'\right] = \pm\frac{1}{m}W(f,g) \tag{28}$$

Wronskian

$$W(f,g) = fg' - f'g \tag{29}$$

which is constant for f, g both solutions to $y'' = ay$.

In 3D

Flux in three dimensions

$$\mathbf{j_x} = \frac{1}{m}\Im\left[\psi^* \nabla\psi\right] \tag{30}$$

In spherical coordinates

$$\nabla\psi = \frac{d\psi}{dr}\hat{\mathbf{r}} + \frac{1}{r}\frac{d\psi}{d\theta}\hat{\boldsymbol{\theta}} + \frac{1}{r\sin\theta}\frac{d\psi}{d\phi}\hat{\boldsymbol{\phi}}. \tag{31}$$

Flux of Plane and Spherical Waves

Plane wave $\exp(ikx)$

$$j_{x_0} = \frac{1}{m}\Im\left[\exp(-ikx)ik\exp(ikx)\right]_{x_0} = \frac{k}{m} \qquad (32)$$

(and in 3D: $\mathbf{j} = \mathbf{k}/m$)
$\exp(\pm ikx)$ are travelling to the right/left
Spherical wave $\frac{1}{r}\exp(ikr)$

$$j_r = \frac{1}{m}\Im\left[\frac{ik}{r^2} - \frac{1}{r^3}\right] \qquad (33)$$

(k/m flux through surface element $r^2 d\Omega$)
$\exp(\pm ikr)/r$ are travelling outwards/inwards
Constant flux expected because these are $f \pm ig$ functions for free particle.

Lippmann-Schwinger

Partition $\hat{H} = \hat{H}_0 + \hat{V}$
Schrödinger equation

$$\left(E - \hat{H}_0\right)|\psi\rangle = \hat{V}|\psi\rangle \tag{34}$$

$$|\psi\rangle = \left(E - \hat{H}_0\right)^{-1} \hat{V}|\psi\rangle??? \tag{35}$$

Lippmann-Schwinger

$$|\psi\rangle = |\phi\rangle + \left(E - \hat{H}_0 + i\epsilon\right)^{-1} \hat{V}|\psi\rangle \tag{36}$$

where $(E - \hat{H}_0)|\phi\rangle = 0$

Lippmann-Schwinger

$$|\psi\rangle = |\phi\rangle + \left(E - \hat{H}_0 + i\epsilon\right)^{-1} \hat{V}|\psi\rangle \tag{37}$$

In position representation (1D)

$$\langle x|\psi\rangle = \langle x|\phi\rangle + \langle x| \left(E - \hat{H}_0 + i\epsilon\right)^{-1} \int dx' |x'\rangle\langle x'|\hat{V}|\psi\rangle \tag{38}$$

$$= \langle x|\phi\rangle + \int dx' \langle x| \left(E - \hat{H}_0 + i\epsilon\right)^{-1} |x'\rangle V(x') \langle x'|\psi\rangle. \tag{39}$$

Green's function

$$G(x, x') = \langle x| \left(E - \hat{H}_0 + i\epsilon\right)^{-1} |x'\rangle \tag{40}$$

$$= \frac{1}{2\pi} \int dk \langle x|k\rangle \left(E - k^2/2m + i\epsilon\right)^{-1} \langle k|x'\rangle \tag{41}$$

$$= \frac{1}{2\pi} \int dk \frac{\exp\left[ik\left(x - x'\right)\right]}{E - k^2/2m + i\epsilon} \tag{42}$$

(43)

Lippmann-Schwinger III

Re-write denominator using $k_0^2 = 2m(E + i\epsilon)$

$$\frac{1}{E - k^2/2m + i\epsilon} = \frac{-2m}{k^2 - 2m(E + i\epsilon)} = \frac{-2m}{k^2 - k_0^2} = \frac{-2m}{(k - k_0)(k + k_0)} \tag{44}$$

So now the Green's function

$$G(x, x') = \frac{-2m}{2\pi} \int_{-\infty}^{\infty} dk \frac{\exp\left[ik\left(x - x'\right)\right]}{(k - k_0)(k + k_0)} \tag{45}$$

Close contour in upper half-plane, picks up residue at $k = k_0$

$$G(x, x') = \frac{-2m}{2\pi} 2\pi i \frac{\exp\left[ik_0\left(x - x'\right)\right]}{2k_0} = \frac{m}{ik_0} \exp\left[ik_0\left(x - x'\right)\right] \tag{46}$$

Repeat in 3D

$$G(x,x') = \langle x| \left(E - \hat{H}_0 + i\epsilon\right)^{-1} |x'\rangle \tag{47}$$

$$= \frac{1}{(2\pi)^3} \int\int\int d\mathbf{k} \frac{\exp\left[i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')\right]}{E - k^2/2m + i\epsilon} \tag{48}$$

$$= \frac{1}{(2\pi)^3} \int_0^\infty k^2 dk \int_{-1}^{1} d\cos\theta \int_0^{2\pi} d\phi \frac{\exp\left[ik\Delta r\cos\theta\right]}{E - k^2/2m + i\epsilon} \tag{49}$$

$$= \frac{2\pi}{(2\pi)^3} \int_0^\infty k^2 dk \left[\frac{\exp(ik\Delta r\cos\theta)}{ik\Delta r}\right]_{\cos\theta=-1}^{1} \frac{-2m}{k^2 - k_0^2} \tag{50}$$

$$= \frac{2\pi}{(2\pi)^3} \int_{-\infty}^\infty k^2 dk \frac{\exp(ik\Delta r)}{ik\Delta r} \frac{-2m}{k^2 - k_0^2} \tag{51}$$

Close contour in the upper half-plane, residue at $k = k_0$

$$G(x,x') = 2\pi i \frac{1}{(2\pi)^2} k_0^2 \frac{\exp(ik_0\Delta r)}{ik_0\Delta r} \frac{-2m}{2k_0} \tag{52}$$

$$= -m\frac{\exp(ik_0\Delta r)}{2\pi\Delta r} \tag{53}$$

Green's function generates *outgoing*[2] spherical waves

$$G(x, x') = -m \frac{\exp(ik_0 \Delta r)}{2\pi \Delta r} \tag{54}$$

Ingoing plane wave, plus spherical waves originating from the interaction region

$$\psi(x) = \phi(x) + \int dx' \, G(x, x') V(x') \psi(x') \tag{55}$$

at $r = x \gg x'$

$$\psi(\mathbf{r}) \simeq \exp(i\mathbf{k} \cdot \mathbf{r}) + f(\mathbf{k}, \mathbf{k}') \frac{\exp(ikr)}{r} \tag{56}$$

$\mathbf{k}$ is incoming wave vector, $\mathbf{k}' = k\mathbf{r}/r$ is the outgoing wave vector

[2] cf flux discussion

Cross sections

Asymptotic wave function

$$\psi(\mathbf{r}) \simeq \exp(i\mathbf{k}\cdot\mathbf{r}) + f(\mathbf{k},\mathbf{k}')\frac{\exp(ikr)}{r} \tag{57}$$

First term — $\exp(i\mathbf{k}\cdot\mathbf{r})$: Linear flux $j_{\mathbf{k}} = k/m$
Second term — $\frac{\exp(ikr)}{r}$: Radial flux $j_r r^2 d\Omega = k/m$
$\Rightarrow |f(\mathbf{k},\mathbf{k}')|^2$ gives flux through $r^2 d\Omega$ normalized to incoming flux.

$$\frac{d\sigma}{d\Omega} = |f(\mathbf{k},\mathbf{k}')|^2 \tag{58}$$

$$\sigma = \int d\Omega \frac{d\sigma}{d\Omega} = \int_{-1}^{1} d\cos\theta \int_0^{2\pi} d\phi |f(\mathbf{k},\mathbf{k}')|^2 \tag{59}$$

Scattering amplitude from Lippmann-Schwinger

$$\psi(x) = \phi(x) + \int dx'\, G(x,x')V(x')\psi(x') \quad (60)$$

$$G(x,x') = -m\frac{\exp(ik_0\Delta r)}{2\pi\Delta r} \quad (61)$$

$$\Delta r = |\mathbf{x}-\mathbf{x}'| = r\sqrt{1-2\mathbf{x}\cdot\mathbf{x}'/r^2+\mathbf{x}'\cdot\mathbf{x}'/r^2} \quad (62)$$

$$\Delta r \simeq r-\mathbf{x}\cdot\mathbf{x}'/r = r-r'\cos\theta \quad (63)$$

$$\psi(x)-\phi(x) \simeq -\frac{m}{2\pi}\exp(ikr)/r\int dx'\exp(-ikr'\cos\theta)V(x')\psi(x') \quad (64)$$

$$= \exp(ikr)/r\left[\frac{-m}{2\pi}\int dx'\exp(-i\mathbf{k}'\cdot\mathbf{x}')V(x')\psi(x')\right] \quad (65)$$

$$\Rightarrow f(\mathbf{k},\mathbf{k'}) = \frac{-m}{2\pi}\langle\mathbf{k'}|V|\psi\rangle \quad (66)$$

Born

Lippmann-Schwinger:

$$|\psi\rangle = |\phi\rangle + \left(E - \hat{H}_0 + i\epsilon\right)^{-1} \hat{V}|\psi\rangle \tag{67}$$

Born series: Iterative solution

$$\begin{aligned} |\psi^{(0)}\rangle &= |\phi\rangle \\ |\psi^{(1)}\rangle &= |\phi\rangle + \left(E - \hat{H}_0 + i\epsilon\right)^{-1} \hat{V}|\phi\rangle \\ |\psi^{(n+1)}\rangle &= |\phi\rangle + \left(E - \hat{H}_0 + i\epsilon\right)^{-1} \hat{V}|\psi^{(n)}\rangle \end{aligned} \tag{68}$$

Born approximation is lowest order

$$f(\mathbf{k}, \mathbf{k'}) \approx \frac{-m}{2\pi}\langle \mathbf{k'}|V|\mathbf{k}\rangle \tag{69}$$

Optical Theorem

$$r = \sqrt{x^2 + y^2 + z^2} = z(1 + \frac{x^2 + y^2}{2z^2} + \dots) \tag{70}$$

$$r^{-1} = \left(x^2 + y^2 + z^2\right)^{-1/2} = 1/z(1 - \frac{x^2 + y^2}{2z^2} + \dots) \tag{71}$$

$$\psi(\mathbf{r}) = \exp(ikz) + f(\theta)\frac{\exp(ikr)}{r} \tag{72}$$

$$\approx \exp(ikz) + f(0)\frac{\exp(ikz)\exp(ik\frac{x^2+y^2}{2z})}{z} \tag{73}$$

$$d\psi/dz = ik\psi + \mathcal{O}(z^{-2})$$

$$\psi^* \frac{d}{dz}\psi = ik\left[1 + f(0)\frac{\exp(ik\frac{x^2+y^2}{2z})}{z} + f(0)^*\frac{\exp(-ik\frac{x^2+y^2}{2z})}{z} + \mathcal{O}(z^{-2})\right] \tag{74}$$

Optical Theorem II

$$\psi^* \frac{d}{dz}\psi = ik\left[1 + f(0)\frac{\exp(ik\frac{x^2+y^2}{2z})}{z} + f(0)^*\frac{\exp(-ik\frac{x^2+y^2}{2z})}{z} + \mathcal{O}(z^{-2})\right] \tag{75}$$

Using the Gaussian integral (Requires making k slightly complex)

$$\int_{-\infty}^{\infty} dx \exp(-x^2) = \sqrt{\pi} \tag{76}$$

$$\frac{1}{z}\int\int \exp(-ik\frac{x^2+y^2}{2z})dx\ dy = \frac{2\pi}{ik} \tag{77}$$

$$\int\int dxdy\psi^* \frac{d}{dz}\psi = ik - 2\pi(f - f^*) \tag{78}$$

Flux reduced from k/m by $\frac{4\pi}{m}\Im[f(0)]$

$$\sigma = \frac{4\pi}{k}\Im[f(0)] \tag{79}$$

Partial wave expansion

Plane wave

$$\exp(i\mathbf{k}\cdot\mathbf{z}) = \sum_l i^l(2l+1)j_l(kr)P_l(\cos\theta) \tag{80}$$

$$\simeq \frac{i}{2kr}\sum_l(2l+1)\left[(-1)^l\exp(-ikr)-\exp(ikr)\right]P_l(\cos\theta) \tag{81}$$

Scattered wave

$$f(\mathbf{k},\mathbf{k}') = \sum_l(2l+1)f_lP_l(\cos\theta) \tag{82}$$

$$f(\mathbf{k},\mathbf{k}')\frac{\exp(ikr)}{r} = \frac{1}{r}\sum_l(2l+1)f_l\exp(ikr)P_l(\cos\theta) \tag{83}$$

Total wave function

$$\psi \simeq \frac{i}{2kr}\sum_l(2l+1)\left[(-1)^l\exp(-ikr)-\exp(ikr)S_l\right]P_l(\cos\theta) \tag{84}$$

S-matrix and scattering amplitude

$$S_l = \exp(i2\delta_l) = 1+2ikf_l \tag{85}$$

Spherical Bessel function primer

Spherical Bessel functions

$$
\begin{aligned}
j_0(x) &= \sin(x)/x \\
j_l(x) &\simeq \sin(x - \ell\pi/2)/x \\
y_l(x) &\simeq -\cos(x - \ell\pi/2)/x
\end{aligned} \tag{86}
$$

Spherical Hankel functions

$$
\begin{aligned}
h_l^{(1)}(x) &= j_l(x) + iy_l(x) \\
h_l^{(2)}(x) &= j_l(x) - iy_l(x)
\end{aligned} \tag{87}
$$

Asymptotic form

$$
\begin{aligned}
h_\ell^{(1)}(x) &\simeq i^{\ell+1}\exp(ix) \\
j_\ell(x) &= \frac{1}{2}\left[h_\ell^{(1)}(x) + h_\ell^{(2)}(x)\right] \\
&= \frac{i}{2}\left[i^{\ell}\exp(ix) - i^{-\ell}\exp(-ix)\right]
\end{aligned} \tag{88}
$$

S-matrix, T-matrix, and cross sections again

$$S_l = \exp(i2\delta_l) = 1 + 2ikf_l \quad (89)$$

$$f_l = \frac{1}{2ik}(S_l - 1) = \frac{1}{2ik}T_l \quad (90)$$

Cross section

$$f(\cos\theta) = \sum_l (2l+1) f_l P_l(\cos\theta) \quad (91)$$

$$\sigma = \int\int d\Omega |f(\cos\theta)|^2 = 4\pi \sum_l (2l+1)|f_l|^2 = \frac{\pi}{k^2}\sum_l (2l+1)|T_l|^2 \quad (92)$$

Phase shift: $T = \exp(i2\delta) - 1$

$$|T| = |\exp(i\delta) - \exp(-i\delta)| = |2i\sin(\delta)| \quad (93)$$

$$\sigma = \frac{4\pi}{k^2}\sum_l (2l+1)\sin^2\delta_l \quad (94)$$

Wave packets

Plane wave ⇒ Gaussian wave packet

$$\begin{aligned}\psi &= \int dk \exp(ikx) \exp\left[-(k-k_0)^2 d^2\right] \\ &= \exp(ik_0 x) \int dk' \exp(ik'x) \exp(-k'^2 d^2)\end{aligned} \tag{95}$$

Complete square $(kd - ix/2d)^2 = k^2 d^2 - ikx - x^2/4d^2$:

$$\begin{aligned}\ldots &= \exp(ik_0 x) \int dk \exp\left[-(kd - i/2d)^2 - x^2/4d^2\right] \\ &= \exp(ik_0 x) \exp(-x^2/4d^2) \int dk \exp\left[-(kd - i/2d)^2\right]\end{aligned} \tag{96}$$

Plane wave with finite spatial extent

$$\psi \simeq \exp(ik_0 x) \exp(-x^2/4d^2) \tag{97}$$

Wave packets II

Time dependence

$$\begin{aligned}
\psi(t) &= \int dk \exp\left(-i\frac{k^2}{2m}t\right)\exp(ikx)\exp\left[-(k-k_0)^2 d^2\right] \\
&= \exp(-k_0^2 d^2)\int dk \exp\left(-i\frac{k^2}{2m}t - k^2 d^2 + 2kk_0 d^2 + ikx\right) \\
&= \exp(-k_0^2 d^2)\int dk \exp\left(-k^2\tilde{d}^2 + ik\tilde{x}\right) \qquad (98)
\end{aligned}$$

where

$$\begin{aligned}
\tilde{d}^2 &= d^2 + \frac{i}{2m}t, \\
\tilde{x} &= x - 2ik_0 d^2. \qquad (99)
\end{aligned}$$

Neglecting time dependence of width $\tilde{d}$

$$\psi \simeq \exp\left(-\frac{\tilde{x}^2}{4\tilde{d}^2}\right) \approx \exp(ik_0 x)\exp\left[-\frac{(x-\frac{k_0}{m}t)^2}{4d^2}\right] \qquad (100)$$

Wave packets IIb

Again, define:

$$\tilde{d}^2 = d^2 + \frac{i}{2m}t,$$
$$\tilde{x} = x - 2ik_0 d^2. \tag{101}$$

Now for $\tilde{x}^2/4\tilde{d}^2$:

$$1/\tilde{d}^2 = \frac{\tilde{d}^{2*}}{|\tilde{d}^2|^2} \approx 1/d^2(1 - \frac{i}{2md^2}t),$$
$$\tilde{x}^2 \approx x^2 - 4ik_0 d^2 x.$$
$$\frac{\tilde{x}^2}{\tilde{d}^2} = \frac{x^2}{d^2} - \frac{2k_0 x}{md^2}t - 4ik_0 x - \frac{ix^2 t}{2md^4} \tag{102}$$

Neglecting time dependence of width $\tilde{d}$

$$\psi \simeq \exp\left(-\frac{\tilde{x}^2}{4\tilde{d}^2}\right) \approx \exp(ik_0 x)\exp\left[-\frac{(x - \frac{k_0}{m}t)^2}{4d^2}\right] \tag{103}$$

Wave packets III

Now make wave packets of scattering wave functions

$$\exp(ikx) \to \exp(ik \cdot r) + f(\theta)\frac{\exp(ikr)}{r} \tag{104}$$

Second term

$$f(\theta)\int_0^\infty k^2 dk \frac{\exp(ikr)}{r}\exp(-i\frac{k^2}{2m}t)\exp\left[-(k-k_0)^2 d^2\right] \tag{105}$$

Complete square identically

$$f(\theta)\frac{1}{r}\exp(-\frac{\tilde{r}^2}{4\tilde{d}^2})\int_0^\infty k^2 dk \exp(-k^2) \tag{106}$$

$$\psi \simeq f(\theta)\frac{1}{r}\exp(ik_0 r)\exp\left[-\frac{(r-\frac{k_0}{m}t)^2}{4d^2}\right] \tag{107}$$

Exponentially suppressed at $t < 0$.
At large t: Gaussian wave packet moving outward at radial velocity k_0/m.

Hard-sphere scattering, s-wave

$$\left[-\frac{d^2}{dr^2}+\frac{\hat{l}^2}{r^2}+2\mu V(r)-2\mu E\right][r\psi(r)]=0,$$

$$\left[-\frac{d^2}{dr^2}+\frac{l(l+1)}{r^2}-k^2\right][r\psi_l(r)]=0. \quad (108)$$

With boundary condition $\psi(a)=0$.
For $l=0$ s-wave

$$\begin{aligned} r\psi_0(r) &= \sin[k(r-a)] = [\exp(ikr-ika)-\exp(-ikr+ika))/2i \\ &= \exp(ika)[\exp(-i2ka)\exp(ikr)-\exp(-ikr)]/2i, \\ \psi &= \frac{i}{2kr}\sum_l(2l+1)\left[(-1)^l\exp(-ikr)-\exp(ikr)S_l\right]P_l(\cos\theta) \end{aligned} \quad (109)$$

$\Rightarrow S_0=\exp(-2ika)$ or $\delta_0=-ka$ Cross section

$$\begin{aligned} \sigma &= \frac{4\pi}{k^2}\sin^2(ka) \\ \lim_{k\to 0} &= 4\pi a^2 \end{aligned} \quad (110)$$

Hard-sphere scattering, $l > 0$

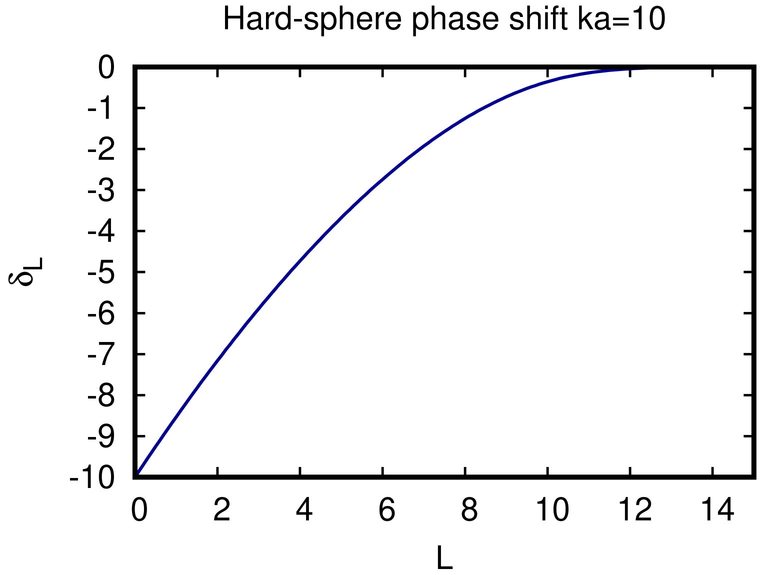
$$\left[\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - k^2\right][r\psi_l(r)] = 0. \tag{111}$$

Boundary condition $\psi(a) = 0$.

$$\psi_l(r) \simeq j_l(kr)\cos\delta_l - y_l(kR)\sin\delta_l$$
$$\tan\delta_l = \frac{j_l(ka)}{y_l(ka)} \tag{112}$$

δ_l is a monotonic function of l starting at $-ka$, decaying where $l \approx ka$. If $ka \gg \pi$, then $\sin^2\delta_l$ is essentially random, and equal to $1/2$ on average.

$$\sigma = \frac{4\pi}{k^2}\sum_l (2l+1)\sin^2(\delta_l)$$
$$\approx \frac{4\pi}{k^2}\sum_{l=0}^{ka}\frac{2l+1}{2} = \frac{2\pi}{k^2}(ka+1)^2 \approx 2\pi a^2 \tag{113}$$



Hard-sphere phase shift ka=10
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
δ_L
0
2
4
6
8
10
12
14
L

Repulsive Soft-sphere, s-wave

Repulsive soft-sphere potential V_1 $(k'^2 = 2\mu(V_1 - E))$

$$\psi_1(r) = c \sinh(k' r) \tag{114}$$
$$\psi_2(r) = \sin(kr + \delta) \tag{115}$$

Continuity of wavefunction and derivative

$$c \sinh(k' a) = \sin(ka + \delta) \tag{116}$$
$$ck' \cosh(k' a) = k \cos(ka + \delta) \tag{117}$$

Yields

$$\delta = -ka + \tan^{-1}\left[\frac{k}{k'} \tanh(k' a)\right] \approx -ka + \frac{k}{k'} \tag{118}$$

Last step for large V_1 $(k' \gg k)$

Cross section from short-range wave function

Scattering amplitude

$$f(\mathbf{k},\mathbf{k'}) = \frac{-m}{2\pi}\langle \mathbf{k'}|V|\psi\rangle \tag{119}$$

s-wave only:

$$\begin{aligned} \langle r|\phi\rangle &= j_0(kr) = \frac{\sin(kr)}{kr}, \\ \langle r|\psi\rangle &= \begin{cases} j_0(kr+\delta) & r > a \\ c\exp(k'r)/kr & r < a \end{cases} \end{aligned} \tag{120}$$

where $c = \sin(ka+\delta)/\exp(k'a)$. Consider $k' \gg k$ or $\delta \approx -ka + k/k'$.

$$\langle \mathbf{k'}|V|\psi\rangle = \frac{c}{k^2}V\int_0^{2\pi}\int_{-1}^{1}\int_0^a \frac{\exp(k'r)}{r}\frac{\sin(kr)}{r}r^2 dr d\Omega \tag{121}$$

$$\int_0^a \exp(k'r)\sin(kr)dr \approx \frac{1}{k'}\exp(k'a)\sin(ka) \tag{122}$$

Cross section from short-range wave function II

$$f(\mathbf{k},\mathbf{k'}) = \frac{-m}{2\pi}4\pi\frac{\sin(ka+\delta)}{k^2\exp(k'a)}V\frac{1}{k'}\exp(k'a)\sin(ka)$$
$$= -\frac{2mV}{k'^2}k'\sin(ka+\delta)\frac{\sin(ka)}{k^2} \qquad (123)$$

Now $ka+\delta = \tan^{-1}[\frac{k}{k'}\tanh(k'a)]$ and $\sin(\tan^{-1}(x)) = x/\sqrt{1+x^2} \approx x$

$$f(\mathbf{k},\mathbf{k'}) = -k'\frac{k}{k'}\tanh(k'a)\frac{\sin(ka)}{k^2} \approx -\frac{\sin(ka)}{k}. \qquad (124)$$

And with $ka \approx \delta$ this gives precisely

$$\sigma = \int |f|^2 d\Omega = \frac{4\pi}{k^2}\sin^2\delta. \qquad (125)$$

Attractive Soft-sphere, *s*-wave

Attractive soft-sphere potential $-V_1$ $(k'^2 = 2\mu(V_1 + E))$

$$\psi_1(r) = c\sin(k'r) \tag{126}$$

$$\psi_2(r) = \sin(kr + \delta) \tag{127}$$

Continuity of wavefunction and derivative

$$c\sin(k'a) = \sin(ka + \delta) \tag{128}$$

$$ck'\cos(k'a) = k\cos(ka + \delta) \tag{129}$$

Yields

$$\begin{aligned}\delta &= -ka + \tan^{-1}\left[\frac{k}{k'}\tan(k'a)\right] \\ &\approx k\left[-a + \frac{1}{k'}\tan(k'a)\right]\end{aligned} \tag{130}$$

Effective hard-sphere radius (scattering length)

$$a_0 = a - \frac{1}{k'}\tan(k'a) \tag{131}$$

Singularity at $k'a = \pi(n + \frac{1}{2})$ WKB quantization.

Numerical Methods

Initialize $\Phi = 0$ at $R_{\rm min}$

$$\Phi(R) = R\Psi(R) \tag{132}$$

Solution to

$$\left[-\frac{d^2}{dR^2} + \frac{l(l+1)}{R^2} + 2mV(R) - 2mE\right]\Phi(R) = 0 \tag{133}$$

Finite differences

$$\frac{d^2}{dR^2}\Phi \approx \frac{\Phi(R-\Delta) - 2\Phi(R) + \Phi(R+\Delta)}{\Delta^2} \tag{134}$$

Insert in radial Schrödinger equation, and solve for $\Phi(R_{n+1})$ from previous two values, $\Phi(R_n)$ and $\Phi(R_{n-1})$. Finally, match to asymptotic form

$$\psi \simeq \frac{i}{2kr}\sum_l (2l+1)\left[(-1)^l \exp(-ikr) - \exp(ikr)S_l\right] P_l(\cos\theta) \tag{135}$$

Inelastic scattering

Non-central potential $V(R,\xi)$
Total wave function expanded in "channels"

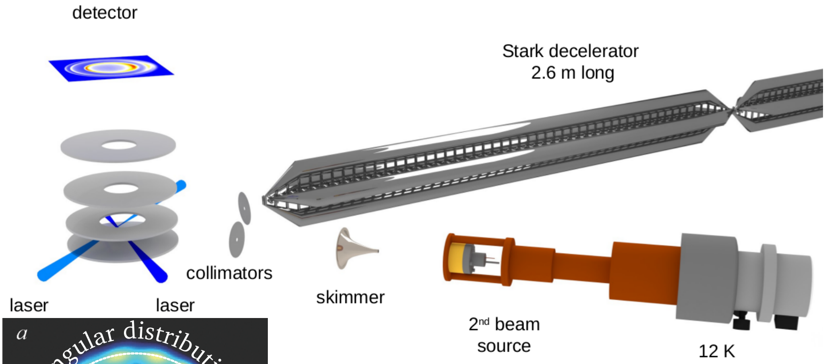
$$\Psi(R,\xi) = \frac{1}{R}\sum_n \Phi_n(R)|n\rangle \tag{136}$$

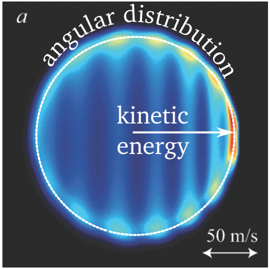
Propagate coupled equations numerically and match to

$$\psi_n \simeq \frac{i}{2kr}\sum_{l,l',n'}(2l+1)\left[(-1)^l \exp(-ikr)\delta_{l,l'}|n\rangle - \exp(ikr)S_{nl;n'l'}|n'\rangle\right] C^*_{l,0}(\mathbf{k})C_{l',m'}(\mathbf{R}). \tag{137}$$

Cross sections for $n \to n'$ from $S_{nl;n'l'}$.

Crossed Molecular Beams





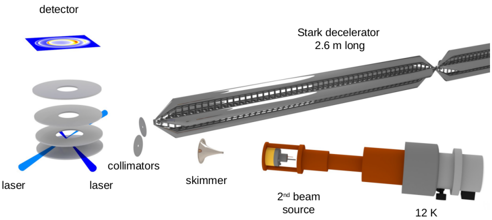
- State-to-state cross sections
- Velocity controlled

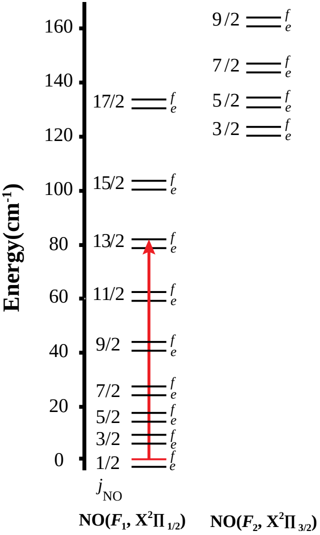
Bas van de Meerakker (Nijmegen)

NO – Rg Quantum Stereodynamics

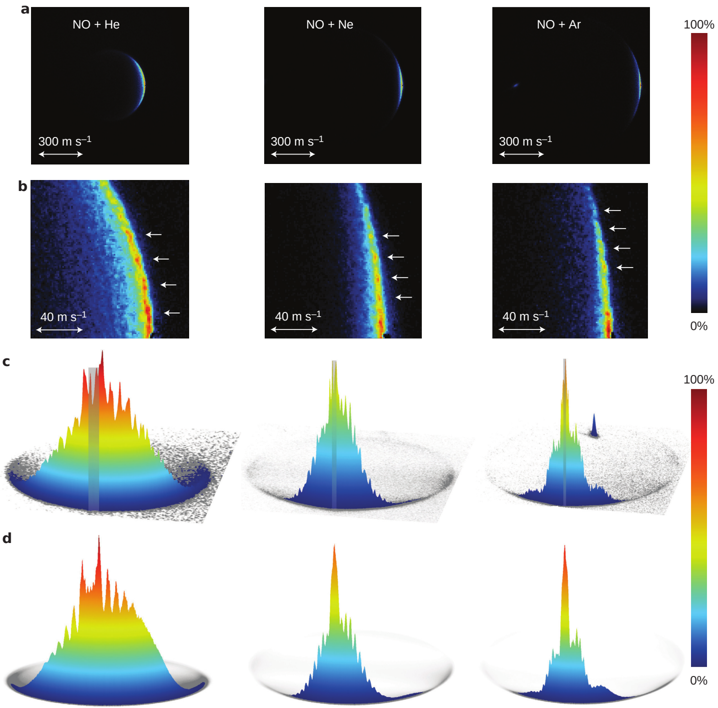
[Onvlee, *et al.* Nature Chem., **9**, 226 (2016)]

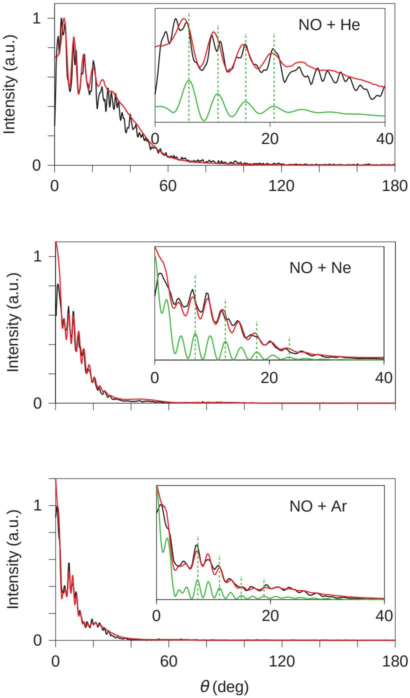
Crossed Molecular Beam





NO—He/Ne/Ar/Kr/Xe
500—700 cm^{-1}
700—1000 K

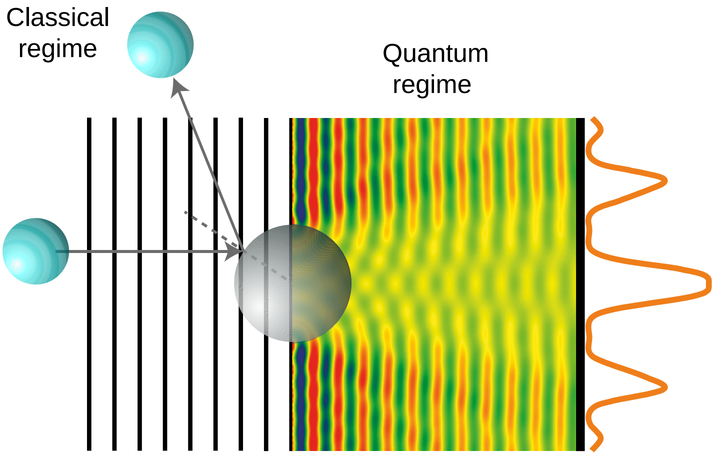

a
NO + He
NO + Ne
NO + Ar
300 m s–1
b
40 m s–1
c
d
100%
0%

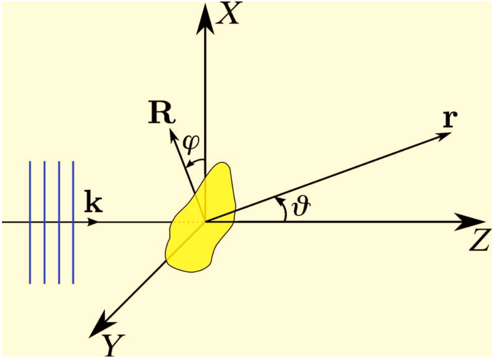


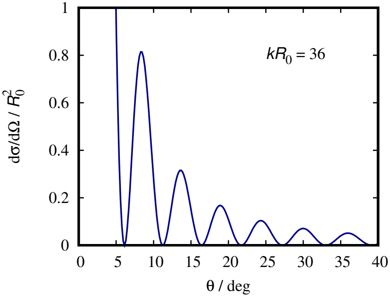
— Experimental intensity

— Simulated intensity
Based on theoretical DCS

— Theoretical DCS


Classical
regime
Quantum
regime





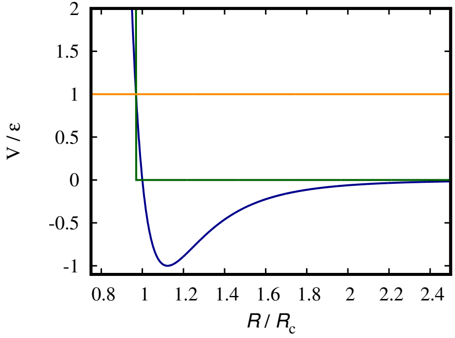
[M. Faubel J. Chem. Phys. **81**, 5559 (1984)]

[M. Lemeshko and B. Friedrich J. Chem. Phys. **129**, 024301 (2008)]

Fraunhofer cross section for spherical target

$$\frac{d\sigma}{d\Omega} = R_0^2 \left[\frac{J_1(kR_0 \sin\theta)}{\sin\theta} \right]^2 \tag{138}$$

Oscillations of order $\Delta\theta = \pi / kR_0$



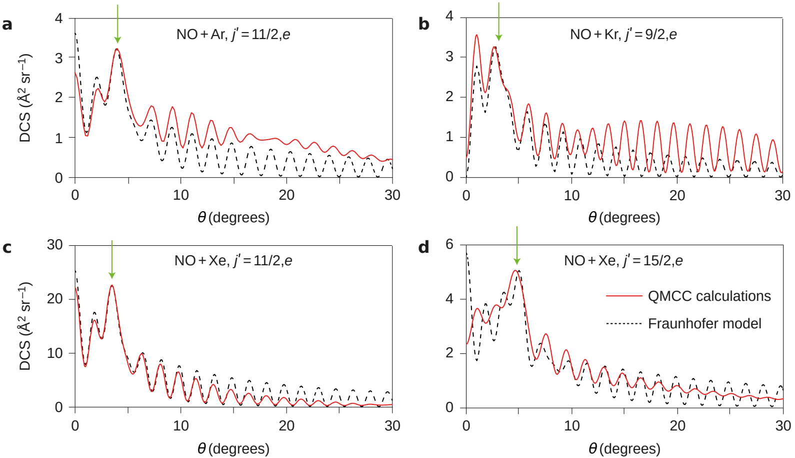
Expansion of hard shell

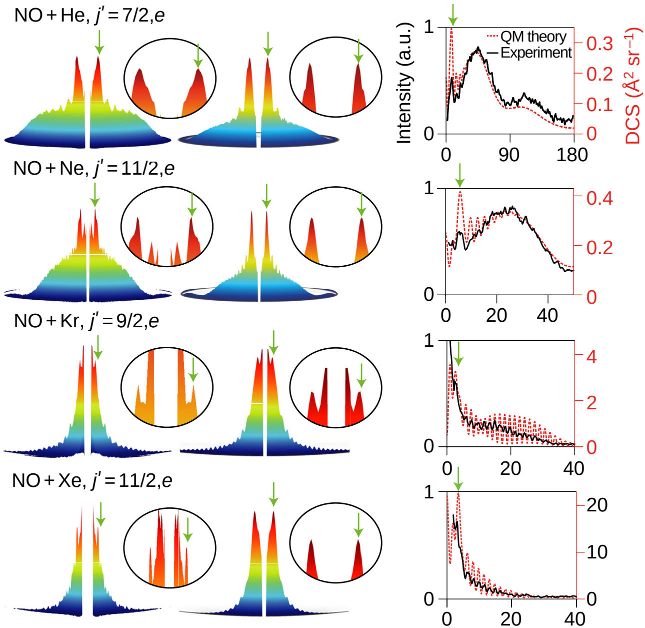
$$R(\beta) = R_0 + \sum_{\kappa>0} \Xi_\kappa P_\kappa(\beta) \quad (139)$$

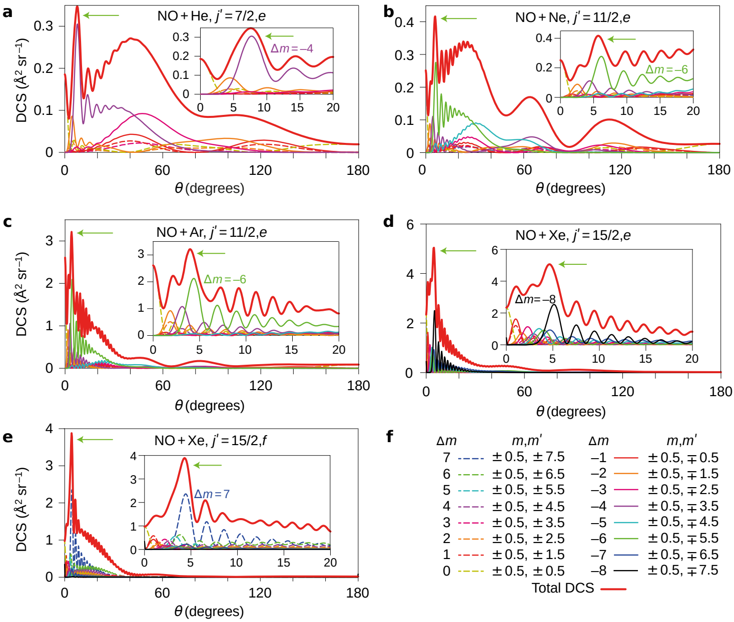
Scattering amplitude

$$f_{\epsilon,j,m\to\epsilon',j',m'}(\theta) = \frac{ikR_0}{4\pi} J_{|\Delta m|}(kR_0\theta) \sum_{\kappa>0} Q(\kappa, j, m, j', m') \left[(-1)^\kappa + \epsilon\epsilon'(-1)^{\Delta j}\right] \quad (140)$$

$$Q(\kappa, j, m, j', m') \propto \Xi_\kappa \quad (141)$$


a
NO + Ar, j′ = 11/2,e
b
NO + Kr, j′ = 9/2,e
c
NO + Xe, j′ = 11/2,e
d
NO + Xe, j′ = 15/2,e
QMCC calculations
Fraunhofer model
DCS (Å² sr⁻¹)
θ (degrees)


NO + He, j′ = 7/2,e
NO + Ne, j′ = 11/2,e
NO + Kr, j′ = 9/2,e
NO + Xe, j′ = 11/2,e
Intensity (a.u.)
DCS (Å² sr⁻¹)
QM theory
Experiment


a
NO + He, j′ = 7/2,e
Δm = –4
DCS (Å² sr⁻¹)
θ (degrees)
b
NO + Ne, j′ = 11/2,e
Δm = –6
c
NO + Ar, j′ = 11/2,e
Δm = –6
d
NO + Xe, j′ = 15/2,e
Δm = –8
e
NO + Xe, j′ = 15/2,f
Δm = 7
f
Δm m,m′ Δm m,m′
7 ±0.5, ±7.5 –1 ±0.5, ∓0.5
6 ±0.5, ±6.5 –2 ±0.5, ∓1.5
5 ±0.5, ±5.5 –3 ±0.5, ∓2.5
4 ±0.5, ±4.5 –4 ±0.5, ∓3.5
3 ±0.5, ±3.5 –5 ±0.5, ∓4.5
2 ±0.5, ±2.5 –6 ±0.5, ∓5.5
1 ±0.5, ±1.5 –7 ±0.5, ∓6.5
0 ±0.5, ±0.5 –8 ±0.5, ∓7.5
Total DCS

Expansion hard-shell radius

$$R(\beta) = R_0 + \sum_{\kappa>0} \Xi_\kappa P_\kappa(\beta) \tag{142}$$

Scattering amplitude

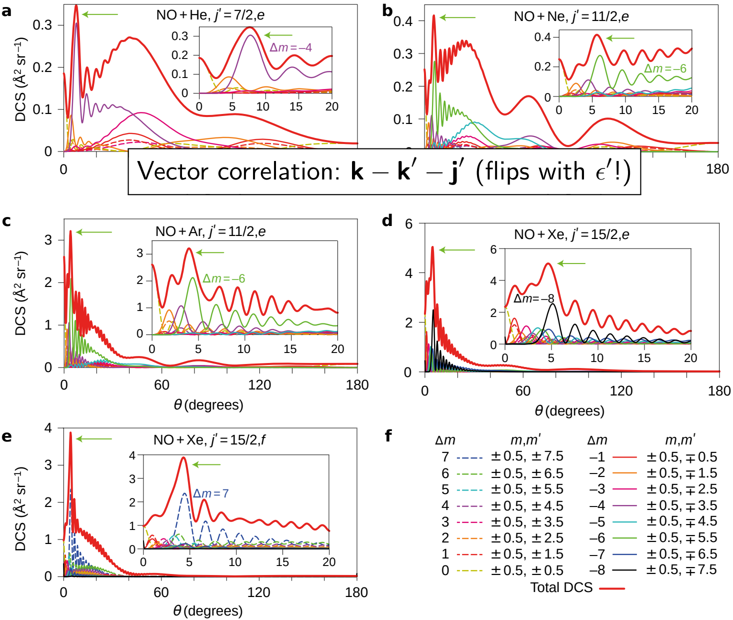
$$f_{\epsilon,j,m\to\epsilon',j',m'}(\theta) = \frac{ikR_0}{4\pi} \boxed{J_{|\Delta m|}(kR_0\theta)} \sum_{\kappa>0} \boxed{Q(\kappa,j,m,j',m')} \boxed{\left[(-1)^\kappa + \epsilon\epsilon'(-1)^{\Delta j}\right]} \tag{143}$$

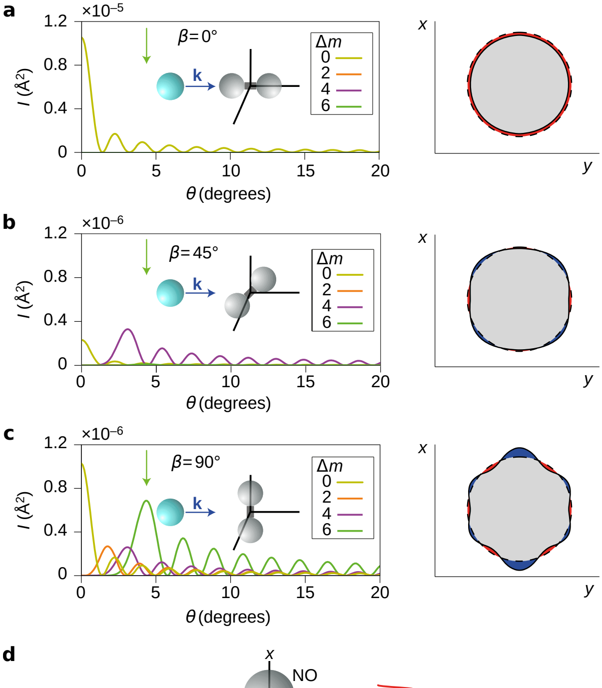
$$Q(\kappa,j,m,j',m') \propto \Xi_\kappa \tag{144}$$

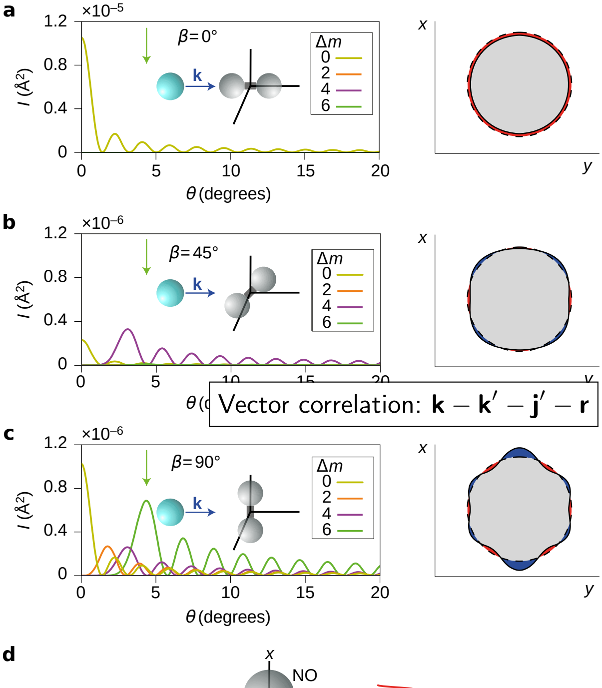
$j = 1/2 \Rightarrow \kappa = j' \pm 1/2$
Parity selects single κ
Q maximum for $\Delta m = j'\epsilon\epsilon' - 1/2$ (meaning $m' = \pm j'$)
First peak most intense, θ_f increases with $|\Delta m|$.

Vector correlation: $\mathbf{k} - \mathbf{k}' - \mathbf{j}'$

Vector correlation: $\mathbf{k} - \mathbf{k}' - \mathbf{j}'$ (flips with ϵ'!)




a
×10⁻⁵
1.2
0.8
0.4
0
I (Å²)
β = 0°
k
Δm
0
2
4
6
0
5
10
15
20
θ (degrees)
x
y
b
×10⁻⁶
β = 45°
c
×10⁻⁶
β = 90°
d
x
NO

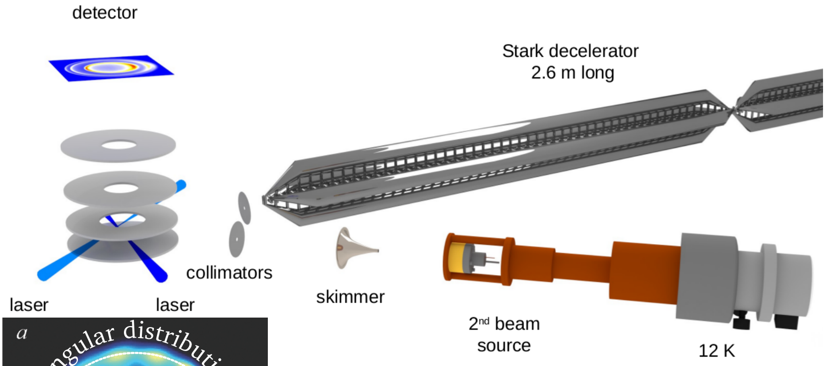


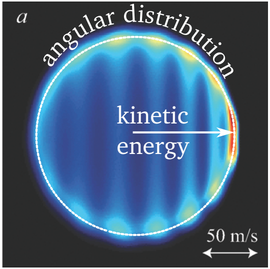
Vector correlation: $\mathbf{k} - \mathbf{k}' - \mathbf{j}' - \mathbf{r}$

$NO - H_2$ Resonances

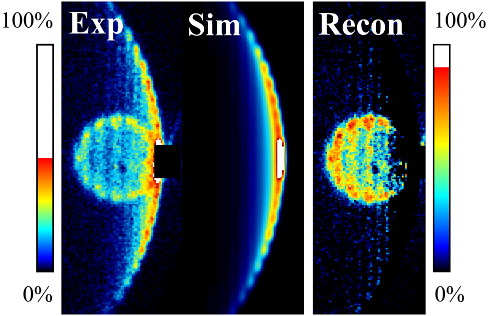
[Vogels, Karman, *et al.* Nature Chem. **10**, 435 (2018)]

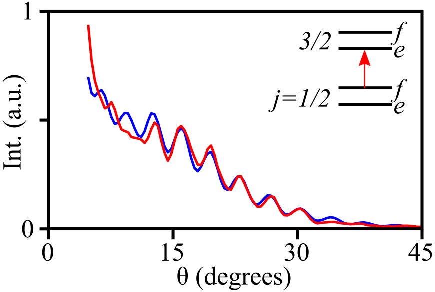
Molecular beam experiment





H_2 seeded in neon.



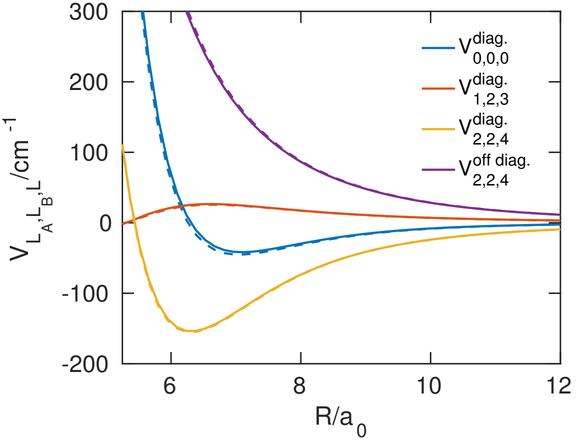


- Exp:
  Outer ring: Exp NO−Ne
  Inner ring: Exp NO − H_2
- Sim:
  Simulated NO−Ne signal
- Recon:
  Reconstructed
  NO − H_2 signal
- Bottom:
  Exp and Sim NO−Ne
  signal and as reference
  for ICS.

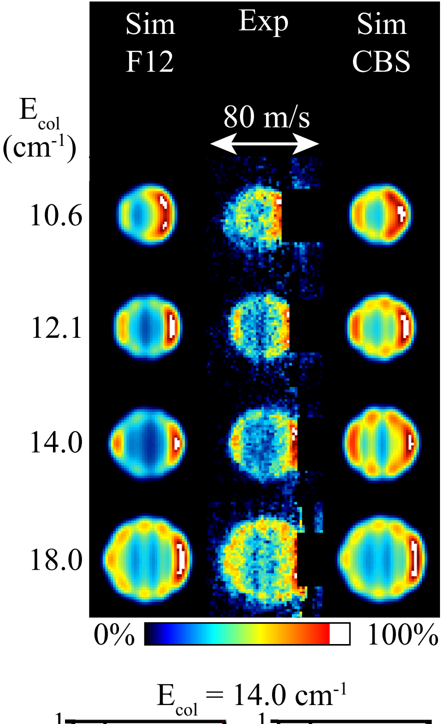
NO – H_2 potential

- - - **F12**-CCSD(T) / avtz+midbond / high-symmetry points
[Kłos *et al.* J. Chem. Phys., **146**, 114301 (2017)]

—— CCSD(T) / **CBS**(avtz,avqz) / quadrature points
[de Jongh, Karman, *et al.* J. Chem. Phys., **147**, 013918 (2017)]

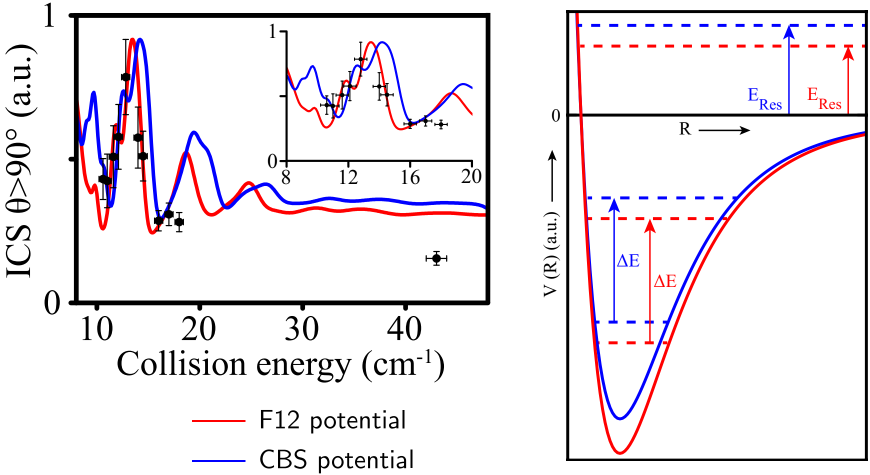


Simulation
F12 potential
[Kłos *et al.*
J. Chem. Phys., **146**,
114301 (2017)]



Simulation
CBS potential
[de Jongh *et al.*
J. Chem. Phys., **147**,
013918 (2017)]

Integral cross sections

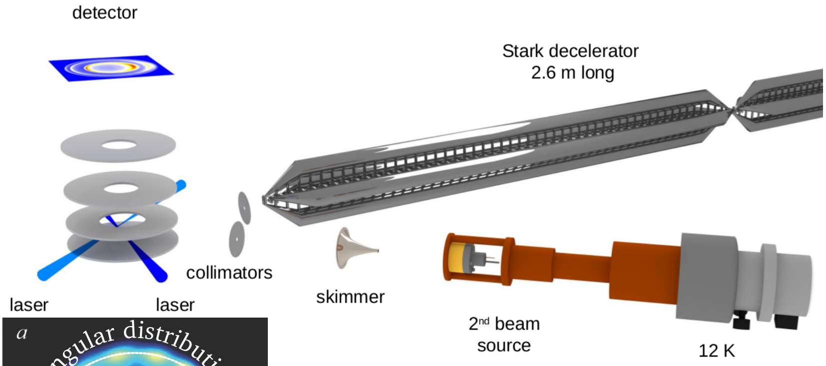


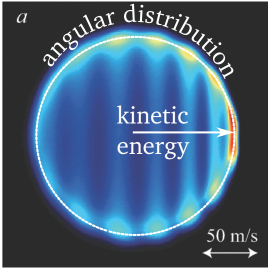
Deeper F12 potential fortuitously more accurate:
Discrepancy experiment and "gold standard" CCSD(T) resolved.

$NO - O_2$ Correlated Excitations

[Gao, Karman, *et al.* Nature Chem. **10**, 469 (2018)]

Molecular beam experiment

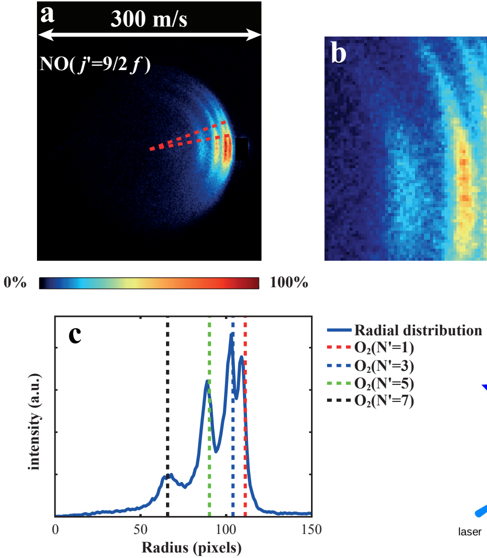


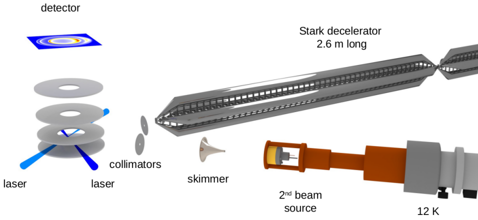


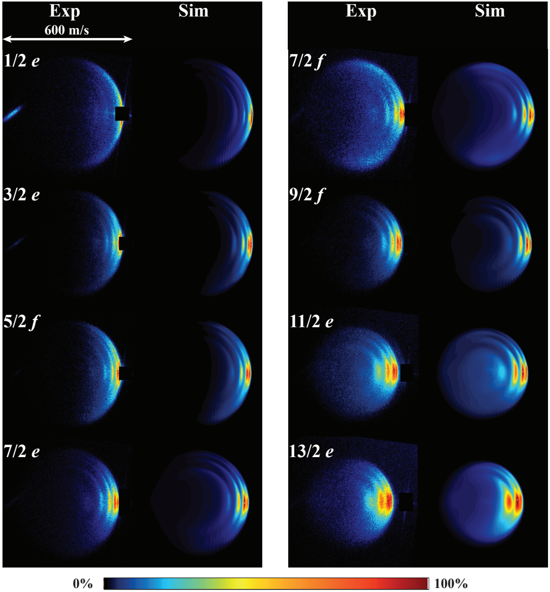
NO$-$O$_2$

Collision energy 160 cm^{-1}

Rotational "product pairs"

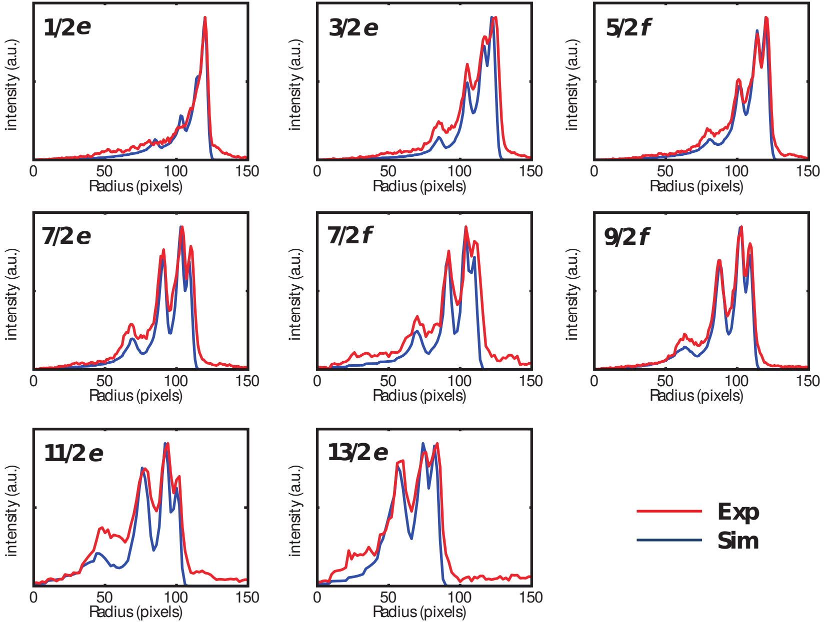






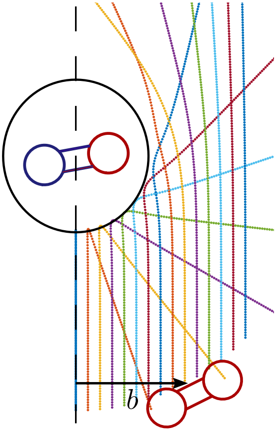
- Good agreement for both angular and radial distributions
- Clear trend:
  - Low NO states, O_2 scatters elastically
  - High NO states, O_2 inelastic channels dominate
- Violation energy-gap law

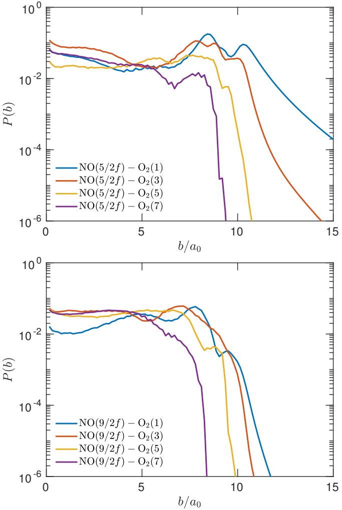
Radial distributions



Energy gap law — Opacity functions $P(b)$

$$\sigma = 2\pi \int_0^\infty P(b)\ b\ db$$



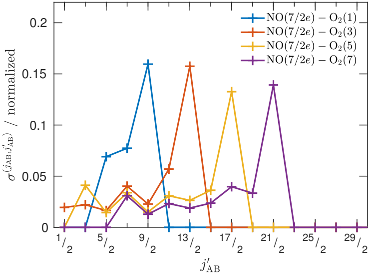


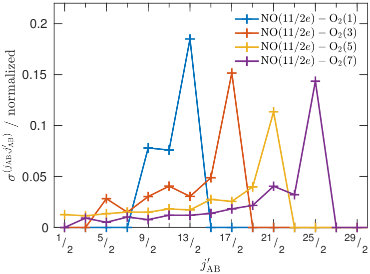
Low NO excitation

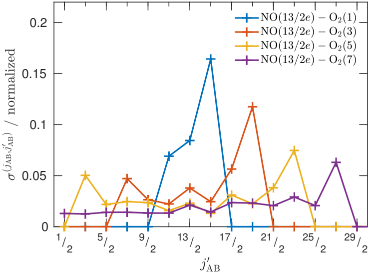
High NO excitation

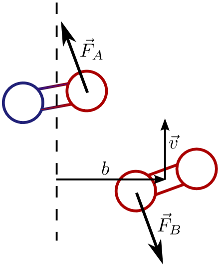
Head-on collisions / Glancing collisions

Vector correlation $\vec{j}_A$ and $\vec{j}_B$ stretched









Summary

- Plane, Spherical, and Partial Waves
- Wave Packets
- Lippmann-Schwinger
- Born Series and Approximation
- Optical Theorem
- Hard/Soft-Sphere Problems
- Sketch of Numerical Approach and Inelastic scattering
- Current Research