Two-dimensional coherent spectroscopy of doped Helium nanodroplets

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Outline

- Introduction
  - Femtosecond experiments
  - Coherent multidimensional spectroscopy

- 2d-coherent spectroscopy of doped helium nanodroplets
  - Wave packet dynamics of Rb dimers
  - Dynamics of dopant molecules with the helium environment

- Conclusion
Femtosecond methods

a) Time-dependance of an action signal

b) Wave packet dynamics (Tannor-Kosloff-Rice)

c) Wave packet interferometry (Brumer-Shapiro)

d) Multidimensional coherent spectroscopy
Simulations: M. Barranco et al. (Uni Barcelona)

Rb*  

Rb: equal electron density surface

5s

5p

HeN

Pump probe Rb⁺ Velocity Map Imaging
a) Time-dependance of an action signal

b) **Wave packet dynamics (Tannor-Kosloff-Rice)**

c) Wave packet interferometry (Brumer-Shapiro)

d) Multidimensional coherent spectroscopy
Femtosecond methods

a) Time-dependance of an action signal

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Quantum interferences of K atoms – nJ pulse energies

Multi-Path Interference

\[ \Delta E_{so} = 57.72 \text{ cm}^{-1} \]
Conventional pump-probe

Conventional pump-probe setups use femtosecond (fs) laser pulses to excite a sample and then probe the sample with a delayed laser pulse. The signal detected is proportional to the convolution of the pump and probe pulses with the system's response function. Mathematically, this can be represented as:

\[ S \propto c + \sum a_i \cos(\omega_i \tau) \]

where \( a_i \) are the system's resonance frequencies and \( \tau \) is the delay between the pump and probe pulses. The diagram shows the sequence of events: the fs-laser pulse first excites the sample, followed by the pump pulse, and then the probe pulse, which is delayed by \( \tau \). The signal detected by the detector is then analyzed.

Three-level system:

- \( |e_2\rangle \)
- \( |e_1\rangle \)
- \( |g\rangle \)

The system transitions between levels with rates that can be measured using pump-probe techniques.
Phase-modulated pump-probe technique

\[ S \propto c + \sum a_i \cos(\omega_{el} \tau + \Omega_{21} t) \]

\[ S_{dm} \propto \sum a_i \cos \left( (\omega_{el} - \omega_M) \tau \right) \]

\[ S_{ref} = \cos(\omega_M \tau + \Omega_{21} t) \]

Comparison of phase modulation technique to conventional WPI

Conventional pump-probe:

Phase-modulated pump-probe:

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2-dimensional spectroscopy

Frequency resolved probe process

Frequency resolved pump process

*pulse 1* pulse 1 pulse 2 pulse 2 pulse 3 pulse 3 pulse 4 pulse 4

*\( \phi_1 \) \( \phi_2 \) \( \phi_3 \) \( \phi_4 \) \( \phi_5 \) \( \phi_6 \) \( \phi_7 \) \( \phi_8 \)*

electronic wave packet interferometry

Detector frequency

Excitation frequency

Intensify
2D spectroscopy – FMO complex, light harvesting

Four-wave mixing

Mask defining phase matching conditions e.g. \(k_1-k_2+k_3=k_4\)

Robin M. Hochstrasser PNAS 04, 14190 (2007)
2-D spectroscopy at dilute samples: Phase matching – Phase cycling

**Four-wave mixing:**
- Advanced geometry of the optical setup
- Macroscopic ensemble effect, no option for small particle numbers
- Low sensitivity, photon detection

**Phase cycling:**
- Detection of population states (charged particles, photons, absorption, ...)
- High sensitivity and phase stability
- Collinear optical pulse sequence (still advanced optical setup)
Phase-modulated 2D electronic spectroscopy

2×FT → $S(\tau, T, t)$

photo electron/ion yield or fluorescence signal

detection unit

doped droplet beam

electronic wave packet interferometry

$\delta\omega \delta T$

$\delta\tau \delta t$

$\omega_\tau$

$T$

$p^{(3)}$

$|e\rangle$

$|g\rangle$

$p^{(3)}$

$\phi_4$

$\phi_3$

probe

pulse 4

pulse 3

$\phi_2$

$\phi_1$

pump

pulse 2

pulse 1

time evolution

$S(\omega, T, t)$

$P$

$\phi_5$

$\phi_6$

$\phi_7$

$\phi_8$

$|g\rangle$

$|e\rangle$

$\mathcal{P}$

$\mathcal{P}$

time evolution

Phase-modulated 2D electronic spectroscopy
Optical setup

- Spirit fs-laser
  - Tuneable rep rate (0-200) kHz
  - 1040 nm
  - Pulse width <400 fs
  - 80 μJ p.P.

- NOPA
  - Tunable wavelength (325-450) nm; (650-1000) nm
  - Pulse width <25 fs
  - ~3 μJ p.P.

- 4H gen.

- MZI 1
  - Delay stage
  - BS3
  - AOM1
  - Monochromator 1
  - PMT2
  - 8 kHz signal

- MZI 2
  - Delay stage
  - BS5
  - AOM4
  - Monochromator 2
  - PMT1
  - 5 kHz signal

- Frequency mixer

- Nozzle
- Source chamber
- Doping chamber
- Detector chambers:
  1. LIF
  2. Magnetic bottle
  3. TOF

- QMS/LT detector

- LIA 1
  - Rephasing signal

- LIA 2
  - Nonrephasing signal

- Ref 3 kHz signal
- Ref 13 kHz signal

- Detector signals
Droplet beam apparatus

b) Beam creation | Doping | Laser interaction & detection

LIF | MB | TOF MS | LT

Rare gas
He gas
Cryocooler
Skimmer
Nozzle
Pick-up cells
Chopper/Shutter
PMT
MCP
Ion+
CEM
Re-wire

7E^-7 mbar
1200 l/s
300 l/s
300 l/s
300 l/s
4E^-9 mbar
80 l/s
2-dimensional electronic spectroscopy at molecular beam targets

weakly-bound high-spin molecules

Photoionization, target density: $10^7 \text{ cm}^{-1}$

2-dimensional electronic spectroscopy at molecular beam targets

**Graphical Elements:**
- **Diagram:**
  - Energy levels (E) vs. internuclear distance (R).
  - Transitions labeled as SE, ESA, GSB, CP.
- **Legend:**
  - SE: Stimulated emission
  - ESA: Excited state absorption
  - GSB: Ground state bleach
  - CP: Cross peak
- **Cartoon Diagram:**
  - Pump and probe with delay T
  - SE, ESA, GSB transitions indicated

**Key Terms:**
- (1)^3Π_g
- a^3Σ_u
- Ground state bleach (GSB)
- Cross peak (CP)
- Stimulated emission (SE)
- Excited state absorption (ESA)
Comparison with fluorescence absorption spectra

Bruder et al., Nat. Comm. 9, 4823 (2018)
Comparison with fluorescence emission spectra

Bruder et al., Nat. Comm. 9, 4823 (2018)
Comparison with fluorescence emission spectra

Detection of ions and electrons

**Electrons**
- Rb$_3$ $^1A'_2 \rightarrow ^1A''_{1,2}$
- $\phi_1$, $\phi_2$, $\phi_3$, $\phi_4$
- $T=0$ fs
- 730 nm

**Ions**
- Rb$_2$ $^1\Sigma_u^+ \rightarrow ^3\Pi_g$
- $\phi_1$, $\phi_2$, $\phi_3$, $\phi_4$, $\phi_5$
- $T=200$ fs
- 670 nm, 720 nm

(RP SE, RP ESA2 transitions shown)

**Energy Levels**
- |i⟩, |f⟩, |e⟩, |g⟩

**Energy Spectra**
- $\omega_r (\times 10^3$ cm$^{-1}$) for PE and PI with $T=0$ fs and $T=200$ fs.
Mass-resolved detection

**TOF trace**

Ion time-of-flight (TOF) gated with boxcar integrator

**Pulse scheme**

Mass resolution → additional information (e.g. dissociation channels)
Molecule – matrix interaction

A

ω_r (x10^3 cm^-1)

12.0

13.0

14.0

15.0

0 250 500 750 1000 1250 1500 1750 2000 2250

T=0fs

ω_r (x10^3 cm^-1)

13.0

14.0

15.0

Rb3

GSB

ESA

Δ1

Δ2

T

Pump

GSB

SE

z (Rb3-He_N)

z_eq
Molecule–matrix interaction

Peak position along $\omega_t$ (cm$^{-1}$)

- GSB
- SE
- ESA

$T < 300$ fs
Conclusions

- 2-dimensional electronic spectroscopy of molecular beams at target densities of $10^7 \text{cm}^{-3}$
  - Unprecedented spectro-temporal resolution
  - “Complete” information on energies and the dynamics
- $\text{Rb}_2$: Dynamics of wave packet propagation and relaxation into lower states
- $\text{Rb}_3$: Dynamics of interaction with the helium surface

Outlook

- Application to organic excitation and charge transfer complexes to unravel complex dynamics
- Phase modulation enables efficient and selective detection of higher order processes
  - Many-body effects of interacting ensembles
  - HHG light sources: coherent multidimensional schemes are possible without direct XUV pulse manipulation
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More details on phase-modulated coherent spectroscopy

See Posters:

Ulrich Bangert
Two-dimensional electronic spectroscopy of Rb$_3$ in helium nanodroplet isolation

Daniel Uhl
Photoelectron two-dimensional coherent spectroscopy

Marcel Binz
Peak shape modulations in two-dimensional electronic spectroscopy caused by intense laser pulses

Friedemann Landmesser
Two-dimensional electronic spectroscopy of isolated, cold molecular nanosystems