Development of Frequency-Domain Multidimensional Spectroscopy

—Beyond Two Dimensions—

Blaise Thompson

University of Wisconsin–Madison

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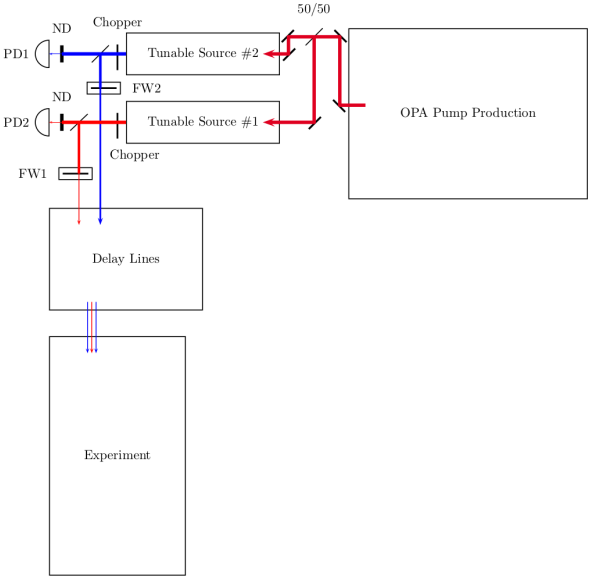
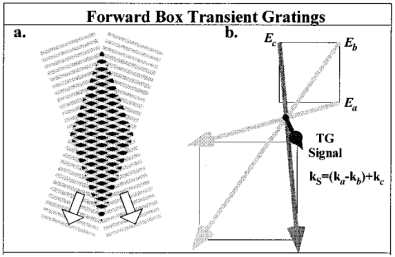
Introduction to CMDS

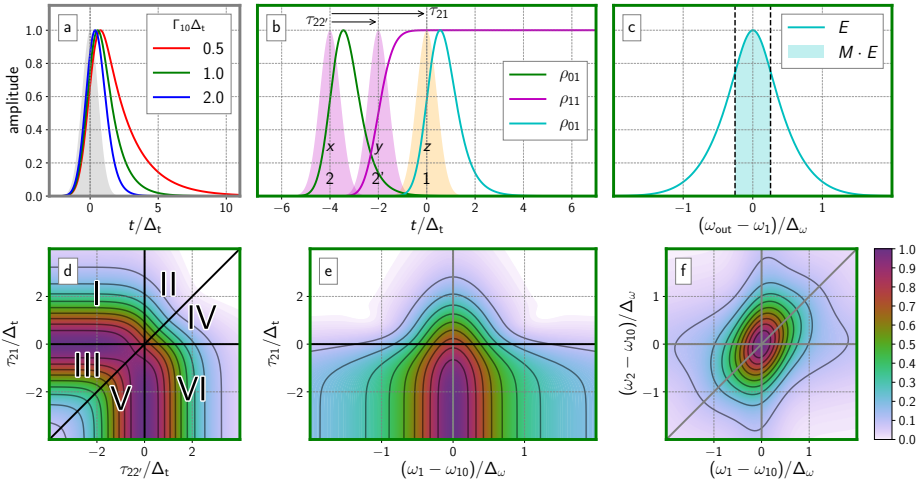




$$\vec{k_{\text{sig}}} = \vec{k_a} - \vec{k_b} + \vec{k_c}$$

Figure:
Brown, E., Zhang, Q. and Dantus, M. (1999).
The Journal of Chemical Physics, 110(12), pp.5772-5788.

Introduction to CMDS



Diversity

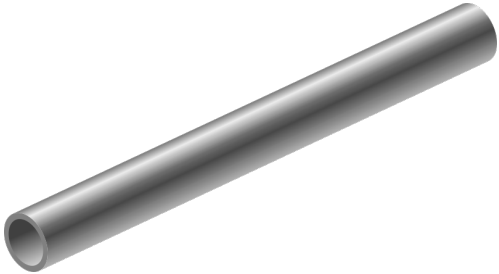
Great diversity of experimental strategies.

Different phase matching conditions...

- transient grating $\vec{k}_a - \vec{k}_b + \vec{k}_c$
- transient absorption
- DOVE

But also different color combinations and dimensions explored.

Pipeline



What does the “pipeline” of MR-CMDS data acquisition and processing look like in the Wright Group?

How to increase data throughput and quality, while decreasing frustration of experimentalists?

MR-CMDS development

[SUMMARY SLIDE FOR REMAINDER OF PRESENTATION]

Control and Calibration of Optical Parametric Amplifiers

Two strategies for CMDS

Two strategies for collecting multidimensional spectra:

Time Domain

- broadband pulses
- resolve spectra interferometrically
- fast (even single shot)
- robust

Frequency Domain

- narrowband pulses
- resolve spectra by tuning OPAs directly
- slow (lots of motor motion)
- fragile

Two strategies for CMDS

Time Domain

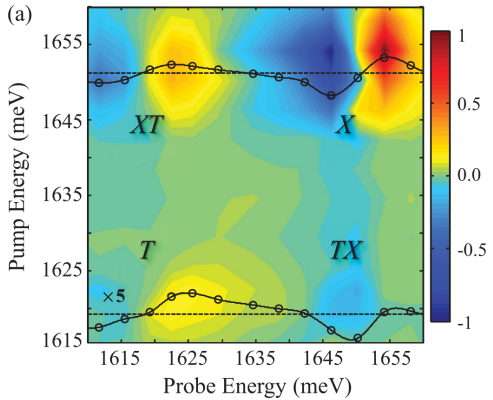
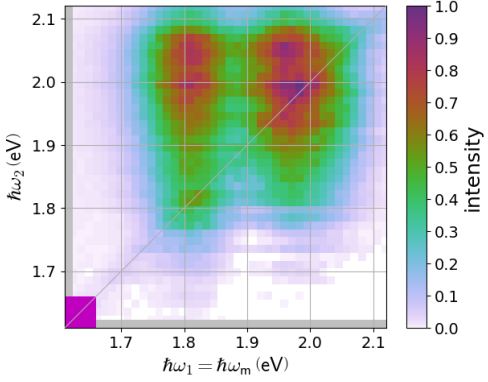


Figure:
Singh, A., Moody, G., Wu, S., Wu, Y., Ghimire, N., Yan, J., Mandrus, D., Xu, X. and Li, X. (2014). Coherent Electronic Coupling in Atomically Thin $MoSe_2$. Physical Review Letters, 112(21).

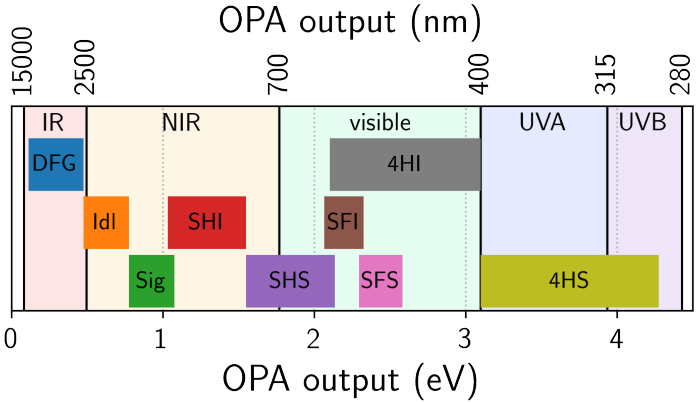
Frequency Domain



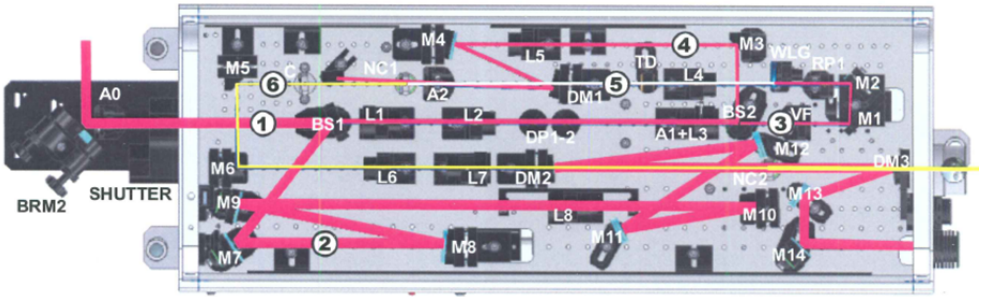
More bandwidth. Crucial for electronic states, band structure.

Bandwidth

A lot more bandwidth... through the usage of OPAs

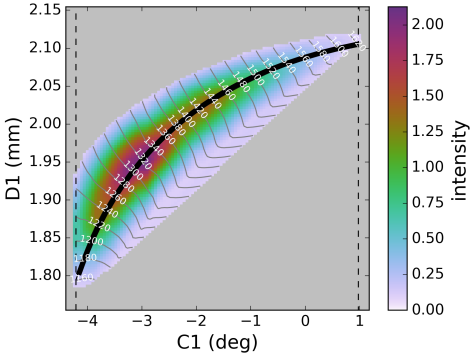


TOPAS-C



Two “stages”, each with two motorized optics.

Automation



Fully automated OPA tuning

- less than 1 hour per OPA
- can be scheduled for odd times
- high quality from global analysis
- reproducible
- unambiguous representations automatically generated

Other calibration steps also automated.

Control of the MR-CMDS Instrument

The instrument

Many kinds of component hardware

- monochromators
- delay stages
- filters
- OPAs

$\sim$ 10 settable devices, $\sim$ 25 motors, multiple detectors.

Acquisition

PyCMDS—unified software for controlling hardware and collecting data.

Central loop

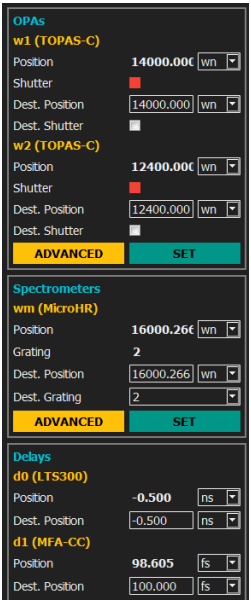
At its core, PyCMDS does something very simple...

Set, wait, read, wait, repeat.

Everything is multi-threaded (simultaneous motion, simultaneous read).

- decrease scan time by up to $\sim 2\times$, more for complex experiments

Extensibility

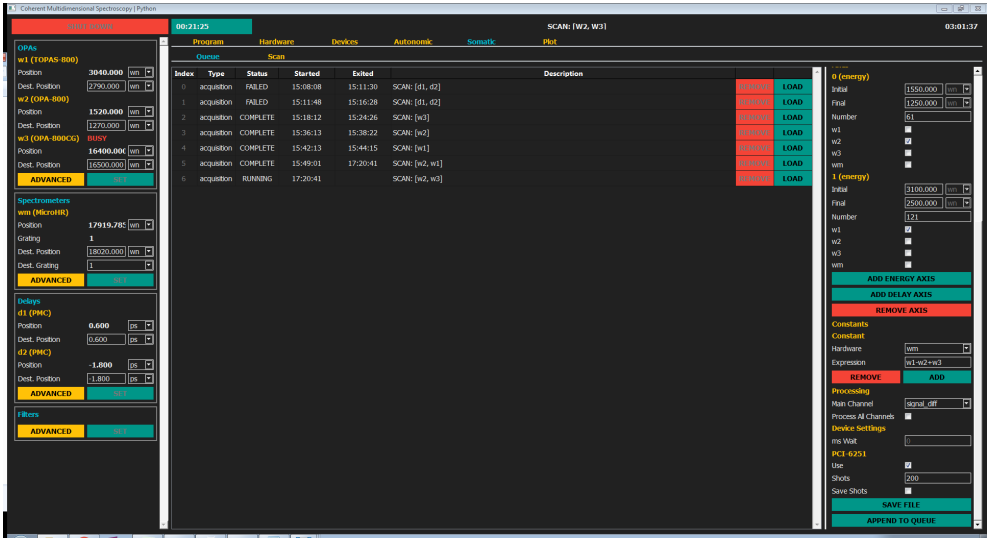


A modular hardware system that can be easily added to

- When a new OPA was installed on the picosecond system, PyCMDS was back in action the next day.
- Darien inherited a new delay stage from the Crim Group, and added it to PyCMDS in less than two days.
- New *kinds* of hardware also possible to add, although this is more difficult.

just need to copy a script and modify...

Queue


Coherent Multidimensional Spectroscopy | Python
Shut Down
00:21:25
SCAN: [W2, W3]
03:01:37
Program
Hardware
Devices
Autonomic
Somatic
Plot
Queue
Scan
OPAs
w1 (TOPAS-800)
Position 3040.000 wn
Dest. Position 2790.000 wn
w2 (OPA-800)
Position 1520.000 wn
Dest. Position 1270.000 wn
w3 (OPA-800CG) BUSY
Position 16400.00(wn
Dest. Position 16500.000 wn
ADVANCED
SET
Spectrometers
wm (MicroHR)
Position 17919.785 wn
Grating 1
Dest. Position 18020.000 wn
Dest. Grating 1
ADVANCED
SET
Delays
d1 (PMC)
Position 0.600 ps
Dest. Position 0.600 ps
d2 (PMC)
Position -1.800 ps
Dest. Position -1.800 ps
ADVANCED
SET
Filters
ADVANCED
SET
Index Type Status Started Exited Description
0 acquisition FAILED 15:08:08 15:11:30 SCAN: [d1, d2]
1 acquisition FAILED 15:11:48 15:16:28 SCAN: [d1, d2]
2 acquisition COMPLETE 15:18:12 15:24:26 SCAN: [w3]
3 acquisition COMPLETE 15:36:13 15:38:22 SCAN: [w2]
4 acquisition COMPLETE 15:42:13 15:44:15 SCAN: [w1]
5 acquisition COMPLETE 15:49:01 17:20:41 SCAN: [w2, w1]
6 acquisition RUNNING 17:20:41 SCAN: [w2, w3]
LOAD
0 (energy)
Initial 1550.000 wn
Final 1250.000 wn
Number 61
w1
w2
w3
wm
1 (energy)
Initial 3100.000 wn
Final 2500.000 wn
Number 121
w1
w2
w3
wm
ADD ENERGY AXIS
ADD DELAY AXIS
REMOVE AXIS
Constants
Constant
Hardware wm
Expression w1-w2+w3
REMOVE
ADD
Processing
Main Channel signal_diff
Process All Channels
Device Settings
ms Wait 0
PCI-6251
Use
Shots 200
Save Shots
SAVE FILE
APPEND TO QUEUE

Queue

This strategy can be incredibly productive!

- Soon after the queue was first implemented, we collected more pixels in two weeks than had been collected over the previous three years.

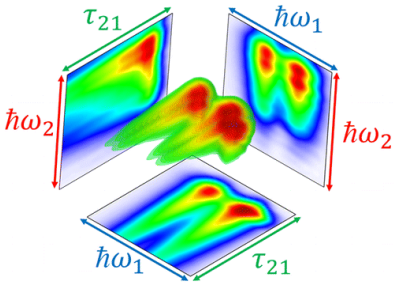
Artifact Rejection

Shots Processing

[DIGITAL SHOTS PROCESSING—NO MORE BOXCARS]

Data Processing

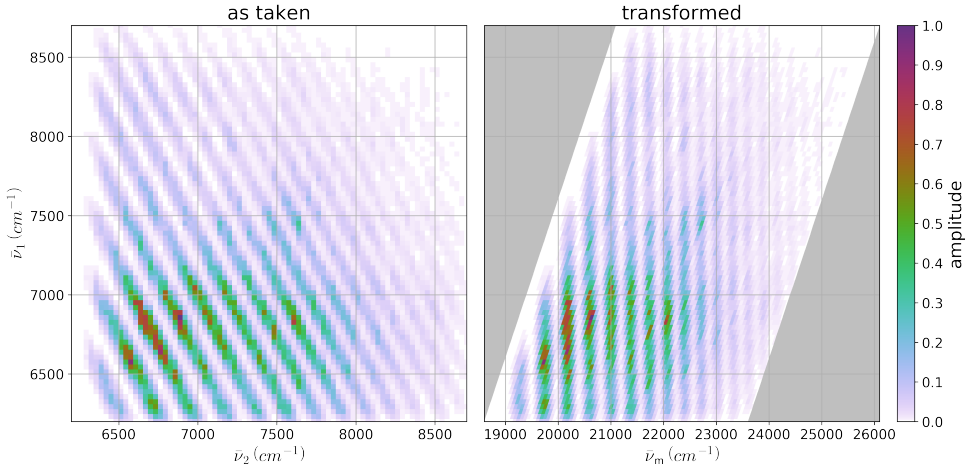
Dimensionality



TEST

Flexible data model

Flexibility to transform into any desired “projection” on component variables.



Universal format

WrightTools defines a *universal file format* for CMDS.

- store multiple multidimensional arrays
- metadata

Import data from a variety of sources.

- previous Wright Group acquisition software
- commercial instruments (JASCO, Shimadzu, Ocean Optics)

Conclusion

[CONCLUSION]

Acknowledgments

Wright Group

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- Skye Kain
- John
- (and more...)

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- Randall Goldsmith
- Tim Bertram

UW-Madison Chemistry Department

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- Pam Doolittle
- Bill Goebel
- Steve Myers

You, the audience! Questions?

Tuning

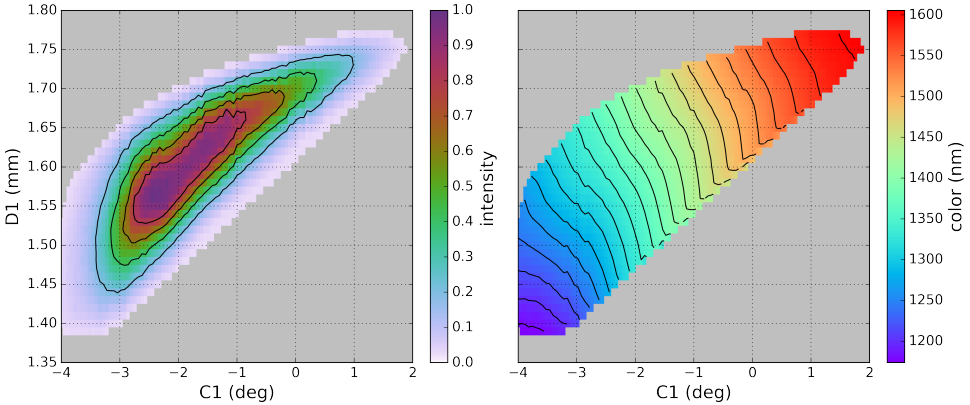
Tuning curves—recorded correspondence between motor positions and output color.

Exquisite sensitivity to alignment and lab conditions—tuning required roughly once a week.

Manual tuning is difficult...

- high dimensional motor space
- difficult to asses overall quality
- several hours of work per OPA (sometimes, an entire day for one OPA)

Preamp



Modular hardware model

```
Hardware
├── Delay
│   ├── Aerotech
│   ├── LTS300
│   ├── MFA
│   └── PMC
├── Filter
│   └── Homebuilt
├── OPA
│   ├── OPA800/PMC
│   └── TOPAS
│       ├── TOPAS-C
│       └── TOPAS-800
└── Spectrometer
    └── MicroHR
```

Modular sensor model

Can have as many sensors as needed.

Each sensor contributes one or more channels.

Sensors with size contribute new variables (dimensions).

Domains of CMDS

CMDS can be collected in two domains:

- time domain
- frequency domain

Time domain

Multiple broadband pulses are scanned in *time* to collect a multidimensional interferogram (analogous to FTIR, NMR).

A local oscillator must be used to measure the *phase* of the output.

This technique is...

- fast (even single shot)
- robust

pulse shapers have made time-domain CMDS (2DIR) almost routine.

Frequency domain

In the Wright Group, we focus on *frequency* domain "Multi-Resonant" (MR)-CMDS.

Automated Optical Parametric Amplifiers (OPAs) are used to produce relatively narrow-band pulses. Multidimensional spectra are collected "directly" by scanning OPAs against each-other.

This strategy is...

- slow (must directly visit each pixel)
- fragile (many crucial moving pieces)

but! It is incredibly flexible.

Selection rules

MR-CMDS can easily collect data without an external local oscillator.

This means... [BOYLE]

MR-CMDS theory

Mixed domain

[FIGURES FROM DAN'S PAPER]