Real time dynamics of doped helium nanodroplets

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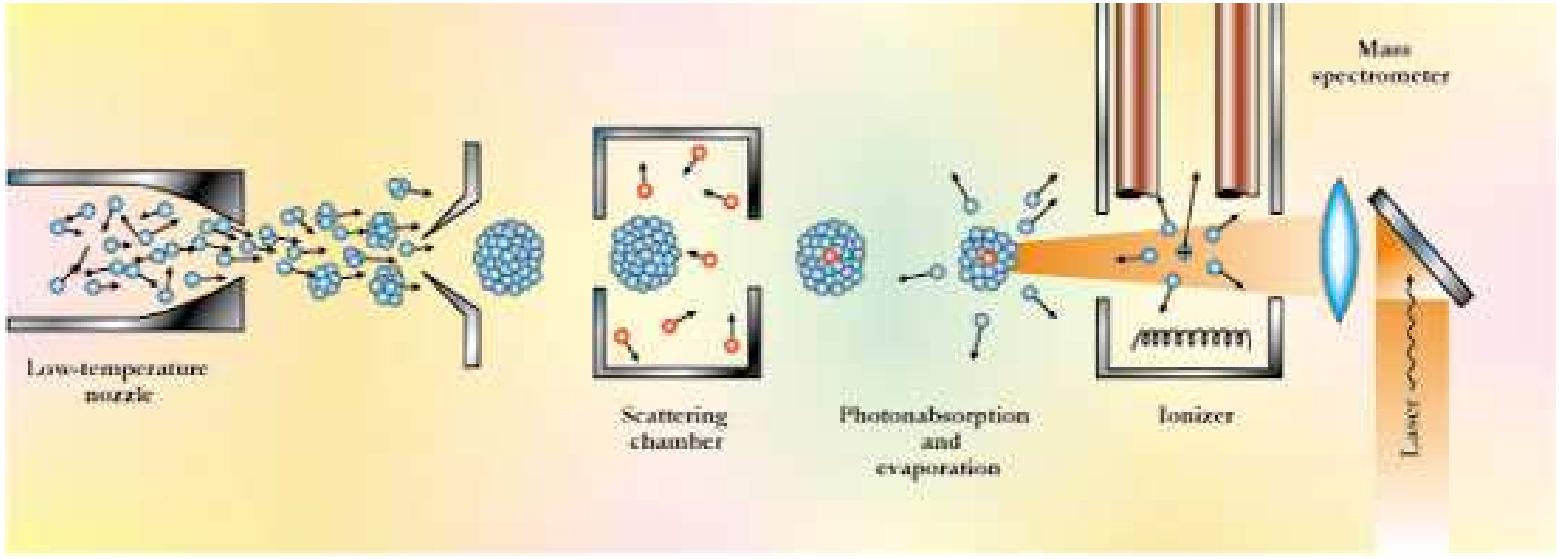
Helium nanodroplets:

- clusters of 500 to over 10^8 atoms



from Toennies, Phys. Today 2001

$T \simeq 0.4\ K$ from rotationally resolved spectra

Helium nanodroplets: Why study them?

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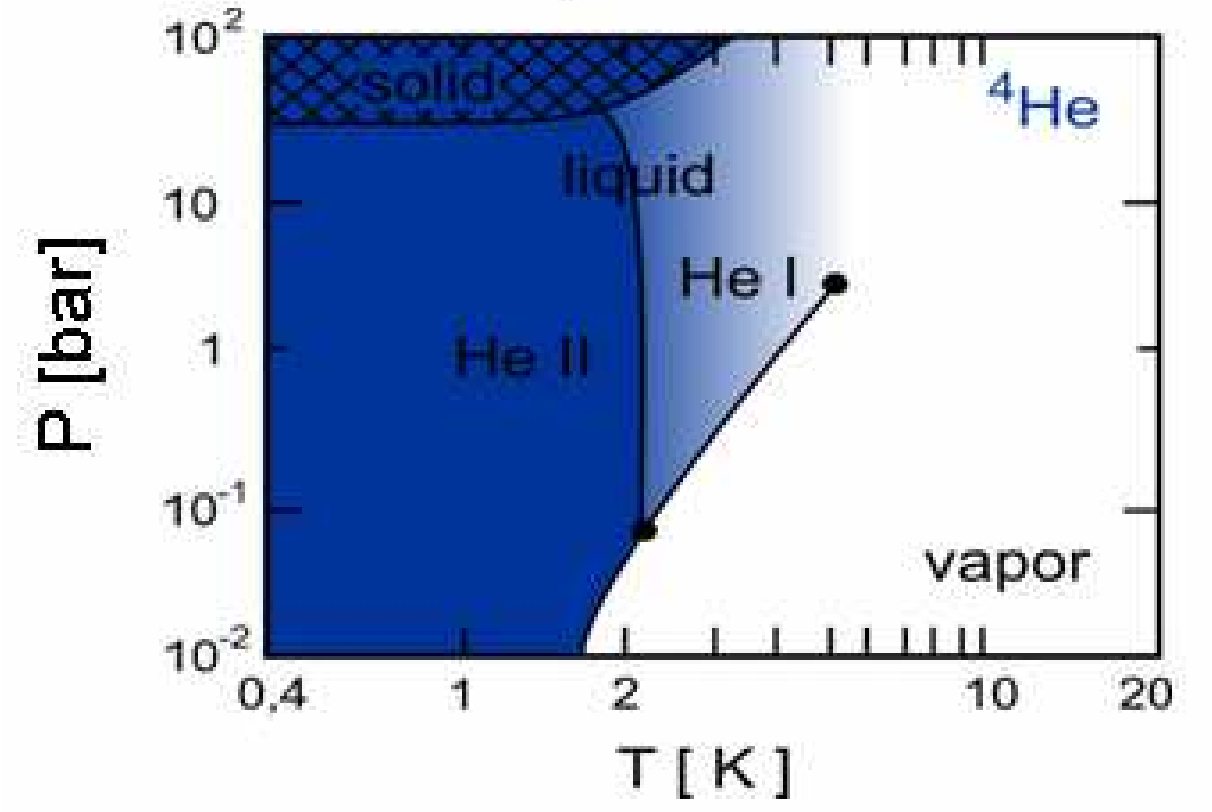

Helium nanodroplets: Why study them?

superfluidity in a finite size system?

- "Frictionless" motion: molecular rotation, existence of a Landau critical velocity?
- Very high heat conductivity
- Zero-phonon lines separated from phonon wings
- Quantized vortices

Quantum "solvent"

- Helium droplets will pick up "anything"
  - atoms, molecules...
  - e^- metastable

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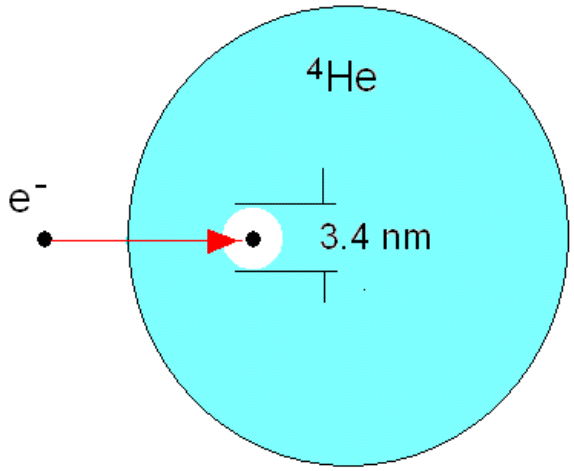

He-electron interaction repulsive

$\longrightarrow$ empty bubble around e^-

(picture from G. Benedek)

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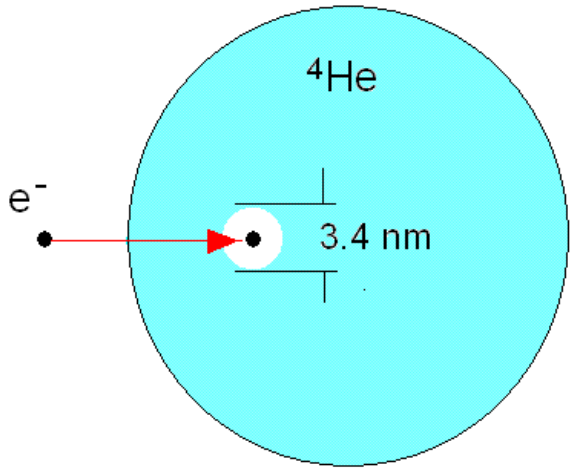

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- Location of the dopant:
  – M will sit near the center,
  – except alkalis, Ba, Sr, alkali clusters (which size?), A-Rg$_n$ to solvate them...

Nanolab's experiments

- ^4He_N: A "solvent" with very special properties:
  - extremely cold (0.4 K)
  - (super-)fluid
  - chemically inert

$\rightarrow$ high resolution spectroscopy

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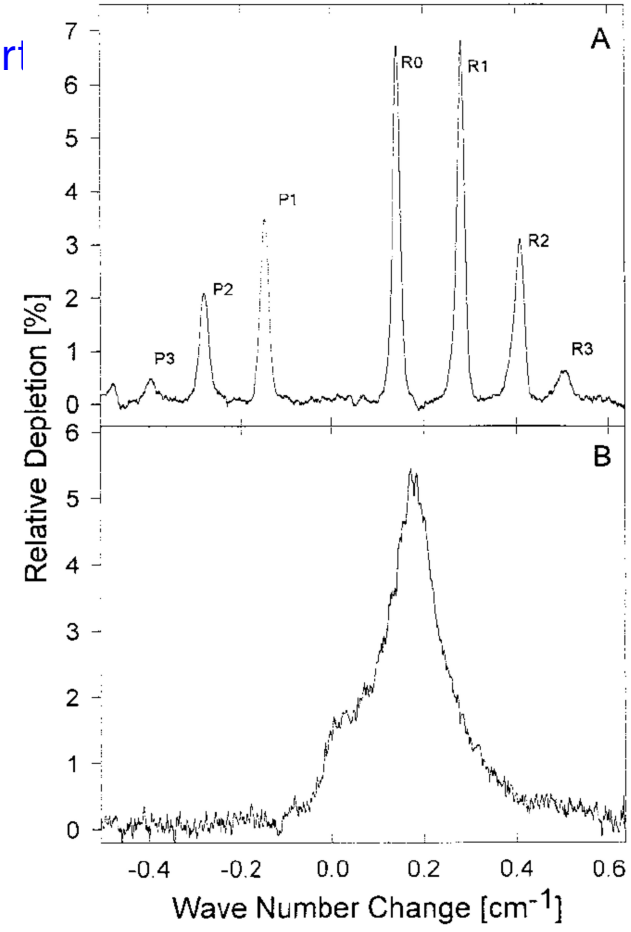
OCS rotational resolution in ^{4}He!

OCS rovibrational IR spectroscopy



Grebenev, Toennies, Vilesov, Science 1998

Nanolab's experiments

PTCDA electronic spectroscopy

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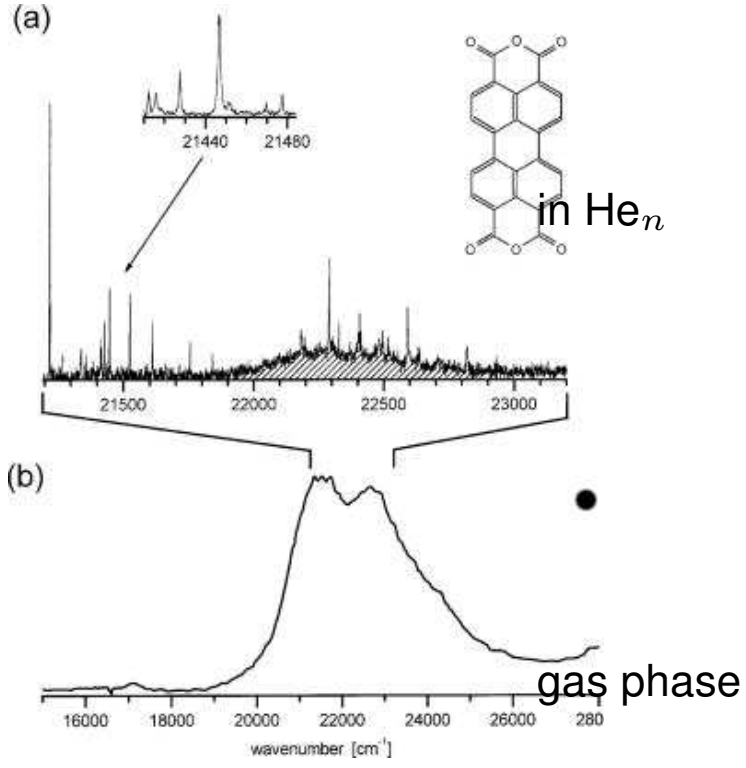

in He$_n$

gas phase

(from Stienkemeier and Vilesov, J.Chem.Phys. 2001)

$\rightarrow$ e.g., Gert Von Helden: Catching proteins in liquid heliu

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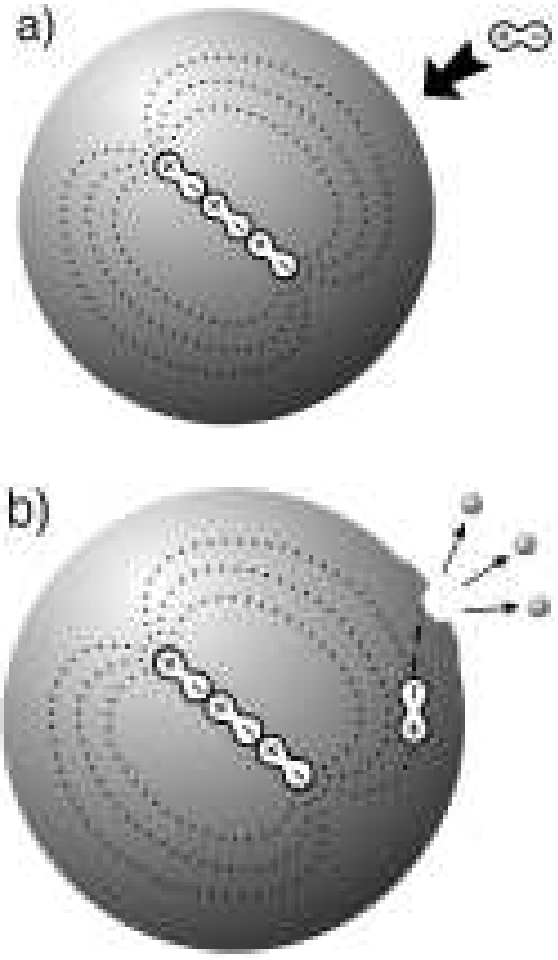
  - very high heat conductivity → fast cooling

→ Exotic clustering

HCCCN clustering



chain formation

driven by electrostatics

(exp. Nauta, Moore and Miller 1999, from Toennies, Angew.Chem. 2004)

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→ Chemical reactions: highly reactive species, low barriers...

  → *e.g., Gary E. Douberly: Spectroscopy and reactions of hydrocarbon radicals in helium nanodroplets*

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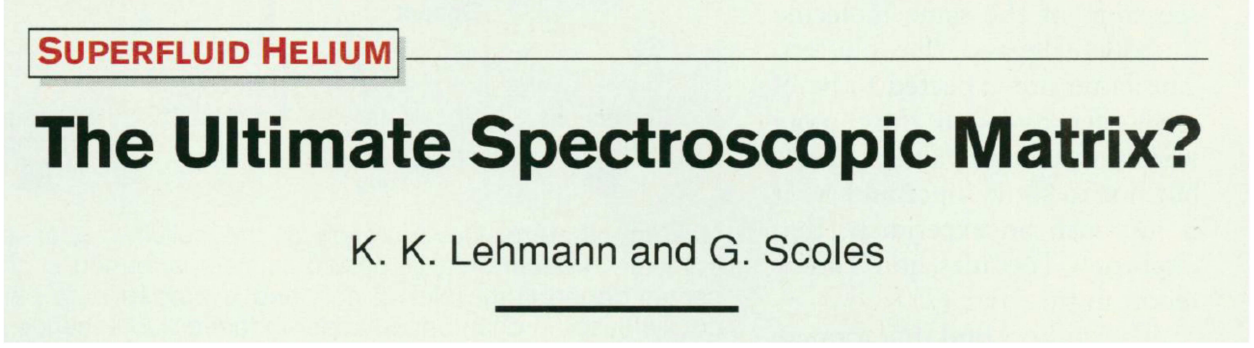
SUPERFLUID HELIUM

The Ultimate Spectroscopic Matrix?

K. K. Lehmann and G. Scoles

Science 279, 2065 (1998)

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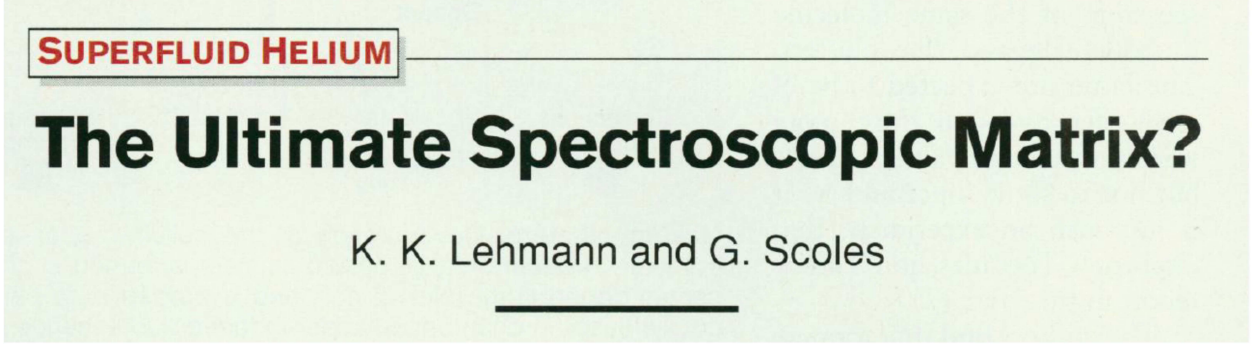
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But the influence of the superfluid helium environment is not well known...

Dynamics in the ground electronic state: Pickup and Clustering by superfluid ^{4}He droplets

- Pickup by $^4\mathrm{He}_N$:
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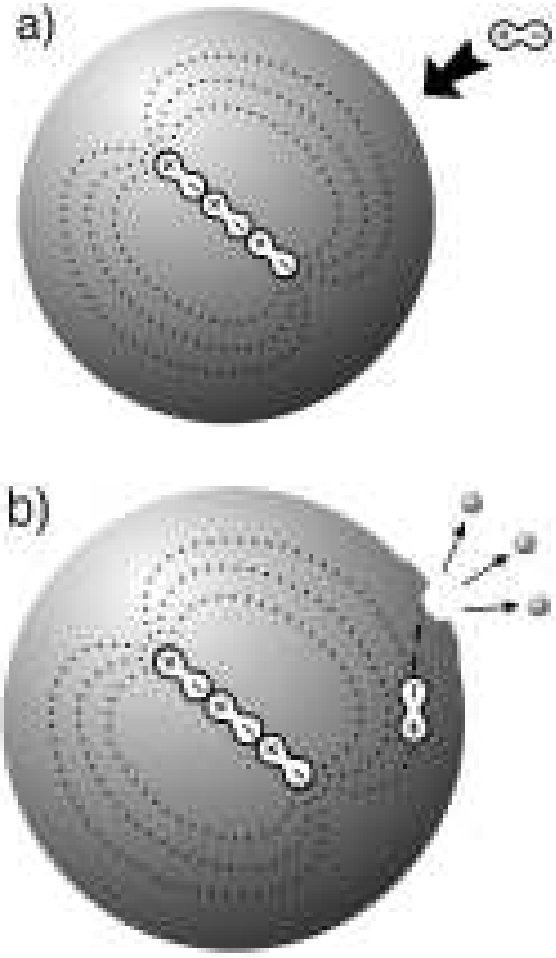

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- Pickup + Clustering by He_N hosting Vortices
  – visualize vortices with Xe atoms
  – filament-shaped clusters

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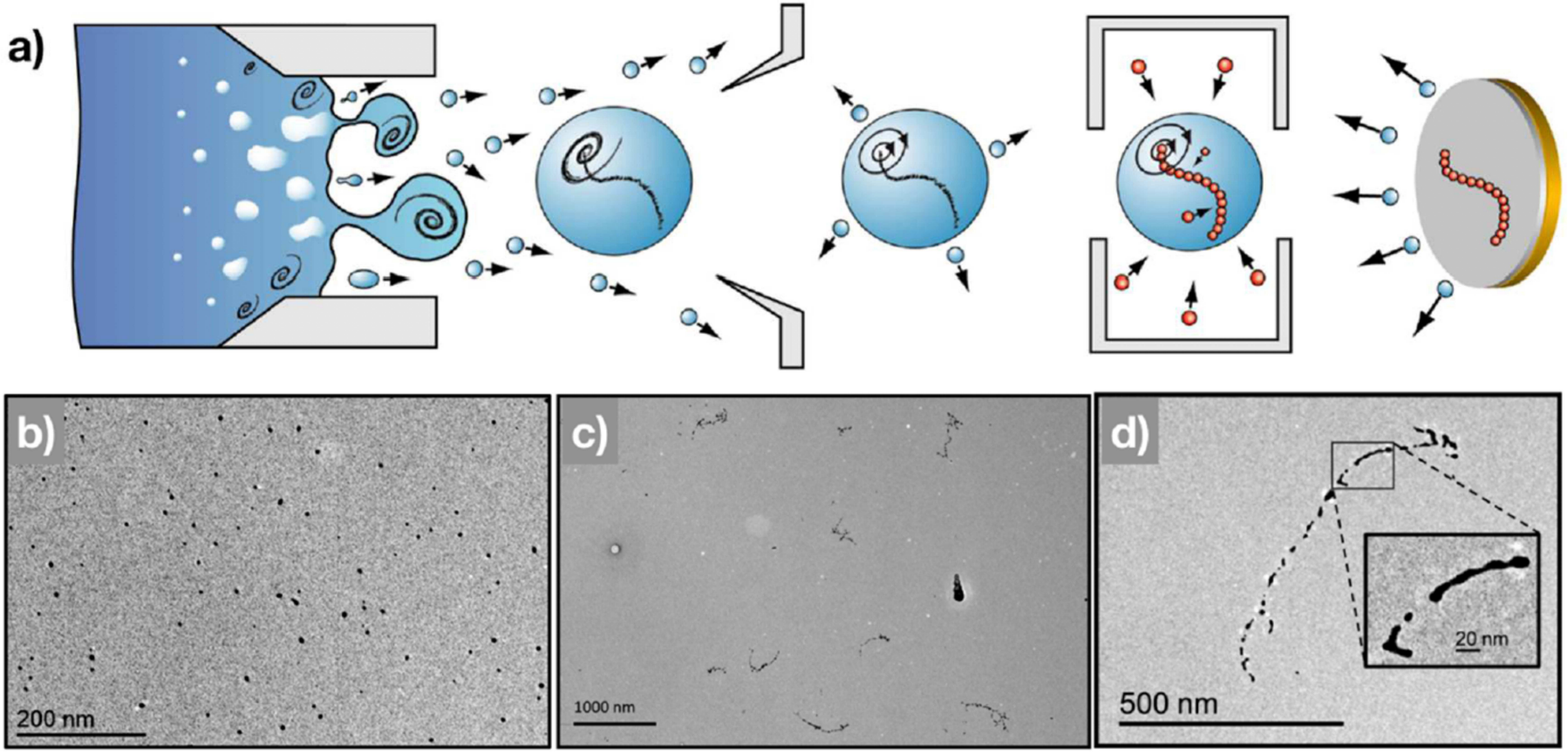

Ag-doped very large droplets $\rightarrow$ filament-shaped clusters vizualizing vortices

(Gessner and Vilesov, Annu. Rev. Phys. Chem. ***70****, 173 (2019))*

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$\rightarrow$ Study pickup and clustering by superfluid helium droplets hosting or not vortices...

Theoretical simulation: ^{4}He-DFT for A@He$_N$

Total energy of the system as a function of the ^{4}**He density** $\rho(\mathbf{r})$:

$$E[\rho] = \int d\mathbf{r} \left\{ \frac{\hbar^2}{2m_{\rm He}} \left|\nabla\sqrt{\rho(\mathbf{r})}\right|^2 + \mathcal{E}[\rho(\mathbf{r})] \right\} + \int d\mathbf{r}\, \rho(\mathbf{r})\, V_{\rm A}(|\mathbf{r}_{\rm Rb} - \mathbf{r}|)$$

Orsay-Trento density functional : *[F. Dalfovo, A. Lastri, L. Pricaupenko, S. Stringari & J. Treiner, PRB 1995; F. Ancilotto, M. Barranco, F. Caupin, R. Mayol & M. Pi, PRB 2005.]*

$$\begin{aligned}
\mathcal{E}_c[\rho] \quad = \quad & \frac{1}{2}\int \mathrm{d}\mathbf{r}'\rho(\mathbf{r})V_{LJ}(\mathbf{r}-\mathbf{r}'|)\rho(\mathbf{r}') + \frac{1}{2}c_2\,\rho(\mathbf{r})\,[\bar{\rho}(\mathbf{r})]^2 + \frac{1}{3}c_3\,\rho(\mathbf{r})\,[\bar{\rho}(\mathbf{r})]^3 \\
& -\frac{\hbar^2}{4m}\alpha_s \int \mathrm{d}\mathbf{r}'\,F(|\mathbf{r}-\mathbf{r}'|)\,[1-\tilde{\rho}(\mathbf{r})/\rho_{0s}]\,\nabla\rho(\mathbf{r})\cdot\nabla'\rho(\mathbf{r}')\,\left[1-\tilde{\rho}(\mathbf{r}')/\rho_{0s}\right] \\
& -\frac{m}{4}\int d\mathbf{r}'\,V_J(|\mathbf{r}-\mathbf{r}'|)\,\rho(\mathbf{r})\,\rho(\mathbf{r}')\,[\mathbf{v}(\mathbf{r})-\mathbf{v}(\mathbf{r}')]^2 + C\,\rho(\mathbf{r})\{1+\tanh[\beta\,(\rho(\mathbf{r})-\rho_{\rm m})]\}
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Statics: Minimize $E[\rho]$ with respect to $\Psi(\mathbf{r}) = \sqrt{\rho(\mathbf{r})}$: $\rightarrow$ Euler-Lagrange equation:

$$\left\{ -\frac{\hbar^2}{2m_{\mathsf{He}}} \nabla^2 + \frac{\delta\mathcal{E}}{\delta\rho} + V_{\mathrm{A}}(|\mathbf{r}_{\mathsf{A}} - \mathbf{r}|) \right\} \Psi(\mathbf{r}) = \mu\, \Psi(\mathbf{r}) \,, \qquad \Psi(\mathbf{r}) = \sqrt{\rho(\mathbf{r})}$$

Sum of pairwise interactions with V_{A} from the literature (Aziz)

Imaginary time propagation on a 3-D grid $\rightarrow \rho_0(\mathbf{r}) = \Psi_0^2(\mathbf{r})$

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Dynamics: Time-dependent DFT Minimize the action / $\Psi_{\rm He}(\mathbf{r}, t)$
$\Psi_{\rm He}(\mathbf{r}, t)$ coupled to classical $\mathbf{r}_{\rm A}$ (mean field)

$$\begin{cases} i\hbar\dfrac{\partial}{\partial t}\Psi_{\rm He} &= \left[-\dfrac{\hbar^2}{2m_{\rm He}}\nabla^2 + \dfrac{\delta\mathcal{E}}{\delta\rho} + V_{\rm A}(\mathbf{r} - \mathbf{r}_{\rm A}) \right] \Psi_{\rm He} \quad \rightarrow \quad \rho_{\rm He}(\mathbf{r}, t) = |\Psi_{\rm He}(\mathbf{r}, t)|^2 \\ m_{\rm A}\ddot{\mathbf{r}}_{\rm A} &= -\nabla_{\mathbf{r}_{\rm A}} \left[\int d\mathbf{r} \rho(\mathbf{r}) V_\lambda(\mathbf{r} - \mathbf{r}_{\rm A}) \right] = -\int d\mathbf{r}\, \nabla\rho(\mathbf{r}) V_{\rm A}(\mathbf{r} - \mathbf{r}_{\rm A}) \end{cases}$$

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With vortices: work in the co-rotating frame ω: $\{\mathcal{H}[\rho] - \omega\hat{L}_Z\}\Psi(\mathbf{r}) = \mu\Psi(\mathbf{r})$

He-TDDFT simulation: Xe 200 m s^{-1} collision with He_{1000}

(thermal energy $\leftrightarrow$ 240 m s^{-1})

$b = 0$ $b = 22.2$ *Å*

He-TDDFT simulation: Xe 200 m s^{-1} collision with He_{1000}

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If $b >$Droplet radius (22 Å), no capture

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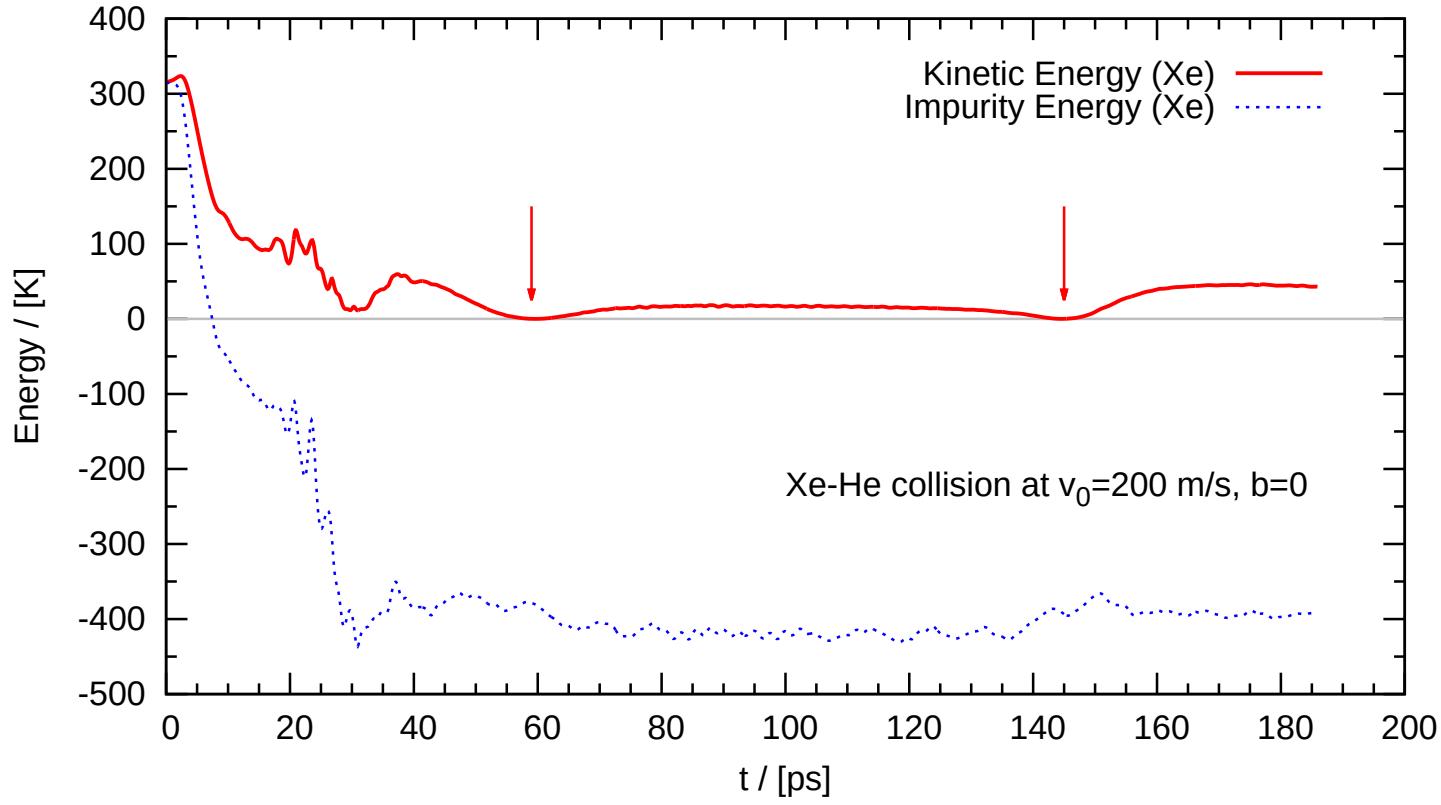

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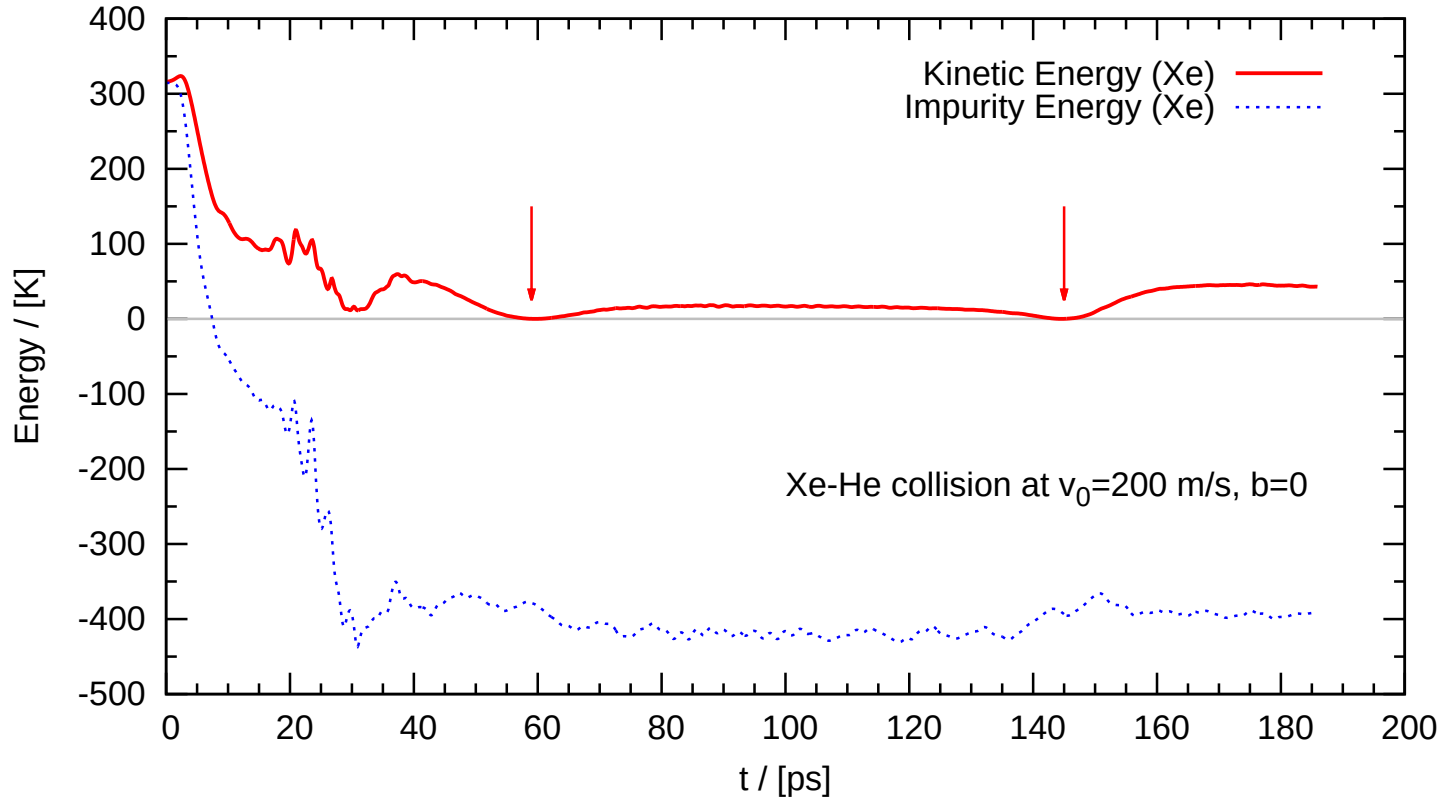

Capture cross section $\simeq$ geometrical cross section

*Coppens, Leal, Barranco, Halberstadt, Pi, JLTP **187**, 439 (2017);*

With a vortex
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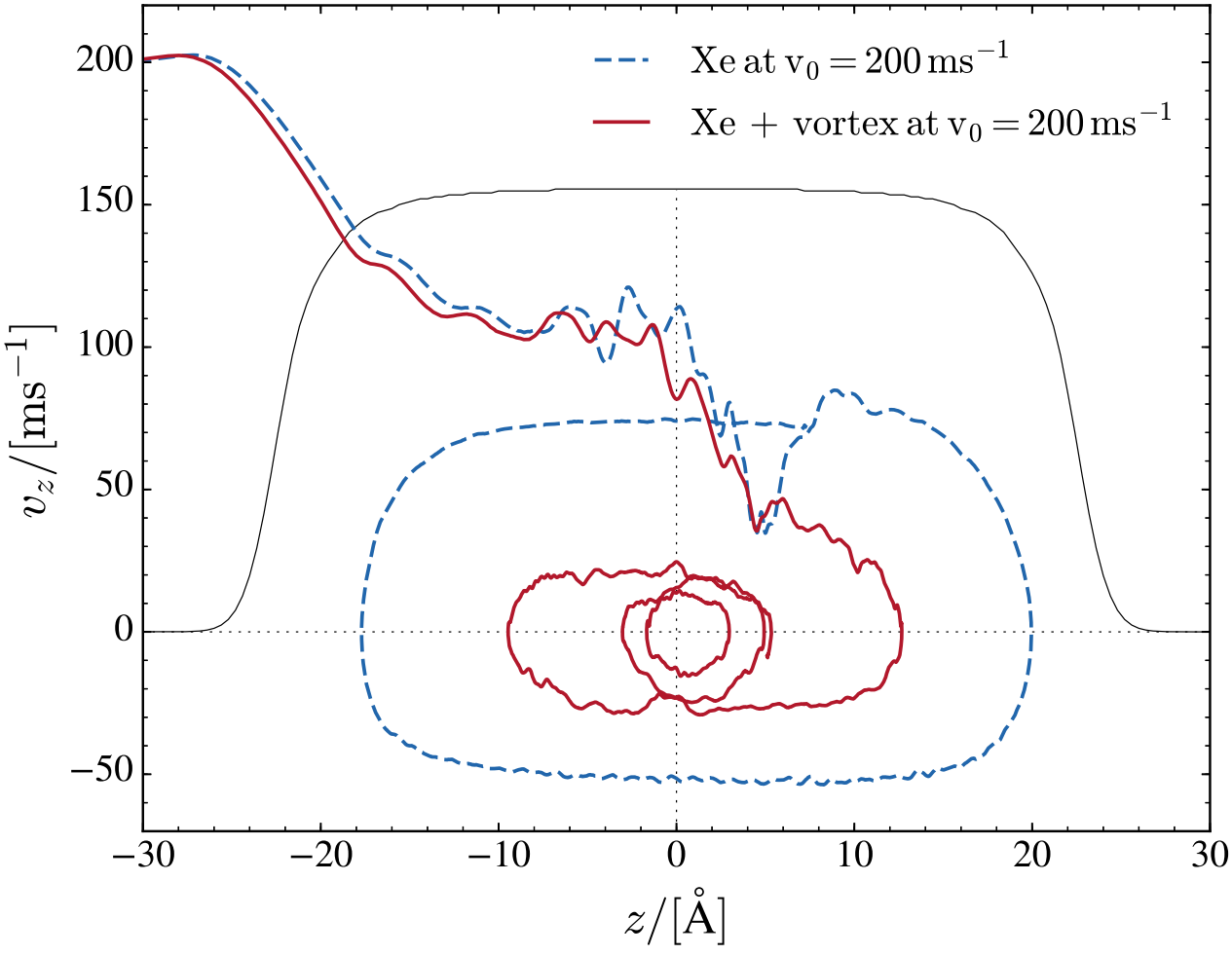

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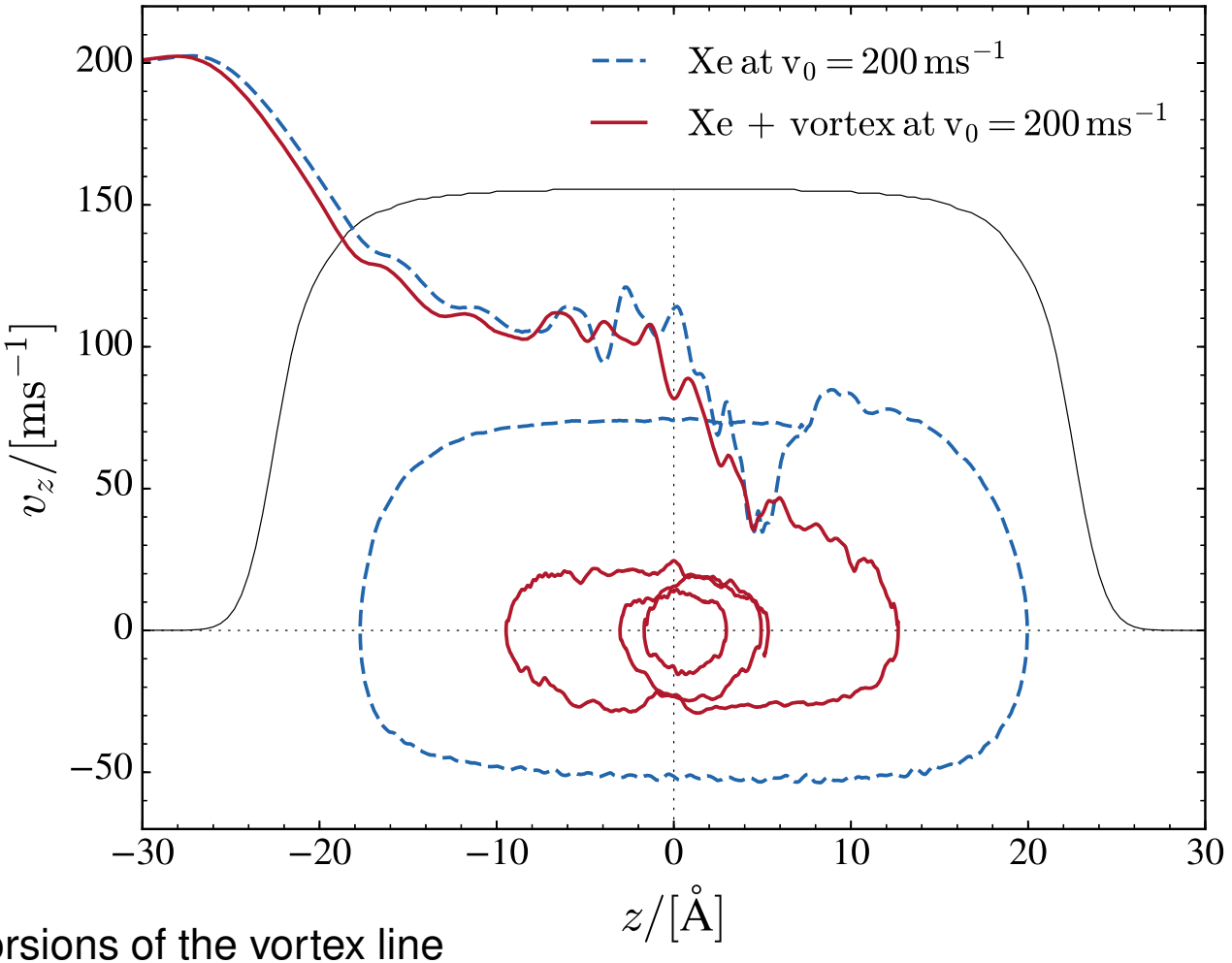


Strong distorsions of the vortex line

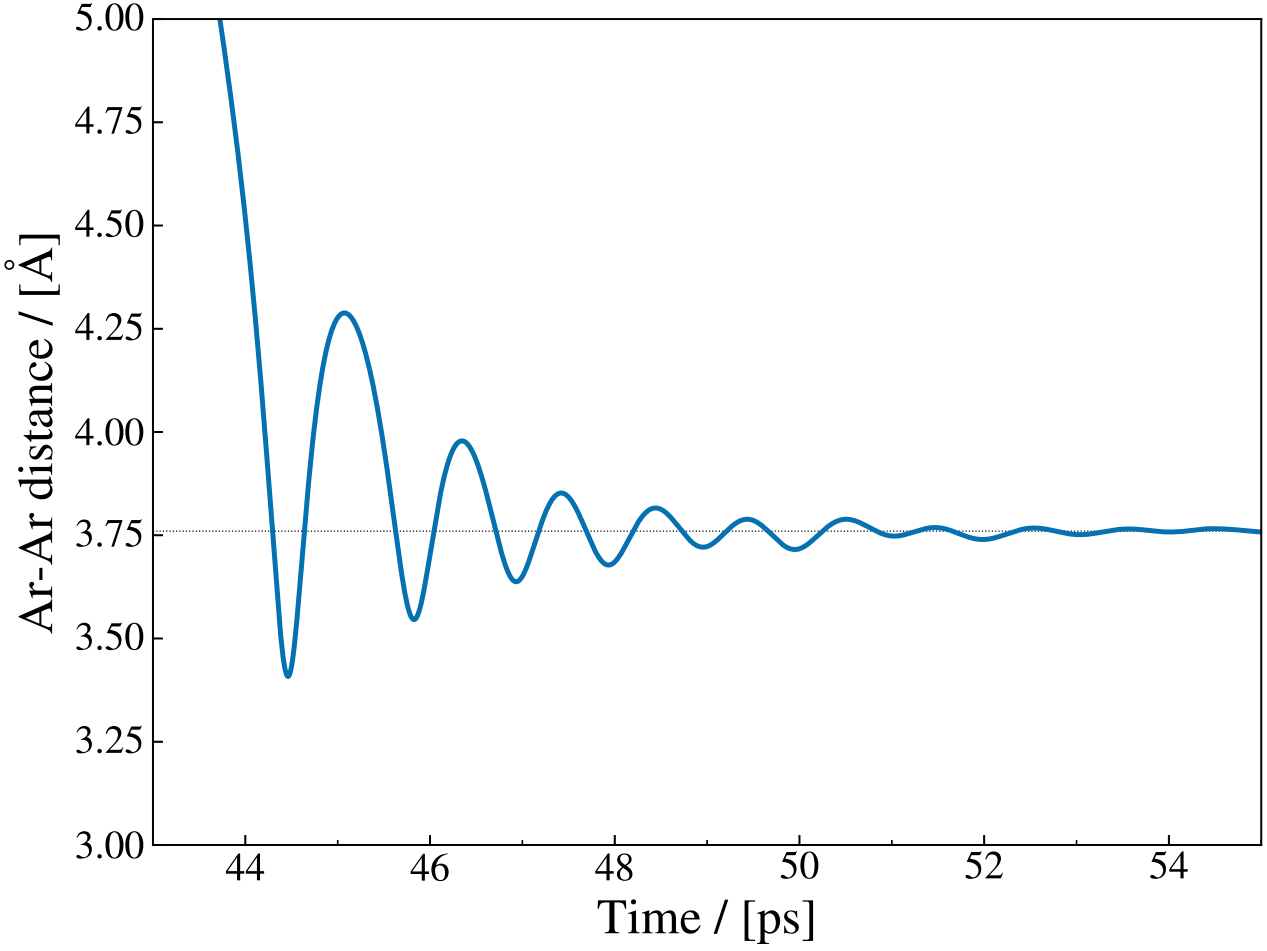
Xe ends up bound to the vortex

*Coppens et al., JLTP **187**, 439 (2017); Coppens et al., PCCP **19**, 24805 (2017)*

Clustering: Ar_2
2 Ar, 360 m s^{-1} collision with He_{5000}

$$b = 0$$

Clustering: Ar_2



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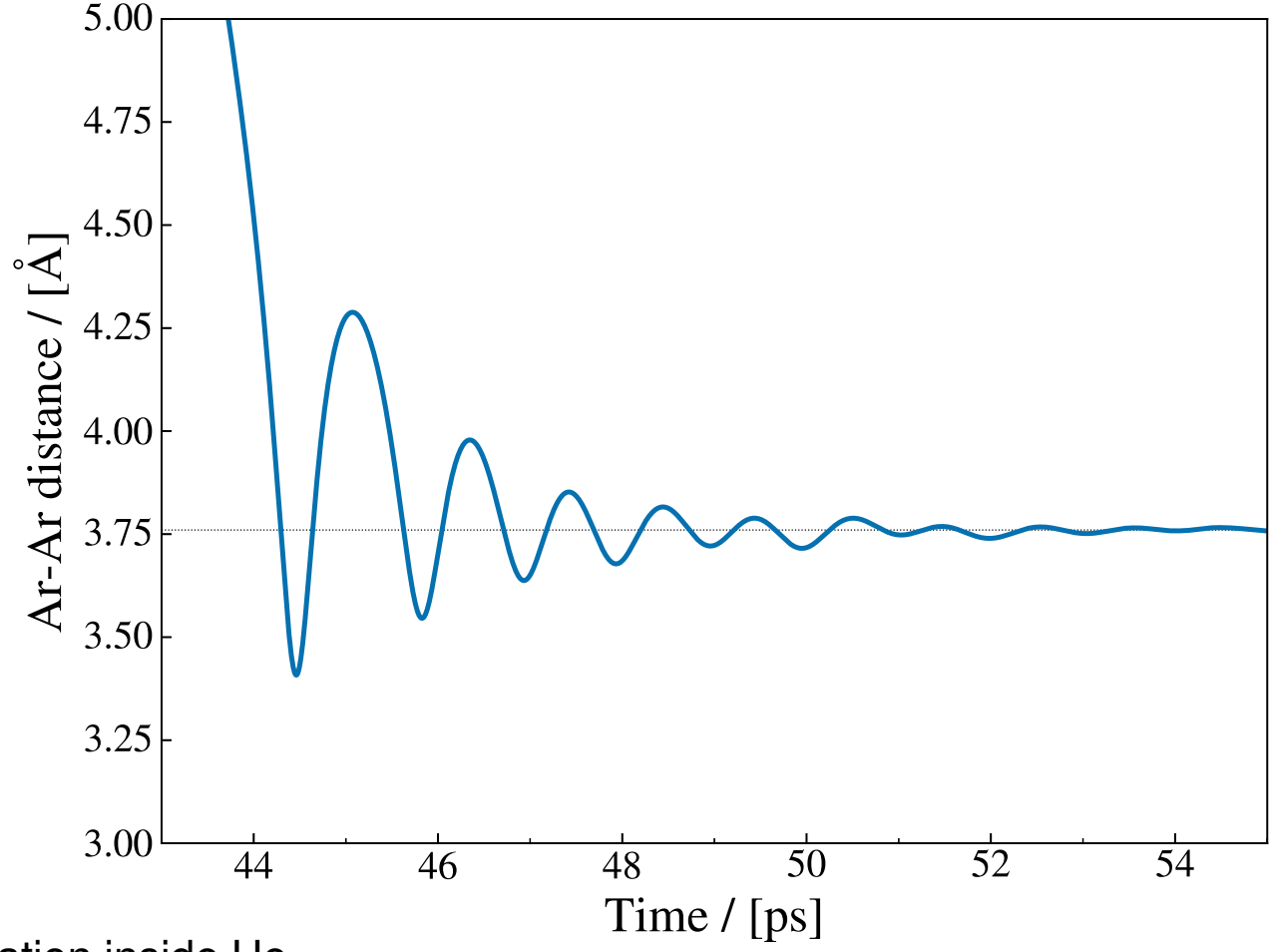

Dimer formation inside He_{5000}

Coppens et al., Phys.Chem.Chem.Phys. ***21****, 17423 (2019)*

Clustering: Ar_6
6 Ar 360 m s^{-1} *collision with* He_{5000}

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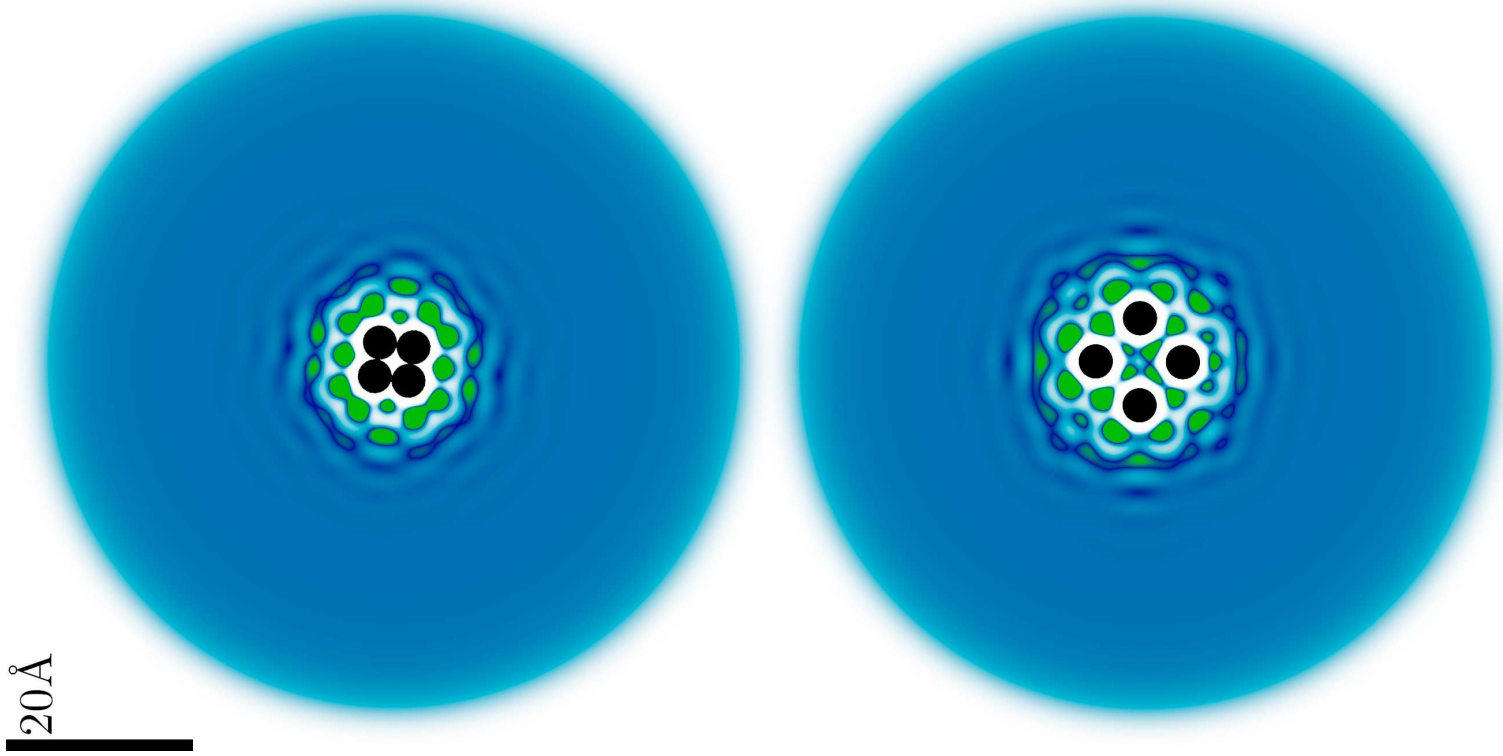

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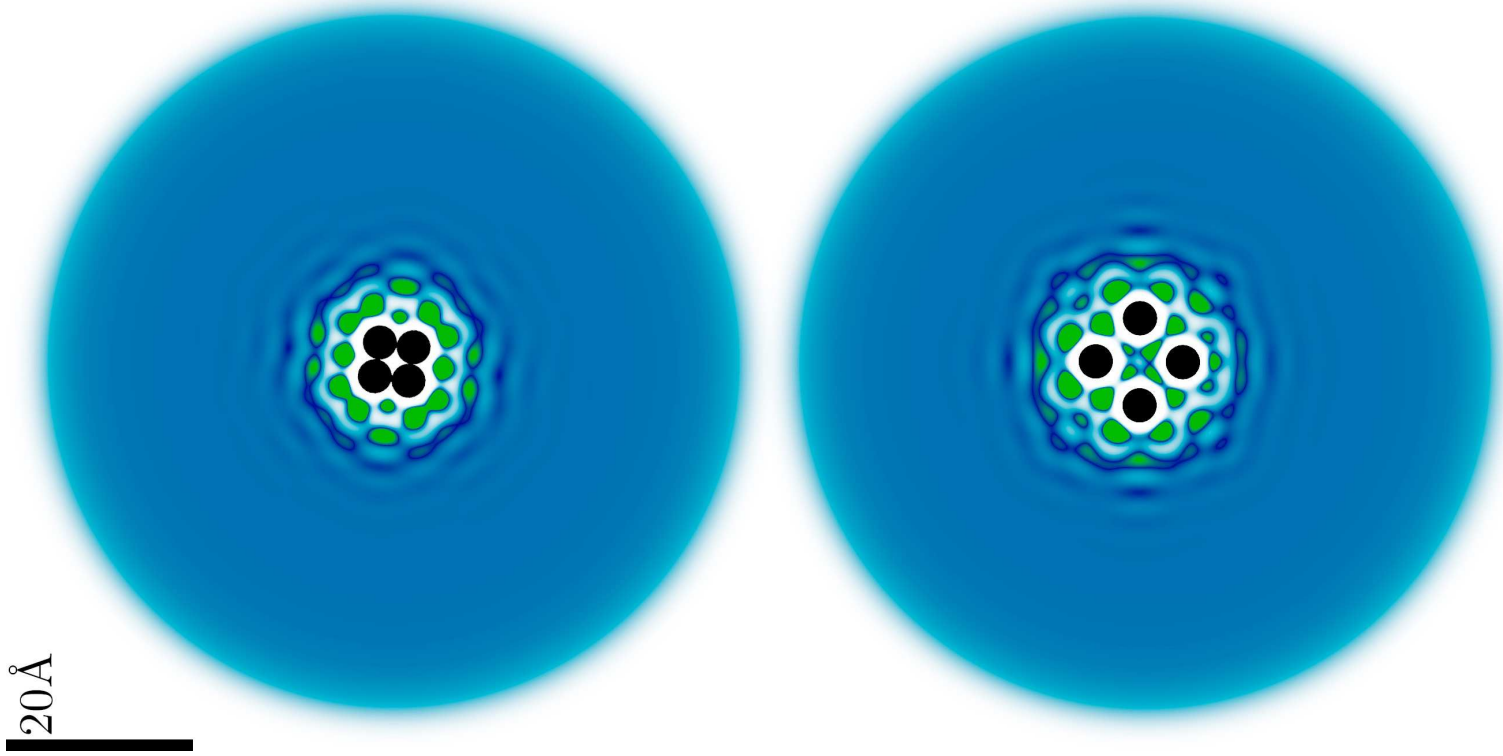

Ar_6 formation inside He_{5000} hindered by He shell structure: “dilute” Ar_6

Coppens et al., Phys.Chem.Chem.Phys. ***21****, 17423 (2019)*

Clustering: Ar_6 with 6 vortices

$$b = 0$$

Clustering: Ar_6 with 6 vortices

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A dilute Ar_6 cluster is formed, bound to the central cluster line
Coppens et al., Phys.Chem.Chem.Phys. ***21****, 17423 (2019)*

Conclusion for cluster formation

- Capture cross section $\simeq$ geometrical cross section
- Capture and cluster formation release a lot of energy in the droplet
  $\rightarrow$ necessity to describe the He droplet dynamics
- Clustering is well described by He-TDDFT (dimer formation)
- Clustering can be hindered by the He solvation structure
- Atoms are attracted to the vortex line(s) and end up bound to them
- Cluster formation along the vortex lines?

Would require longer time dynamics, with more Ar atoms and even larger droplets...

Also: Vary initial conditions

Excited state dynamics: He-induced electronic transitions?

He is chemically inert, at T$\simeq$ 0.4 K it looks “inoffensive”

Excited state dynamics: He-induced electronic transitions?

He is chemically inert, at T$\simeq$ 0.4 K it looks “inoffensive”, and yet:

Laser-induced fluorescence of alkali atoms in He

(cold dense gas, superfluid liquid , solid, droplets):

$\rightarrow$ electronic relaxation

Also for molecules: Cl_2^*(B)

$\longrightarrow$ **study case: Ak* at He$_N$**

Ak → Ak Dynamics @ He droplets*

- many experiments: LIF, beam depletion, VMI... (Scoles, Stienkemeier, Ernst, Drabbels, Mudrich,...)
- LIF experiments: Ak sits in a “dimple” at the He droplet surface (shift/liquid He)
- Photoexcitation: leads to Ak* or He$_n$Ak* desorption [except for Rb*($5\Pi_{1/2}$) and Cs*($6\Pi_{1/2}$) low energy side]

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Theory

- Pseudo-diatomic model (He_N)—Ak remarkably valid for spectroscopy
- Ring Polymer MD for K* He_{300} (Takayanagi and Shiga, PCCP 2004): one of the first dynamics studies
- He-DFT, TDDFT (Ancilotto, Callegari, Hernando, Matteo, Leal, Barranco, Pi, Eloranta, Dalfovo,...)

Ak → Ak Dynamics @ He droplets*

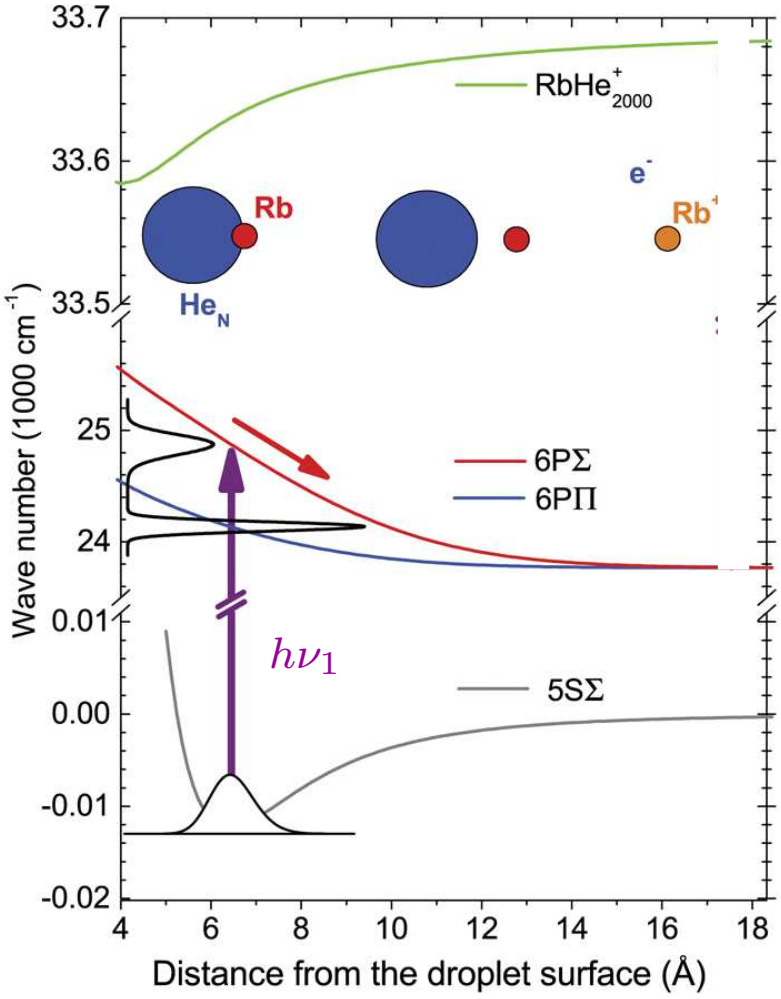
- many experiments: LIF, beam depletion, VMI... (Scoles, Stienkemeier, Ernst, Drabbels, Mudrich,...)
- LIF experiments: Ak sits in a "dimple" at the He droplet surface (shift/liquid He)
- Photoexcitation: leads to Ak* or He_nAk* desorption [except for Rb*($5\Pi_{1/2}$) and Cs*($6\Pi_{1/2}$) low energy side]

Theory

- Pseudo-diatomic model (He_N)—Ak remarkably valid for spectroscopy
- Ring Polymer MD for K* He_{300} (Takayanagi and Shiga, PCCP 2004): one of the first dynamics studies
- He-DFT, TDDFT (Ancilotto, Callegari, Hernando, Matteo, Leal, Barranco, Pi, Eloranta, Dalfovo,...)

This work: collaboration with Von Vangerow, Stienkemeier, Mudrich
First direct time-dependent observation of the dynamics

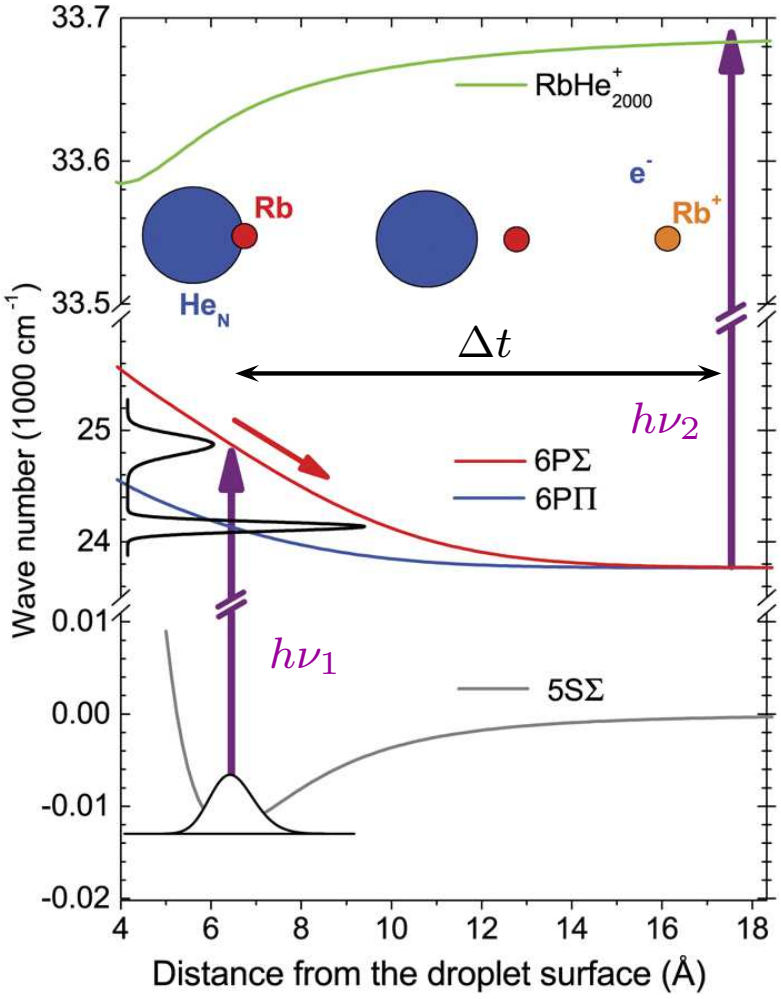
Desorption dynamics of Rb(5p, 6p)*



Principle of the experiment

*J. von Vangerow, O. John, F. Stienkemeier, and M. Mudrich, JCP **143**, 034302 (2015)*

Desorption dynamics of Rb(5p, 6p)*

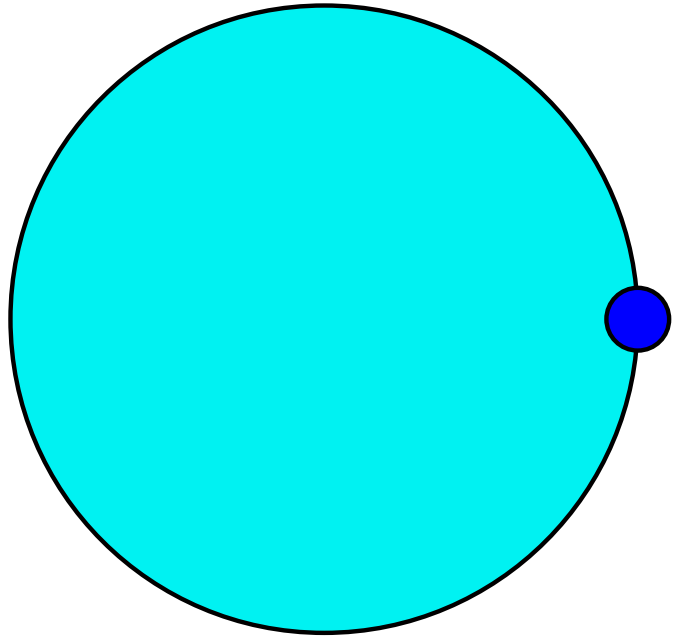


Principle of the experiment

*J. von Vangerow, O. John, F. Stienkemeier, and M. Mudrich, JCP **143**, 034302 (2015)*

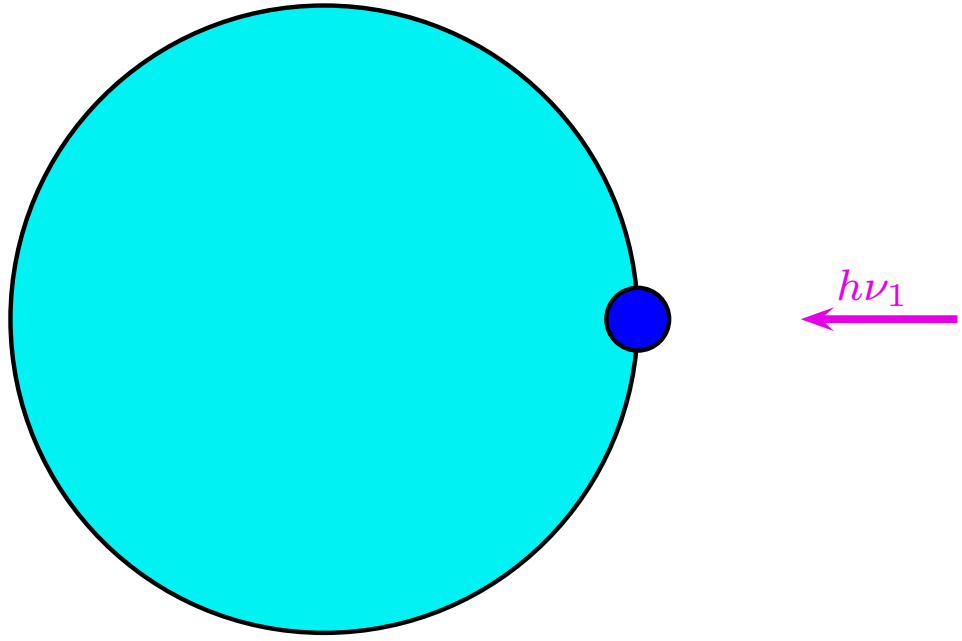
Principle of the experiment

initial state: Rb(5s,Σ)@He$_N$



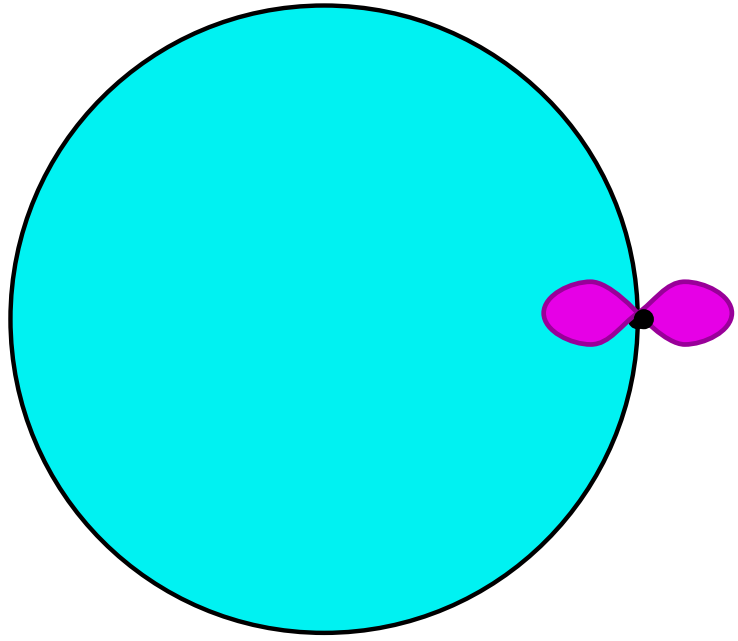
Principle of the experiment

laser 1 excitation



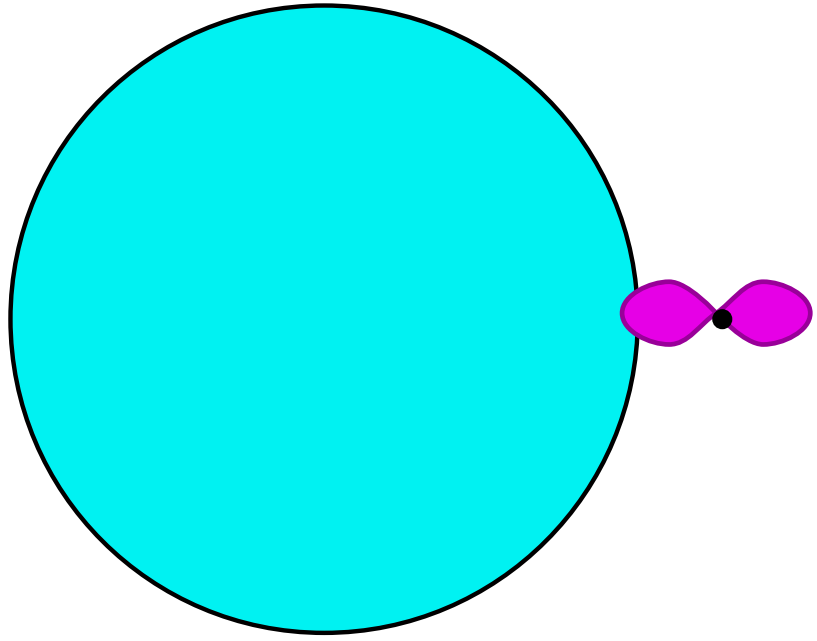
Principle of the experiment

Rb(5s,Σ)$\rightarrow$Rb* (np,Σ)@He$_N$



Principle of the experiment

ejecting Rb (np,Σ)*



Principle of the experiment

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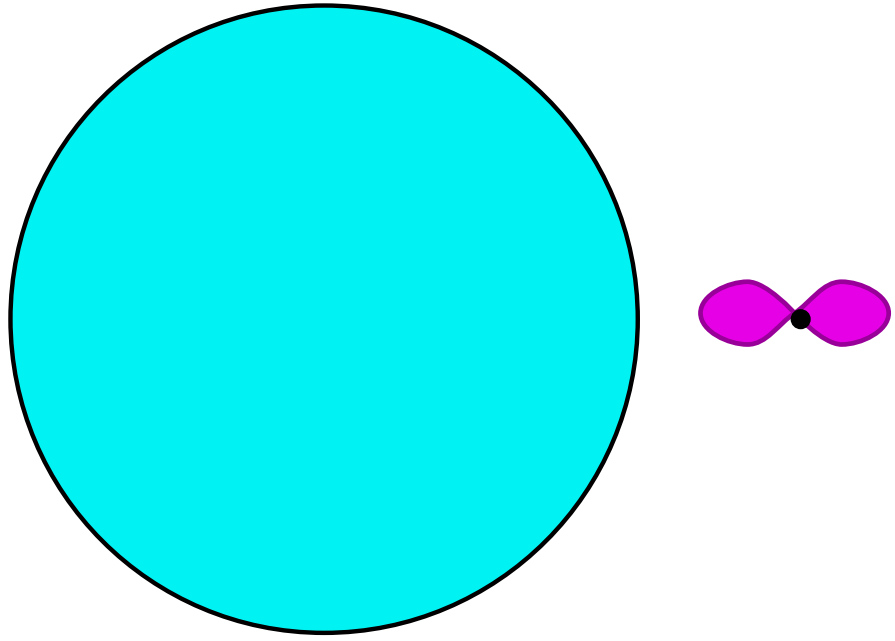
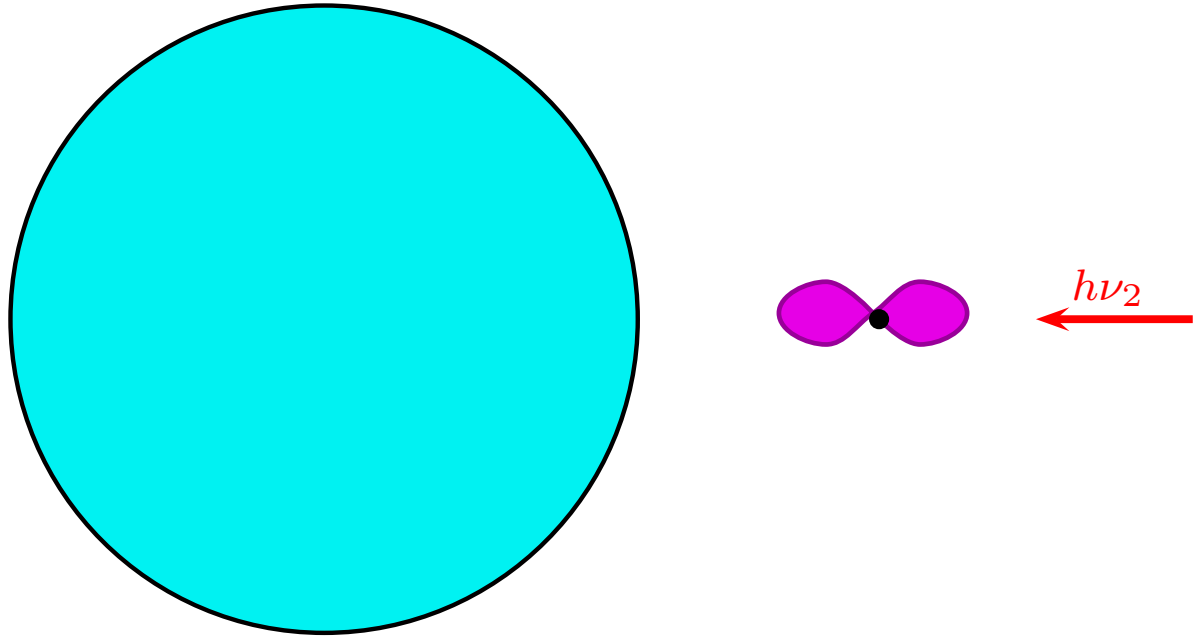


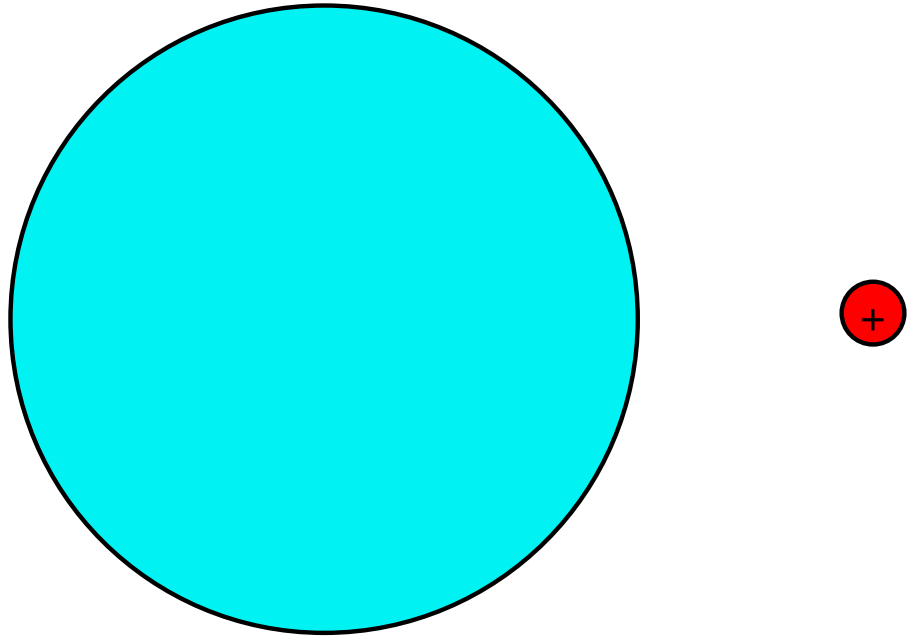
Principle of the experiment

laser 2 ionization



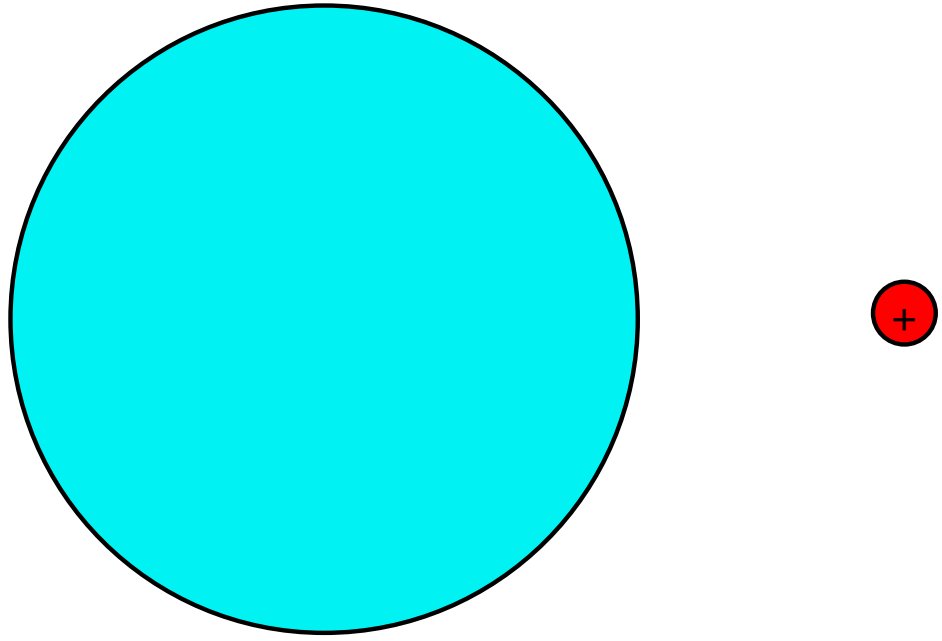
Principle of the experiment

Rb^+



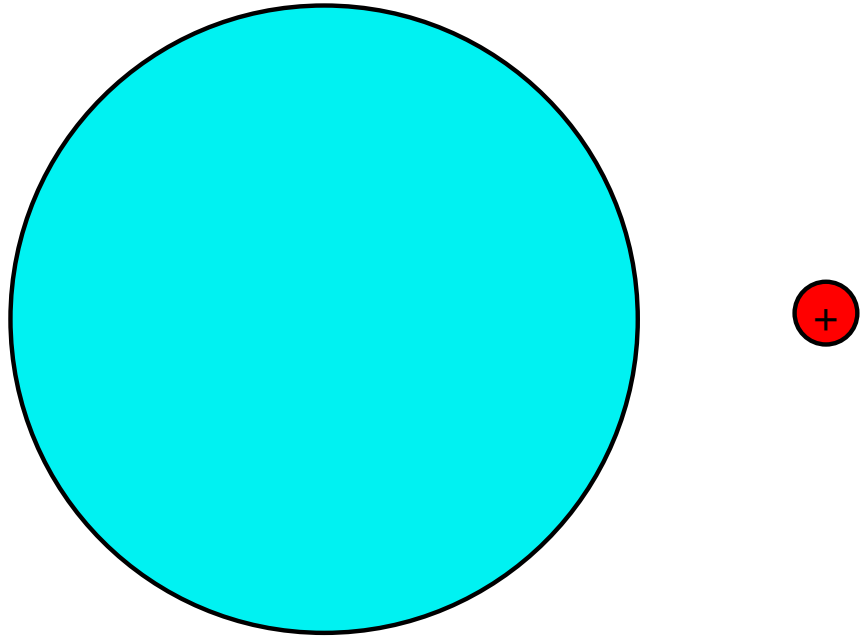
Principle of the experiment

slow down due to Rb^+ -He attraction



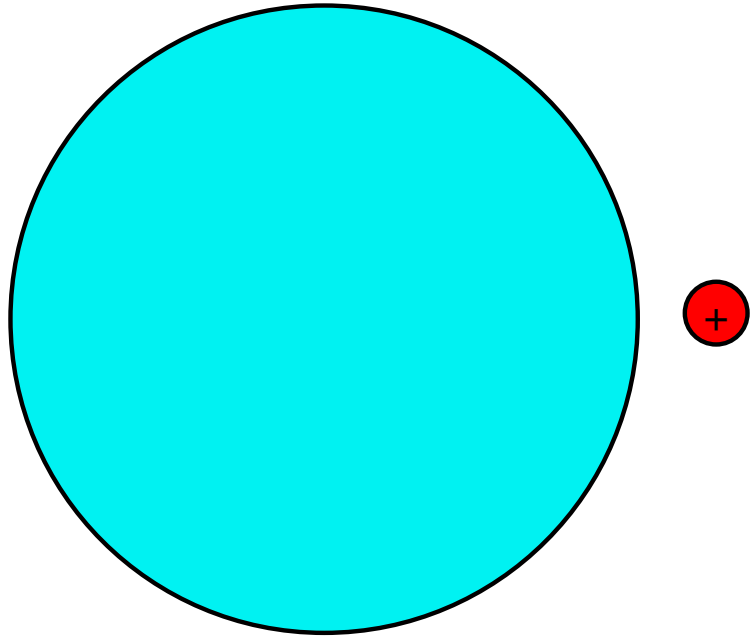
Principle of the experiment

Rb^+ possible turnaround and ...



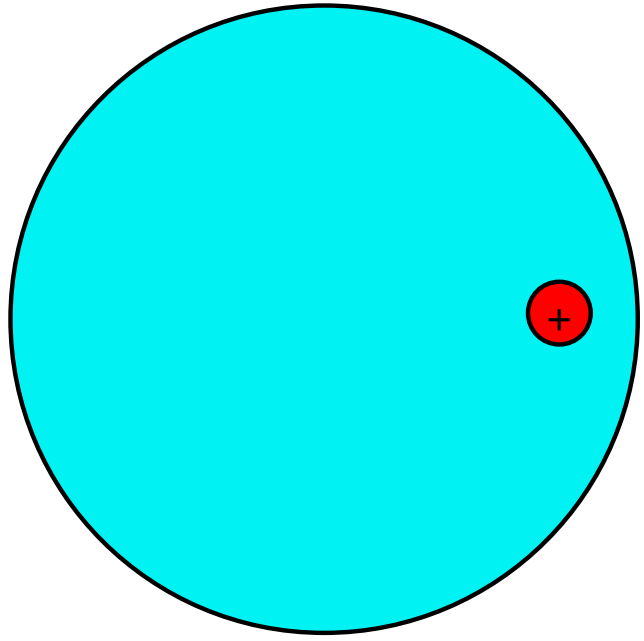
Principle of the experiment

Rb^+ possible turnaround and ...



Principle of the experiment

Rb^+ possible turnaround and solvation

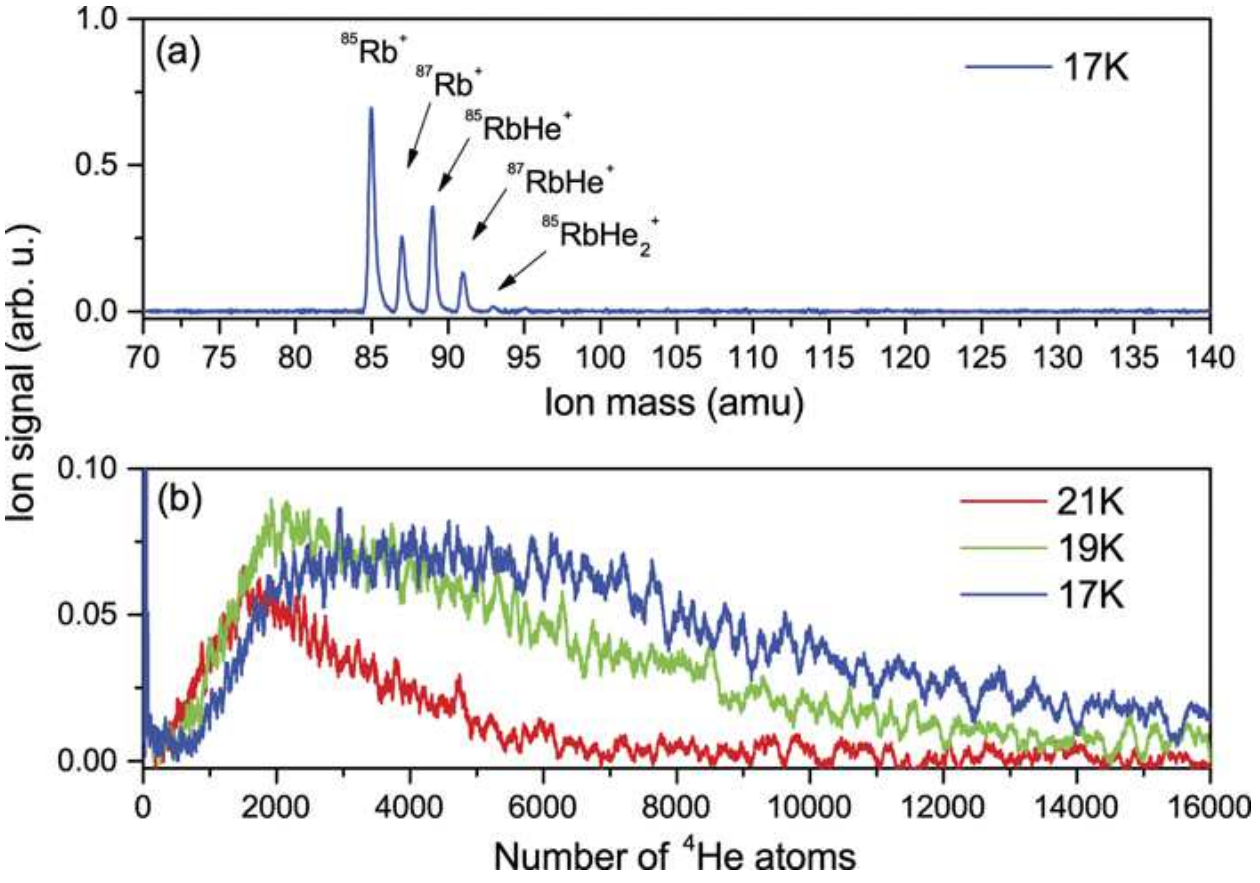


Experimental mass spectra

415 nm (24100 cm^{-1}) excitation (6pΠ)

Δt = 5 ps

single pulse
(Δt = 0)



*J. von Vangerow, O. John, F. Stienkemeier, and M. Mudrich, JCP **143**, 034302 (2015)*

Theoretical simulation: ^{4}He-DFT for A@He$_{1000}$

Total energy of the system as a function of the ^{4}**He density** $\rho(\mathbf{r})$:

$$E[\rho] = \int d\mathbf{r} \left\{ \frac{\hbar^2}{2m_{\rm He}} \left|\nabla\sqrt{\rho(\mathbf{r})}\right|^2 + \mathcal{E}[\rho(\mathbf{r})] \right\} + \int d\mathbf{r}\, \rho(\mathbf{r})\, V_X(|\mathbf{r}_{\rm Rb} - \mathbf{r}|)$$

* Orsay-Trento density functional *[F. Dalfovo, A. Lastri, L. Pricaupenko, S. Stringari & J. Treiner, PRB 1995; F. Ancilotto, M. Barranco, F. Caupin, R. Mayol & M. Pi, PRB 2005.]*

$$\begin{aligned}
\mathcal{E}_c[\rho] \;=\; & \frac{1}{2}\int \mathrm{d}\mathbf{r}'\rho(\mathbf{r})V_{LJ}(\mathbf{r}-\mathbf{r}'|)\rho(\mathbf{r}') + \frac{1}{2}c_2\,\rho(\mathbf{r})\,[\bar{\rho}(\mathbf{r})]^2 + \frac{1}{3}c_3\,\rho(\mathbf{r})\,[\bar{\rho}(\mathbf{r})]^3 \\
& -\frac{\hbar^2}{4m}\alpha_s \int \mathrm{d}\mathbf{r}'F(|\mathbf{r}-\mathbf{r}'|)\,[1-\tilde{\rho}(\mathbf{r})/\rho_{0s}]\,\nabla\rho(\mathbf{r})\cdot\nabla'\rho(\mathbf{r}')\,\left[1-\tilde{\rho}(\mathbf{r}')/\rho_{0s}\right] \\
& -\frac{m}{4}\int d\mathbf{r}'\,V_J(|\mathbf{r}-\mathbf{r}'|)\,\rho(\mathbf{r})\,\rho(\mathbf{r}')\,[\mathbf{v}(\mathbf{r})-\mathbf{v}(\mathbf{r}')]^2 + C\,\rho(\mathbf{r})\{1+\tanh[\beta\,(\rho(\mathbf{r})-\rho_{\rm m})]\}
\end{aligned}$$

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Statics: Minimize $E[\rho]$ with respect to $\Psi(\mathbf{r}) = \sqrt{\rho(\mathbf{r})}$: $\rightarrow$ Euler-Lagrange equation:

$$\left\{ -\frac{\hbar^2}{2m_{\mathrm{He}}} \nabla^2 + \frac{\delta\mathcal{E}}{\delta\rho} + V_X(|\mathbf{r}_{\mathrm{Rb}} - \mathbf{r}|) \right\} \Psi(\mathbf{r}) = \mu\, \Psi(\mathbf{r})\,, \qquad \Psi(\mathbf{r}) = \sqrt{\rho(\mathbf{r})}$$

Sum of pairwise interactions with V_X from the literature (Patil 1991)

Imaginary time propagation on a 3-D grid $\rightarrow \rho_0(\mathbf{r}) = \Psi_0^2(\mathbf{r})$

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Sum of pairwise interactions with V_X from the literature (Patil 1991)
Imaginary time propagation on a 3-D grid $\rightarrow \rho_0(\mathbf{r}) = \Psi_0^2(\mathbf{r})$

Dynamics: Time-dependent DFT Minimize the action / $\Psi_{\mathrm{He}}(\mathbf{r}, t)$

$\Psi_{\mathrm{He}}(\mathbf{r}, t)$ coupled to electronic wave packet $|\lambda\rangle$ and to classical $\mathbf{r}_{\mathrm{Rb}^*}$ (mean field)

$$\begin{cases} i\hbar\dfrac{\partial}{\partial t}\Psi_{\mathrm{He}} &= \left[-\dfrac{\hbar^2}{2m_{\mathrm{He}}}\nabla^2 + \dfrac{\delta\mathcal{E}}{\delta\rho} + V_\lambda(\mathbf{r} - \mathbf{r}_{\mathrm{Rb}^*}) \right] \Psi_{\mathrm{He}} \quad \rightarrow \quad \rho_{\mathrm{He}}(\mathbf{r}, t) = |\Psi_{\mathrm{He}}(\mathbf{r}, t)|^2 \\ i\hbar\dfrac{\partial}{\partial t}|\lambda\rangle &= \mathcal{H}_{\mathrm{el}}\,|\lambda\rangle = (\mathcal{H}_{\mathrm{DIM}} + \mathcal{H}_{\mathrm{SO}})\;|\lambda\rangle \\ & \text{where} \quad \boxed{|\lambda\rangle = \textstyle\sum_{is} \lambda_{is}(t)\,|p_i, m_s\rangle} \quad \longrightarrow \quad V_\lambda = \langle\lambda|\mathcal{H}_{\mathrm{el}}|\lambda\rangle \\ m_{\mathrm{Rb}}\ddot{\mathbf{r}}_{\mathrm{Rb}^*} &= -\nabla_{\mathbf{r}_{\mathrm{Rb}^*}} \left[\int d\mathbf{r}\rho(\mathbf{r}) V_\lambda(\mathbf{r} - \mathbf{r}_{\mathrm{Rb}^*}) \right] = -\int d\mathbf{r}\,\nabla\rho(\mathbf{r}) V_\lambda(\mathbf{r} - \mathbf{r}_{\mathrm{Rb}^*}) \end{cases}$$

He-TDDFT simulation

t_1: 1^{st} laser excitation

$$He_N \cdots Rb(5s\,^2\Sigma_{1/2}) \rightarrow He_N \cdots Rb^*(5p\,^2\Sigma_{1/2})$$

t_2: 2^{nd} laser ionization

$$He_N \cdots Rb^*(5p\,^2\Sigma_{1/2}) \rightarrow He_N \cdots Rb^+$$

$t_2 = 55$ *ps* $\qquad\qquad$ $t_2 = 20$ *ps*

Von Vangerow, Coppens, Leal, Pi, Barranco, Halberstadt, Stienkemeier and Mudrich, JPCL ***8****, 307 (2017)*

He-TDDFT simulation

t_1: 1st laser excitation

$$He_N \cdots Rb(5s\,^2\Sigma_{1/2}) \rightarrow He_N \cdots Rb^*(5p\,^2\Sigma_{1/2})$$

t_2: 2nd laser ionization

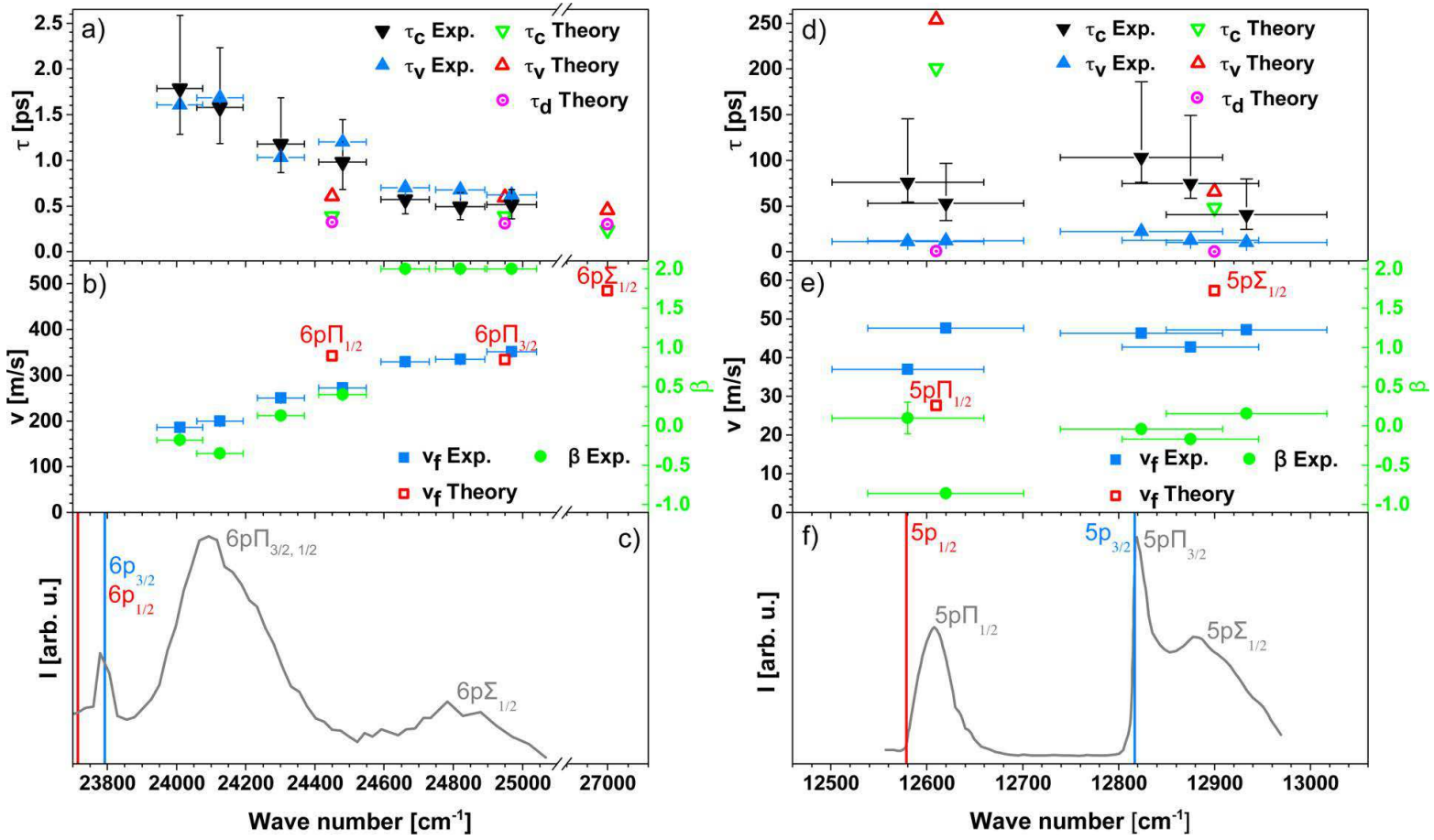
$$He_N \cdots Rb^*(5p\,^2\Sigma_{1/2}) \rightarrow He_N \cdots Rb^+$$

Critical time delay τ_c:

- if $t_2 - t_1 > \tau_c$, Rb^+ escapes;
- if $t_2 - t_1 < \tau_c$, Rb^+ turns around and gets solvated.

*Von Vangerow, Coppens, Leal, Pi, Barranco, Halberstadt, Stienkemeier and Mudrich, JPCL **8**, 307 (2017)*

Comparison with experiments



Von Vangerow et al., J. Phys. Chem. Lett. ***8****, 307 (2017)*

Everything works...

- He-TDDFT gives a good qualitative description of Rb$^*(6p, {}^2\Sigma_{1/2}, {}^2\Pi_{3/2}, {}^2\Pi_{1/2})$ and Rb$^*(5p, {}^2\Sigma_{1/2}, {}^2\Pi_{1/2})$ photodissociation from He$_N$
- 2 orders of magnitude difference for critical fall-back times between 5p and 6p excitation well reproduced

except for Rb$^*(5\,{}^2\Pi_{3/2})$:

- ejected exciplex in experiment
- bound exciplex in our simulations

- initial Rb position? (zero-point delocalization or $T = 0.4$ K):
- initial electronic excitation could be mixed?
- non-adiabatic transition to ${}^2\Pi_{1/2}$? *(Moroshkin et al. 2006 solid He; several Ak* experiments)*

$\rightarrow$ existence of **He-induced electronic relaxation** (non-radiative transitions)**?**

Including spin-orbit relaxation

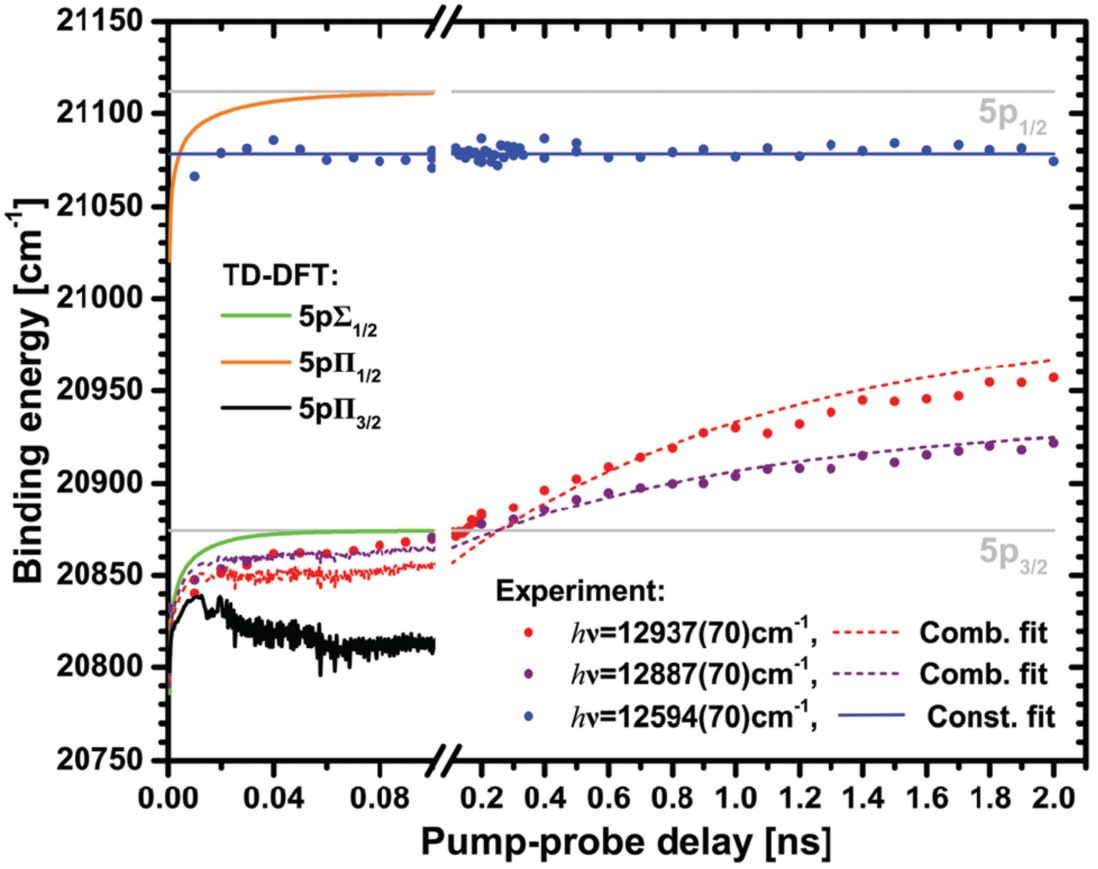
Model:

- He-TDDFT for Rb(5p$^2\Pi_{3/2}$)
  $\rightarrow$ bound exciplex

- after 60 ps, jump down to $^2\Pi_{1/2}$;
  transfer x% of ΔE to Rb
  $\rightarrow$ He-Rb ejection ?

He-TDDFT for x=12.5

Including spin-orbit relaxation



12.5% of ΔE=165 cm^{-1} is enough to eject the exciplex

Fit to the slow electrons binding energies as a function of time:

$^2\Pi_{3/2} \rightarrow {}^2\Pi_{1/2}$ relaxation time = 700 ps

Coppens et al., Phys. Chem. Chem. Phys. ***20****, 9309 (2018)*

He-induced electronic transitions:

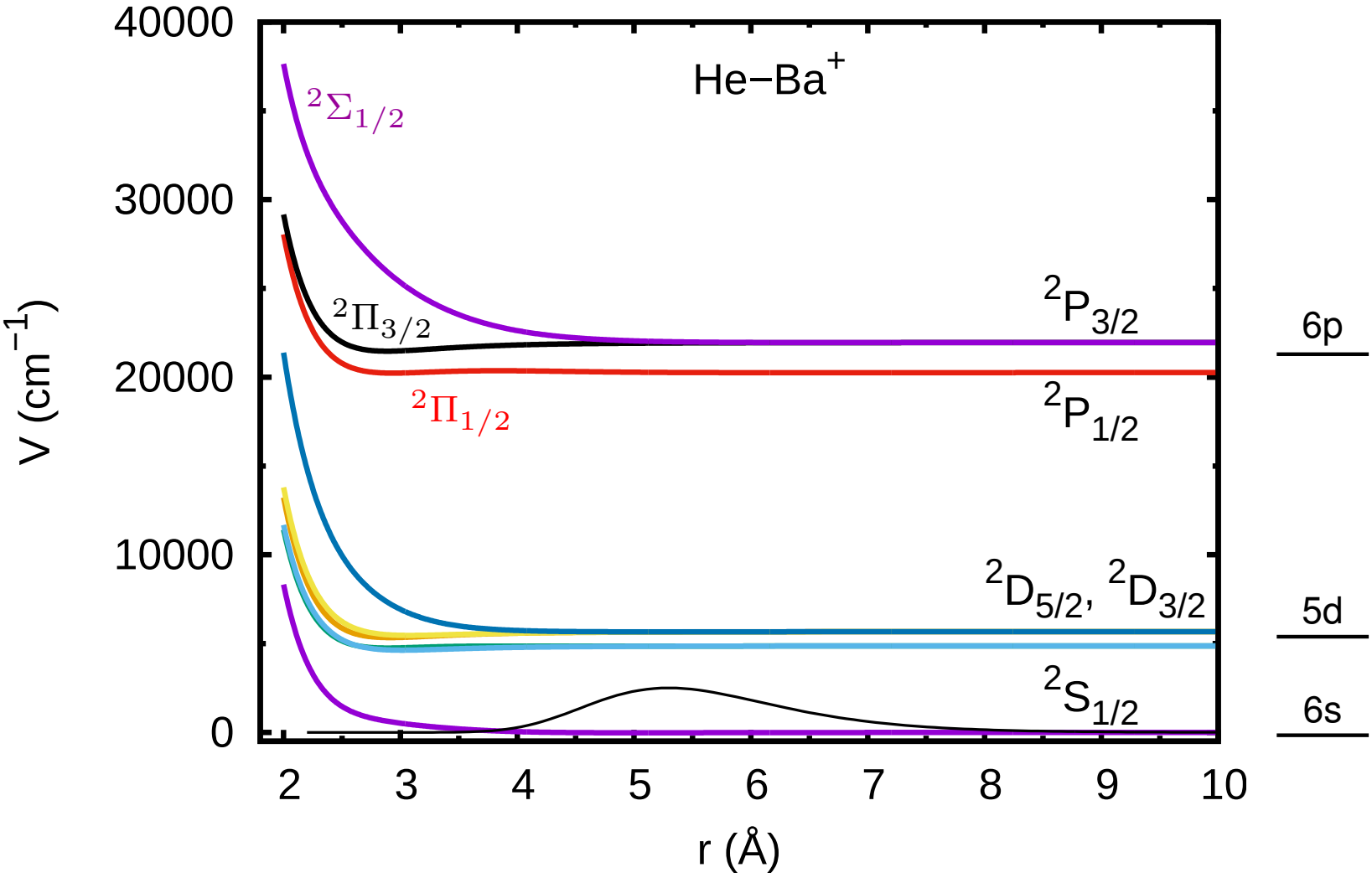
How to predict them?

He-induced electronic transitions:

How to predict them? The case of Ba^+

- He-TDDFT gives very good results for Ba^+ solvation upon ionization,
- also for its absorption and emission spectrum once it is solvated
- but Zhang and Drabbels observed Ba^+ ejection upon $6p \leftarrow 6s$ excitation which could not be reproduced

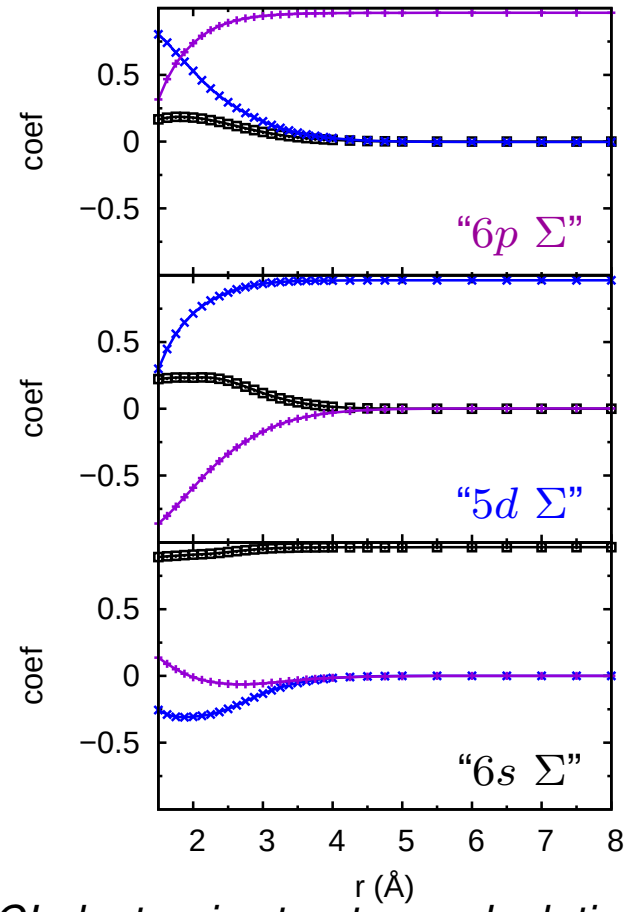
He-Ba$^+$ potential energy curves



*PEC from M. Mella and MF. Cargnoni, JPCA **118**, 6473 (2014)*

Model for potential energies and couplings

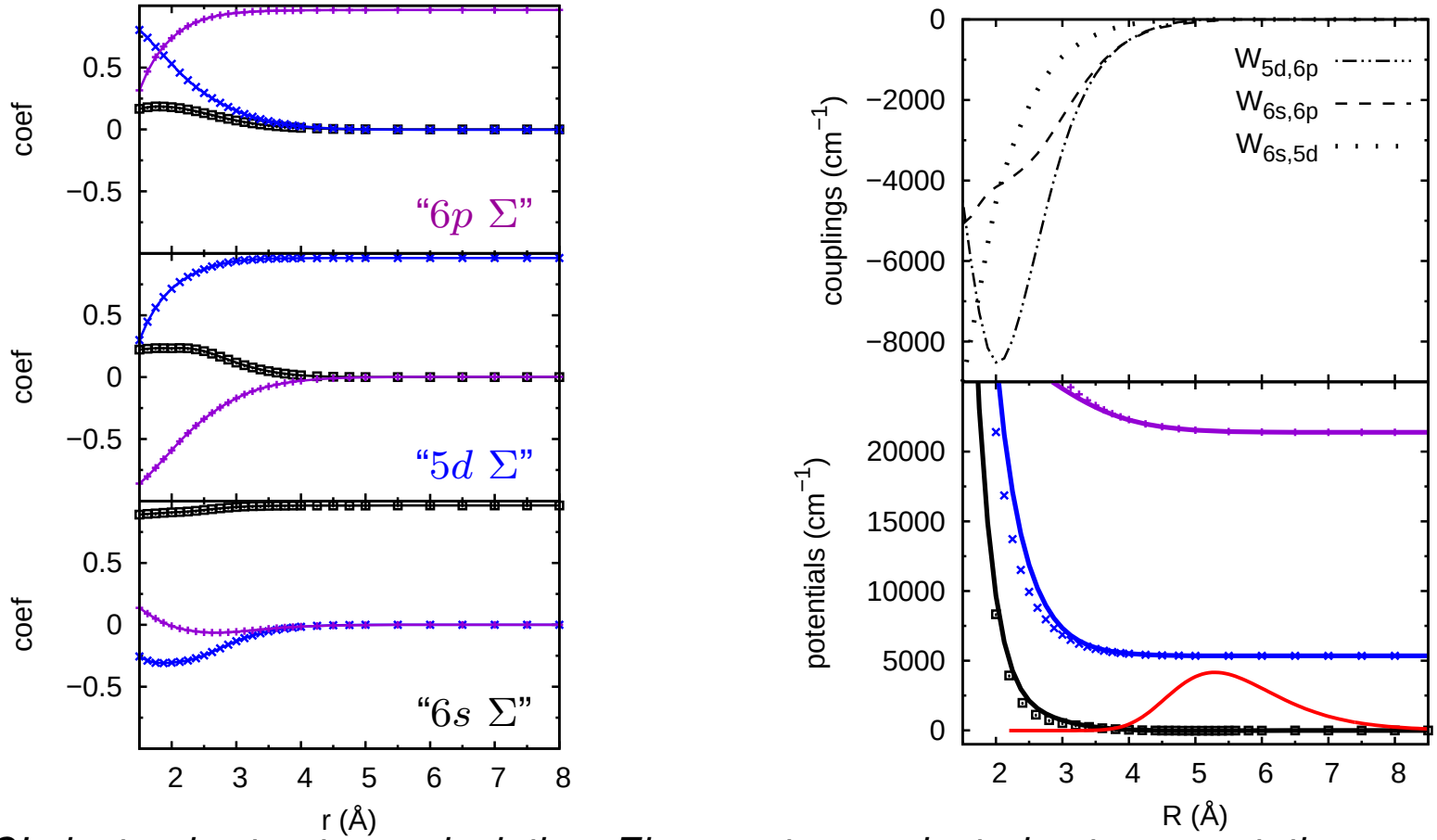
$\Lambda = 0$ mixing coefficients



MRCI electronic structure calculation; Eigenvectors projected onto asymptotic ones:
Ba^+ 6s, 5d, 6p

Model for potential energies and couplings

$\Lambda = 0$ mixing coefficients $\rightarrow$ $\Lambda = 0$ PEC and couplings



MRCI electronic structure calculation; Eigenvectors projected onto asymptotic ones: Ba^+ 6s, 5d, 6p

Eigenvector coefficients = Transformation matrix to Ba^+ states $\rightarrow$ *diabatic curves and couplings*

Model for potential energies and couplings

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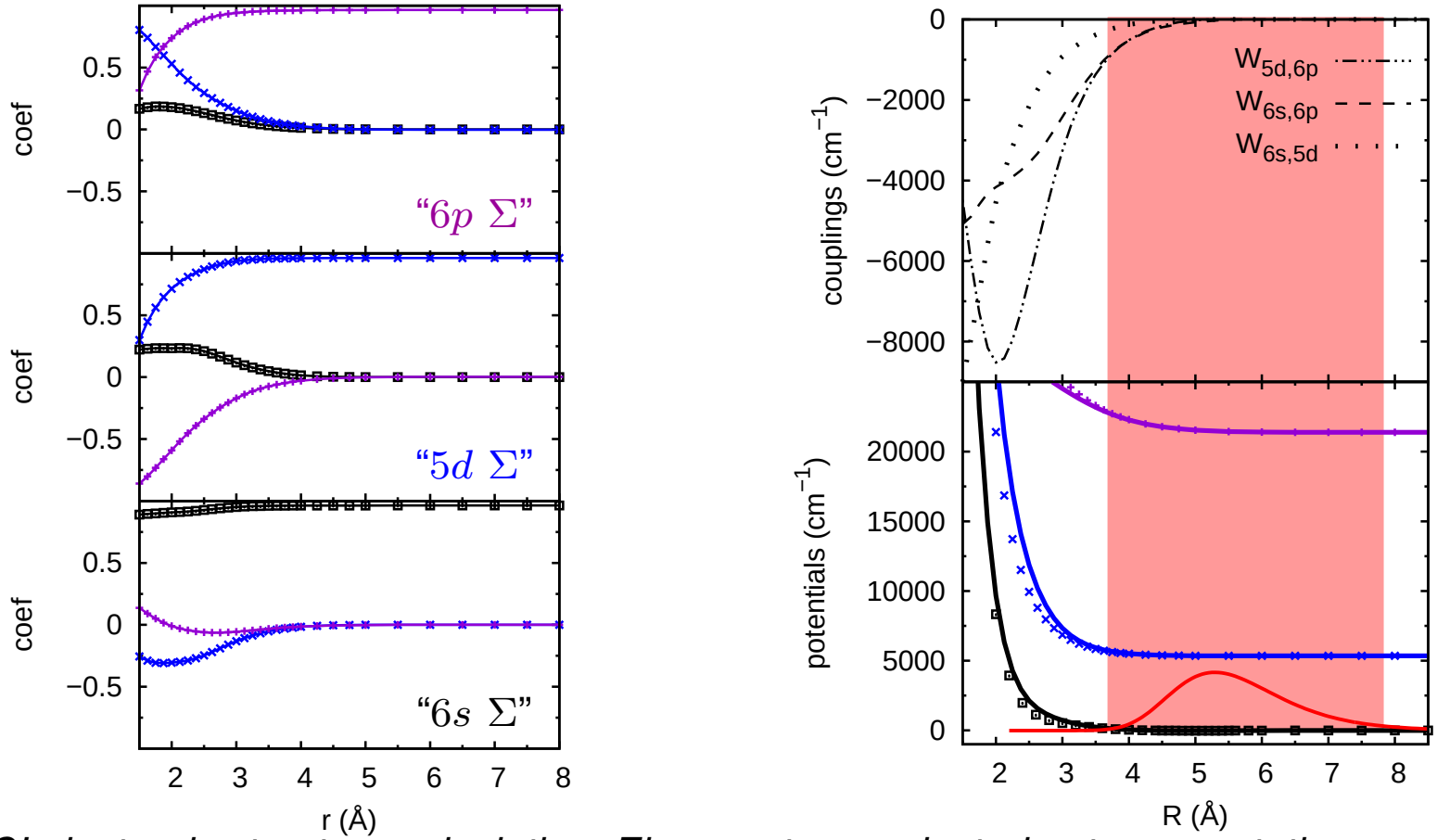


MRCI electronic structure calculation; Eigenvectors projected onto asymptotic ones: Ba^+ 6s, 5d, 6p

Eigenvector coefficients = Transformation matrix to Ba^+ states $\rightarrow$ *diabatic curves and couplings*

So from this potential model:

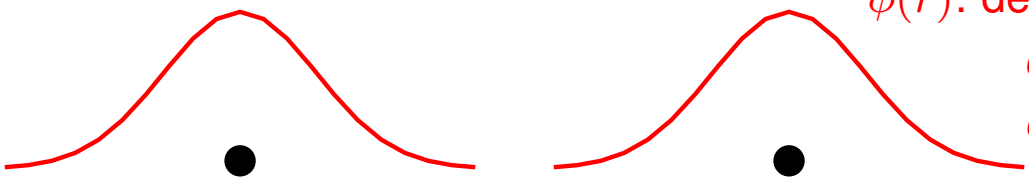
- Model for He-Ba^+ electronic Hamiltonian $\rightarrow$ diabatic representation (potentials, couplings) for 6s, 5d, 6p mixing
- Couplings are too weak to induce electronic relaxation in $HeBa^+$
- But they can induce electronic relaxation in configurations with more He atoms
- More relaxation when getting out of cylindrical symmetry (vibrations)

Vindel Zandbergen et al., J. Phys. Chem. ***148****, 144302 (2018);*

$\longrightarrow$ Dynamics study !

Influence of the Helium nanodroplet environment: Explicit Zero-Point Averaged He dynamics (ZPAD)

- ZPAD Dynamics *cf. David Bonhommeau's thesis on* Rg_n^+ He_N
  - $(Ba^+)^*$ - He_N DIM + SO; Molecular Dynamics with Quantum Transitions (Tully)
  - He_N: classical (adiabatic) taking the ZPE effects into account on average

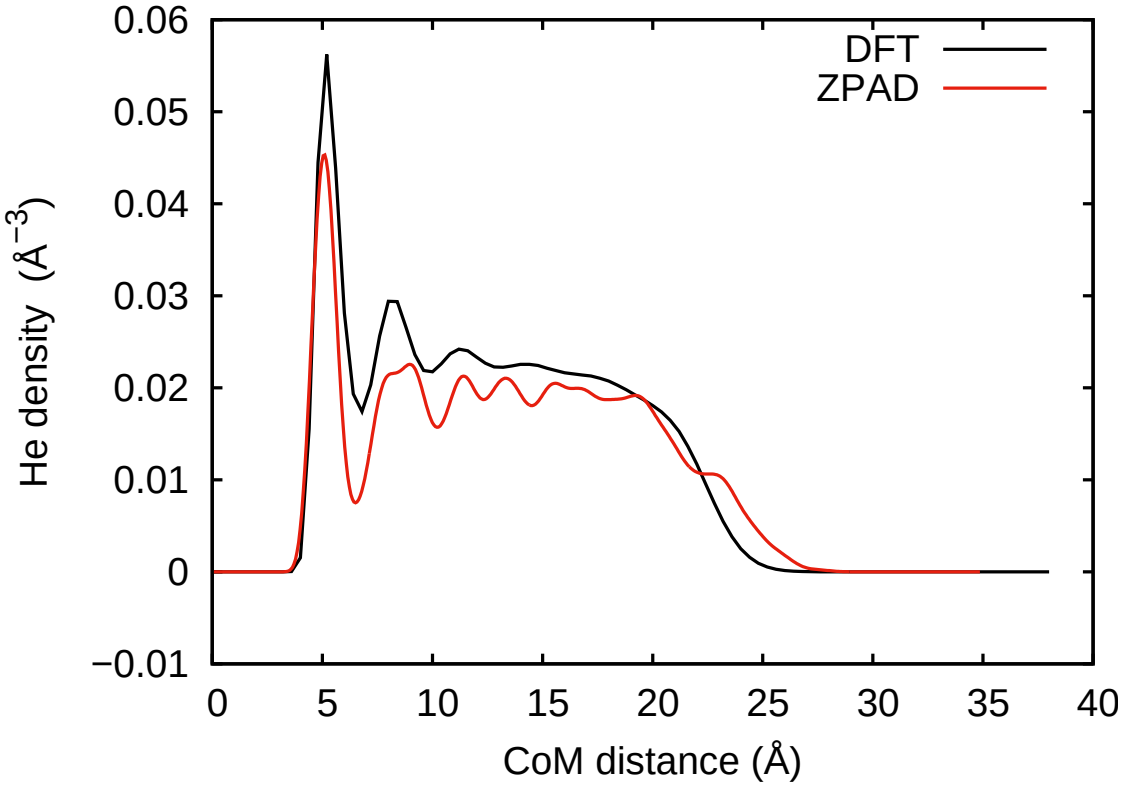


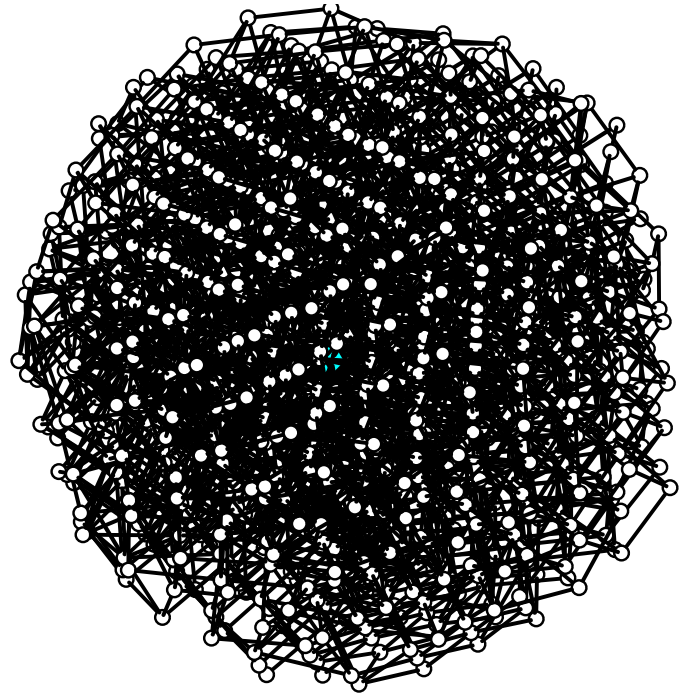
$\phi(r)$: delocalization of He atoms
determined iteratively:
one He in the (spherical)
mean field of the cluster

- Potentials
  - He ··· He: ZPAD equivalent to **classical dynamics** with **effective potential**
    (He-He potential averaged over the He wave function)
    (Portwich 1995,Slavíček et al., JPCA 2003; Sterling et al., JCP 1995)
  - He ··· Ba^+, He ··· $(Ba^+)^*$ Σ, Π: analytic forms fitted to F.Cargnoni's curves
    averaged over the He wave function

(TDDFT; semiclassical path integral centroid MD by Takayanagi and Shiga, multiple hard sphere collisions by Drabbels, CBF by Zillich; but most are mean field)

Reasonable initial conditions

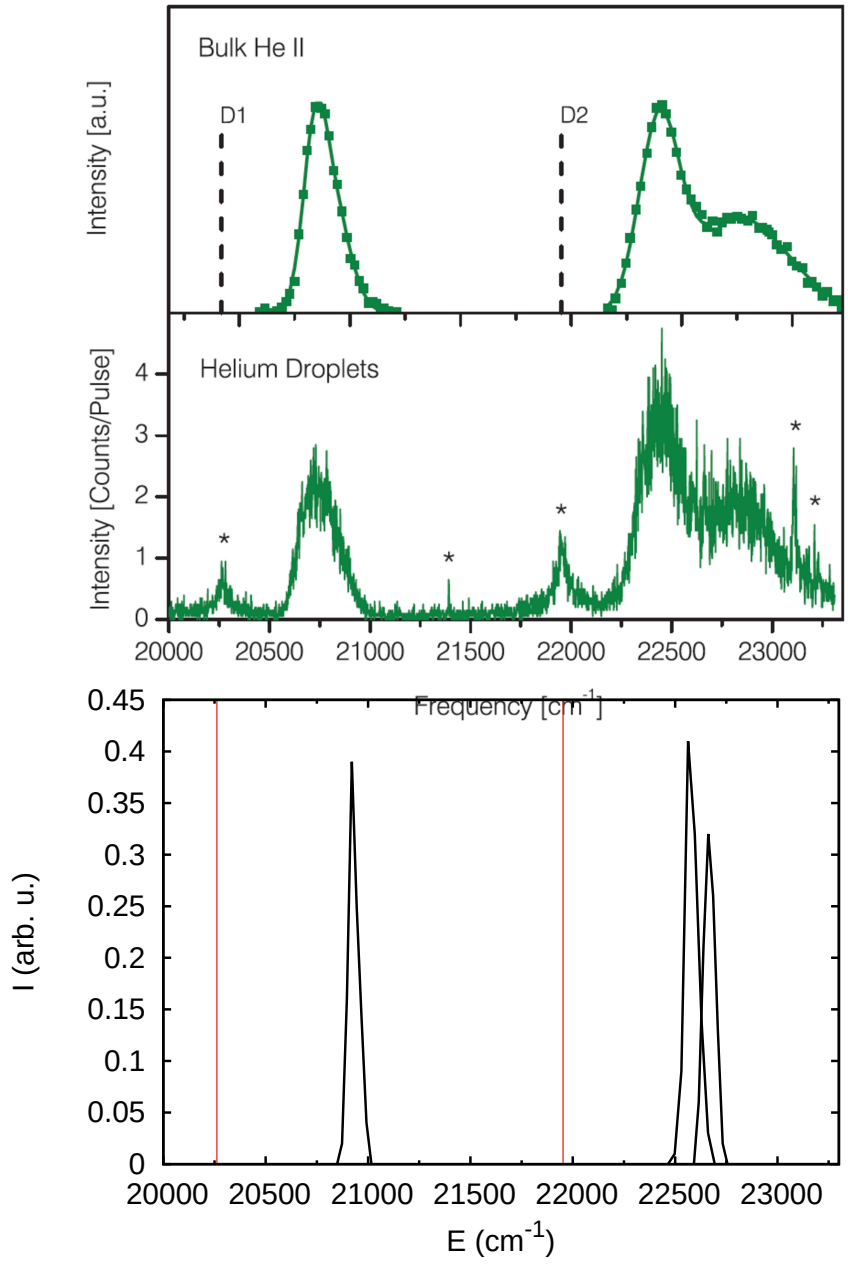




He-DFT from Leal, Mateo, Hernando, Pi, Barranco, Ponti, Cargnoni and Drabbels, PRB ***90****, 224518 (2014).*

$He_{1000}Ba^{+}$ ZPAD structure calculated by David Bonhommeau

Absorption spectrum



Zhang and Drabbels,

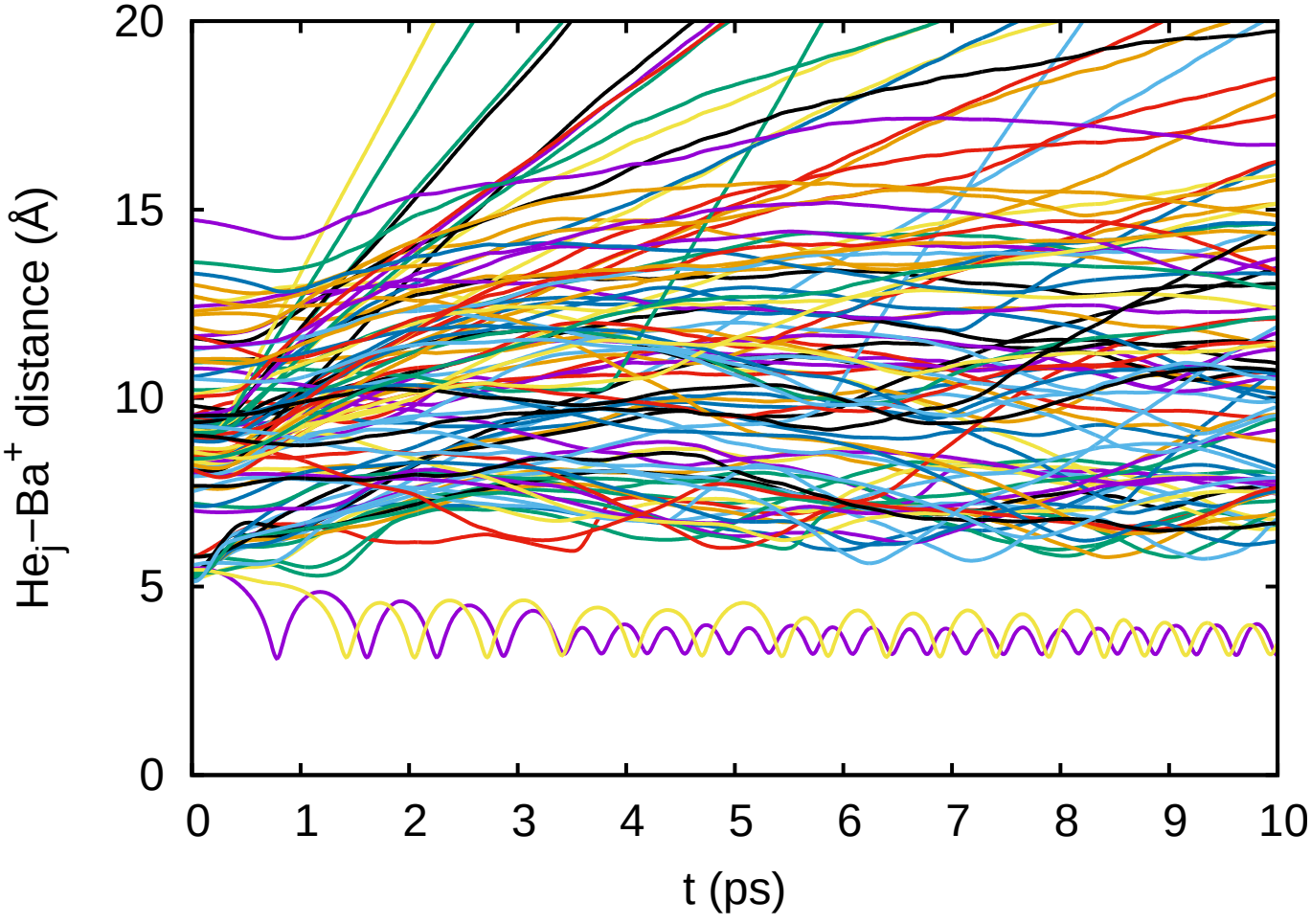
*JCP **137**, 051102 (2012)*

shift $\sim$ correct,

width too small

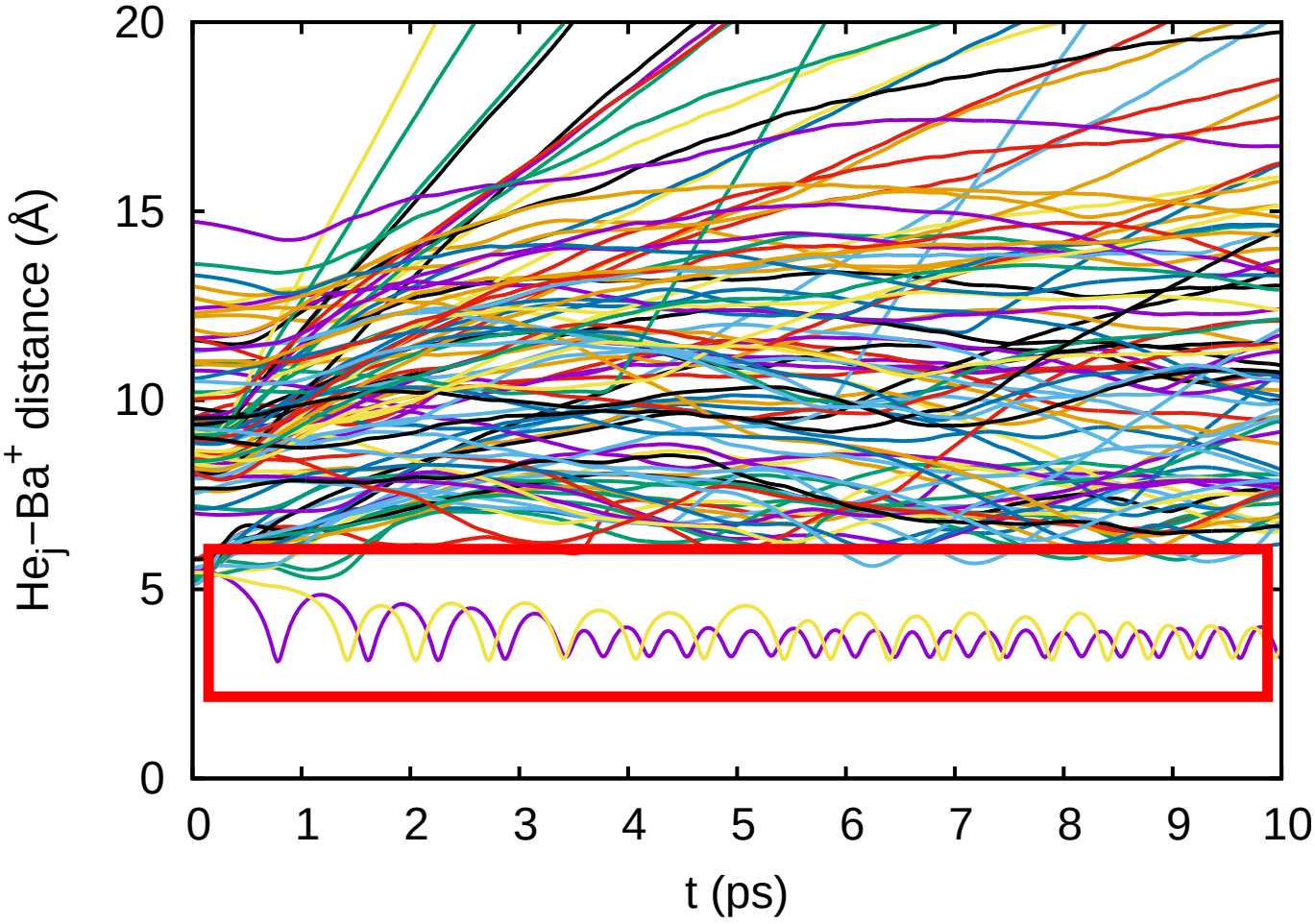
missing quantum fluctuations

Dynamics for Ba^+ $^2\Sigma_{1/2}$ excitation: typical trajectory



As expected, many He dissociate, some of them fast and early.

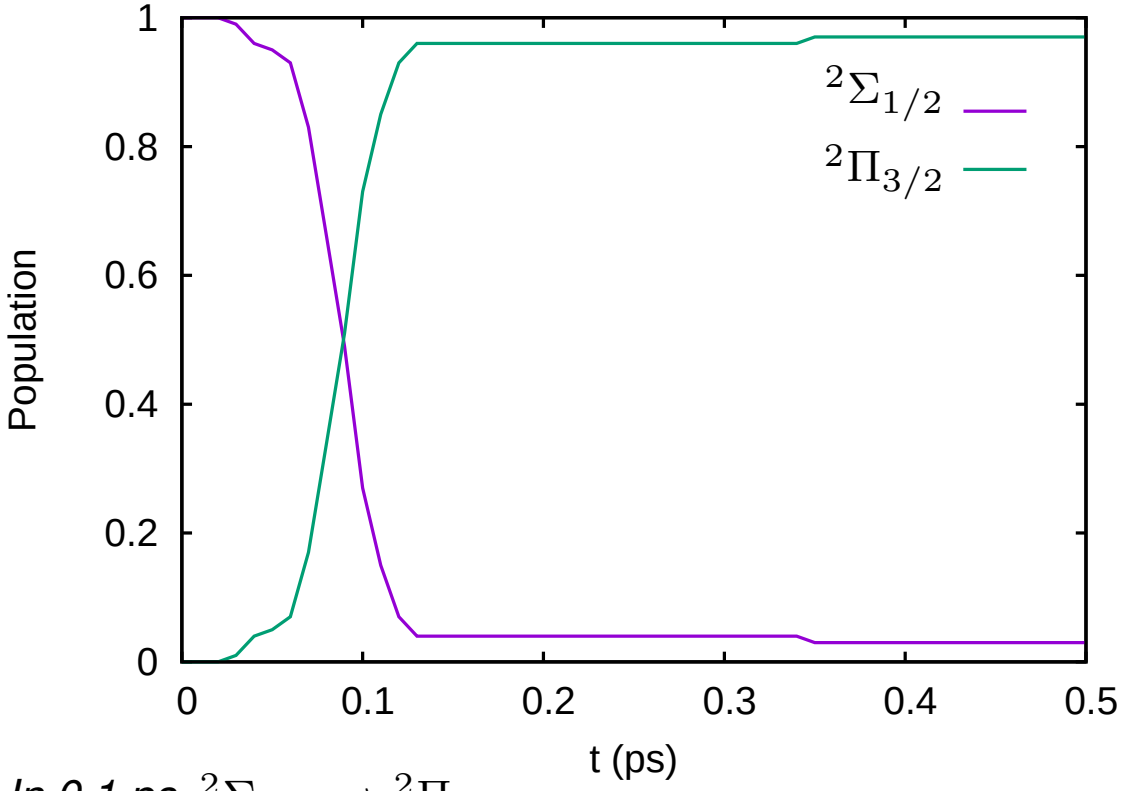
Dynamics for Ba^+ $^2\Sigma_{1/2}$ excitation: typical trajectory



As expected, many He dissociate, some of them fast and early.

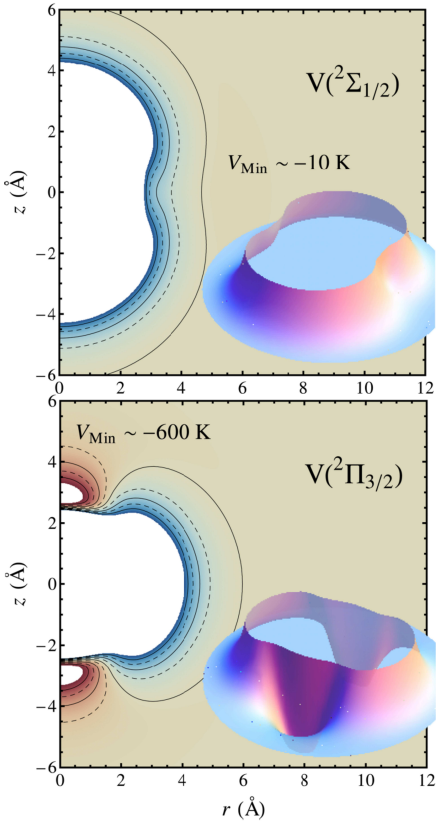
BUT: *a double excimer is formed??? This normally only happens for* $^2\Pi_{3/2}$

Electronic transition at work



In 0.1 ps, $^2\Sigma_{1/2} \rightarrow {}^2\Pi_{3/2}$

(here: averaged over 100 trajectories)

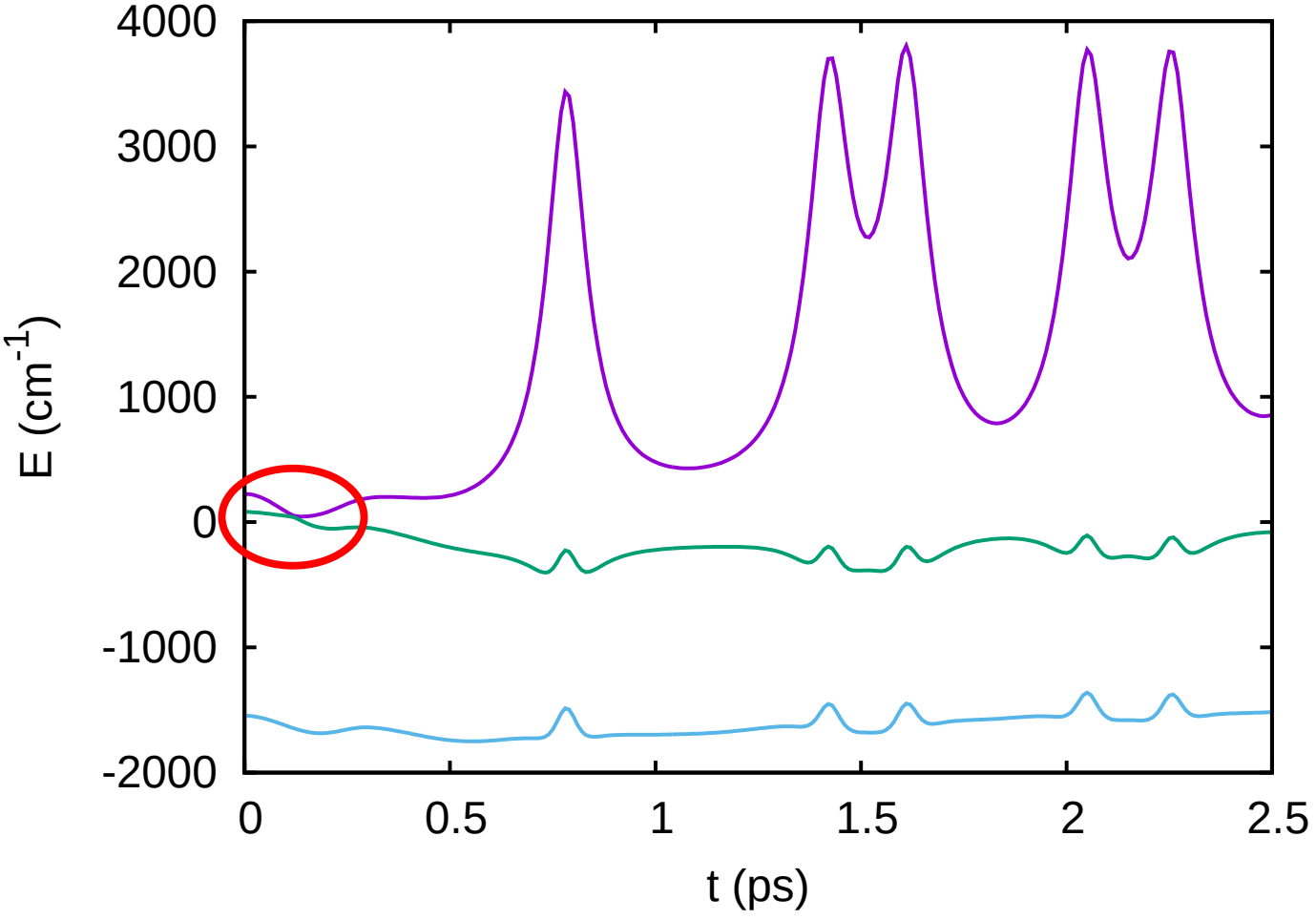


3D PES from Leal et al.,

JCP 144, 094302 (2016)

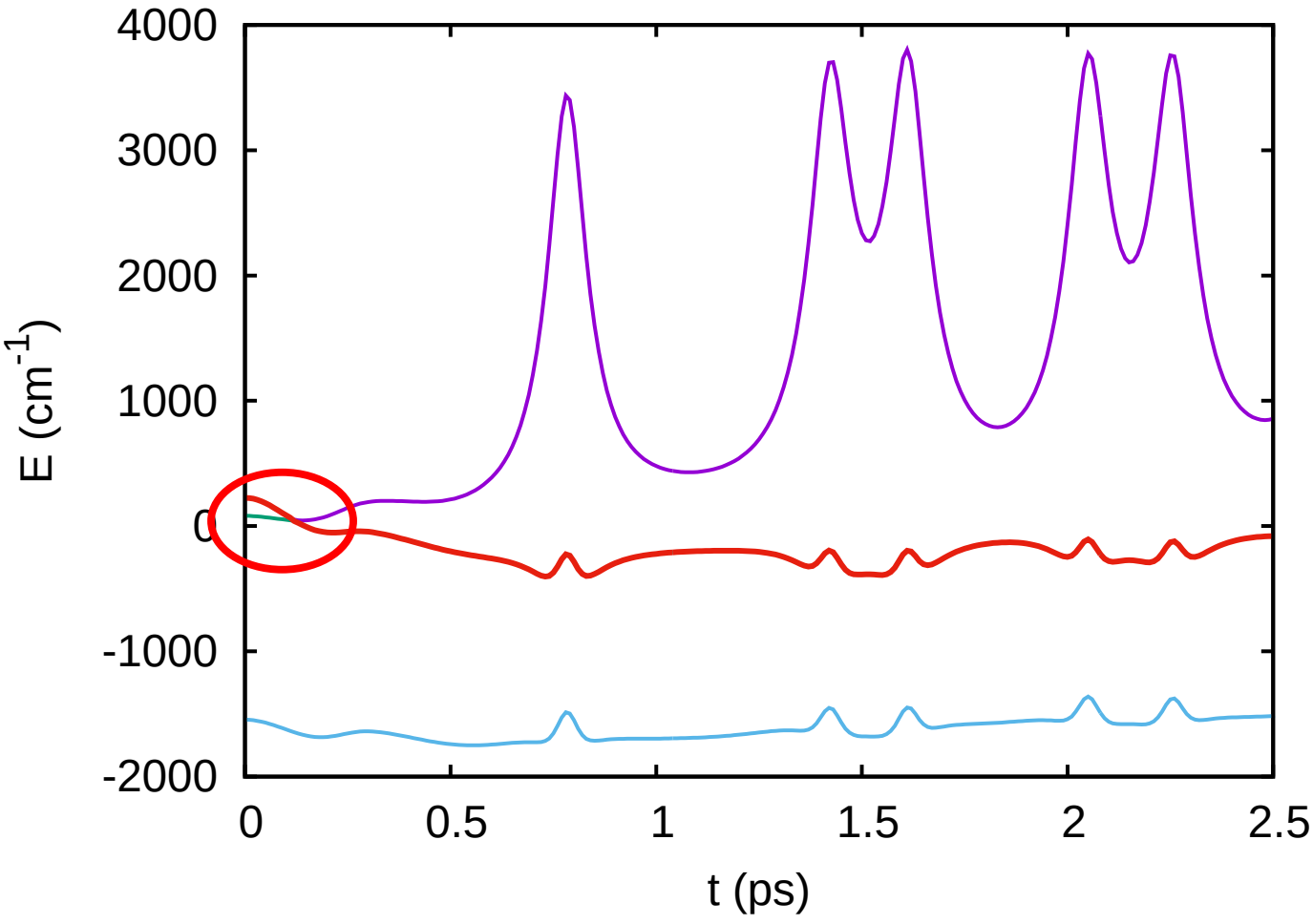
How did that happen?

Potential energy curves during the “typical” trajectory



How did that happen?

Potential energy curves during the “typical” trajectory



At $\sim$0.1 ps, $^2\Sigma_1/2$ and $^2\Pi_{3/2}$ come very close: $\Delta \simeq 20$ cm^{-1} (quasi-spherical symmetry) $\rightarrow$ strong coupling $\rightarrow$ “hop” (electronic transition)

Conclusion/Perspectives

- Yes, there are electronic transitions induced by He at 0.4 K!
- He-(TD)DFT is a very accurate and realistic tool to describe doped He droplet structures and dynamics
- It can describe the dynamics following an electronic transition
- Molecular model is complementary since it can describe potentials and couplings, and predict transitions
- Approximate (ZPAD) quantum molecular dynamics for Ba^+ at He_N (not finished): include quantum fluctuations in the initial conditions, ...

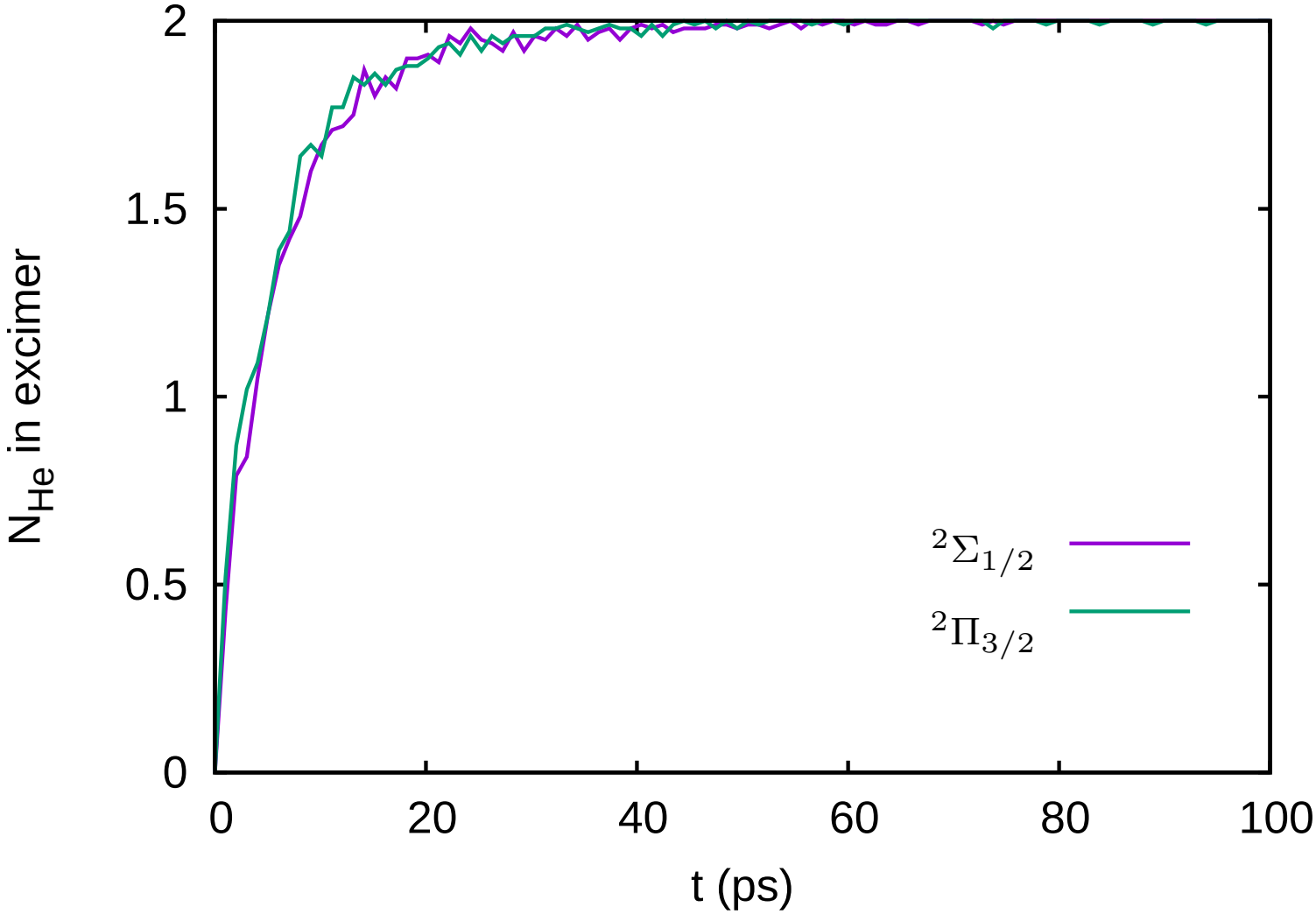
$\rightarrow$ couple TDDFT to other dynamics

Many thanks for your attention!

Programme Chaires d'Attractivité

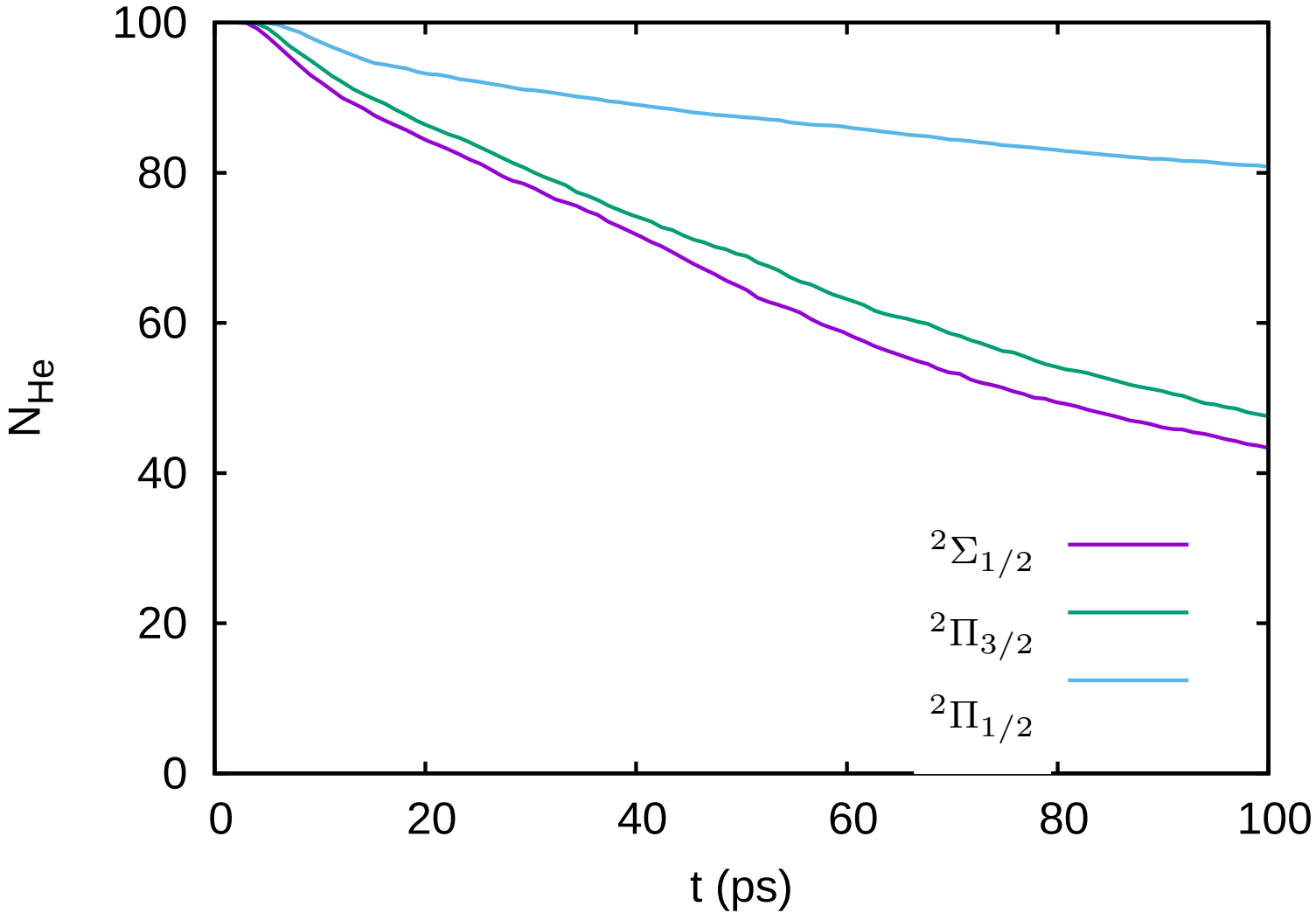
Manuel Barranco

Excimer formation dynamics



excimer formation: same kinetics for $^2\Pi_{3/2}$ *and* $^2\Sigma_{1/2}$

He evaporation dynamics



Slower dynamics for $^2\Pi_{1/2}$