# Elastic, Inelastic, and Reactive Collisions Between Open-shell Polar Molecules

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# Outline

- OH $(^2\Pi_{3/2})$ + NO $(^2\Pi_{1/2})$ (Experiment FHI Berlin)
  - Stark controlled OH beam
  - Hexapole NO beam
  - Controlled collision energy: $70 - 300$ cm$^{-1}$
  - Theory and experiment for 4 inelastic channels
  - $\Rightarrow$ follow up of 2006 Xe+OH study

Gilijamse *et al.*, Science **313**, 1617 (2006): Xe+OH

Kirste *et al.*, Science **338**, 1060 (2012): OH+NO

- $^{15}$NH $(^3\Sigma^-)$+ $^{15}$NH $(^3\Sigma^-)$
  - Ultra cold collisions in magnetic trap $(1\mu K - 1K)$
  - Allow for reactive collisions ($\rightarrow$ $N_2$+$H_2$, $HN_2$+H)
  - Question: is evaporative cooling possible?

Liesbeth Janssen *et al.*, Phys. Rev. Lett. **110**, 063201 (2013)

# Acknowledgements

Theory Nijmegen

- Liesbeth Janssen
- Ad van der Avoird
- Koos Gubbels
- Tijs Karman

Theory Durham

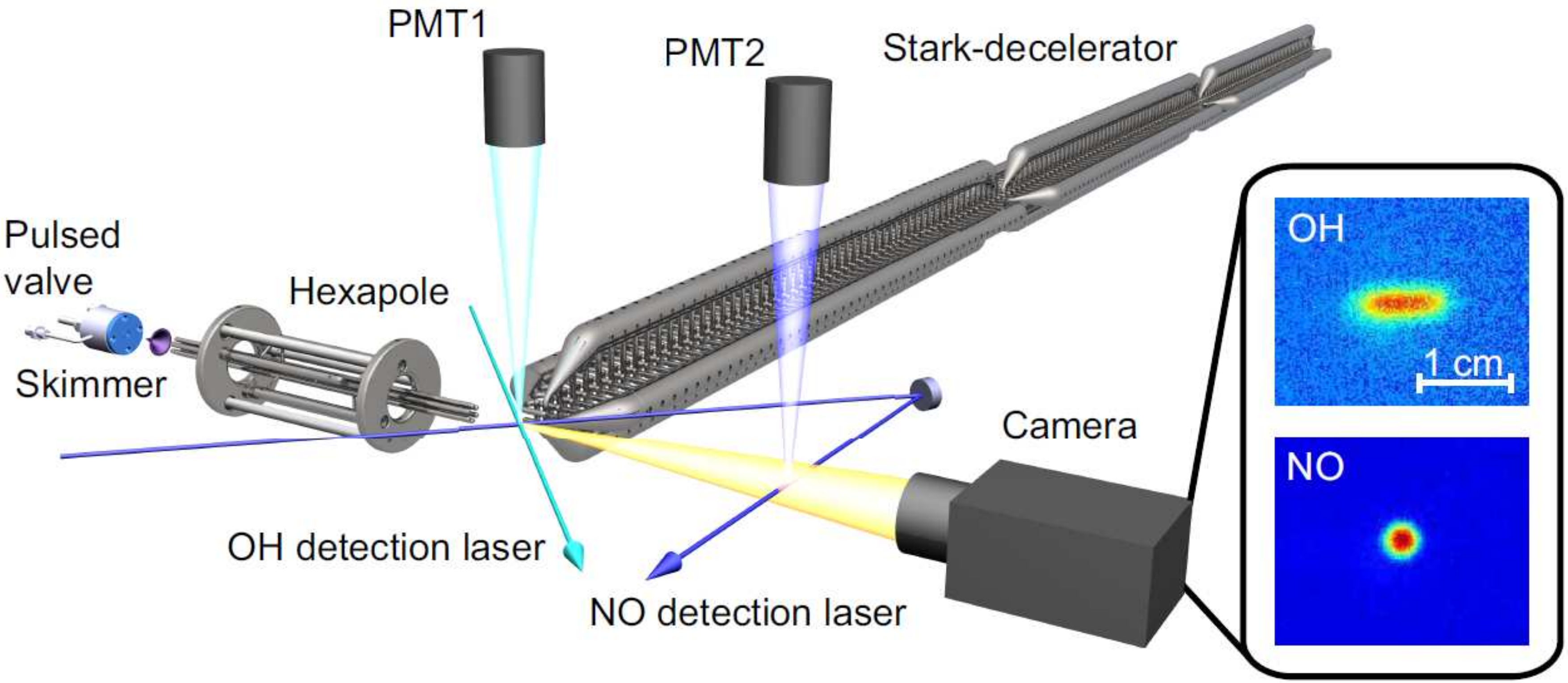
- Piotr Żuchowski
- Jeremy Hutson

OH+NO experiment FHI Berlin

- Moritz Kirste
- Xingan Wang
- H. Christian Schewe
- Kopin Liu (IAMS)
- Gerard Meijer
- Bas van de Meerakker

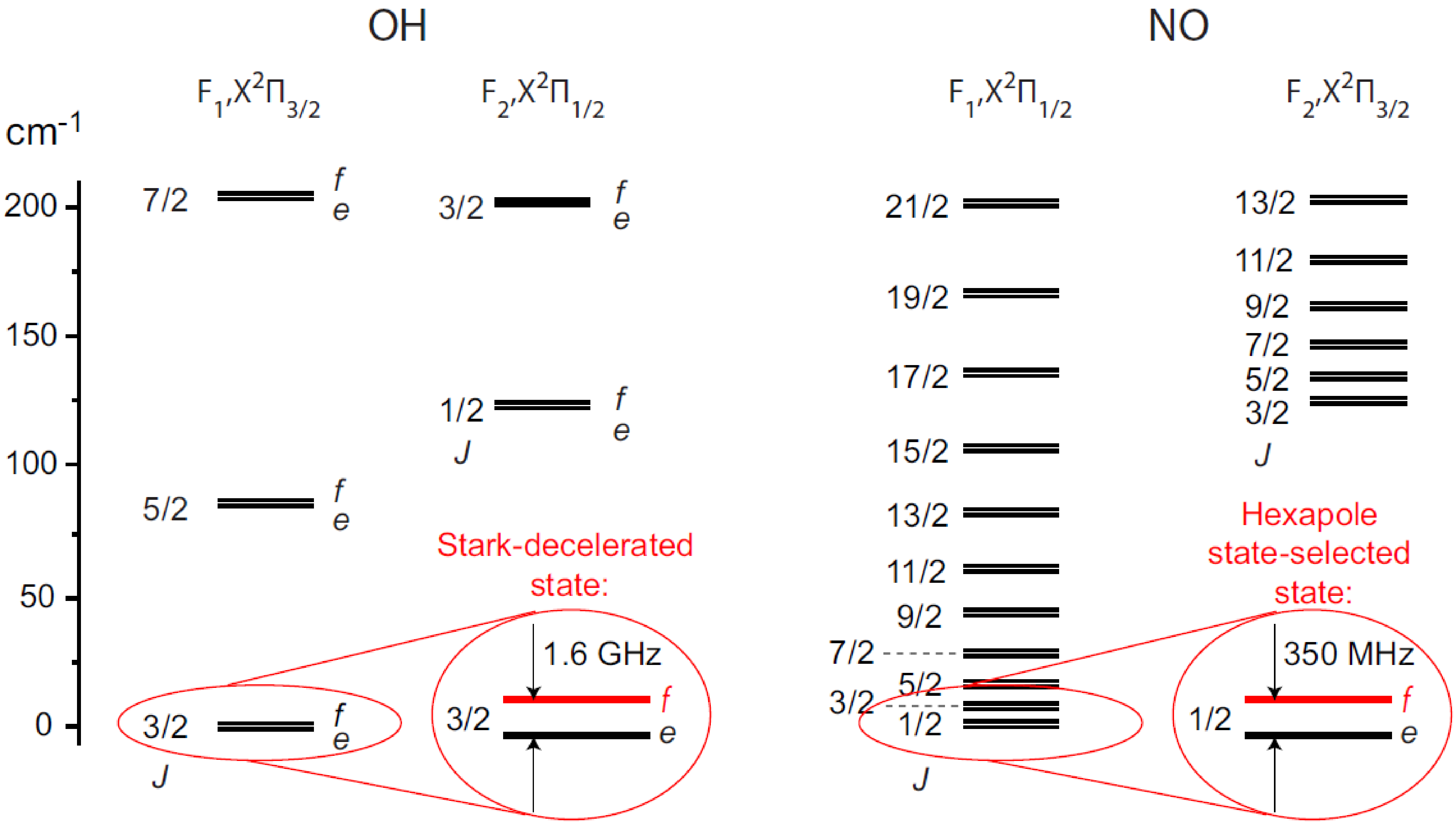
€: NWO-CW ECHO, ESF

# OH+NO Experiment (FHI, Berlin)



Moritz Kirste, Xingan Wang, Christian Schewe, Gerard Meijer, Kopin Liu, Bas vd Meerakker

# OH+NO energy levels



# **OH** $(X^2\Pi)$ **+ NO** $X(^2\Pi)$ **Hamiltonian**

$$\hat{H} = -\frac{1}{2\mu R}\frac{\partial^2}{\partial R^2}R + \frac{\hat{l}^2}{2\mu R^2} + \hat{H}_{\mathrm{OH}} + \hat{H}_{\mathrm{NO}} + \hat{V}$$

Monomers, using spectroscopy constants:

$$\hat{H}_X = \hat{H}_{\mathrm{rotation}} + \hat{H}_{\mathrm{spin-orbit}} + \hat{H}_{\Lambda-\mathrm{doubling}}$$

Interaction potential $\hat{V}$

- Doublet + doublet → singlet + triplet
- $\Pi \times \Pi \rightarrow$ four potentials (some reactive)

8 adiabatic potentials + nonadiabatic couplings: hopeless

Our hope: main inelastic channels dominated by long range

# Diabatic long range model

$$\hat{V} = \hat{V}_{\text{electrostatic}} - \frac{C_{6,\text{disp}} + C_{6,\text{ind}}}{R^6} + e^{-2(R-1.5)}$$

$$\hat{V}_{\text{electrostatic}} = \sum_{l_A m_A m'_A l_B m_B m'_B} \frac{C_{l_{AB},m_{AB}}(\theta_R,\phi_R)}{R^{l_A+l_B+1}} (-1)^{l_B} \begin{pmatrix} 2l_{AB} \\ 2l_A \end{pmatrix}^{\frac{1}{2}}$$

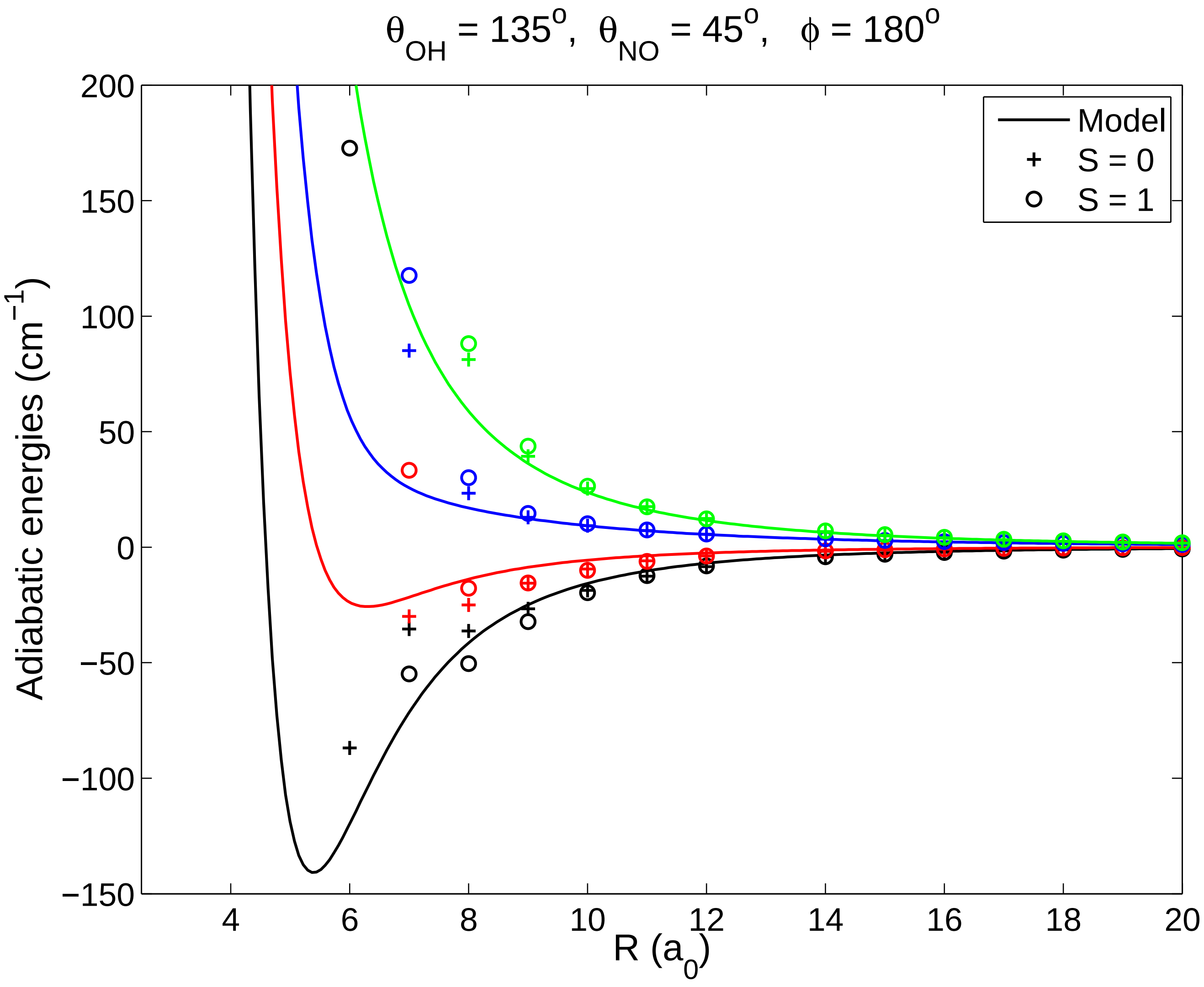
$$\hat{Q}_{l_A m_A} D^{(l_A)*}_{m'_A m_A}(\phi_A,\theta_A,0)\hat{Q}_{l_B m_B} D^{(l_B)*}_{m'_B m_B}(\phi_B,\theta_B,0)\langle l_A m_A l_B m_B | l_{AB} m_{AB}\rangle$$

OH and NO multipole moments included:

| | |
|---|---|
| Dipole | $Q_{1,0}$ |
| Quadrupole | $Q_{2,0}$, $Q_{2,\pm 2}$ |
| Octupole | $Q_{3,0}$, $Q_{3,\pm 2}$ |

# Test model potential

Comparison of adiabats with *ab initio* points

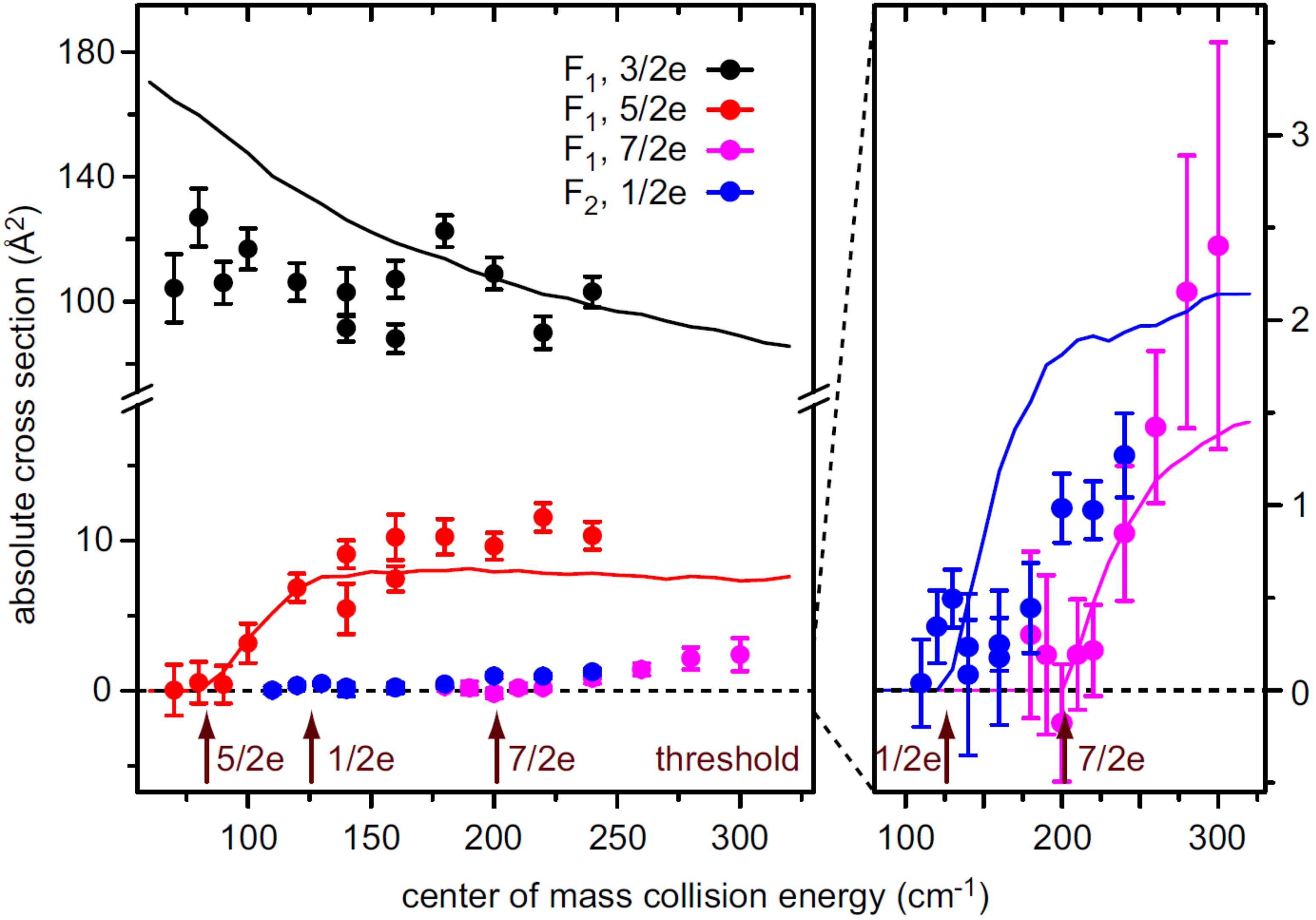


# Coupled channels calculation

- Space-fixed, parity adapted, coupled ($J_{\text{tot}}$) basis
- All (18) OH states with $j \leq 9/2$
- All (14) NO states with $j \leq 7/2$
- Partial waves: $0 \leq J_{\text{tot}} \leq 225$
- Total number of coupled channels: 4408
- $R$-grid: 3 to 35 $a_0$ in steps of 0.08 $a_0$
- Renormalized Numerov propagator

# $OH(^2\Pi)+NO(^2\Pi)$ inelastic cross sections

Theory (solid lines) vs experiment on absolute scale



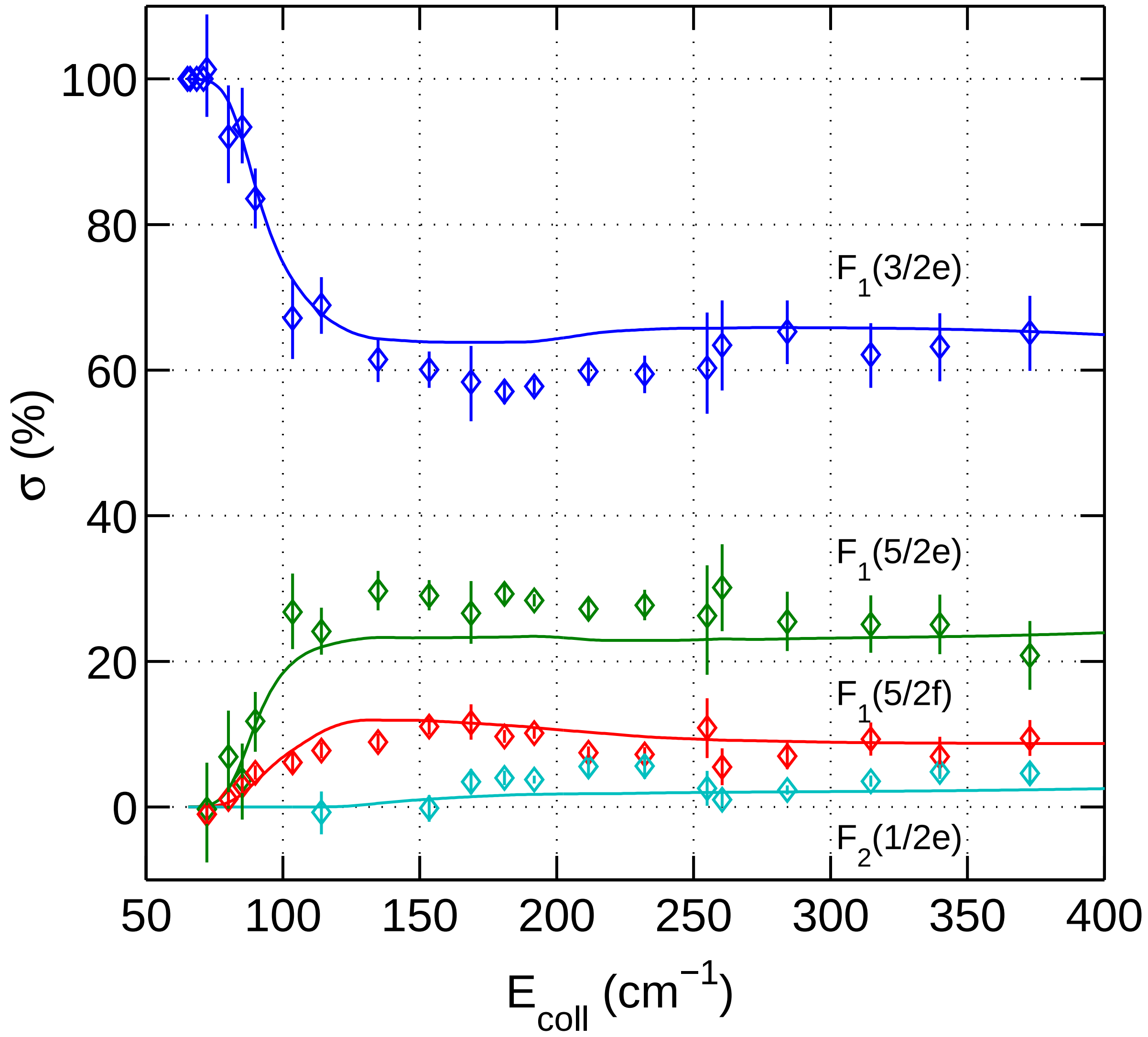
Experiment at $E = 220$ cm$^{-1}$, OH$(F_1, 3/2e)$: $90 \pm 38$ Å$^2$

# Correlated state-to-state cross sections

$$\mathrm{OH}[F_1(3/2f)] + \mathrm{NO}[F_1(1/2f)] \rightarrow \mathrm{OH}[F_1(3/2e)] + \mathrm{NO}$$

| $E_{\rm col}$ (cm$^{-1}$):<br>NO | 10 | 50 | 300 | |
|---|---|---|---|---|
| $F_1(1/2e)$ | 152 | 55 | 15 | $ff \rightarrow ee$ dipole-dipole |
| $F_1(1/2f)$ | 45 | 26 | 4 | |
| $F_1(3/2e)$ | 19 | 21 | 10 | |
| $F_1(3/2f)$ | 18 | 47 | 30 | |
| $F_1(5/2e)$ | | 9 | 5 | |
| $F_1(5/2f)$ | | 7 | 13 | |
| $F_1(7/2e)$ | | 5 | 4 | |
| $F_1(7/2f)$ | | 5 | 6 | |
| $F_2(3/2e)$ | | | $< 1$ | |
| elastic | 410 | 265 | 166 | $ff \rightarrow ff$ dominant |

# Xe+OH ($^2\Pi$)



- OH($F_1, 3/2e$) less dominant
- 2D *ab initio* PES
- relative cross sections

Gilijamse, Hoekstra, van de Meerakker, Groenenboom, Meijer, Science **313**, 1617 (2006)

# Parameters used for OH+NO

| | | OH | NO |
|---|---|---|---|
| $B_0$ | (cm$^{-1}$) | 18.5487 | 1.69611 |
| $A$ | (cm$^{-1}$) | -139.21 | 123.1393 |
| $p$ | (cm$^{-1}$) | 0.235 | 0.01172 |
| $q$ | (cm$^{-1}$) | -0.0391 | 0.00067 |
| $Q_{1,0}$ | $(ea_0)$ | 0.6472 | 0.07195 |
| $Q_{2,0}$ | $(ea_0^2)$ | 1.2709 | -0.8257 |
| $Q_{2,\pm2}$ | $(ea_0^2)$ | -1.1589 | 1.0158 |
| $Q_{3,0}$ | $(ea_0^3)$ | 2.3023 | 0.8946 |
| $Q_{3,\pm2}$ | $(ea_0^3)$ | -0.02894 | -1.4067 |
| $\alpha_0$ | $(a_0^3)$ | 7.4774 | 11.5180 |

Dispersion (isotropic part) $C_{6,\mathrm{disp}} = 45.2 E_h a_0^6$

Induction (isotropic part) $C_{6,\mathrm{ind}} = 4.91 E_h a_0^6$

For Xe+OH: 2-D aug-cc-pVQZ/CCSD(T) $A'$ and $A''$ PESs

# OH+NO conclusions

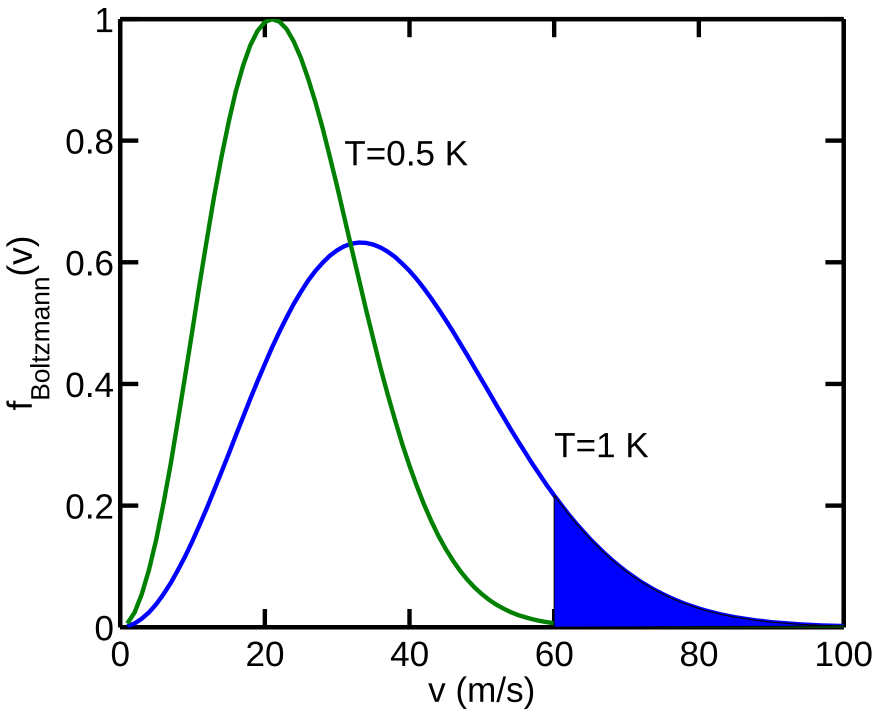
- Absolute, state-tot-state, inelastic cross sections
- Energy dependent
- OH $(F_1, 3/2f \rightarrow e)$ parity changing dominant

Diabatic long range model:

- OH parity changing, 50% impact parameter $> 12\ a_0$
- Dipole-dipole interaction dominant at low energy
- Many NO states contribute at higher energy
- Uncertainty in dominant channel: $\sim 8\%$.

M. Kirste, X. Wang, H. C. Schewe, G. Meijer, K. Liu, A. van der Avoird, L. M. C. Janssen, K. B. Gubbels, G. C. Groenenboom, and Bas van de Meerakker, Science, **338**, 1060 (2012)

# Evaporative cooling

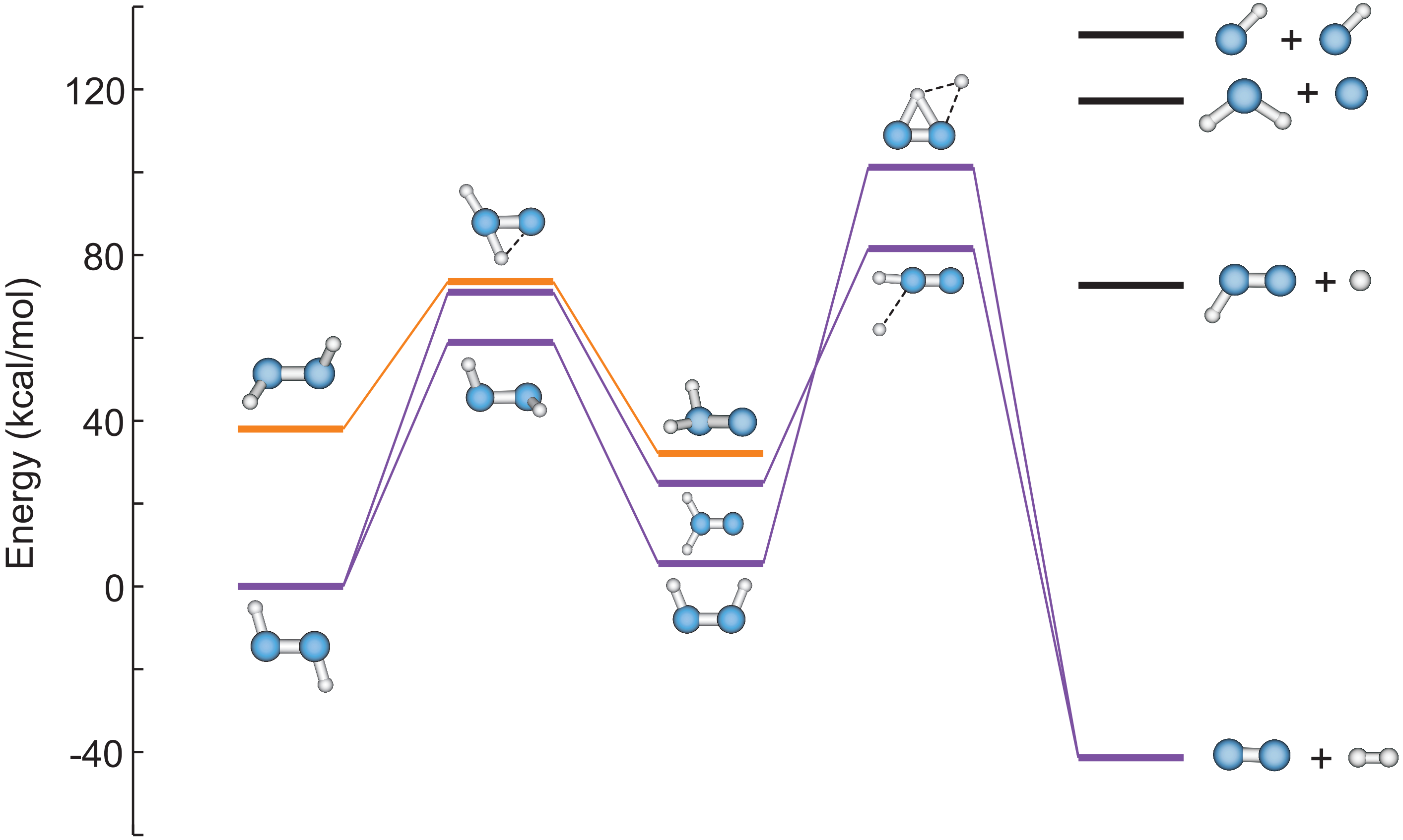


- Elastic collisions $\Rightarrow$ thermalizing
- Inelastic/spin changing collisions $\Rightarrow$ trap loss
- Condition: $K_{\rm el} \gg K_{\rm in}$

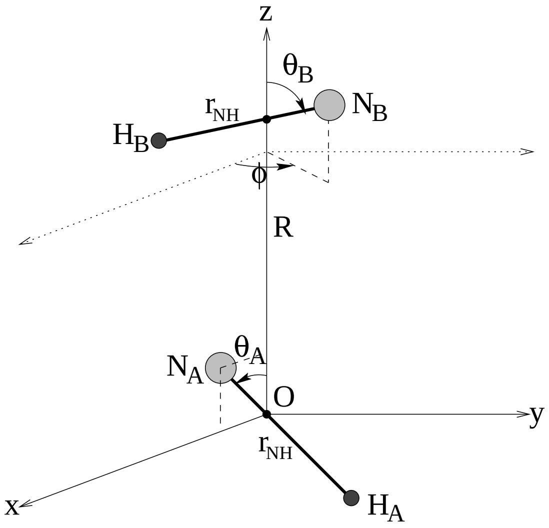
For He$^*$: $n \approx 10^{12}$ cm$^{-3}$ at $T \approx 500$ mK $\longrightarrow$ 5 $\mu$K BEC

Doret, Connoly, Ketterle, Doyle, Phys. Rev. Lett. **103**, 103005 (2009)

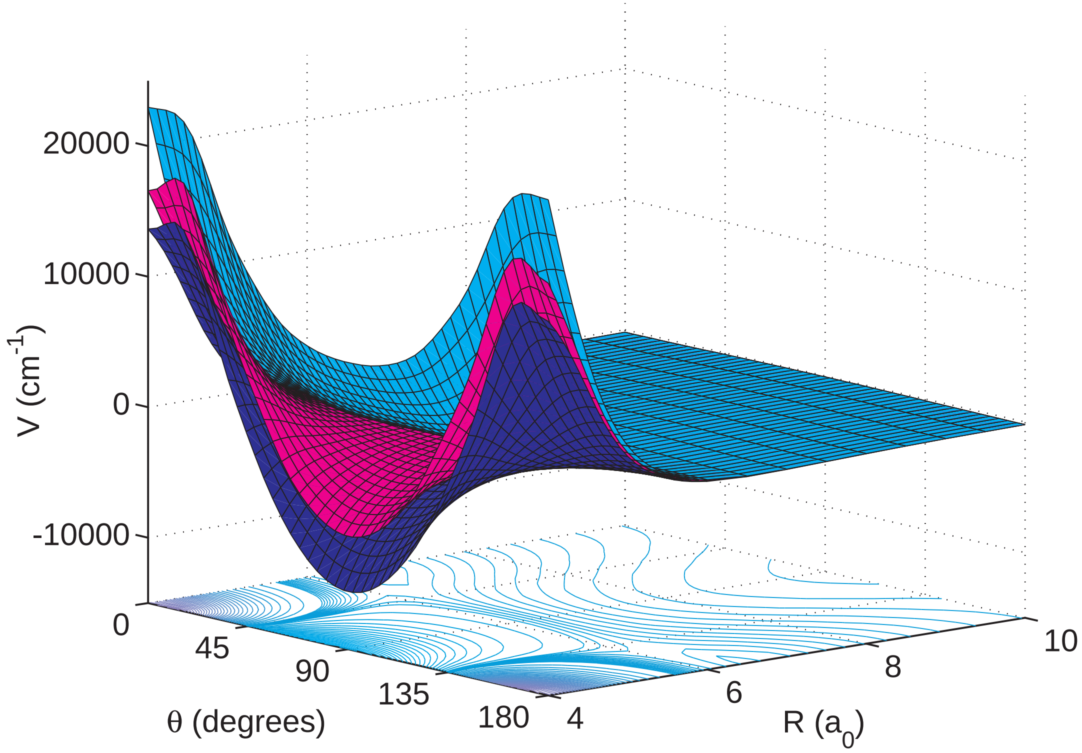
# NH $(^3\Sigma^-)$+NH $(^3\Sigma^-)$ chemistry



# $NH(^3\Sigma^-)$-$NH(^3\Sigma^-)$ 4D PESs

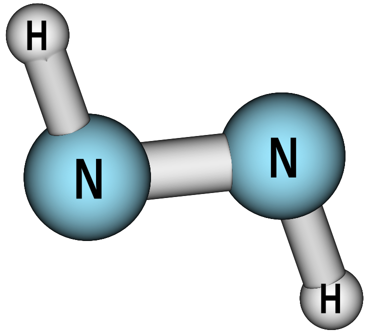


$r_{NH} = 1.0362$ Å (fixed)



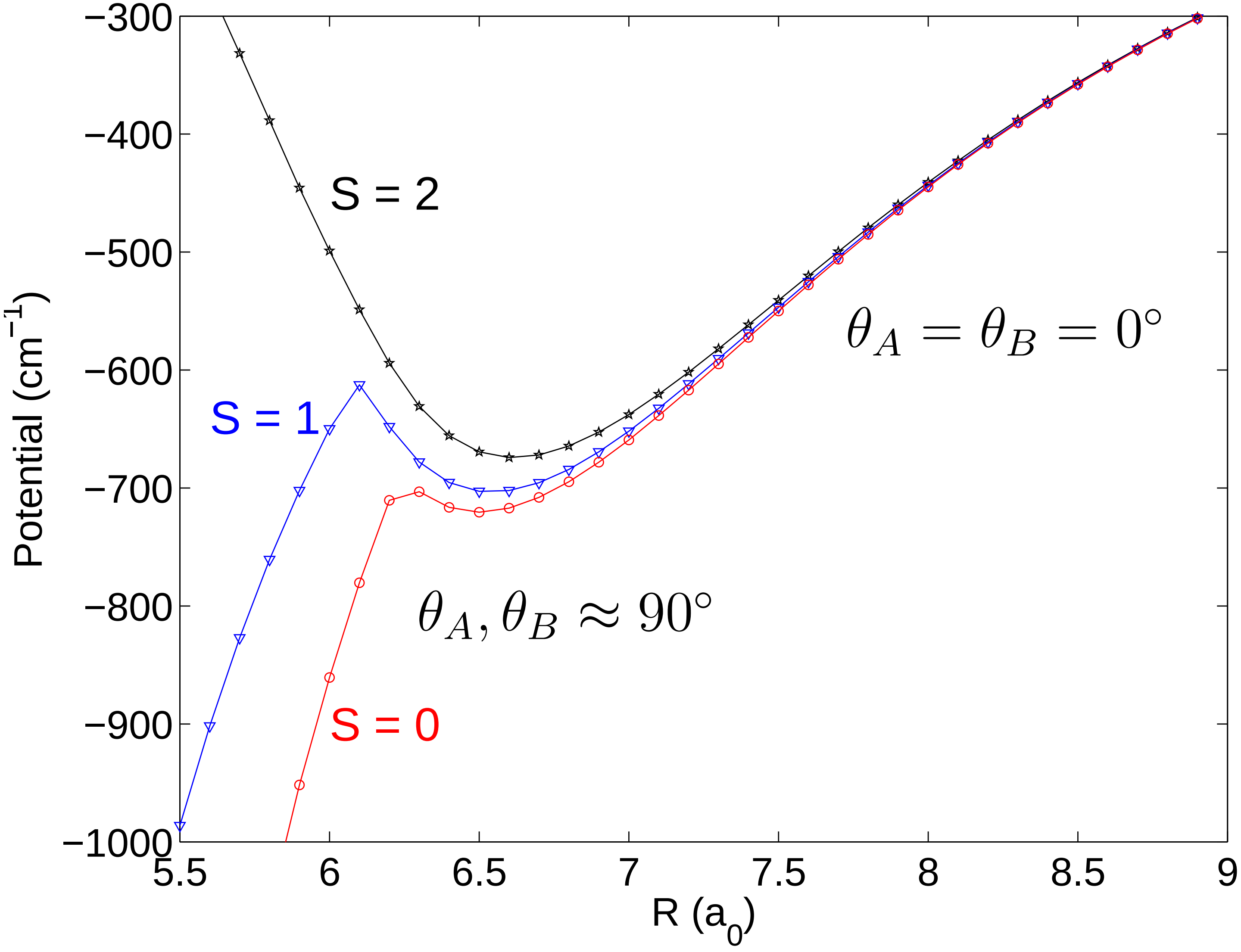
$\theta_A = \theta_B = \theta$

$$\text{triplet+triplet} \rightarrow \begin{cases} \text{quintet} & (S=2) \\ \text{triplet} & (S=1) \\ \text{singlet} & (S=0) \end{cases}$$



Janssen, GCG, vd Avoird, Żuchowski, and Podeszwa, J. Chem. Phys., **131**, 224314 (2009)

# NH-NH: all angles optimized



Dhont, van Lenthe, Groenenboom, and van der Avoird, J. Chem. Phys., **123**, 184302 (2005)

# NH-NH Hamiltonian

$$\underbrace{\frac{-\hbar^2}{2\mu R}\frac{\partial^2}{\partial R^2}R}_{\text{kinetic}}+\underbrace{\frac{\hat{l}^2}{2\mu R^2}}_{\text{centrifugal}}+\underbrace{\hat{V}(R,\theta_A,\theta_B,\phi)}_{\text{potential}}+\underbrace{\hat{H}_A+\hat{H}_B}_{\text{monomer terms}}+\underbrace{\hat{H}^{(\text{magn})}_{\text{dip}-\text{dip}}}_{\text{inter molecular}}$$

## Monomer terms:

$$\hat{H} = B_{\text{rot}}\hat{N}^2 + \gamma_{\text{SR}}\hat{N}\cdot\hat{S} + \frac{2}{3}\lambda_{\text{SS}}(3\hat{S}_z - \hat{S}^2) + \underbrace{g_e\mu_B\hat{B}\cdot\hat{S}}_{\text{Zeeman term}}$$

$$\left(B_{\text{rot}} = 16.3\ \text{cm}^{-1}, \gamma_{\text{SR}} = -0.055\ \text{cm}^{-1}, \lambda_{\text{SS}} = 0.92\ \text{cm}^{-1}\right)$$

## Magnetic dipole-dipole term

$$\hat{H}^{(\text{magn})}_{\text{dip}-\text{dip}} = -\sqrt{6}\frac{\alpha^2}{R^3}g_S^2\mu_B^2\sum_q(-1)^q C_{2,-q}(\hat{R})\left[\hat{S}_A\otimes\hat{S}_B\right]^{(2)}_q$$

# Scattering calculations

- Uncoupled basis set to include magnetic field

$$|N_A M_A\rangle|S_A M_{S_A}\rangle|N_B M_B\rangle|S_B M_{S_B}\rangle|L M_L\rangle$$

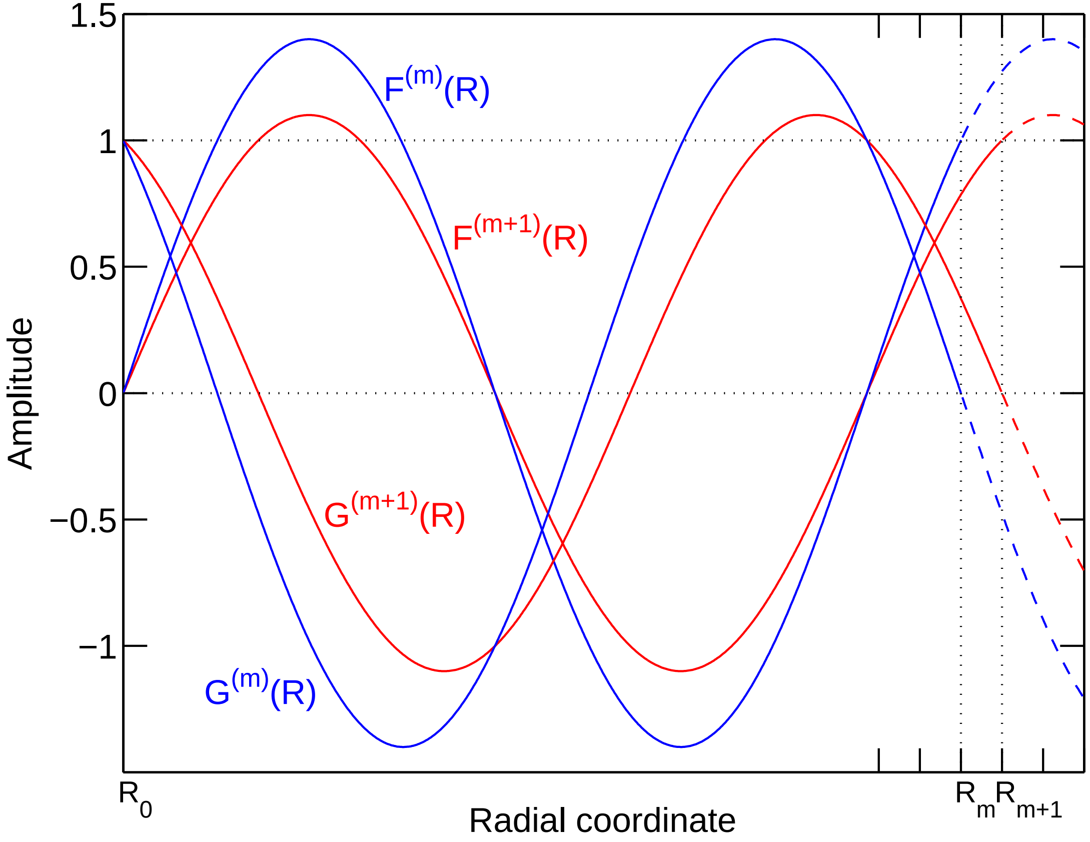
- Initial state: $N_A = N_B = 0, \quad M_{S_A} = M_{S_B} = 1$
- Basis set: $N_A, N_B \leq 2$, $L \leq 6$, $M_{\rm tot} = 2$

- Single arrangement reactive boundary conditions
- New renormalized Numerov type propagator

“Universal limit”, Z. Idziaszek, P. S. Julienne, Phys. Rev. Lett. **104**, 113203 (2010)

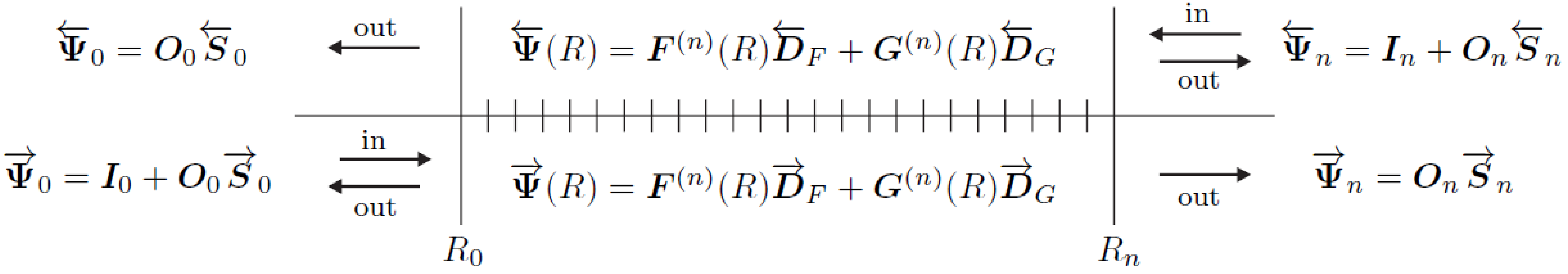
$$\begin{aligned} R_6 &= \frac{1}{2}(2\mu C_6/\hbar^2)^{\frac{1}{4}} && \text{van der Waals radius} \\ \bar{a} &= 4\pi R_6/\Gamma(1/4)^2 && \text{mean scattering length} \\ \sigma_{\rm elastic}(k) &= 4g\bar{a}^2 && (g=2) \\ \sigma_{\rm reactive}(k) &= 2g\bar{a}/k \end{aligned}$$

# Reactive Numerov propagator



- $F^{(m)}(R)$: regular solutions (inelastic scattering)
- $G^{(m)}(R)$: irregular solutions

# Reactive boundary conditions

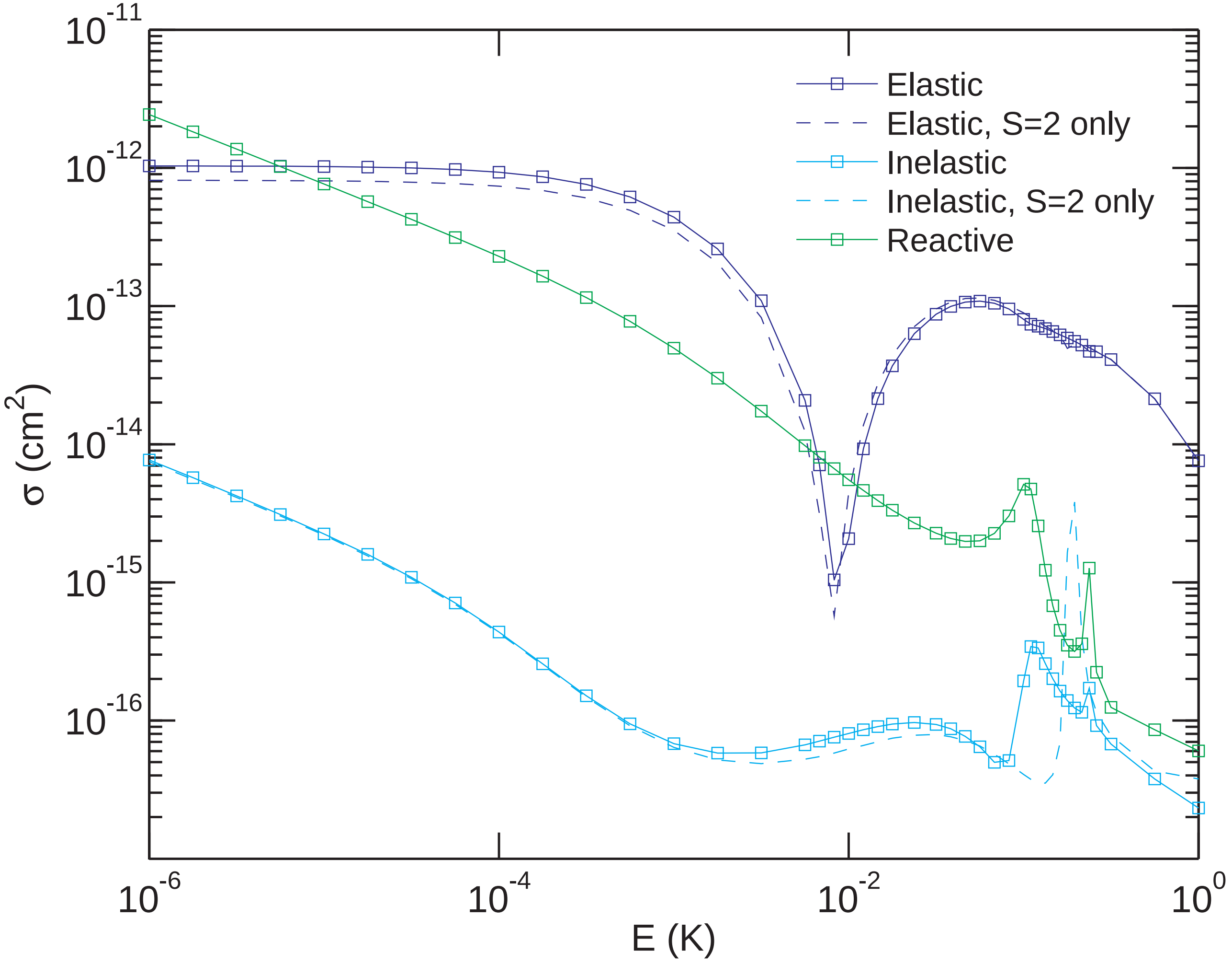


$$\overleftarrow{\boldsymbol{\Psi}}_0 = \boldsymbol{O}_0 \overleftarrow{\boldsymbol{S}}_0 \qquad \overleftarrow{\boldsymbol{\Psi}}(R) = \boldsymbol{F}^{(n)}(R)\overleftarrow{\boldsymbol{D}}_F + \boldsymbol{G}^{(n)}(R)\overleftarrow{\boldsymbol{D}}_G \qquad \overleftarrow{\boldsymbol{\Psi}}_n = \boldsymbol{I}_n + \boldsymbol{O}_n \overleftarrow{\boldsymbol{S}}_n$$

$$\overrightarrow{\boldsymbol{\Psi}}_0 = \boldsymbol{I}_0 + \boldsymbol{O}_0 \overrightarrow{\boldsymbol{S}}_0 \qquad \overrightarrow{\boldsymbol{\Psi}}(R) = \boldsymbol{F}^{(n)}(R)\overrightarrow{\boldsymbol{D}}_F + \boldsymbol{G}^{(n)}(R)\overrightarrow{\boldsymbol{D}}_G \qquad \overrightarrow{\boldsymbol{\Psi}}_n = \boldsymbol{O}_n \overrightarrow{\boldsymbol{S}}_n$$

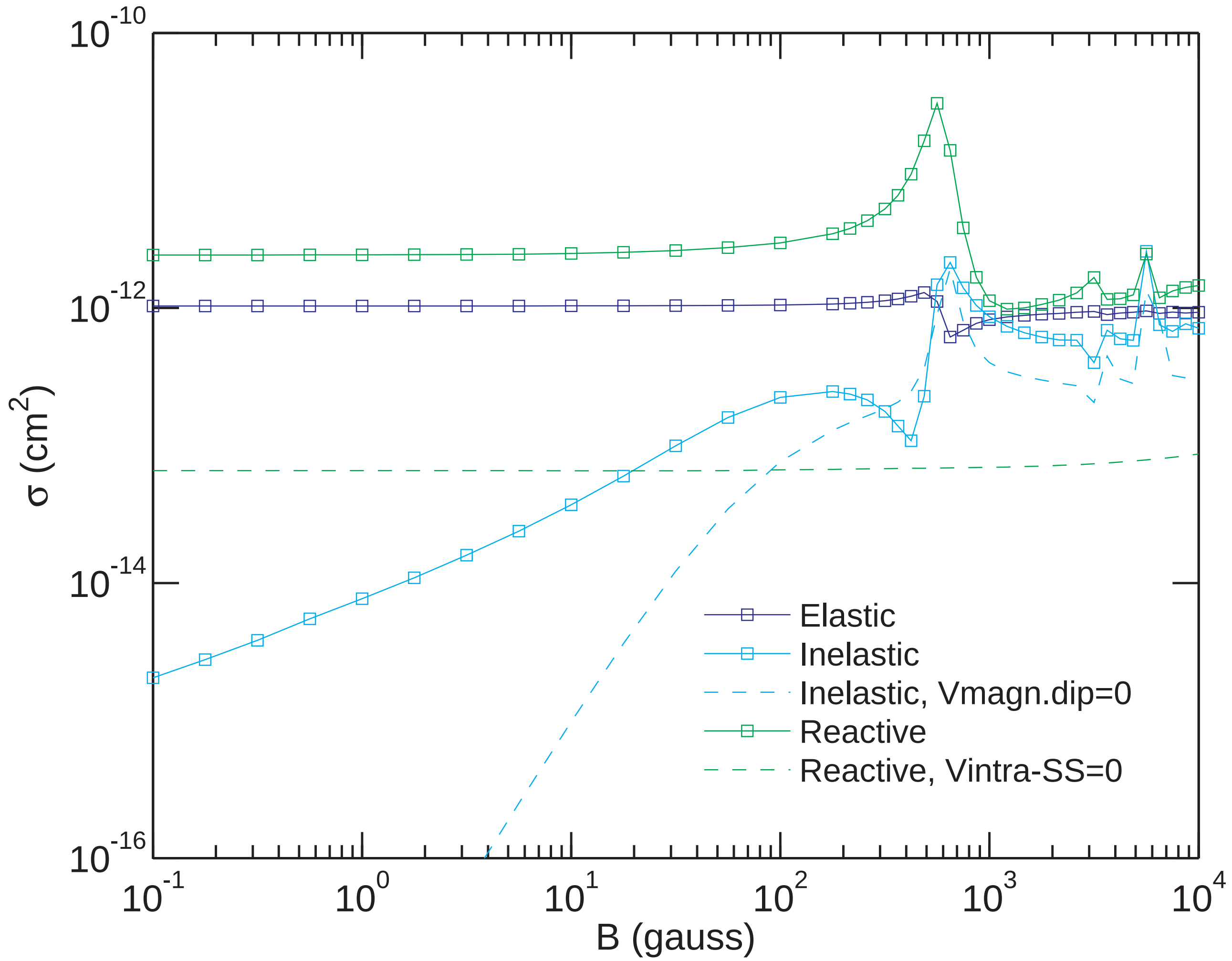
- Propagation: real functions
- Apply any boundary condition *after* propagation
- S-matrix is unitary
- Interval $[R_a, R_b]$+$[R_b, R_c] \rightarrow [R_a, R_c]$: parallel code

# $^{15}$NH+$^{15}$NH cross sections, $B = 1$ gauss



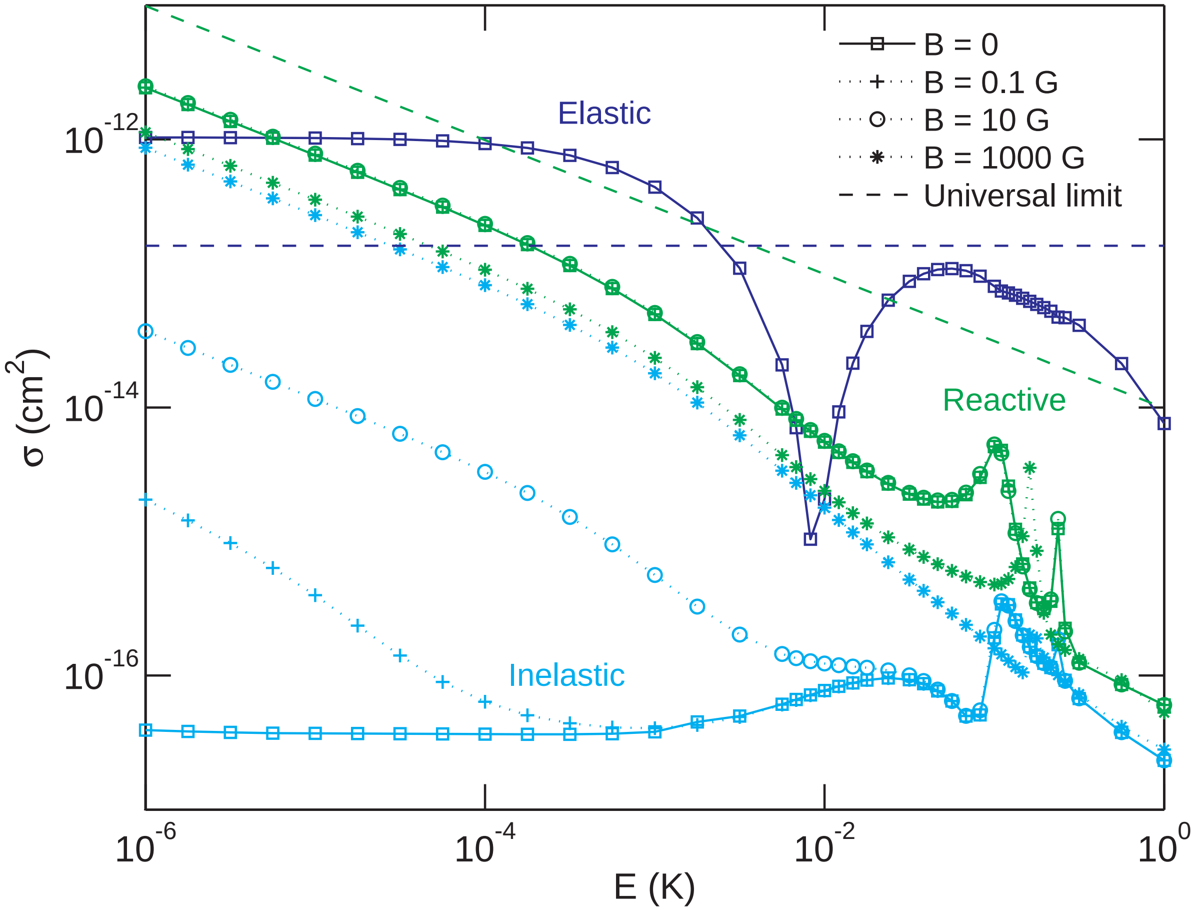
- Surprise: reaction > inelastic (below 0.1 K)
- Only quintet potential needed for elastic & inelastic

# $^{15}$NH+$^{15}$NH cross sections, $E = 1\mu$K



- Inelastic: long range inter-molecular spin-spin
- Reactive: short range intra-molecular spin-spin

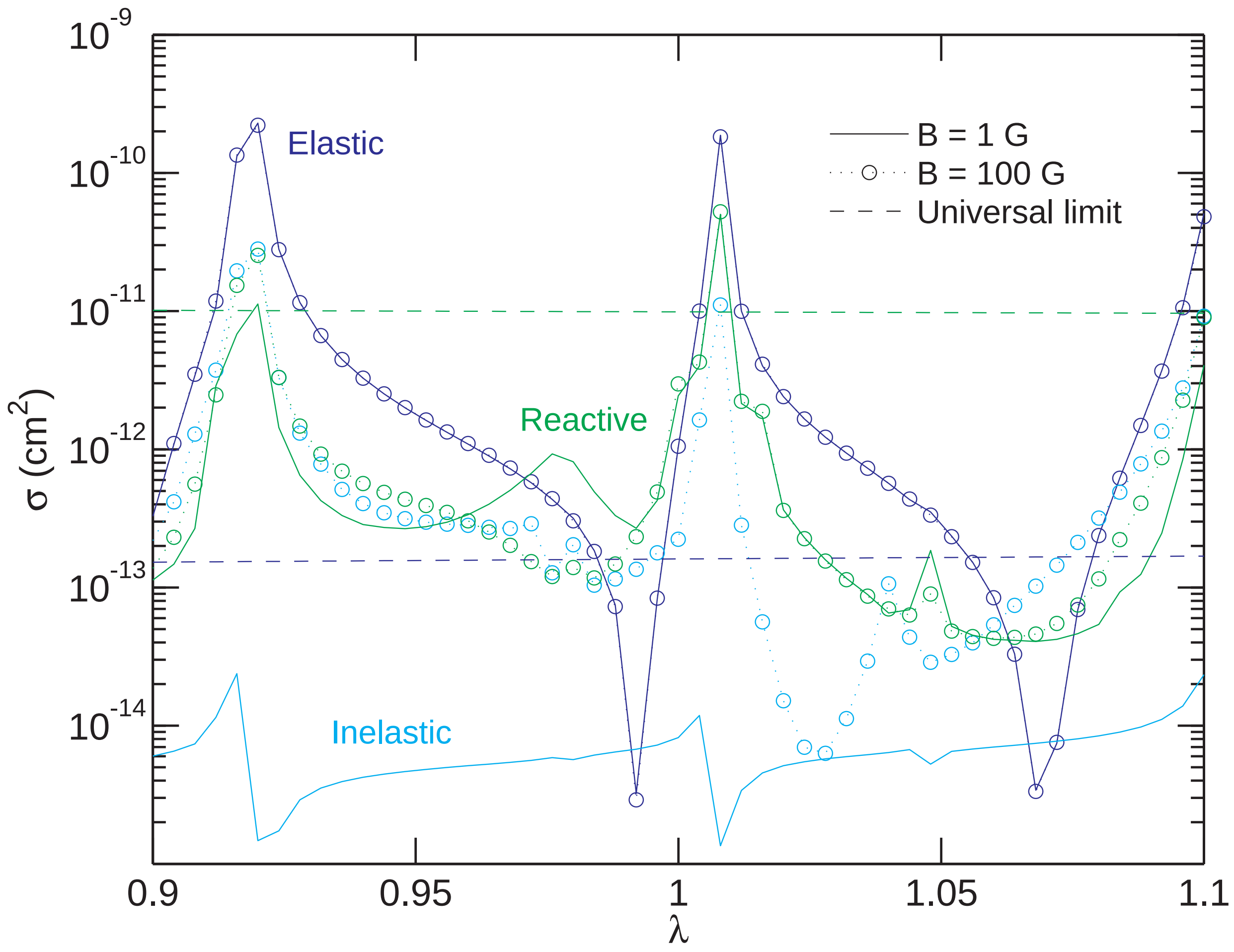
# $^{15}$NH+$^{15}$NH cross sections + universal limit



- Reactive cross sections: not universal
- Reaction weakly dependent on magnetic field

Threshold behavior: Janssen *et al.*, Eur. Phys. J. D, **65**, 177 (2011)

# NH+NH cross sections, λ-scan, $E = 1\mu\mathrm{K}$



- Evaporative cooling not possible in universal limit
- Inelastic suppressed for low magnetic field
- Reative collisions not universal, but still large

# Conclusions for $^{15}$NH($^3\Sigma^-$) +$^{15}$NH($^3\Sigma^-$)

- Reaction mechanism: short range (intra-spin spin)
- Inelastic mechanism: long range (inter-spin spin)
- “non universal”
- Elastic and inelastic only require quintet potential

- Below 100 mK reaction more likely than inelastic
- Reaction weakly dependent on magnetic field
- Reaction may hamper evaporative cooling

L. Janssen, A. van der Avoird, G. C. Groenenboom, Phys. Rev. Lett. **110**, 063201 (2013)