



# Quantum Monte Carlo calculations on open shell species inside helium clusters

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Marius Lewerenz. Quantum Monte Carlo calculations on open shell species inside helium clusters. 2013. hal-00832967

**HAL Id: hal-00832967**

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Submitted on 11 Jun 2013

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# Quantum Monte Carlo calculations on open shell species inside helium clusters

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## Acknowledgments

**Paris-Est:**

**Ji Jiang, Ph.D student,  $\text{Ar}^+ @ \text{He}_n$ ,  $\text{I}^q @ \text{He}_n$**

**Mirjana Mladenović,  $\text{CO}^+ @ \text{He}_n$**

**Prague:**

**Petr Slavíček,  $\text{Pb}^{q+} @ \text{He}_n$**

**ANR project DYNHELIUM (Toulouse, Rennes, Paris)**

# What makes helium clusters interesting?

- Helium-helium interaction is of **weak van der Waals** type, closed shell atoms of very low polarisability,  $D_e \approx 7.6 \text{ cm}^{-1}$
- Helium atoms have a relatively small mass.
- Large zero point energy effects ( $D_0$  for  $\text{He}_2 \approx 0.001 \text{ cm}^{-1}$ ).
- Helium clusters are small chunks of a quantum liquid.
- Quantum statistical effects: **bosonic**  $^4\text{He}$ , fermionic  $^3\text{He}$ .
- **Superfluidity** in bulk liquid  $^4\text{He}$  below 2.17 K, in  $^3\text{He}$  at mK level
- **A very special solvent: Is there a new chemistry?**
- Implantation of dopants through (multiple) inelastic collisions.
- Weak interactions with dopant.
- Binding energy and position of dopants depend on quantum effects.

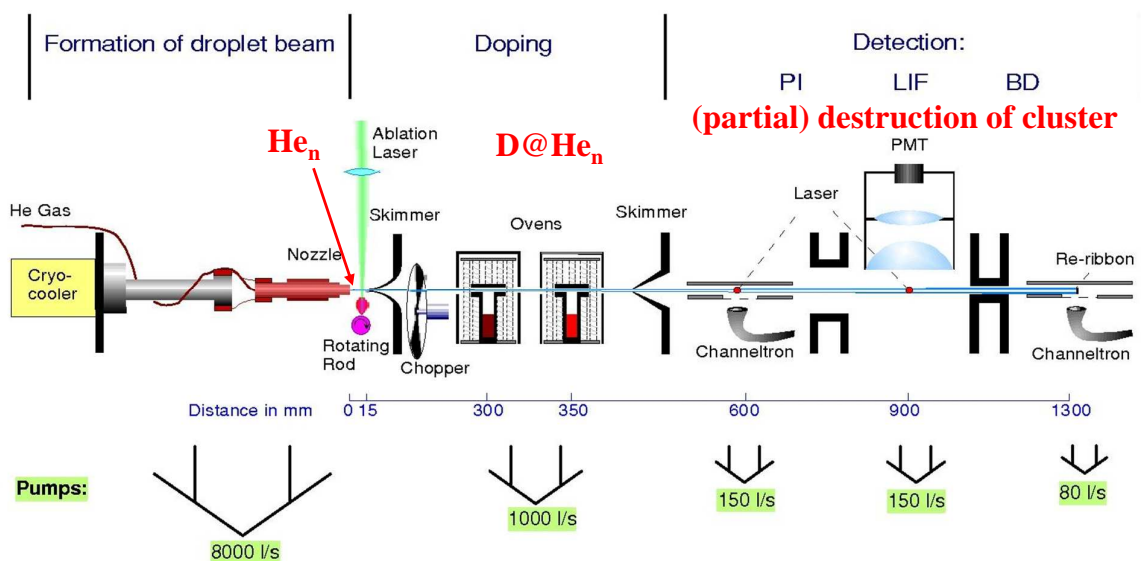
**Delicate balance between potential and quantum kinetic energy**

**Plenty of interesting experiments but theoretical difficulties!**

## Recent applications of helium clusters

- Matrix spectroscopy with minimal perturbations: **OCS, (HF) $_n$ , biomolecules at 0.4 K, radicals**
- Reaction dynamics at very low temperatures:  **$\text{Ba} + \text{N}_2\text{O} \rightarrow \text{BaO} + \text{N}_2$**
- Preparation of reactive intermediates:  **$\text{HF} \cdots \text{CH}_3$ ,  $\text{HCN} \cdots \text{CH}_3$  etc.**
- Preparation of high spin metal polymers:  **$\text{Na}_3$ ,  $\text{K}_3$ ,  $\text{Rb}_3$  etc.**
- Assembly of cold clusters:  **$\text{Ag}_n$ ,  $\text{Mg}_n$**
- Thermodynamically unstable isomers: **linear  $(\text{HCN})_n$**
- Nanomodels for molecule-surface interactions:  **$\text{HCN} \cdots \text{Mg}_3$  etc.**
- Container for soft ionisation for analytical mass spectrometry?
- Energy dissipation by coupling to the bath?
- Confinement medium for cluster ignition and Coulomb explosion.
- Spacer for interatomic Coulombic decay (ICD).

# A typical helium droplet experiment



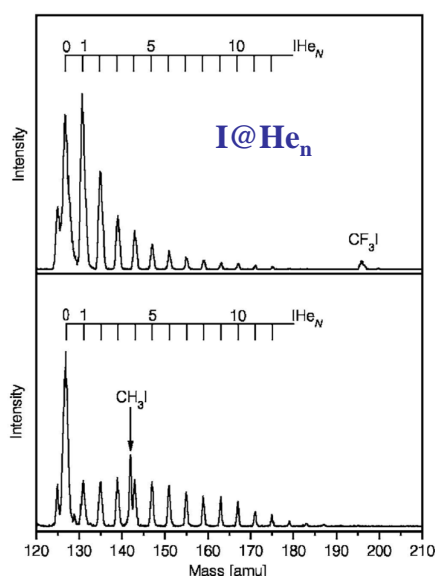
Observation of ionic clusters resulting from fragmentation or ejected photo fragments

Marius Lewerenz

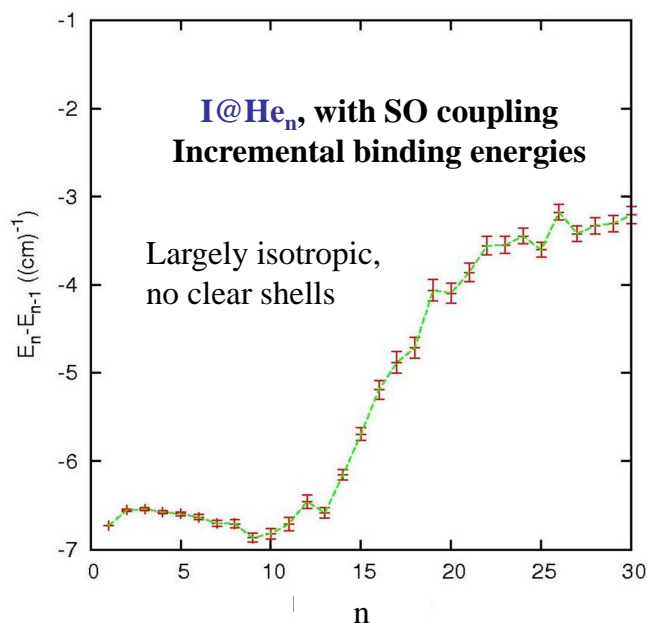
Helsinki, 13.11.2012

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## I@He<sub>n</sub> from CH<sub>3</sub>I → CH<sub>3</sub> + I. Experimental fragment distributions vs. ab initio+diffusion quantum Monte Carlo results



Braun and Drabbs 2007



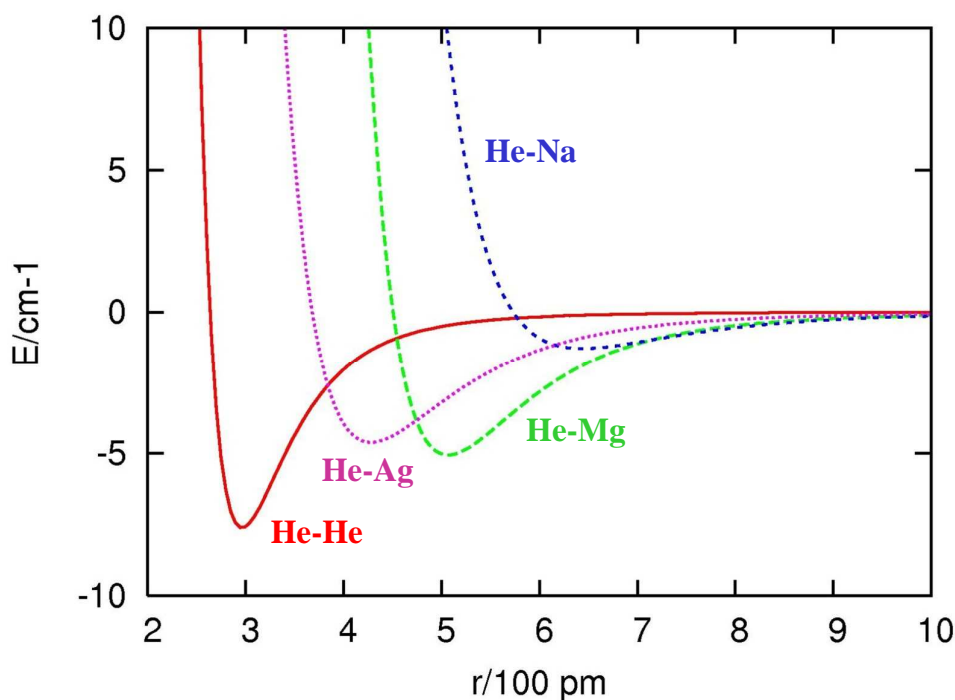
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PRAHA2012, 8.9.2012

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# Pair potentials involving helium and metals

Shallower well than He-He and larger equilibrium distance for He-M



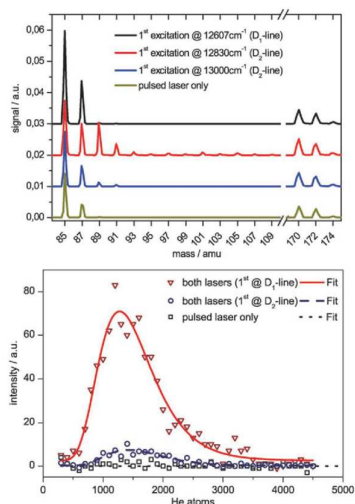
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Helsinki, 13.11.2012

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## Ions in helium clusters

- Massive change of interaction potential
- Polarisation forces
- Enhanced localisation of helium atoms
- “Snowball” formation



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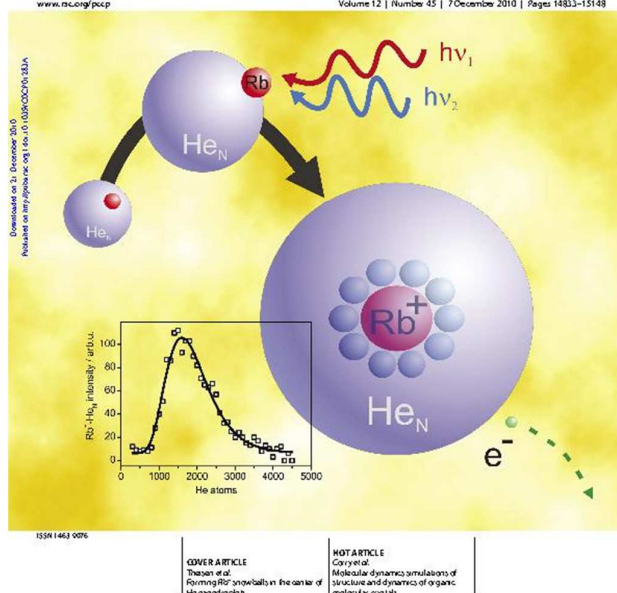
PCCP

Two step photoionisation  
Theisen et al., TU Graz

Physical Chemistry Chemical Physics

www.rsc.org/pccp

Volume 12 | Number 45 | 7 December 2010 | Pages 14833–15148



# Modelling open shell species inside helium clusters

**ANR project DYNHELIUM (Paris , Rennes, Toulouse):**

**Dissociation, recombination/caging and/or cluster exit of reaction products**

Our ultimate test problem, well known in the gas phase:

**Photodissociation of  $\text{CH}_3\text{I} \rightarrow \text{CH}_3 + \text{I}$  inside  $\text{He}_n$**

We need global potential energy surfaces for ground and excited  $\text{CH}_3\text{I}@\text{He}_n$  and for the relevant fragments  $\text{CH}_3@\text{He}_n$  and  $\text{I}@\text{He}_n$  (electronic anisotropy!).

**Isoelectronic warm up system:**

$\text{Ar}^+$  ions ( $s^2p^5$  valence shell,  $X^2\Sigma^+$  and  $A^2\Pi$  states for  $\text{Ar}^+\text{He}$ ).

Spin-orbit coupling between  $\Sigma$  and  $\Pi$  states has to be included in the model.

Spin-orbit splitting is typically larger than the van der Waals interaction:

$\Delta = 1432 \text{ cm}^{-1}$  for  $\text{Ar}^+$ ,  $\Delta = 7600 \text{ cm}^{-1}$  for  $\text{I}$

Include non additive induced dipole – induced dipole interaction for charged species

## Diffusion quantum Monte Carlo (DMC)

- Isomorphism between **time dependent Schrödinger equation** and a **multi dimensional diffusion equation** (Fermi, Ulam)
- Exact solution except for statistical errors

$$i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t} = \left\{ -\frac{\hbar^2}{2} \sum_{j=1}^n \frac{1}{m_j} \nabla_j^2 + \{ \textcolor{red}{V}(\vec{r}) - \textcolor{red}{E}_{ref} \} \right\} \Psi(\vec{r}, t)$$

$$\frac{\partial C(\vec{r}, t)}{\partial t} = \left\{ \sum_{j=1}^n D_j \nabla_j^2 - \textcolor{red}{k}(\vec{r}) \right\} C(\vec{r}, t) .$$

**Solution by propagation of an ensemble of random walkers in imaginary time**  
**Cartesian coordinates, precision  $\sigma_E/E = 10^{-6} - 10^{-3}$**

# DMC calculations for $\text{Ar}^+\text{He}_n$

## Potential model:

Anisotropy due to  $\text{Ar}^+$   $s^2p^5$  valence shell  $\rightarrow$   $\mathbf{X}^2\Sigma^+$  and  $\mathbf{A}^2\Pi$  states for  $\text{Ar}^+\text{He}$ .

**IP(Ar)=15.76 eV**  $\rightarrow$   $\text{He}^++\text{Ar}$  channel is unimportant, single configuration.  
RCCSD(T) calculations with (aug)-cc-pVXZ basis sets (**MOLPRO**).

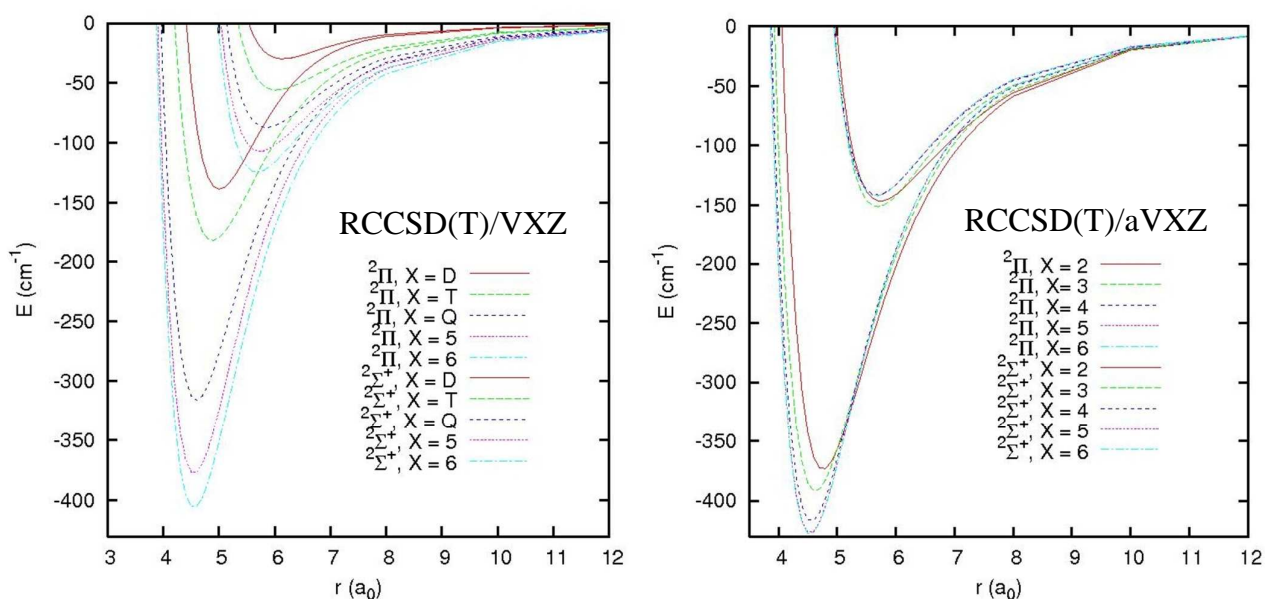
Infinite basis set ab initio points fitted to **HFD-style analytical form**  
with fixed  $C_4$  coefficient computed from  $\alpha_{\text{He}} = 1.41 \text{ a}_0^3$ .

Strong **spin-orbit interaction** in  $\text{Ar}^+$  ( $\Delta = 1432 \text{ cm}^{-1}$ ):

Non additive many body potential model including induced dipoles on He  
with additional spin-orbit mixing included using atomic  $\Delta_{\text{Ar}^+}$   
(**complex 6 x 6 matrix** to diagonalise in each DMC step).

## $\text{Ar}^+\text{He}$ : convergence of interaction energy

RCCSD(T) calculation, standard and augmented basis sets





# Ar<sup>+</sup>He: spectroscopic observables

CCSD(T), infinite basis extrapolated potentials (aQ56), atomic  $\Delta_{\text{so}}$ ,  
variational rovibrational calculation in Laguerre basis,  $^4\text{He}^{40}\text{Ar}^+$

## Vibrational transition frequencies in cm<sup>-1</sup>

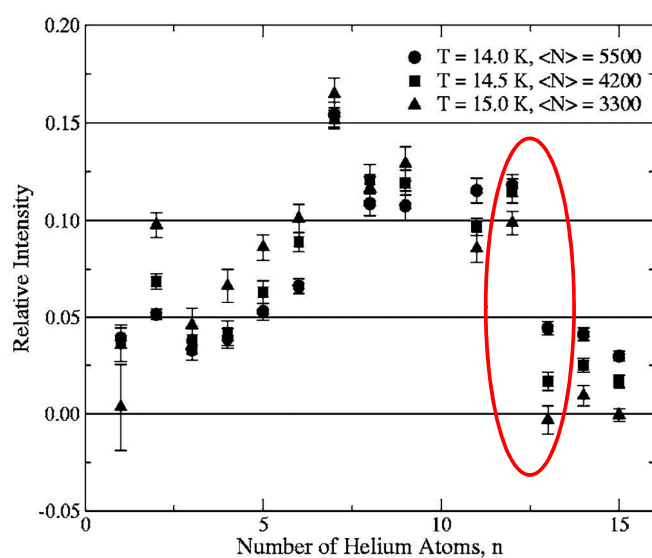
$v$	$X^2\Sigma_{1/2}^+$			$A_1^2\Pi_{3/2}$		$A_2^2\Pi_{1/2}$		
	exp	S96	This work	S96	This work	exp	S96	This work
0	<b>92.9</b>	83.9	<b>92.47</b>	52.9	55.91	<b>69.2</b>	64.0	<b>69.19</b>
1	<b>66.2</b>	55.2	<b>64.88</b>	26.9	29.20		35.1	38.82
2		30.7	38.55	11.9	11.73		15.7	17.59
3		14.1	17.81					

## Expectation values for rotational constants in cm<sup>-1</sup>

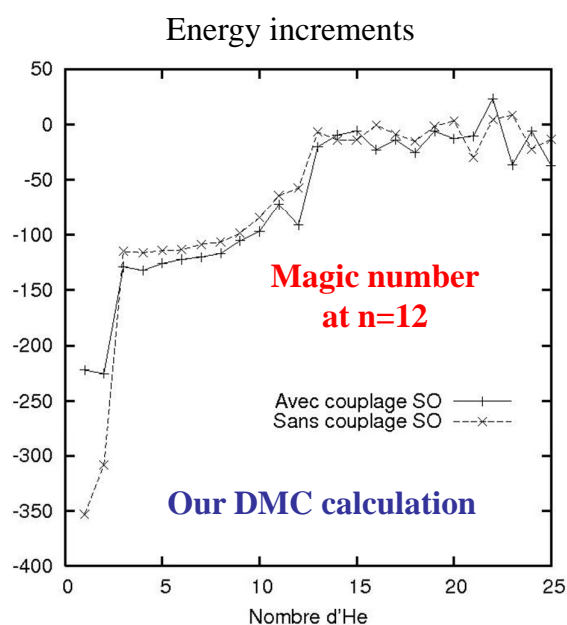
0	<b>0.659</b>	0.614	<b>0.650</b>	0.460	0.469	<b>0.515</b>	0.501	<b>0.514</b>
1	<b>0.551</b>	0.518	<b>0.559</b>	0.355	0.365	<b>0.420</b>	0.397	<b>0.412</b>
2	<b>0.39</b>	0.404	<b>0.450</b>	0.241	0.255		0.282	0.298
3		0.282	0.324	0.168	0.087		0.182	0.180
4		0.182	0.196					

**Our Ar<sup>+</sup>He potential is excellent !**

# Ar<sup>+</sup>He<sub>n</sub> : DMC ground state energies vs. exp.



Fragmentation after ionisation of Ar@He<sub>N</sub>,  
Brindle et al. 2005



**Spin orbit coupling is responsible for magic character of n=12 cluster**



# DMC calculations for I@He<sub>n</sub>

**Motivation:** Photodissociation of  $\text{CH}_3\text{I} \rightarrow \text{CH}_3 + \text{I}$  inside He<sub>n</sub>.

We need global potential energy surfaces for ground and excited  $\text{CH}_3\text{I}@He_n$  and for the relevant fragments  $\text{CH}_3@He_n$  and  $\text{I}@He_n$

## Potential model:

Anisotropy due to I  $s^2p^5$  valence shell  $\rightarrow$   $X^2\Sigma^+$  and  $A^2\Pi$  states for I-He.  
RCCSD(T) calculations with aug-cc-pVXZ basis sets and relativistic pseudopotential (ECP) from K. Petersen.

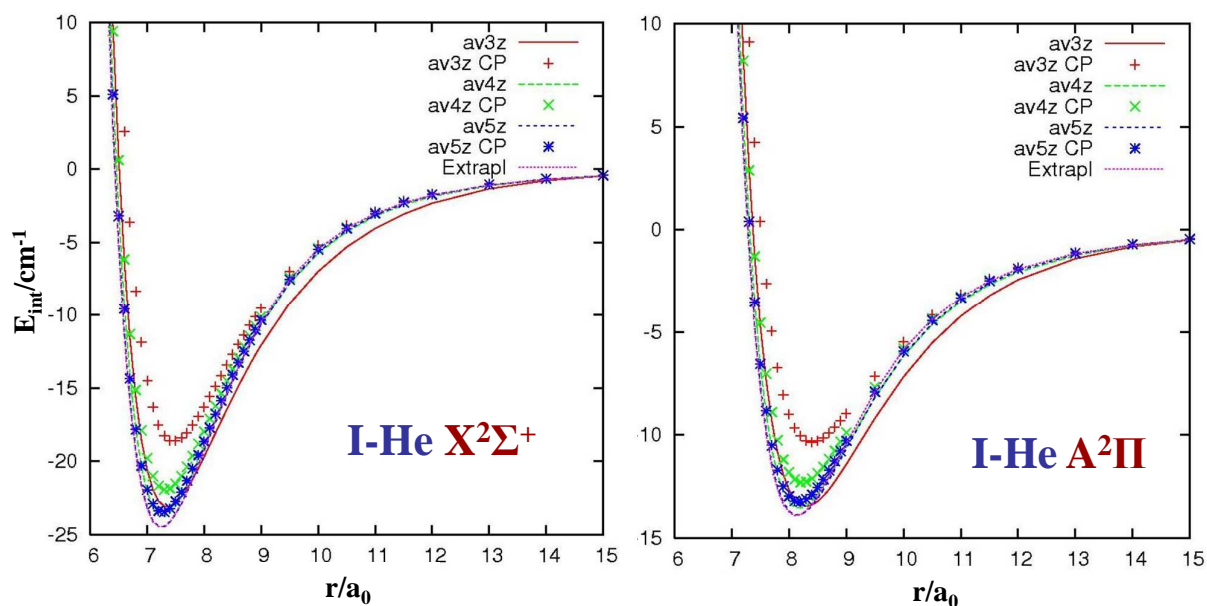
Ab initio points fitted to extended Tang-Toennies analytical form.

Very strong spin-orbit interaction in I:

Non additive many body potential model with additional spin-orbit mixing using atomic  $\Delta_I$  (complex 6 x 6 matrix to diagonalise in each DMC step).

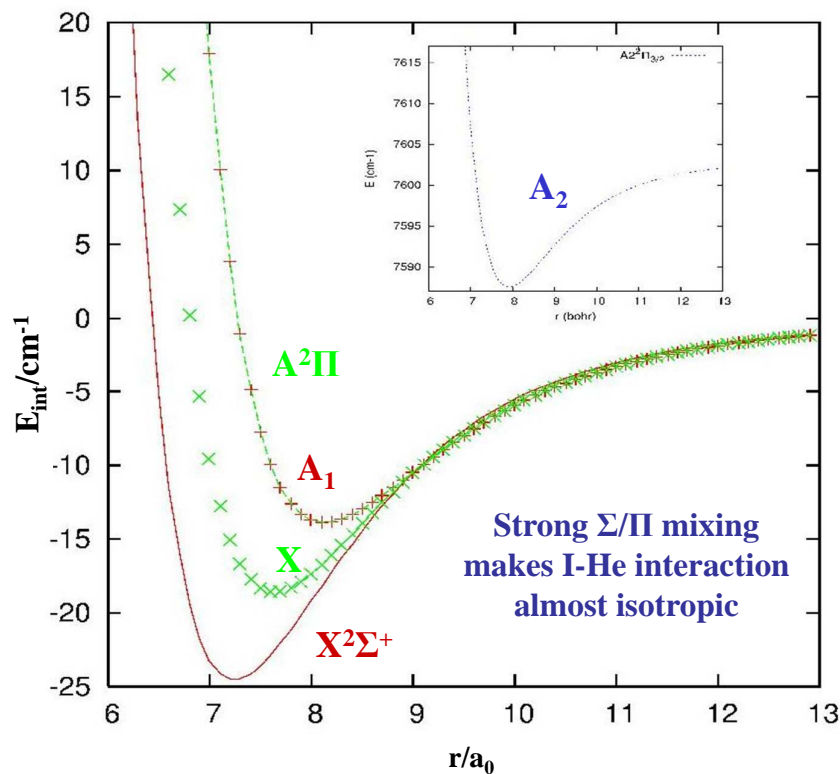
$\Delta_{\text{SO}}$  dominates so much over  $E_{\text{vdW}}$  that SO mixing is almost perfect!

## I-He: Convergence of RCCSD(T)/ECP calculations



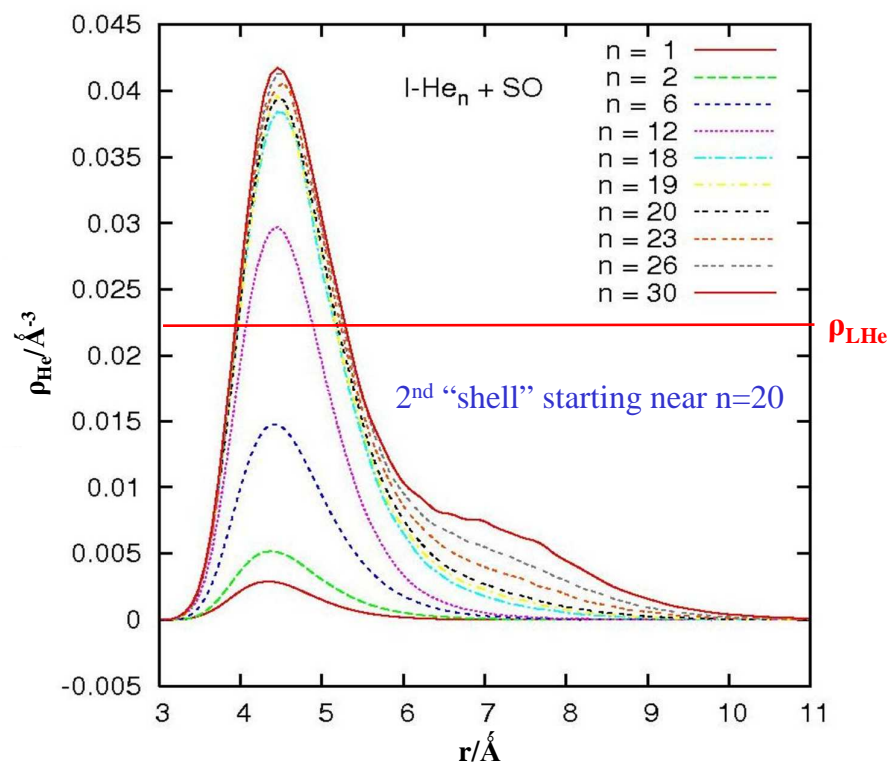
Spin-orbit coupling mixes the  $^2\Sigma_{1/2}$  and  $^2\Pi_{1/2}$  components: 6x6 complex matrix

# I-He: Interaction potential with SO coupling

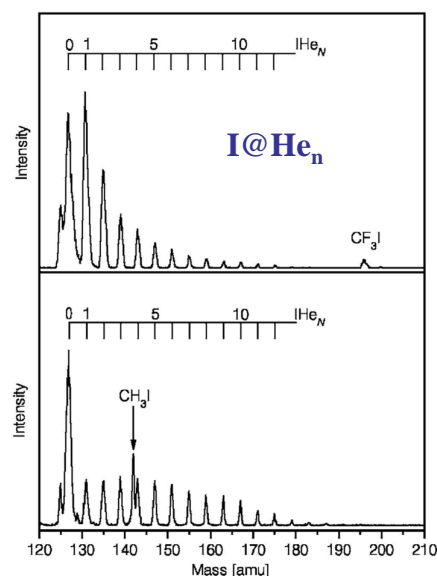
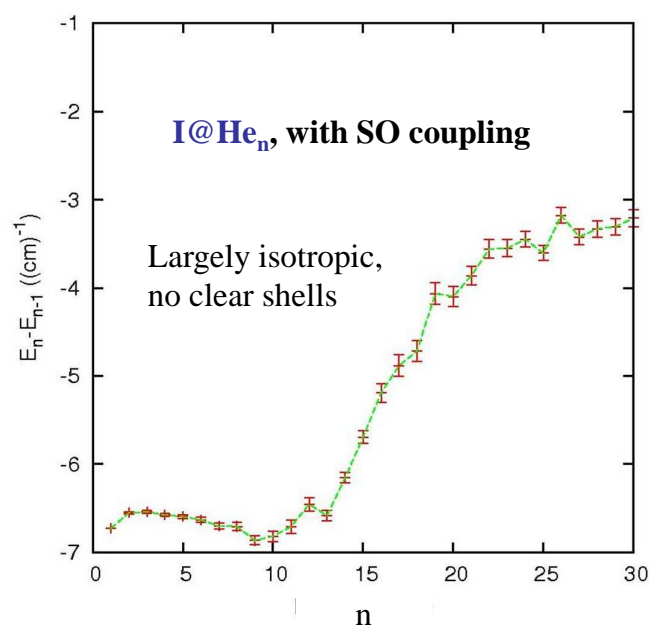


RCCSD(T),  
small core ECP,  
MOLPRO code,  
infinite basis  
extrapolation,  
experimental  
atomic SO  
constant.

# I@He<sub>n</sub>: Radial helium density from DMC

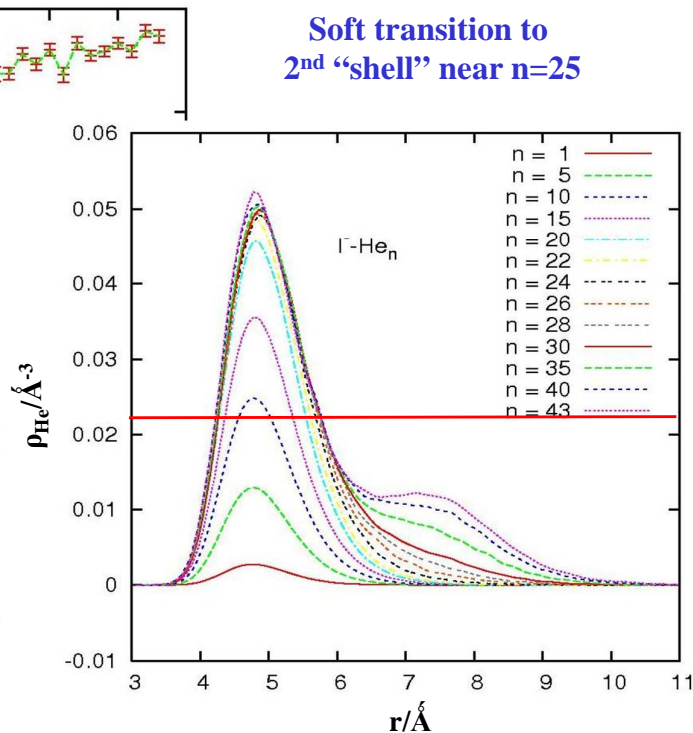
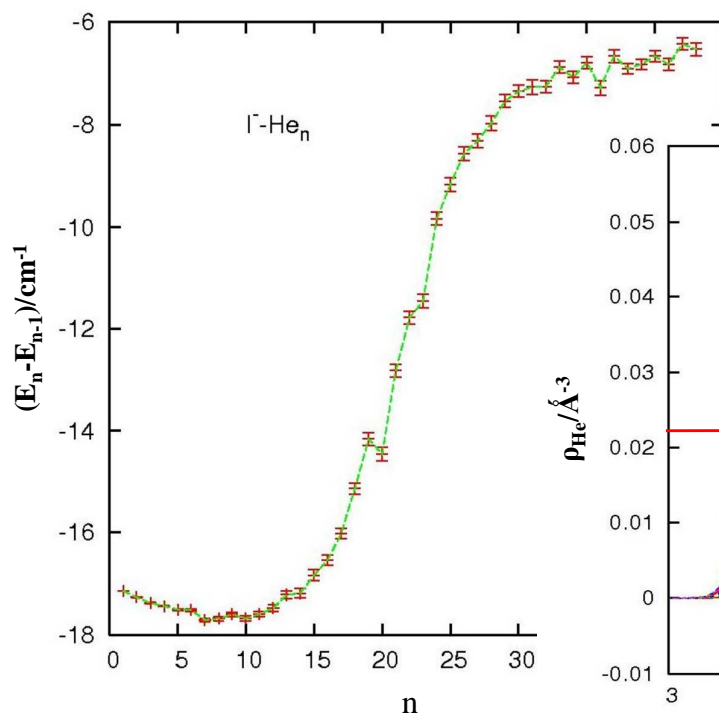


# I@He<sub>n</sub>: Incremental binding energies from DMC

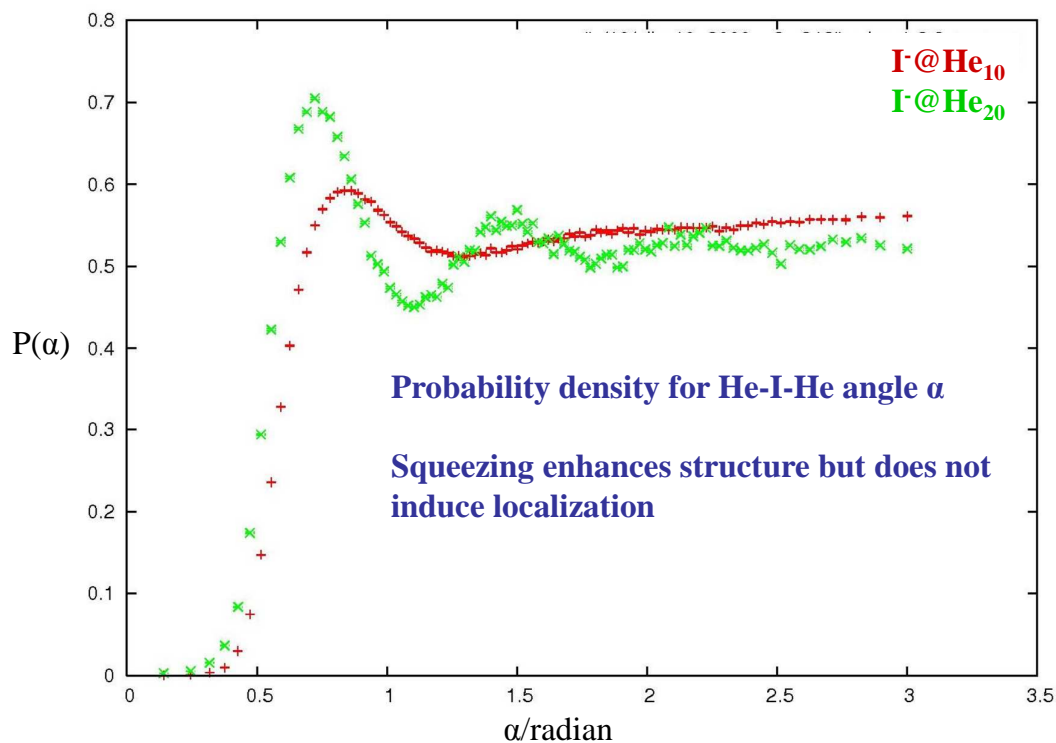


Braun and Drabbels 2007

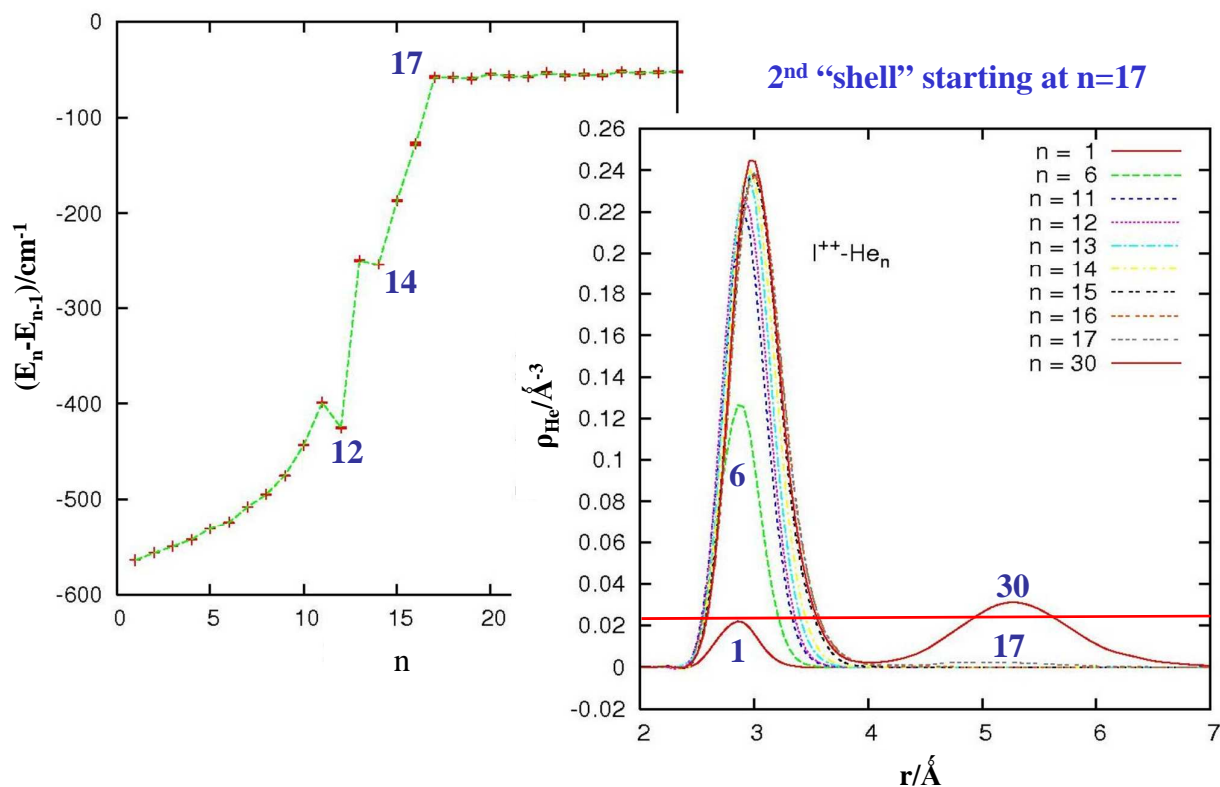
# I<sup>-</sup>@He<sub>n</sub>: Binding energy and radial helium density



## I<sup>-</sup>@He<sub>n</sub>: Angular correlations



## I<sup>2+</sup>@He<sub>n</sub>: Binding energy and radial helium density



# CO<sup>+</sup>-He and CO<sup>+</sup>@He<sub>n</sub>

Evidence for formation of CO<sup>+</sup>He ions in several drift tube experiments.

**No experimental spectroscopic information.**

Mixed cluster ions of the composition CO<sup>+</sup>He<sub>n</sub> should be accessible in drift tube experiments, mixed gas expansions coupled to electric discharges, or CO ionization inside large He clusters.

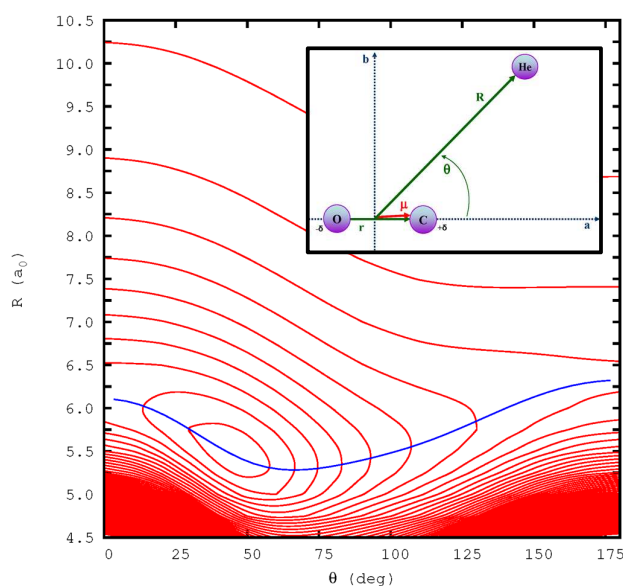
Ionisation of CO barely changes the rotational constants but strongly affects the interaction with helium: CO@He<sub>n</sub> and CO<sup>+</sup>He<sub>n</sub> are an ideal pair to understand **rotation in helium clusters** by separating effects due to mass and interaction.

Potential surface can be checked by ion depletion spectroscopy (see N<sub>2</sub><sup>+</sup>-He<sub>n</sub>).

## Astrophysical motivation

CO is rather abundant in interstellar space and CO<sup>+</sup> has been identified in 1993. Low energy collisions with **helium** atoms, its second most abundant and **non reactive collision partner**, are governed by the weak intermolecular interaction leading to the van der Waals complex He-CO<sup>+</sup>.

## Features of the CO<sup>+</sup>-He surface



**2D contour plot of the RCCSD(T) PES.**

Contour lines at intervals of 25 cm<sup>-1</sup>, first contour placed at -250 cm<sup>-1</sup>. The **blue line** shows the variation of the Jacobi distance R along the minimum energy path in the direction of the Jacobi angle  $\theta$ .

**RCCSD(T) surface extrapolated to complete basis set limit.**

$$V_{\min} = -275.3 \text{ cm}^{-1}$$

$$E_0 = -195.0 \text{ cm}^{-1}$$

$$A_0 = 7.168 \text{ cm}^{-1}$$

$$B_0 = 0.466 \text{ cm}^{-1}$$

$$C_0 = 0.411 \text{ cm}^{-1}$$

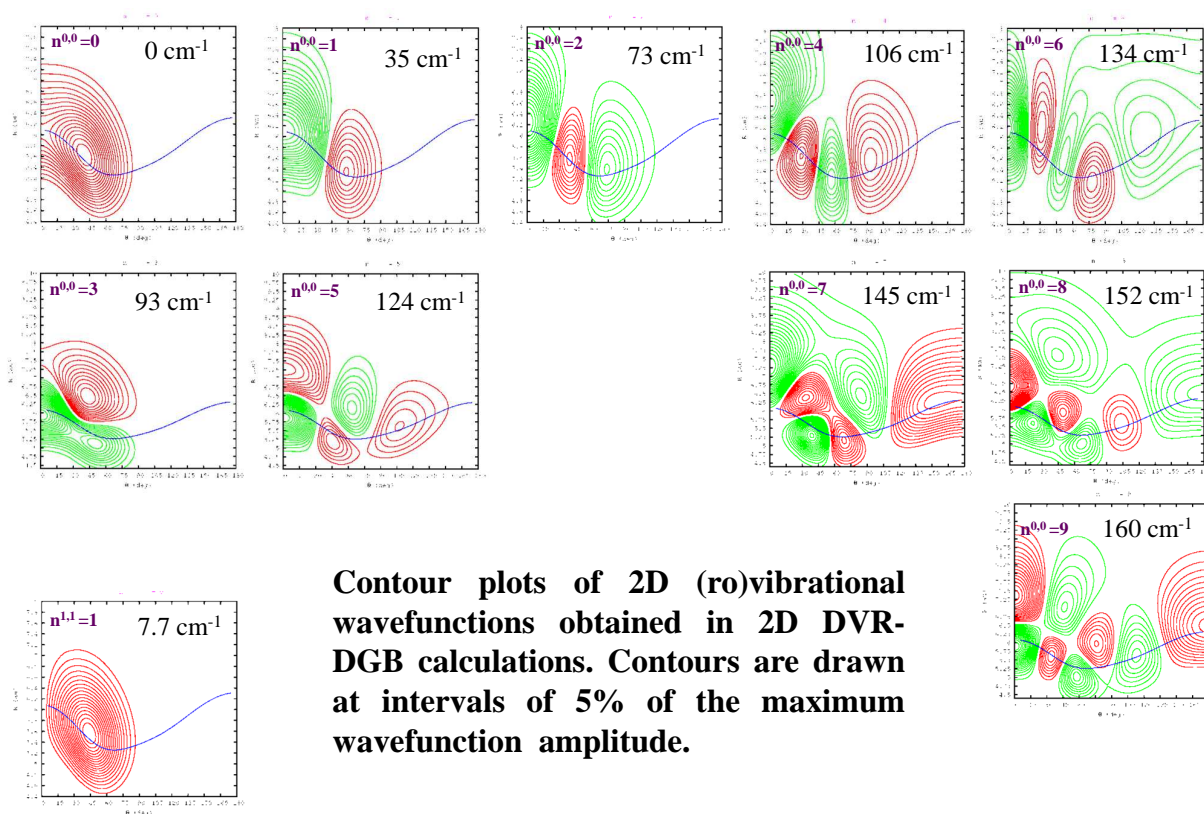
**Quasilinear molecule with strong permanent dipole moment and strong IR transition moment.**

**Low energy scattering resonance.**

# Spectroscopic results from DVR-DGB calculations

He-CO<sup>+</sup>(X<sup>2</sup>Σ<sup>+</sup>) 2D RCCSD(T) potential energy surfaces V(R,θ) at r(CO)=1.11783 Å

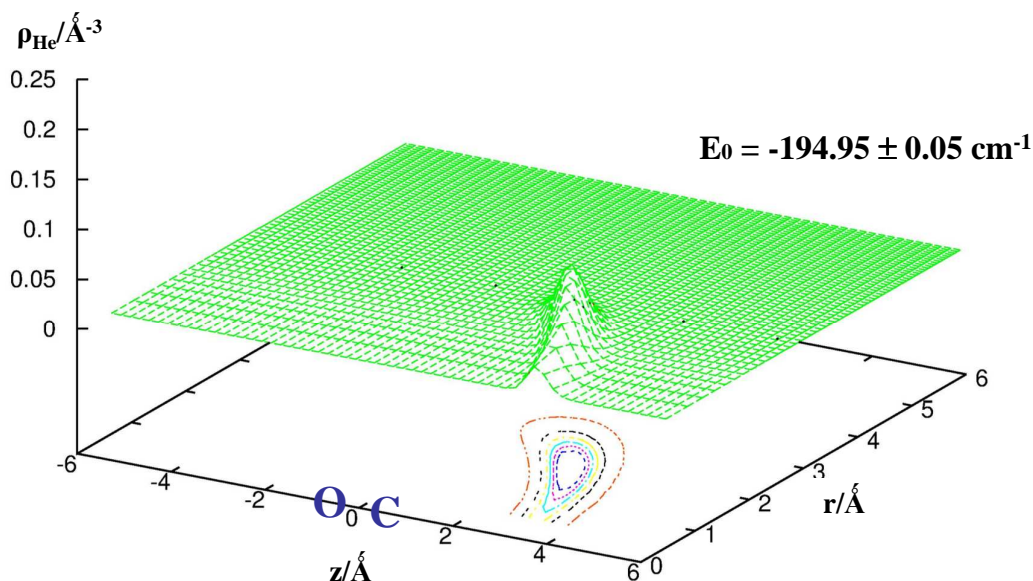
	avtz	avtz <sub>corr</sub>	avqz	avqz <sub>corr</sub>	av5z	av5z <sub>corr</sub>	av∞z
$R_e/\text{Å}$	2.898	2.905	2.870	2.878	2.868	2.871	2.866
$\theta_e/\text{deg}$	43.8	46.2	45.8	46.0	46.1	46.1	46.3
$V_{\min}/\text{cm}^{-1}$	-285.8	-252.4	-281.6	-269.0	-277.7	-274.0	-275.3
$E_0/\text{cm}^{-1}$	-209.7	-177.5	-201.3	-189.9	-197.6	-194.2	-195.0
$A_0/\text{cm}^{-1}$	10.3	7.315	7.679	7.328	7.362	7.256	7.168
$B_0/\text{cm}^{-1}$	0.444	0.454	0.462	0.462	0.465	0.465	0.466
$C_0/\text{cm}^{-1}$	0.395	0.400	0.408	0.407	0.410	0.409	0.411
$\nu_2/\text{cm}^{-1}$	31.9	32.8	34.3	34.4	34.7	34.7	34.9
$\nu_3/\text{cm}^{-1}$	94.8	86.5	94.2	91.3	93.6	92.8	93.3
$\Delta_1/\text{cm}^{-1}$	0.049	0.055	0.056	0.055	0.055	0.055	0.056
$\kappa$	-0.990	-0.984	-0.985	-0.984	-0.984	-0.984	-0.983
$\gamma_0$	-0.31	0.08	0.08	0.12	0.12	0.14	0.15



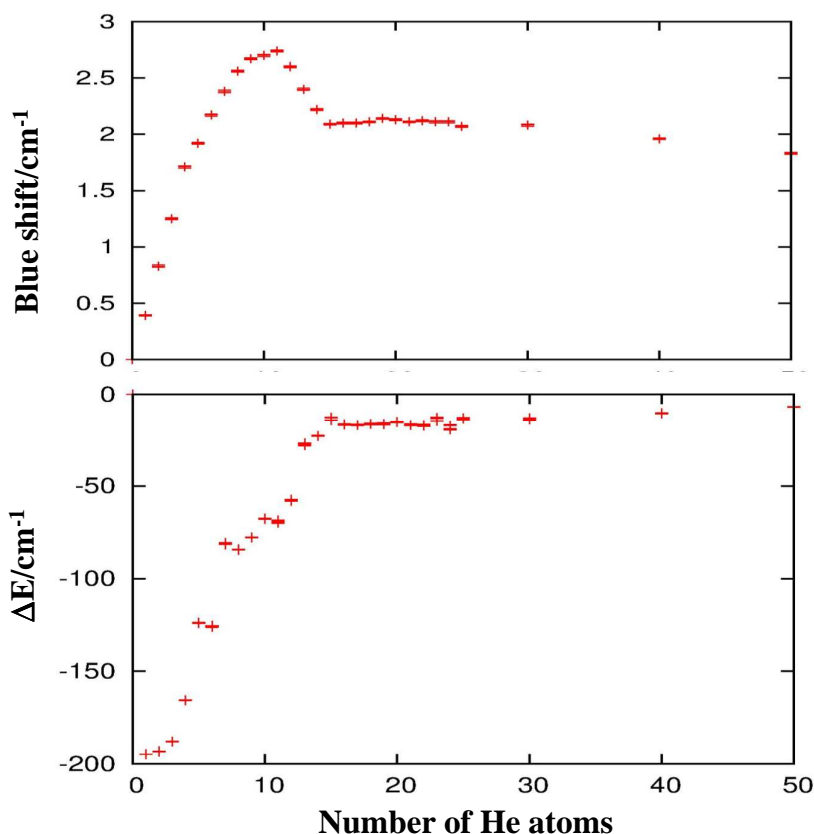


# CO<sup>+</sup>-He ground state as seen by DMC: He density histogram in cylinder coordinates (z,r)

O→C defines z-axis, origin at c.o.m. of CO unit



Contour lines at  $\rho_{\text{He}} = 0.001, 0.01, 0.02, 0.03, 0.04, 0.05, 0.1, 0.15, 0.20, 0.25 \text{ Å}^{-3}$



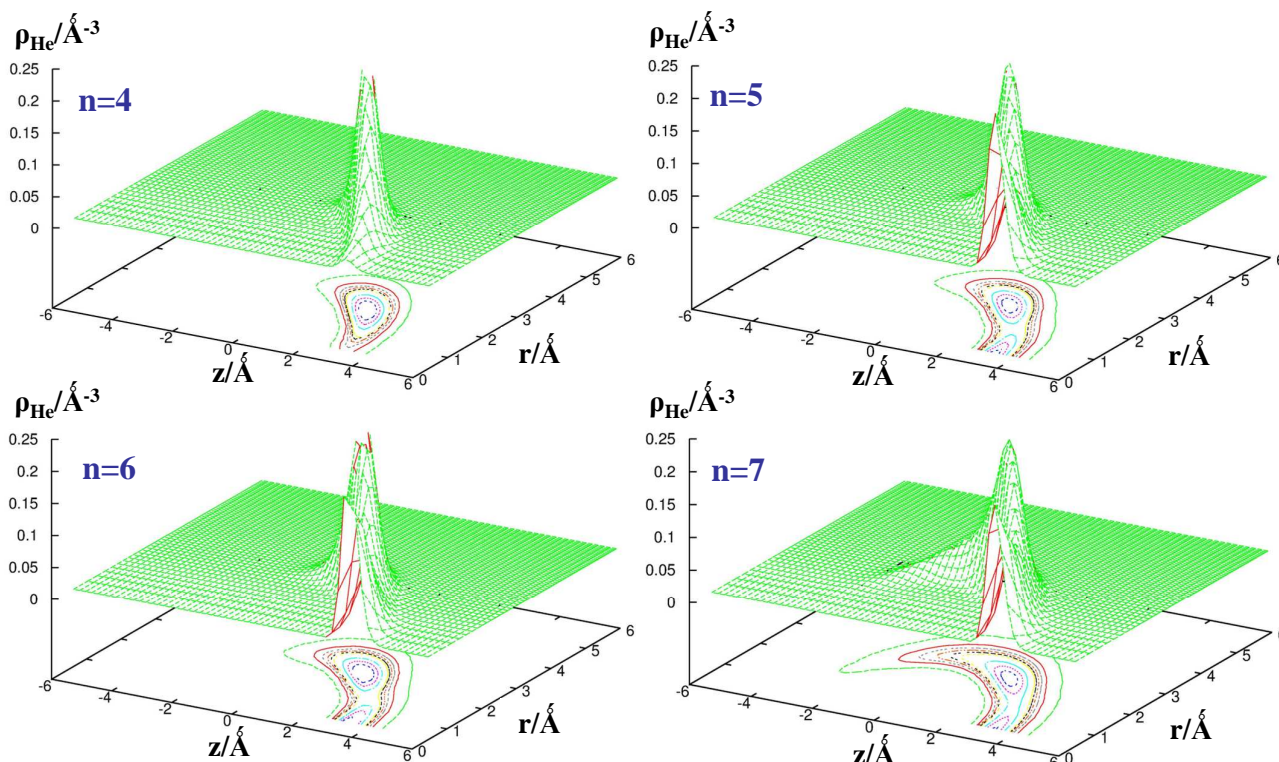
## CO<sup>+</sup>@He<sub>n</sub>

**Energy increments  $\Delta E$**  (chemical potential, bottom graph) and **CO<sup>+</sup> frequency shift** (upper graph) from adiabatic method (intermolecular potential as parametric function of the CO<sup>+</sup> vibrational state). Many body model with induced dipoles.

Note the turn-around of the frequency shift at the last “magic” size.



# CO<sup>+</sup>He<sub>n</sub> ground state densities from DMC

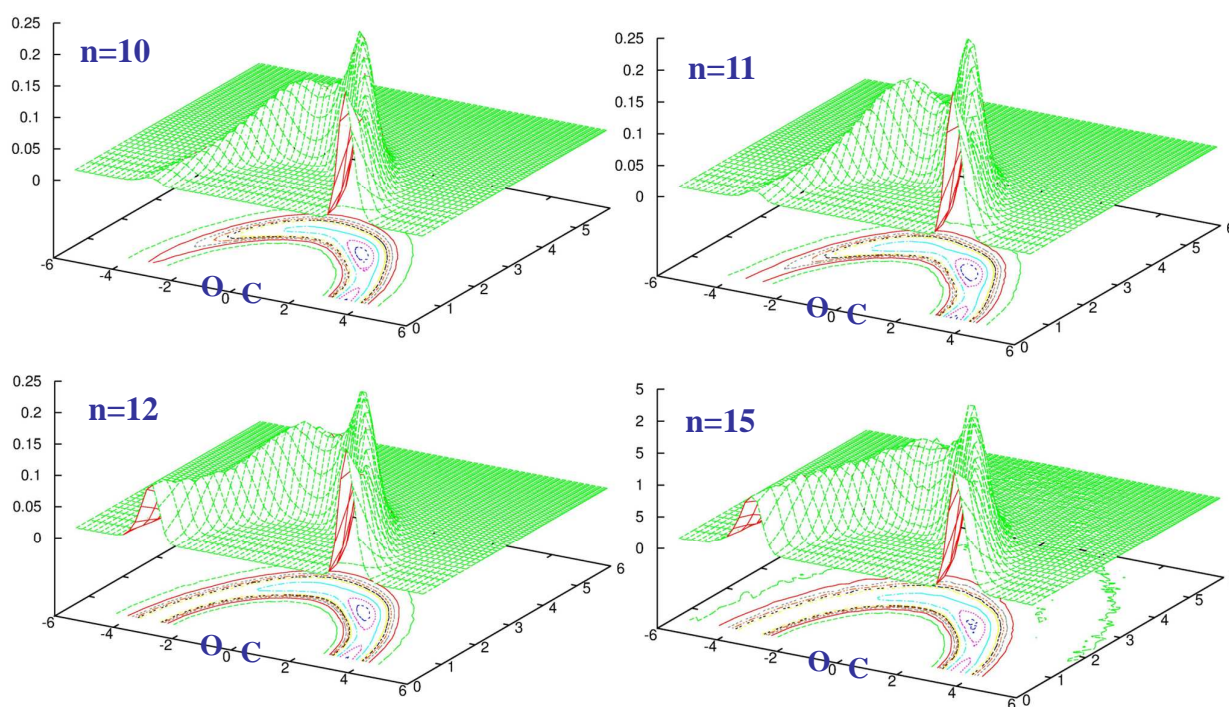


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## CO<sup>+</sup>He<sub>n</sub> DMC ground state densities: build up of strongly anisotropic first helium shell

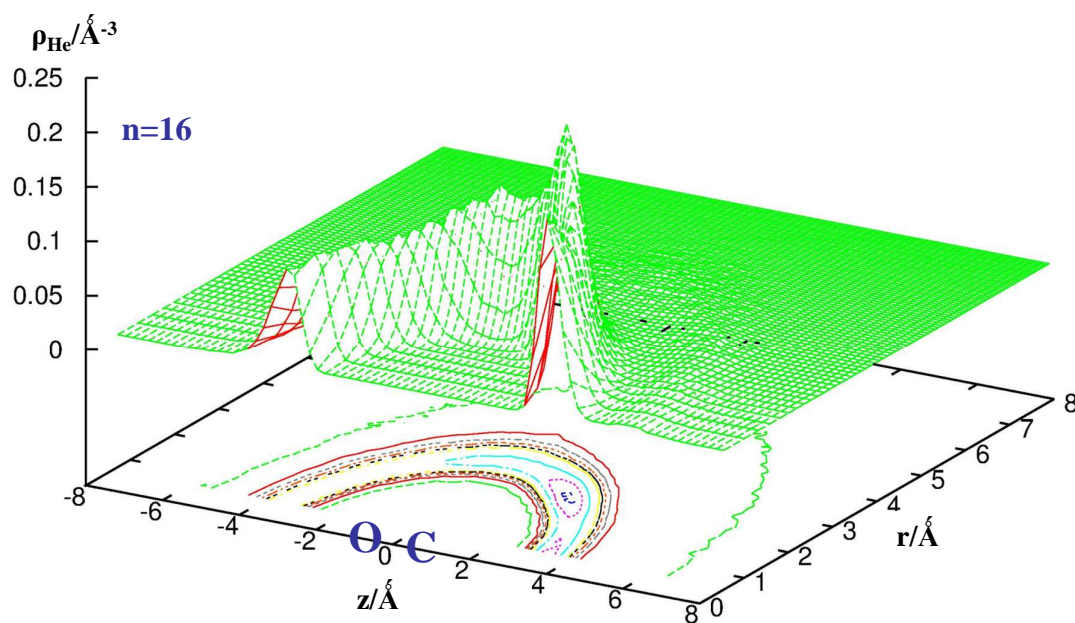


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# CO<sup>+</sup>He<sub>n</sub> DMC ground state densities: onset of second helium shell at n=16

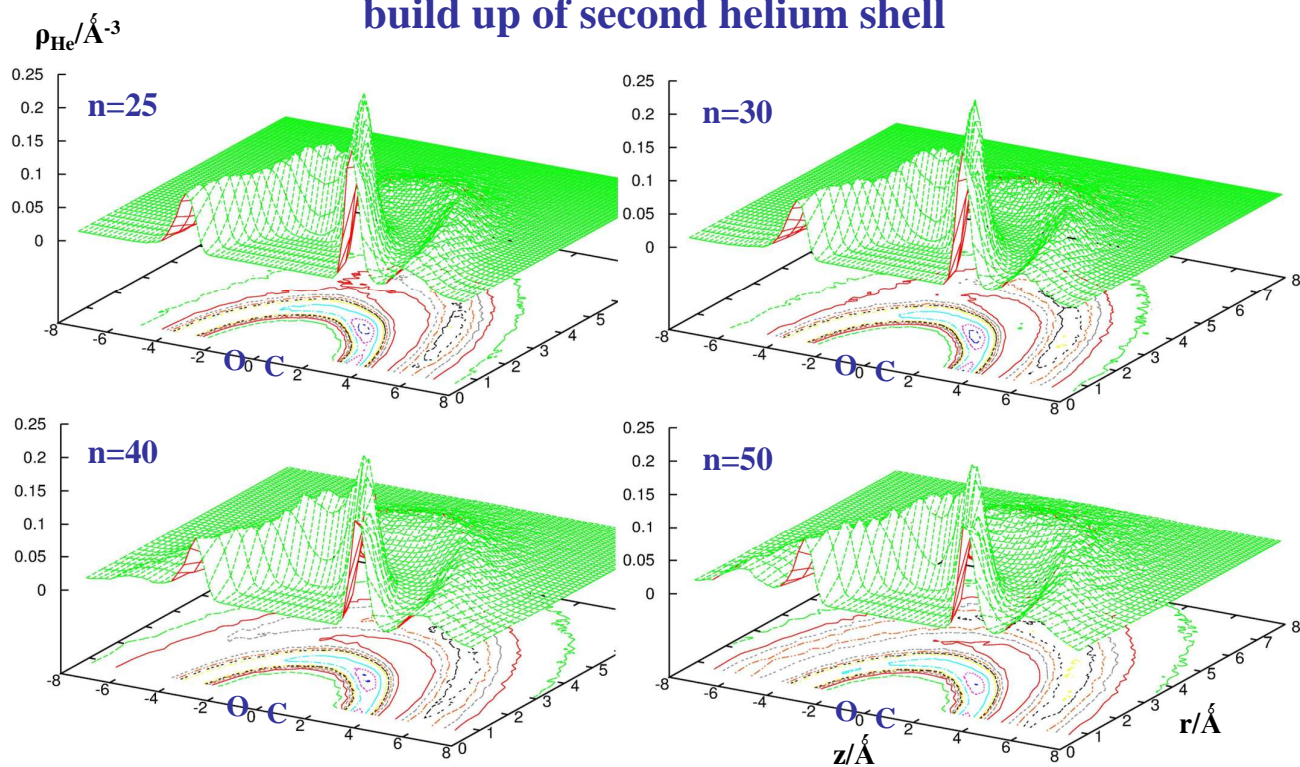


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# CO<sup>+</sup>He<sub>n</sub> DMC ground state densities: build up of second helium shell



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# CH<sub>3</sub>-He

- Ab initio **RCCSD(T)** calculations with **aug-cc-pVXZ** basis sets (**X=D,T,Q,5**)
- **CH<sub>3</sub>** keeping C<sub>3v</sub> symmetry and fixed C-H distance: only **umbrella angle  $\alpha$**
- **He** position relative to **CH<sub>3</sub>** center of mass in **spherical coordinates  $R, \theta, \phi$**
- Several 3D surfaces assembled into 4D surface including **CH<sub>3</sub>** relaxation
- Overall about 3000 potential energy points

Analytical representation with **angle dependent HFD** form expanded over real spherical harmonics  $T_{lm}$  with symmetry restrictions on  $l, m$ :

$$V(R, \theta, \phi) = A \exp\{-b(\theta, \phi) [R - R_e(\theta, \phi)]\} - \sum_k C_k(\theta, \phi)/R^k$$

$$X(\theta, \phi) = \sum_{lm} x_{lm} T_{lm}(\theta, \phi) \quad X=b, R_e, C_k$$

500-1000 points per 3D cut are fitted with 38 parameters and rms < 0.1 cm<sup>-1</sup>

## Outlook

- Effective rotational constants for CO<sup>+</sup> in helium (DMC/PIMC in collaboration with P. N. Roy).
- CH<sub>3</sub> radicals in helium, reactive complexes.
- Photodissociation of CH<sub>3</sub>I and CF<sub>3</sub>I (ZPAD, DMC etc.)
- Dopant spectroscopy (Mg<sup>\*</sup>, Ag<sup>\*</sup>, Ag<sup>+</sup> etc.).
- Transport properties (Mg<sup>+</sup>, Na<sup>+</sup>).
- DMC and ZPAD calculations on Xe<sub>n</sub>He<sub>m</sub>.
- DMC with constraints ((H<sub>2</sub>)<sub>n</sub>, He<sub>n</sub>(H<sub>2</sub>)<sub>m</sub> possible).
- SBDMC: soft body DMC allowing feedback between dopant and bath vibrations, quaternions for rotation.

**ANR project DYNHELIUM (Toulouse, Rennes, Paris)**