SAND2022-11226C

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The Development of an Optical Centrifuge for Chemical Dynamics Studies as Probed through Time-Resolved Coherent Raman Scattering

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SPIE Optics and Photonics

August 21, 2022

Sandia National Laboratories

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Optical centrifuge first demonstrated through rotational dissociation of Cl_2

VOLUME 85, NUMBER 3 PHYSICAL REVIEW LETTERS 17 JULY 2000

Forced Molecular Rotation in an Optical Centrifuge

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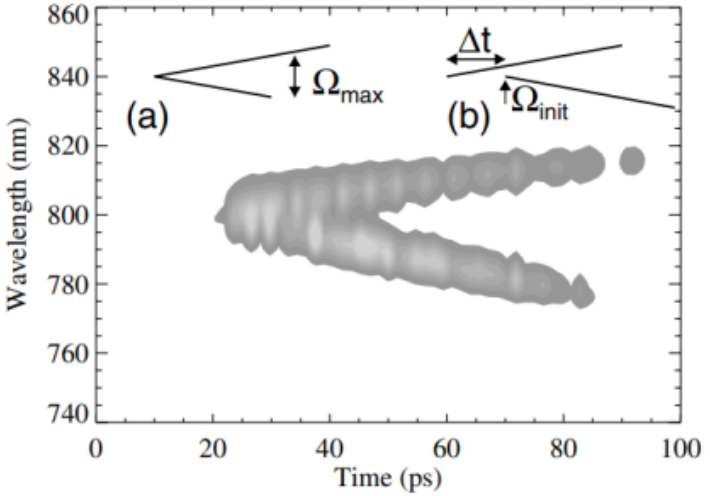
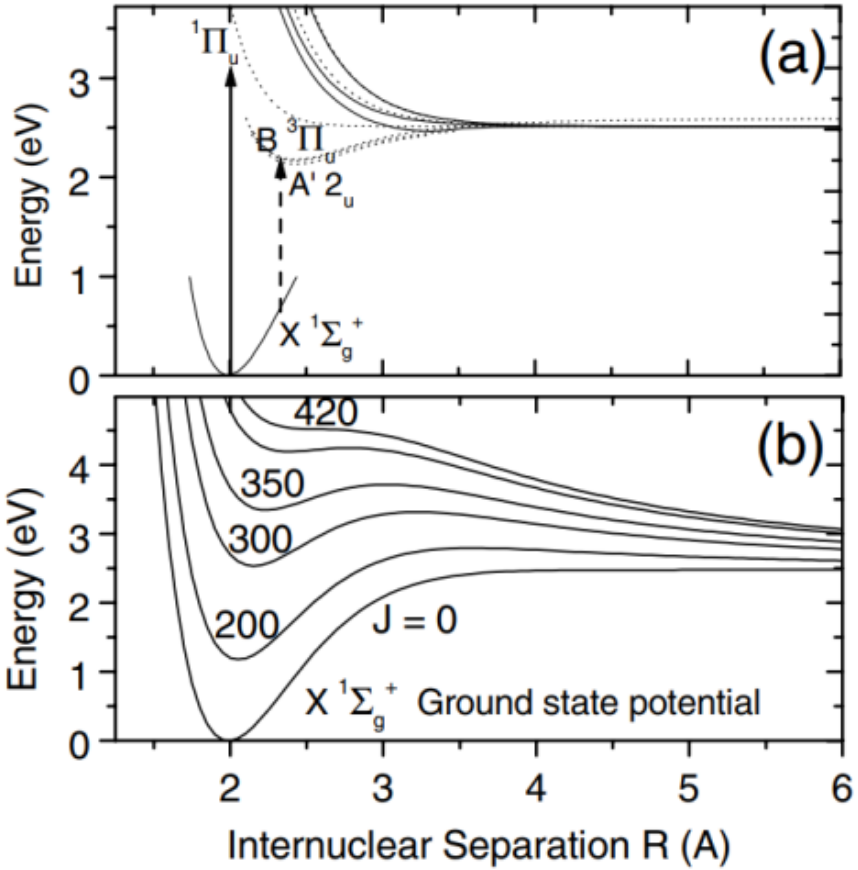
(Received 17 February 2000)

- First experimental demonstration by Corkum and coworkers in 2000.
- Rotational dissocation of Cl_2 observed through TOF-MS





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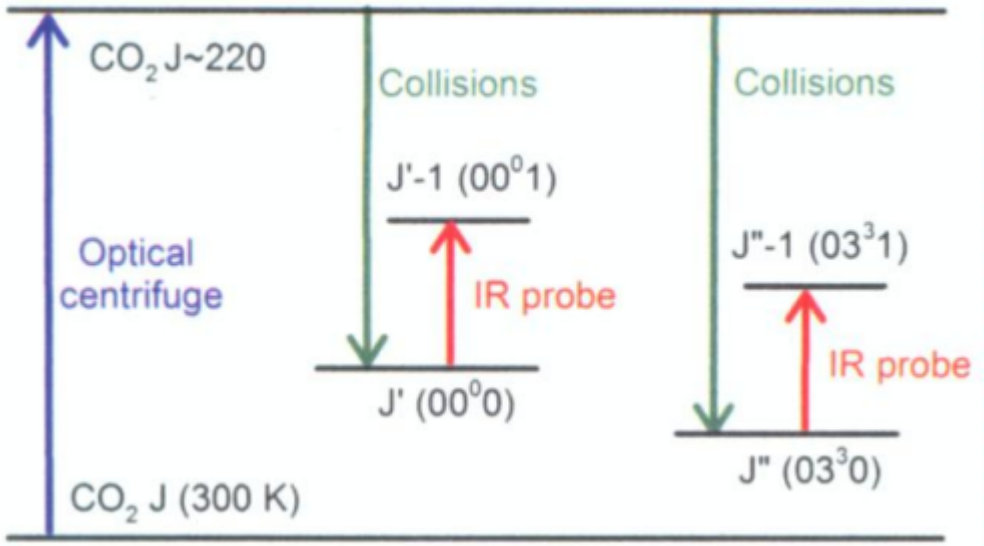
Subsequent measurements demonstrated “super-rotor” reduction in collisional energy transfer rate



- Mullin and coworkers have made measurements using transient IR absorption for centrifuged CO2, CO, and N2O.
- Provides for the first time the ability to both centrifuge and study the energy transfer dynamics of molecules in high angular momentum states.

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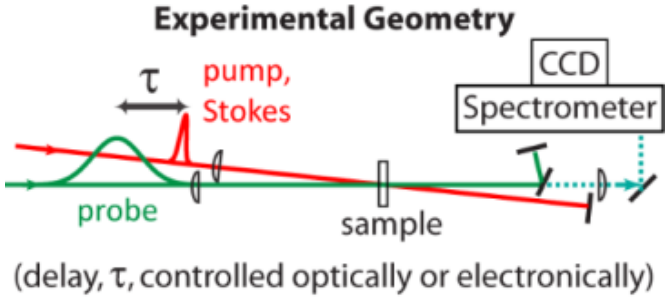
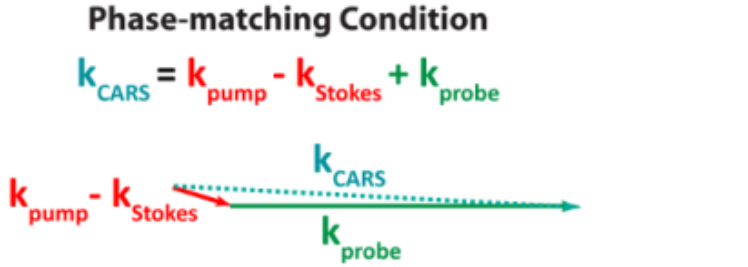
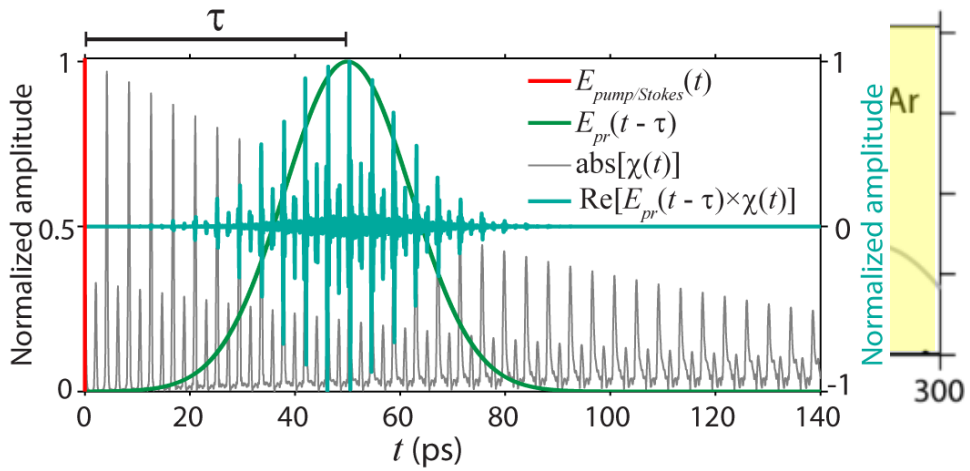
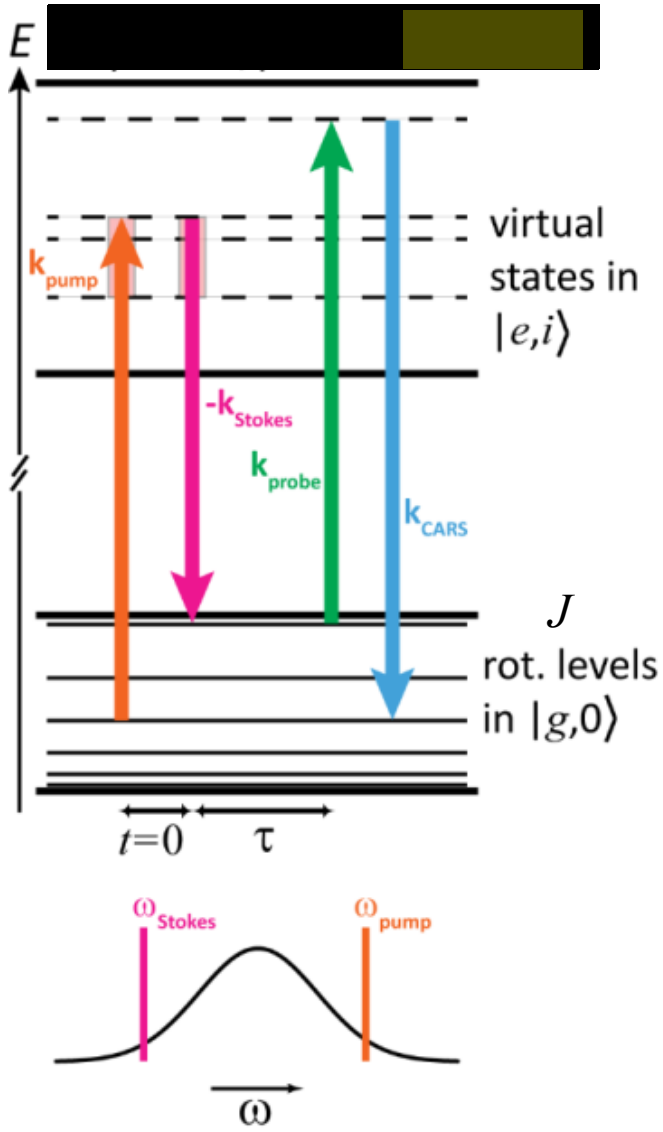
Two-Beam Hybrid Femtosecond/Picosecond RCARS









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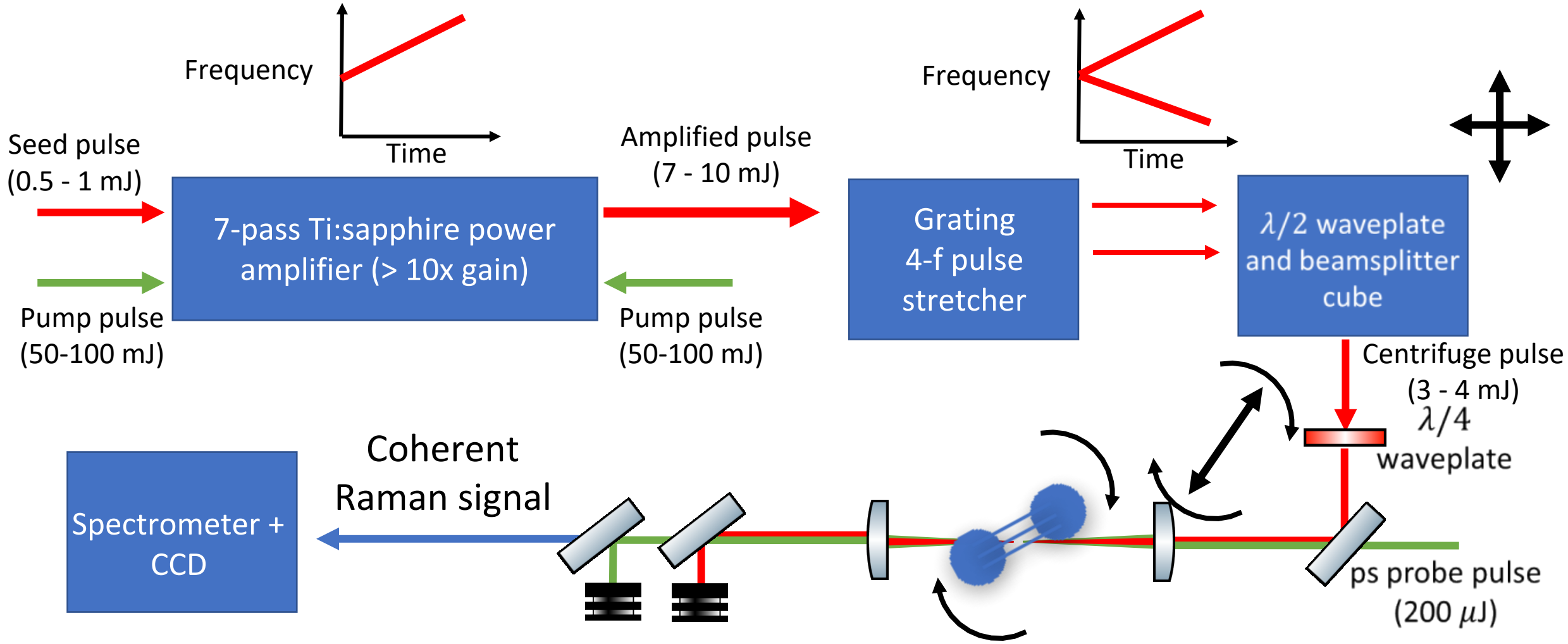
Home-built Optical Centrifuge and Coherent Raman Probe



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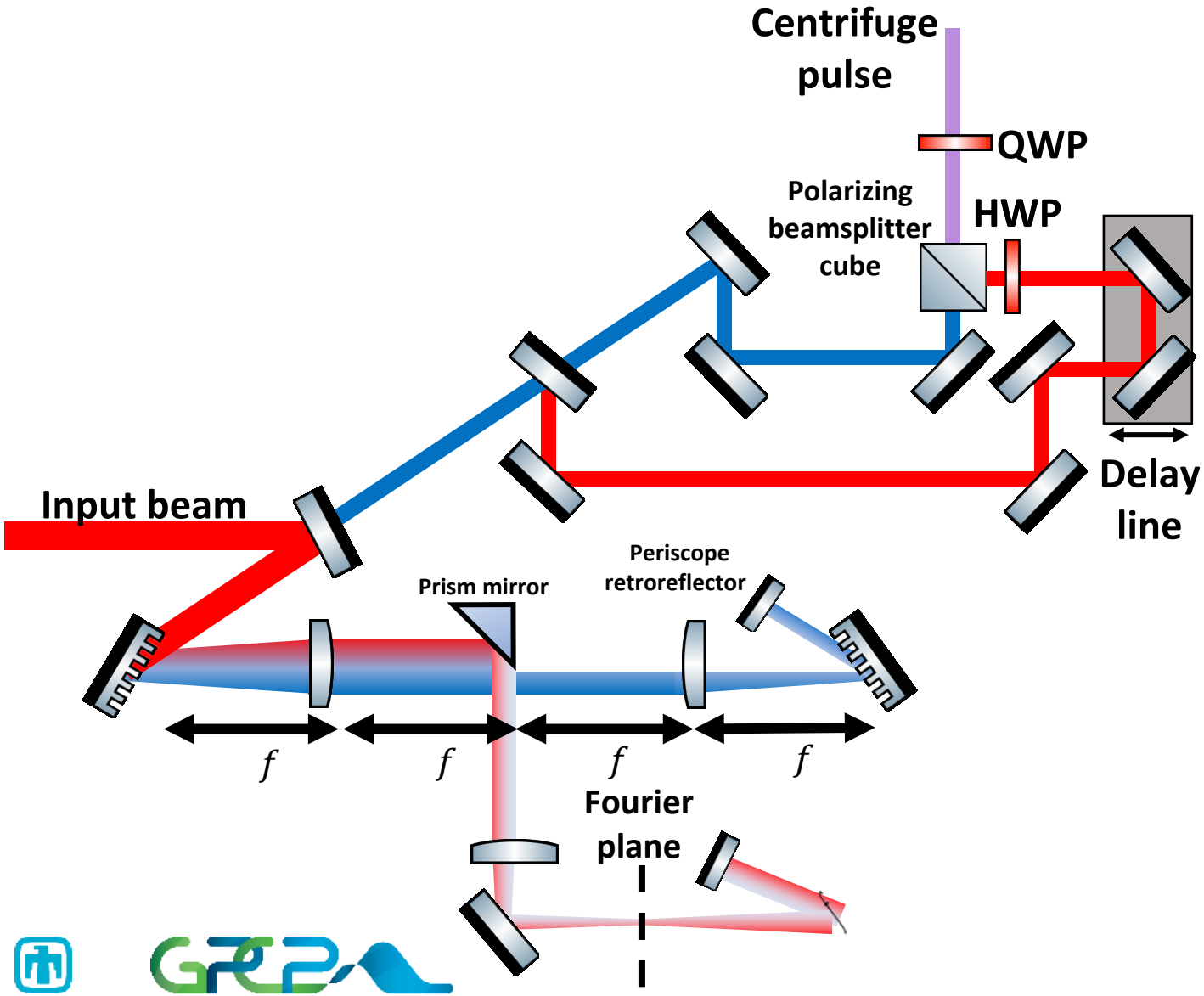

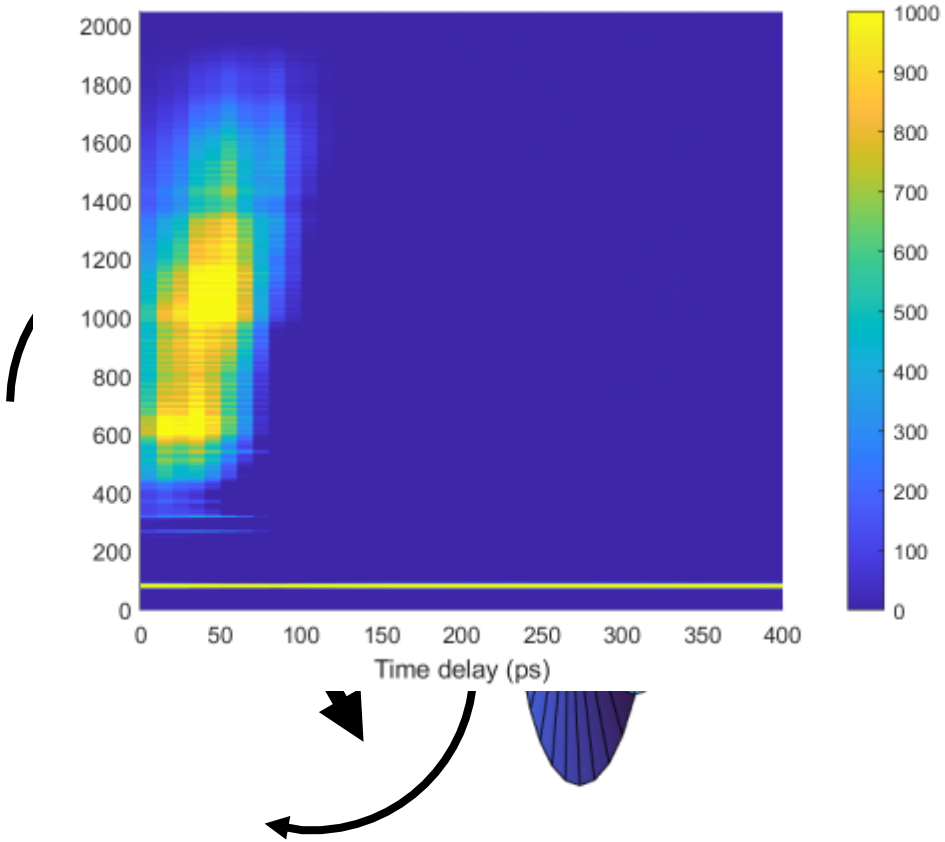

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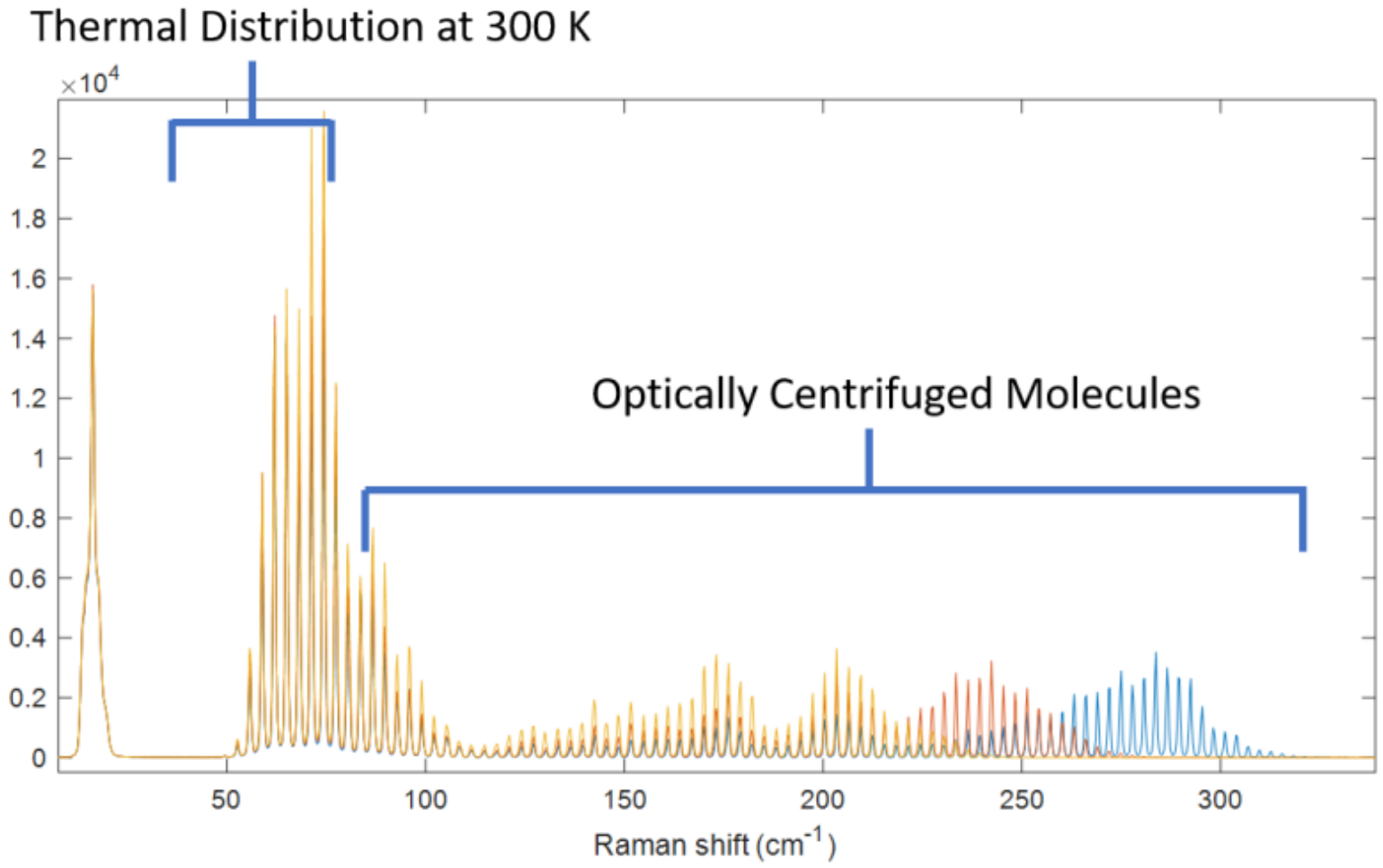
Demonstrated Centrifuge of CO_2 to J=250, E_{rot} = 24000 cm^{-1}



- Chopping one of the centrifuge arms in the stretcher allows control over the final J-state distribution
- Can be limited to thermal distribution for comparison

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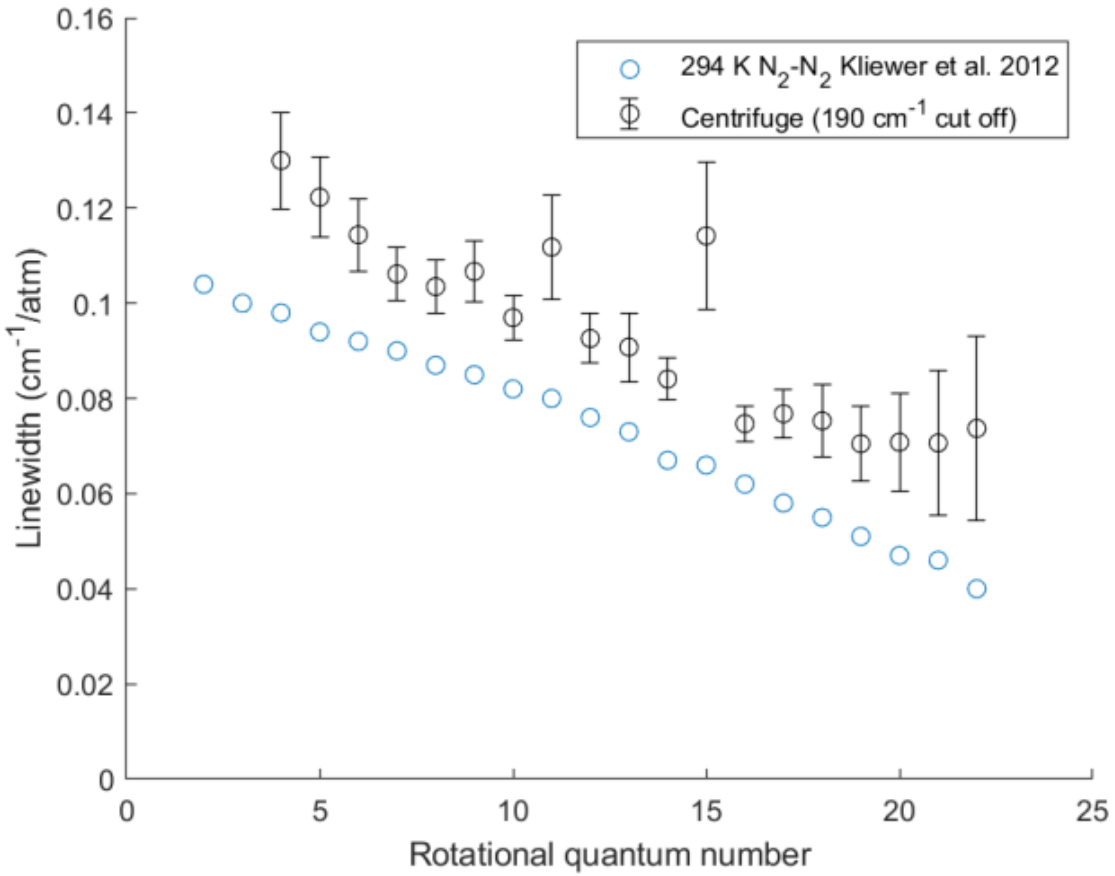
Linewidths in the centrifuge for N2 are significantly larger than at 294 K



- High-finesse coherence decays have been recorded in our lab for extreme accuracy in molecular thermometry
- Oriented angular momentum appears to modify collisional energy exchange rate

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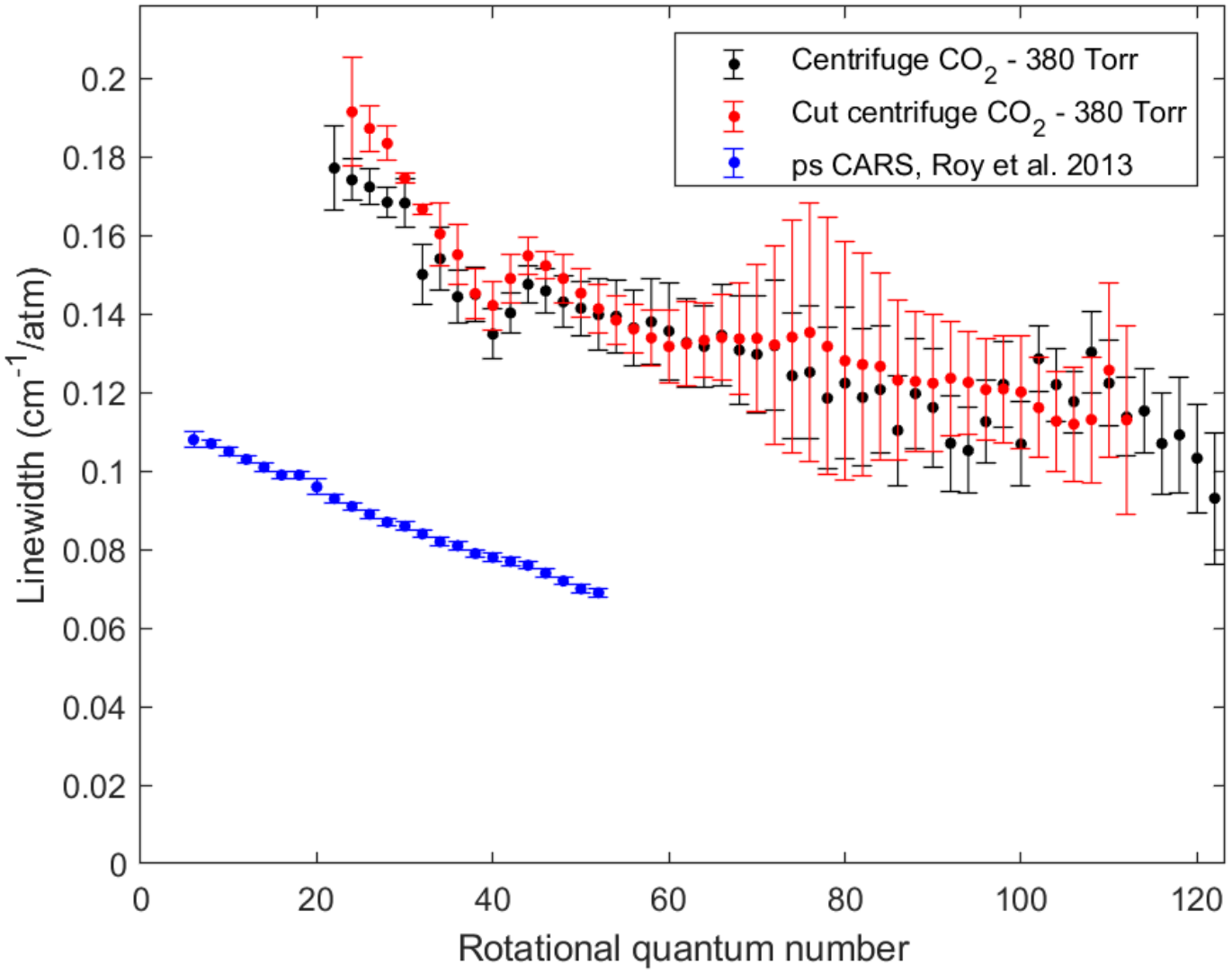
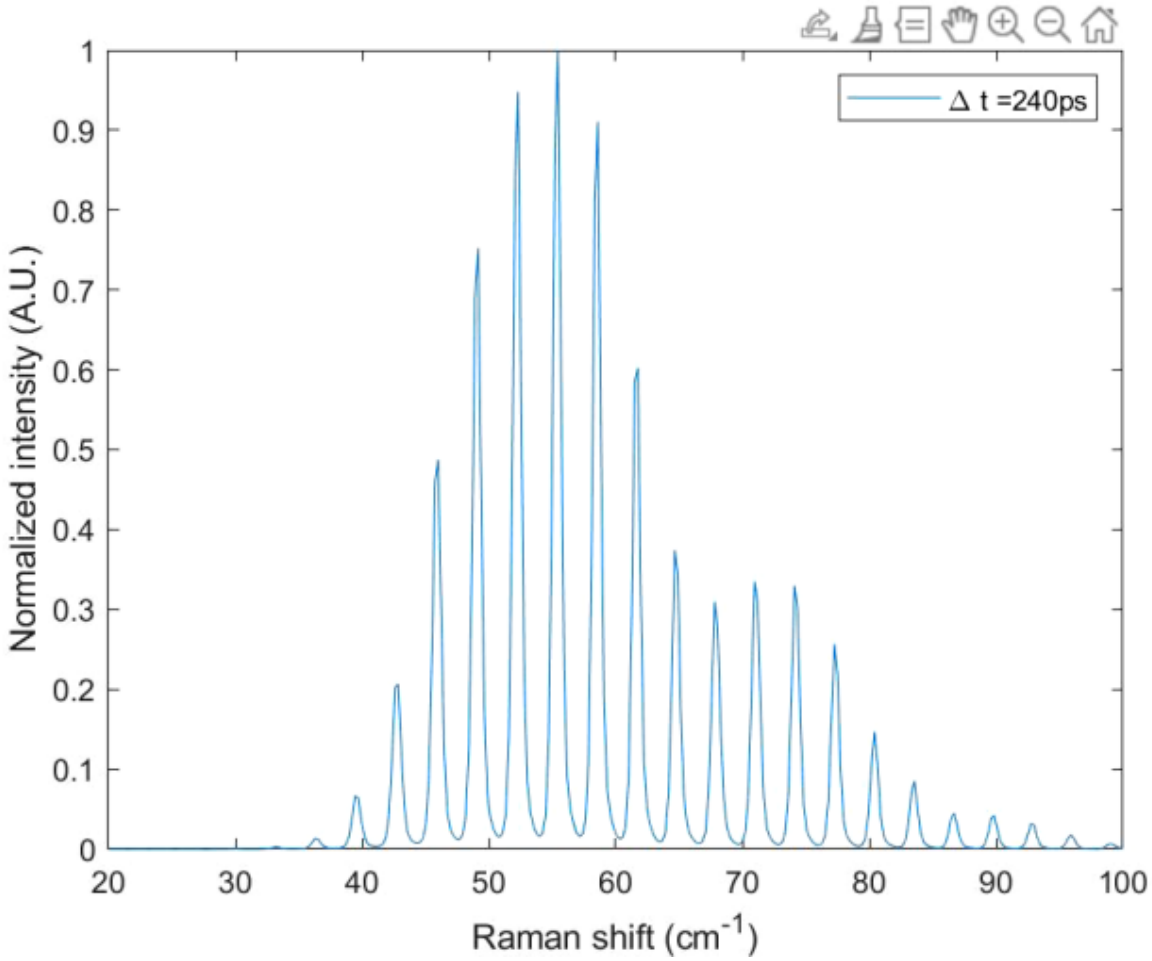
Comparison of collisional dephasing rates for CO_2 reveals significant difference for centrifuged molecules



- Dramatic enhancement of collisional dephasing rate observed for centrifuged CO2 molecules.
- Comparison to earlier time-domain measured decoherence rates using fs/ps CARS reveals more than a factor of 2X faster dephasing.
- Comparison to thermally limited ensemble still results in enhanced decay rates.

Time evolution of thermally limited centrifuge pulse reveals growth of vibrational excitation

- Fits well to the rotational shift expected from v=1 CO_2 bending mode.
- Interesting because molecules are limited to thermal distribution
- Special collisional energy exchange due to oriented angular momentum?
- Resolution of vibrational excitation limited by standard grating-spectrometer solution



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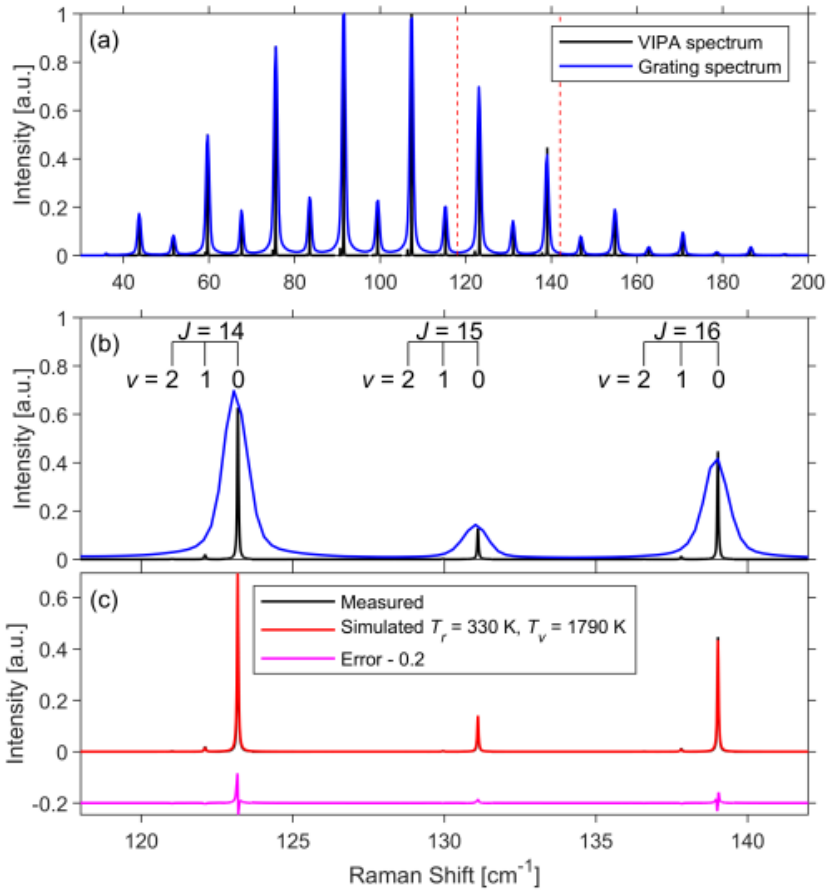
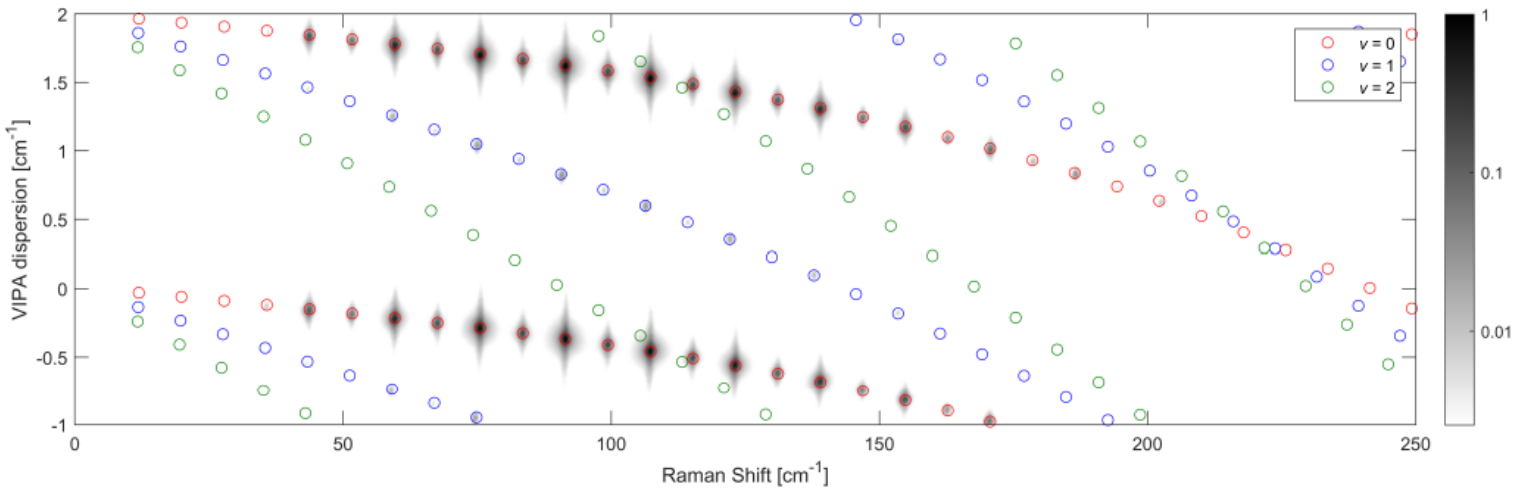
VIPA-based CARS spectrometer allows for spectral resolution down to ~100 MHz





- The vibrational population of N2 during plasma discharge is assessed from the shift in the pure-rotational spectrum

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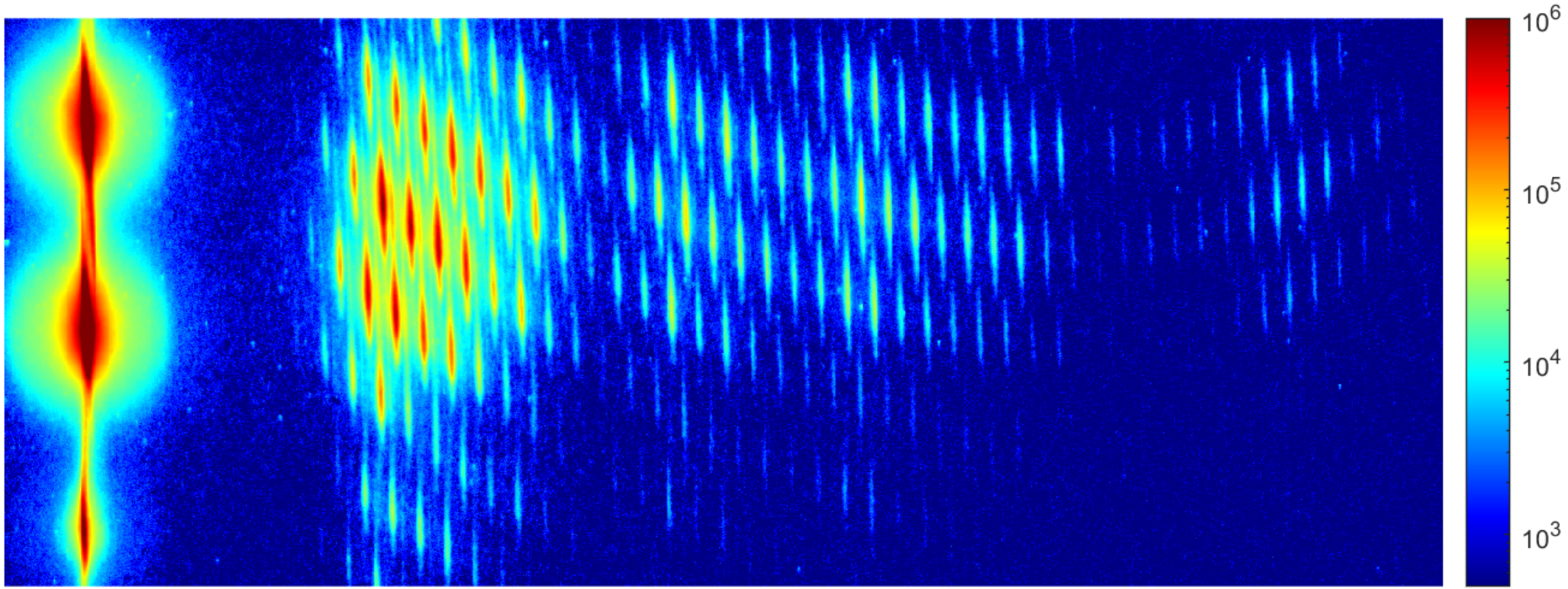
VIPA-based CARS spectrometer isolates signal from ground and excited vibrational states



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Future Directions

- Chemical dynamics studies coupled to velocity mapped imaging apparatus

- Energy exchange with surfaces where rotational energy is sufficient to drive surface reactions.
- Pulse shaping approaches to selectively spin up single rotational axes within polyatomic molecules.

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Conclusions

- We have built and demonstrated a molecular optical centrifuge (3rd group in world to do so), coupled to a coherent Raman probe to assess the time-domain evolution of the excited rotational coherence.
- Surprising changes to coherence lifetimes observed for molecules for which the sense of rotation is controlled. Indicates modification to efficacy of collisional energy exchange.
- VIPA-based coherent Raman spectrometer allows high-spectral resolution analysis of pure-rotational scattering, and the separation of excited vibrational populations.

Thank you for your time!

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Acknowledgements

Sandia Team:
Timothy Chen (Lead postdoc)
Brian Patterson
Scott Steinmetz
Dave Chandler

External Collaborators/Discussions:
Ahren Jasper (Argonne)

Funding: BES GPCP

Happy to take your questions.

This material is based upon work supported by the Division of Chemical Sciences, Geosciences and Biosciences, Office of Basic Energy Sciences (BES), U.S. Department of Energy (USDOE). Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the USDOE's National Nuclear Security Administration under contract DE-NA0003525. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the USDOE or the United States Government.


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