Development of Frequency-Domain Multidimensional Spectroscopy

—Beyond Two Dimensions—

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Introduction to CMDS

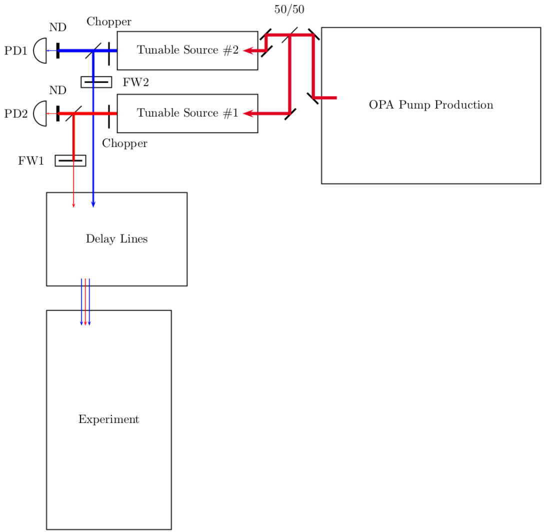
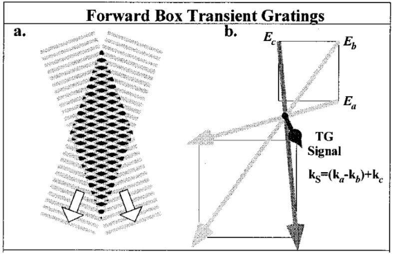


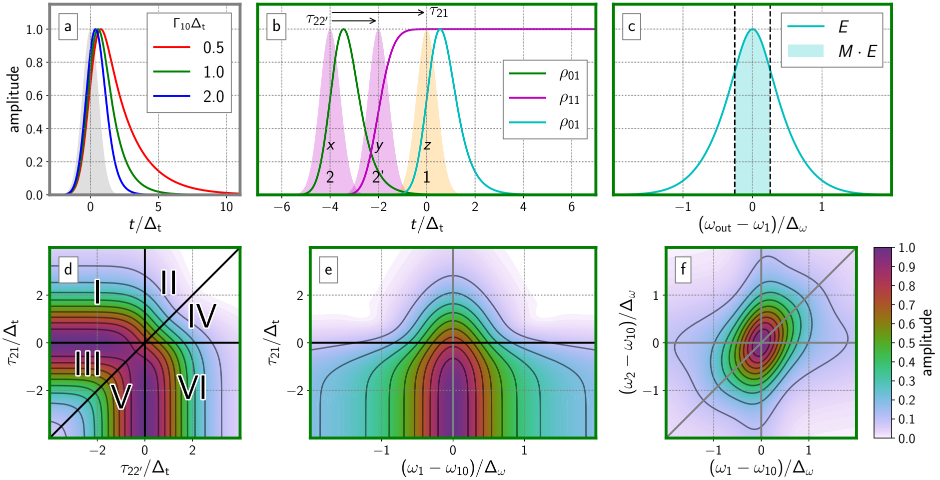
Figure courtesy of Schuyler Kain



$$\vec{k}_{\text{sig}} = \vec{k}_a - \vec{k}_b + \vec{k}_c$$

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

Introduction to CMDS: microscopic picture



Diversity

Great diversity of experimental strategies under the “umbrella” of CMDS:

Experimental geometry...

- $\vec{k}_a - \vec{k}_b + \vec{k}_c$
- $\vec{k}_a + \vec{k}_b + \vec{k}_c$
- $\vec{k}_a - \vec{k}_a + \vec{k}_b + \vec{k}_c + \vec{k}_d$

Dimensions explored...

- MIR & visible: DOVE, TRSF
- fully visible: TREE, CARS
- frequency-frequency: 2DES/2DIR, “Resonant-(Raman/IR)”
- frequency-delay: TG, TA
- delay-delay: 3PE, MUPPETS

Or 3D.. or 4D: many possibilities not yet popular enough to name

My focus

Focus on the *pipeline* of CMDS:

- throughput
- quality
- diversity

Unlock the true potential of these instruments:

- automated calibration
- 2D, 3D, 4D...
- full diversity of possible hardware combinations, rapid development
- powerful and flexible detection strategies
- data processing tools

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

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Tunability

Acquisition

Measurement enhancements

Processing

Universal format

Flexible data model

Integrations

Conclusion

Supplement

Two strategies for CMDS

Time Domain

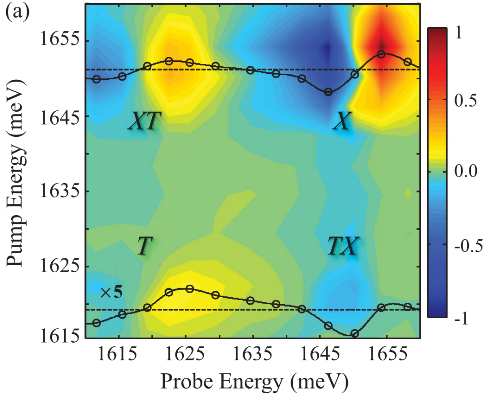
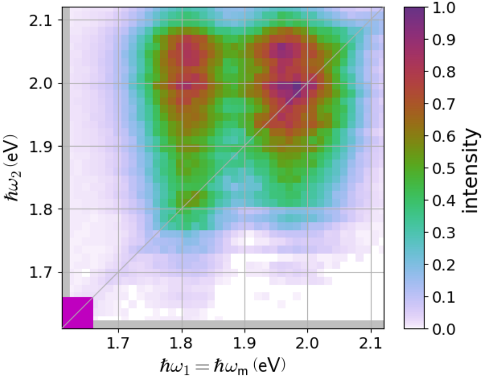


Figure:
Singh, A., Moody, G., Wu, S., Wu, Y., Ghimire, N., Yan, J., Mandrus, D., Xu, X. and Li, X. (2014). Coherent Electronic Coupling in Atomically Thin $MoSe_2$. Physical Review Letters, 112(21).

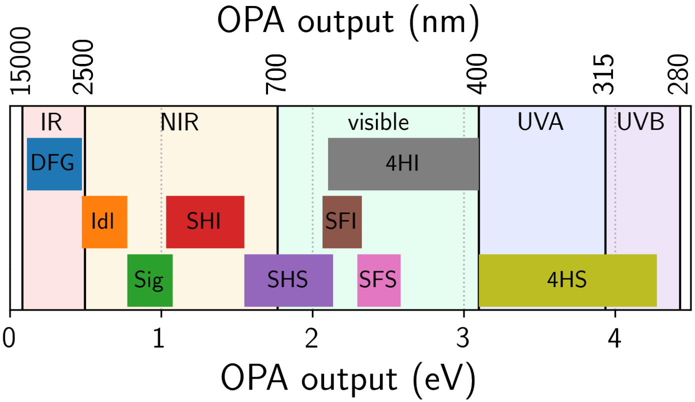
Frequency Domain



More bandwidth. Crucial for electronic states, band structure.

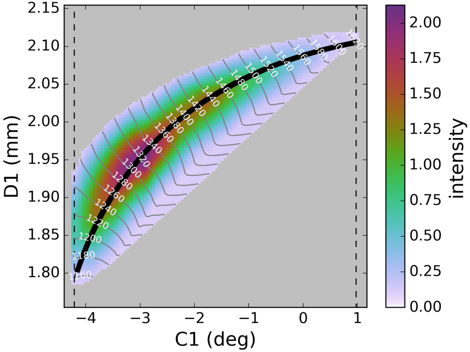
Bandwidth

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



but how to make this strategy easy and robust?

Automation



Fully automated OPA tuning

- less than 1 hour per OPA
- can be scheduled during down time
- high quality from global analysis
- reproducible
- unambiguous representations automatically generated to assess health

Other calibration also needed, 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.

Coordination problem.

Acquisition

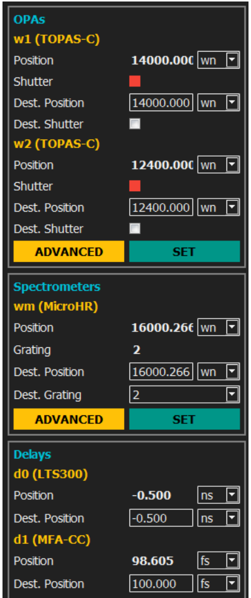
PyCMDS—unified software for controlling hardware and collecting data.

Acquisition

Capabilities of PyCMDS:

- reconfigures itself based on available hardware (modularity)
- multithreaded (up to 2x speed enhancement)
- queued acquisitions
  - long scans, short window of calibration—large duty cycle needed
  - shortly after implementation, two weeks of data collection yielded as many pixels as the previous three years
- extensibility
  - easy to add new hardware, new sensors, and new acquisition strategies
  - typical addition $\sim$ 100 lines of new Python code

Extensibility



Easy to add new hardware to PyCMDS

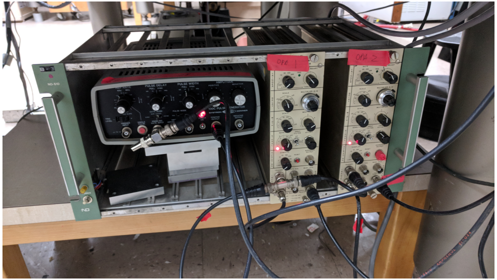
- In 2016, a new OPA was added to the picosecond system in one day.
- In 2017, we added multiple delay stages to the femtosecond system. Implementation took between one and four hours.

Once added, new hardware is immediately available for scanning in a multidimensional space with other hardware—no additional programming needed!

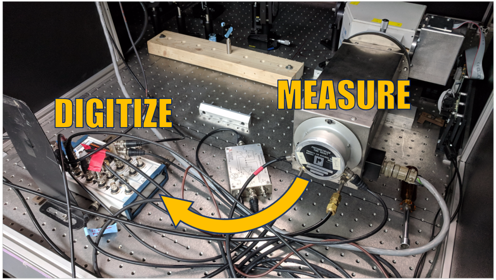
Measurement enhancements

Digital processing

boxcar averager

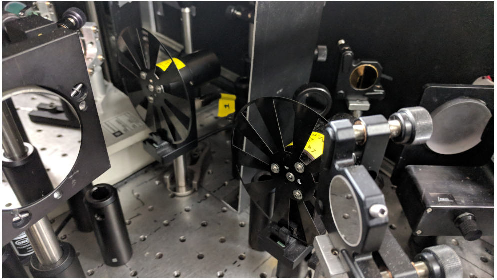


digitize immediately



- cheaper, fewer points of failure
- more flexibility for different detector configurations
- shot-level statistics, processing sequences
  - configurable through simple python script
- $\sim 3\times$ faster

Dual chopping



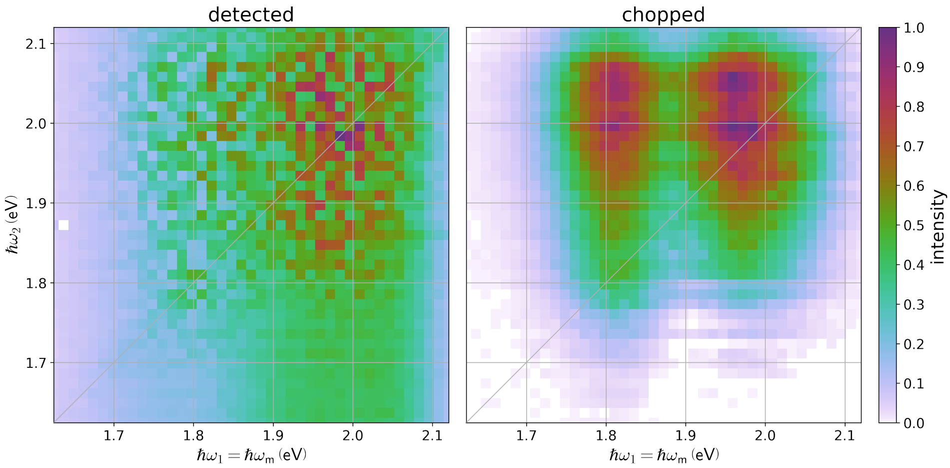
	A	B	C	D
signal			✓	
scatter 1		✓	✓	
scatter 2			✓	✓
other	✓	✓	✓	✓

$$I_{\text{signal}} = A - B + C - D$$

Isolate signal that depends on *all* indecent beams.

- no scatter
- no competing signals
- no voltage offset or room lights

Digital processing



Data processing

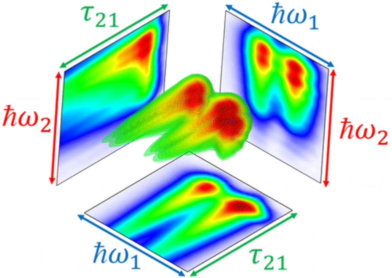
Processing

Great! We have *lots* of CMDS data.
Now what?

Working with multidimensional data is hard...

- storage
- visualization
- post-processing
- fitting, modeling

and the dimensions are always changing!



WrightTools—software to process CMDS.

Universal format

WrightTools defines a *universal file format* for CMDS.

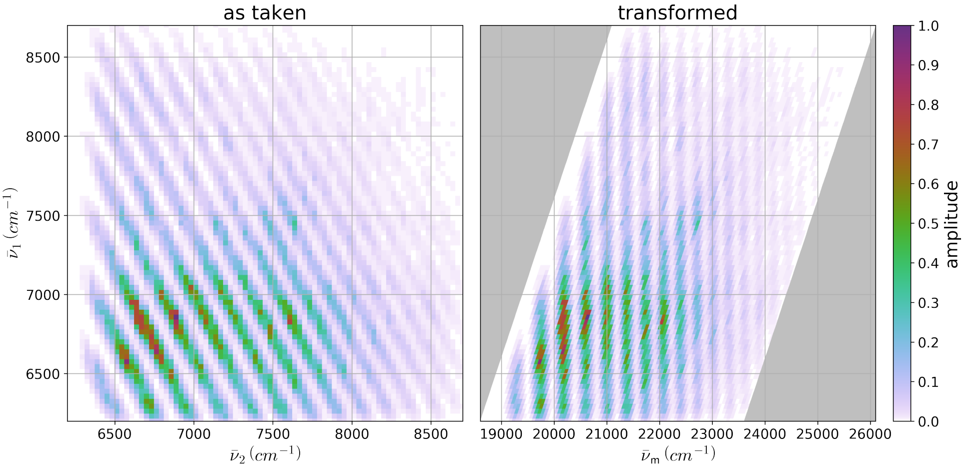
- store multiple multidimensional arrays
- metadata

Import data from a variety of sources.

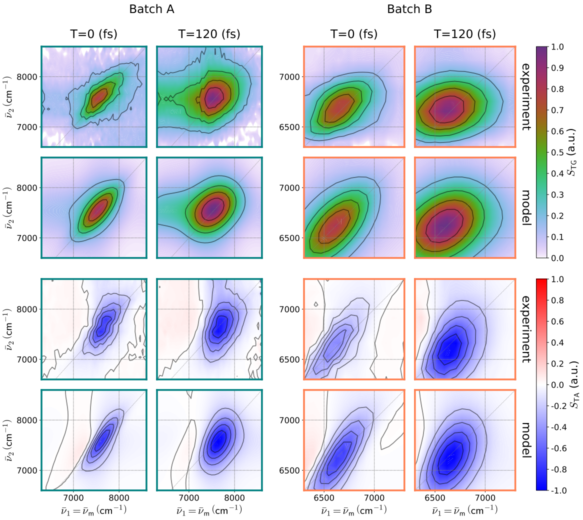
- previous Wright Group acquisition software
- commercial instruments (JASCO, Shimadzu, Ocean Optics)
- simulation packages

Flexible data model

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



Integrations



- WrightTools as a backend
- puts models and experiments on the same footing
- makes custom modeling work easier
- more general-purpose modeling coming soon

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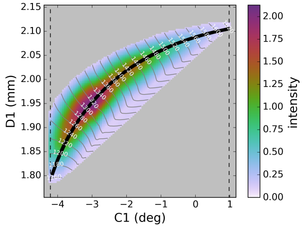
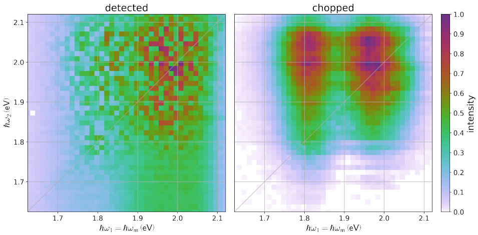
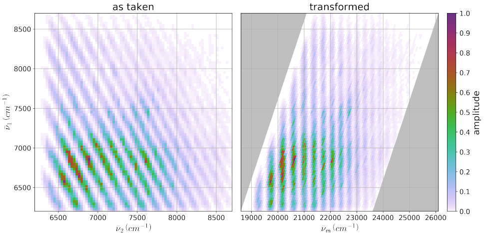
Conclusion







Acknowledgments

Wright Group

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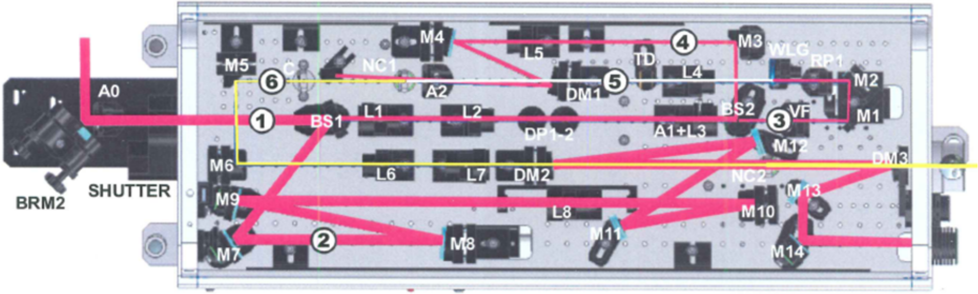
- Steve Myers

Friends and family

You, the audience! Questions?

TOPAS-C

One of four models of OPAs used within the Wright Group.



Two "stages", each with two motorized optics.

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)

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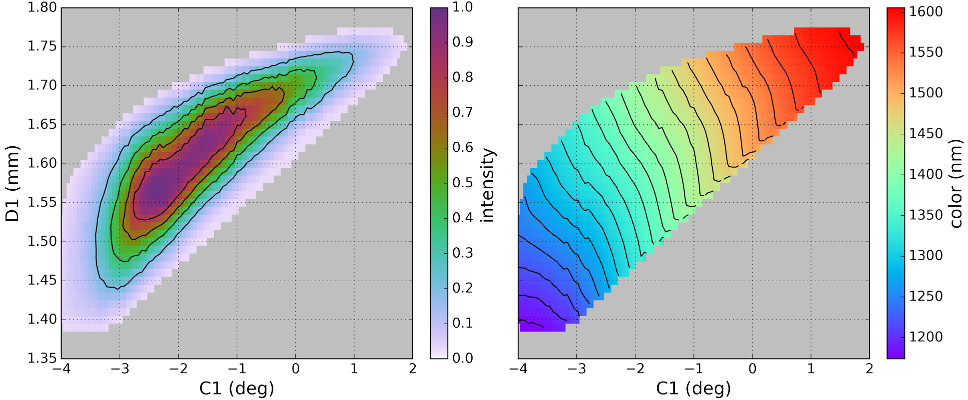
Preamp



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]

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