From continuous waves to femtosecond pulses: time-resolved *in situ* laser diagnostics of non-equilibrium plasma methane reforming

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Online Low Temperature Plasma Seminar

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Talk outline

1. Overview of laser sources and laser spectroscopies for plasmas

2. Time-resolved laser measurements of plasma CH_4 reforming and model validation

3. *In situ* laser probing of electric field and electron property coupling in CH_4/Ar ns-DBD discharges

4. Conclusions

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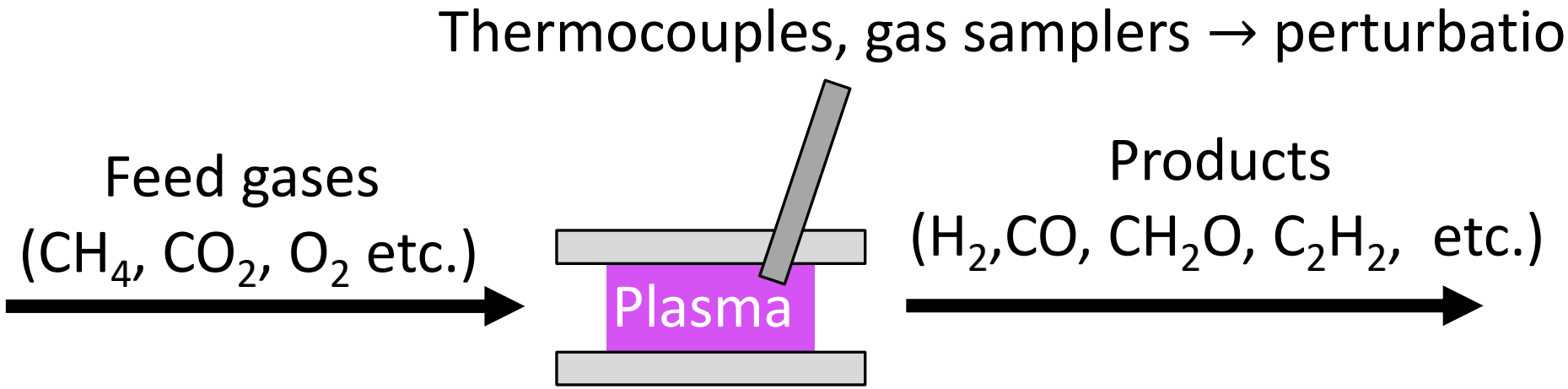
Challenges of studying non-equilibrium plasma- Need *in situ* diagnostics

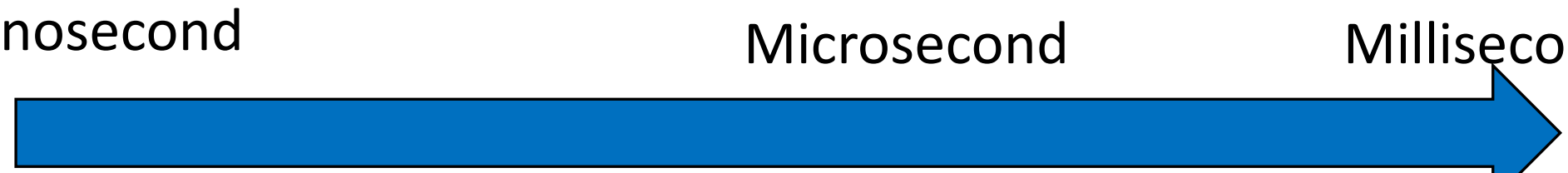


Chemical kinetics?

Plasma physics?

Properties of interest: species concentrations, electric field, electron density, electron temperature, gas rotational and vibrational temperature

Challenges of studying non-equilibrium plasma- Multi-time scale reacting flow



O(1-100 ns)

- Electron energy transfer
- Plasma self-shielding

O(100 ns -100 μs)

- Excited state relaxation
- Electron-ion recombination
- Gas phase reactions

O(>100 μs)

- Convection and diffusion
- Gas phase reactions

Need high temporal resolution→ laser diagnostics

Commercially available lasers can be broadly categorized by pulse-width (or lack thereof)

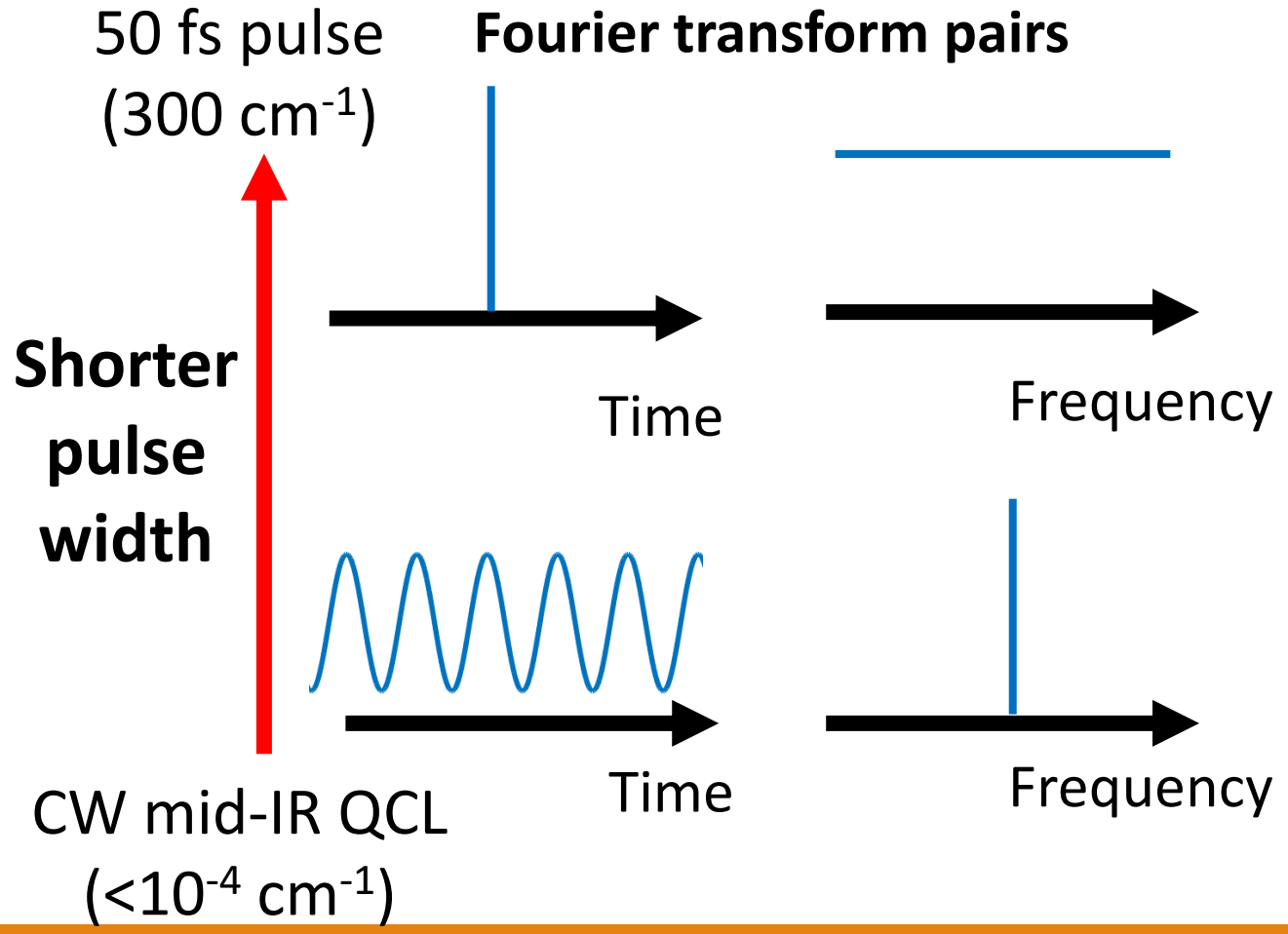
	Continuous wave (CW)	Nanosecond (10^{-9} s)	Picosecond (10^{-12} s)	Femtosecond (10^{-15} s)
	 Photo credit: Thorlabs Inc.	 Photo credit: Amplitude Laser	 Photo credit: EKSPLA Co.	 Photo credit: Coherent Inc.
Peak power (photons/time):	~mW to 10 W	~100-200 MW	~1 GW	~0.1-1 TW*
Repetition rate and pulse-width:	Mid-IR CW lasers can scan at 1 MHz	10 Hz to 10 kHz 6 to 10 ns FWHM	10 Hz to 1 kHZ 20 to 80 ps FWHM	1-5 kHz (amplified) 35 to 100 fs FWHM

Linear spectroscopies (single photon interactions)

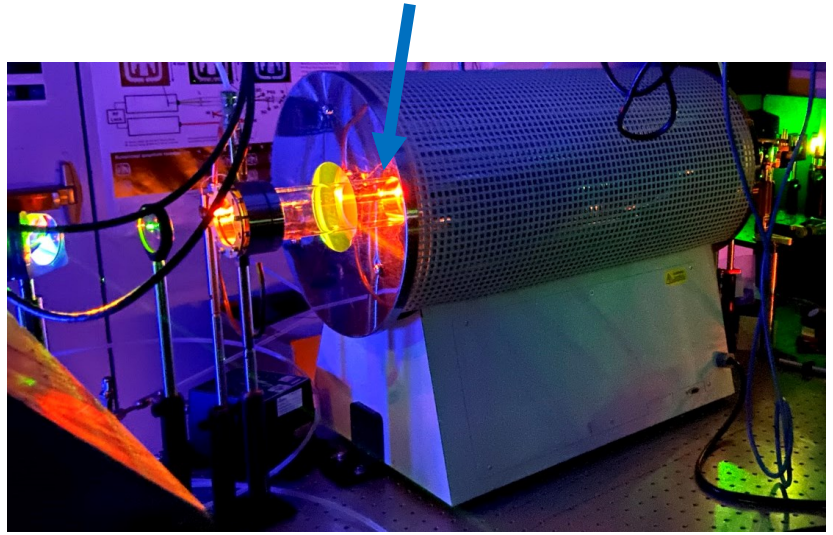
Nonlinear spectroscopies (multi-photon interactions)

*PW (10^{15} W!) fs lasers have been built

Transform-limited ultrafast pulsed lasers are fundamentally different than CW lasers



orange light from <7 fs "supercontinuum" pulse, 550-900 nm



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Bandwidth: $< 10^{-4}$ cm^{-1}	3×10^{-3} cm^{-1} (seeded)	0.2 to 0.7 cm^{-1}	200 to 400 cm^{-1}
Spectroscopies: Laser absorption	Rayleigh/Raman/Thomson scattering, laser induced fluorescence (LIF), LIF-dip, coherent anti-Stokes Raman scattering (CARS)	2 and 3 photon LIF, 4 wave mixing, electric field-induced second harmonic generation (EFISH), hybrid fs/ps CARS	

<u>Narrowband</u> linear spectroscopies (single photon interactions)

<u>Broadband</u> nonlinear spectroscopies (multi-photon interactions)

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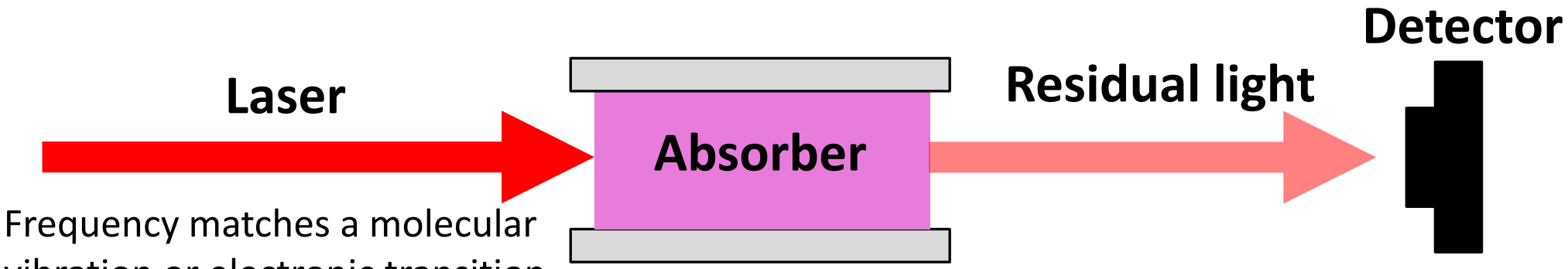
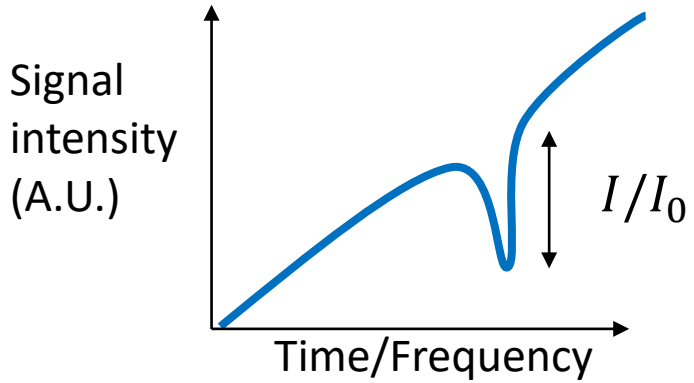
Laser absorption measures absolute number densities





Beer-Lambert law: $I/I_0 = \exp(-k_v L)$

$k_v \propto \boldsymbol{n_{absorber}}$, L is path length

Advantages:

- Absolute and calibration-free
- Can scan multiple transitions to get temperature

Disadvantage:

- Path-length averaged
- Multi-pass cells needed for weak-transitions

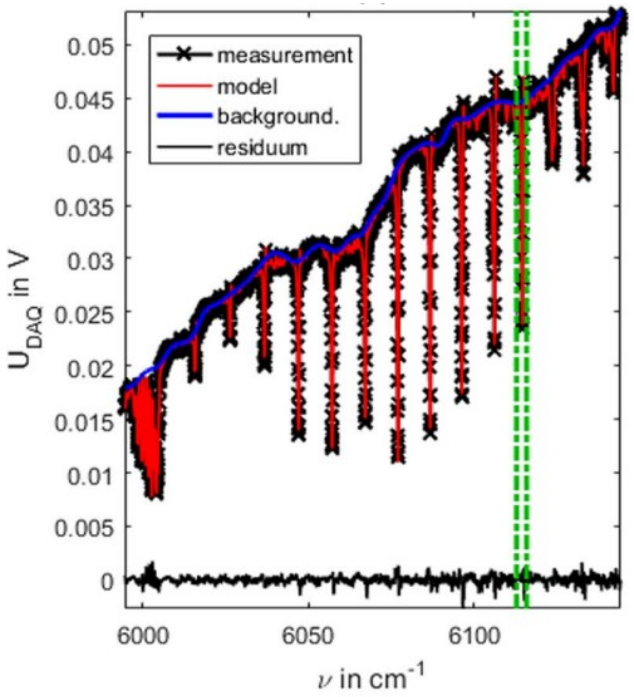
Ronald K. Hanson's Combustion Summer School lecture notes and recordings are a great resource for details:
https://cefrc.princeton.edu/combustion-summer-school/archived-programs/2018-session/lecture-notes
https://www.youtube.com/user/PrincetonCEFRC/playlists

Pulsed ultrafast lasers are also useful in absorption spectroscopy

Advantages:

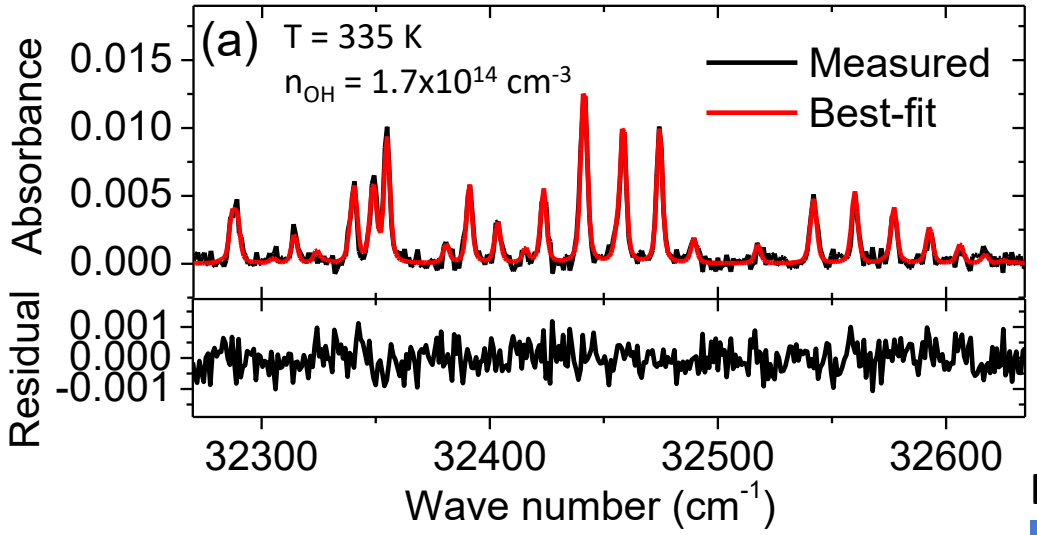
- Simultaneous acquisition of spectrum
- Temporal resolution limited by path length
  - 1 cm path length → ~30 ps

CH_4 "supercontinuum laser absorption spectroscopy" (SCLAS)



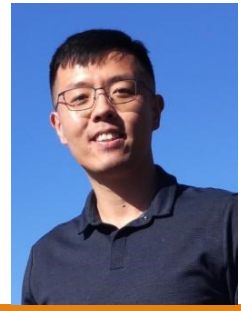
CH_4/air, 1 bar, 296 K
Emmert et al. Sci. Rep. (2018)

OH "fs UV laser absorption" (fs-UV-LAS)

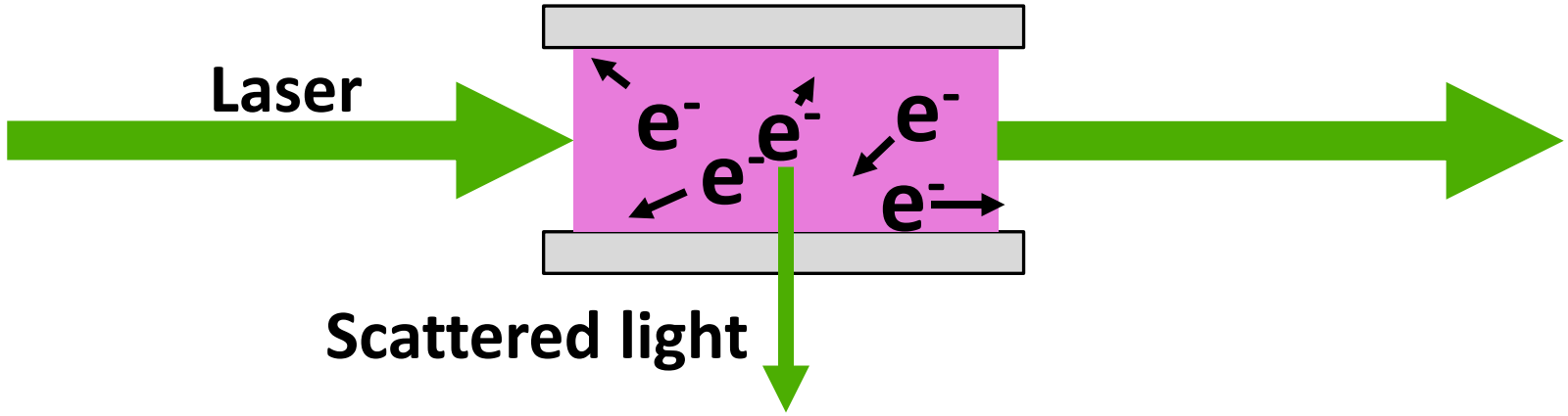


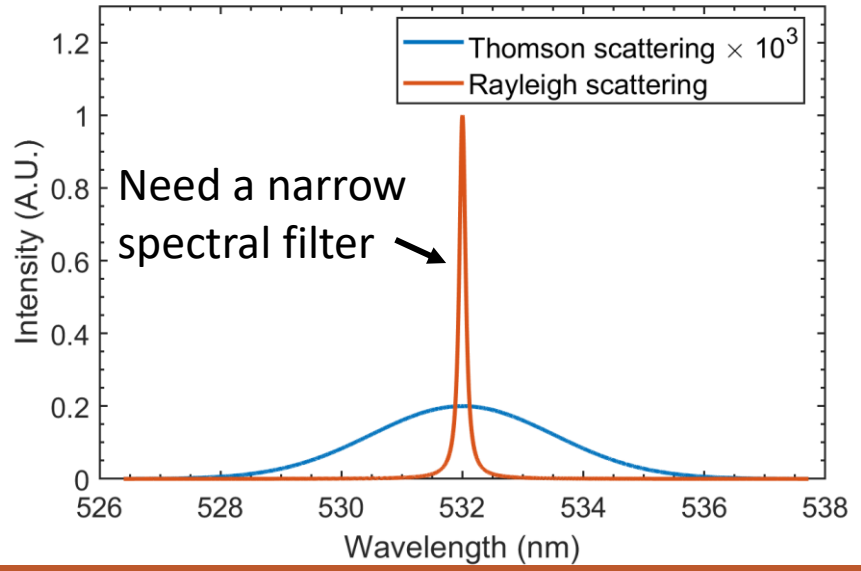
H_2O/He ns-DBD, 5 mm gap, 200th pulse
N. Liu et al. *submitted (2022)*

Dr. Ning Liu



Thomson scattering directly measures electron density and temperature





$$\frac{\sigma_{Thomson} n_e}{\sigma_{Rayleigh}\, n_{gas}} \approx 10^{-4}$$

Useful resources: MJ van de Sande, PhD Thesis (2002), K. Muraoka and A. Kono, JPhysD (2011), AFH van Gessel et al. PSST (2012), E Carbone and S Nijdam, PPCF 2014

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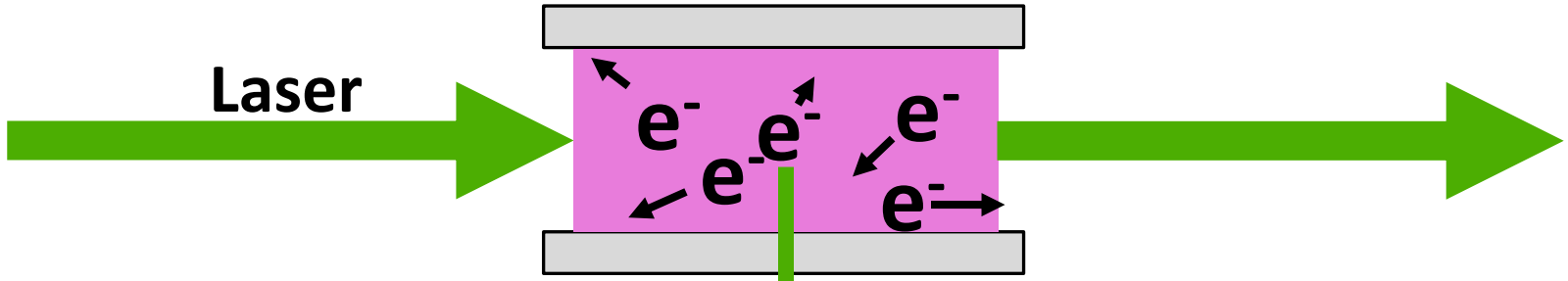
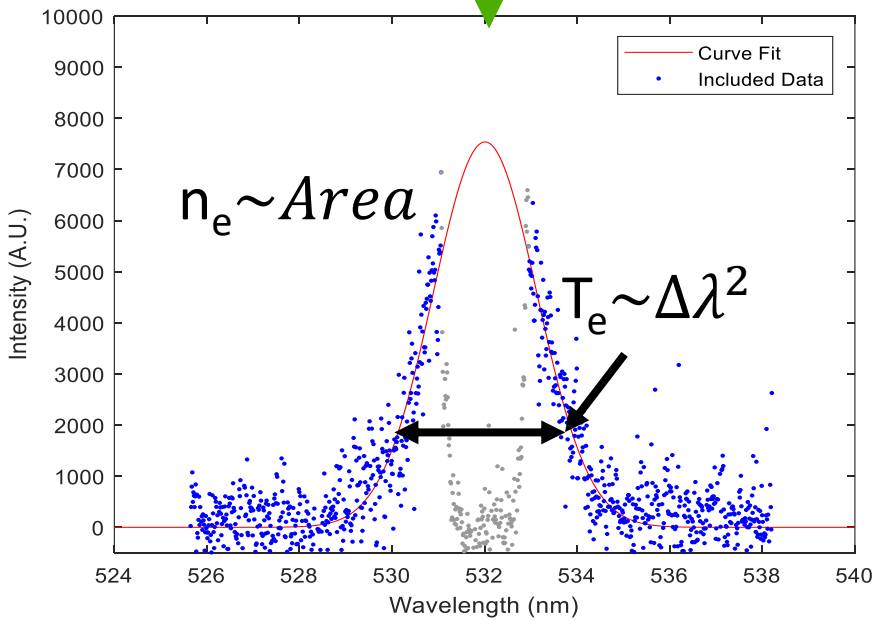




Advantages:

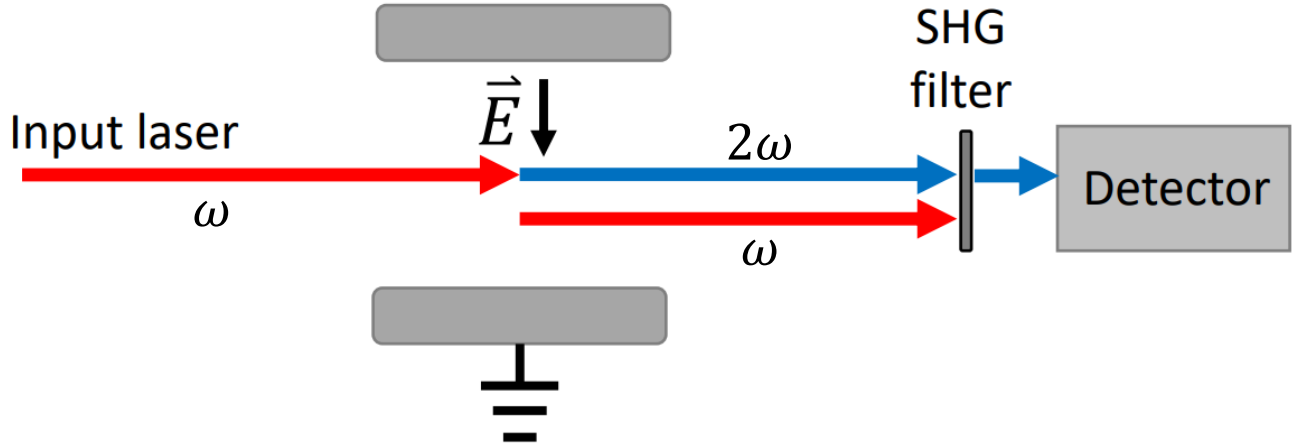
- Direct measurement of electron properties
- Can be spatially-resolved

Disadvantages:

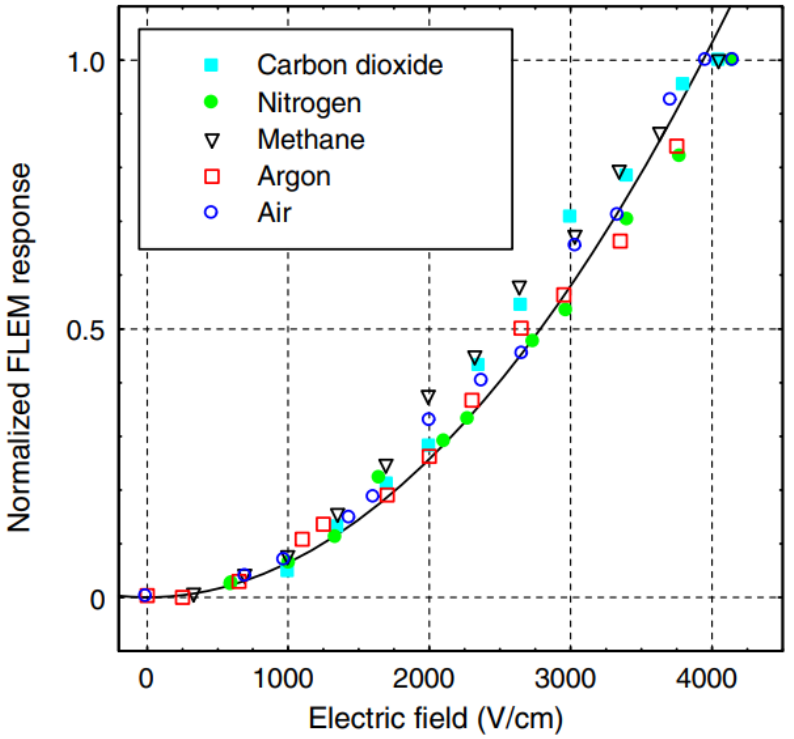
- Need a narrow spectral filter and **a lot** of averaging (>10,000 laser shots) for $n_e < 10^{13}$ cm^{-3}
- Interference with rotational Raman peaks in molecular plasmas

T.Y. Chen et al. J.Phys.D 2019

Electric field induced second harmonic generation (EFISH) enables sub-ns measurements of electric fields



$$I^{(2\omega)} = A \cdot N^2 (E_{Ext})^2 \left(I_{Pump}\right)^2$$



A. Dogariu et al. Phys. Rev. Appl. 2017

- Second harmonic generation (SHG) forbidden in centro-symmetric media like a gas
- External electric field breaks symmetry and allows 3rd order optical nonlinear process to occur
- Use of ps and fs lasers enable sub-ns electric field measurements

A. Dogariu et al. Phys. Rev. Appl. 2017, M. Simeni Simeni et al. PSST (2018), B.M. Goldberg Opt. Lett. 2019, K. Orr. et al. PSST 2020, TL Chng et al. PSST 2019, A. Rousso et al. PSST 2020, T.L. Chng et al. PSST 2020, T.L. Chng et al. PSST 2022, Y. Tang et al. Combust. Flame (2022)

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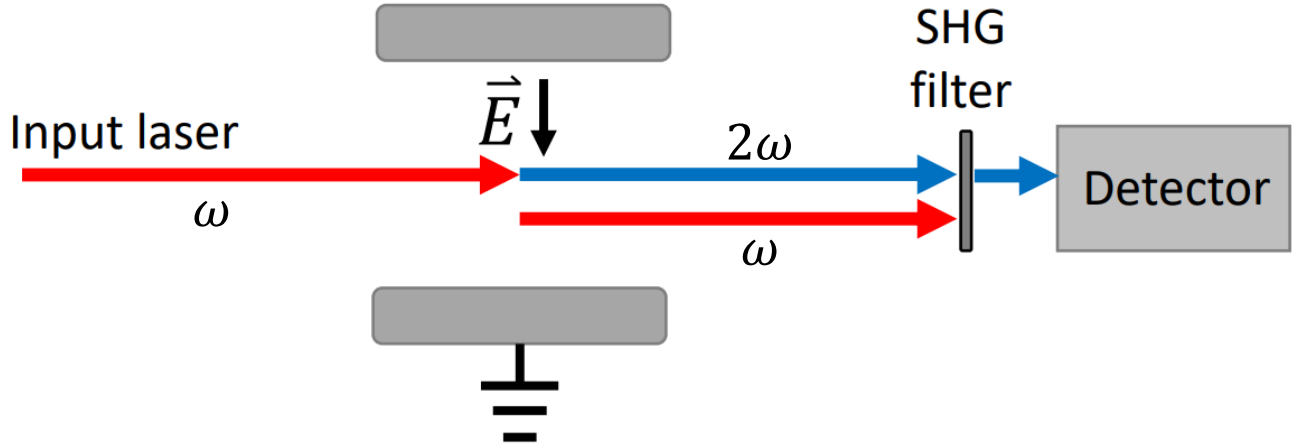

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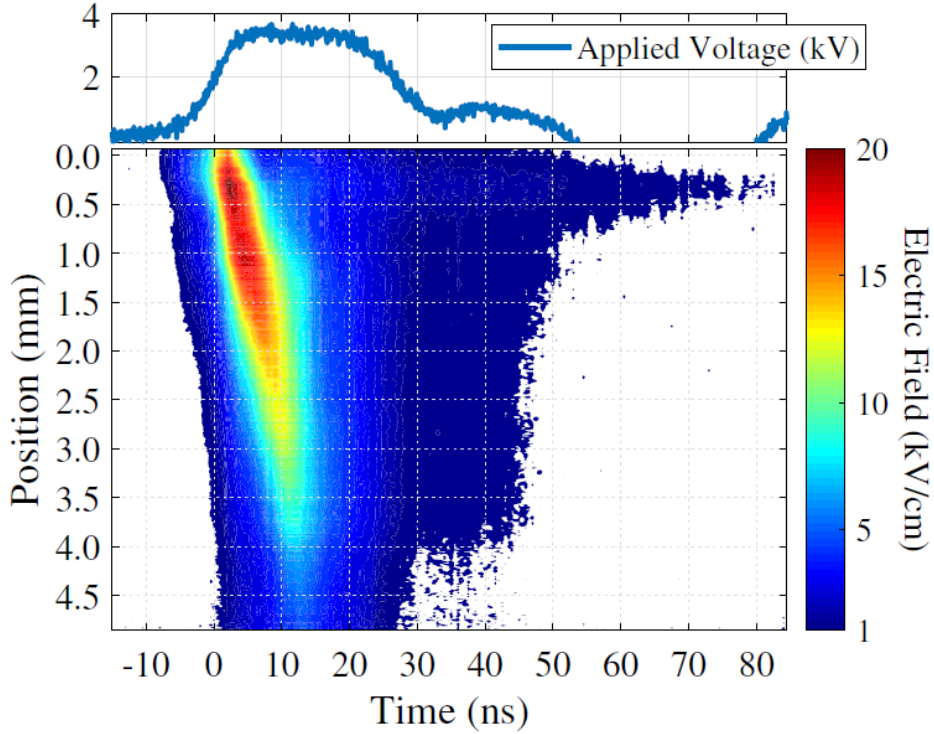

B.M. Goldberg et al. Opt. Lett. 2019

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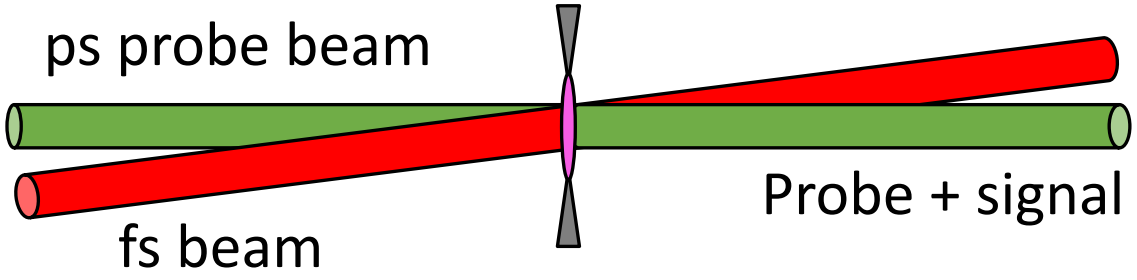
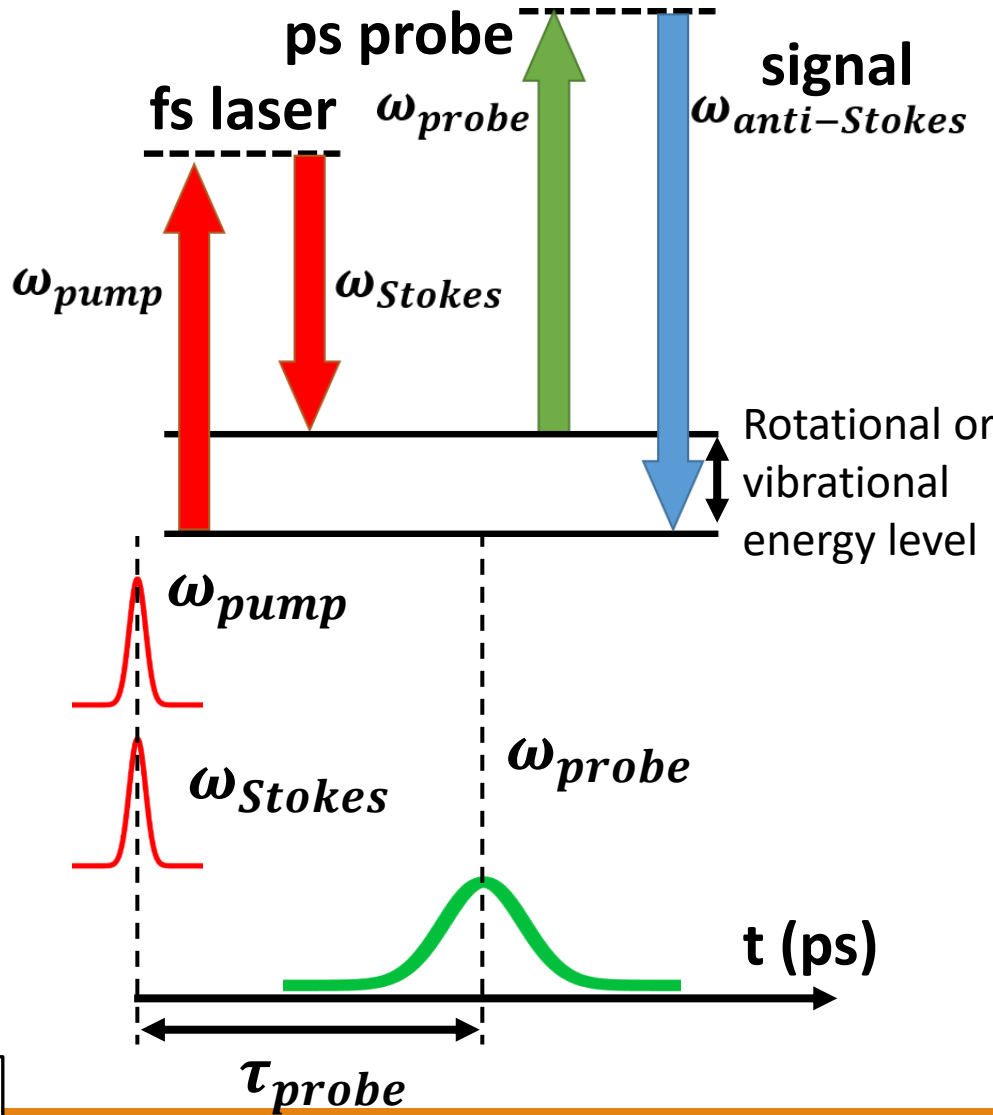
What is hybrid fs/ps CARS?

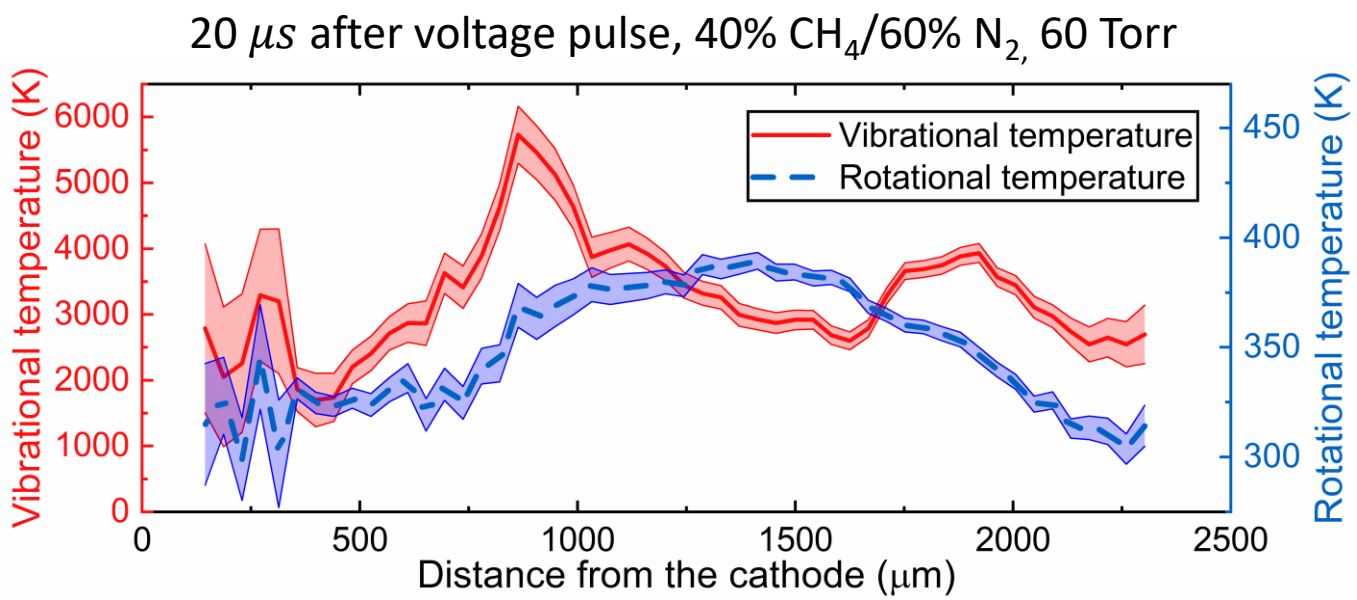


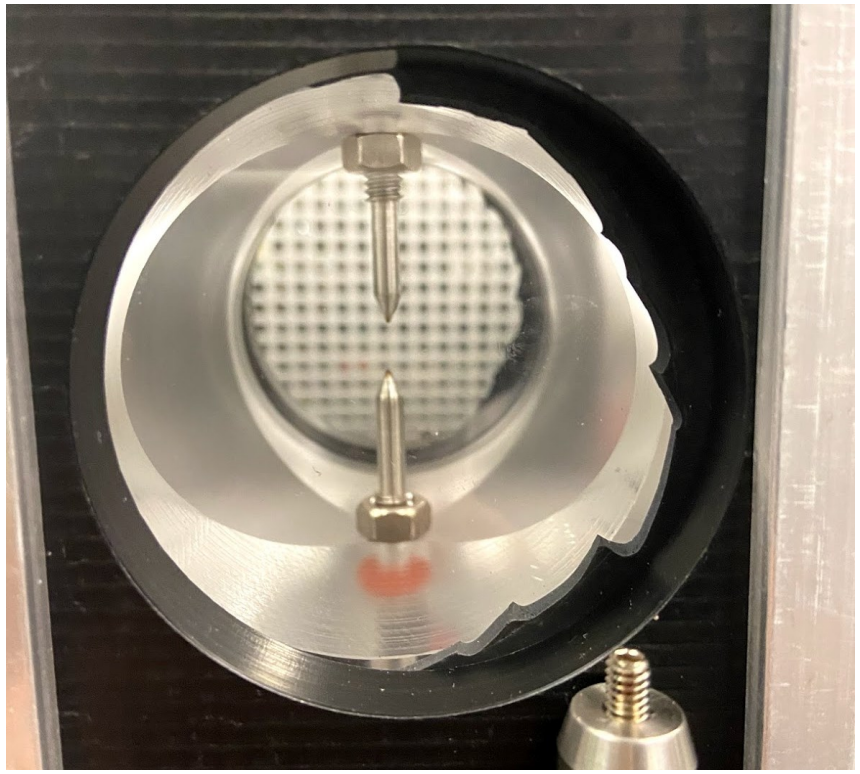
- Use broadband femtosecond pulse for simultaneous acquisition of many Raman transitions and picosecond probe for spectral resolution [1-8]
- Several advantages:
  - $I_{CARS} \propto I_{fs}^2 * I_{ps} \rightarrow$ 1-D or 2-D imaging of temperature and species concentrations within 50 μm of surface [4-7]
  - No need to scan Stokes frequency and only needs 2 beams



[1] B Prince et al. J Chem Phys (2006), [2] D Pestov et al., Science (2007), [3] C Dedic et al. Optica (2018), [4] A Bohlin et al. J. Chem. Phys (2013), [5] J Retter et al. Combust. Flame (2018) [6] A Bohlin et al. Proc. Combust. Inst. (2017), [7] Chen et al. Opt. Lett. (2019) [8] Chen et al. Combust. Flame (2021)

Can get both T_{rot} and T_{vib} from pure rotational fs/ps CARS





Demonstrated 1-D imaging of rotation-vibration non-equilibrium with 40 μm resolution

Chen T.Y. et al. Opt. Lett. *(2020)*

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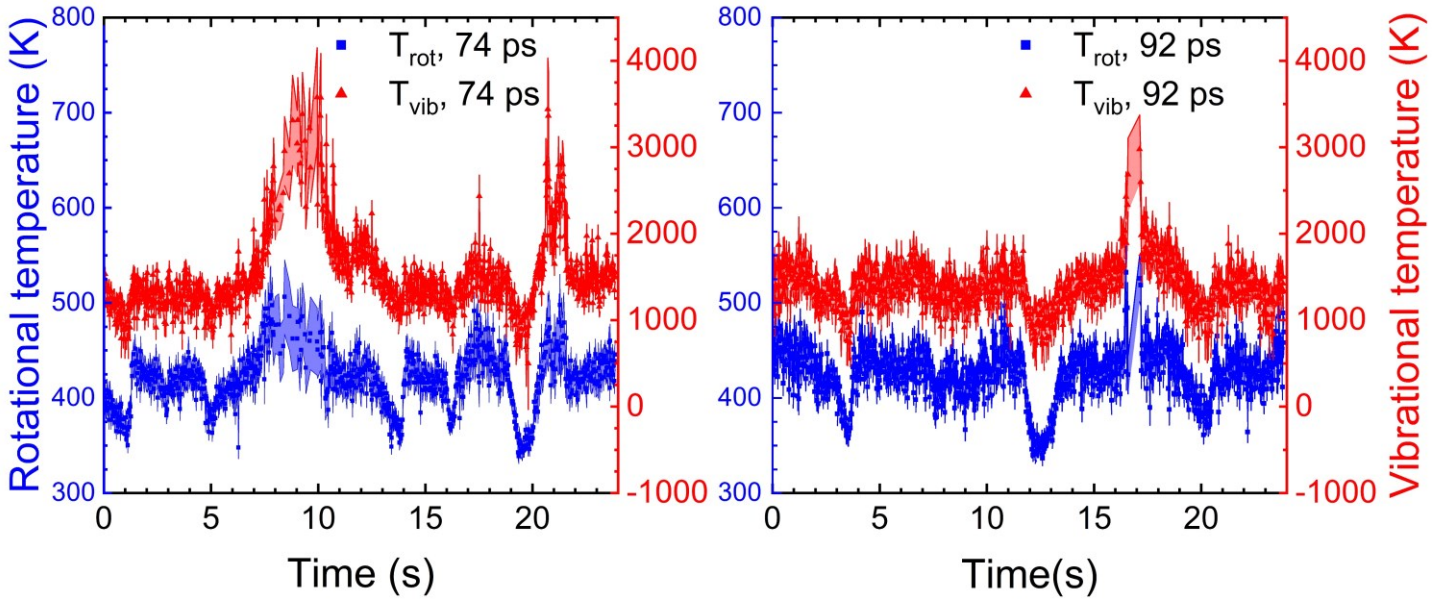

75 Torr pure N_2 DC discharge, 7mm gap
100 kOhm ballast resistor, 500 V at the anode,
1500 V drop across resistor

Can also do single shot measurements using ps probe pulse generated from the fs laser for kHz rate monitoring

Chen T.Y. et al. Opt. Lett. *(2022)*

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T.Y. Chen et al. Proc. Combust. Inst. 2021

Why study non-equilibrium plasma CH_4 reforming?

- Deep reductions in CH_4 and CO_2 emissions required to avoid more than 1.5°C increase in global warming [1]
- 149 billion cubic meters of natural gas were flared in 2016 -> 1% of global annual CO_2 emissions [2-3]
- CH_4 emissions identified as contribution >20% of increase in warming to date [4]
- Plasma processing of CH_4 and CO_2 to chemicals could be a more modular alternative to high pressure thermal catalysis [5]

Varodrig, Wikimedia Commons

[1] IPCC, *Global Warming of 1.5°C*, https://www.ipcc.ch/sr15/
[2] The World Bank, "New Gas Flaring Data Shows Mixed Results", 2017.
[3] T. Boden, B. Andres, and G. Marland, Oak Ridge National Laboratory, 2017
[4] M Saunois et al. Env. Res. Lett. 2016
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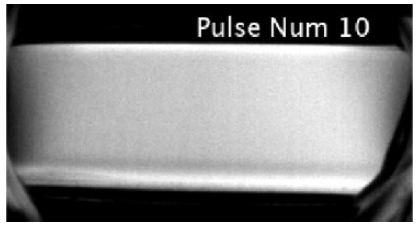
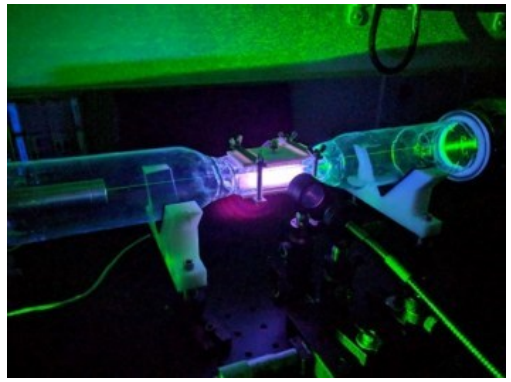
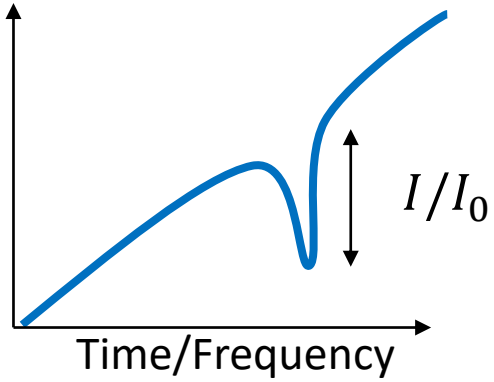
What are the key reactions and processes in plasma CH_4 reforming?

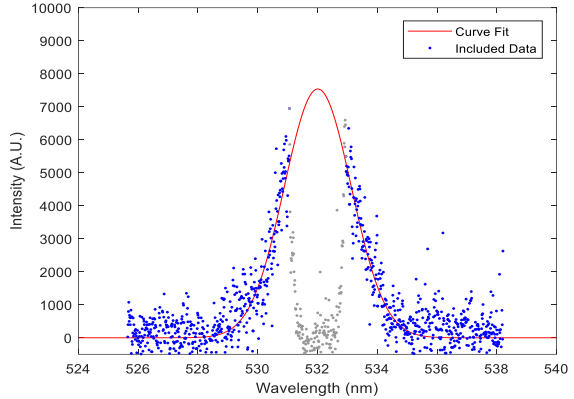


Rousso et al. PSST (2020)



Signal intensity (A.U.)





Uniform ns-DBD plasma flow reactor for plasma chemistry studies

Tunable mid-infrared laser absorption (species concentrations) and Thomson scattering (n_e, T_e)

Discharge geometry, voltage input

Plasma kinetic model

Experimental validation

Reaction path flux toward products

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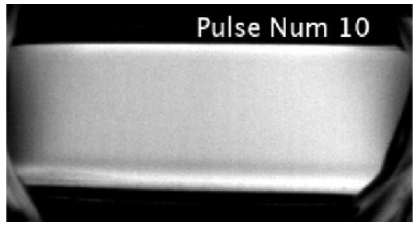

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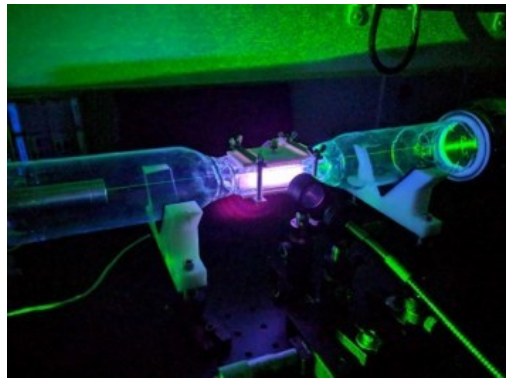

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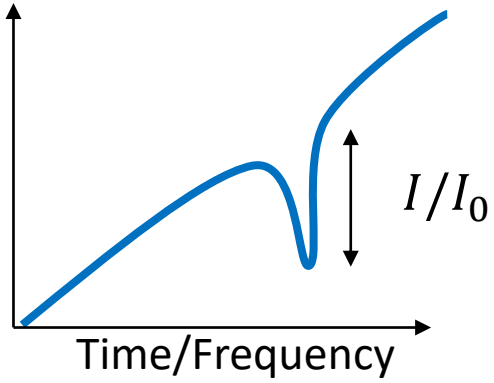

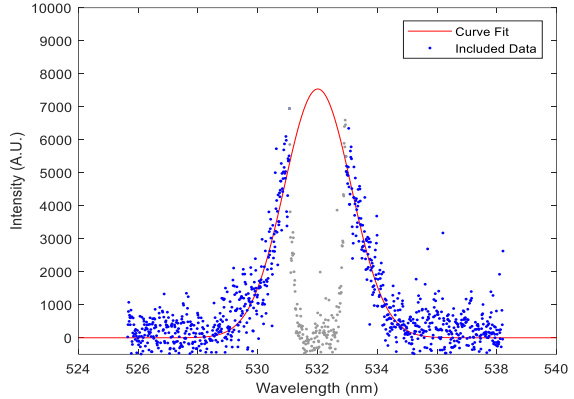

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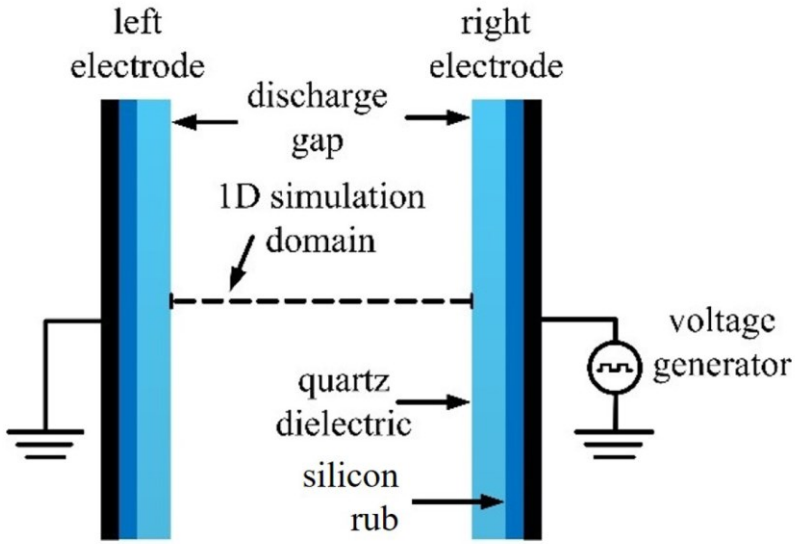
1-D Numerical Model

- Plasma chemistry mechanism from [6] and Helium reactions from [7-8]
- To reduce computation time, O_2 and O_3 and vibrational excitation of CH_4 and CO_2 was not included
- Electric field is solved for using 1-D Poisson equation and fitted voltage waveform [9]
- Electron impact rate & transport coefficients solved using BOLSIG+ [10]



Collaboration with Prof. Suo Yang and Taaresh Taneja at UMN-Twin Cities

[6] Wang et al JPhysD 2018
[7] Martens et al. Anal Bioanal Chem (2007)
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[9] Yang et al. JPhysD (2017)
[10] Hagelaar & Pitchford, PSST (2005)

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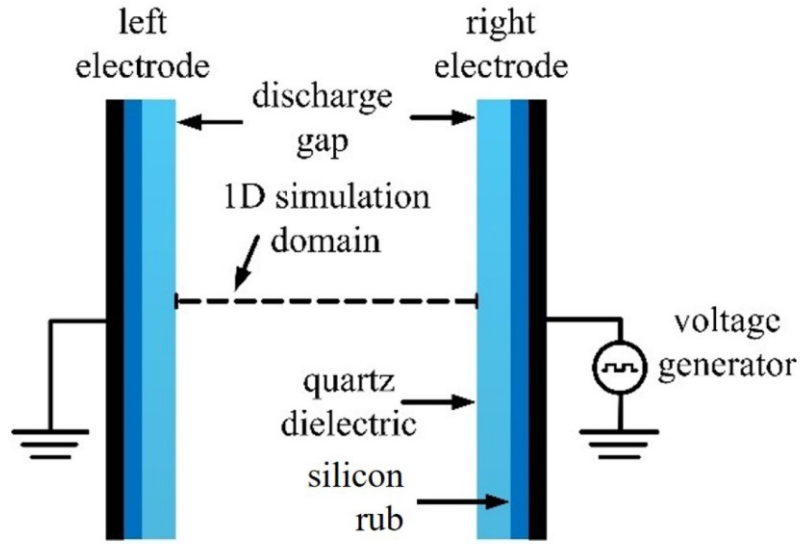

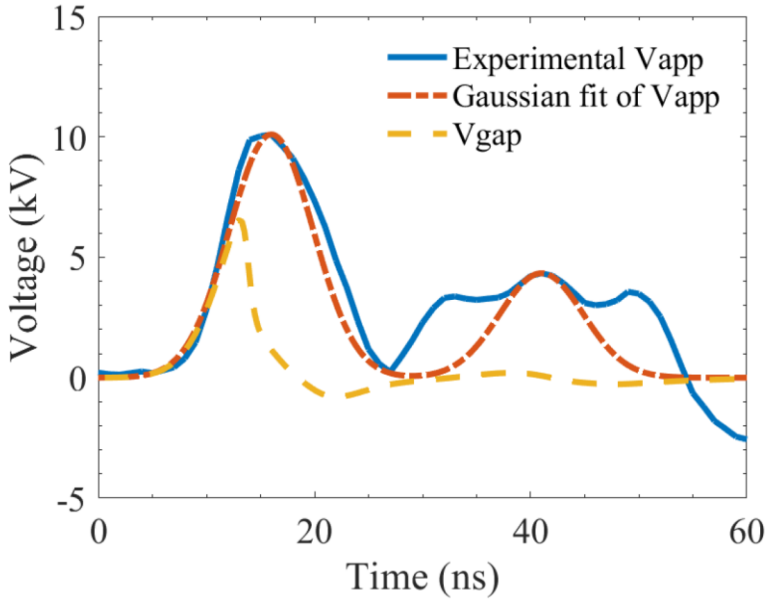

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[10] Hagelaar & Pitchford, PSST (2005)

Laser absorption setup

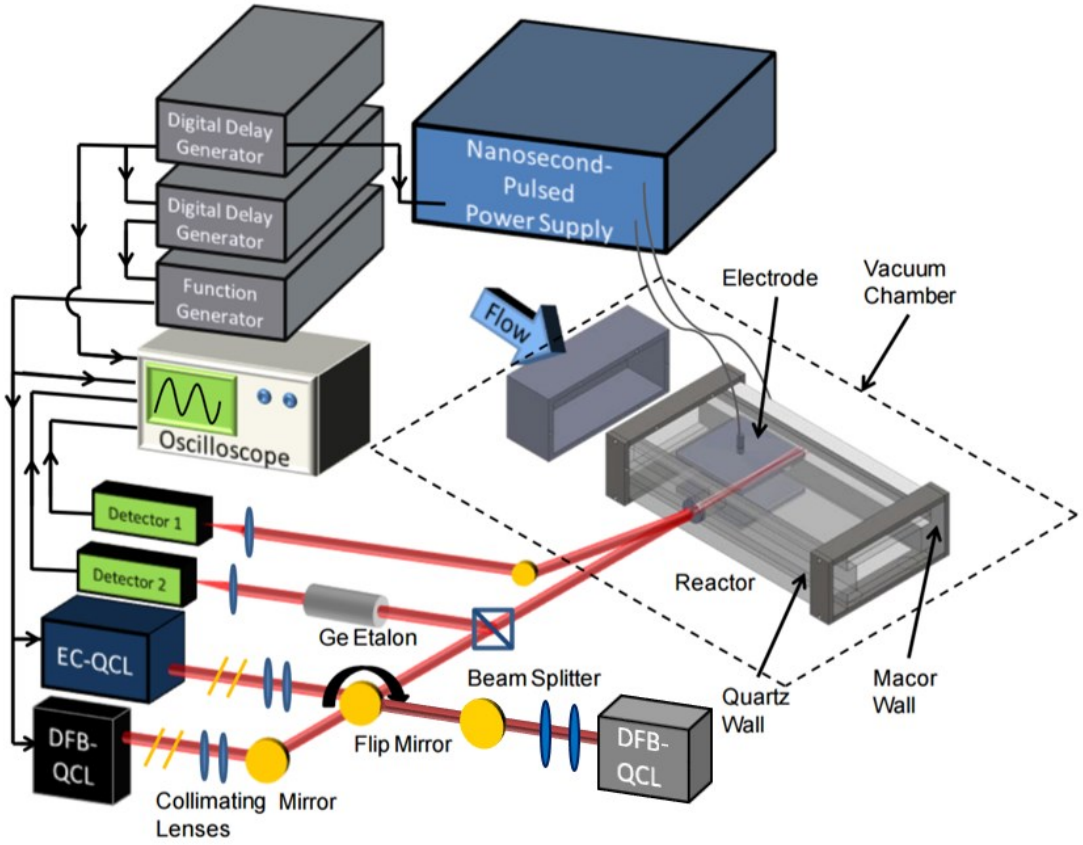
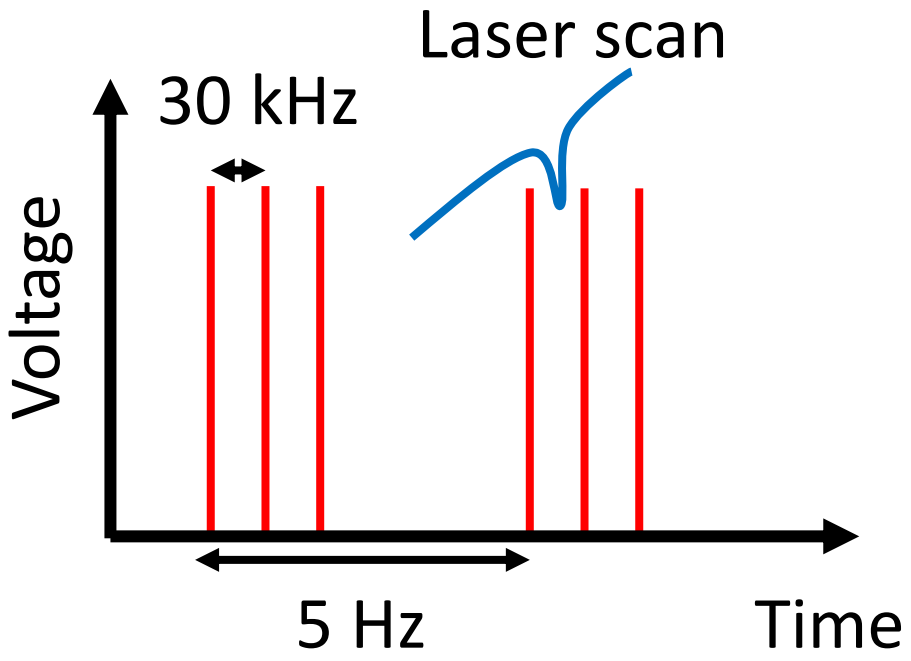


Fig. 3.1.1, J. Lefkowitz, PhD Thesis, 2016

Species	Line location (cm^{-1})	Laser
CH_4 and Temperature	1343.56, 1343.63	EC-QCL
CH_2O	1726.9	DFB-QCL
C_2H_2	1321.03	EC-QCL
H_2O	1312.55	EC-QCL

- Mixture: 15% CH_4/15% CO_2/70% He, 60 Torr
- 300-pulse burst, 10 kV pulse, 30 kHz pulse repetition rate, 0.2 m/s flow speed
- Direct laser absorption using 24 pass Herriott cell
- Discharge geometry is the same as the Thomson Scattering setup

Laser absorption setup



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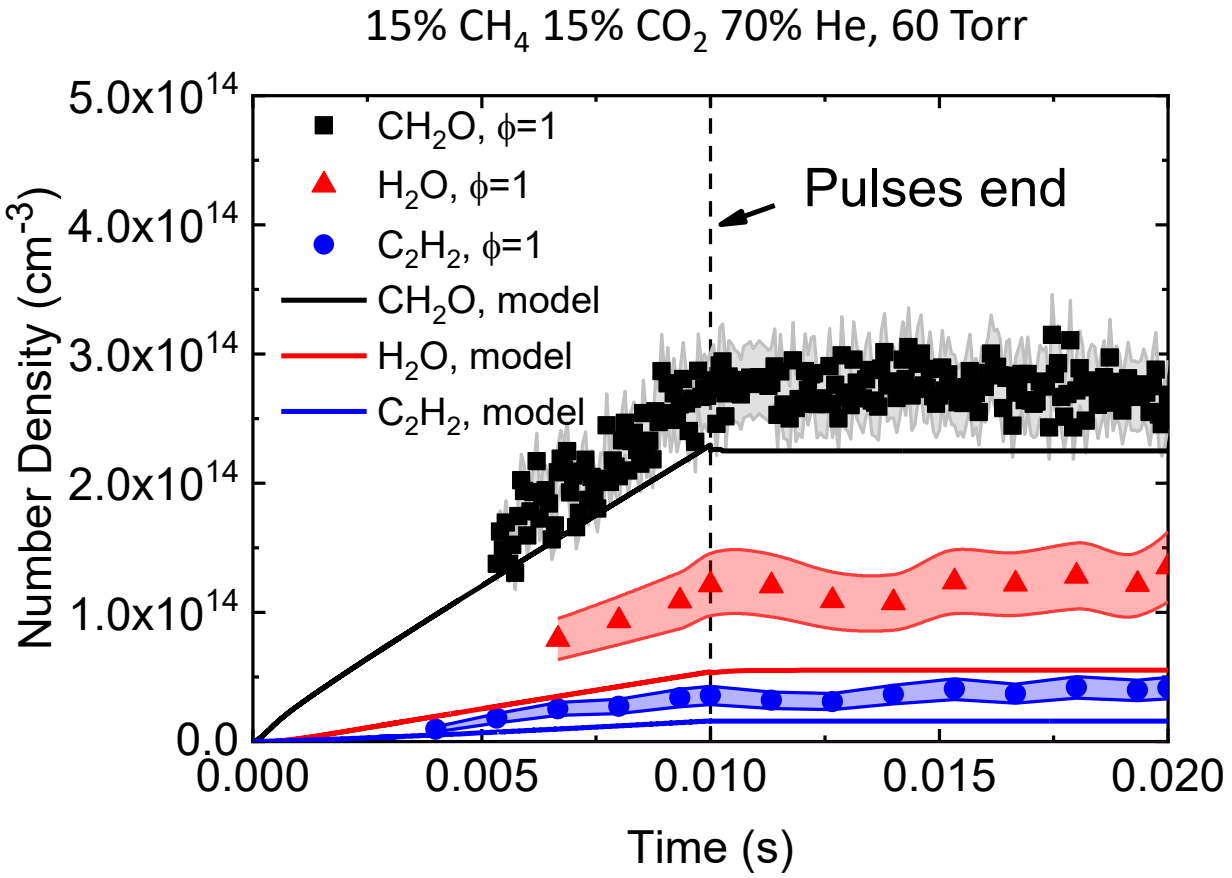
Comparison of plasma chemistry predictions and experiment

- Fairly well predicted CH_2O but poor predictions of H_2O and C_2H_2
- Can assume the reaction pathways for CH_2O are the main channels
- Indicates there could be missing reactions in the mechanism for production of H_2O and C_2H_2



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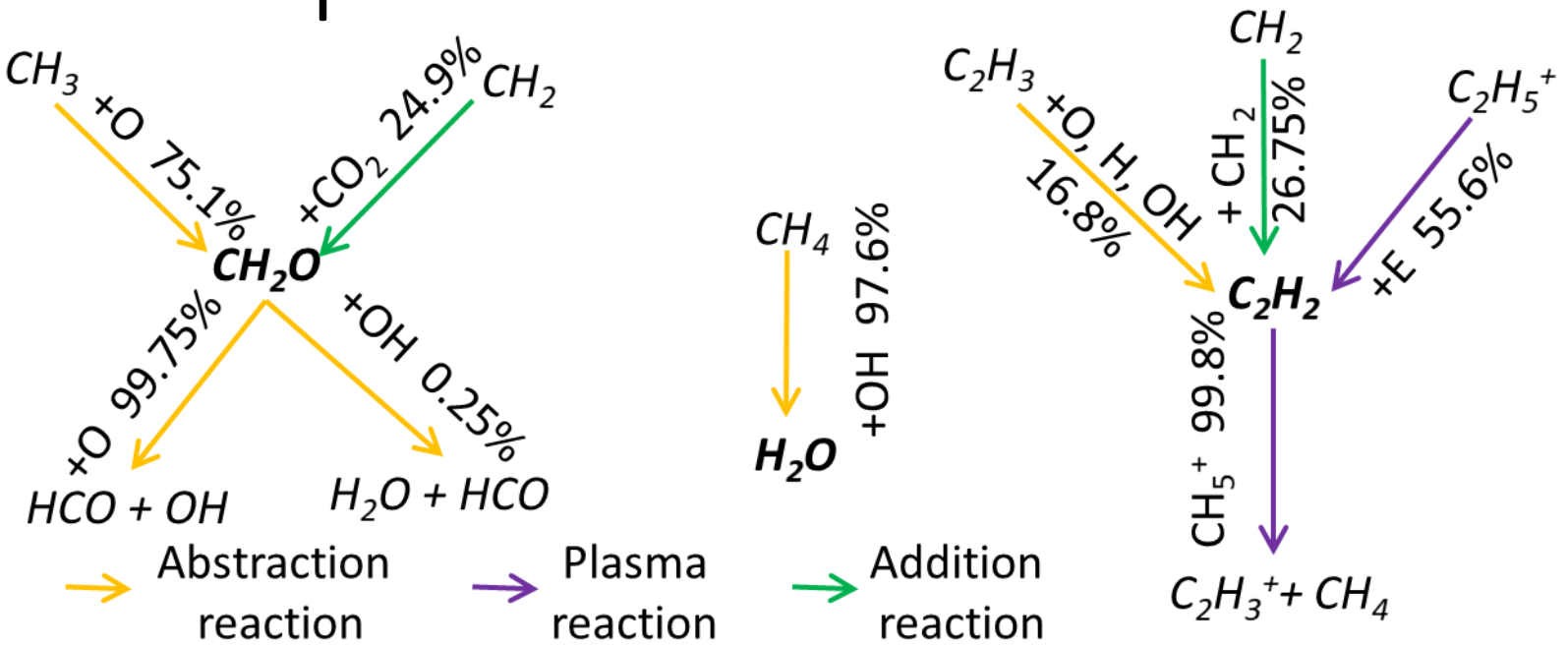
Predicted reaction path flux for measured species



- 50%-300% uncertainty in the reaction rates that form C_2H_2 [10]
- Mao et al. suggest updated branching ratios of e^- + CH_4^+ dissociative recombination for more CH_2 formation [15]
- Low uncertainty in CH_4 +OH indicates missing pathway for H_2O formation

T.Y. Chen et al. Proc. Combust. Inst. 2021

[10] Wang et al. JPhysD (2018).
[15] Mao et al. Energy Convers. Manag. (2019).

Summary – CH_4/CO_2 plasma reforming

- Time-resolved *in situ* Thomson scattering and laser absorption measurements were used as validation targets for a 1-D numerical model
- CH_2O was predicted within 25% of the measured value while H_2O and C_2H_2 were underpredicted by factor of 2
  - Likely due to uncertainties in reaction rates and missing reaction pathways in the mechanism

Talk outline

1. Overview of laser sources and laser spectroscopies for plasmas

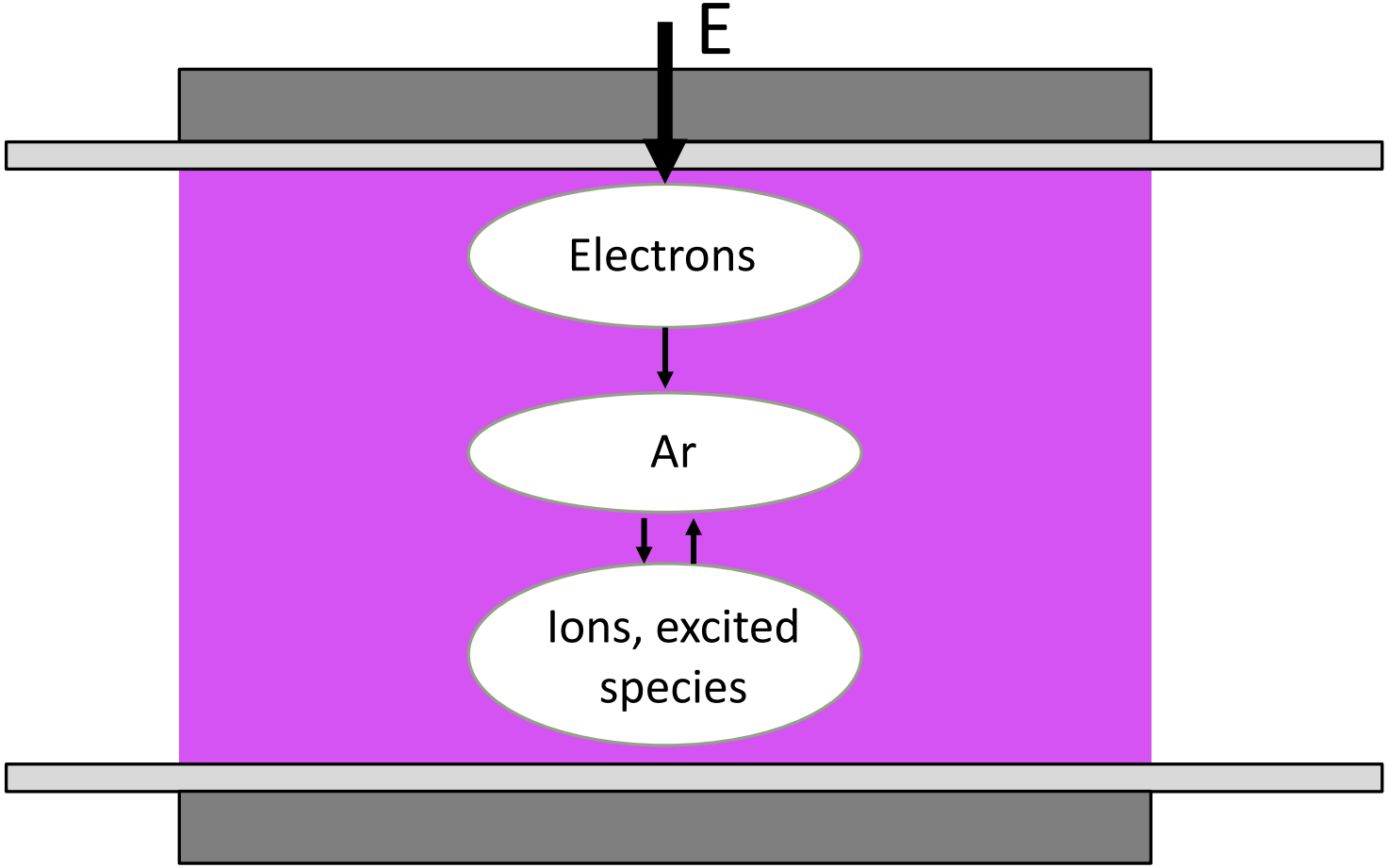
2. Time-resolved laser measurements of plasma CH_4 reforming and model validation

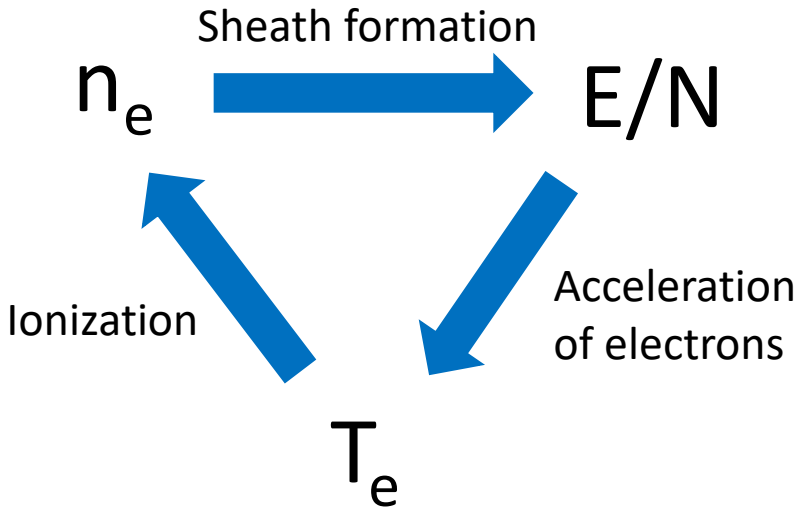
3. *In situ* laser probing of electric field and electron property coupling in CH_4/Ar ns-DBD discharges

4. Conclusions and future directions

T.Y. Chen et al. *manuscript in preparation*

With CH_4 addition to Ar ns-DBD, how does E, T_e, and n_e vary and couple?





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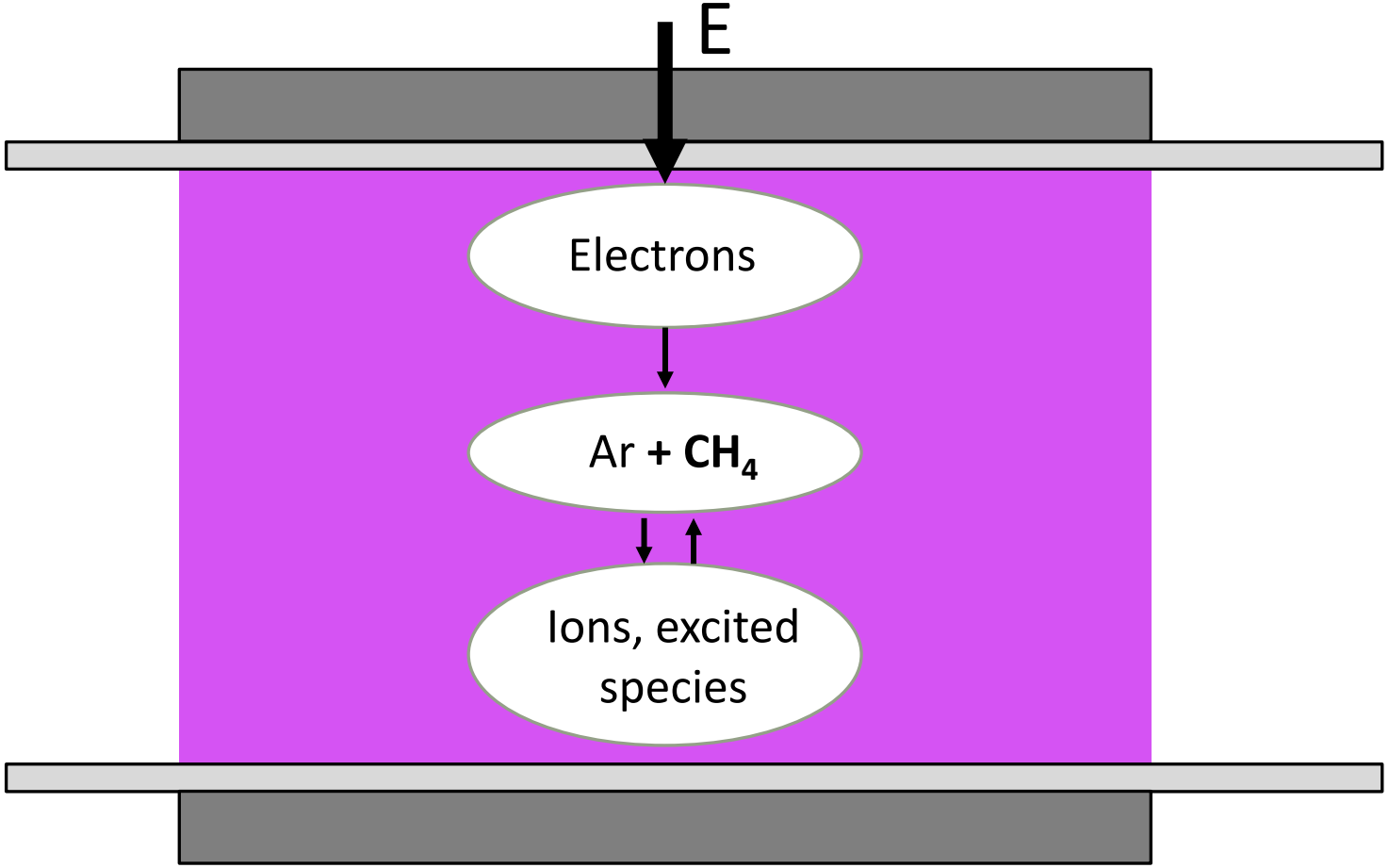
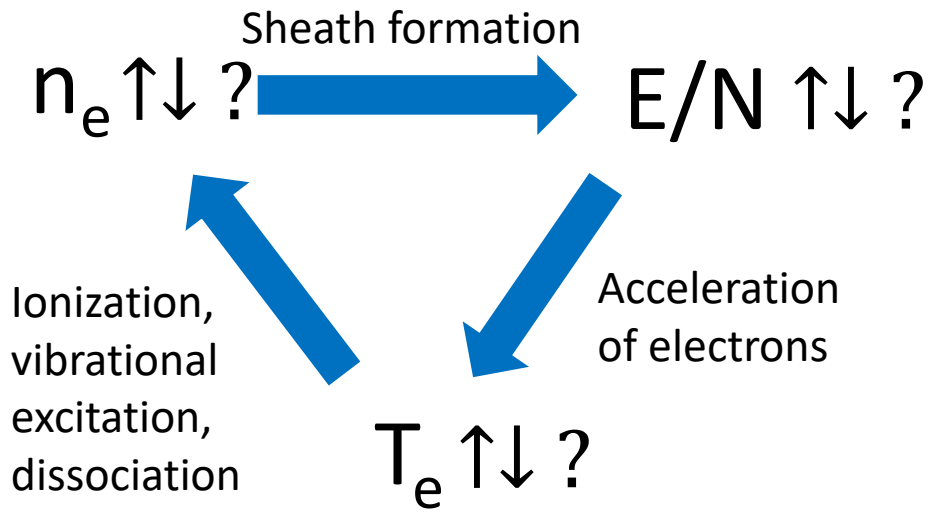
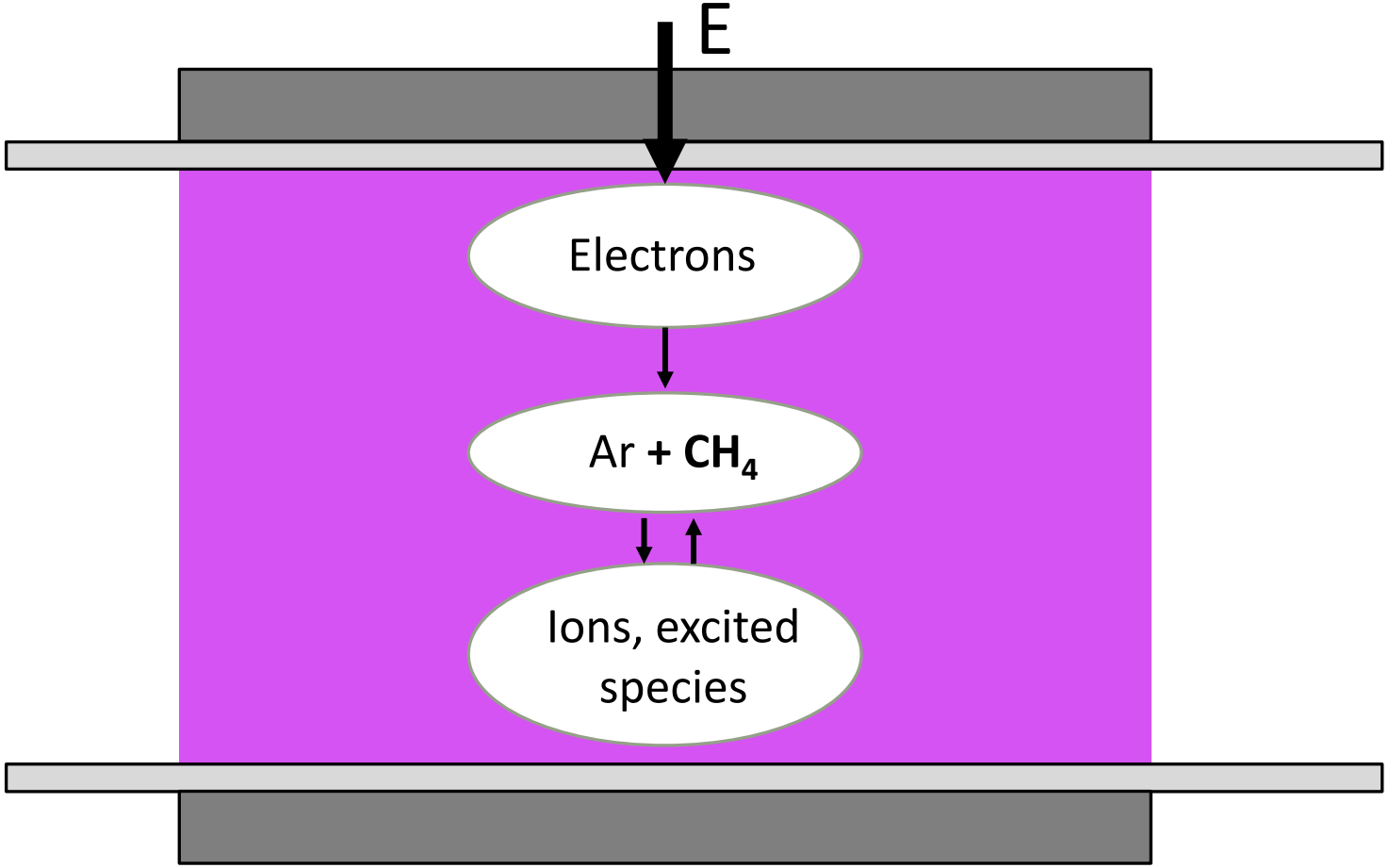
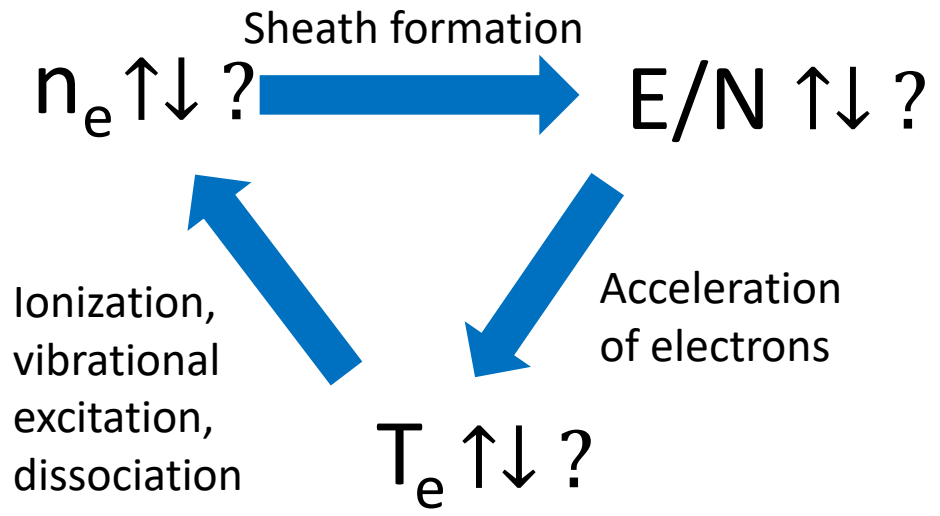




With CH_4 addition to Ar ns-DBD, how does E, T_e, and n_e vary and couple?

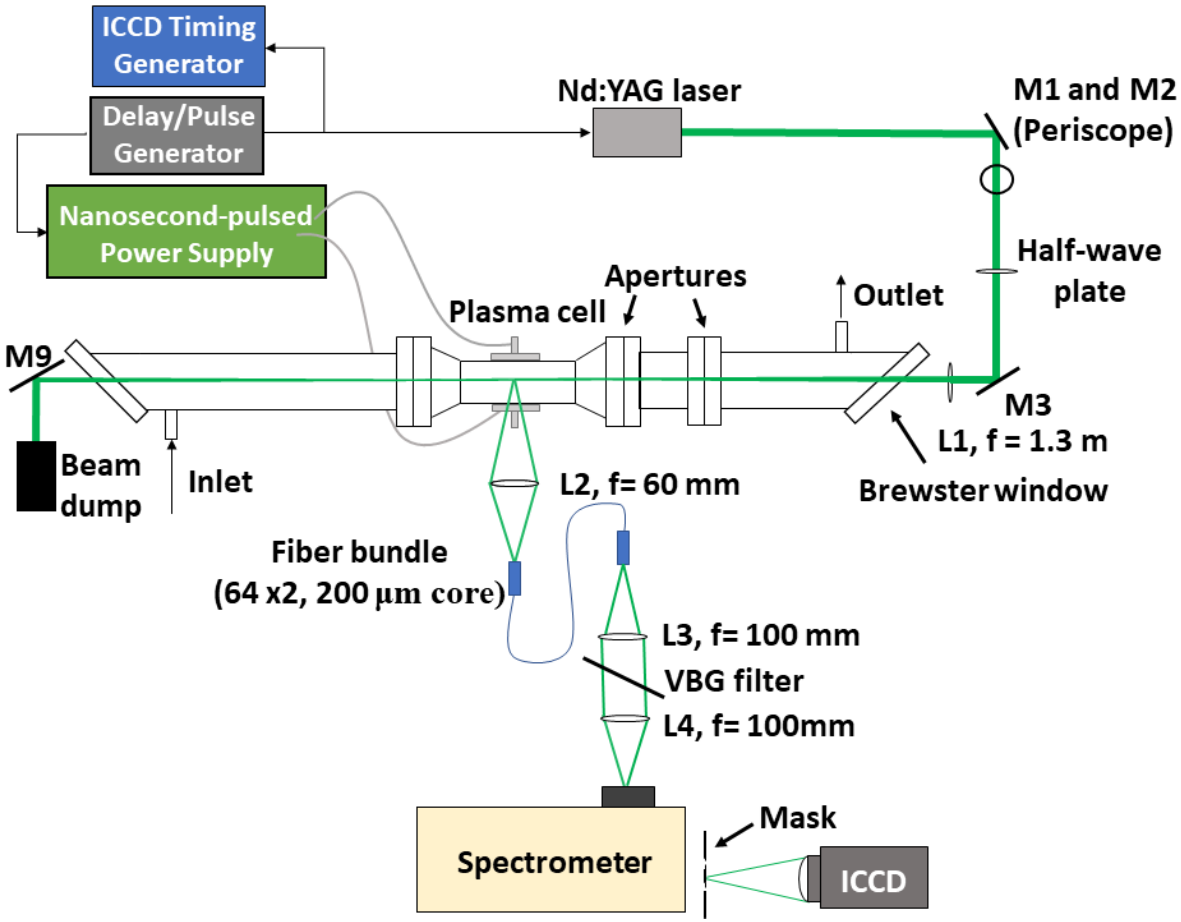




We can measure |E|, T_e, and n_e with EFISH and Thomson scattering!

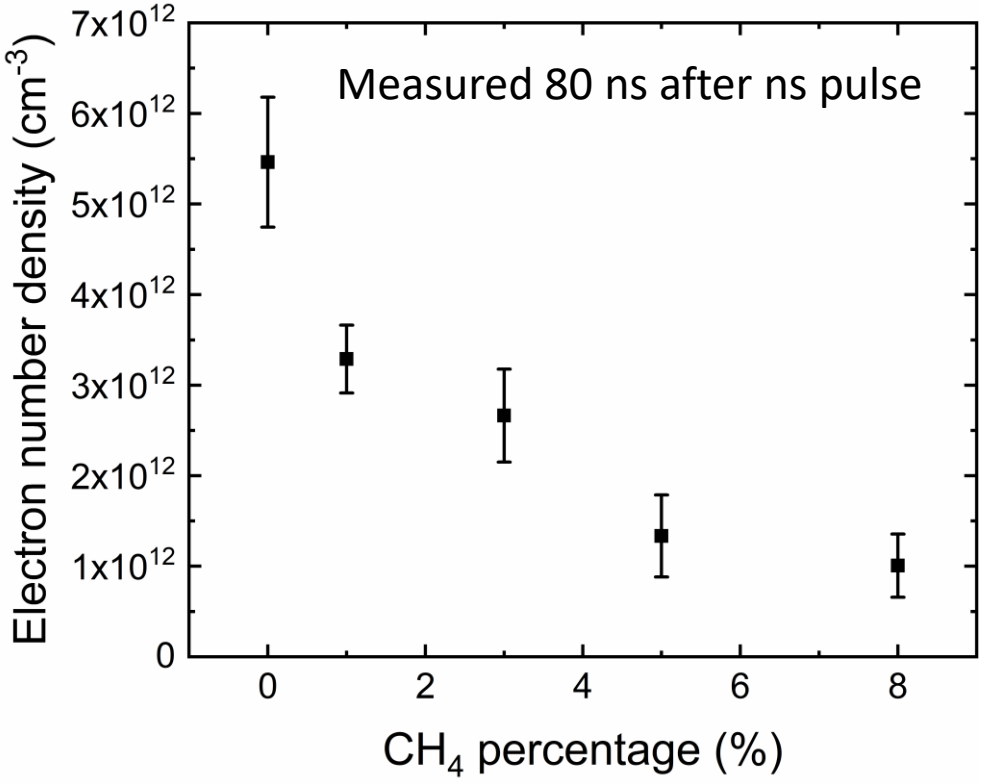
Thomson scattering setup

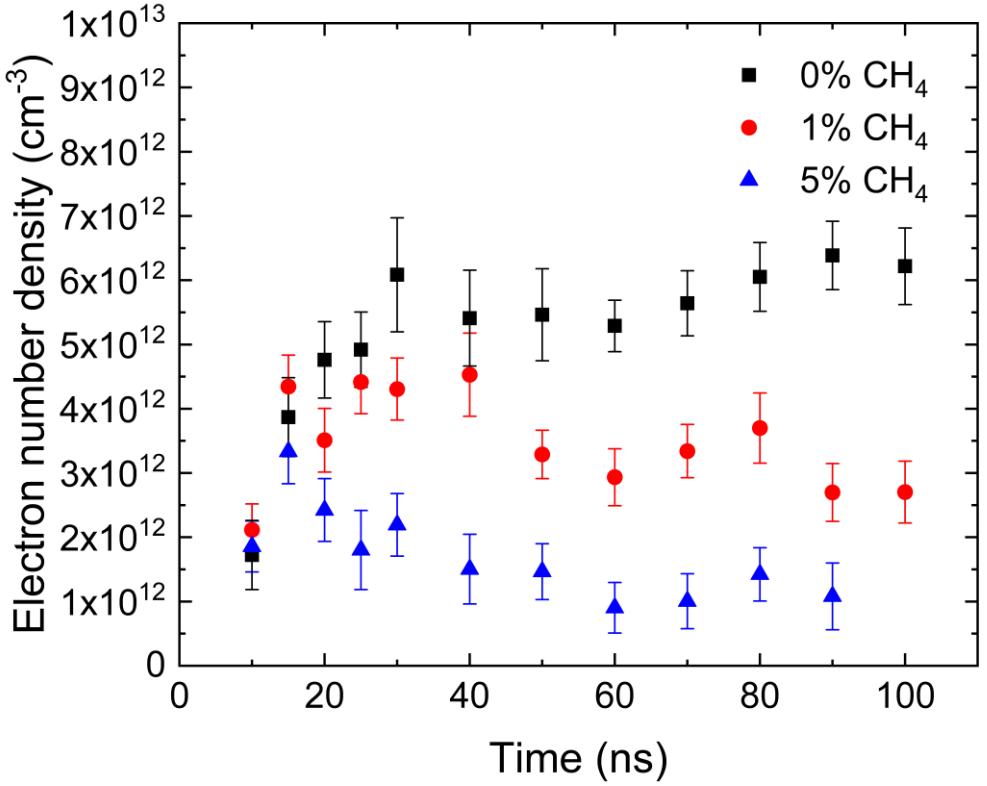
- Blackened aluminum mask and volume Bragg grating (VBG) notch filter block 532 nm light
- Allows for background subtraction of remaining light to obtain Thomson scattering spectrum
- 2nd harmonic of Nd:YAG laser (532 nm), 390 mJ laser energy, 6 ns FWHM pulse width
- Plasma reactor:
  - Dielectric barrier discharge (DBD), 14 mm gap, 44.5 mm x 44.5 mm electrodes
  - 75 Torr, Ar bath gas, 0-8% CH_4, ~9kV, 12 ns pulse 500 Hz



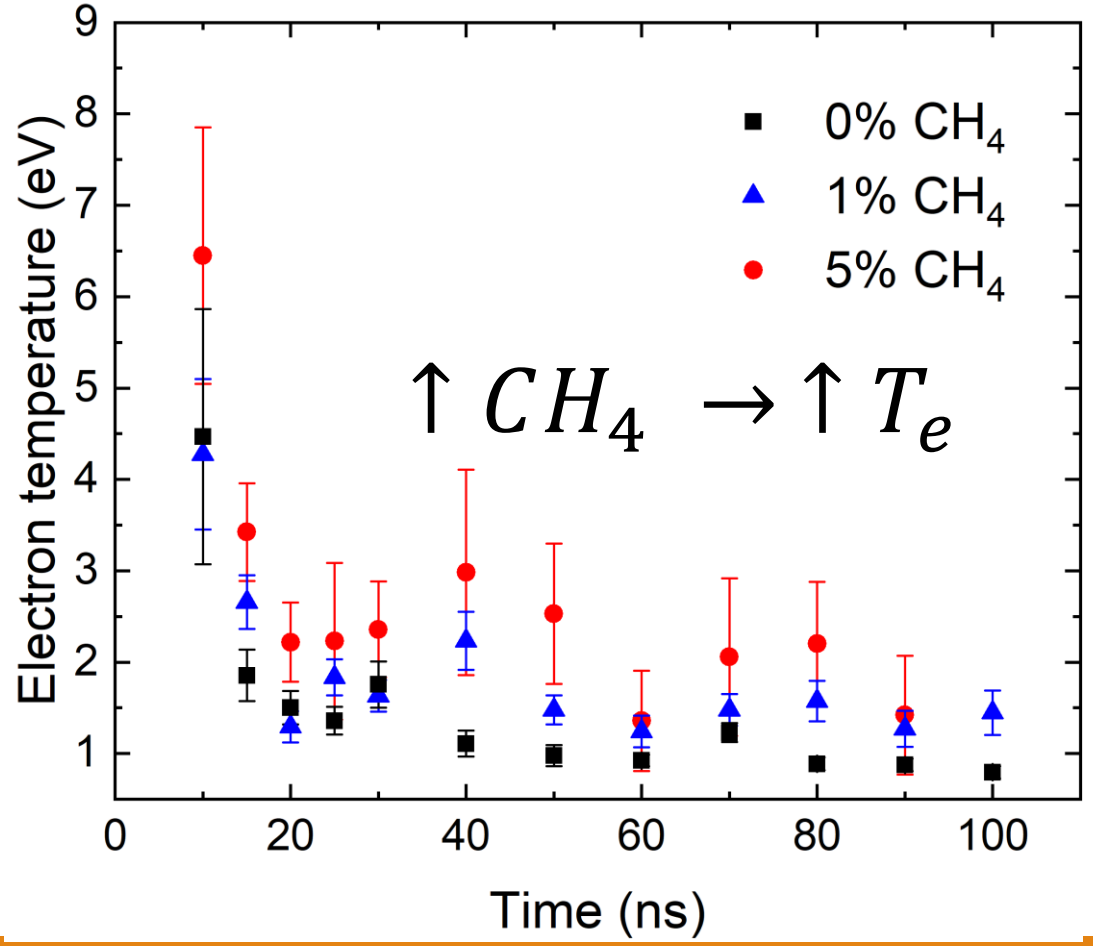
CH_4 addition to Ar ns-DBD has nonlinear effect on n_e

$$\uparrow CH_4 \rightarrow \downarrow n_e$$

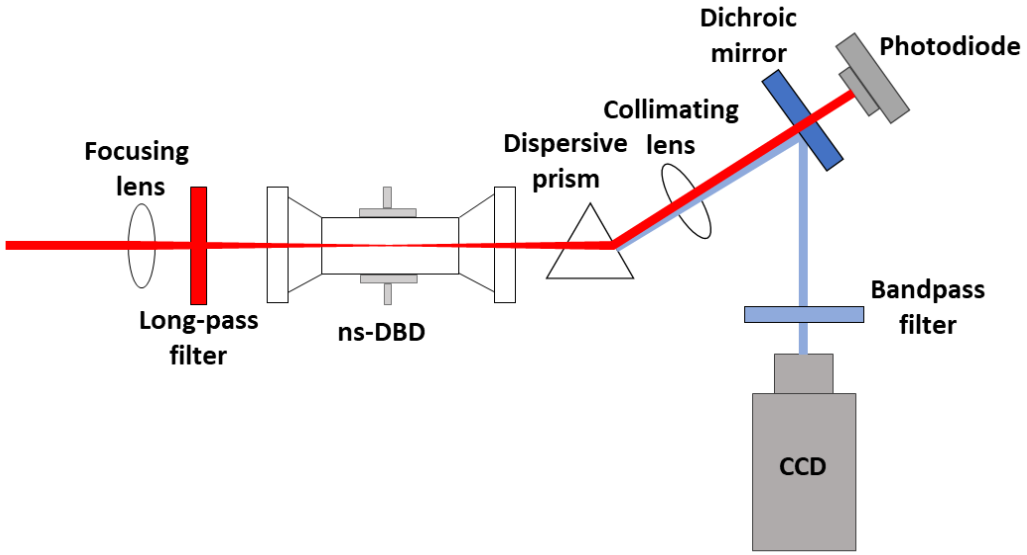




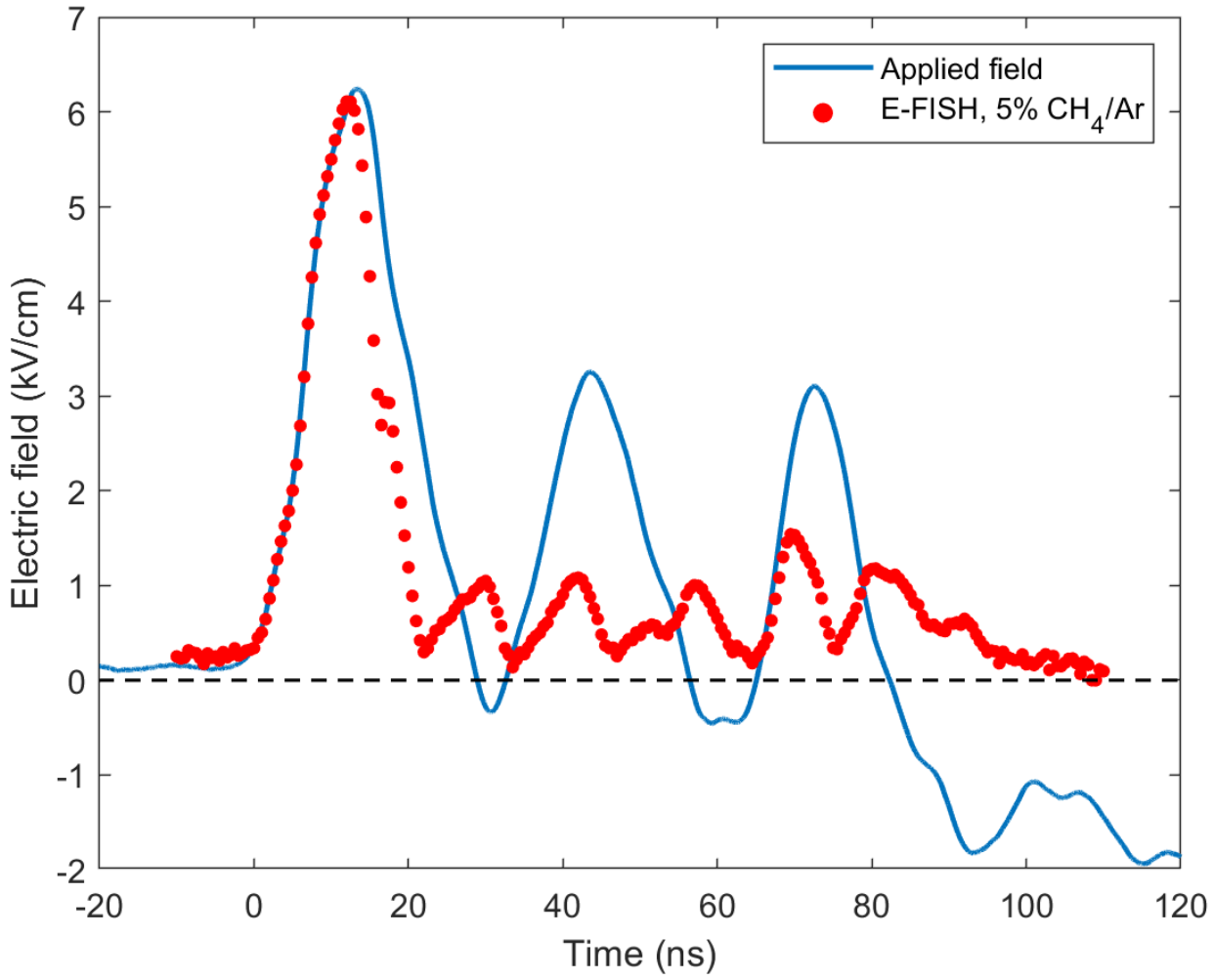
Time-resolved CH_4/Ar electron temperature



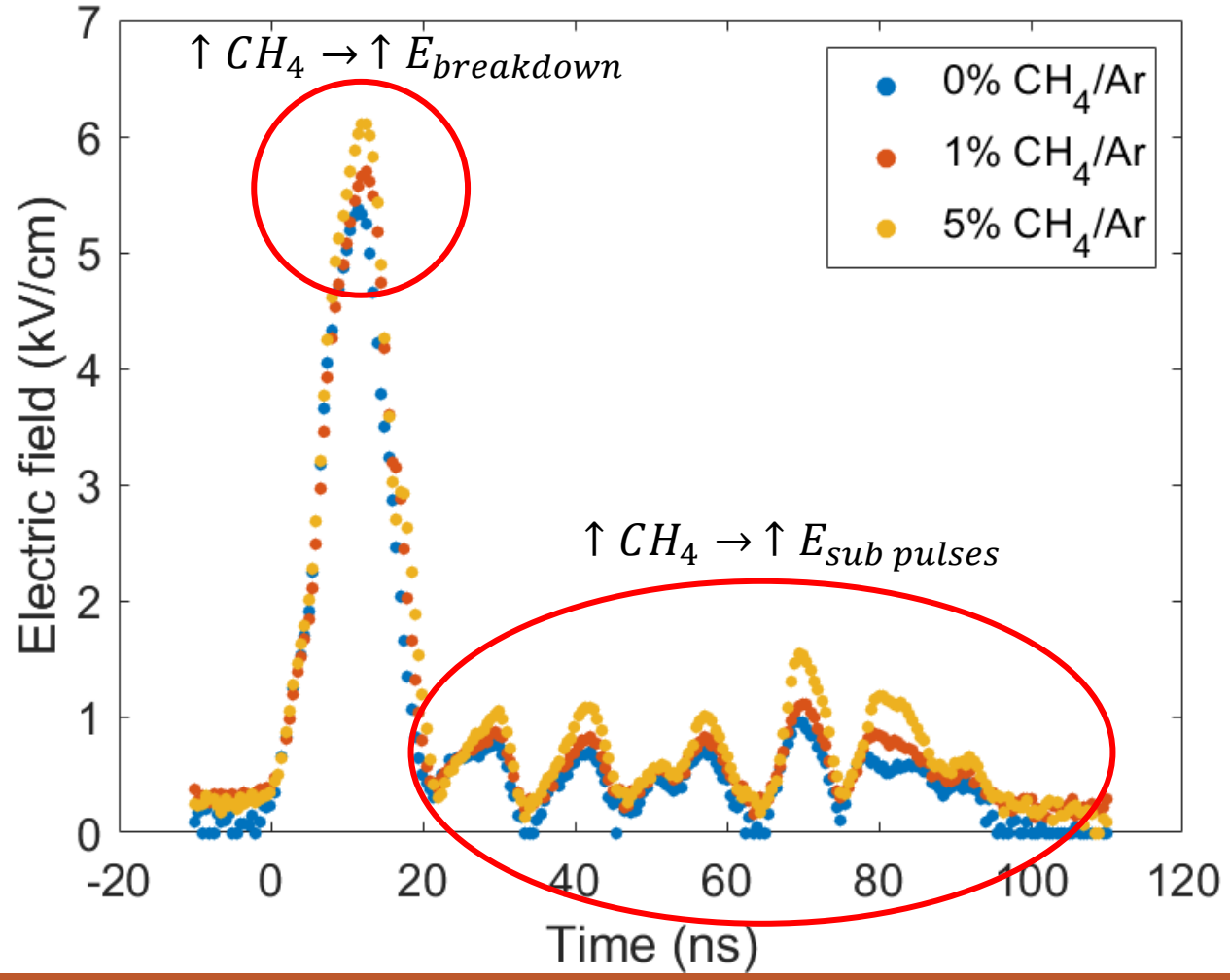
Can E-FISH help us understand T_e trends?



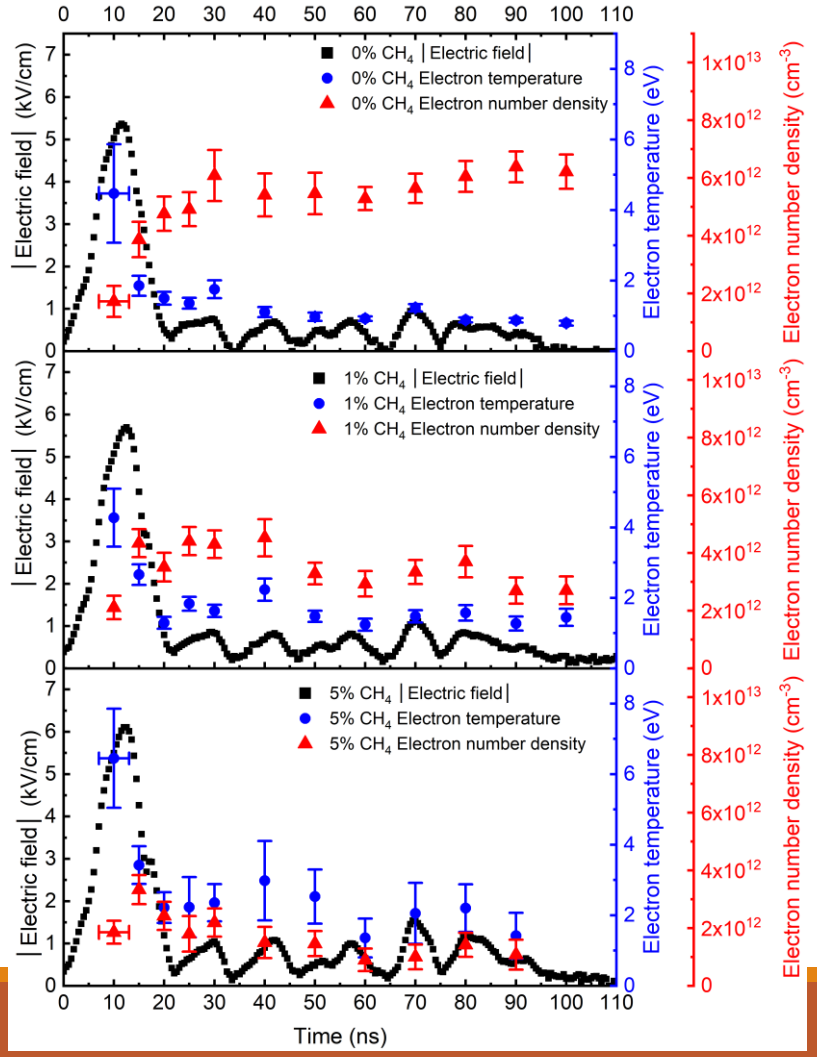
- 0.5 ns time steps, 80 fs pulses, 500 Hz voltage pulse repetition rate
- Averaged 800 laser shots per point, timing jitter <300 ps
- Calibrated with AC power supply



Higher CH_4 concentration leads to larger measured electric fields



From combined E, n_e, and T_e measurements, we can identify their coupling



Additional electron energy deposition pathways

$CH_4 \uparrow$

Ionization, **vibrational excitation, dissociation, attachment**

$n_e \downarrow$

Delay of breakdown and slower shielding of rapid applied field changes

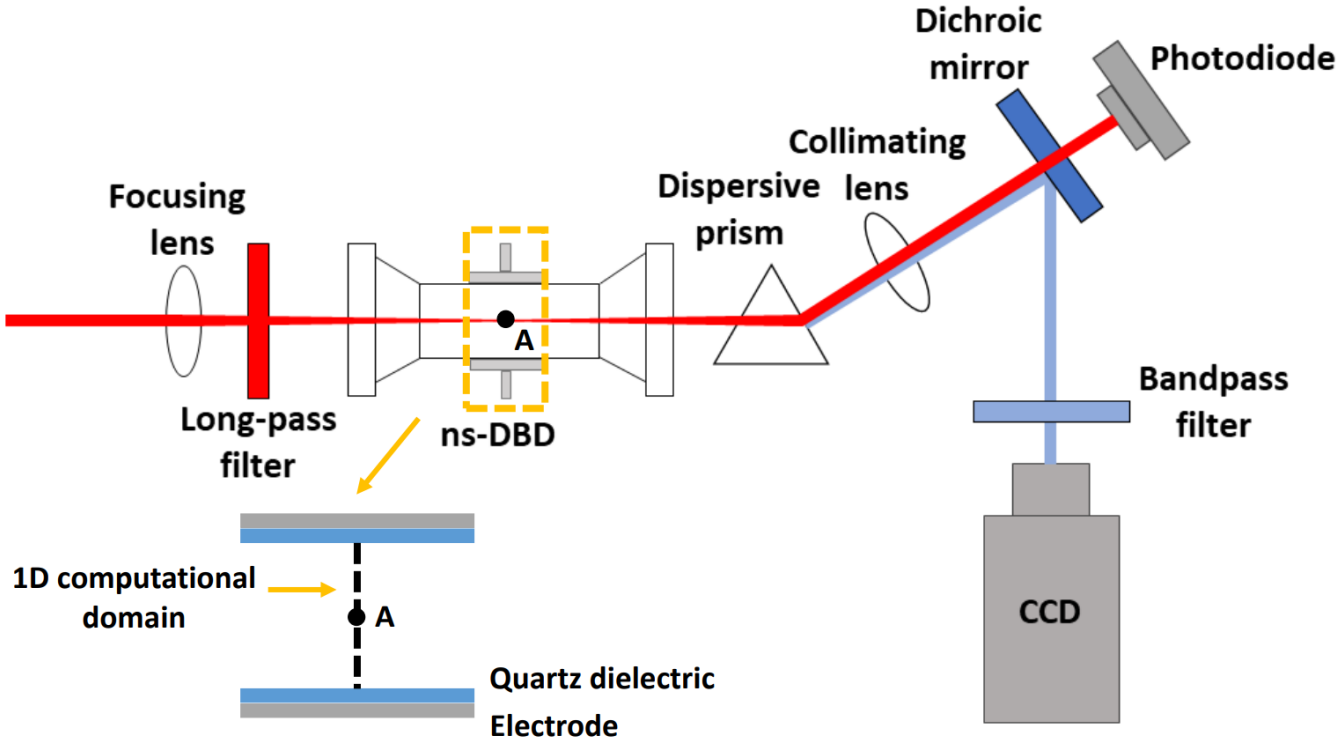
$E/N \uparrow$

$T_e \uparrow$

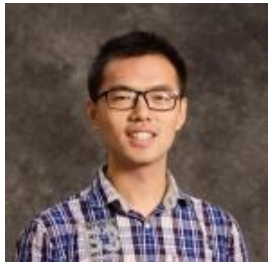
Heated electrons

Comparison with numerical modelling

1-D plasma kinetics model based off MARCS-PAC [16], 16 species, 48 reactions



Collaboration with Dr. Xingqian Mao and Hongtao Zhong

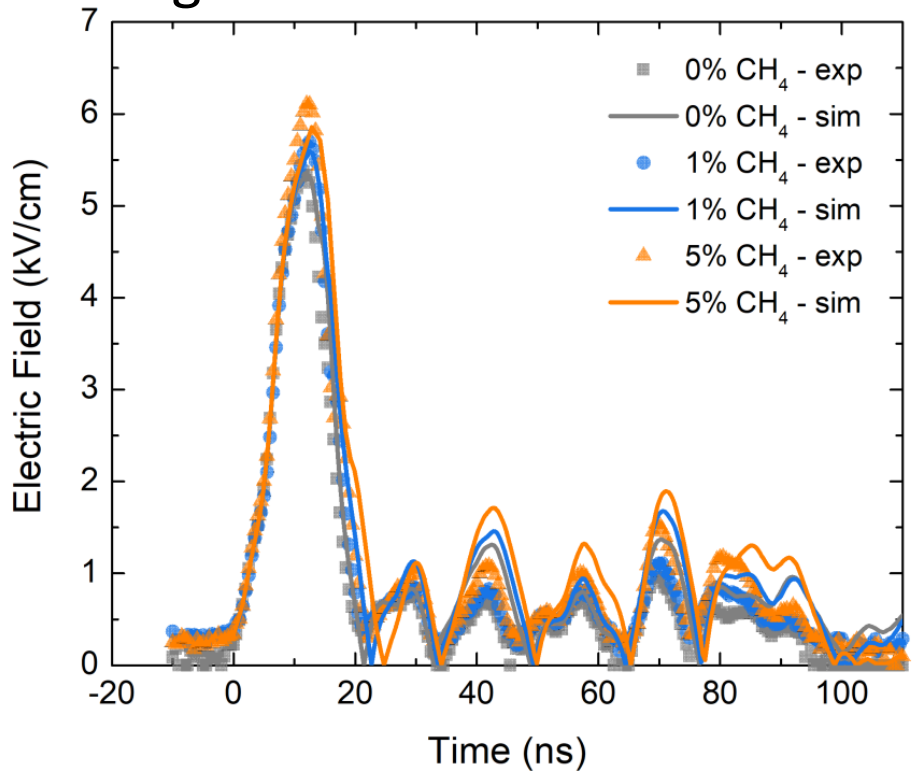


[16] X. Mao et al. Combust. Flame (2022)

Comparison with numerical modelling

1-D plasma kinetics model based off MARCS-PAC [16], 16 species, 48 reactions

Modelling matches the electric field trends well



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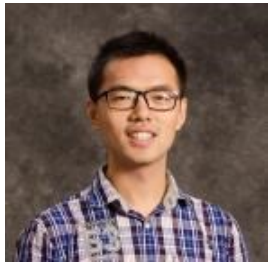
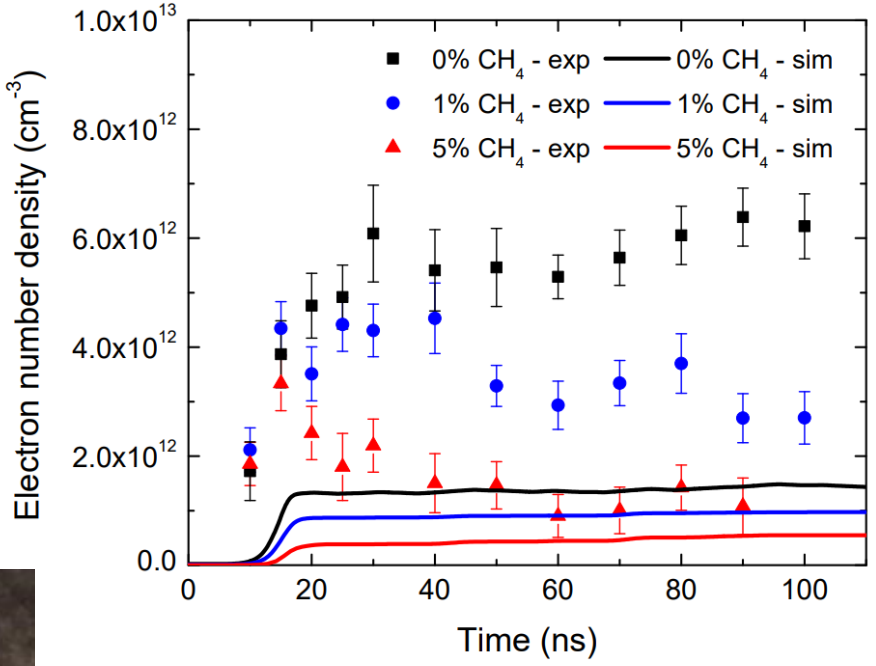


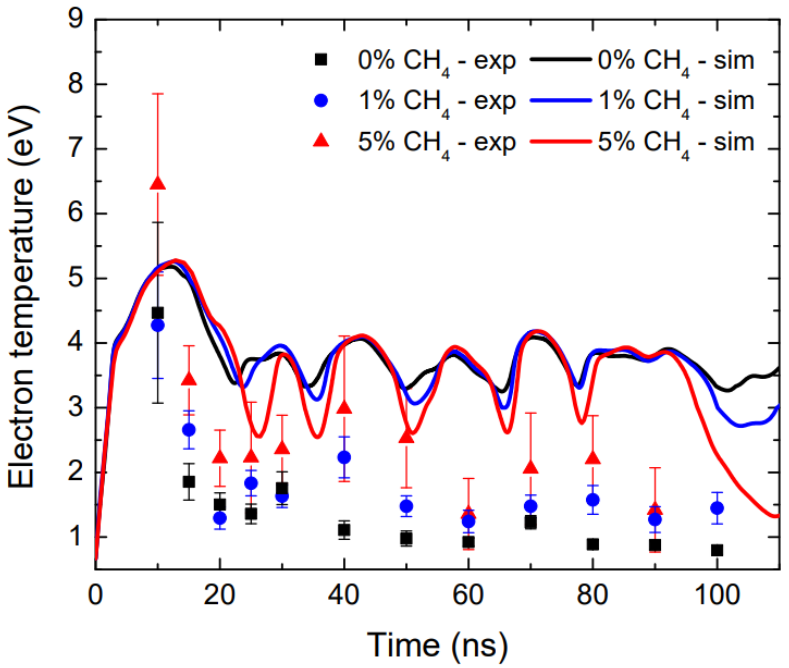
[16] X. Mao et al. Combust. Flame (2022)

Comparison with numerical modelling

But electron properties under and over predicted →

matching E does not guarantee T_e and n_e will be correct





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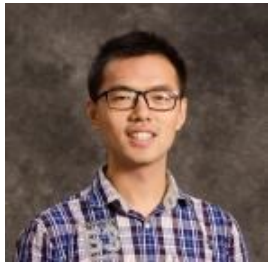


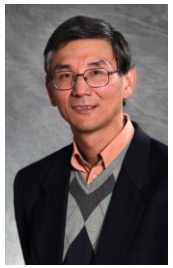
Need more multi-parameter measurements!

Conclusions

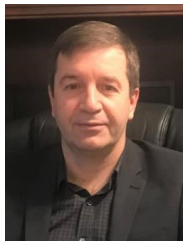
- Advances in CW to fs laser sources and *in situ* time-resolved laser diagnostics have enabled unprecedented ability to probe non-equilibrium plasmas and plasma chemistry
- Combined laser diagnostics and numerical modelling to better understand plasma CH_4 reforming
  - Radical-radical and ion reactions important pathways for products but rate constants uncertain
- Multi-parameter measurements of E, n_e, and T_e reveal how they vary due to CH_4 addition
  - Combination with numerical modelling show that validated E-fields do not guarantee quantitative prediction of n_e and T_e
  - **Need more multi-parameter measurements!**

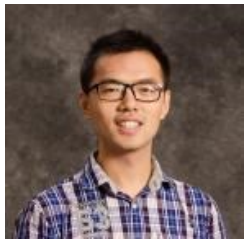
Acknowledgements

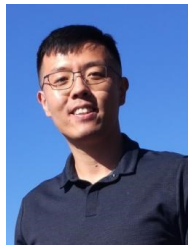
Thesis advisors: Yiguang Ju (Princeton) and Egemen Kolemen (Princeton)
Collaborators: Suo Yang (UMN), Taaresh Taneja (UMN), Christopher Kliewer (Sandia), Arthur Dogariu (Texas A&M) , Benjamin Goldberg (LLNL), Xingqian Mao (Princeton), Hongtao Zhong (Princeton) Aric Rousso (LLNL), Ning Liu (Princeton)







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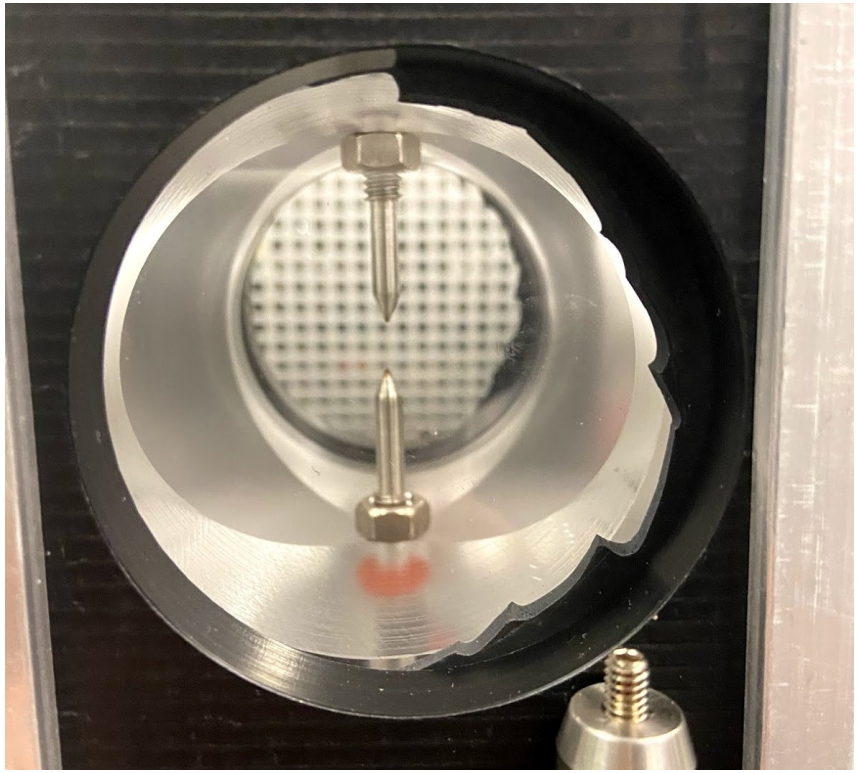
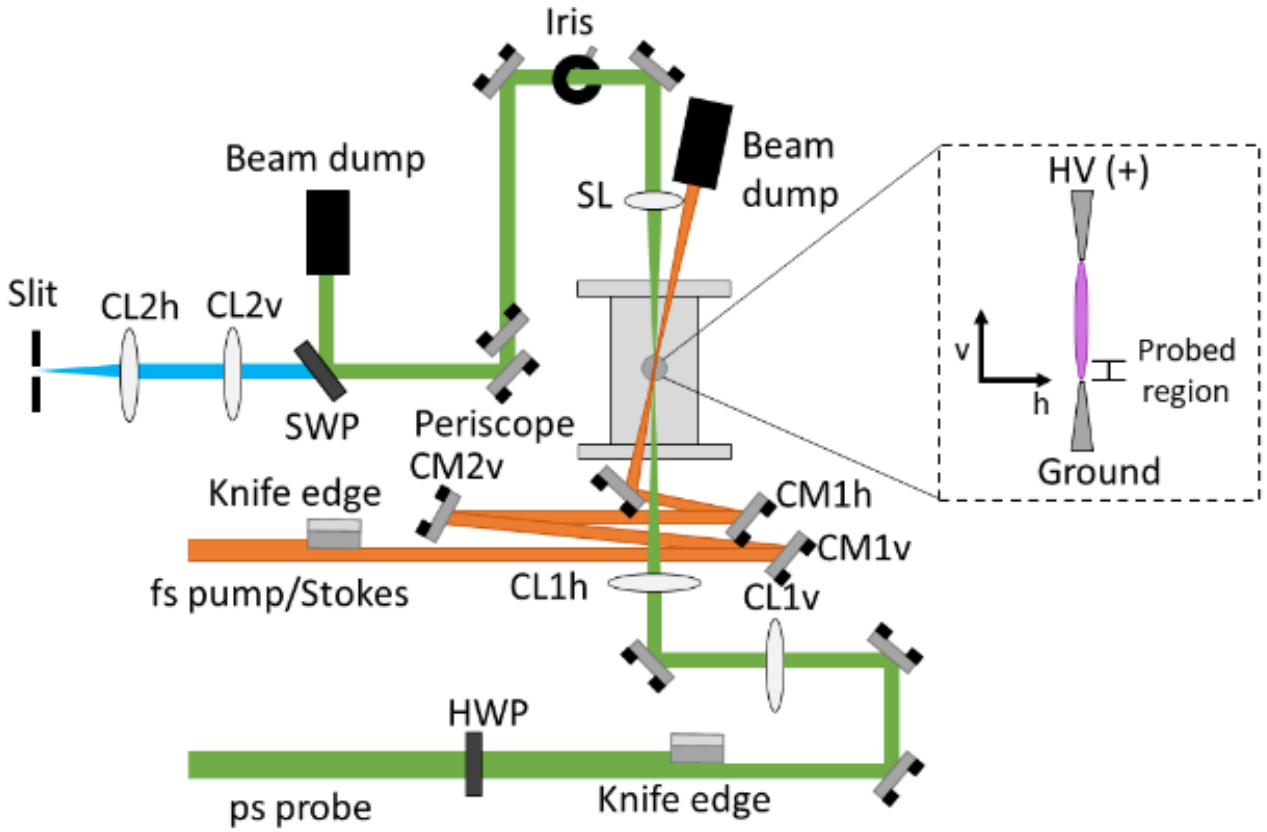
Questions?

Backup slides

Discharge geometry and experimental setup





- 40% CH_4, 60% N_2, 60 Torr
- 4 kV, 500 ns pulse width, 20 Hz, 8 mm gap, 220 Ω resistor
- fs laser: <7 fs, 0.6 mJ (bandwidth to CH_4 vibrations)

Chen T.Y. et al. Opt. Lett. *(2020)*

Is there a way to use rotational CARS to measure both rotational and vibrational temperatures?

Rotational energy level $F(v,J)$

$$F(v,J) = B_v\big(J(J+1)\big) - D_v(J^2(J+1)^2)$$

$$B_v = B_e - \alpha\left(v+\frac{1}{2}\right) + \gamma_e\left(v+\frac{1}{2}\right)^2$$

v = vibrational quantum number
J = rotational quantum number
B_v = rotational constant
α = rotation-vibration coupling constant
D_v = centrifugal constant

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$$B_v = B_e - \boldsymbol{\alpha}\left(\boldsymbol{v} + \frac{\mathbf{1}}{\mathbf{2}}\right) + \gamma_e\left(v + \frac{1}{2}\right)^2$$

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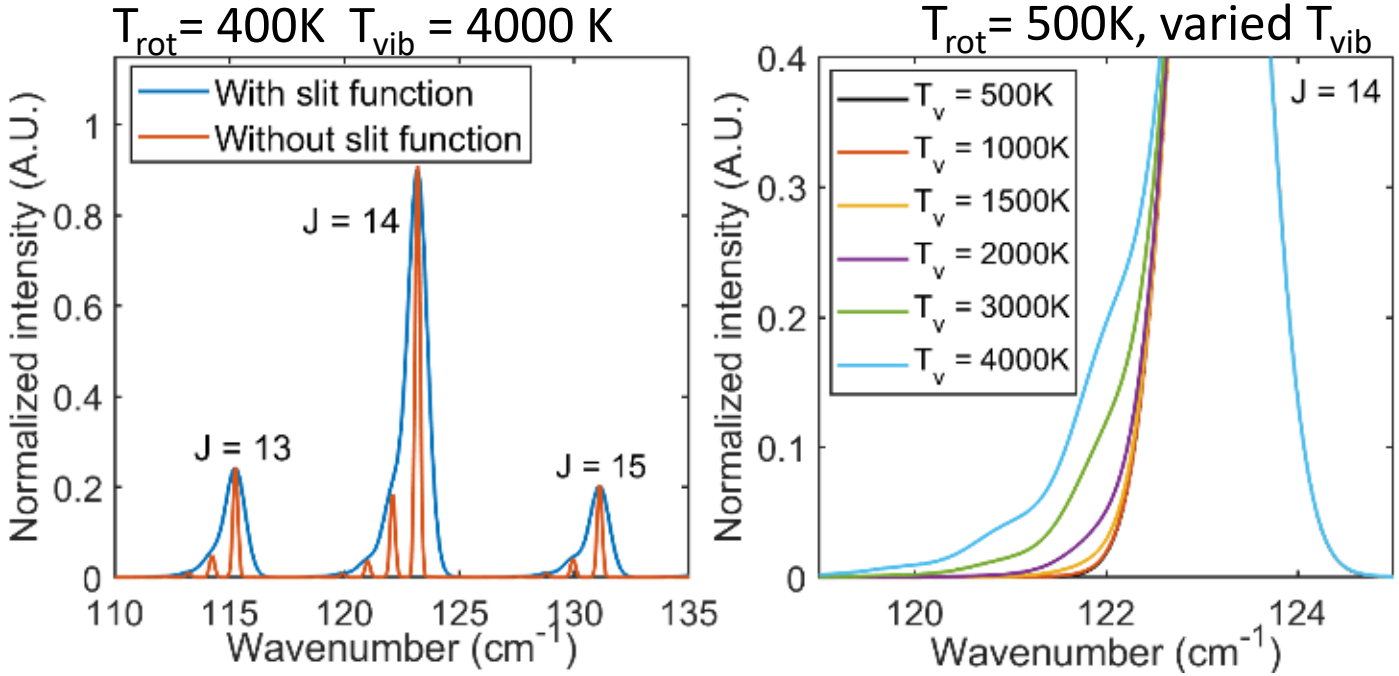
J = rotational quantum number
B_v = rotational constant
α = rotation-vibration coupling constant
D_v = centrifugal constant

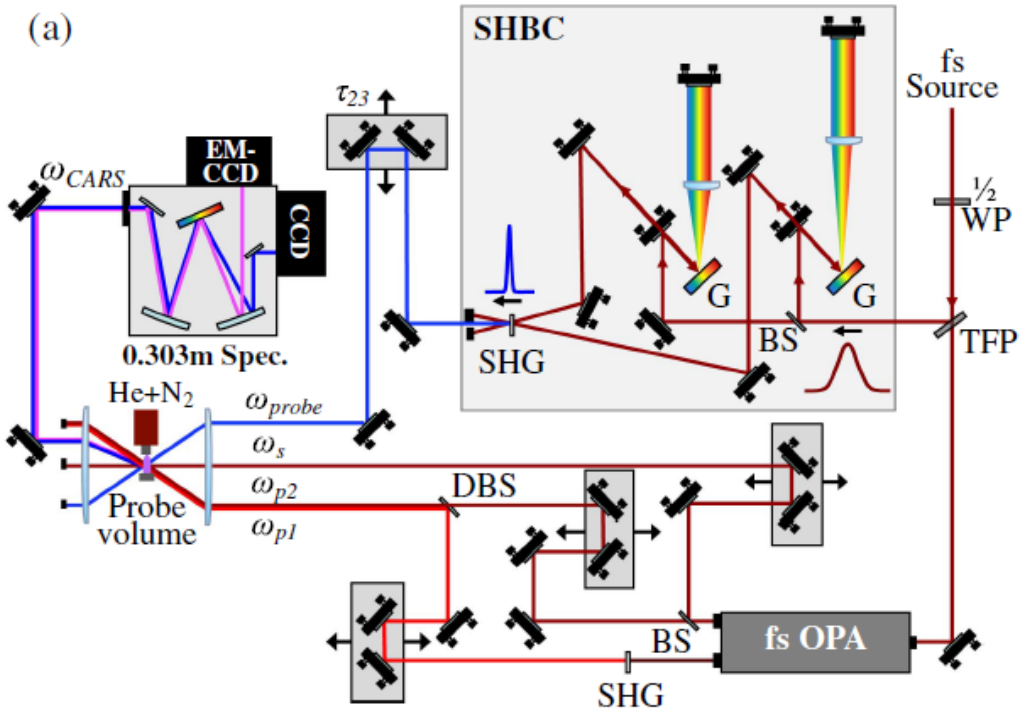
Simulated rotational N_2 CARS spectra



Chen T.Y. et al. Opt. Lett. *(2020)*

Is there a simpler method?

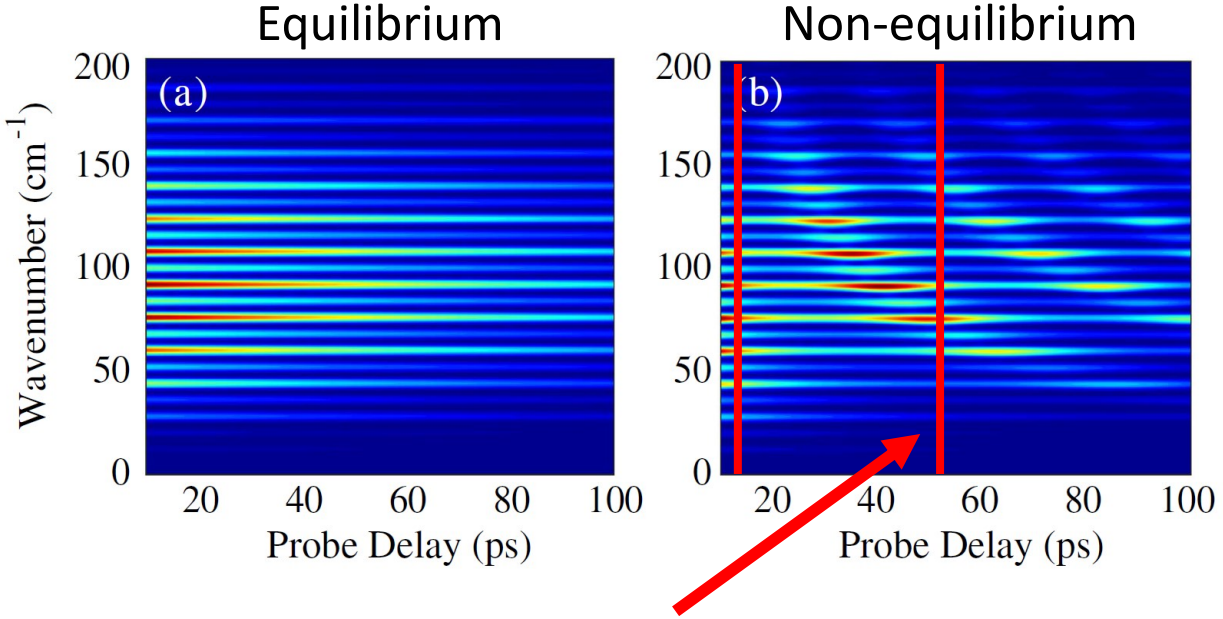
Dual pump fs/ps CARS is sensitive uses one fs laser but needs **4 beams**



Dedic, C.E. et al., *Optica*, (2017)

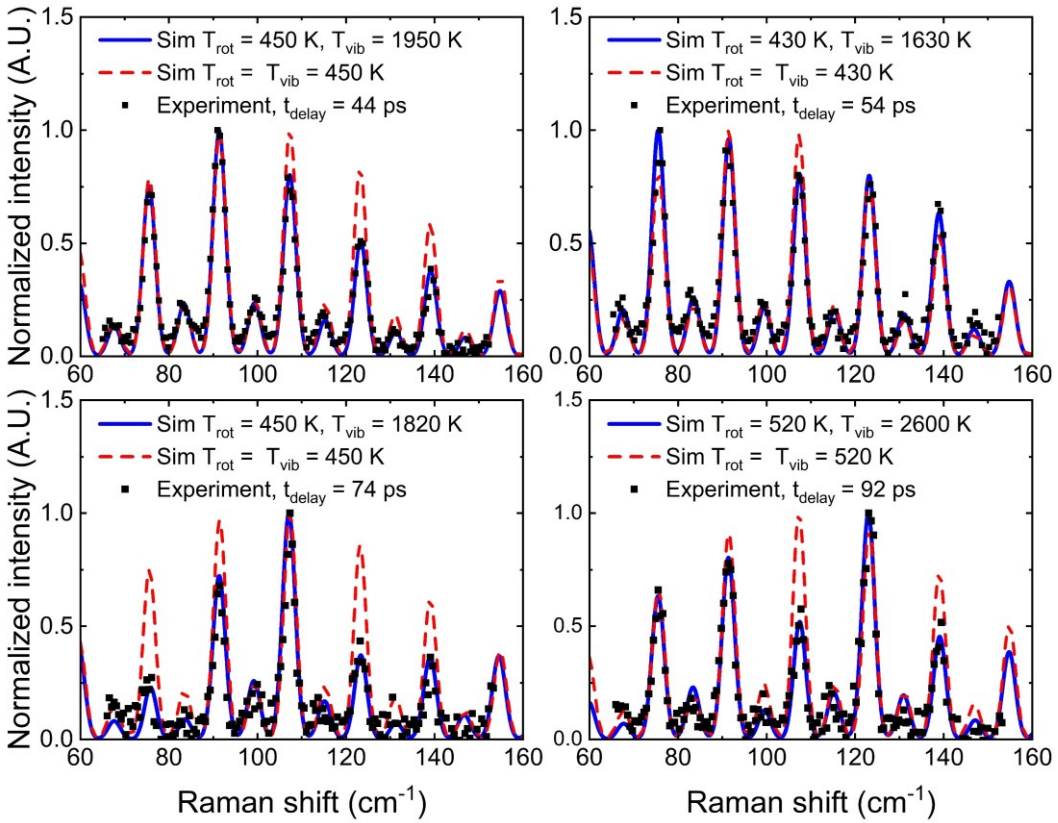
2 to 3 cm^{-1} probe bandwidth > 1 cm^{-1} vibrational shift

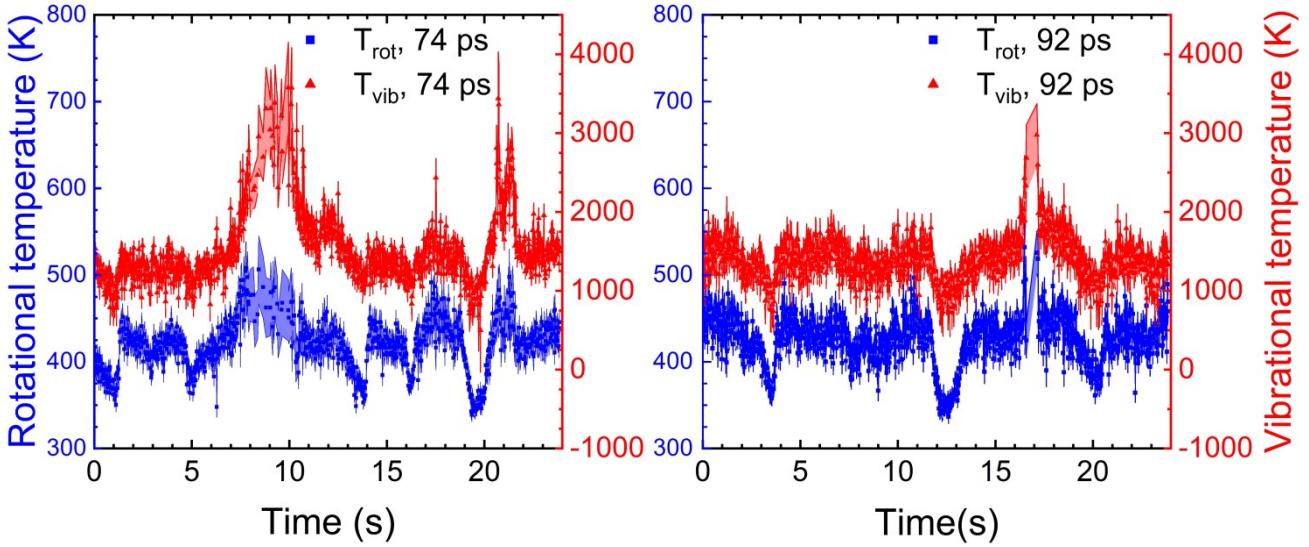
→ *coherence beating*



If we know probe delay and beating pattern, can we extract T_{vib} and T_{rot} ?

T_{rot} and T_{vib} can be simultaneously determined using coherence beating of pure rotational fs/ps CARS spectra!

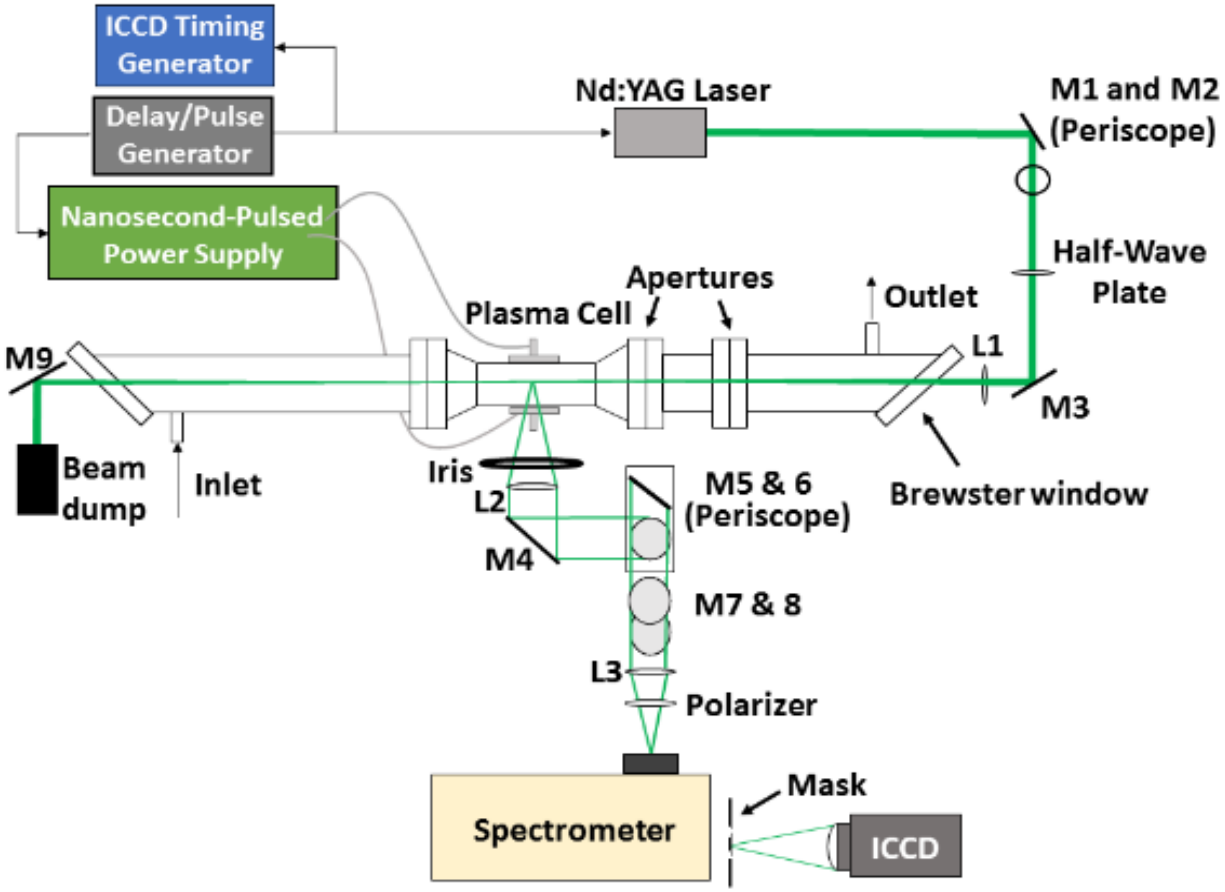




Chen T.Y. et al. Opt. Lett. *(2022)*

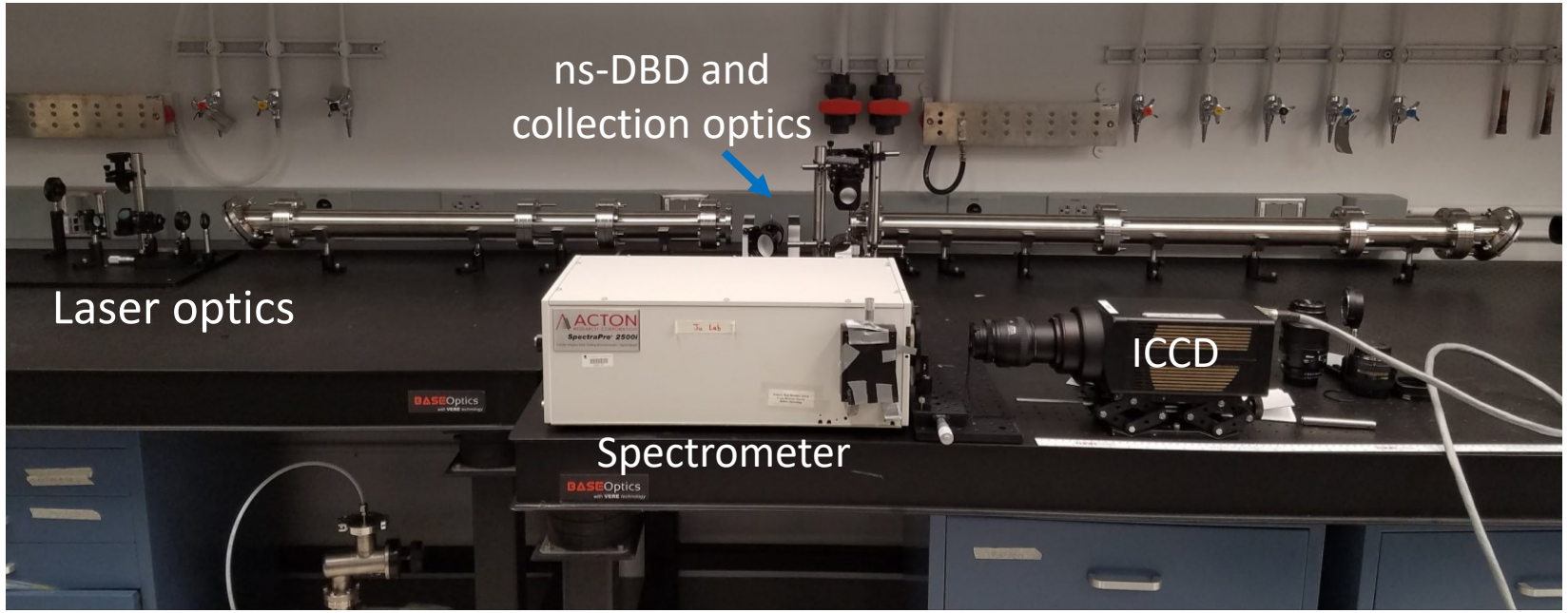
Thomson scattering setup (2019)

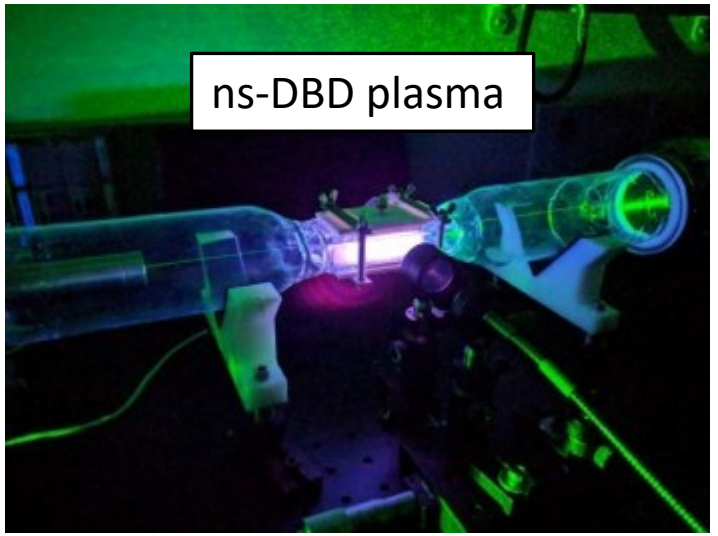
- Blackened aluminum mask blocks stray light at the spectrometer output
- Allows for background subtraction of remaining light to obtain Thomson scattering spectrum
- 2nd harmonic of Nd:YAG laser (532 nm), 230 mJ laser energy, 6 ns pulse width
- Plasma reactor:
  - Dielectric barrier discharge (DBD), 14 mm gap, 44.5 mm x 44.5 mm electrodes
  - 60 Torr, He bath gas, 0-2% CH_4, ~9kV, 12 ns pulse 100 Hz

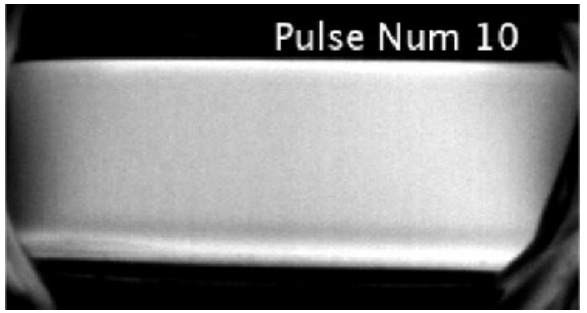


T.Y. Chen et al. J.Phys.D 2019

Thomson scattering setup

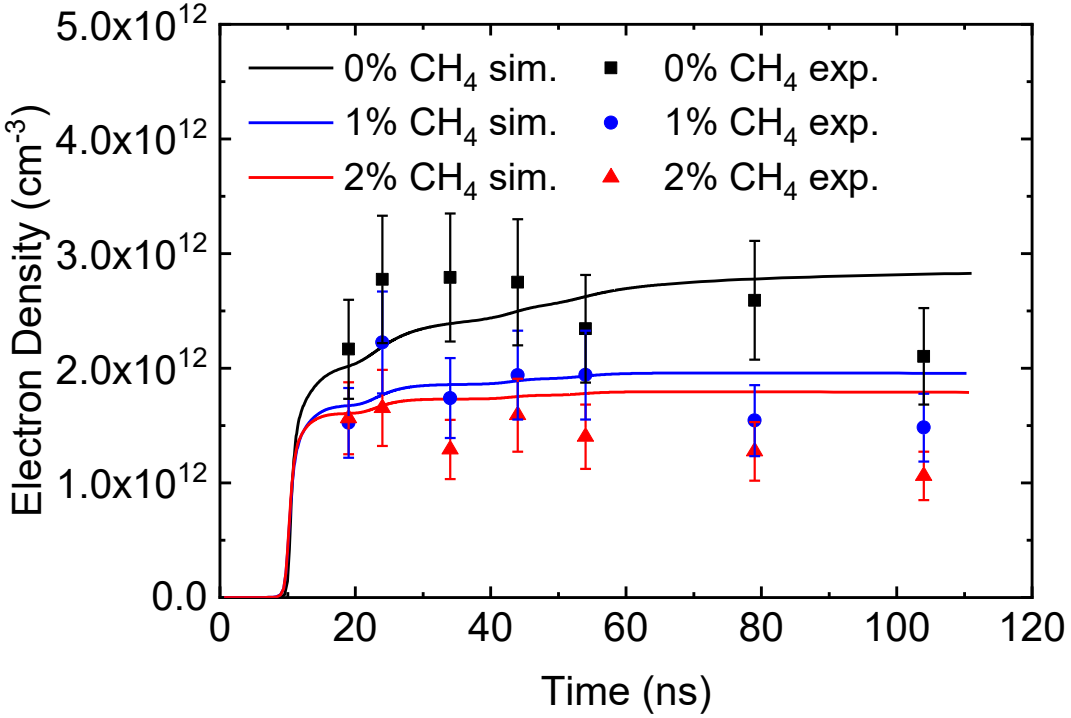


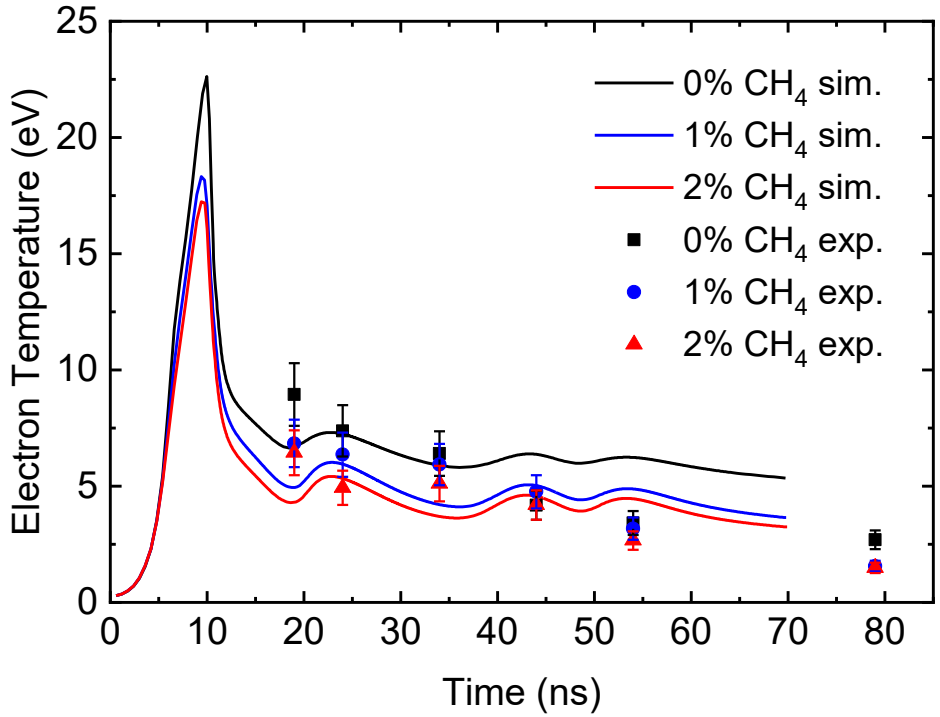




CH_4/Ar 1 μs gate image from Rousso et al. Plasma Sources Sci. Technol. (2020)

CH_4 addition decreases n_e and T_e





- More CH_4 → lower overall n_e and T_e
- Nonlinear decrease in n_e and T_e with CH_4 addition
- Both trends captured by model

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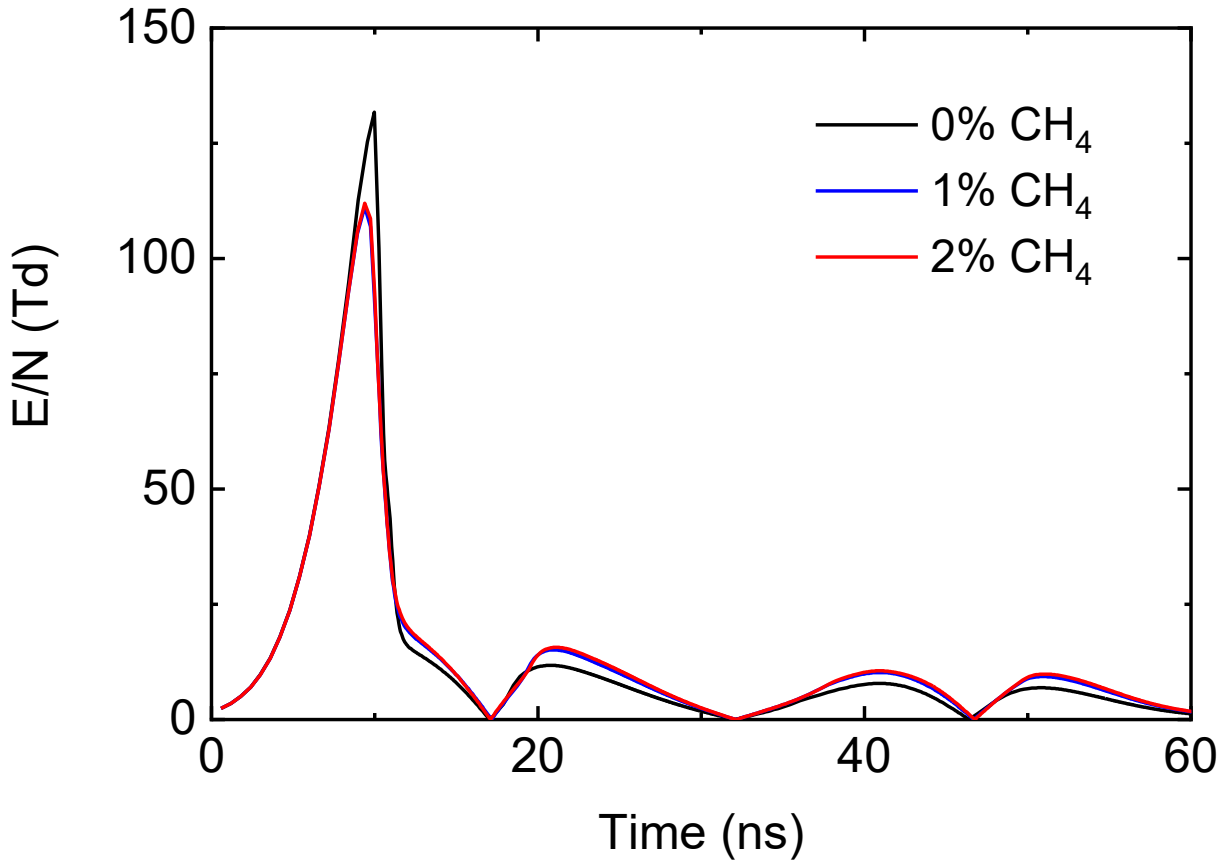
CH_4 addition to He has nonlinear effect on reduced electric field (E/N)

- Computed E/N shows significant difference between 0 and 1% CH_4
- Lower E/N suggests that breakdown occurs earlier due to lower ionization potential of CH_4
- Adding more CH_4 does not affect E/N
  - Additional differences due to increased electron-impact reactions with CH_4



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