Development of Frequency Domain Multidimensional Spectroscopy

—Beyond Two Dimensions—

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2018-04-23

Development of Frequency Domain Multidimensional Spectroscopy

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Tunability

Acquisition

Extensibility

Processing

Conclusion

Supplement

Brown et al. (1999)

JOURNAL OF CHEMICAL PHYSICS VOLUME 110, NUMBER 12 22 MARCH 1999

Femtosecond transient-grating techniques: Population and coherence dynamics involving ground and excited states

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(Received 11 May 1998; accepted 23 December 1998)

Time-resolved transient grating techniques (TG) arising from four-wave mixing (FWM) processes are explored for the study of molecular dynamics in gas-phase systems ranging from single atoms to large polyatomic molecules. For atomic species such as Ar and Xe, each TG signal shows only a peak at zero time delay when all three incident pulses are overlapped temporally. For diatomic O_2 and N_2 and linear triatomic CS_2 molecules, the TG signals exhibit ground state rotational wave packet recurrences that can be analyzed to obtain accurate rotational constants for these molecules. With heavier systems such as HgI_2, ground state vibrational and rotational wave packet dynamics are observed. Resonant excitation allows us to select between measurements that monitor wave packet dynamics, i.e., populations in the ground or excited states or coherences between the two electronic states. To illustrate these two cases we chose the $X \rightarrow B$ transition in I_2. TG measurements yield dynamic information characteristic of vibrational and rotational wave packets from the ground and excited states. Reverse transient grating (RTG) experiments monitor the time evolution of an electronic coherence between the ground and excited states which includes vibrational and rotational information as well. Early time TG signal for the polyatomic samples CH_2Cl_2, CH_2Br_2, benzene, and toluene exhibit a coherence coupling feature at time zero followed by rotational dephasing. Differences in the amplitude of these two components are related to the contributions from the isotropic and anisotropic components of the molecular polarizability. A theoretical formalism is developed and used successfully to interpret and simulate the experimental transients. The measurements in this study provide gas-phase rotational and vibrational dephasing information that is contrasted, in the case of CS_2, with liquid-phase measurements. This comparison provides a time scale for intramolecular dynamics, intermolecular collisions, and solvation dynamics. [S0021-9606(99)02012-7]

I. INTRODUCTION

The past decade has witnessed rapid growth of real-time molecular dynamics investigation using ultrashort laser pulses.[1–4] Various probing techniques have been exploited in this endeavor. Particularly, third- or higher-order nonlinear techniques have been employed increasingly in recent years for studying molecular dynamics in the gas-phase environment. Techniques similar to coherent transient birefringence in vapor samples, pioneered by Heritage *et al.* in the picosecond regime,[5] were recognized by Fayer and co-workers for their potential for probing gas-phase dynamics.[6–8] Examples of such novel techniques extended to the femtosecond time scale include degenerate four-wave mixing (DFWM)[9,10] and coherent anti-Stokes Raman scattering (CARS).[11,12] In this study, we examine the different types of dynamics that can be observed by time-resolved transient-grating (TG) techniques involving four-wave mixing (FWM) nonlinear optical processes. The name ''transient grating'' is used here to highlight the fact that most of the information obtained in these experiments derives from the time-ordering of various ultrashort pulses and not from high-resolution frequency tuning. We explore the TG signals from a series of atomic, diatomic, and polyatomic systems. A theoretical framework is included that takes into account the different third-order nonlinear processes that contribute to the observed signals. From this analysis formulae are derived to analyze the vibrational and rotational dynamics observed in the experimental transients for both resonant and off-resonant excitation.

Most ultrafast experiments on molecular dynamics in the gas phase have been carried out using the pump–probe technique.[1–4] In these experiments, a pump laser initiates the dynamics of a system typically through a one-photon excitation process. In a few studies multiphoton excitation by the pump laser has been utilized to access higher-lying electronic or vibrational states.[13–17] For the probe process, various techniques have been used; examples include linear techniques such as absorption and laser induced fluorescence (LIF) and nonlinear techniques such as fluorescence up-conversion and multiphoton excitation followed by photoionization or photoelectron detection.[1–4] The formalisms for quantitative analysis of these measurements, i.e., the extraction of vibrational and rotational populations, are well known.[18–20] One of the goals of this work is to extend this level of understanding to the quantitative analysis of ultrafast

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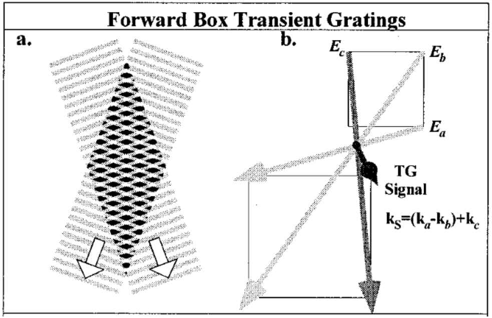
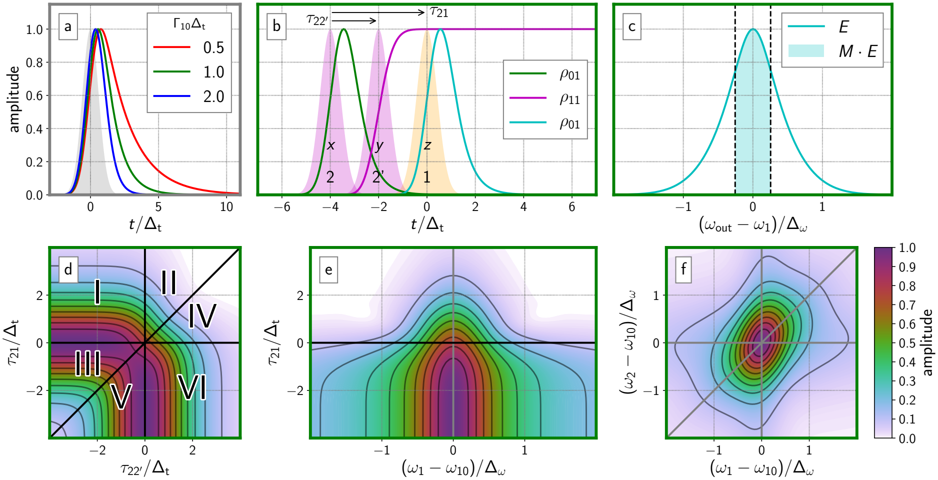


$$\vec{k}_{\mathrm{sig}} = \vec{k}_a - \vec{k}_b + \vec{k}_c$$

Overview


a
$\Gamma_{10}\Delta_t$
0.5
1.0
2.0
amplitude
t/Δ_t
b
$\tau_{22'}$
τ_{21}
x
y
z
2
2'
1
ρ_{01}
ρ_{11}
ρ_{01}
t/Δ_t
c
E
$M \cdot E$
$(\omega_{out} - \omega_1)/\Delta_\omega$
d
I
II
III
IV
V
VI
τ_{21}/Δ_t
$\tau_{22'}/\Delta_t$
e
τ_{21}/Δ_t
$(\omega_1 - \omega_{10})/\Delta_\omega$
f
$(\omega_2 - \omega_{10})/\Delta_\omega$
$(\omega_1 - \omega_{10})/\Delta_\omega$
amplitude

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.

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

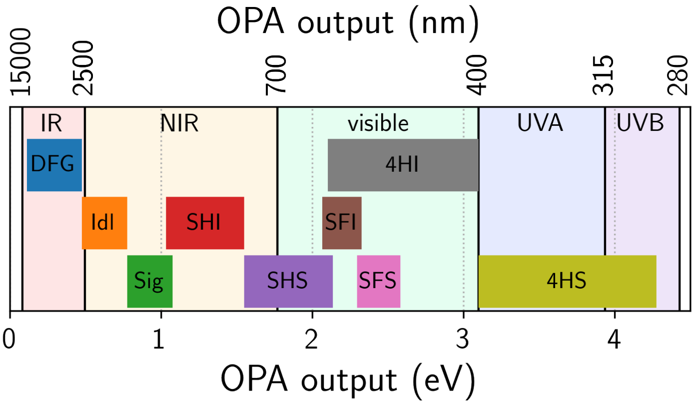
Postage stamp

[FIGURE FROM LIT]

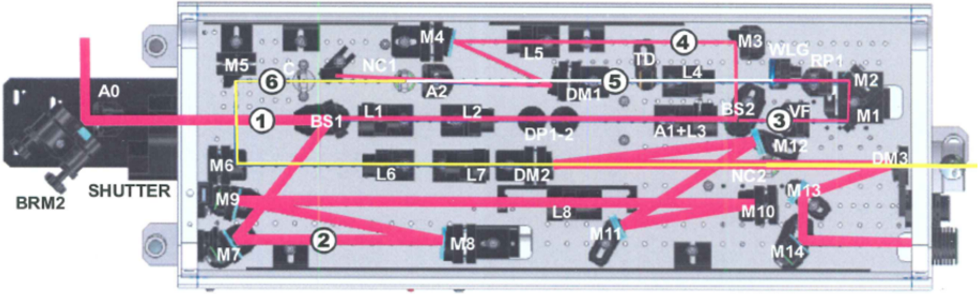
Czech

[FIGURE FROM CZECH]

Bandwidth


OPA output (nm)
15000
2500
700
400
315
280
IR
NIR
visible
UVA
UVB
DFG
4HI
Idl
SHI
SFI
Sig
SHS
SFS
4HS
0
1
2
3
4
OPA output (eV)

TOPAS-C



Two “stages”, each with two motorized optics.

Tuning

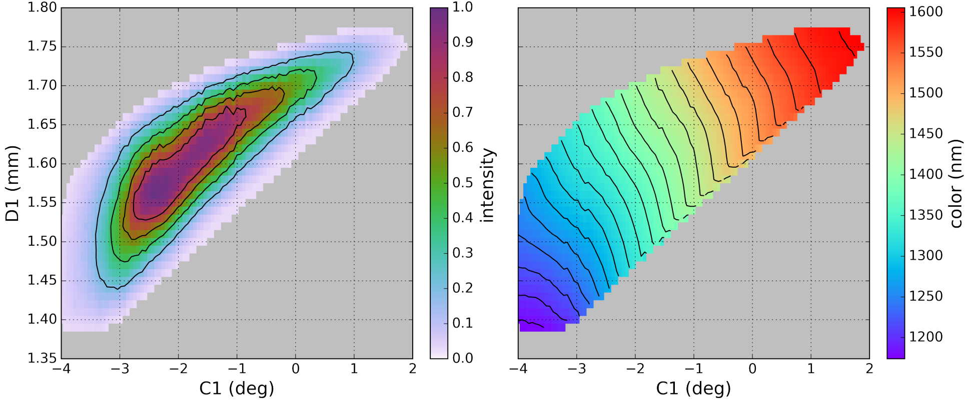
Tuning curves—recorded correspondence between motor positions and output color.

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

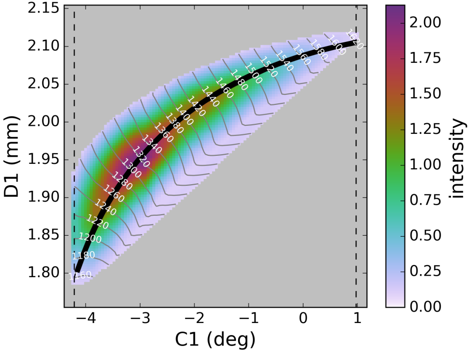
Manual tuning is difficult...

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

Preamp


1.80
1.75
1.70
1.65
1.60
1.55
1.50
1.45
1.40
1.35
D1 (mm)
−4
−3
−2
−1
0
1
2
C1 (deg)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
intensity
C1 (deg)
1600
1550
1500
1450
1400
1350
1300
1250
1200
color (nm)

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

Other calibration steps also automated.

Control of the MR-CMDS Instrument

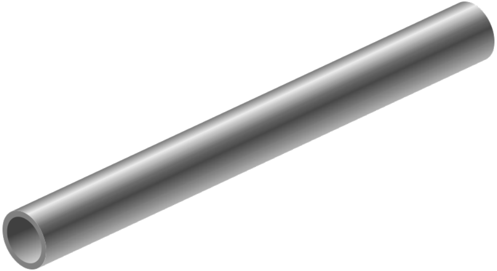
The instrument

Many kinds of component hardware

- monochromators
- delay stages
- filters
- OPAs

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

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?

Acquisition

PyCMDS—unified software for controlling hardware and collecting data.

Abstraction

Hardware—something that has a position that can be set.

Sensor—something that has a signal that can be read.

Central loop

Set, wait, read, wait, repeat.

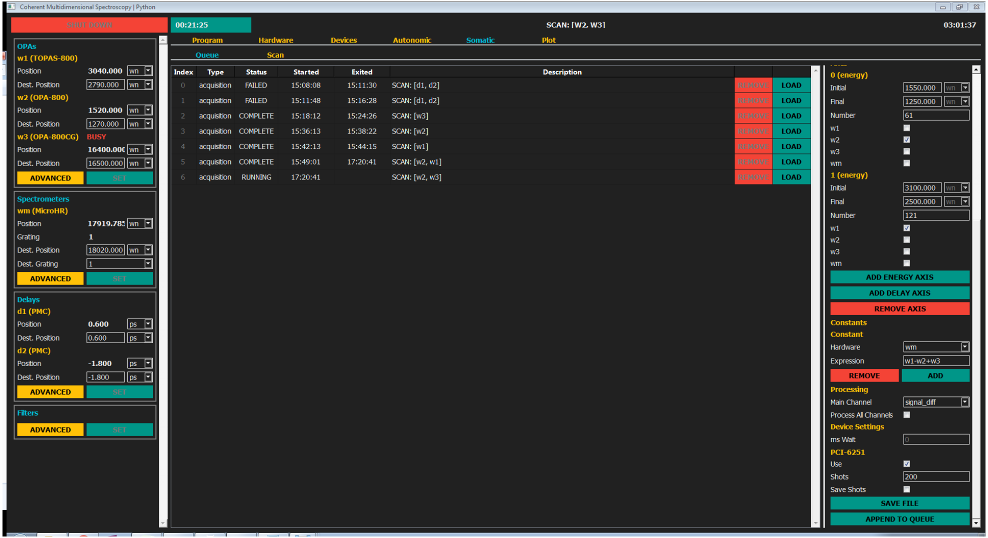
Everything is multi-threaded (simultaneous motion, simultaneous read).

Acquisitions

Acquisition—a particular set of actions.

Acquisition modules—a GUI that accepts a user instruction.

Queue.


Coherent Multidimensional Spectroscopy | Python
SHUT DOWN
00:21:25
SCAN: [W2, W3]
03:01:37
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 16400.000 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
Program Hardware Devices Autonomic Somatic Plot
Queue Scan
Index Type Status Started Exited Description
0 acquisition FAILED 15:08:08 15:11:30 SCAN: [d1, d2] REMOVE LOAD
1 acquisition FAILED 15:11:48 15:16:28 SCAN: [d1, d2] REMOVE LOAD
2 acquisition COMPLETE 15:18:12 15:24:26 SCAN: [w3] REMOVE LOAD
3 acquisition COMPLETE 15:36:13 15:38:22 SCAN: [w2] REMOVE LOAD
4 acquisition COMPLETE 15:42:13 15:44:15 SCAN: [w1] REMOVE LOAD
5 acquisition COMPLETE 15:49:01 17:20:41 SCAN: [w2, w1] REMOVE LOAD
6 acquisition RUNNING 17:20:41 SCAN: [w2, w3] REMOVE 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.

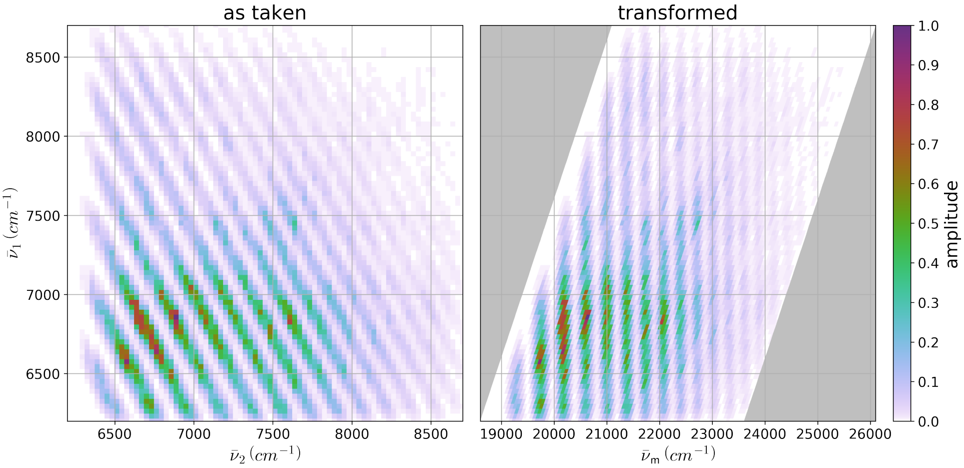
Processing

WrightTools.

TOC

Flexible data model

Flexibility to transform into any desired "projection" on component variables.



Conclusion

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).

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)

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]