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A New Experimental Approach to Determine Low-Temperature Product Branching in Multichannel Reactions

Baptiste Joalland¹, Chamara Abyasekara¹, Lindsay N. Zack¹, Nuwandi Ariyasingha¹, James M. Oldham¹, Kirill Prozument², G. Barratt Park², Ian R. Sims³, Robert W. Field⁴, and Arthur G. Suits¹

¹ Department of Chemistry, Wayne State University, 5101 Cass Ave., Detroit, MI 48202, USA
² Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA
³ Institut de Physique de Rennes, CNRS-UR 6251, Université de Rennes 1, 263 du Général Leclerc, 35042, Rennes, France

Nearly all kinetics studies report the observed rate of reactant disappearance, with product identity and branching largely unknown. This limitation arises from considerable experimental challenges inherent in the quantitative detection of the full range of products of a given reaction, particularly for large polyatomic systems. Recent advances have relied upon tunable synchrotron photoionization or low-energy electron impact ionization to achieve selective product detection in dynamics, kinetics, and flame studies. Challenges remain, however, as these studies require fitting of composite and often incompletely resolved spectra to infer branching, and clear product signatures are often lacking. To address these issues, we have developed an alternative approach, which incorporates chirped-pulse Fourier transform microwave spectroscopy [1] in low-temperature uniform supersonic flows [2] (“chirped-pulse / uniform flow”, C-PUF). This technique provides clear quantifiable spectroscopic signatures of polyatomic products in bimolecular or unimolecular reactions for virtually any species with a modest electric dipole moment.

Chirped-Pulse / Uniform Flow

Schematic

- Flow Chamber: The pulsed uniform flow source consists of a piezoelectric stack valve connected to mass flow controllers (MFCs) and an Laval nozzle mounted on one end of a polycarbonate vacuum chamber. A quartz window is located on the other end of the chamber to allow radiation from an AIF excimer laser to propagate down the axis of the Laval nozzle, such that the core of the flow is irradiated. 
- Spectroscopy: CP-FTMW: Linearly chirped pulses (0.25–3.75 GHz) are produced in an arbitrary waveform generator (AWG) and then mixed with a local oscillator (frequency 8.125 GHz) phase-locked to a 10 MHz active frequency multiplier, and matched by a PGOPHER waveform generator (AWG; Tektronix AWG7082C), which is used to amplify the output signal produced by the AWG to the desired power. The signal is then sent to a digital oscilloscope (Tektronix DPO70804C) and then to its abundance could be obtained from the noise

Applications for reaction dynamics and astrochemistry

Photodissociation of SO₂

SO₂ + hv (193 nm) → SO (v, J) + O (P₂)

Time evolution of SO spectra generated from the photodissociation of SO₂ with 193 nm radiation. SO begins to appear 20 μs after the laser is fired at 65% in the v = 2 vibrational level. This value is in good agreement with the nascent vibrational populations determined from imaging studies. Ref. [5]

Product Branching for CN + C₂H₄

Product branching in percent, at 22 K with 2σ uncertainty in the last digit:

<table>
<thead>
<tr>
<th>Product Branching</th>
<th>Best estimation</th>
<th>Least estimation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂CN</td>
<td>68%</td>
<td>53%</td>
</tr>
<tr>
<td>CH₃CN</td>
<td>32%</td>
<td>47%</td>
</tr>
</tbody>
</table>

Relative product populations is deduced from the spectra using the relationship between the integrated line intensities (W) and column densities (N₂₀): W = 4ν₀¹/² α₀² β₀² ν₂₀² S₂₀² ε₂₀² N₂₀ e⁻/kT₂₀ c₂₀²/kT₂₀

Segmented macroscopic scan that targets transitions of HCCCN, CH₂CCHCN, and CH₃CCHCN. J = 8–9 transition at 81.811 GHz, νCH₂ = 16, νCH₃ = 15, νCCCN = 81.814 GHz and Jₙ = 200 – 190 at 82.527 GHz. The inset shows the K = 0, 1, 2, and 3 transitions of CH₂CCHCN. Ref. [8]

References


Note: The references are not included in the text as per the instruction.