

Cold Chemistry with $\text{OH}+\text{NO}$ and $\text{NH}+\text{NH}$

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Outline

● $^{15}\text{NH} (^3\Sigma^-) + ^{15}\text{NH} (^3\Sigma^-)$

- Ultra cold collisions in magnetic trap ($1\mu\text{K} - 1\text{K}$)
- Allow for **reactive** collisions ($\rightarrow \text{N}_2 + \text{H}_2, \text{HN}_2 + \text{H}$)
- Question: is evaporative cooling possible?

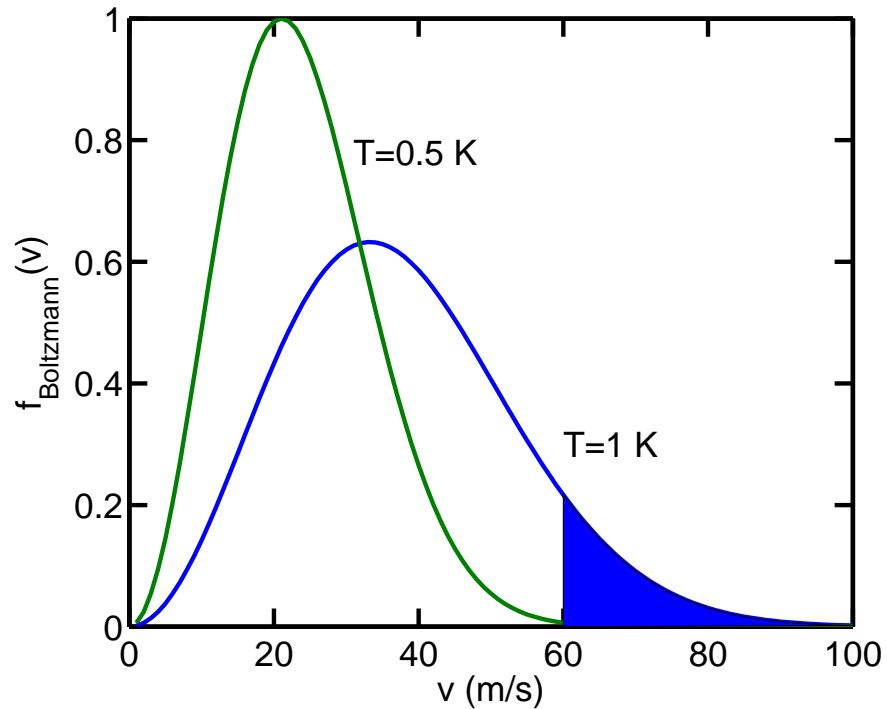
Liesbeth Janssen *et al.*, Phys. Rev. Lett. 1-Feb (2013), arXiv:1301.1931

● $\text{OH} (^2\Pi) + \text{NO} (^2\Pi)$ (Experiment FHI Berlin)

- Stark controlled OH beam
- Hexapole NO beam
- Controlled collision energy: $70 - 300 \text{ cm}^{-1}$
- Theory and experiment for 4 inelastic channels
- \Rightarrow follow up of 2006 Xe+OH study

Moritz Kirste *et al.*, Science 338, 1060 (2012)

Evaporative cooling

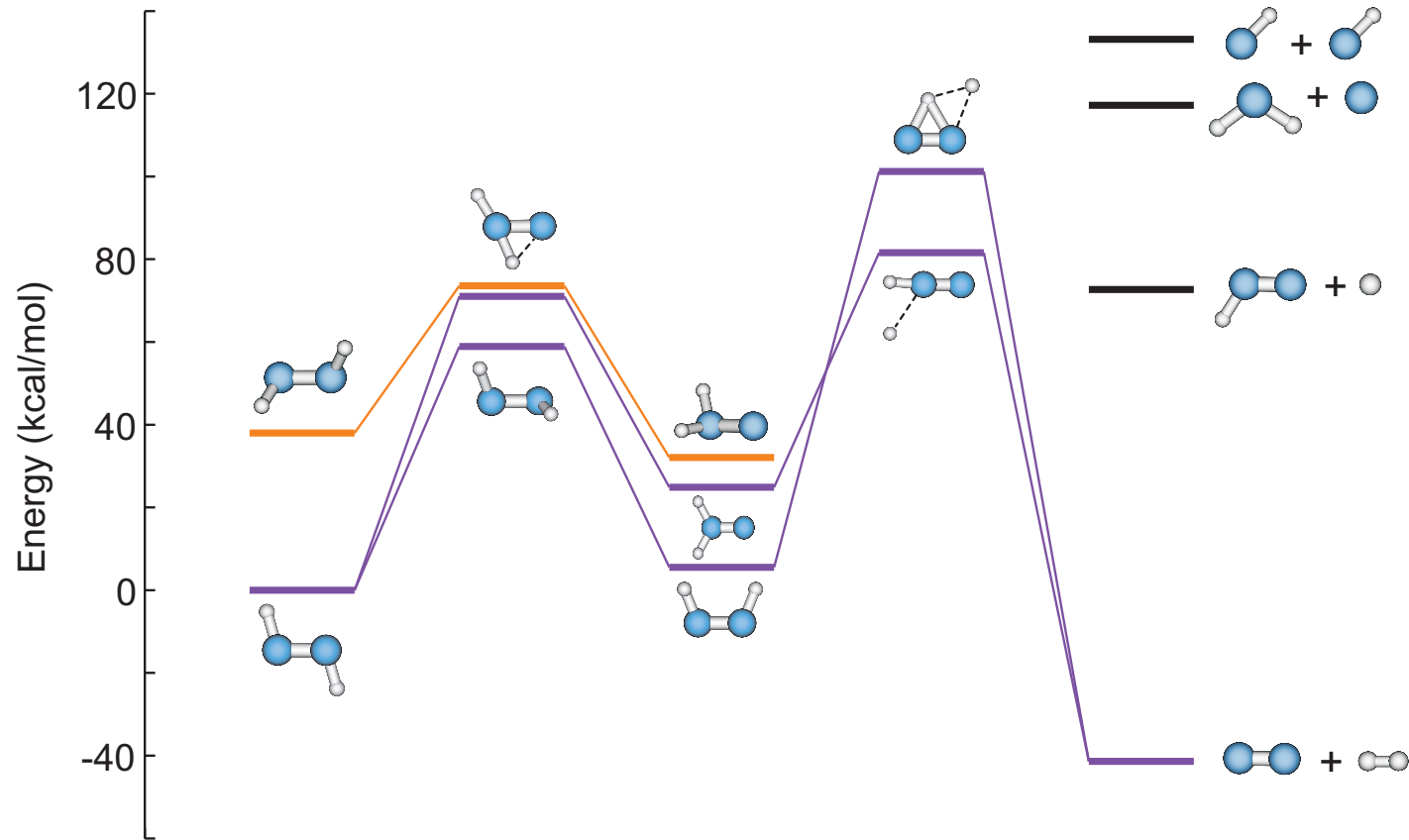


- Elastic collisions \Rightarrow thermalizing
- Inelastic/spin changing collisions \Rightarrow trap loss
- Condition: $K_{\text{el}} \gg K_{\text{in}}$

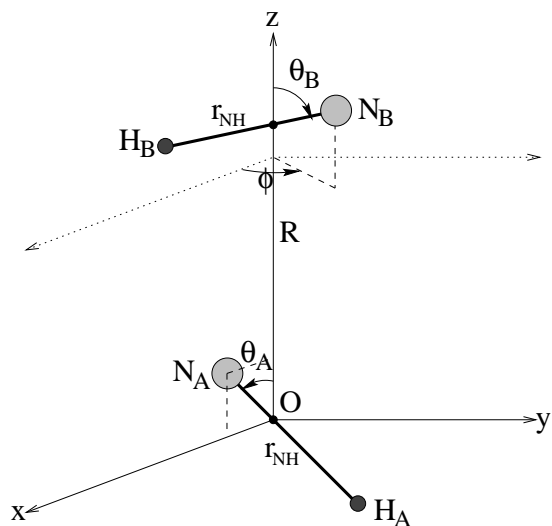
For He^* : $n \approx 10^{12} \text{ cm}^{-3}$ at $T \approx 500 \text{ mK} \rightarrow 5 \mu\text{K BEC}$

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

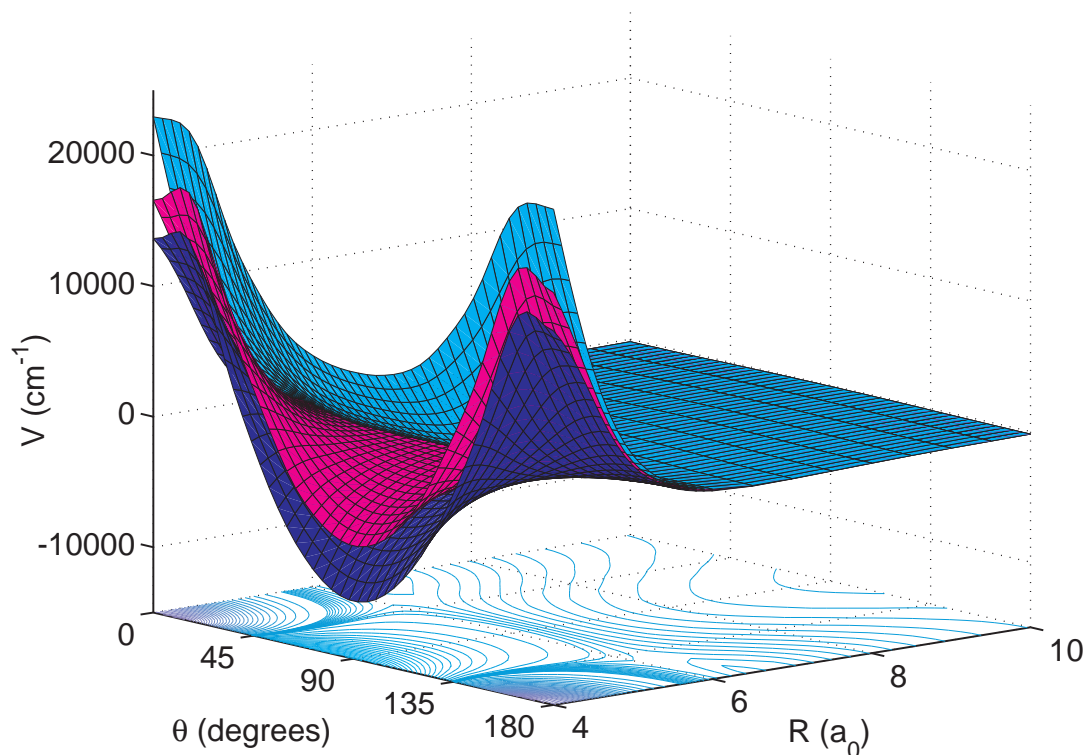
NH+NH chemistry



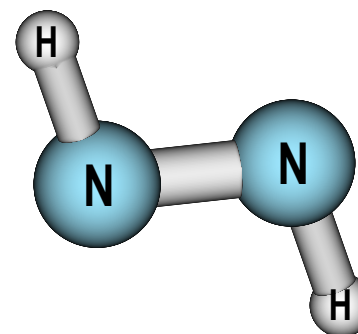
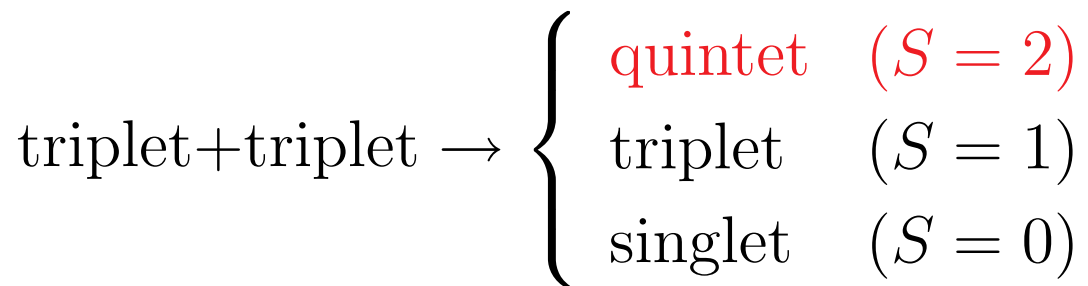
NH($^3\Sigma^-$)-NH($^3\Sigma^-$) 4D PESs



$r_{\text{NH}} = 1.0362 \text{ \AA}$ (fixed)



$$\theta_A = \theta_B = \theta$$



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

NH-NH Hamiltonian

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

Monomer terms:

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

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

Magnetic dipole-dipole term

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

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: $N_A = N_B = 0$, $M_{S_A} = M_{S_B} = 1$
- Basis set: $N_A, N_B \leq 2$, $L \leq 6$, $M_{\text{tot}} = 2$
- Single arrangement **reactive** boundary conditions
- New renormalized Numerov type propagator

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

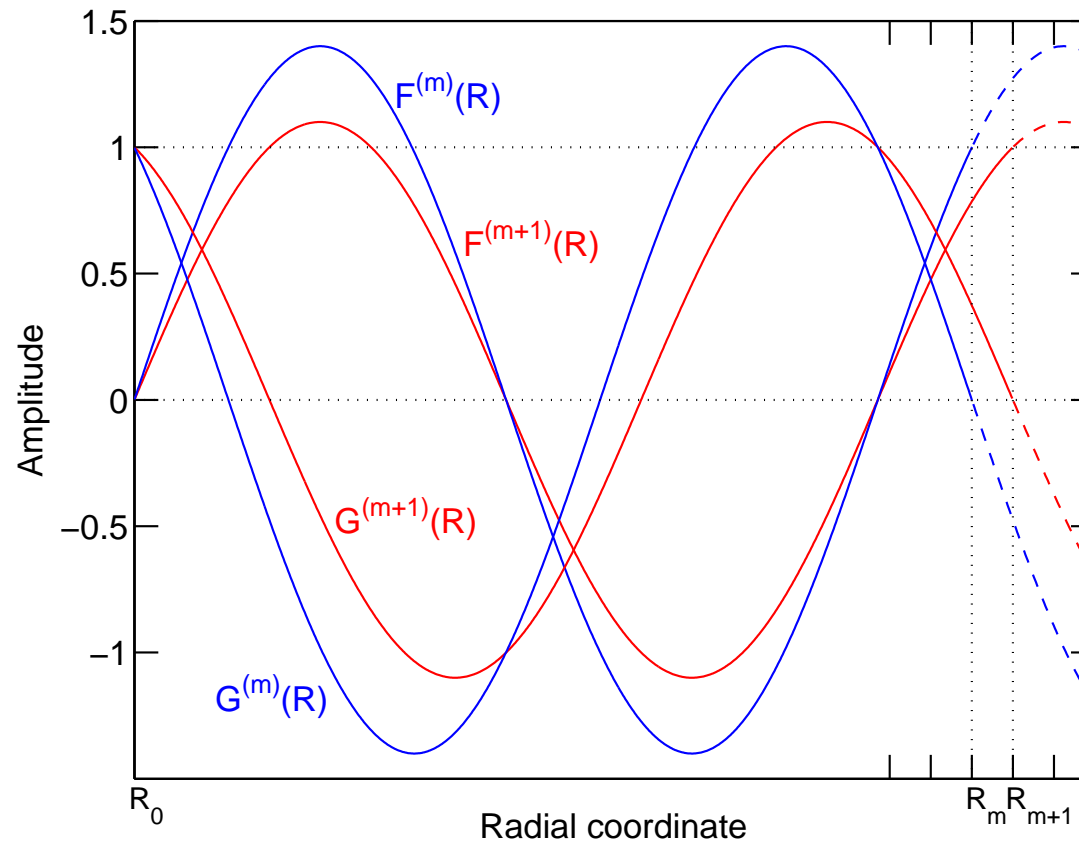
$$R_6 = \frac{1}{2} (2\mu C_6 / \hbar^2)^{\frac{1}{4}} \quad \text{van der Waals radius}$$

$$\bar{a} = 4\pi R_6 / \Gamma(1/4)^2 \quad \text{mean scattering length}$$

$$\sigma_{\text{elastic}}(k) = 4g\bar{a}^2 \quad (g = 2)$$

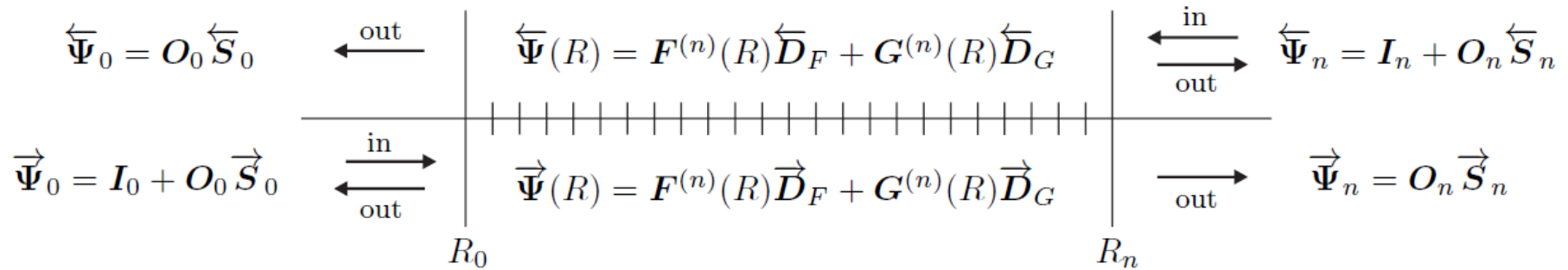
$$\sigma_{\text{reactive}}(k) = 2g\bar{a}/k$$

Reactive Numerov propagator



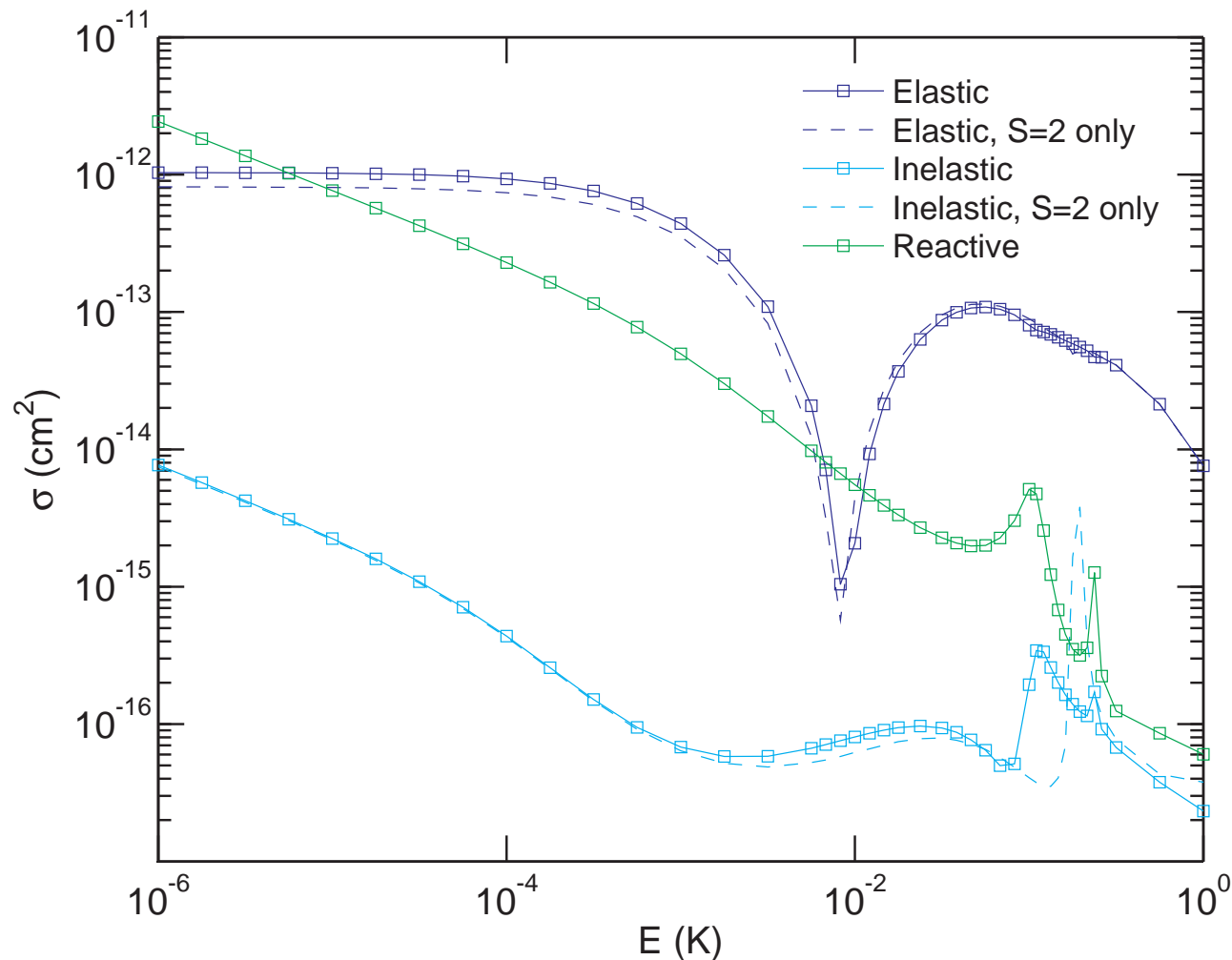
- $F^{(m)}(R)$: regular solutions (inelastic scattering)
- $G^{(m)}(R)$: irregular solutions

Reactive boundary conditions



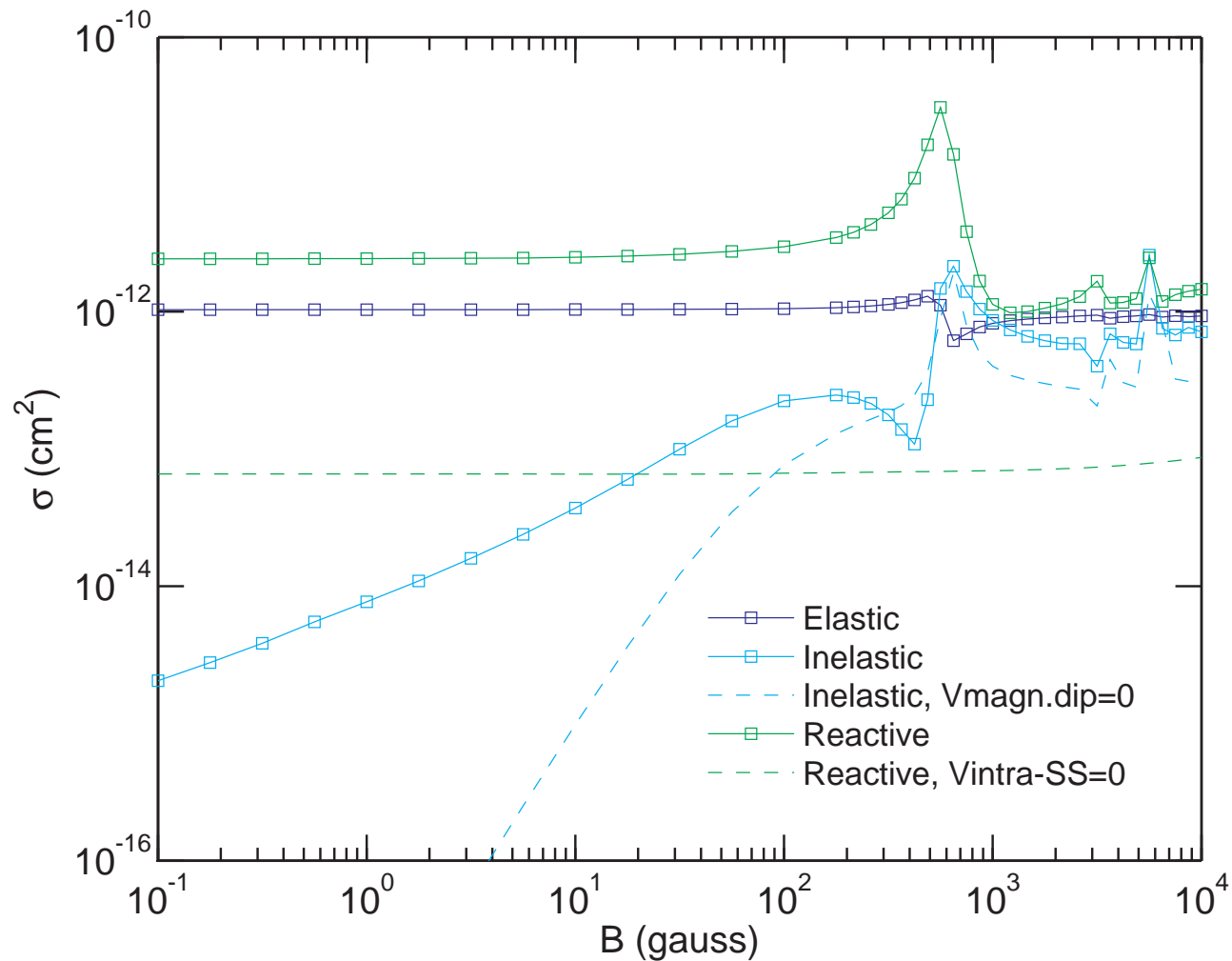
- Propagation: real functions
- Apply any boundary condition *after* propagation
- S-matrix is unitary
- Interval $[R_a, R_b] + [R_b, R_c] \rightarrow [R_a, R_c]$: parallel code

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



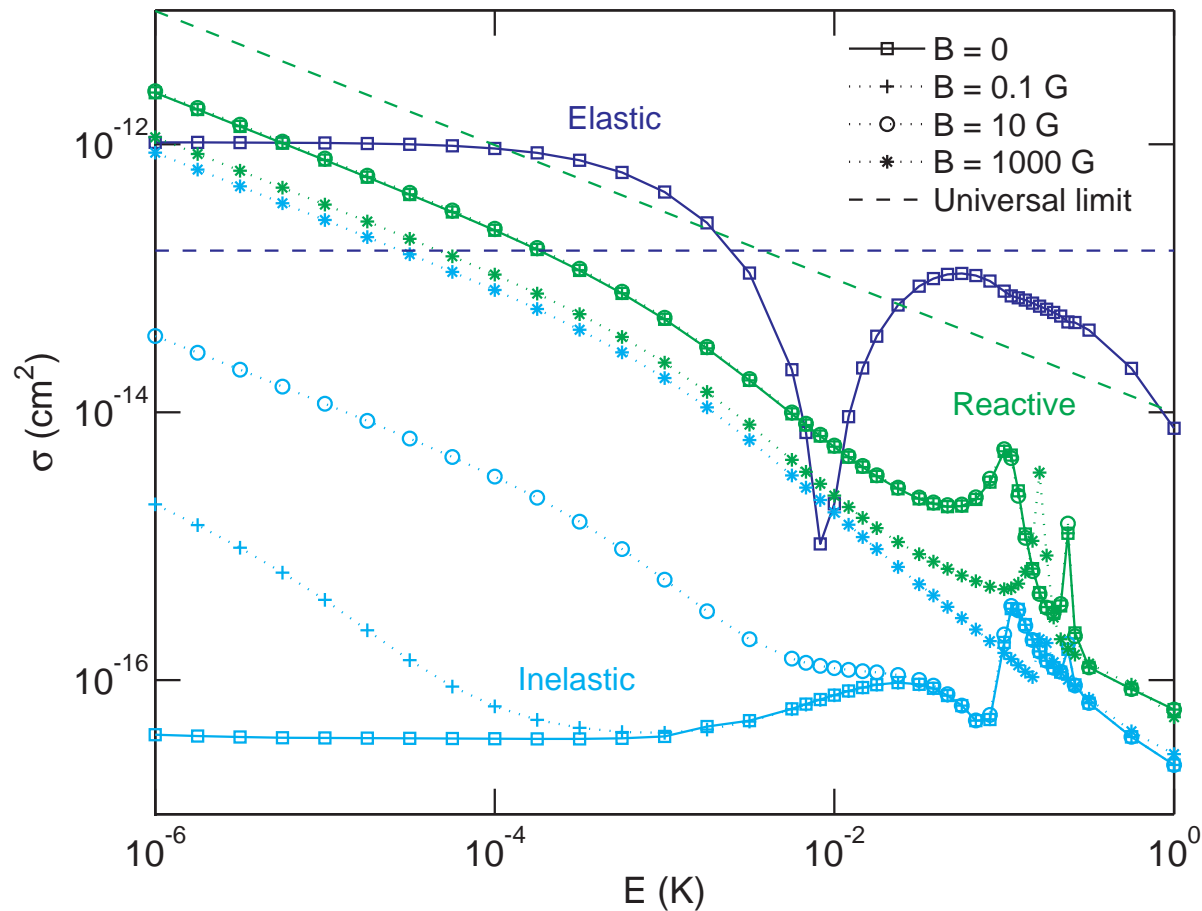
- **Surprise:** reaction $>$ inelastic (below 0.1 K)
- Only quintet potential needed for elastic & inelastic

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



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

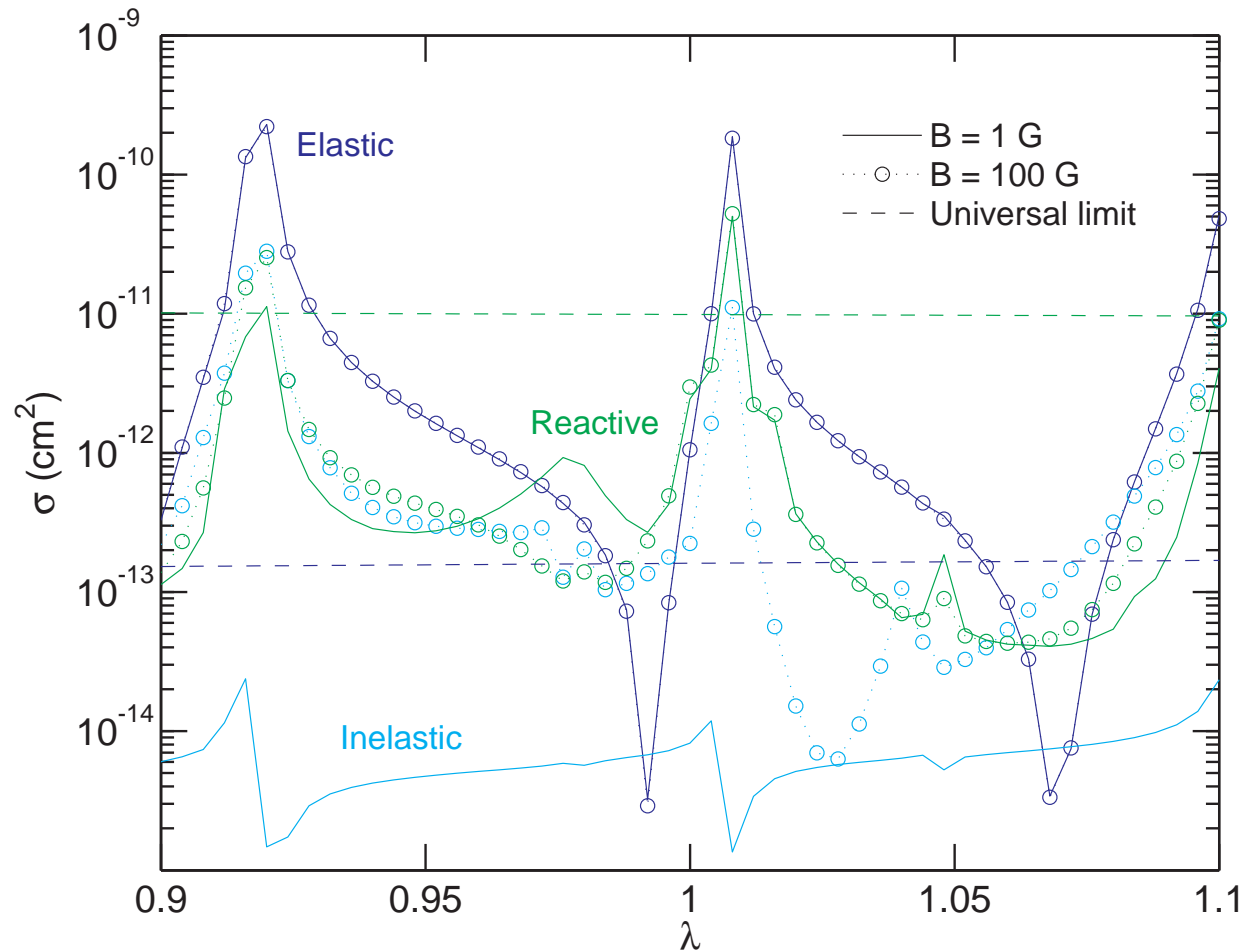
$^{15}\text{NH} + ^{15}\text{NH}$ cross sections + universal limit



- 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, $E = 1\mu\text{K}$



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

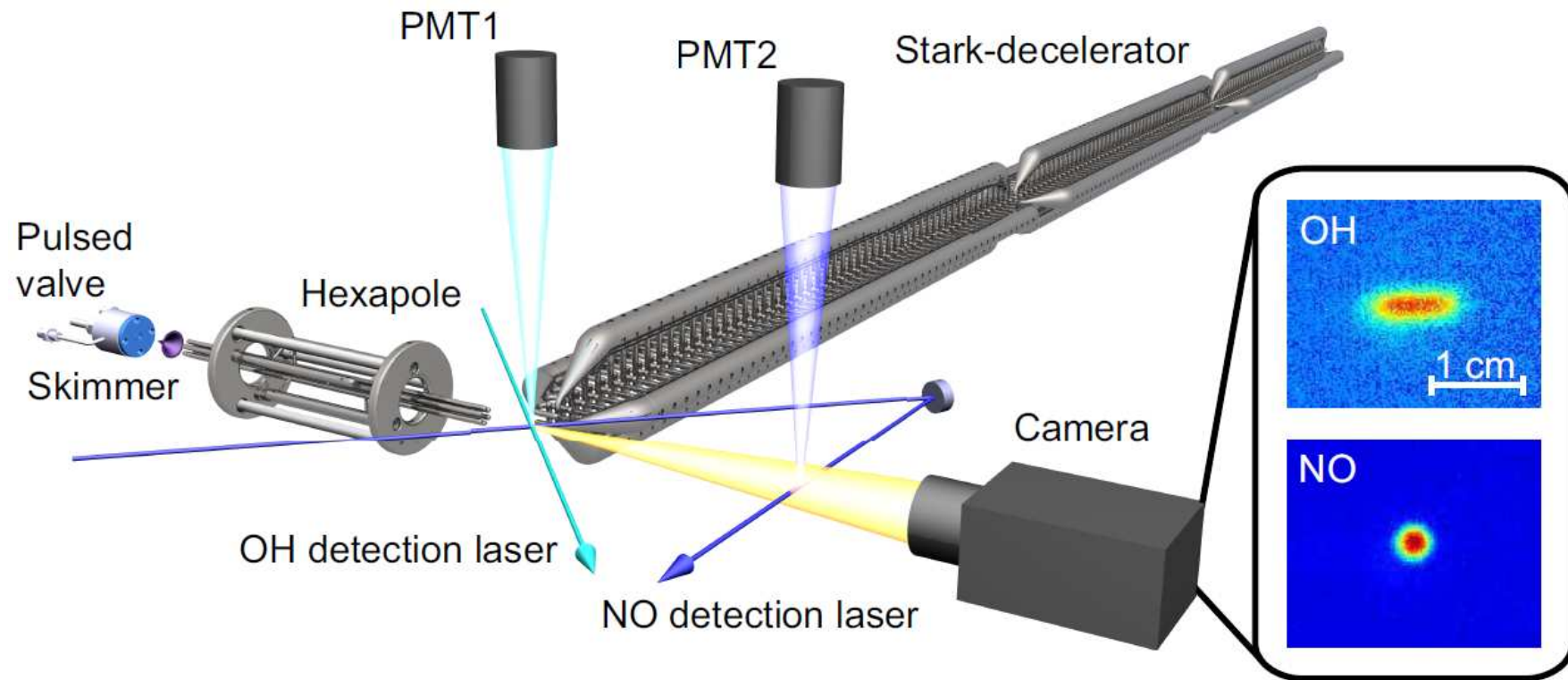
Conclusions for $^{15}\text{NH}(^3\Sigma^-) + ^{15}\text{NH}(^3\Sigma^-)$

- 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. M. C. Janssen, A. van der Avoird, G. C. Groenenboom, Phys. Rev. Lett. 1-Feb (2013)

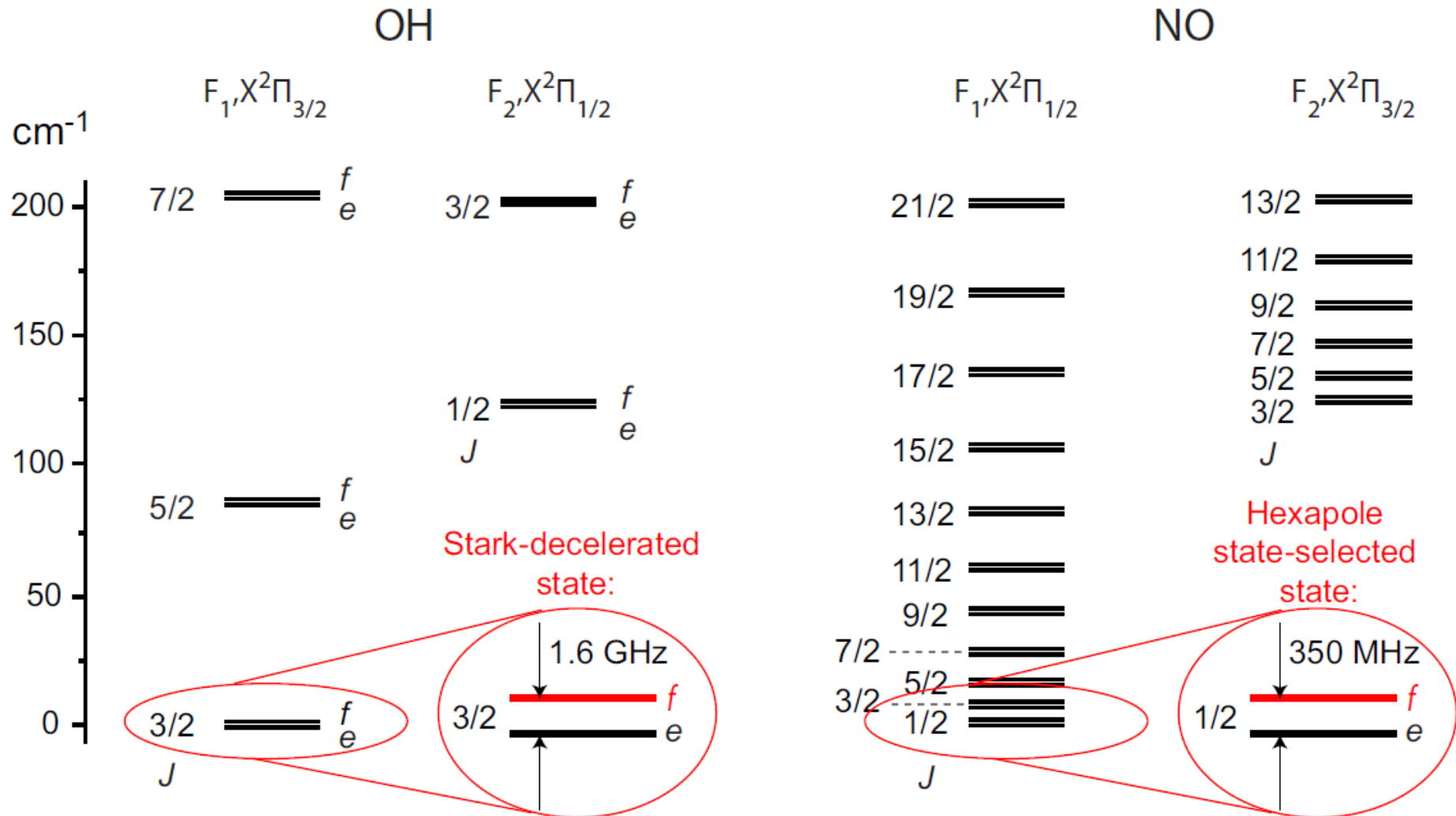
www.theochem.ru.nl/files/theses/janssen-phdthesis-2012.pdf

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

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

Monomers, using spectroscopy constants:

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

Interaction potential \hat{V}

- Doublet + doublet \rightarrow 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

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

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

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

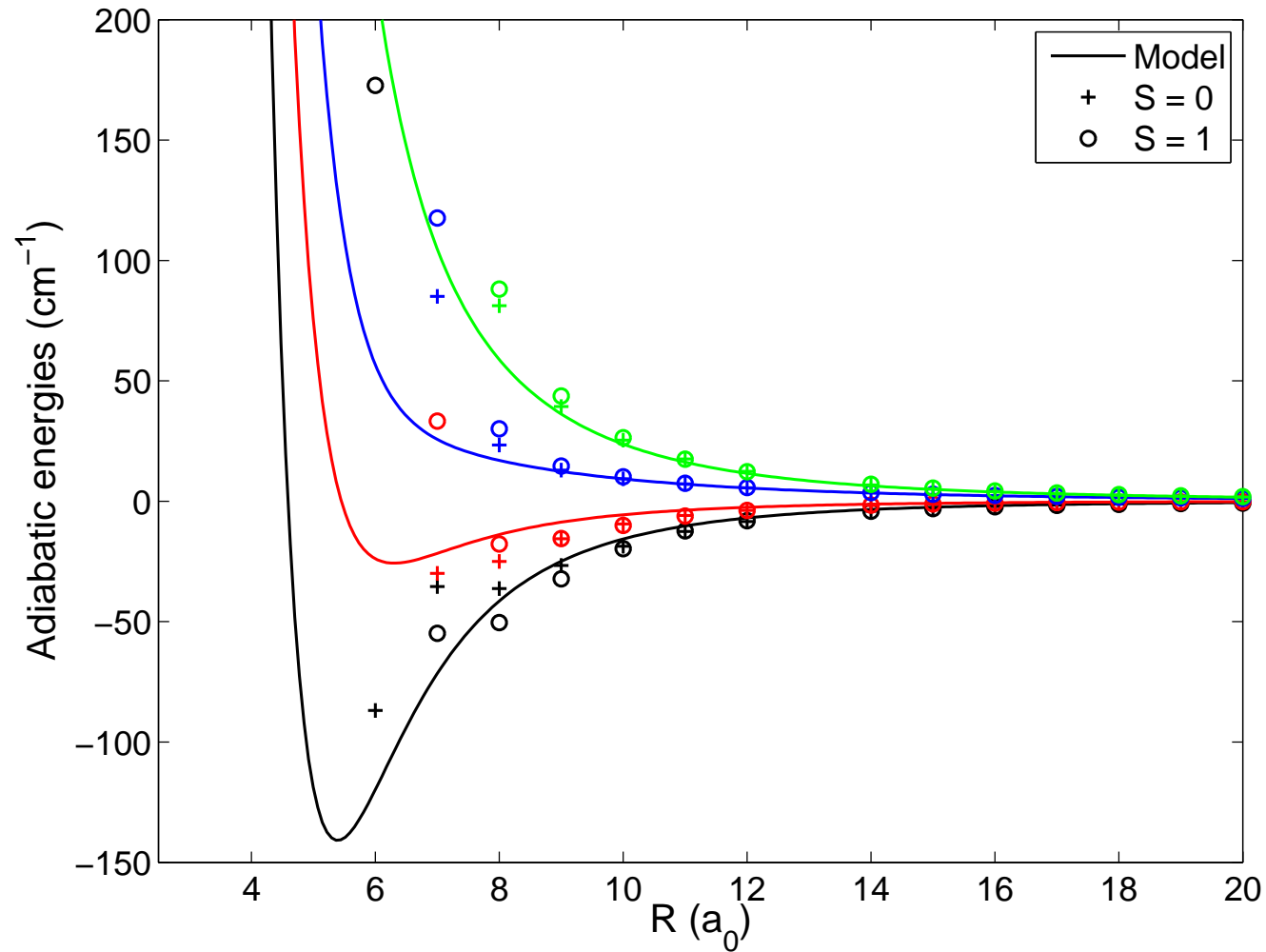
OH and NO multipole moments included:

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

$$\theta_{\text{OH}} = 135^\circ, \theta_{\text{NO}} = 45^\circ, \phi = 180^\circ$$

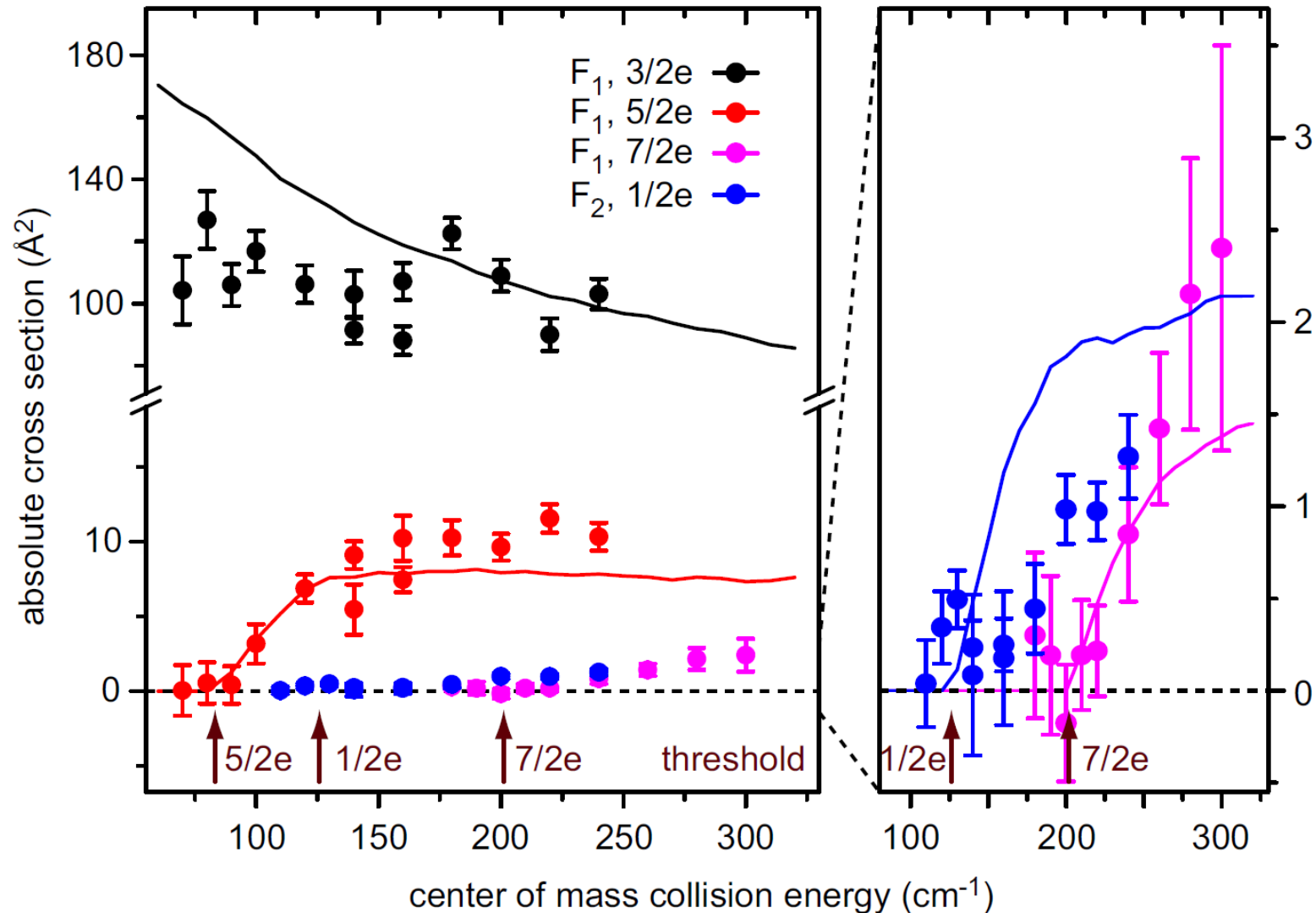


Coupled channels calculation

- Space-fixed, parity adapted, coupled (J_{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

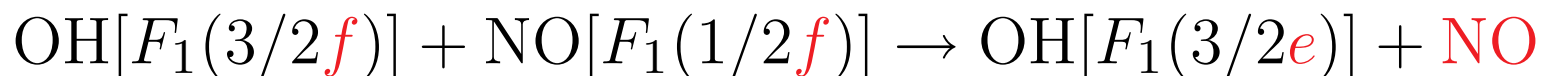
OH($^2\Pi$)+NO($^2\Pi$) inelastic cross sections

Theory (solid lines) vs experiment on **absolute scale**



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

Correlated state-to-state cross sections

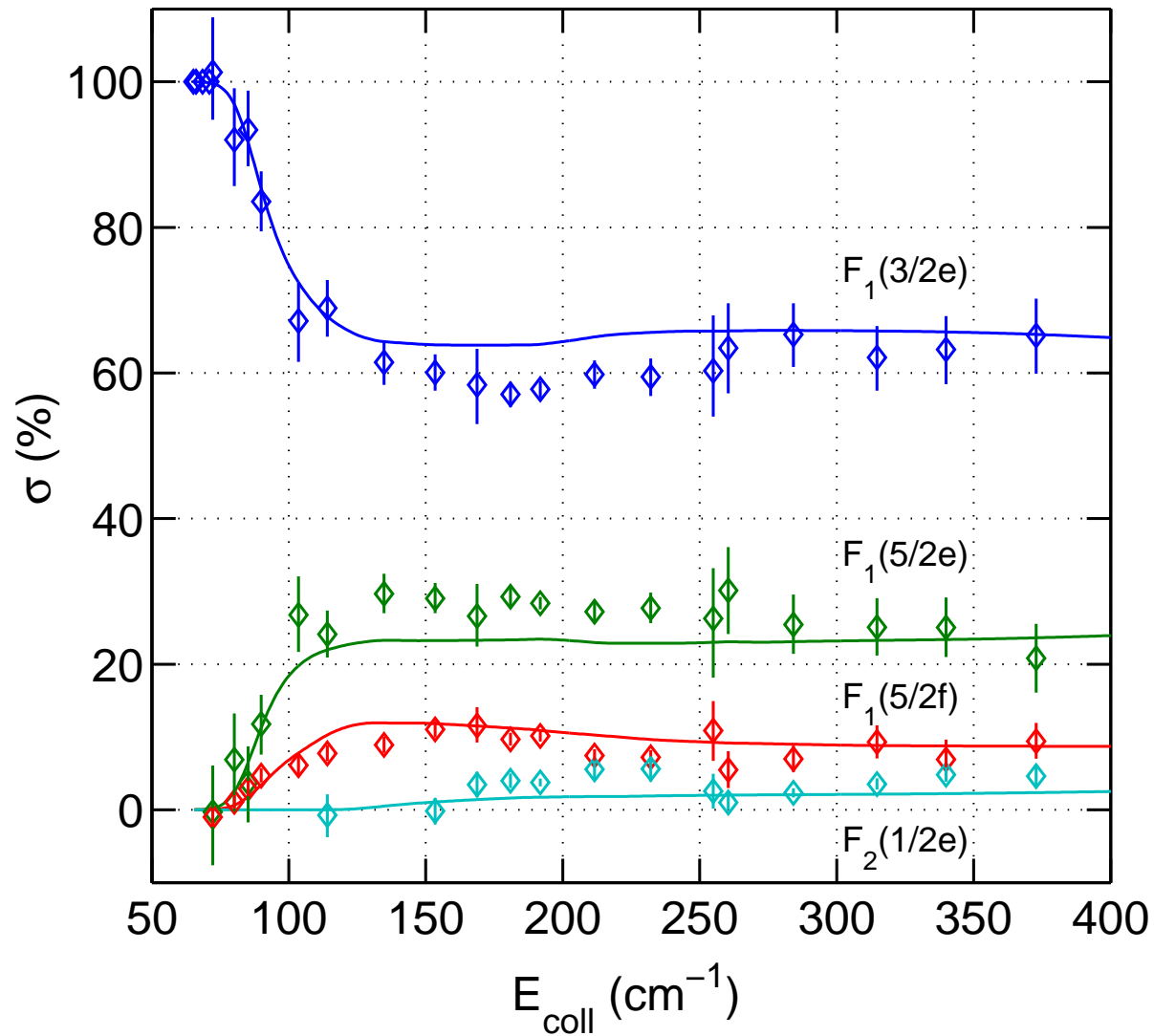


E_{col} (cm⁻¹): 10 50 300

NO

$F_1(1/2e)$	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

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

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)

Acknowledgements

Theory Nijmegen

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

Theory Durham

- Piotr Żuchowski
- Jeremy Hutson

OH+NO experiment FHI Berlin

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- Bas van de Meerakker

€: NWO-CW ECHO, ESF