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Time domain and level-specific investigations of collisions using picosecond two-color resonant four-wave-mixing spectroscopy: OH $X\,^2\Pi$ collisions in flames

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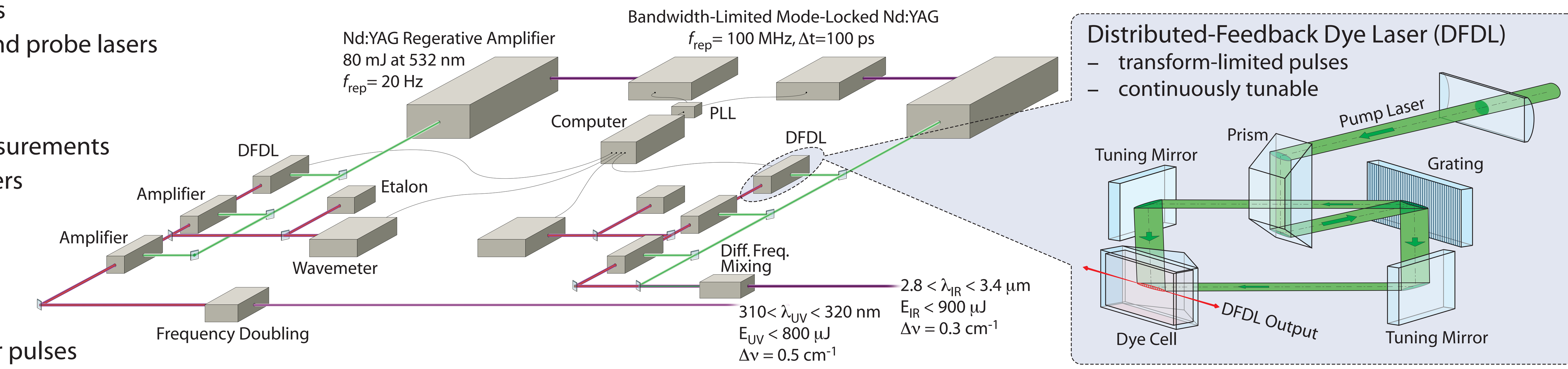
Overview

Time-resolved two-color resonant four-wave-mixing spectroscopy (TC-RFWM) provides a powerful means to investigate both inelastic and elastic collisions. This technique is demonstrated using custom-built picosecond laser systems, which produce nearly transform-limited laser pulses. The 50-ps pulses provide adequate time and spectral resolution for rotationally resolved studies of collisions affecting ground-state hydroxyl radicals in an atmospheric-pressure methane-air flame. The combination of double resonance, time-delayed probing, and independent control of the polarization of each of the four fields involved in the wave-mixing process enables rotational-level-specific measurement of the decay of laser-induced population, alignment, and orientation, as well as state-to-state transfer of these three moments.

Picosecond TC-RFWM for collision studies

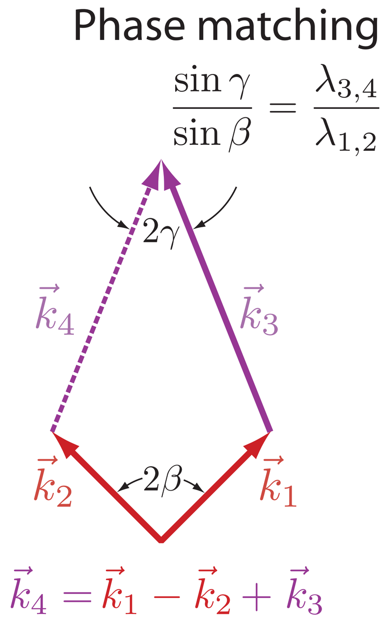
- Picosecond pump-probe technique
  - direct measurement of collision rates in time domain
  - requires sufficiently ***short*** laser pulses
  - requires ***synchronization*** of pump and probe lasers
- Two-color (double resonance)
  - enables rotational-level-specific measurements
  - requires sufficiently ***narrowband*** lasers
- Coherent spectroscopy ($\chi^{(3)}$ process)
  - sensitve to alignment/orientation
  - immune to background in flames
  - requires sufficiently ***high-power*** laser pulses

Custom picosecond laser system enables time-domain studies in atmospheric-pressure flames

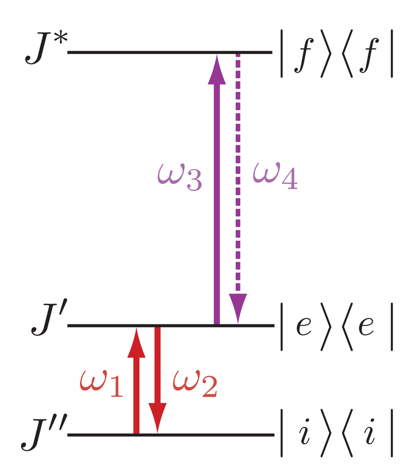


Experimental parameters dictate relevant wave-mixing physics

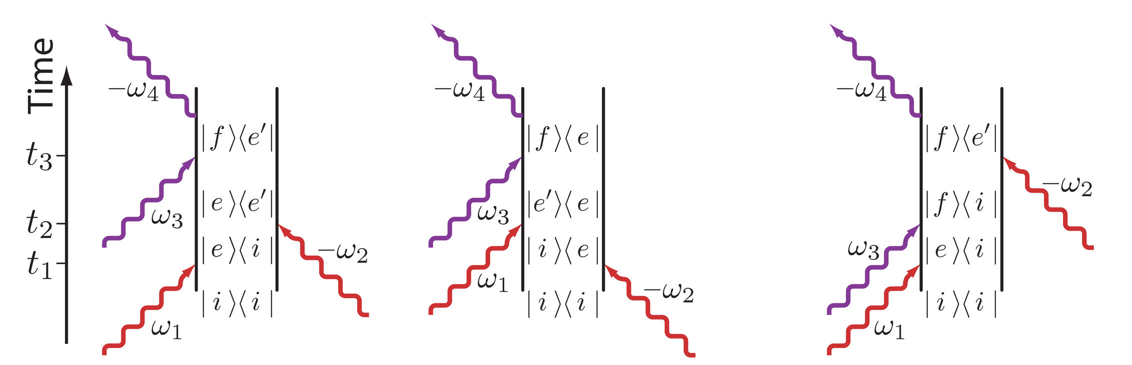
Phase matching



Pump/probe tuning



Time ordering of photon-molecule interactions



Two pump-molecule interactions at $t=t_1, t_2$ produce an intermediate-state grating, $\rho^{(2)}(t_2) = |e\rangle\langle e|$, that evolves, field-free, under the influence of collisions.

$$\rho^{(2)}(t; t_2 \le t \le t_3) = \rho^{(2)}(t_2)\, e^{\Gamma_{K_2}^{J_e}(t-t_2)}$$

Time-delayed pulse probes collisional decay rates $\Gamma_{K_2}^{J_e}$.

The additional coherent interaction, shown above, contributes to the signal only when the two pump pulses and the probe pulse are overlapped in time.

Polarization dependence of time-domain TC-RFWM

The contribution to the signal electric field with polarization $\vec{\epsilon}_4$ resulting from each relevant Feynman diagram can be expressed as follows using diagrammatic pertubation theory.

$$[\mathbf{P}^{(3)} \cdot \vec{\epsilon}_4^{\,*}] = C\,\Phi \sum_K F(\vec{\epsilon}_1\vec{\epsilon}_2\vec{\epsilon}_3\vec{\epsilon}_4; K)\, G(J''J'J^*; K)$$

Spherical tensor analysis is used to express the problem in terms of the three ranks, K, of the state multipoles.

- $K=0$ Population
- $K=1$ Orientation
- $K=2$ Alignment

The constant C contains the signal dependence on molecular number density, pump and probe field amplitiudes, and transition linestrengths.

$$C = \frac{N_i\,\mathcal{E}_1\mathcal{E}_2\mathcal{E}_3}{8i\hbar^3}\,\frac{|\langle J^*||\mu^{(1)}||J'\rangle|^2}{2J'+1}\,\frac{|\langle J'||\mu^{(1)}||J''\rangle|^2}{2J''+1}$$

The phase term for the first two Feynman diagrams on the left is given below. The second exponential term describes dephasing resulting from motion of molecules forming the intermediate-state grating $\vec{k}_G = \vec{k}_1 - \vec{k}_2$.

$$\Phi = e^{-i(\omega_4 t - \vec{k}_4\cdot\vec{r})}\, e^{-i\vec{v}\cdot[\vec{k}_4(t_4-t_3) + \vec{k}_G(t_3-t_2)]}\, e^{-\Gamma_{fe}(t_4-t_3)}$$

The signal dependence on electric-field polarization is contained in F. Control of polarization can be used to ensure signal is dependent only on population or orientation or alignment by forcing $F \neq 0$ for only one K.

$$F(\vec{\epsilon}_1\vec{\epsilon}_2\vec{\epsilon}_3\vec{\epsilon}_4; K) = \sum_{Q_1Q_2Q_3} (-1)^{K-Q_2}(2K+1)(\vec{\epsilon}_1)^{(1)}_{-Q_1}(\vec{\epsilon}_2^{\,*})^{(1)}_{Q_1-Q_2}(\vec{\epsilon}_3)^{(1)}_{Q_2-Q_3}(\vec{\epsilon}_4^{\,*})^{(1)}_{Q_3} \times \begin{pmatrix} 1 & 1 & K \\ Q_1 & Q_2-Q_1 & -Q_2 \end{pmatrix}\begin{pmatrix} 1 & 1 & K \\ Q_3 & Q_2-Q_3 & -Q_2 \end{pmatrix}$$

G contains dependencies on the spectroscopic transition branches and the decay rates $\Gamma_K^{J'}$ for the $K^{\rm th}$ moment of the intermediate level J'.

$$G(J''J'J^*; K) = (2J'+1)\begin{Bmatrix} 1 & 1 & K \\ J' & J' & J'' \end{Bmatrix}\begin{Bmatrix} 1 & 1 & K \\ J' & J' & J^* \end{Bmatrix} e^{-\Gamma_K^{J'}(t_3-t_2)}$$

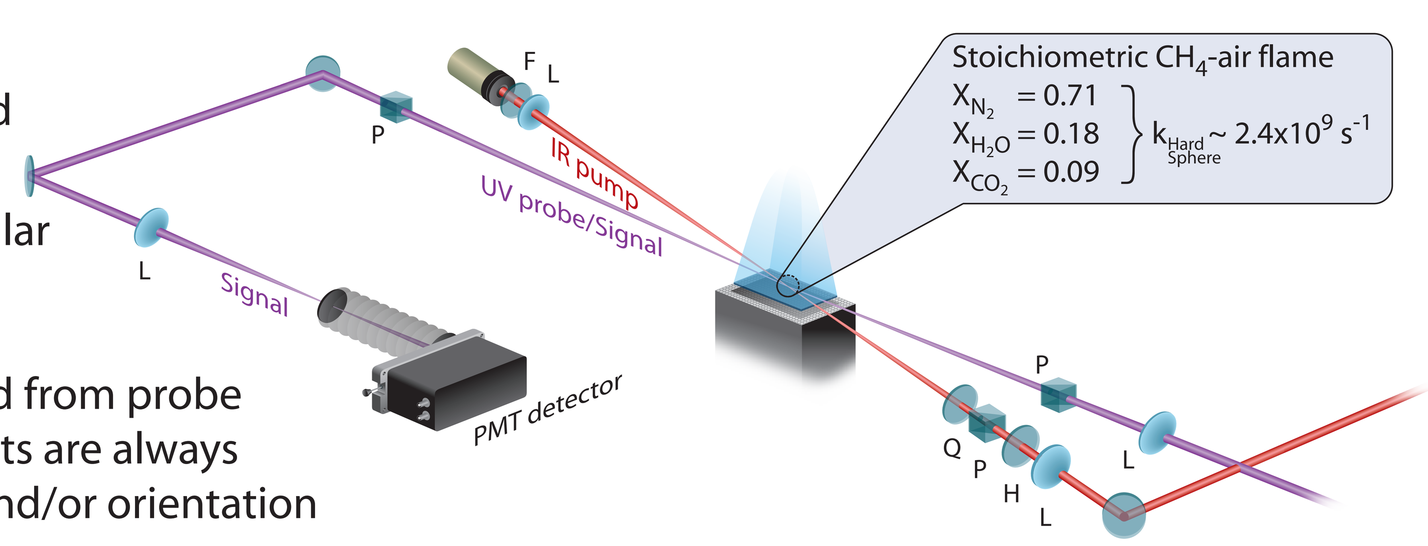
Polarization/excitation schemes

$$|F(\vec{\epsilon}_1\vec{\epsilon}_2\vec{\epsilon}_3\vec{\epsilon}_4; K)\, G(J''J'J^*; K)|\; e^{+\Gamma_K^{J'}(t_3-t_2)}$$

	$K=0$	$K=1$	$K=2$
Population			
CC ↑ ↑ P P	$\frac{1}{9.07}$	0	$\frac{1}{177}$
CC ↑ ↑ P Q	$\frac{1}{9.07}$	0	$\frac{1}{177}\frac{2J'-1}{J'+1}$
→→ ↑ ↑ P Q	$\frac{1}{9.14}$	0	$\frac{1}{91.4}\frac{2J'-1}{J'+1}$
Pump "magic angle" ~ 54.9° (phase match: $\beta=5^\circ$, $\gamma=1^\circ$)			
↗↗ ↑ ↑ P P	$\frac{1}{9.09}$	0	0
Orientation			
CC ↑ → P P	0	$\frac{1}{12.05}$	$\frac{1}{39{,}400}$
CC ↑ → P Q	0	$\frac{1}{12.05}\frac{1}{J'+1}$	$\frac{1}{39{,}400}\frac{2J'-1}{J'+1}$
Alignment			
↗↗ ↑ → P Q	0	$\frac{1}{7{,}890}\frac{1}{J'+1}$	$\frac{1}{60.2}\frac{2J'-1}{J'+1}$

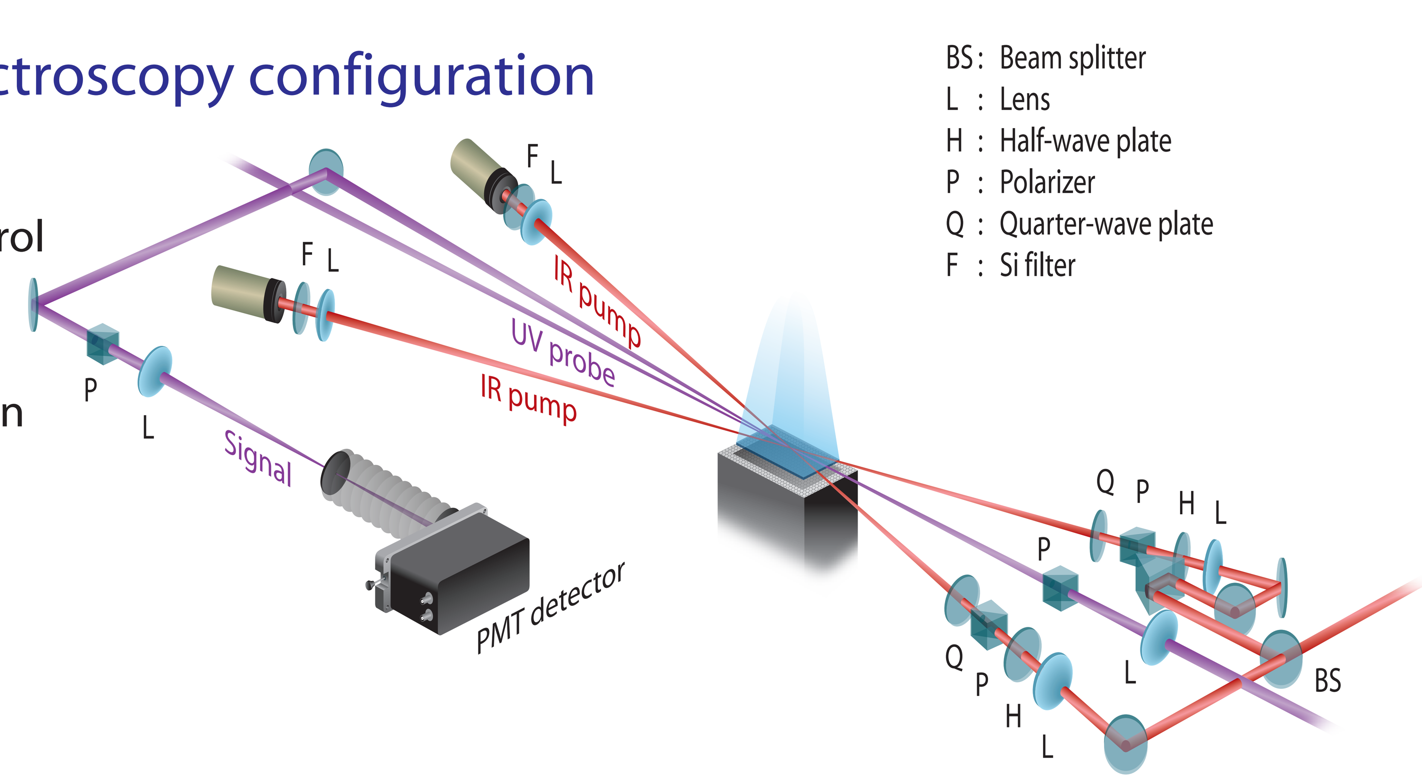
Two-beam, polarization spectroscopy configuration

- Simplest set-up
- Automatically phase matched
- Detect component of signal with polarization perpendicular to probe polarization
  - $\vec{\epsilon}_4 \perp \vec{\epsilon}_3$
  - Susceptible to background from probe
  - Collision rate measurements are always influenced by alignment and/or orientation

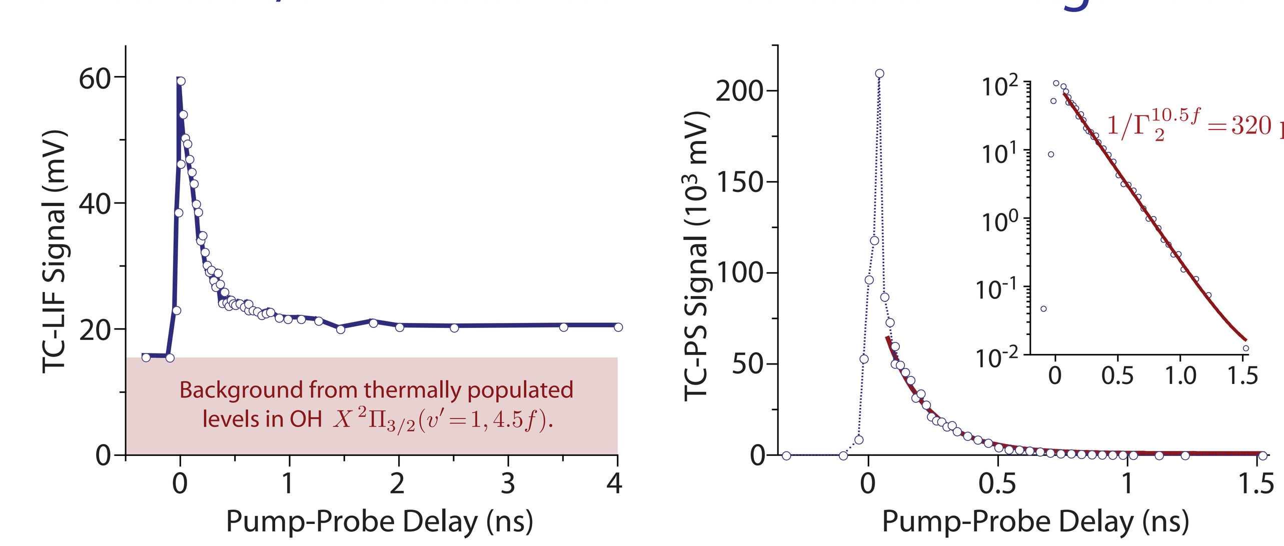


Four-beam, grating spectroscopy configuration

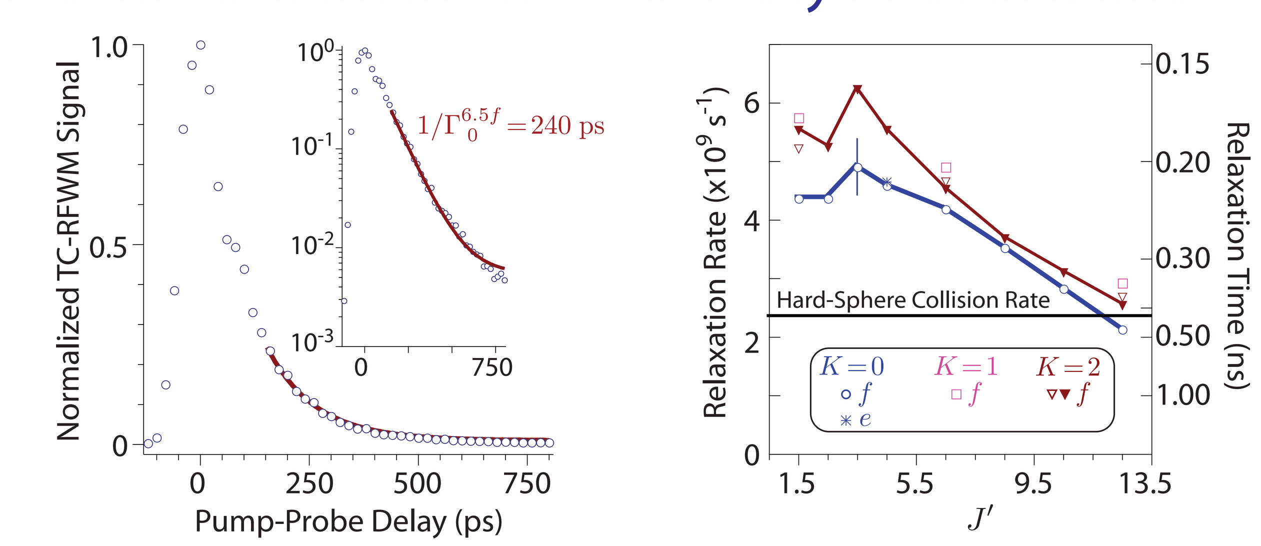
- Phase matching is critical
- Complete experimental control over polarization of all three waves driving $\chi^{(3)}$
- Polarization-specific detection
  - population
  - orientation
  - alignment



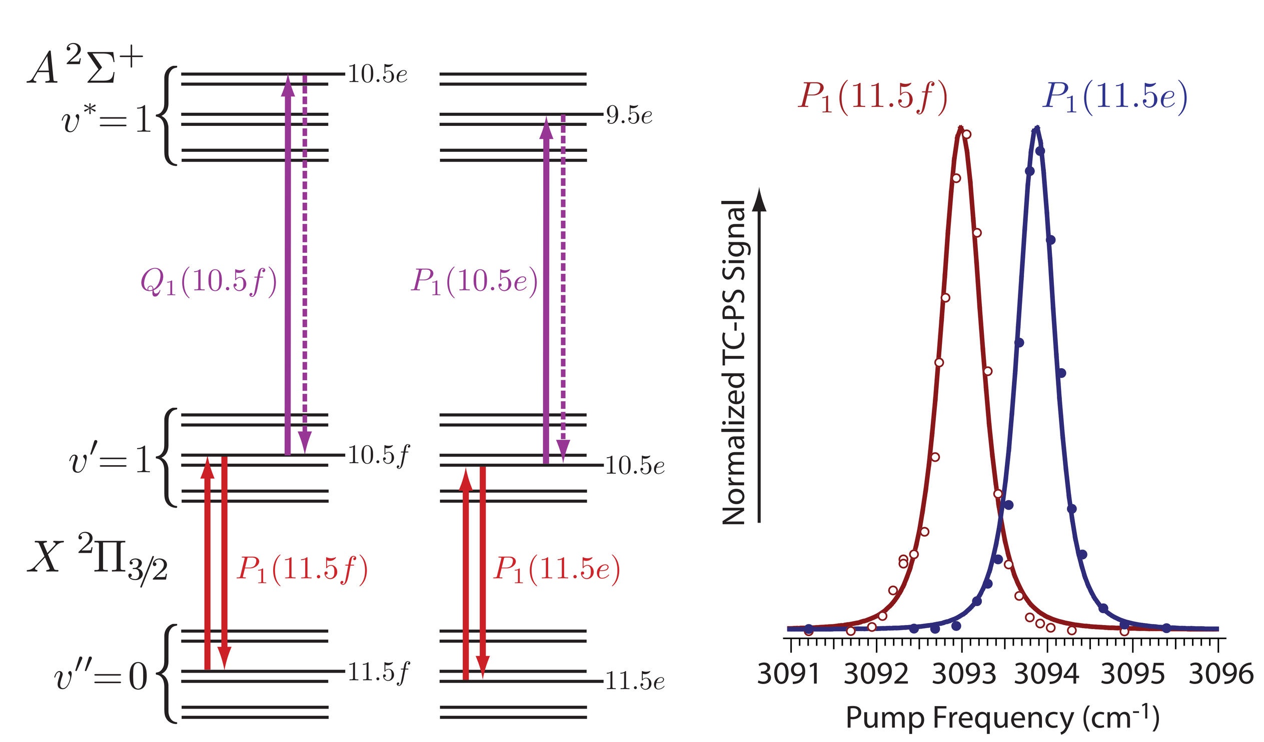
TC-RFWM/PS is immune to thermal background



Direct measurement of total decay rates in flame



Λ-doublet resolution and sub-ns time resolution



Level-to-level transfer of population/anisotropy