

# High-level *ab-initio* NO-He potential energy surfaces and scattering resonances in NO-He collisions.

A collaboration between theory and experiment.

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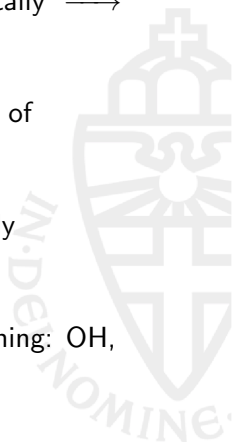
With DAN-II we try to understand the lifecycle of molecules in the interstellar medium:



**Rate coefficients** are used in astrochemical models to predict the evolution of molecules in the interstellar medium.

# Obtaining rate coefficients

- **Rate coefficients** not directly obtained experimentally  $\longrightarrow$  quantum calculations.
- **Benchmark** these calculations to the highest level of experiment.
- NO is a perfect benchmark system: experimentally convenient.
- **Extend** to astronomically relevant systems containing: OH, CH, NH<sub>3</sub>, H<sub>2</sub>, CO,...



# Calculating scattering cross sections

Rate coefficients are derived from **scattering cross-sections** obtained by solving the nuclear Schrödinger equation using the following Hamiltonian:

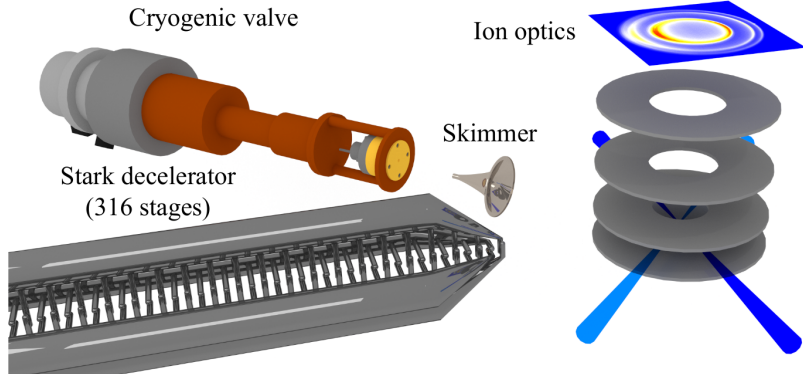
$$\hat{H} = -\frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial R^2} R + \frac{\hat{\ell}^2}{2\mu R^2} + \hat{H}_A(\mathbf{r}_A) + \hat{H}_B(\mathbf{r}_B) + \hat{V}(\mathbf{r}_A, \mathbf{r}_B, R)$$

**Potential energy surface** (PES) obtained from electronic structure calculations.

An accurate **PES** is essential to the scattering dynamics.

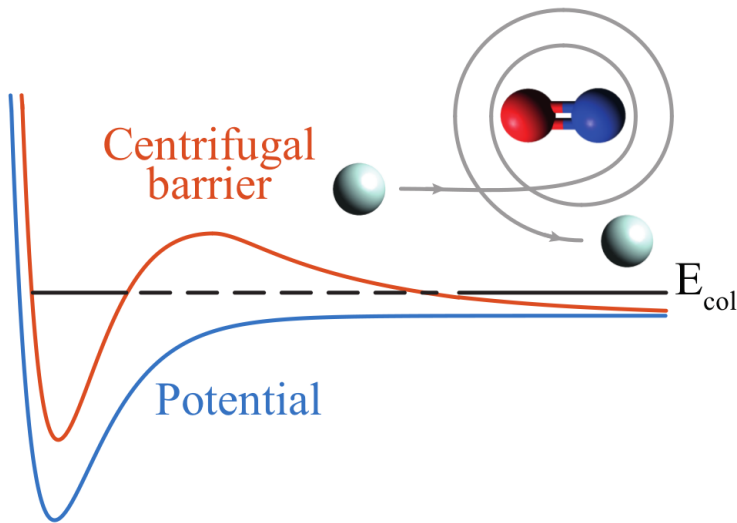


Cold and controlled collision experiments to test PESs.



- Low collision energies: PES sensitive to resonances.

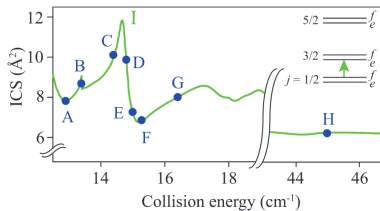
# Scattering resonances at low collision energies



Shape resonance

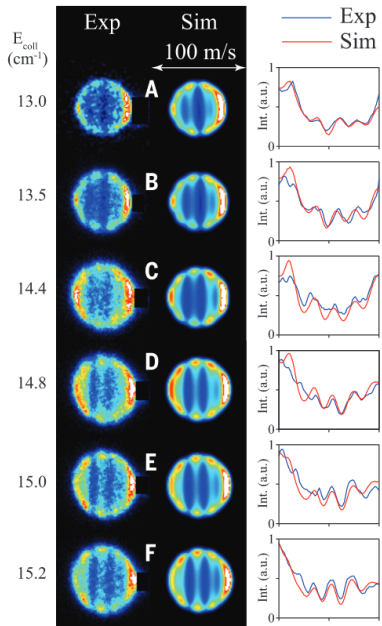
# NO-He collision experiments

Nearly perfect agreement  
between theory and experiment.



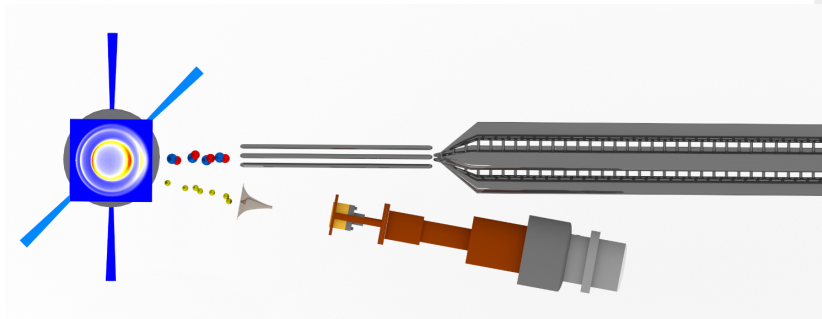
Scattering resonances are  
observed.

$$1 \text{ cm}^{-1} \approx 1.5 \text{ Kelvin}$$



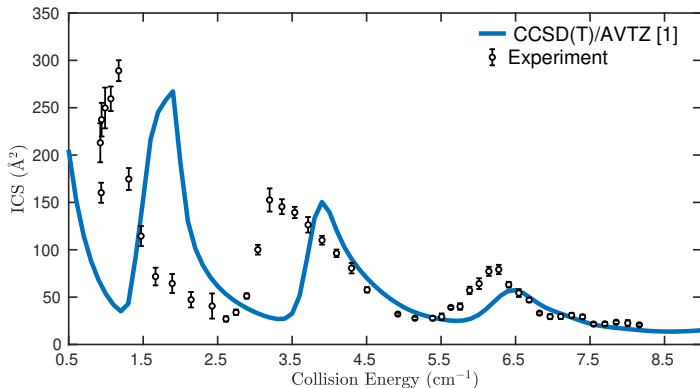
# Change of experimental set-up

Decreased scattering angle to  $10^\circ$   $\rightarrow$  lower collision energies.



# New NO-He collision experiments at lower energies

Position of measured and **theoretically calculated** resonances do not match for the  $j_{NO} = 0.5f \rightarrow j'_{NO} = 0.5e$  transition.



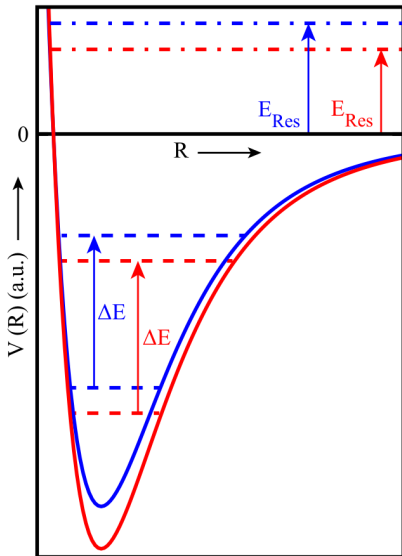
NO-He PES is not sufficiently accurate.

[1] J. Kłos et al., Chem. Phys. 112, 2195 (2000).

# Shift in resonances

Deeper potential well  $\rightarrow$  shift in scattering resonances to lower energies.

Depth of the well is directly probed with scattering experiments.



# Computation of NO-He PESs

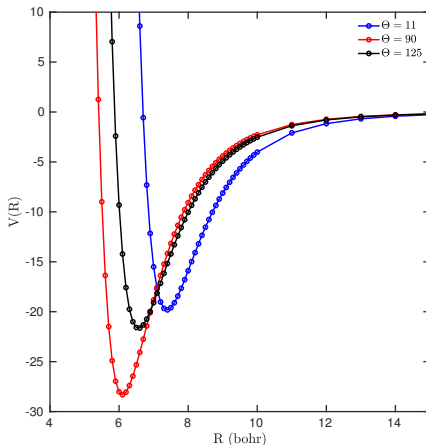
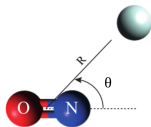
NO is an **open-shell**  $\Pi$ -state molecule (in the ground state).

$$V(R, \Theta) = (E_{NO-He} - E_{NO} - E_{He})$$

We use the **CCSD(T)** method.

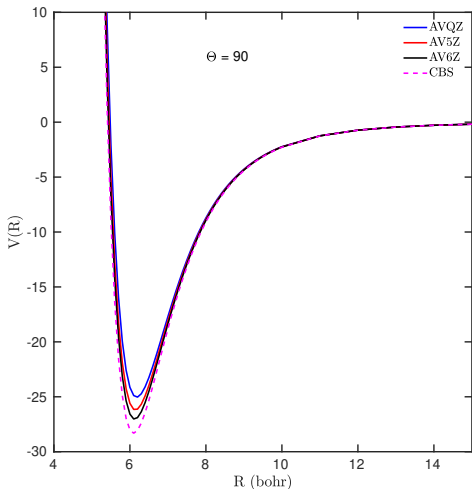
1824 unique *ab-initio* points, 12 hours per point (AV6Z).

$r_{NO}$  is kept fixed  $\rightarrow$  2D-potential.



Increasing the size of basis-sets gives improved interaction energies.

**Complete Basis Set (CBS)** extrapolation estimates the interaction energy as if a complete basis-set is used.

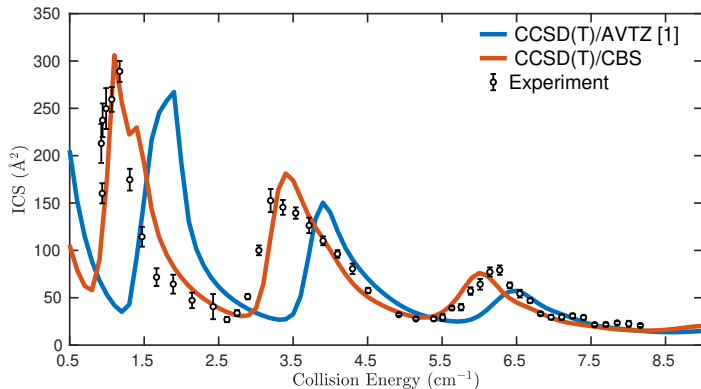




# Cross-sections with the CBS potential

The CBS potential shows a significant improvement.

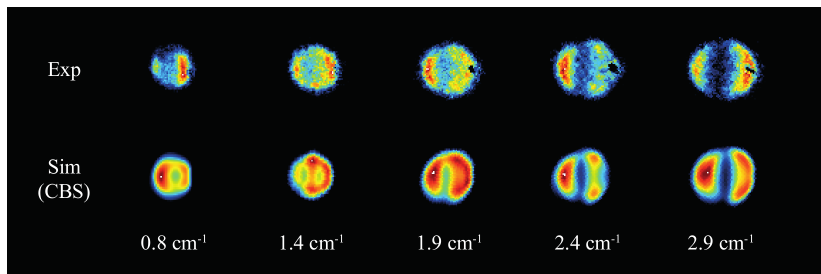
$$j_{NO} = 0.5f \rightarrow j'_{NO} = 0.5e$$



Remaining disagreement due to:  
vibrational motion, electron correlation effects, Born-Oppenheimer approximation?

[1] J. Kłos et al., Chem. Phys. 112, 2195 (2000).

# Angular distributions



Agreement not perfect at **CCSD(T)/CBS**.

# Scattering resonances in bimolecular collisions between NO radicals and H<sub>2</sub> challenge the theoretical gold standard

Sjoerd N. Vogels<sup>1,4</sup>, Tijds Karman<sup>1,4</sup>, Jacek Kłos<sup>2</sup>, Matthieu Besemer<sup>1</sup>, Jolijn Onvlee<sup>1,3</sup>, Ad van der Avoird<sup>1</sup>, Gerrit C. Groenenboom<sup>1\*</sup> and Sebastiaan Y. T. van de Meerakker<sup>1\*</sup>

Over the last 25 years, the formalism known as coupled-cluster (CC) theory has emerged as the method of choice for the ab initio calculation of intermolecular interaction potentials. The implementation known as CCSD(T) is often referred to as the gold standard in quantum chemistry. It gives excellent agreement with experimental observations for a variety of energy-transfer processes in molecular collisions, and it is used to calibrate density functional theory. Here, we present measurements of low-energy collisions between NO radicals and H<sub>2</sub> molecules with a resolution that challenges the most sophisticated quantum chemistry calculations at the CCSD(T) level. Using hitherto-unexplored anti-seeding techniques to reduce the collision energy in a crossed-beam inelastic-scattering experiment, a resonance structure near 14 cm<sup>-1</sup> is clearly resolved in the state-to-state integral cross-section, and a unique resonance fingerprint is observed in the corresponding differential cross-section. This resonance structure discriminates between two NO-H<sub>2</sub> potentials calculated at the CCSD(T) level and pushes the required accuracy beyond the gold standard.

Intermolecular interactions determine the properties of gases and liquids, and play a key role in biochemistry. These interactions depend on the electronic structure of the interacting molecules. To describe or predict the electronic structure, physicists and chemists in principle need to solve only one equation: the electronic Schrödinger equation. Yet, solving this equation exactly is impossible for molecules, as all electrons interact with each other, leading to the notorious electron correlation problem. Synergy between experiment and theory has proven essential to develop and refine the methods to calculate intermolecular potentials with ever higher accuracy.

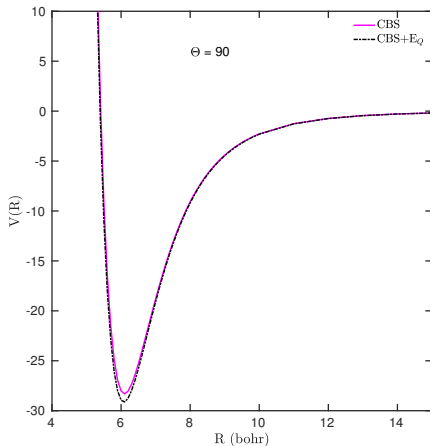
To numerically solve the electronic Schrödinger equation in the best possible approximation, a method technically known as the coupled-cluster method with the inclusion of single and double

levels of the complex. Collision experiments also probe the repulsive parts of potentials that determine the shape of molecules, as well as the much weaker long-range interactions between molecules. The most global and sensitive probes of molecular interaction potentials are the scattering resonances that can occur in low-energy collisions. Resonances are sensitive to the repulsive and long-range interactions that determine the shape of the potential well, and in particular to the depth of this well. As illustrated in Fig. 1, a small difference in potential well depth directly results in an observable shift of the scattering resonance energy  $E_{\text{res}}$ , whereas the spectroscopically accessible differences in bound-state energies,  $\Delta E$ , are less strongly affected.

As a consequence, the observation of scattering resonances in low-energy collisions has received a great deal of attention in recent

# From CCSD(T) to CCSDT(Q)

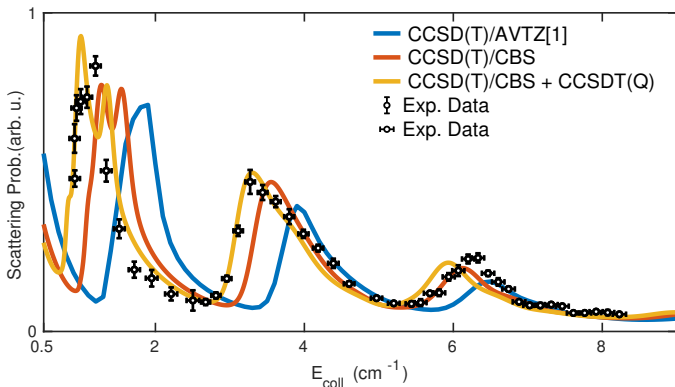
CCSDT(Q) deepens the well by as much as  $0.8 \text{ cm}^{-1}$  compared to CCSD(T)/CBS.



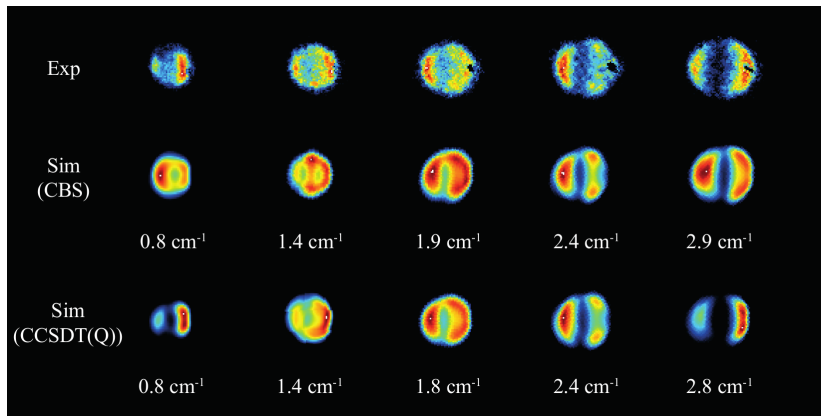
# Cross sections with the CCSDT(Q) potential

Some parts agree better with the experiment.

$$j_{NO} = 0.5f \rightarrow j'_{NO} = 0.5e$$



# Angular distributions



Better agreement at CBS+CCSDT(Q) level.

**Born-Oppenheimer (BO) approximation:** assumes separation between nuclear and electronic motion.

Not accurate for NO due to first derivative coupling terms ( $\Pi_x/\Pi_y$ ).

Second derivative coupling terms are small and normally ignored.

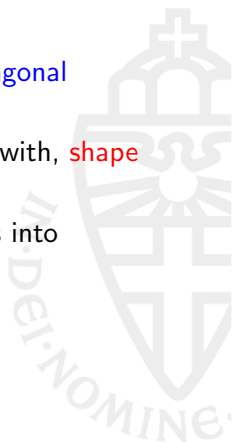
The **Diagonal Born-Oppenheimer Correction (DBOC)** partially accounts for second derivative coupling terms:

$$E_{DBOC} = \sum_I^{N_{coord}} \langle \Psi_e | -\frac{1}{2M_I} \nabla_I^2 | \Psi_e \rangle$$

Calculated with the **CFOUR** program:

- Works fine for closed-shell systems (CO-He).
- Difficult for open-shell systems (**Work in progress!**)

- We will investigate the effect of including the **Diagonal Born-Oppenheimer Correction**.
- Analyze what types of resonances we are dealing with, **shape** or **Feshbach**.
- Analyze and decompose differential cross-sections into individual partial wave contributions.





## Molecule-Atom/Molecule collisions:

- $\text{NH}_3\text{-H}_2$
- $\text{CH}_4\text{-He}$  (Taha Selim)
- $\text{CO-H}_2$  (Ad van der Avoird)
- $\text{CO}_2\text{-He}$  (Taha Selim)
- $\text{HCCH-He}$  (Taha Selim)
- $\text{NH}_3\text{-NO}$  (Daan Snoeken & Matthieu Besemer)

Molecule-Molecule collisions can have **pair-correlated** cross-sections.



# Acknowledgments

My supervisors:



**Prof. Bas van de  
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**Prof. Ad van  
der Avoird**



**Prof. Gerrit C.  
Groenenboom**

My Colleagues:



**Daan Snoeken**



**MSc. Taha Selim**

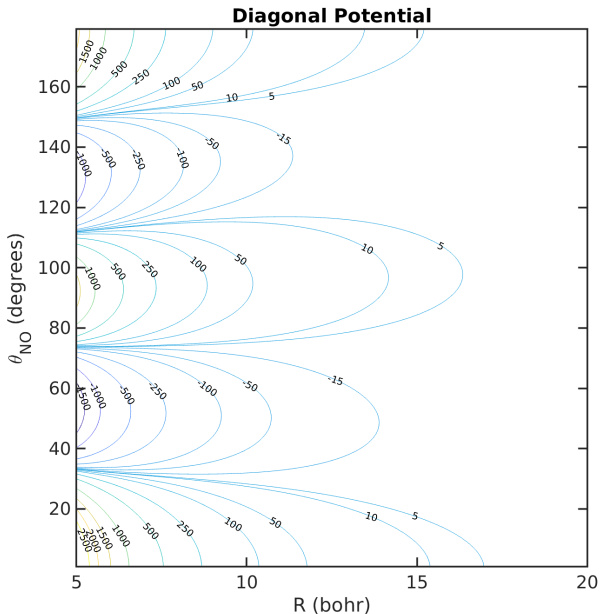
MSc. Tim de Jongh

Dr. Quan Shuai

# Exciting project on $\text{NH}_3\text{-NO}$



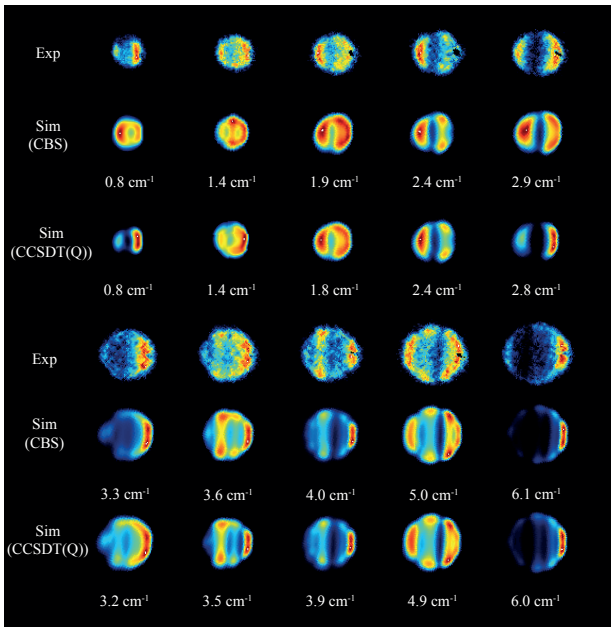
Master student:  
Daan Snoeken



Questions?



# Back-up slides: Angular distributions at the resonances

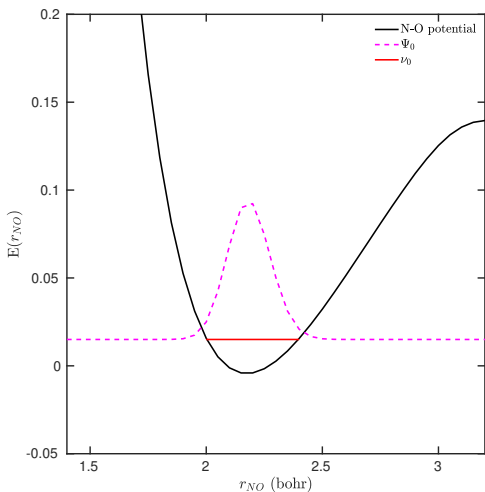


# Back-up slides: Vibrational averaging of N-O

The NO molecule is not rigid. Ideally, one would like to construct a full 3D-potential. However, an approximation can be made.

Calculate the interaction energy of the NO-He complex at different  $r_{NO}$  values and average them.

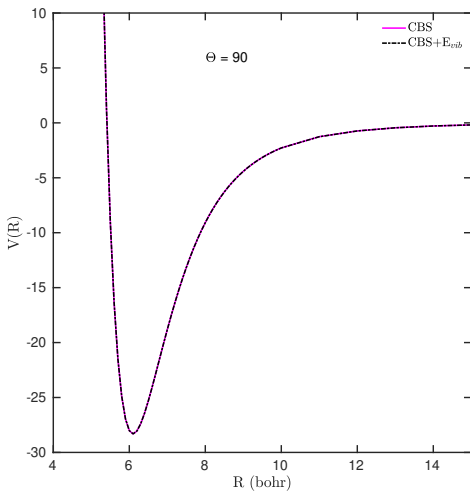
$$\langle V(R) \rangle = \frac{\langle \Psi_0(r) | V(r, R) | \Psi_0(r) \rangle}{\langle \Psi_0(r) | \Psi_0(r) \rangle}$$



# Back-up slides: Effect of vibrational averaging of N-O on ICS

Averaging over the vibrational motion of NO has no significant effect on the interaction potential of the NO-He complex.

So we need something else that will explain the differences between theory and experiment.



In the **Born-Oppenheimer approximation** one assumes a separation between the nuclear and electronic motion.

If you start from the exact Schrödinger equation you end up with two *non-adiabatic coupling terms*.

In the Born-Oppenheimer approximation all the coupling terms are neglected.

In general, the Born-Oppenheimer approximation is accurate when the separation of the electronic energies is large, for NO this is not the case.



The diagonal Born-Oppenheimer correction is a correction to the electronic energy due to the nuclear motion:

$$E_{DBOC} = \sum_I^{N_{\text{coord}}} \langle \Psi_e | -\frac{1}{2M_I} \nabla_I^2 | \Psi_e \rangle$$

There are two ways of calculating this quantity:

- 1 analytical gradient techniques
- 2 the finite differences approach

