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Title: Advances in Optical Methods for Standoff Detection of Explosives

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Advances in Optical Methods for Standoff Detection of Explosives

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ABSTRACT

The detection of explosives is a notoriously difficult problem, especially at stand-off distances, due to their (generally) low vapor pressure, environmental and matrix interferences, and packaging. Recent advances both at Los Alamos and elsewhere are reviewed for their capabilities to detect explosives at standoff distances, especially Raman spectroscopy. Finally, we are exploring optimal dynamic detection to exploit the best capabilities of recent advances in laser technology and recent discoveries in optimal shaping of laser pulses for control of molecular processes to significantly enhance the standoff detection of explosives. The core of the ODD-Ex technique is the introduction of optimally shaped laser pulses to simultaneously enhance sensitivity of explosives signatures while reducing the influence of noise and the signals from background interferents in the field (increase selectivity). These goals are being addressed by operating in an optimal nonlinear fashion, typically with a single shaped laser pulse inherently containing within it coherently locked control and probe sub-pulses. With sufficient bandwidth, the technique is capable of intrinsically providing orthogonal broad spectral information for data fusion, all from a single optimal pulse.

Advances in Optical Methods for Standoff Detection of Explosives

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with:
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Homeland Security

PRINCETON UNIVERSITY

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Outline

- Some General Considerations about Optical (Laser) Methods for Remote Explosives Detection
- Raman as Stand-off Detection Example
  - Raman / Stand-off Raman
- Other Demonstrated Stand-off Methods
- Stand-off CARS
- Optimal Dynamic Detection

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Some Considerations for (Standoff) Detection

A) In general, there is a $1/r^2$ Dependence for Return Signal:

(for most cases, light scattering or emission is a diffuse process

$\Rightarrow$ $1/r^2$ Signal Strength)

Red = specular
Green = diffuse scattering

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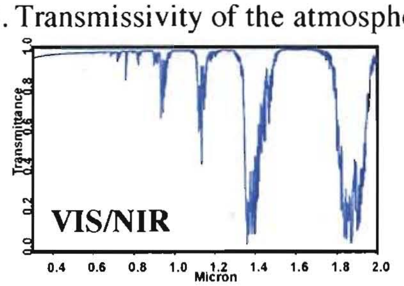
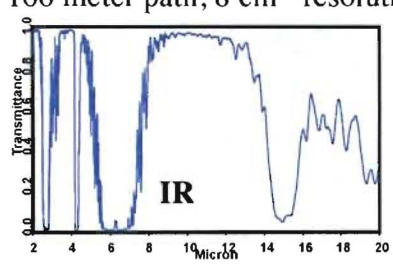
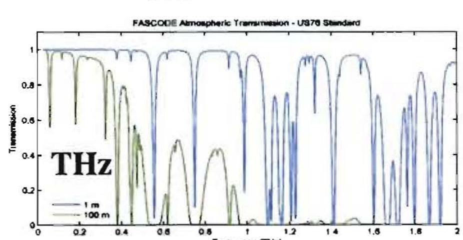
Some Considerations for (Standoff) Detection

B. Transmissivity of the atmosphere – 100 meter path, 8 cm^{-1} resolution







1 m and 100 m path THz

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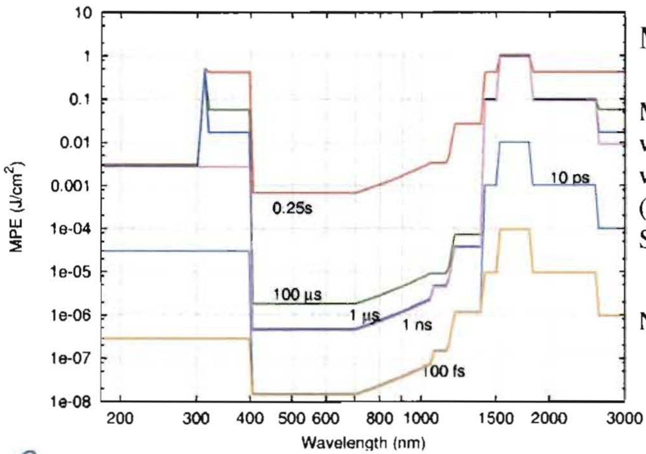
Some Considerations for (Standoff) Detection

C. Eyesafe laser operation



Maximal permissible Energy (J/cm^2)

MPE as energy density versus wavelength for various exposure times (pulse durations).

Source: Wikipedia, ANSI

Note the log axis

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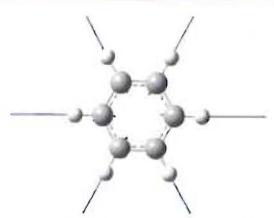
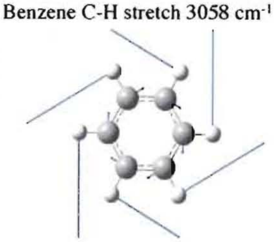
Molecular Vibrations and IR absorption / Raman scattering



Benzene C-H stretch 3058 cm^{-1}



Benzene frust. rotation 1367 cm^{-1}

- Molecules vibrate at very discrete frequencies determined by the masses of the individual atoms and the strength of the bonds between the atoms.
- Example: H_2O – three frequencies, two stretches, one bend.
- Typical frequencies range from about 400 to 4,000 cm^{-1}, in the 10^{13} to the 10^{14} Hz range, (OO 1000 cm^{-1})
- Infrared spectroscopy is DIRECT absorption by light of same frequency – exact match of light frequency to vibrational freq.
- Raman spectroscopy – frequency difference corresponds to 1 quantum of vibration. Different selection rules IR

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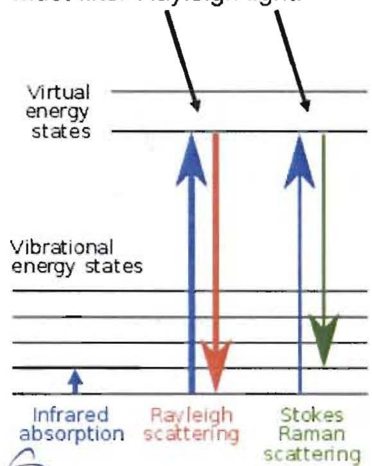
The Raman Effect

1,000,000x less Raman than Rayleigh scattering. Must filter Rayleigh light!



- Two-photon process: The Incident (laser) photon & scattered photon.
- Uses UV/Vis/NIR lasers and detectors
- Raman scattering strength goes at $1/\lambda^4$
- MOST (99.9999+%) of light is scattered at same frequency (Rayleigh effect) – no info. Raman effect is VERY weak!
- Need extreme care at signal collection and filtering
- For Raman effect, scattered photon usually of lower frequency.
- Frequency difference corresponds to one quantum of vibrational energy.
- Can be performed at distances
- Note: Zero background experiment

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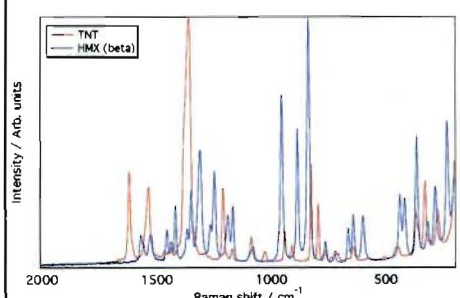
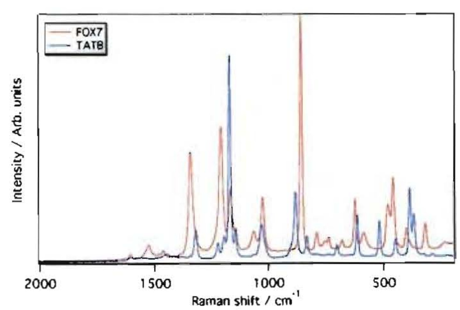
Raman - Advantages



Narrow linewidths / many features, so great specificity, i.e. few false positives



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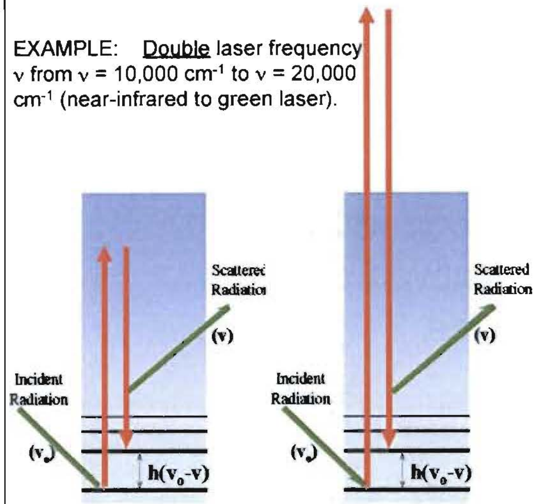
Raman Effect – Choice of Wavelength

EXAMPLE: <u>Double</u> laser frequency ν from ν = 10,000 cm^{-1} to ν = 20,000 cm^{-1} (near-infrared to green laser).



- In the one case the scattered light is at 19,000 cm^{-1}, the other at 9,000 cm^{-1} for a molecular vibration that corresponds to 1,000 cm^{-1}
- Vibrational frequency (i.e. the difference) remains the same, but the choice of laser wavelength dictates type of detector, electronics, etc.
- Usually better to use higher frequency laser since the **signal intensity grows as ν^4.** Double the frequency, get 16x as much light – a good thing!
- But other considerations, visible light – e.g. daylight interference, eyesafe, etc.

⇒ 2x Frequency Get 16 x as much signal!!! ☺

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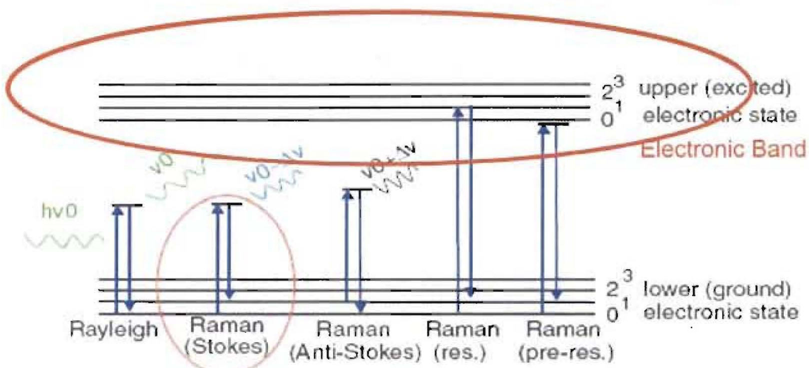
However, Light Scattering/Absorption



- However, increasing laser frequency also has ever-greater probability of laser light causing absorption then fluorescence (signal swamping) at shorter wavelengths.
- Using longer wavelength excitations cut signal as ν^4, but typically may improve upon the fluorescence background – either from the sample or impurities

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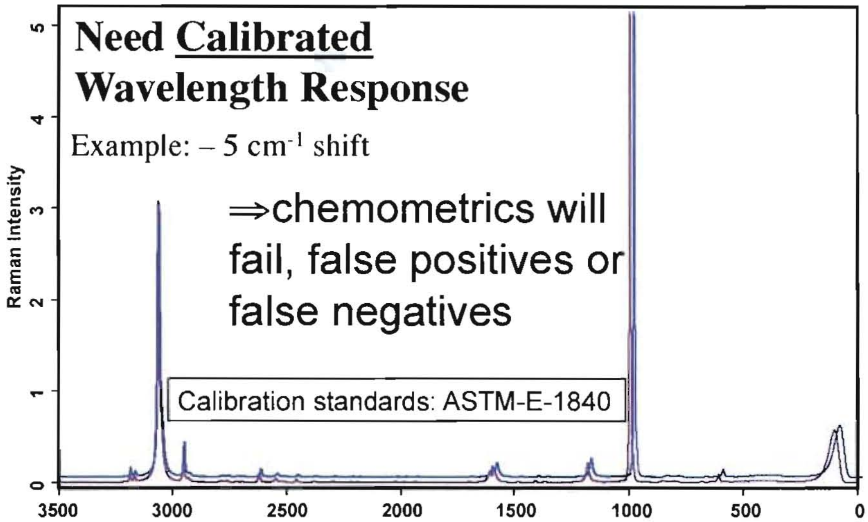
Wavelength Calibration (Libraries)

Need Calibrated Wavelength Response

Example: – 5 cm^{-1} shift

⇒chemometrics will fail, false positives or false negatives

Calibration standards: ASTM-E-1840



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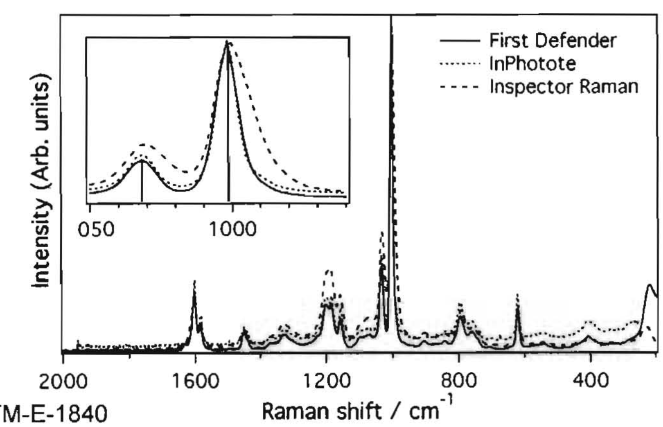
Intensity Calibration (Libraries)

Need Calibrated Intensity Response

These differences apparently occur because of inadequate (or lack of) ordinate spectral responsivity correction, and could affect library search outcomes



Solid vertical lines: ASTM-E-1840

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Raman Practical Limitations

Limitations: Weak signal, (interferent) fluorescence, signal decrease with distance, reference data compatibility

A. Fluorescence problems – both analytes and impurities – especially in the visible, near-UV. Deep UV or IR better.

B. Even though you can point the laser, the scattered Raman signal drops as $1/r^2$ with distance

C. Good reference libraries / methods are critical – need excellent wavelength calibration, good intensity calibration / portability major issue

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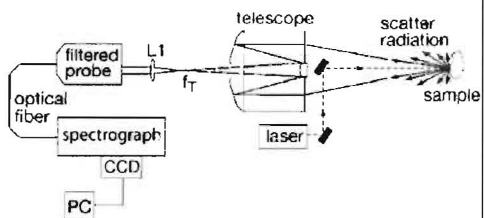
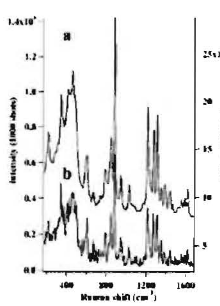
Standoff (UV) Raman

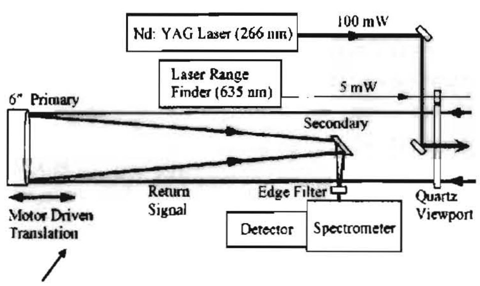
- Several groups involved
- 50 m standoff of fingerprint on bare metal surface
  - Background and matrix interference problems



RDX in silica matrix
a) 100 s integration
b) 1 s integration

Next steps:
UV excitation < 266 nm
Long pulse laser (1 μs)
ICCD detector





SOURCE: Sedlacek et al. Rev. of Sci. Instrum.. 71 (9) 3485 (2000)

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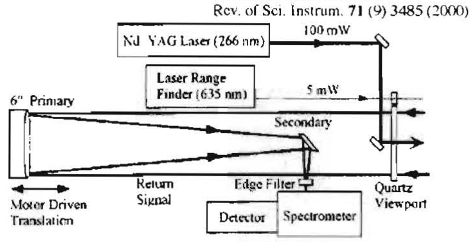
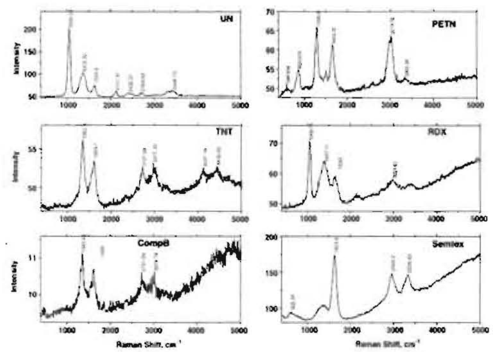
Other Standoff Raman

SOURCE: Sedlacek et al.
Rev. of Sci. Instrum. 71 (9) 3485 (2000)



- Univ. of Hawaii, Sharma, Misra et al.
  - 532 doubled Nd:YAG, compact 50 m
- Östmark, Wallin, Pettersson, Sweden
  - 532 nm at 55 meter thru snow!
- Sedlacek et al, Brookhaven Nat'l Lab
  - UV mini Raman LIDAR
  - 266 nm excitation
- Nagli and Gaft, Israel
  - Compare several UV wavelengths
    - 785, 355, 266, 248 nm
  - Signature studies



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Standoff Raman

Pros

- **No Sample preparation**
- **Solids, liquids much easier**
- **(near) Real-time analysis**
- **Very narrow linewidths, so great specificity, few false positives**
- **Light, portable, robust (now)**
- **Relatively inexpensive**
- **Standoff detection realized**

Cons

- **Raman inherently weak effect**
- **Interference from Daylight**
- **Need high power lasers and sensitive detectors**
- **Eyesafe? (dep. wavelength)**

Future directions

- **Highly specific, better instrumentation needed, filters, detectors, lasers (NIR or UV, eyesafe).**
- **Raman IMAGING – just coming of age (Chemimage)**
- **smaller, better, faster, cheaper…**

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Other Standoff Methods Demonstrated

- Laser Induced Breakdown Spectroscopy - LIBS
- Laser Induced Fluorescence – LIF
- Laser Evaporation + LIF
- Infrared Spectroscopy
  - Vapor phase
    - Active and Passive
  - Solid phase
    - Mid-IR Quantum Cascade Laser Imaging
    - Mid-IR QCL photothermal detection
    - Pulsed laser fragmentation with mid-IR QCL
    - Passive IR imaging
- THz Spectroscopy and Imaging
- Coherent anti-Stokes Raman

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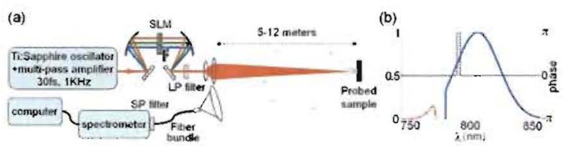
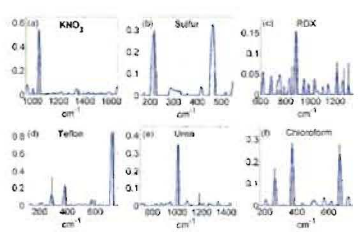
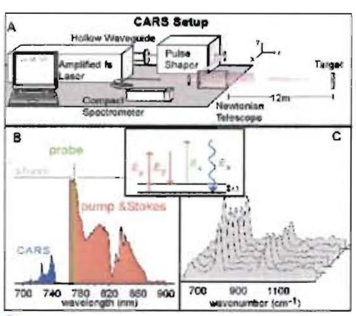
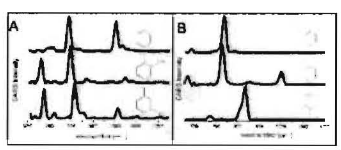
Coherent Anti-Stokes Raman Spectroscopy - CARS





O. Katz et al., Appl. Phys. Lett.. 92:171116 (2008)





H.W. Li et al., Optics Express 16:5499 (2008)

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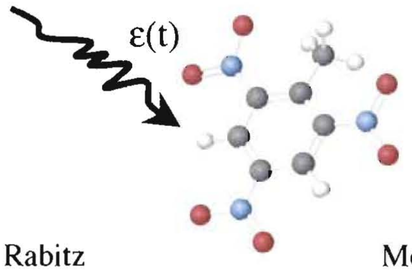
Optimal Dynamic Detection of Explosives (ODD-EX)
with Shaped Laser Pulses as Photonic Reagents



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Department of the Navy ONR Science & Technology

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Participants and Outline

- **Princeton:**
  - Herschel Rabitz; Jon Roslund; Vinny Beltrani
- **Los Alamos:**
  - David Moore; Shawn McGrane; Jason Scharff; Margo Greenfield

Outline

- Background
- ODD basics
- Stilbene photochemistry testbed
- Bandwidth broadening / vibronic control
- Multiplex CARS / mixtures
- Multiobjective optimization
- Summary

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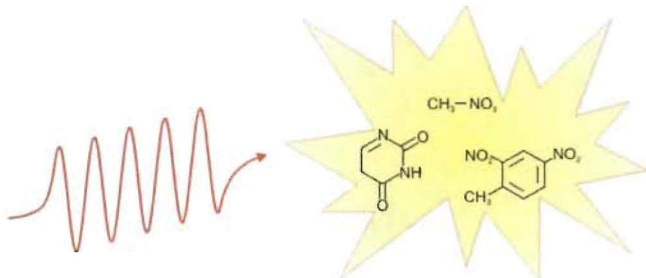
Linear spectroscopy - unshaped pulses

- Conventional steady-state or linear spectroscopy using unshaped pulses
  - Poor molecular discrimination



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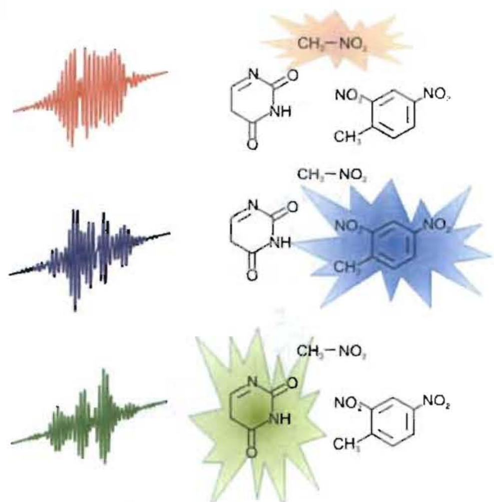
Quantum Optimal Dynamic Discrimination (ODD)

- Concept: Optimally tailored laser pulses (photonic reagents)
  - Enables selective addressing of different species



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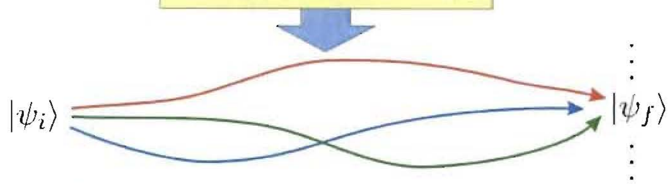
Control of Quantum Systems

- **Customization** of molecular Hamiltonian by optimally shaped field

$$H(t) = H_0 - \mu\epsilon(t)$$

- **Optimally drive** quantum system towards desired final state

Laser Control Field $\epsilon(t)$



  - Constructive interference for $|\psi_f\rangle$
  - Destructive interference for $|\psi_{f'}\rangle \neq |\psi_f\rangle$

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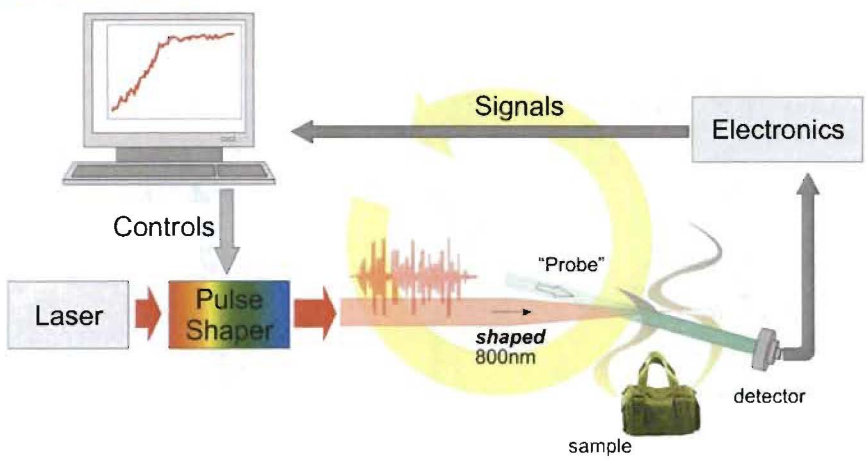
Discovery of Optimal Photonic Reagents

- **Fully automated** high duty cycle closed-loop operation



- **High finesse control** of system without a priori model of the physical sample

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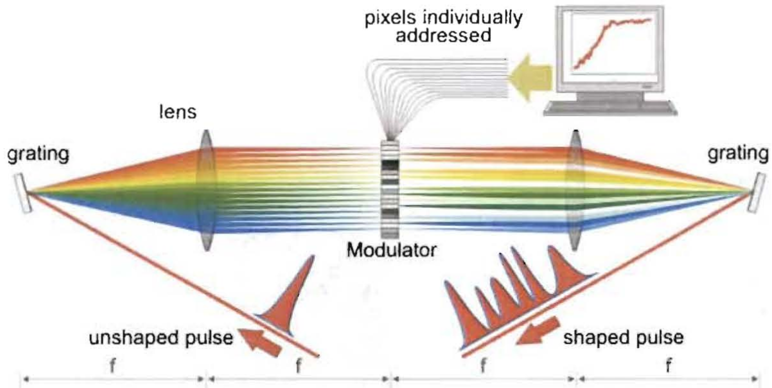
Creating Photonic Reagents on Demand



- Start with raw, featureless, ultrafast laser pulse (30-100 fs)
- Filter spectral amplitude and phase (SLM or AOM)
- Fully automated computer generation of photonic reagents

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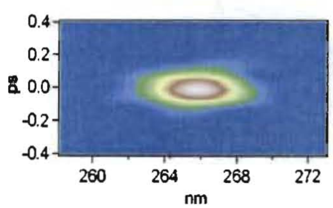
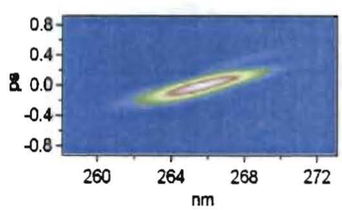
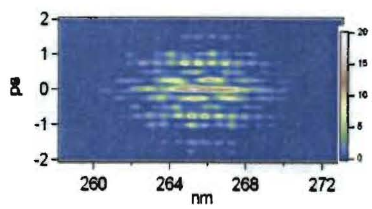
Examples of Shaped Pulses



Transform limited ~150fs



Simple linear chirp



Dual sine waves

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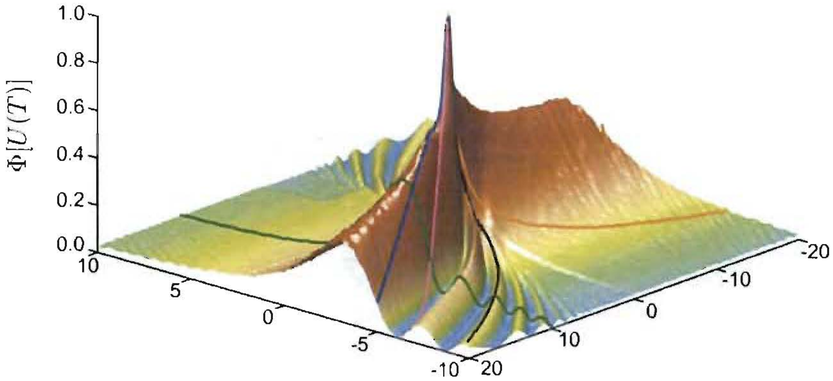
Hiking Over Coherent Control Landscapes

$$J = \Phi[U(T)] - \lambda \int_0^T f[\epsilon(t)]dt$$

$$\Phi[U(T)] = Tr[U(T)\rho(0)U^\dagger(T)\Theta]$$



- Generic lack of traps allows "easy" optimization

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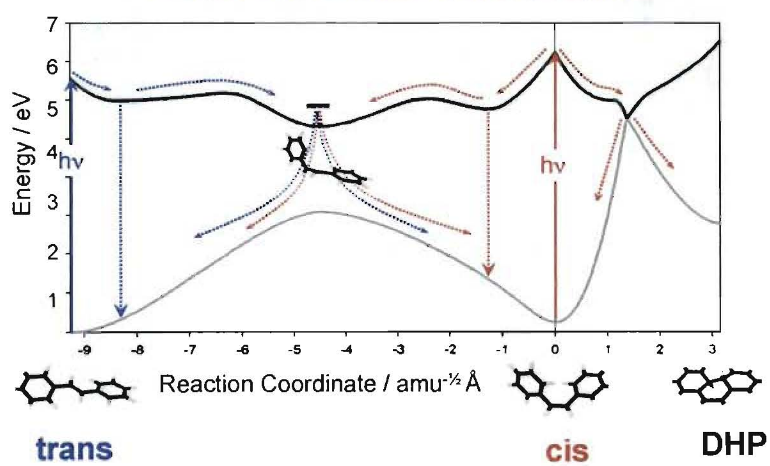
Coherent Control of Chemistry

Control cis-stilbene isomerization



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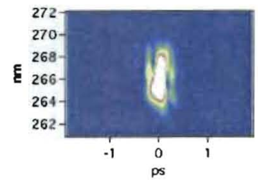
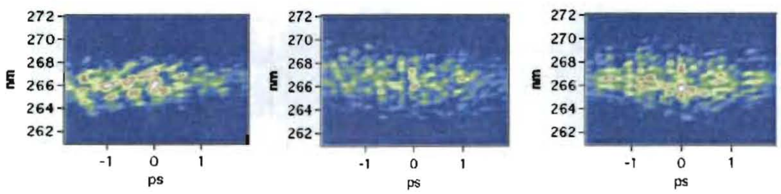
Optimize trans-stilbene product

- Compressed pulse: normal yield (1x)



- Pulse shapes achieving up to 2.08X larger trans-stilbene product



Results showed us we had inadequate control bandwidth to fully optimize!

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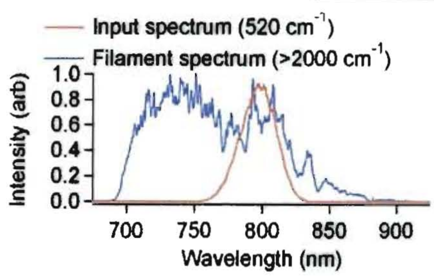
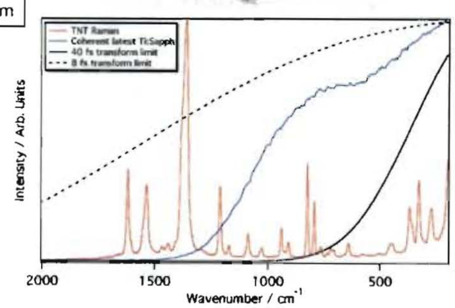
Increasing the Control Bandwidth

Filamentation



New Laser Technology



~2000 cm^{-1} bandwidth is comparable to vibrational fingerprint region

- Allows coherent Raman spectroscopies
  - and vibronic control of emission

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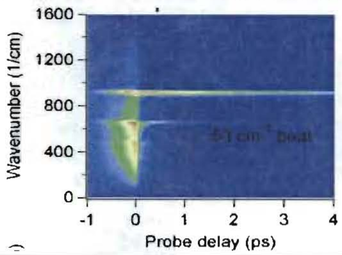
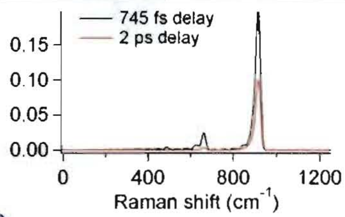
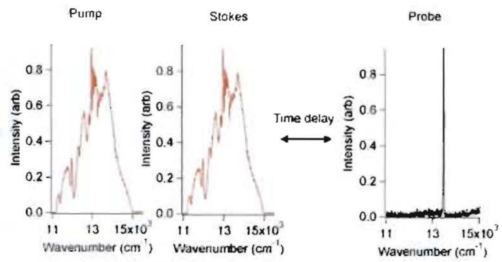
Broadband Coherent Raman

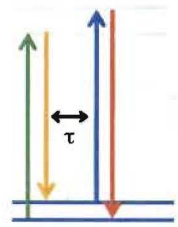
Multiplex CARS in nitromethane



Records full spectrum each laser pulse







Coherence created with first 2 pulses probed by 3rd pulse induces emission of 4th pulse

Pump + Stokes delay τ Probe+CARS

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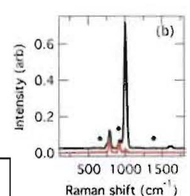
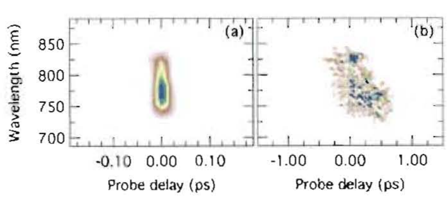
Controlled Detection of Mixture Components

Offers selectivity through pulse shaping

CARS of mixture:
- toluene
- acetone
- cis-stilbene
- nitromethane



black: compressed pulse
red: Optimized pulse for NM



Spectrograms:
left: compressed pulse
right: Optimized pulse

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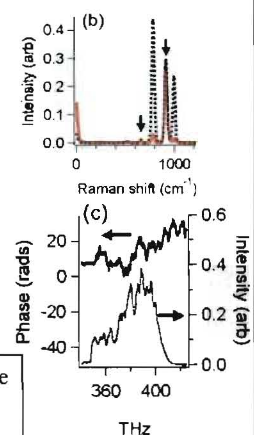
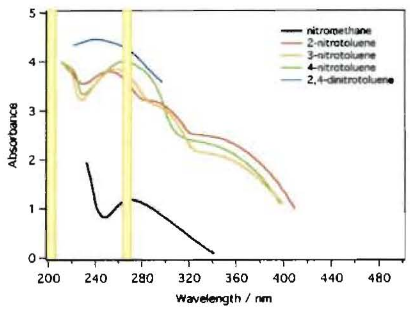
CARS of mixture:
- toluene
- acetone
- nitromethane



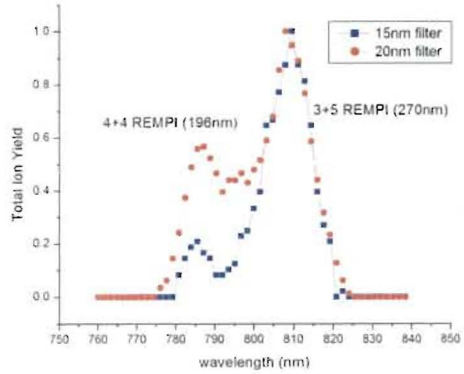
Optimized pulse retains NM peaks while suppressing solvent peaks

Use Electronic Resonances

- Nitrotoluenes have resonances near 266 nm and 200 nm
- Excellent fit to Ti:sapphire harmonics



- Measure multi-order REMPI spectrum
- Obvious 3 and 4 photon resonances



Exploit these two multiphoton resonances to generate interferences

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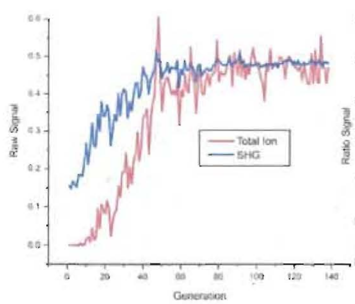
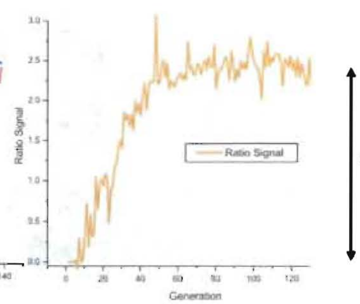
Multiobjective Optimization Needed

- Need to discriminate against intensity dependence - use fitness function:

$$f = \frac{\mathcal{J}_{Ion}}{SHG^{\alpha}}$$

- Use 60 nm bandwidth to cover both 3 and 4 photon resonances for enhanced discrimination
- Use MOTC algorithm: Derandomized Evolution Strategies (DES) with extractable covariance matrix information





= 13 σ

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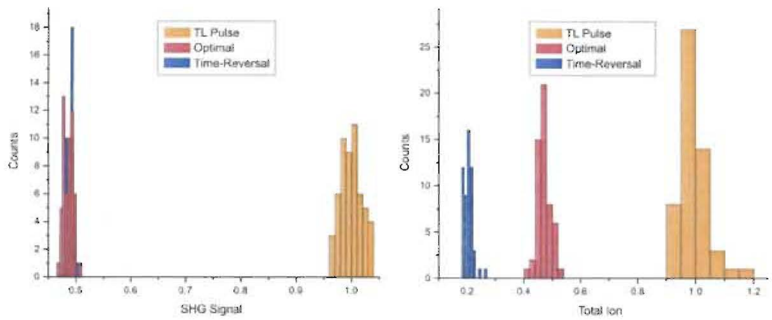
Is This Just an Intensity Effect?

- Time ordering of colors in shaped pulse doesn't matter for purely intensity dependent processes
- Test effect of reversed color ordering in optimal pulse:



Expected result for SHG, but...
Total Ion depends on color ordering!

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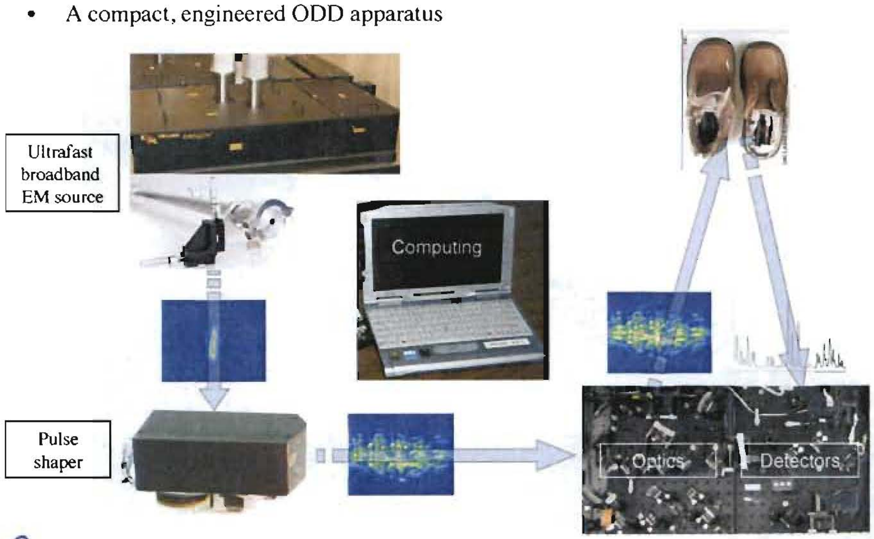
Building Blocks for ODD-Ex

- A compact, engineered ODD apparatus



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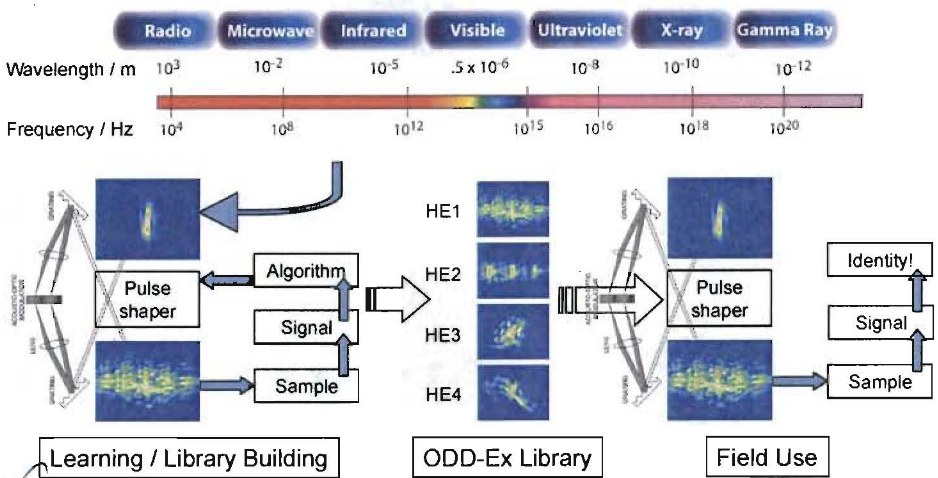
Optimal Control Space

- Not only UV/visible spectroscopic regions can be controlled, but anywhere in the entire EM spectrum where source bandwidth is available for manipulation
- Extent of application will depend only on technology



Summary

- Optimal Dynamic Detection offers a viable path to significant improvements in selectivity and sensitivity
- Photonic reagents are optimally tailored electromagnetic pulses that enable selective addressing of different species
- Single pulse photonic reagent can be designed to create a tailored wavepacket in the analyte excited state and interrogate the system by a stimulated signal
  - The optimally controlled multispectral stimulated signal is sensitive to detailed sample vibronic structure and dynamics
- Large bandwidth sources allow coherent Raman spectroscopies and vibronic control of emission
- Multiobjective optimization allows
  - Discrimination against unwanted nonlinear effects or other interferences
  - Balancing e.g., selectivity versus sensitivity

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