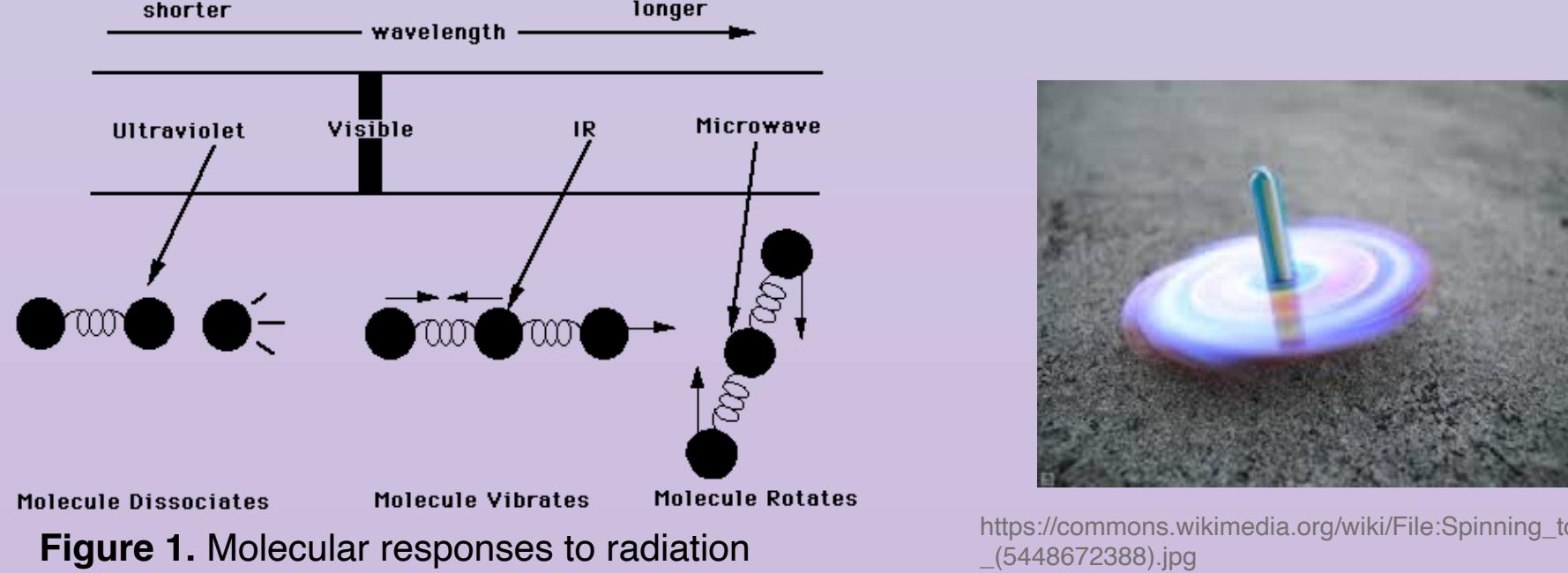


Using Rotational Coherence Spectroscopy to Measure the Ro-vibrational Energy Distribution of a Photodissociation Reaction

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Introduction

What is spectroscopy? When a molecule interacts with light, energy can be transferred from the light to the molecule. Different wavelengths of radiation excite different degrees of freedom of a molecule (Fig. 1). The study of exactly how molecules and their degrees of freedom exchange energy with light is called spectroscopy.¹ For a molecule in the gas phase, angular momentum and rotational energy are particularly important.



What is angular momentum? An object's moment of inertia, I , is dependent on the mass of the object and its distance from its axis of rotation.² In other words, as a mass gets further from its axis of rotation, the more force (or torque, in the case of rotation) is required to keep it in rotation. Angular momentum is a product of an object's moment of inertia and its angular velocity.² As a result, if an object's moment of inertia changes, its angular velocity must also change in order for total angular momentum to be conserved.

$$L = I\omega \quad I = \sum m_i r_i^2$$

Rotational Spectroscopy probes the angular momentum of molecules. Quantum theory dictates that molecules are not free to rotate at all speeds, but rather can only rotate at certain predictable speeds.² In other words, rotational energy states of a molecule in the gas phase are quantized; this follows from the quantization of angular momentum. Because angular momentum is conserved, rotational spectroscopy provides the strictest tests of our theories of molecular quantum mechanics.^{3,4}

Linear molecules (such as CO₂, CS₂, and OCS) can be treated as if their component atoms are point masses at a fixed distance from their center of mass. In a linear model, rotation about an axis is associated with quantized energy levels described by a rotational constant, B , and a single quantum number, J .⁵

$$E(J) = BJ(J + 1) \quad B = \frac{\hbar}{4\pi cI}$$

The rotational constant, B , is related to the molecule's moment of inertia about its center of mass. The quantum number, J , counts how many "quanta" of total rotational angular momentum are in the molecule.

Through analysis of spectroscopic data, moment of inertia for a molecule rotating about its center of mass can be quantitatively solved for.^{4,5} From this, the most precise determinations of molecular bond lengths, bond angles, and structure can be obtained.

Here, I will demonstrate the use of rotational coherence spectroscopy (RCS) to measure the ro-vibrational energy distribution of a photodissociation reaction.

Background

Critical measurements of spectroscopy can be made using frequency-domain or time-domain techniques. The characteristic and resonant frequencies of a system can be determined by testing each frequency separately or by exciting the sample impulsively and following the subsequent dynamics. A time domain approach for measuring rotational structure was demonstrated by Felker *et. al.*⁶ This method was later adapted by Morgen *et. al.* for pure rotational spectroscopy.⁷ In these experiments, a femtosecond laser pulse prepares a coherent superposition of rotational states; such a superposition will show periodic revivals as the molecules rotate. As rotational coherence spectroscopy (RCS) has developed into a sophisticated and powerful spectroscopy technique,⁸ it now becomes reasonable to further explore the use of RCS as a complementary technique for measuring the rotational information contained in molecular systems.

Experimental Goals

In this project, I built an RCS apparatus from the literature, with the goal of recording rotational revivals from the photodissociation reactions of carbon disulfide (CS₂) and carbonyl sulfide (OCS).

Experiment Overview

Replicate	Introduce Target Molecule	Measure and Compare	The Goal
Replicate RCS apparatus from literature (Feng <i>et. al.</i>) and systematically modify it for improved sensitivity and dynamic range, using room air as a test sample. Once CO ₂ can be detected, the instrument will be sufficient to proceed.	Introduce CS ₂ (known to photodissociate to CS+S after absorbing 2 photons at 400nm) and OCS (known to photodissociate to OC+S and OS+C) as target molecules	Measure revival structures of the products and compare them to expectations based on frequency-domain spectroscopy. Results should be approximately equivalent.	To build an RCS apparatus with the goal of recording revivals from a photodissociation reaction. This technique could potentially allow us to follow the dynamics of a molecule during a chemical reaction in real time.

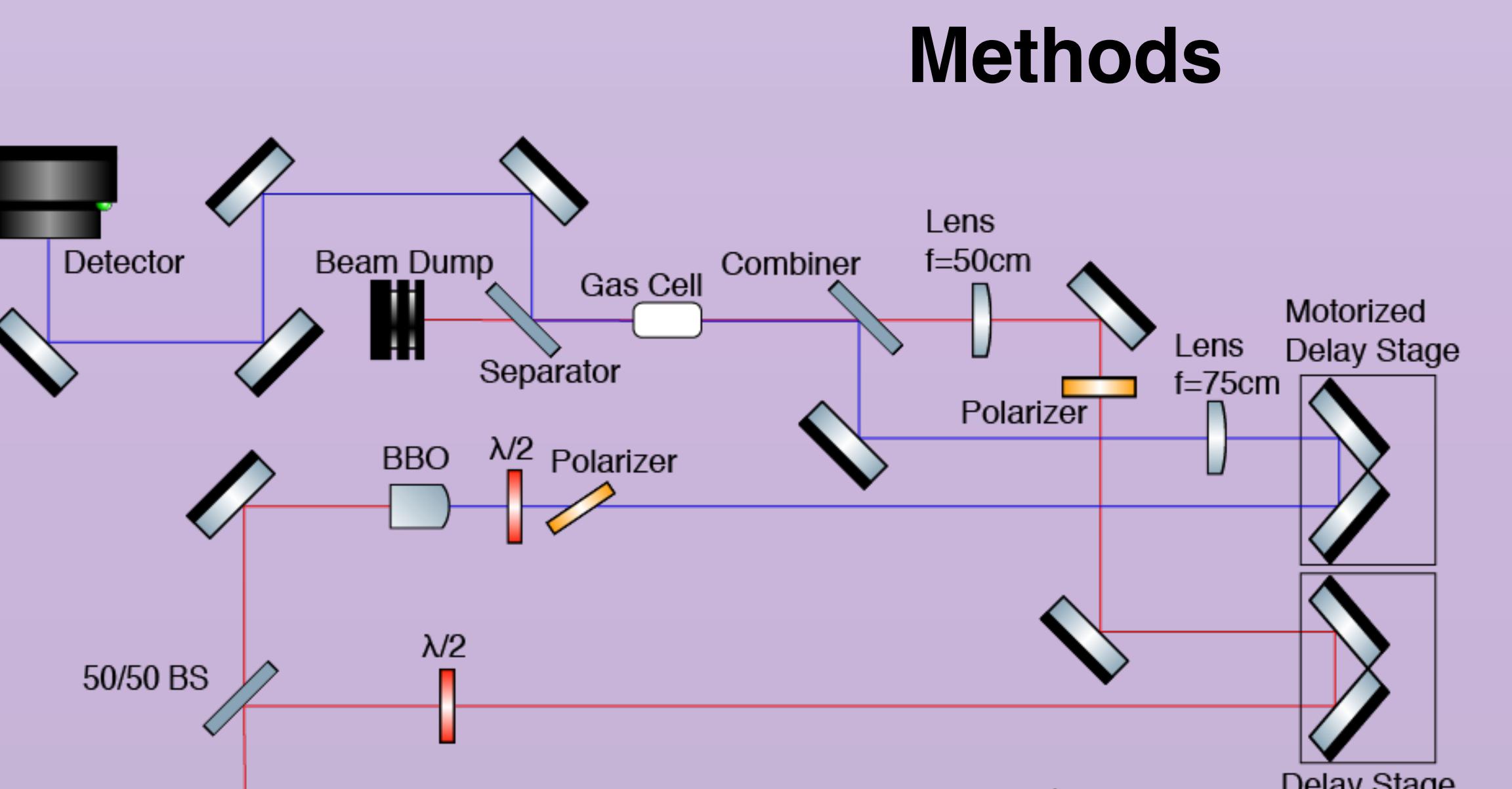


Figure 2. Diagram of Experiment Setup

- Rotational coherences detected using a method based on transient focusing and defocusing
- Since the index of refraction of a molecule is dependent on orientation, a probe pulse will experience a different index of refraction if the molecule is aligned parallel or perpendicular to its polarization direction.^{9,10}
- Strategy produces a signed response, offering slightly more information than other RCS techniques^{9,10}

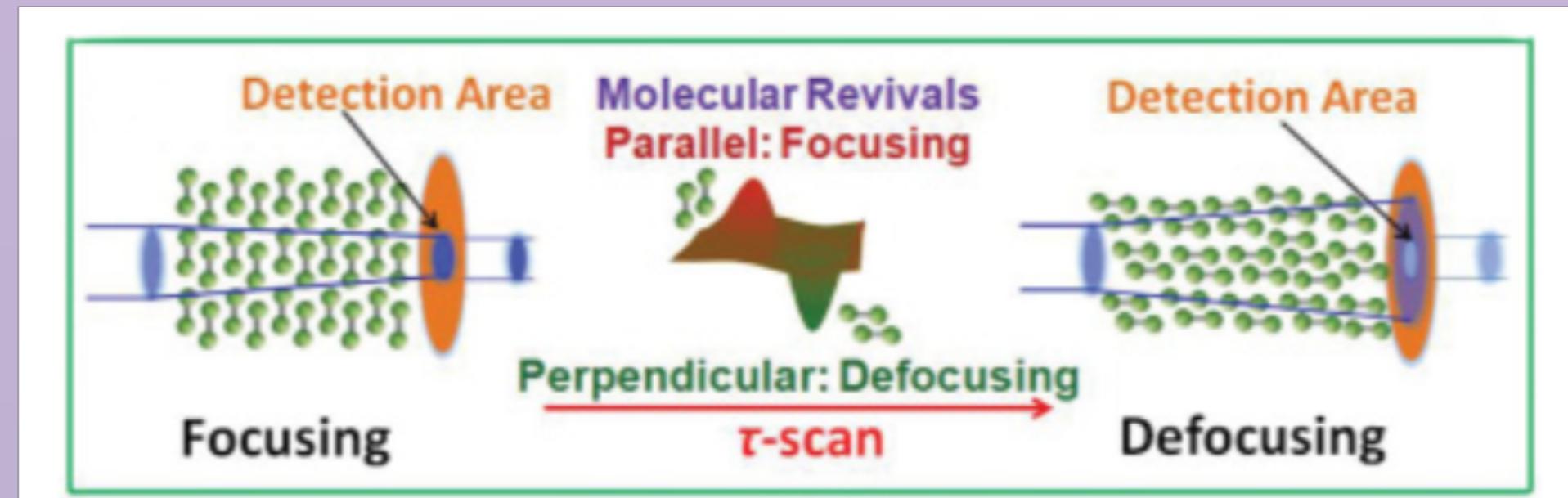


Figure 3. Detection method based on transient (de)focusing effects
Phys Rev A 85, 052515 (2012)

Current Progress

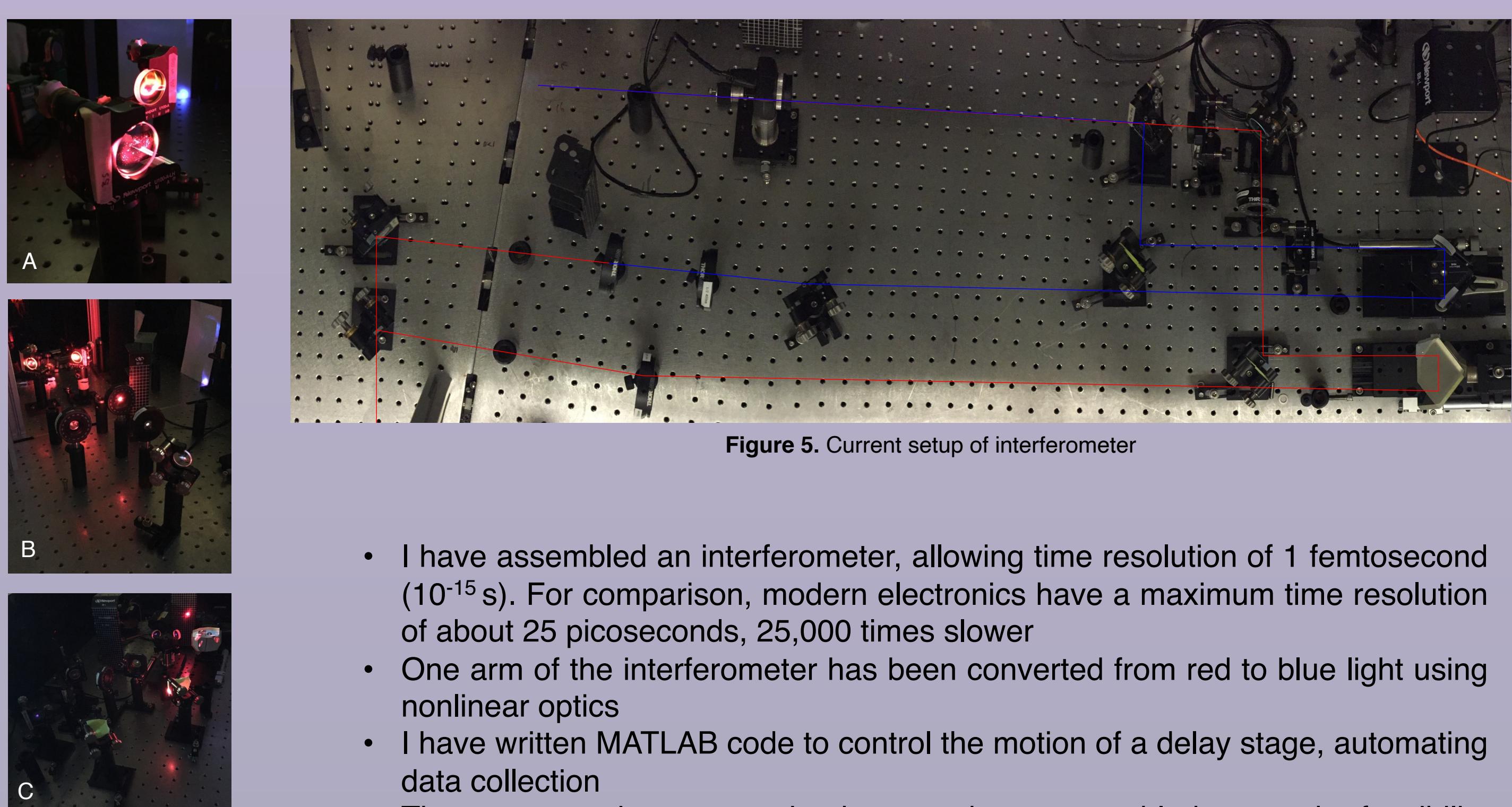


Figure 4.

- I have assembled an interferometer, allowing time resolution of 1 femtosecond (10^{-15} s). For comparison, modern electronics have a maximum time resolution of about 25 picoseconds, 25,000 times slower
- One arm of the interferometer has been converted from red to blue light using nonlinear optics
- I have written MATLAB code to control the motion of a delay stage, automating data collection
- The necessary instrumentation has now been assembled to test the feasibility of using RCS to record rotational information from a photodissociation reaction.

Expected Results

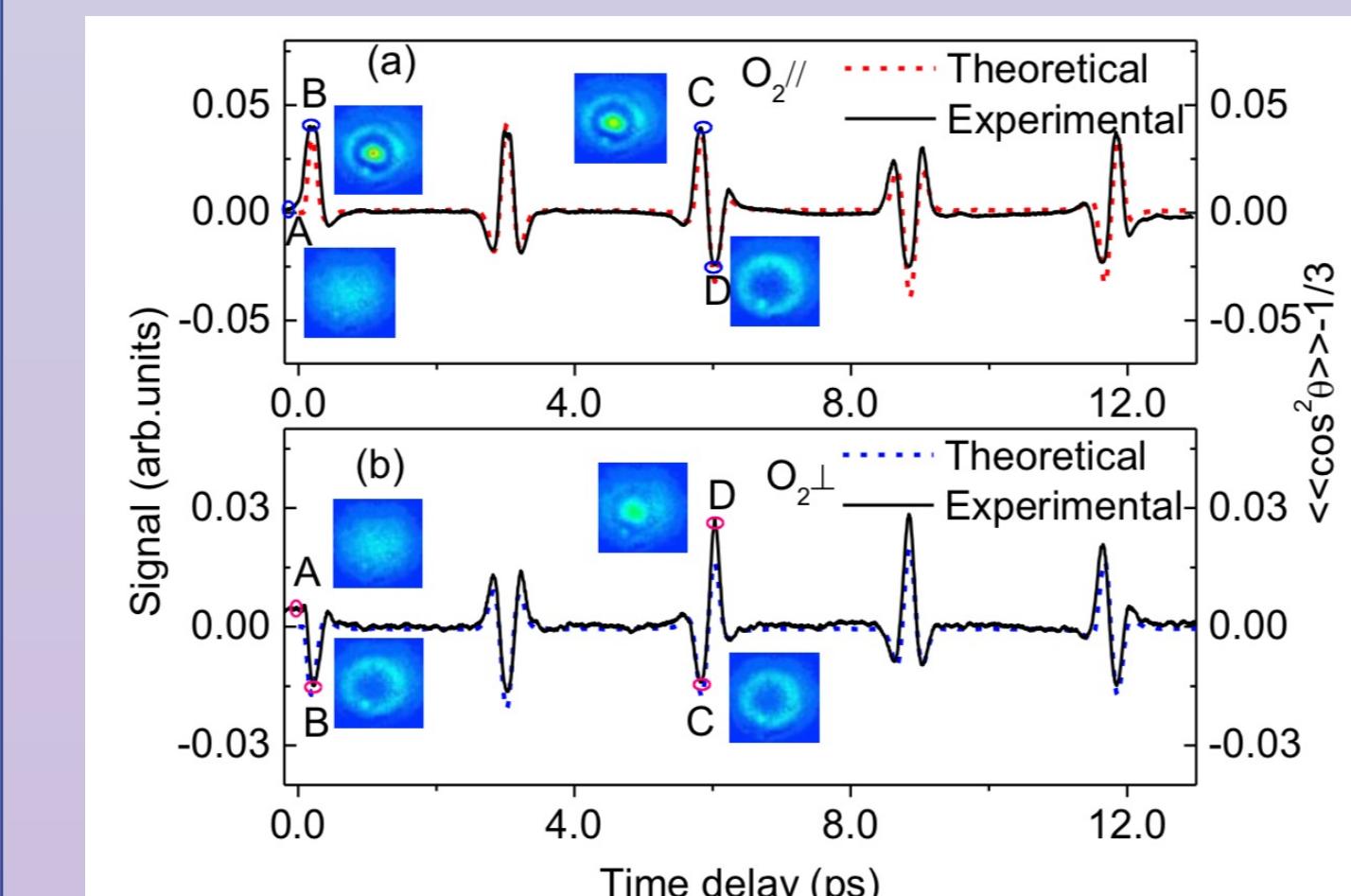


Figure 6. Measured and simulated molecular alignment signals of room temperature O₂ at 1 atm, when the polarization of the probe pulse is (a) parallel and (b) perpendicular to that of the pump pulse. The insets show the probe beam patterns captured by CCD. Optics Express 19, 2852-2857 (2011)

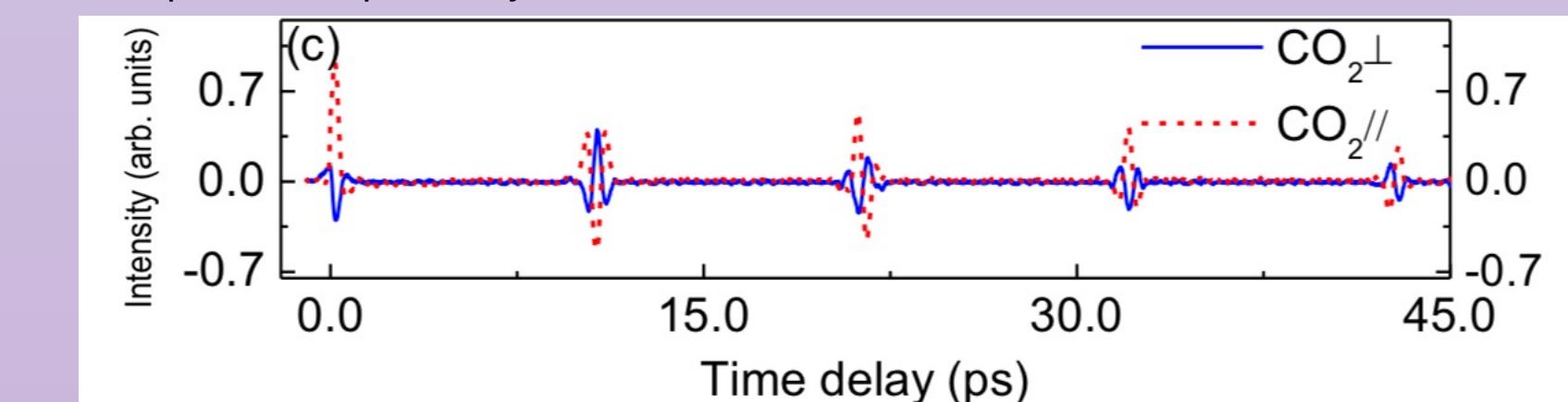


Figure 7. Measured molecular alignment signals of CO₂ when the polarization of the probe pulse is perpendicular or parallel to that of the pump pulse. Optics Express 19, 2852-2857 (2011)

Further Research

Further exploring the applications of RCS will take a promising new technique from the time-domain spectroscopy community and apply it to photodissociation reactions, which are typically studied with frequency-domain techniques.

Next steps in this project include:

- Assemble detection electronics to measure the output of the interferometer
- Optimize for improved sensitivity and dynamic range
- Detect revivals of CO₂ in room air as a test molecule
- Introduce carbon disulfide (CS₂) and carbonyl sulfide (OCS) as target molecules (known to photodissociate to CS+S^{11,12} and CO+S, CS+O, CS+O₂^{13,14} respectively)
- Measure revival structures of product molecules
- Compare to expectations based on frequency-domain spectroscopy

Importance

- The high-resolution structure obtained using rotational spectroscopy can also reveal details of the molecule's vibrational and electronic structures.¹
- Advantages of a time-domain approach:
 - Simpler. All data is collected with the same optics and detectors.
 - Resolving power between peaks is often better.¹⁵
- If the distribution of energy in a product can be measured before the energy is converted to heat by randomized molecular collisions, detailed descriptions of reaction mechanisms can be obtained, which can reveal the effect of energy partitioning on the subsequent chemistry that occurs.
 - Eliminate the need for pressure dependent rate constants in combustion reactions¹⁶
 - Allow for more accurate predictions of ozone concentrations in the atmosphere¹⁷
- Alignment and determination of molecular species in space¹⁸

References

- 1 Swenberg, S. *Atomic and Molecular Spectroscopy*, Fourth Edition, Springer, New York, 2004.
- 2 Wolfson, R., Pasachoff, J. *Physics for Scientists and Engineers*, Third Edition, Addison Wesley, Reading, 1999; pp 293-329, 1045-1070.
- 3 Zare, R. *Angular Momentum*, Wiley Interscience, UK, 1968.
- 4 Frat, D. *Electronic Spectroscopy and Fragmentation of small polyatomic molecules*; Cambridge University Press: New York, 1993.
- 5 Schinke, R. *Photodissociation dynamics: spectroscopy and fragmentation of small polyatomic molecules*; Cambridge University Press: New York, 1993.
- 6 Felker, P. M., Baskin, J. S., Zewail, A. H. *Rephasing of Collisionless Molecular Rotational Coherence in Large Molecules*. *J. Phys. Chem.* 1986, 90 (5), 724-728.
- 7 Morgen, M., Price, W., Hunziker, L.; Ludwigs, P.; Blackwell, M.; Chen, Y. *Femtosecond Raman-induced polarization spectroscopy studies of rotational coherence in O₂, N₂*. *Spectroscopics* 2010, 00, 15.
- 8 Frey, H., Kummel, D.; Löschner, S.; Leutwyler, S. *High-resolution Rotational Raman Spectroscopy with Femtosecond Pulses*. In *Handbook of High Resolution Spectroscopy*; Quack, M., Merkt, F., Eds.; Wiley: West Sussex, 2011; Vol. 2, pp 1291-1295.
- 9 Zare, R. H. *W.; Feng, Y.; Liu, J.; Pan, H.; Zeng, H. Measurement of molecular polarization anisotropy via alignment-induced spatial focusing and defocusing*. *Phys. Rev.* 2012, 85, 052515.
- 10 Feng, Y.; Pan, H.; Liu, J.; Chen, C.; Wu, J.; Zeng, H. *Direct measurement of field-free molecular alignment by spatial (de)focusing effects*. *Optics Express* 2011, 19 (4), 2852-2857.
- 11 Kong, D.; Chang, D.; Gao, Y.; Yu, H.; Zhang, L.; Shi, G.; Zhang, X.; Wang, Y.; Yang, K.; Song, Y. *Nonlinear absorption of CS₂ at the wavelength of 400 nm with femtosecond pulses*. *Journal of Nonlinear Optics Physics & Materials* 2010, 10 (2), 1279-1281.
- 12 Kawasaki, M.; Sato, H.; Kikuchi, T.; Fukuroda, A.; Kobayashi, S.; Arkawa, T. *Angular distributions of photofragments generated in the two-photon dissociation of nitrogen dioxide and carbon disulfide*. *J. Chem. Phys.* 1987, 86, 4425-4430.
- 13 Lee, L. S.; Price, W.; D. C. S. (X'11-X'22) fluorescence from photodissociation of CS₂ and OCS. *J. Chem. Phys.* 1975, 63 (7), 2782.
- 14 Miller, R. L.; Suits, A.; Houston, P.; Toumi, R.; Mack, J.; Wedde, A. *The "Ozone Deficit" Problem: O₃(v=26) + O(P) from 229-nm Ozone Photodissociation*. *Science*, 1994, 265, 1831-1834.
- 15 Shippert, S. *New Techniques in Microwave Spectroscopy*. In *Handbook of High Resolution Spectroscopy*; Quack, M., Merkt, F., Eds.; Wiley: West Sussex, 2011; Vol. 2, pp 801-829.
- 16 Lee, L. S.; Price, W.; D. C. S. (X'11-X'22) fluorescence from photodissociation of CS₂ and OCS. *J. Chem. Phys.* 1975, 63 (7), 2782.
- 17 Miller, R. L.; Suits, A.; Houston, P.; Toumi, R.; Mack, J.; Wedde, A. *The "Ozone Deficit" Problem: O₃(v=26) + O(P) from 229-nm Ozone Photodissociation*. *Science*, 1994, 265, 1831-1834.
- 18 Kickemann, A. *Rotational Coherence Spectroscopy at FLASH: Toward Dynamic Studies in Nanosuperfluids*. Ph.D. Dissertation, University of Hamburg, 2013.