the Crim Group

Vibrationally Mediated Chemistry™

Ultrafast Study of Bromine Radical in Solution

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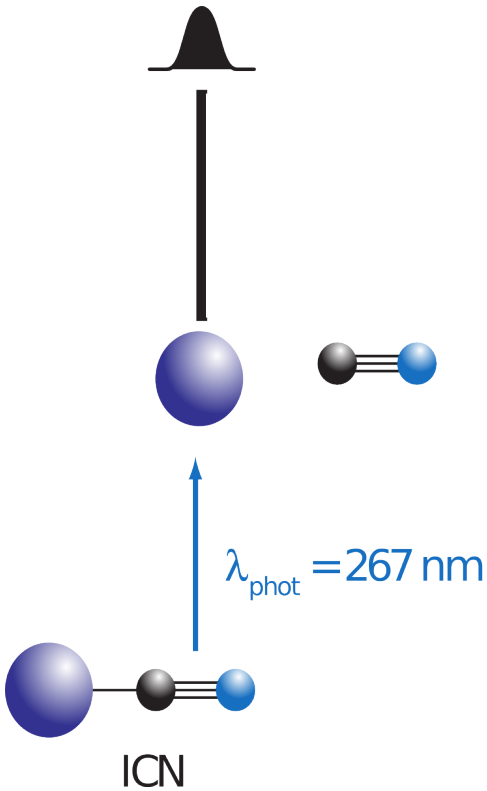
THE UNIVERSITY of WISCONSIN MADISON

Outline

- Previous work on CN
- Bromine system and goals
- Experimental apparatus
- Data and proposed scheme
- Vibrational mediation

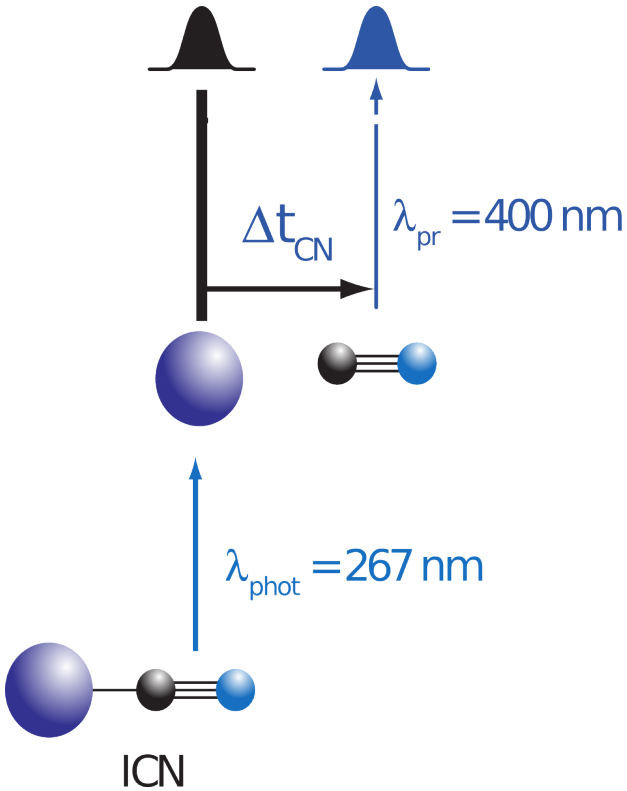
Previous Adventure: ·C≡N



- Photolytic generation of radical (ICN)

Crowther...Crim, JPCA, 2008

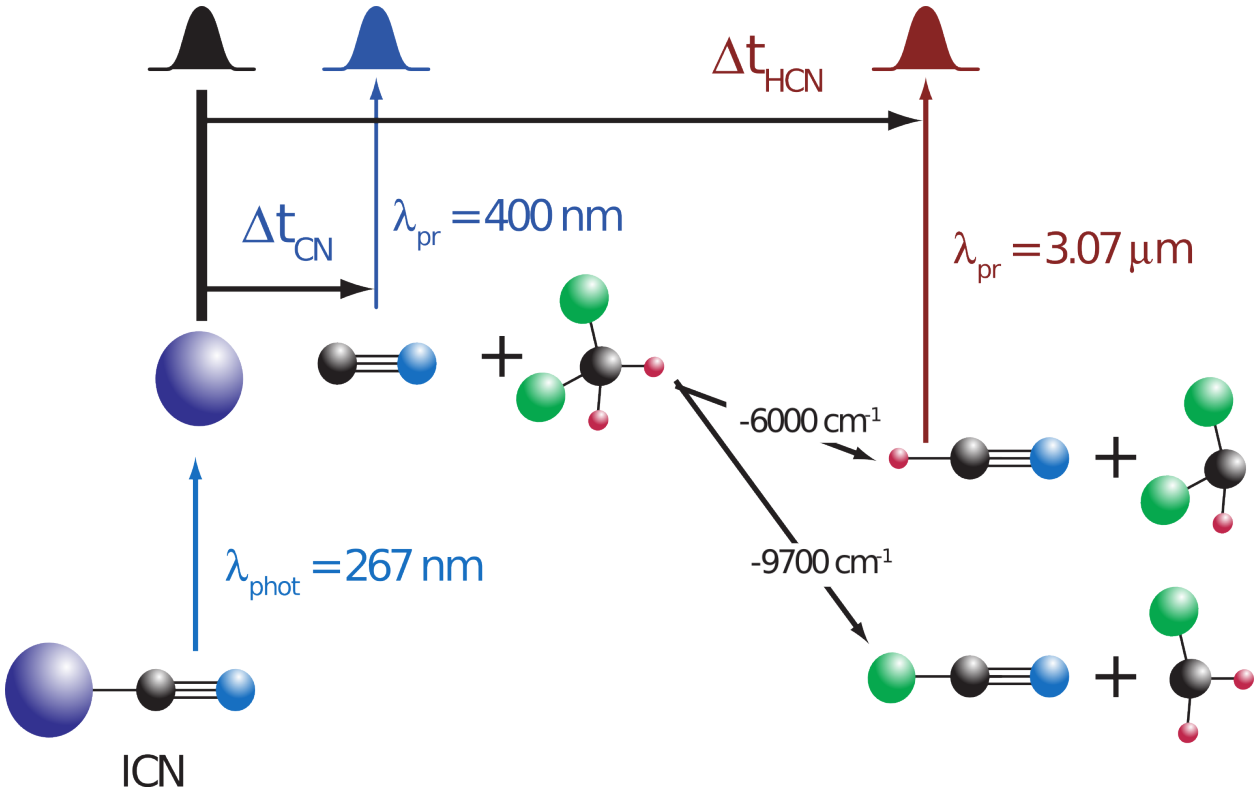
Previous Adventure: ·C≡N



- Photolytic generation of radical (ICN)
- 400-nm probe of ·C≡N decay

Crowther...Crim, JPCA, 2008

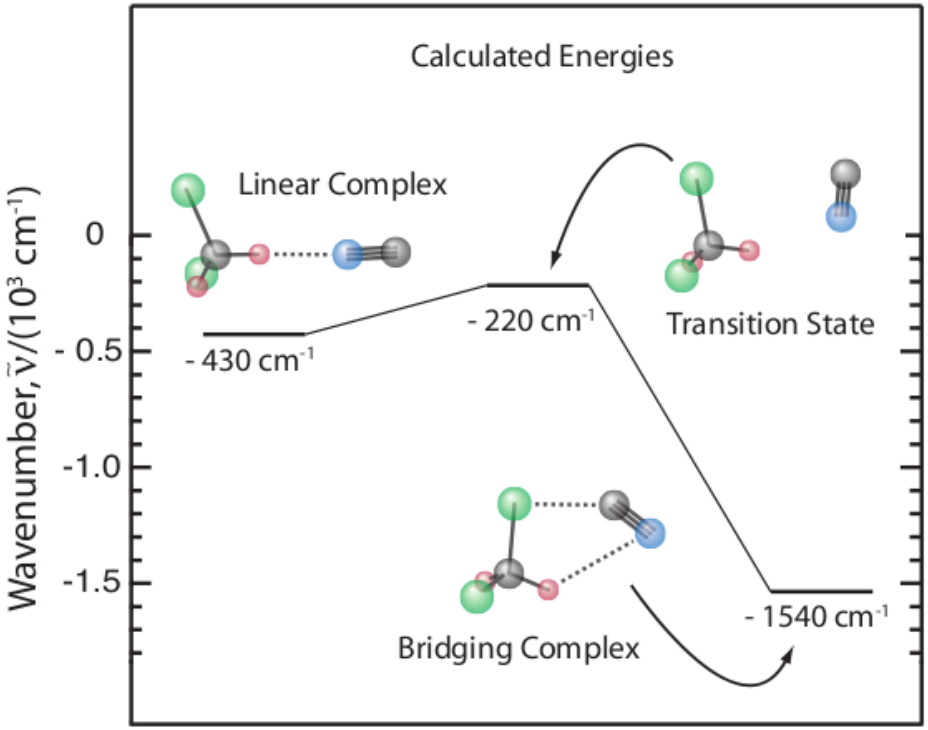
Previous Adventure: ·C≡N



- Photolytic generation of radical (ICN)
- 400-nm probe of ·C≡N decay
- IR probe of HCN rise

Crowther...Crim, JPCA, 2008

Previous Adventure: C≡N·



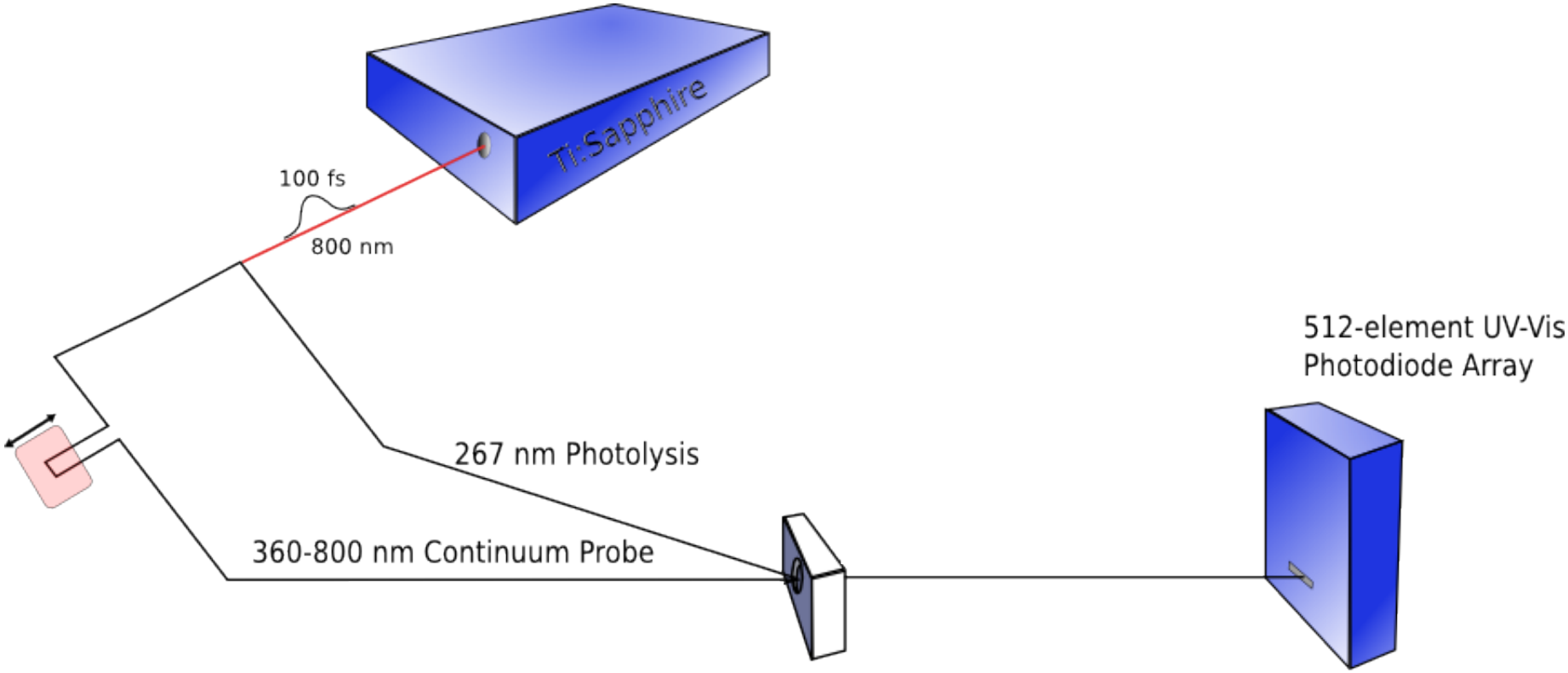
- Two stable complexes with different kinetics
- Complexes do the chemistry in solution

Crowther...Crim, JPCA, 2008

Current System: Br·

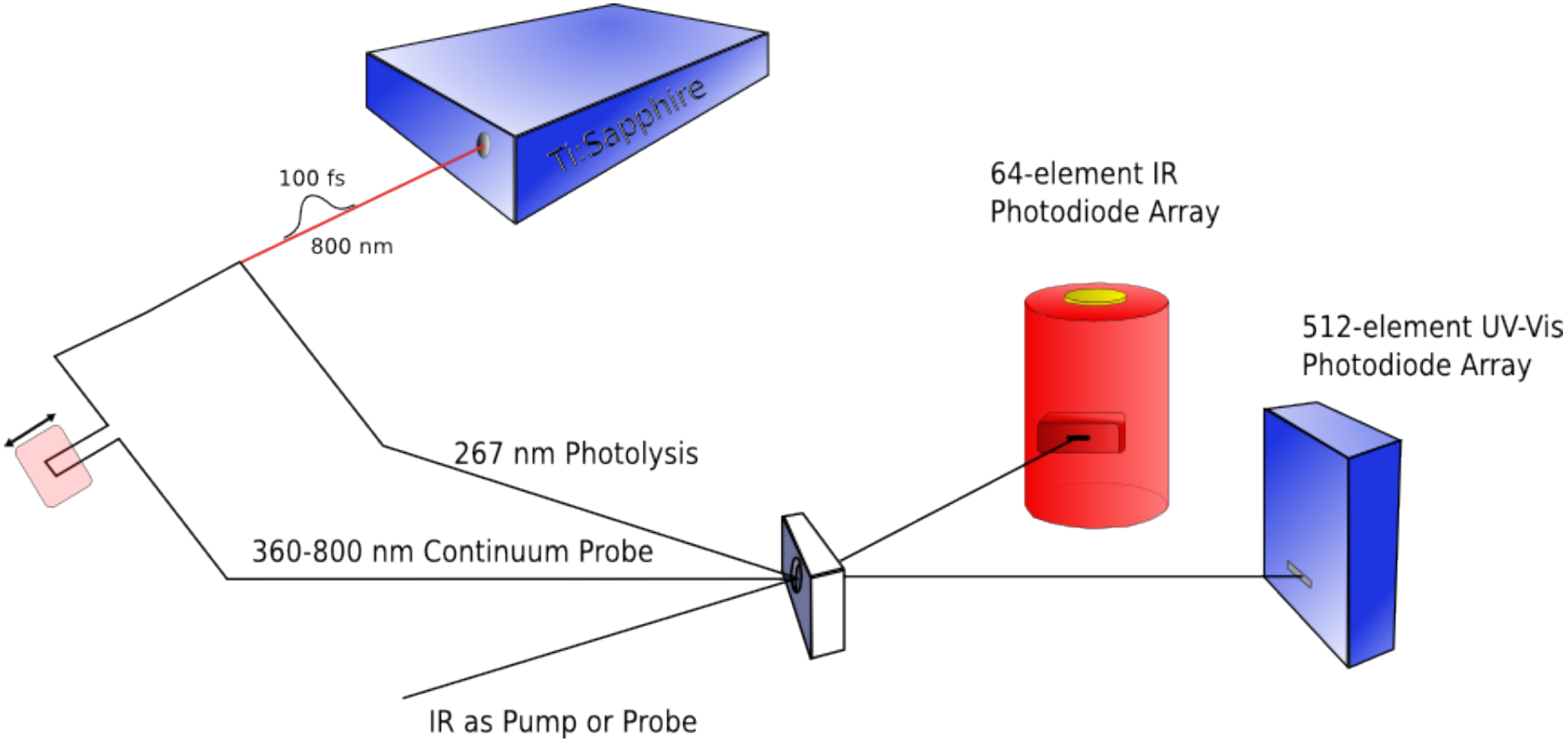
- Generate Br· ($CHBr_3$,CH_2Br_2)
- Probe Br· complex (310-700 nm)
- Drive reaction with IR excitation

Experiment

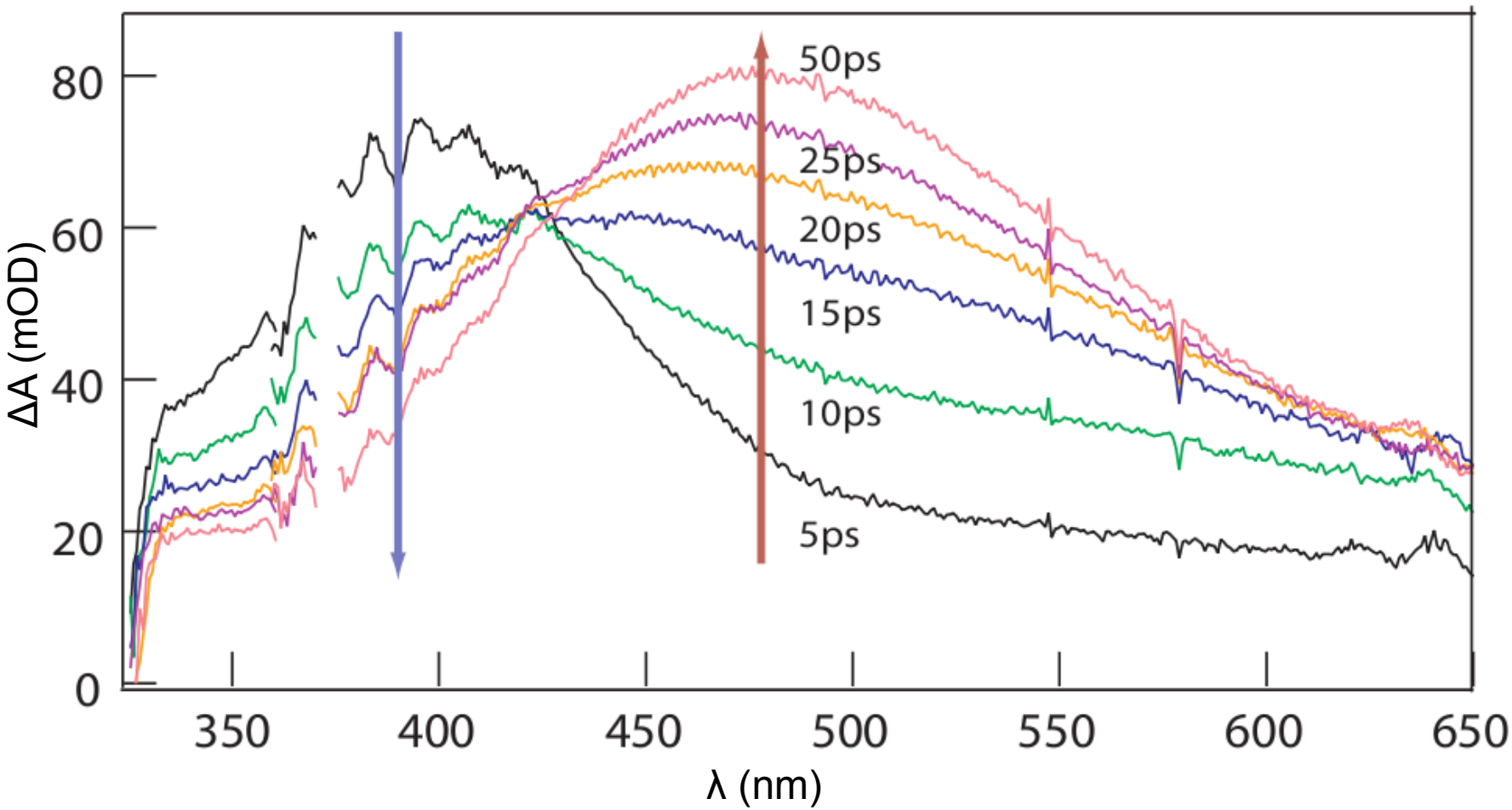


- 2% → 100% v/v $CHBr_3$ in C_6H_{12}
- CH_2Br_2 precursor, CH_3CN solvent

Experiment

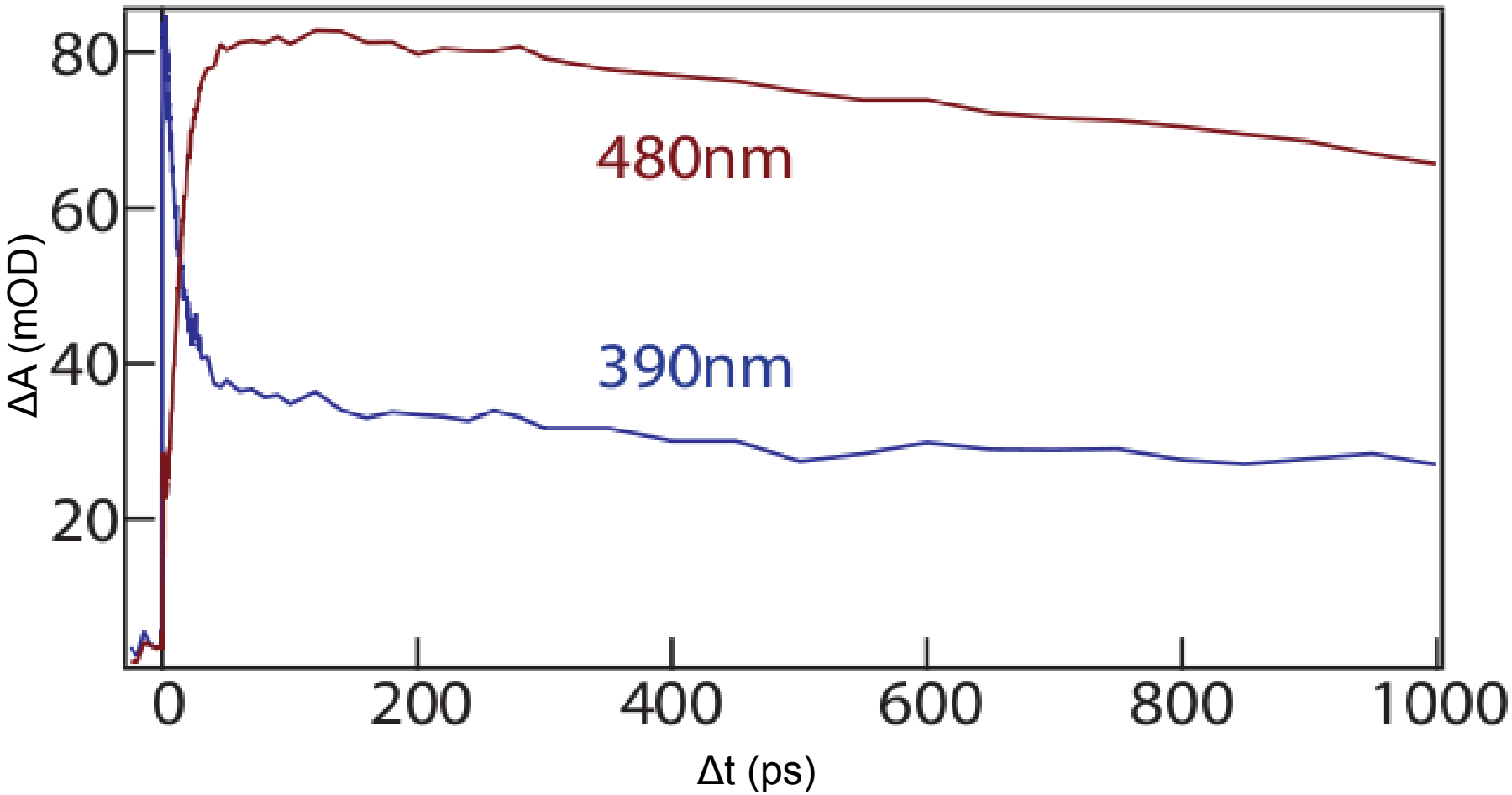

Ti:Sapphire
100 fs
800 nm
64-element IR
Photodiode Array
512-element UV-Vis
Photodiode Array
267 nm Photolysis
360-800 nm Continuum Probe
IR as Pump or Probe

Pure $CHBr_3$



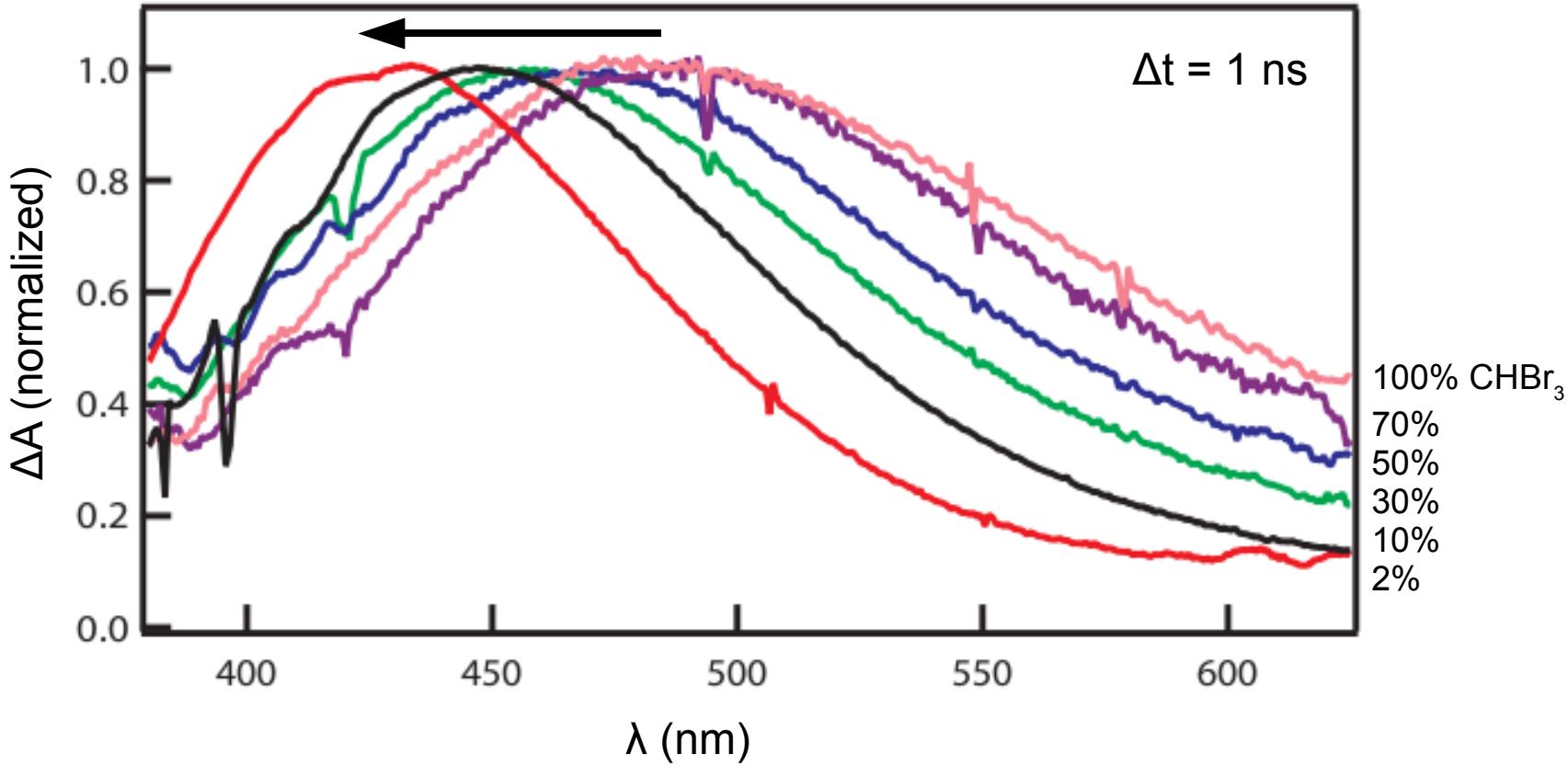
- Resolution-limited rise, centered at 390 nm
- τ=13 ps population transfer to species at 480 nm

Pure $CHBr_3$



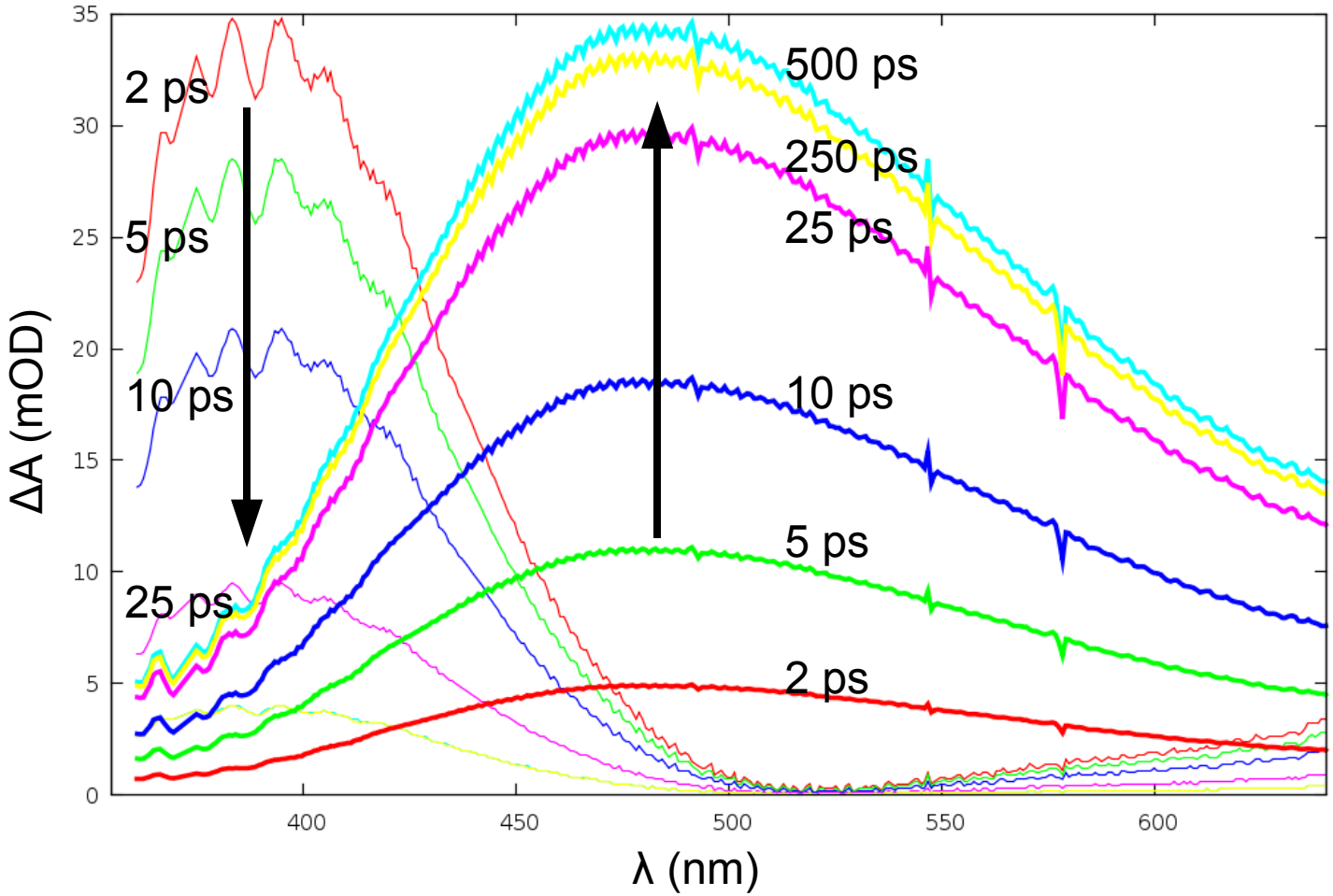
- Resolution-limited rise, centered at 390 nm
- τ=13 ps population transfer to species at 480 nm

$CHBr_3$ in Cyclohexane



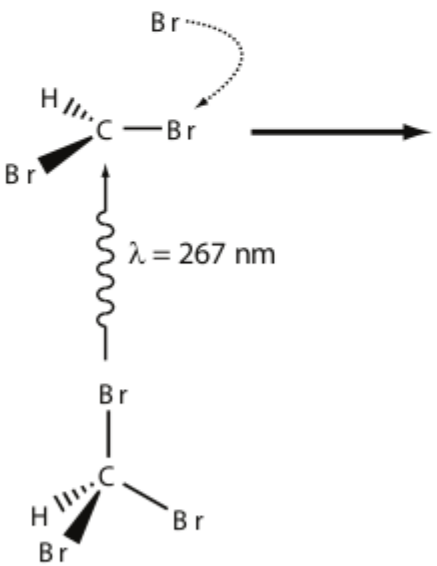
- Short λ peak independent of concentration (390 nm)
- Long λ peak moves with concentration (480 → 430 nm)

Spectral Fits: $CHBr_3$



- Population transfer with τ = 13 ps
- Both species present at 1 ns

Proposed Scheme



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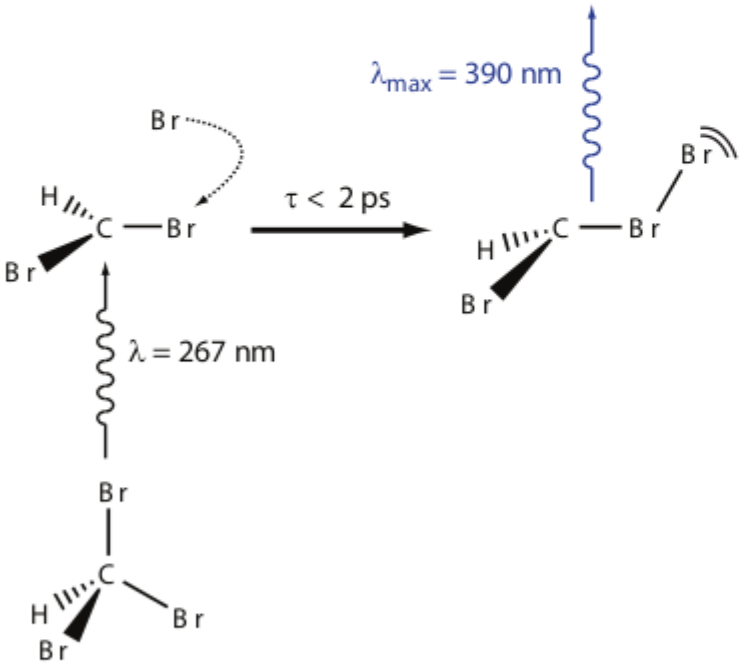

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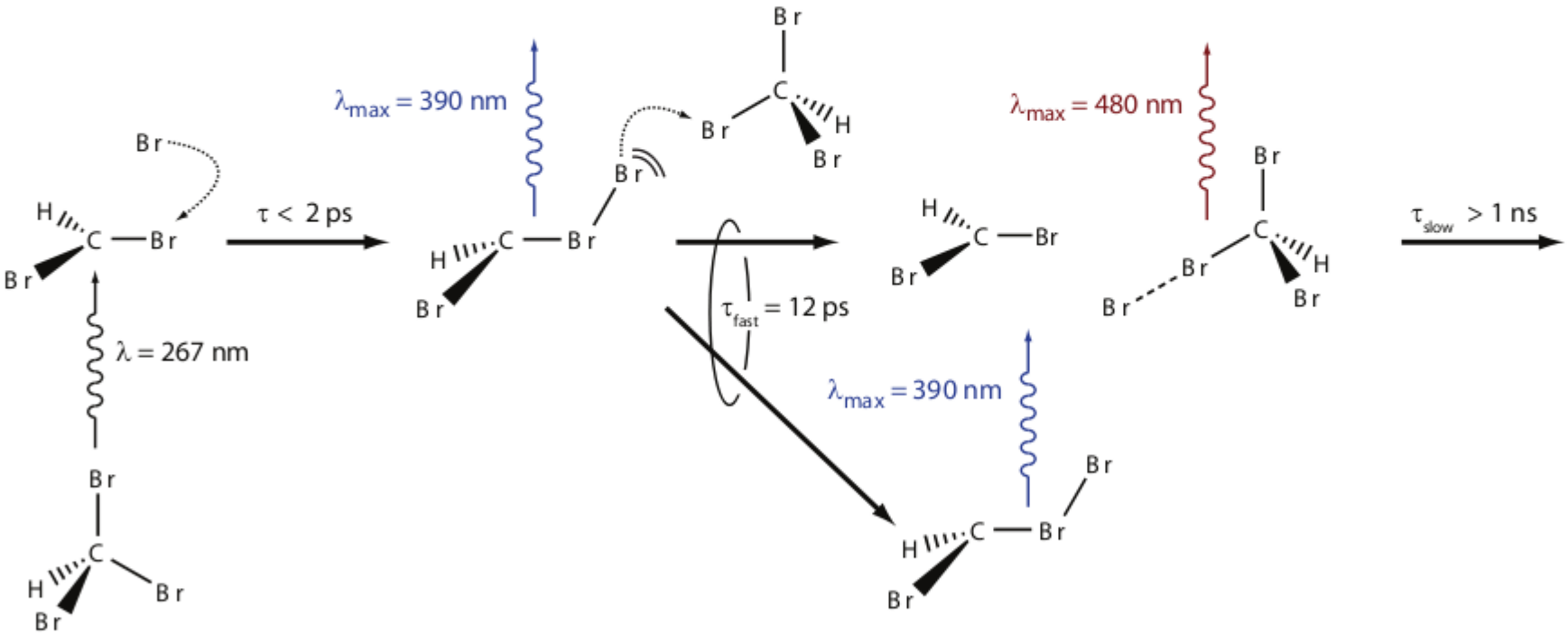

Drive H-abstraction by Br·

- H-abstraction by Br is endothermic by 2000 cm^{-1}
- Pump H-CBr_3 oscillator at 3020 cm^{-1}
- τ_{IVR} = 50 ps

Many Thanks...

- Fleming Crim and group