Femtosecond Photoexcitation Dynamics of Atoms and Molecules inside Helium Nanodroplets

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Quantum Fluid Clusters 2019
Bad Honnef, May 21st, 2019
The Horse in Motion
Eadweard Muybridge 1878

The Molecule in Motion
(inside a He droplet)

1878
2019
Helium nanodroplet experiments

Fragile species: $^4\text{Na}_3$

Science 273, 629 (1996)

Microsolvation: The smallest drop. of acid: HCl$(\text{H}_2\text{O})_4$

Science 324, 1545-1548 (2009)

The smallest piece of ice: $(\text{H}_2\text{O})_6$

Science 287, 293-295 (2000)

Core-shell clusters


Femtochemistry inside $\text{He}_N$

Ahmed Zewail
Time-resolved He$_N$ experiments

**Pure droplets:** Daniel Neumark, Oliver Gessner, et al.


**Alignment & rotation:** Henrik Stapelfeldt, et al.

PRL **120**, 113202 (2018)

**Surface-located alkali-metals:**


Simulations: Manuel Barranco, Marti Pi, et al.

**atoms:**

observe desorption in real time (1-100 ps)

**molecules:** coherent vibrations

Rb$_2$: 1.5 ns

PRA **80**, 042512 (2009)
PCCP **13**, 6816 (2011)

K$_2$: ~5 ps

CPL **490**, 245 (2010)

**2D spectroscopy**

Femtochemistry inside $\text{He}_N$: open questions

Influence of droplets on intra-molecular dynamics?

$I_2$:Kr | PCCP 9, 779 (2007)

$Li$-$\text{He}_N$ | JCP 142, 044303 (2015)

Droplet response to photoexcitation?

$\sim 300 \text{ meV}$

Accessible time frame?

$\text{Ag-He}_N$: PCCP 15, 18388 (2013)
The experiment

Ti:sapphire
25 fs, 3 kHz
4 mJ

Delay Stage

OPA
360-380 nm

SHG
400 nm

TOF
Pick Up

5 μm
18 K
40 bar

He_N source
Droplet response to photoexcitation of atoms

B. Thaler et al.,
JPC A 123, 3977 (2019)
In-$\mathrm{He}_N$: bubble expansion

Time Dependent Helium-Density-Functional-Theory

He density $\rho_{\mathrm{He}}$ as the functional parameter

$\Rightarrow$ solve Schrödinger equation for $\rho_{\mathrm{He}}$

$\Rightarrow$ solve equation of motion for the impurity
Energetics of bubble expansion

0 fs | 200 fs | 500 fs | 1000 fs

- I: 4.5 Å
- II: 5.5 Å
- III: 7.5 Å
- IV: 8.1 Å
Energetics of bubble expansion

- Graph 1: Bubble radius (Å) vs. energy (a.u.)
  - States: $5s^2$, $5s^26s$, $5s^25p$

- Graph 2: Bubble radius (Å) vs. energy (eV)
  - Energy levels: $E_{\text{kin,He}}$, $E_{\text{He}^+,\text{In}^+}$
  - Phases:
    - I: 4.5 Å
    - II: 5.5 Å
    - III: 7.5 Å
    - IV: 8.1 Å
Energetics of bubble expansion
In-He\(_N\): ejection and bubble oscillation
In-He$_N$: ejection and bubble oscillation

Bernhard Thaler et al., Nat. Commun. 9, 4006, 2018
Photoelectrons: sensitive observable

![Graph showing bubble expansion, oscillation, and ejection](image-url)
Wave packet dynamics in a dissipative environment
Wave packet dynamics in a dissipative environment

![Diagram of wave packet dynamics in a dissipative environment](image)

- **dispersion**
- **decoherence**
- **dissipation**

- **ion**
- **ex**
- **gs**

Energy (a.u.) vs. $R_{in-in}$ (Å)
Summary – towards Femtochemistry inside He droplets

- photoelectrons are a good observable
- quantum solvent response to dopant photo excitation:
  - bubble expansion: \(~600\) fs
  - bubble oscillation: \(~30\) ps
  - atom ejection: \(~50\) ps

- little influence on intrinsic dynamics (In$_2$)

He is an exceptional solvent:
- long vibr. coherence (~100 ps)
- (water: <1 ps)

B. Thaler et al., Nat. Comm. 9, 4006, 2018
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