DYNAMIC TIME-RESOLVED CHIRPED-PULSE ROTATIONAL SPECTROSCOPY IN A ROOM TEMPERATURE FLOW REACTOR

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CHEMICAL DYNAMICS AND KINETICS STUDIES

Implementing a deductive scientific approach: first-principles predictions of the behavior of complex chemical systems

Multi-species quantitative spectroscopy is how we will test these predictive kinetic models

Discrepancies between experiments and kinetics models will arise, and some of them will direct extension or revision of the dynamical mechanisms

Time-resolved, quantum state- and isomer- specific quantitative and multi-species spectroscopy is now we will test dynamic mechanisms

1. Dynamic Time-Resolved Chirped-Pulse (DTRCP) Spectroscopy

2. Reactor with well-characterized $T$ and $P$ conditions of the “bath”
ARGONNE DYNAMIC TIME-RESOLVED CHIRPED-PULSE (DTRCP) SPECTROMETER

• 58–92 GHz operating frequency range
• 23 GHz instantaneous bandwidth
• Tunable downconversion local oscillator
• 35 h phase stability

FLOW TUBE REACTOR/CP SPECTROMETER

CP-FTmmW Spectrometer
The Receiver

CP-FTmmW Spectrometer
The Source

Millimeter-wave beam (chirped pulses + FID)

Flow Tube Reactor

To vacuum pump

Mass flow controller

Precursor molecules

Capacitance manometer

Photolysis laser beam

To vacuum pump

Millimeter-wave beam (chirped pulses)
193 NM PHOTOLYSIS OF VINYL CYANIDE (CH₂CHCN)

- Focus on HCN, HNC and HCCCCCN photo-products
DYNAMIC TIME-RESOLVED CP SPECTROSCOPY

- Argonne/BrightSpec DTRCP Spectrometer
- Fine time resolution (10 µs)
- Multiple transitions
- Long post-photolysis observation times (0.5 s)
DYNAMIC TIME-RESOLVED CP SPECTROSCOPY

- Argonne/BrightSpec DTRCP Spectrometer
- Fine time resolution (10 µs)
- Rotational thermalization of hot nascent photoproducts (0 – 1 ms)
- Evacuation of photoproducts from the cell (5 – 500 ms)
- Products branching ratios at 1 – 5 ms
- HNC $\rightarrow$ HCN isomerization
- Wall effects

$P$ (CH$_2$CHCN) = 1 µbar (0.76 mTorr)
$P$ (argon) = 9 µbar (6.8 mTorr)
DYNAMIC TIME-RESOLVED CP SPECTROSCOPY

- Synchronized HDR mode of W-band BrightSpec CP-FTmmW Spectrometer
- Medium time-resolution (0.1 – 1000 ms)
- High duty cycle
- Vibrational population distributions
DYNAMIC TIME-RESOLVED CP SPECTROSCOPY

- Synchronized HDR mode of W-band BrightSpec CP-FTmmW Spectrometer
- Medium time-resolution (0.1 – 1000 ms)
- High duty cycle
- Vibrational population distributions

$t : 1 – 5 \text{ ms}$

HCCCN VPD: 0 – 400 $\mu$s

HCCCN VPD: 1 – 5 ms

**Graphs and Figures:**
- Transition frequency, MHz
- CP-FTmmW signal, mV
- Vibrational energy, cm$^{-1}$
HCN/HCCCN BRANCHING RATIO

Species | CH\textsubscript{2}CHCN | CH\textsubscript{2}CHCN* | HCN | HCCCN
--- | --- | --- | --- | ---
\(n\), cm\textsuperscript{-3} | \(2.46 \times 10^{13}\) | \(1.72 \times 10^{12}\) | \(3.52 \times 10^{11}\) | \(2.15 \times 10^{11}\)
\(N\) | \(1.74 \times 10^{16}\) | \(1.22 \times 10^{15}\) | \(2.49 \times 10^{14}\) | \(1.52 \times 10^{14}\)
REMAINING REACTION CHANNELS

- Main dissociation channel TSH
- Cyanovinyl radical not observed (need more sensitivity)

TSH: \( \text{CH}_2\text{CHCN} \rightarrow \text{CH}_2\text{CCN} + \text{H} \)

\( \text{CH}_2\text{CCN} \rightarrow \text{HCCCN} + \text{H} \)
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CONCLUSIONS AND OUTLOOK

• Implemented time-resolved broadband rotational spectroscopy at room temperature
• A better-characterized flow tube reactor at 295 K
• Pressure can be varied by a factor between 1 and 100 µbar
• A 260–290 GHz spectrometer will increase sensitivity
• Rotational and vibrational collisional relaxation effects observed
• Products branching ratios measured and compared with theory
• The approach is suitable for studying reaction pathways branchings, non-thermal kinetic effects
THANK YOU!