Radically different kinetics at low temperatures

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Summary

Introduction: Radical reactivity at low temperatures

Low temperature environments

Experimental techniques

Polyynes and cyanopolyynes

\[ \text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H} \]
Introduction: Radical reactivity at low temperatures

What kinds of reactions remain rapid at low temperatures?

Why study low temperature reactivity?
Introduction: Radical reactivity at low temperatures

\[ k(T) = A \exp\left(-\frac{E_{\text{act}}}{RT}\right) \]

\[ \ln[k(T)] = \ln A - \frac{E_{\text{act}}}{RT} \]
Introduction: Radical reactivity at low temperatures

The Arrhenius equation

\[ k(T) = A \exp\left(-\frac{E_{\text{act}}}{RT}\right) \]
\[ \ln[k(T)] = \ln A - \frac{E_{\text{act}}}{RT} \]

- associated with absolute barrier to reaction
- Arrhenius plots are often non linear over very wide \( T \) ranges owing to \( T \)-dependent partition functions and QM tunnelling

Non-Arrhenius behaviour

- many radical reactions do not possess barriers
- radical-radical reactions not expected to show Arrhenius behaviour
- many radical-molecule reactions possess no absolute barrier to reaction
- but submerged barriers often exist and may influence temperature dependence through entropic effects
Introduction: Radical reactivity at low temperatures
$CN + O_2$

$k = 6.2 \times 10^{-10} T^{-0.54}$
$CN + O_2$

$k / \text{cm}^3 \text{ molecule}^{-1} \text{s}^{-1} = 6.2 \times 10^{-10} T^{-0.54}$
Introduction: Radical reactivity at low temperatures

CN + C₂H₆ → C₂H₅ + HCN
\[ \text{CN} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5 + \text{HCN} \]
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\[ F + H_2 \rightarrow HF + H \]
Low temperature chemical environments

- Room temperature
- Earth's stratosphere: down to 215 K
- Lowest stratospheric temperature: ca. 180 K
- Interstellar clouds (ISCs): 10—100 K
- Atmosphere of Titan (moon of Neptune): down to 20 K
- Dense, dark ISCs: 10—20 K
Neutral-neutral reactions and astrochemistry

Important low temperature astrochemical processes must be either:

- barrierless and therefore rapid down to low temperatures

and / or

- involve hydrogen as one of the reacting partners

(credit Ben McCall, UIUC)
Summary

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\[ F + H_2 \rightarrow HF + H \]
Isentropic expansion and uniform supersonic flow

axisymmetric Laval nozzle

The CRESU technique

50-100 slm carrier gas (He, Ar or N₂) + precursor + reagent

uniform supersonic flow

T = 15 – 220 K
ρ = 10¹⁶ – 10¹⁸ cm⁻³

boundary layer sets scale of apparatus

chamber pressure 0.1 – 0.25 mbar
pumping speed < 30000 m³ hr⁻¹

Laval nozzle controls expansion of carrier gas: avoids the two main problems of the other methods:

- expansion/cooling is rapid – condensation avoided
- expansion controlled – collisions maintain thermal equilibrium

3 mm – 5 cm

nozzle throat diameter
Laval nozzles – also used in rocket motors
50-100 sℓm carrier gas (He, Ar or N₂) + precursor + reagent

axisymmetric Laval nozzle

uniform supersonic flow

\[ T = 7 - 220 \text{ K} \]
\[ N > = 10^{16} - 10^{18} \text{ cm}^{-3} \]

nozzle throat diameter

3 mm – 5 cm

boundary layer sets scale of apparatus

chamber pressure 0.1 – 0.25 mbar
pumping speed < 30000 m³ hr⁻¹

pitot tube measures impact pressure \( p_i \) – very sensitive to flow conditions

Laval nozzle and isentropic flow
Aerodynamic (Pitot) measurements of flow conditions
Experimental verification of flow conditions

Characterise supersonic flow by **impact pressure** \( (p_i) \) measured by Pitot tube
- can calculate Mach number, \( M \) as \( p_i \) is very sensitive to \( M \)
- temperature, pressure and density, knowing initial conditions in reservoir
- smooth \( p_i \) profile \( \Rightarrow \) isentropic expansion

**PLP-LIF** enables independent verification of \( T \):
- rotationally-resolved CN LIF spectra recorded in flow
- fit to synthetic spectra \( \Rightarrow T_{\text{LIF}} \)
- excellent agreement between \( T_{\text{pitot}}, T_{\text{LIF}} \)
Isentropic expansion and uniform supersonic flow

position downstream / cm

$T / K$ flow

nozzle exit

flow
Isentropic expansion and uniform supersonic flow
Isentropic expansion and uniform supersonic flow
Isentropic expansion and uniform supersonic flow

Temperature (K)

\[ P_{\text{res}} = 88.18 \text{ mbar} \quad T = 23.6 \text{ K} \]
\[ P_{\text{ch}} = 0.171 \text{ mbar} \quad T_{\text{res}} = 295 \text{ K} \]
\[ Q_{\text{He}} = 57.72 \text{ SLM} \]

X (cm)
The CRESU technique

50-100 slm carrier gas (He, Ar or N₂) + precursor + reagent

axisymmetric Laval nozzle

uniform supersonic flow

$T = 15 - 220 \text{ K}$

$\rho = 10^{16} - 10^{18} \text{ cm}^{-3}$

nozzle throat diameter

3 mm – 5 cm

boundary layer sets scale of apparatus

overlapping photolysis / probe pulsed laser beams co-propagate along cold flow

laser-induced fluorescence

chamber pressure 0.1 – 0.25 mbar

pumping speed $\approx 30000 \text{ m}^3 \text{ hr}^{-1}$
The CRESU technique

Provides an ultra-low temperature thermalised (collisional) environment which can operate under heavily supersaturated conditions. It can be used for

**Thermochemistry** of weakly-bound systems e.g.


**Cluster formation** e.g.


**Low temperature kinetics** e.g.


Relaxation towards equilibrium 85—100 K

Alternatively, correct trace for diffusion first: $\exp\left(+k_{\text{diff}} t\right) I_{\text{LIF}} = (A + B \exp(-k_{1st} t))$

$A + B = 5.45$

$A = 1.53$

$T = 95.4 \text{ K}$

$A \over A + B = \left[\text{OH}\right]_{\text{eq}} \over \left[\text{OH}\right]_0 \Rightarrow K_c$
Relaxation towards equilibrium 85—100 K

<table>
<thead>
<tr>
<th>T / K</th>
<th>[O₂] / 10^{17} cm⁻³</th>
<th>A / (A + B) = [OH]_∞ / [OH]₀</th>
<th>K_c [O₂]</th>
</tr>
</thead>
<tbody>
<tr>
<td>87.4</td>
<td>4.55</td>
<td>0.169 ± 0.008</td>
<td>4.93 ± 0.28</td>
</tr>
<tr>
<td>91.5</td>
<td>4.52</td>
<td>0.130 ± 0.034</td>
<td>6.71 ± 2.02</td>
</tr>
<tr>
<td>94.9</td>
<td>4.46</td>
<td>0.325 ± 0.046</td>
<td>2.08 ±0.43</td>
</tr>
<tr>
<td>95.4</td>
<td>5.00</td>
<td>0.280 ± 0.016</td>
<td>2.57 ± 0.21</td>
</tr>
<tr>
<td>96.7</td>
<td>4.66</td>
<td>0.479 ± 0.033</td>
<td>1.09 ± 0.14</td>
</tr>
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<td>97.5</td>
<td>4.75</td>
<td>0.465 ± 0.022</td>
<td>1.15 ± 0.10</td>
</tr>
<tr>
<td>99.8</td>
<td>5.02</td>
<td>0.407 ± 0.086</td>
<td>1.46 ± 0.52</td>
</tr>
</tbody>
</table>

\[
\frac{A}{A + B} = \frac{[\text{OH}]_{\text{eq}}}{[\text{OH}]_0} = r
\]

\[
K_c = \frac{([\text{OH}]_0 - [\text{OH}]_{\text{eq}})}{[\text{OH}]_{\text{eq}} [O_2]}
\]

\[
\Rightarrow K_c [O_2] = \frac{(1 - r)}{r [O_2]}
\]
Derivation of $D_0$ and $\Delta_fH^o_{298\text{K}}$

<table>
<thead>
<tr>
<th>$T / \text{K}$</th>
<th>$[\text{O}_2] / 10^{17} \text{ cm}^{-3}$</th>
<th>$A / (A + B) = [\text{OH}]_\infty / [\text{OH}]_0$</th>
<th>$K_c [\text{O}_2]$</th>
<th>$\ln K_c$</th>
<th>$\ln Q$</th>
<th>$D_0 / \text{kJ mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>87.4</td>
<td>4.55</td>
<td>0.169 ± 0.008</td>
<td>4.93 ± 0.28</td>
<td>−39.063 ± 0.060</td>
<td>−55.376</td>
<td>11.85 ± 0.11</td>
</tr>
<tr>
<td>91.5</td>
<td>4.52</td>
<td>0.130 ± 0.034</td>
<td>6.71 ± 2.02</td>
<td>−38.784 ± 0.301</td>
<td>−55.439</td>
<td>12.70 ± 0.25</td>
</tr>
<tr>
<td>94.9</td>
<td>4.46</td>
<td>0.325 ± 0.046</td>
<td>2.08 ± 0.43</td>
<td>−39.907 ± 0.211</td>
<td>−55.489</td>
<td>12.29 ± 0.22</td>
</tr>
<tr>
<td>95.4</td>
<td>5.00</td>
<td>0.280 ± 0.016</td>
<td>2.57 ± 0.21</td>
<td>−39.81 ± 0.082</td>
<td>−55.496</td>
<td>12.44 ± 0.11</td>
</tr>
<tr>
<td>96.7</td>
<td>4.66</td>
<td>0.479 ± 0.033</td>
<td>1.09 ± 0.14</td>
<td>−40.60 ± 0.135</td>
<td>−55.514</td>
<td>11.99 ± 0.17</td>
</tr>
<tr>
<td>97.5</td>
<td>4.75</td>
<td>0.465 ± 0.022</td>
<td>1.15 ± 0.10</td>
<td>−40.561 ± 0.091</td>
<td>−55.525</td>
<td>12.13 ± 0.12</td>
</tr>
<tr>
<td>99.8</td>
<td>5.02</td>
<td>0.407 ± 0.086</td>
<td>1.46 ± 0.52</td>
<td>−40.382 ± 0.358</td>
<td>−55.557</td>
<td>12.59 ± 0.31</td>
</tr>
</tbody>
</table>

unweighted average 12.3 ± 0.3°

° 95% confidence limits

- $D_0 = RT(\ln K_c – \ln Q) = 12.3 ± 0.3 \text{ kJ mol}^{-1}$
- $\Delta_fH^o_{298\text{K}} = 19.3 ± 0.5 \text{ kJ mol}^{-1}$

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Polyynes and cyanopolyynes

F + H₂ → HF + H

Sidaty Cheikh Sid Ely, Martin Fournier, Sébastien Morales, Jean-Claude Guillemin, Stephen Klippenstein and IRS
Polyynes and cyanopolyynes

**Polyynes**
- linear chain hydrocarbons of generic formula $\text{H-(C≡C)}_n\text{-H}$

**Cyanopolyynes**
- CN-terminated polyynes $\text{H-(C≡C)}_n\text{-C≡N}$
- longest chain interstellar molecule $\text{HC}_{11}\text{N}$ – seen in dark clouds
TMC-1 in the IR

Credit: Five College Radio Astronomy Observatory/Gopal Narayanan/Mark Heyer
Polyynes and cyanopolyynes

Polyynes
- linear chain hydrocarbons of generic formula H-(C≡C)$_n$-H

Cyanopolyynes
- CN-terminated polyynes H-(C≡C)$_n$-C≡N
- longest chain interstellar molecule HC$_{11}$N – seen in dark clouds
- also present in circumstellar shells of red giant/AGB stars
Red Giant / AGB star
IRC+10216

VLT/FORS1 Izan Leao (Universidade Federal do Rio Grande do Norte, Brazil).

Lucas et al. 1995; Guélin et al 1997
Polyynes and cyanopolyynes

Polyynes
- linear chain hydrocarbons of generic formula H-(C≡C)$_n$-H

Cyanopolyynes
- CN-terminated polyynes H-(C≡C)$_n$-C≡N
- longest chain interstellar molecule HC$_{11}$N – seen in dark clouds
- also present in circumstellar shells of red giant/AGB stars
- and strongly implicated in formation of orange haze layer on Titan
Titan as seen by Cassini

Credit: NASA/JPL/Space Science Institute
Polyynes and cyanopolyynes

Possible formation route

\[ \text{C}_2\text{H} + \text{H(C≡C)}_n\text{H} \rightarrow \text{H(C≡C)}_{n+1}\text{H} + \text{H} \]  (1)

\[ \text{CN} + \text{H(C≡C)}_n\text{H} \rightarrow \text{H(C≡C)}_n\text{CN} + \text{H} \]  (2)

\[ \text{C}_2\text{H} + \text{H(C≡C)}_n\text{CN} \rightarrow \text{H(C≡C)}_{n+1}\text{CN} + \text{H} \]  (3)

\[ \text{CN} + \text{H(C≡C)}_n\text{CN} \rightarrow \text{NC(C≡C)}_n\text{CN} + \text{H} \]  (4)

- reactions of type (1) and (2) have been studied by us for the first member of the series, acetylene and found to be fast at low \( T \)
Polyynes and cyanopolyynes

Possible formation route

\[
\begin{align*}
    C_2H + H(C≡C)_nH & \rightarrow H(C≡C)_{n+1}H + H \quad (1) \\
    CN + H(C≡C)_nH & \rightarrow H(C≡C)_nCN + H \quad (2) \\
    C_2H + H(C≡C)_nCN & \rightarrow H(C≡C)_{n+1}CN + H \quad (3) \\
    CN + H(C≡C)_nCN & \rightarrow NC(C≡C)_nCN + H \quad (4)
\end{align*}
\]

- reactions of type (1) and (2) have been studied by us for the first member of the series, acetylene and found to be fast at low \( T \)
- would like to study (1) and (2) for \( n = 2 \) (diacetylene, H-C≡C-C≡C-H) and (3) and (4) CN, \( C_2H + H-C≡C-C≡N \)
Polyynes and cyanopolyynes

Possible formation route

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\begin{align*}
C_2H + H(C\equiv C)_nH & \rightarrow H(C\equiv C)_{n+1}H + H \quad (1) \\
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C_2H + H(C\equiv C)_nCN & \rightarrow H(C\equiv C)_{n+1}CN + H \quad (3) \\
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\]

- reactions of type (1) and (2) have been studied by us for the first member of the series, acetylene and found to be fast at low $T$
- would like to study (1) and (2) for $n = 2$ (diacetylene, H-C≡C-C≡C-H) and (3) and (4) CN, $C_2H + H-C≡C-C≡N$
- major problem is that these reagents are unstable and must be synthesised, and CRESU uses large amounts
- solution: pulse the CRESU
A new pulsed CRESU apparatus: schematic

Sébastien Morales, Sidaty Cheikh Sid Ely, Daniel Travers, Jonathan Courbe, Bertrand Rowe, and IRS
Polyynes and cyanopolyynes

Possible formation route

\[ \text{C}_2\text{H} + \text{H} (\text{C}≡\text{C})_n\text{H} \rightarrow \text{H} (\text{C}≡\text{C})_{n+1}\text{H} + \text{H} \quad (1) \]

\[ \text{CN} + \text{H} (\text{C}≡\text{C})_n\text{H} \rightarrow \text{H} (\text{C}≡\text{C})_n\text{CN} + \text{H} \quad (2) \]

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\[ \text{CN} + \text{H} (\text{C}≡\text{C})_n\text{CN} \rightarrow \text{NC}(\text{C}≡\text{C})_n\text{CN} + \text{H} \quad (4) \]

- Reactions of type (1) and (2) have been studied by us for the first member of the series, acetylene and found to be fast at low \( T \)
- Would like to study (1) and (2) for \( n = 2 \) (diacetylene, H-C≡C-C≡C-H) and (3) and (4) CN, C\(_2\)H + H-C≡C-C≡N
- Major problem is that these reagents are unstable and must be synthesised, and CRESU uses too much to be practicable
- Solution: pulse the CRESU
- First application: measurement of the rate coefficient for the reaction
  \[ \text{CN} + \text{H}-\text{C}≡\text{C}-\text{C}≡\text{N} \rightarrow \text{N}≡\text{C}-\text{C}≡\text{C}-\text{C}≡\text{N} + \text{H} \]
CN + HC₃N: Photochemical methods

Production of CN(\(X^2\Sigma^+\))
- pulsed laser photolysis of ICN at 266 nm

Production of C₂H
- 193 nm photolysis of CF₃C≡CH
- main advantage: appears less reactive with C₂H than C₂H₂

Detection of CN(\(X^2\Sigma^+\))
- pulsed off-resonance LIF in CN(\(B\rightarrow X\)) system
- excitation at 388 nm in (0,0) band
- detection at 421 nm from (0,1) band

Detection of C₂H
- we use the chemiluminescence technique of Peeters and co-workers: the reaction \(C₂H + O₂ \rightarrow CH(A^2\Delta) + CO₂\) generates electronically excited CH
- with excess \([O₂]\), \(CH(A^2\Delta \rightarrow X^2\Pi)\) fluorescence at ca. 430 nm is proportional to \([C₂H]\)
CN + HC$_3$N: Typical 1$^{\text{st}}$ and 2$^{\text{nd}}$ order plots
CN + HC$_3$N: Results

![Graph showing reaction rate constants](image)

Halpern et al. 1989
CN + HC₃N: Results

$T$ (K)

$k$ (cm³ molecule⁻¹ s⁻¹)

Halpern et al 1989
CN + HC$_3$N: Typical 1$^{\text{st}}$ and 2$^{\text{nd}}$ order plots
CN + HC$_3$N: Results

Halpern et al. 1989
CN + HC$_3$N: Results

![Graph showing temperature (T) vs. position downstream (cm)](image)

- Temperature (T) in Kelvin
- Position downstream in centimeters
CN + HC$_3$N: Results

$T$ (K) vs $k$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)

- Halpern et al. 1989

$10^{-11}$

$10^{-10}$

$10^{-9}$

$10^{-8}$
CN + HC$_3$N: Results

$CN + HC_3N$:

$k = 1.79 \times 10^{-11} \left( \frac{T}{298 \text{ K}} \right)^{-0.67} \text{ cm}^3 \text{ s}^{-1}$

Halpern et al. 1989

CRESU

$T$ (K)
CN + HC$_3$N: Results

$\kappa = 1.79 \times 10^{-11} (T / 298 \text{ K})^{-0.67} \text{ cm}^3 \text{ s}^{-1}$

models Halpern et al 1989
$CN + HC_3N$: Results

$CN + HC_3N$

$k = 1.79 \times 10^{-11} \left( T / 298 \text{ K} \right)^{-0.67} \text{ cm}^3 \text{ s}^{-1}$

Faure et al 2008 prediction

CRESU

models

Halpern et al 1989
stationary points for the addition reaction were determined at the CCSD(T)/cc-pVTZ level.

High accuracy predictions for these saddle point energies were obtained from a combination of (i) basis set extrapolated CCSD(T)/CBS evaluations, (ii) core-valence corrections, (iii) CCSDT(Q) corrections, (iv) relativistic corrections, and (v) CCSD(T)/cc-pVTZ zero-point energies.

Expected (2σ) accuracy: 0.2—0.3 kcal mol⁻¹

CN + HC₁C²C³N – only C¹ saddle point submerged below reagent energy (−0.42 kcal mol⁻¹)
TST methodology

- submerged barrier for addition to C¹ implies that there are two transition states involved in the addition at this site.
- a loose outer transition state provides a bottleneck to the formation of a CN…HC₃N van der Waals complex from the CN and HC₃N reactants.
- a tight inner transition state describes the transformation of the CN…HC₃N van der Waals complex into a chemically bound NCCHCCN complex.
- Ab-initio 2 transition state variational TST model
CN + HC₃N: Comparison to theory
CN + HC$_3$N: Comparison to theory

![Graph showing the reaction rate constant ($k$) for the reaction CN + HC$_3$N as a function of temperature ($T$) in Kelvin (K). The graph plots $k$ in units of cm$^3$ molecule$^{-1}$ s$^{-1}$ on a logarithmic scale against $T$. The data points show a decrease in $k$ with increasing temperature, indicating a exothermic reaction. The outer TS (transition state) is indicated on the graph.]}
CN + HC$_3$N: Comparison to theory
CN + HC₃N: Comparison to theory

$T$ (K)

$k$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)

10⁻¹¹ 10⁻¹⁰ 10⁻⁹

CN + HC₃N

outer TS

fixed inner TS

variational inner TS

$T$ (K)
CN + HC$_3$N: Comparison to theory

\[
\begin{align*}
T &\quad (K) \\
10 &\quad 100 &\quad 1000 \\
10^{-11} &\quad 10^{-10} &\quad 10^{-9}
\end{align*}
\]

$k$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)

$T$ (K)

CN + HC$_3$N

outer TS

fixed inner TS

variational inner TS

2 TS
The inner TS is dominant for the full range of temperatures considered here.

Three lowest inner transition state vibrational frequencies are 35, 53, and 72 cm\(^{-1}\) – difficult to obtain accurate estimates of these.

Reducing the saddle point energy by 0.12 kcal mol\(^{-1}\) and decreasing the three transitional mode vibrational frequencies by a factor of 1.15 yields predicted rate coefficients that are essentially within the error bars of the experimental data.
CN + HC$_3$N: Comparison to theory

Graph showing the reaction rate constant ($k$) as a function of temperature ($T$) for CN + HC$_3$N. The graph includes data points and curves for outer TS, fixed inner TS, and variational inner TS.
A roughly equivalent fit is also obtained just by adjusting saddle point down by 0.3 kcal mol$^{-1}$, which is within error limits.

**CN + HC$_3$N**

**Comparison to theory**

$k$ (cm$^3$ molecule$^{-1}$ s$^{-1}$) vs $T$ (K)

- outer TS
- fixed inner TS
- variational inner TS
- 2 TS
- 2 TS adjusted
Polyynes and cyanopolyynes

Possible formation route

\[ C_2H + H(C≡C)_nH \rightarrow H(C≡C)_{n+1}H + H \]  
\[ (1) \]

\[ CN + H(C≡C)_nH \rightarrow H(C≡C)_nCN + H \]  
\[ (2) \]

\[ C_2H + H(C≡C)_nCN \rightarrow H(C≡C)_{n+1}CN + H \]  
\[ (3) \]

\[ CN + H(C≡C)_nCN \rightarrow NC(C≡C)_nCN + H \]  
\[ (4) \]

- reaction type (4) is fast for \( n = 1 \) down to 22 K
- now study  
  \[ C_2H + H-C≡C-C≡N \text{ and } CN, C_2H + H-C≡C-C≡C-H \]
- all three reactions are found to have rapid rate constants down to ca. 20 K
- reaction types (1)—(4) likely to play a role in (cyano)polyyne synthesis in cold environments – collaborations with modellers
Polyynes and cyanopolyynes

C$_3$N kinetics

- previously studied the kinetics of C$_4$H radical reactions (Berteloite et al.), finding very rapid reaction rates at low temperatures with hydrocarbons
- C$_3$N is isoelectronic with C$_4$H (like CN and C$_2$H) and rates of its reactions are included to some extent in models
- there are no kinetics measurements at any temperature for C$_3$N reactions
Polyynes and cyanopolyynes

$C_3N$ kinetics

- we produce $C_3N$ by UV photolysis of $BrC_3N$ and detect by UV LIF at ca. 350 nm (following the work of Endo and co-workers)
Polyynes and cyanopolyynes

**C$_3$N kinetics**

- we produce C$_3$N by UV photolysis of BrC$_3$N and detect by UV LIF at ca. 350 nm (following the work of Endo and co-workers)

![C$_3$N LIF spectrum at 15 K](image)

**FIG. 4.** High resolution LIF spectrum of the $^2\Sigma^+ - ^2\Sigma^+$ band at 28 251.004 cm$^{-1}$. 
Polyynes and cyanopolyynes

$C_3N$ kinetics

- high sensitivity and good signal to noise achieved
C$_3$N + X

Reactions studied include C$_3$N +
- H$_2$
- CH$_4$
- C$_2$H$_4$
- C$_2$H$_6$
- C$_3$H$_4$ (allene and propyne)
- C$_3$H$_6$
- C$_3$H$_8$
- NH$_3$
- O$_2$
Summary

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\[ F + H_2 \rightarrow HF + H \]

Meryem Tizniti, Sébastien Le Picard, François Lique, Coralie Berteloite, André Canosa, Millard Alexander and IRS
HF in the interstellar medium

HF is difficult to observe:
- small moment of inertia
- pure rotational transitions at high frequencies
- strong absorption by the atmosphere
- observations from space needed

Recent detections:
- 1st observed by ISO in 1997 ($J=2\rightarrow1$ 2.463 THz)
- 2nd observation by Herschel in 2010 ($J=1\rightarrow0$ 1.232 THz)
Interstellar fluorine chemistry

A relatively simple chemistry
\[ D_0(\text{HF}) = 5.87 \text{ eV} > D_0(\text{H}_2) = 4.48 \text{ eV} \]
- \( \text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H} \) is exothermic
- HF is not efficiently destroyed in ISM environment
- photodissociation (slowly)
- reactions with ions of low abundances (\( \text{He}^+, \text{H}_3^+, \text{C}^+ \))
  

- HF dominant F-bearing species wherever hydrogen is molecular
- predicted to be more abundant than CO in some areas (\( n(\text{F}) << n(\text{C}) \))
- used as a tracer of molecular hydrogen (HF/H\(_2\) \sim \text{constant})
- detected in dense or diffuse interstellar clouds, circumstellar shells, other galaxies, quasars… HF is ubiquitous!
F(2P) + H₂ → HF + H

- benchmark reaction for quantum scattering calculations and reaction dynamics experiments
- rate constant needed down to ISC temperatures (10-20 K) to connect observations of HF to H₂ density

BUT

- 6 kJ mol⁻¹ barrier: low T reactivity will be entirely due to tunnelling
- quantum mechanical calculations predict very different values between 4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} and 2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} in the 5—10 K temperature range

$F(^2P) + nH_2 \rightarrow HF + H$
$F(^2P) + nH_2 \rightarrow HF + H$
F(²P) + nH₂ → HF + H

Stevens et al. experimental results

Persky and Kornweitz Arrhenius extrapolation
$F(^2P) + nH_2 \rightarrow HF + H$

Zhu et al 2002
Quantum scattering on Stark & Werner surface using ABC quantum reactive scattering program of Skouteris, Castillo, & Manolopoulos

Stevens et al. experimental results

Zhu et al quantum scattering on SW surface

Persky and Kornweitz Arrhenius extrapolation
$\text{F}^{(2P)} + n\text{H}_2 \rightarrow \text{HF} + \text{H}$

Aquilanti et al 2005

I – fit to SW surface
II – with long-range correction
III – and spin-orbit correction in entrance channel

Stevens et al. experimental results
Zhu et al quantum scattering on SW surface
Persky and Kornweitz Arrhenius extrapolation
F(2P) + H₂ → HF + H: Theory by Lique and Alexander


- new hybrid Li-Werner-Alexander-Lique (LWAL)PES
- fits to multi-reference configuration interaction calculations
- used our extensively modified version of the ABC time-dependent, quantum reactive scattering code of Manolopoulos and co-workers
- Born-Oppenheimer calculation performed first on lowest electronic PES
- then full calculation including all levels and non-B.O. effects
F(2P) + nH₂ → HF + H

Stevens et al. experimental results
Zhu et al. quantum scattering on SW surface
Persky and Kornweitz Arrhenius extrapolation
F(\(^2\)P) + \(n\)H\(_2\) \(\rightarrow\) HF + H
F(²P) + H₂ → HF + H : experimental

- generate F by 248 nm excimer laser photolysis of F₂
- follow progress of reaction by detection of H atom product at 121.6 nm
- what about the limitation of the CRESU to \( k_{\text{min}} = 10^{-12} \text{ cm}^3 \text{ s}^{-1} \)??
- using pure H₂ buffer gas this is changed to \( k_{\text{min}} \sim 10^{-14} \text{ cm}^3 \text{ s}^{-1} \)

BUT pure H₂ nozzles give problems
- slow H₂ – H₂ rotational energy transfer
- variation of \( \gamma (= C_p/C_v) \), key aerodynamic parameter
Cryogenically cooled Laval nozzles

γ_{H_2} for normal H_2

γ_{H_2} versus T / K

T / K

γ_{H_2}

0 50 100 150 200 250 300

0 1.40 1.45 1.50 1.55 1.60 1.65 1.70
F(2P) + H₂ → HF + H : experimental

- generate F by 248 nm excimer laser photolysis of F₂
- follow progress of reaction by detection of H atom product at 121.6 nm
- what about the limitation of the CRESU to $k_{\text{min}} = 10^{-12}$ cm³ s⁻¹??
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BUT pure H₂ nozzles give problems
- slow H₂ – H₂ rotational energy transfer
- variation of $\gamma (= C_p/C_v)$, key aerodynamic parameter

SOLUTION
- pre-cool reservoir and double-walled nozzle with liquid N₂
- we now have H₂ nozzles at 5 K, 11 K and 20 K
H₂ nozzle temperature profiles

\[ T_{av} = 20.4 \text{ K and } n_{av} = 5.15 \times 10^{16} \text{ cm}^{-3} \text{ over } 25 \text{ cm / 243 } \mu\text{s} \]

\[ T_{av} = 11.3 \text{ K and } n_{av} = 4.02 \times 10^{16} \text{ cm}^{-3} \text{ over } 22.3 \text{ cm / 185 } \mu\text{s} \]
F(2P) + H₂ : Experimental apparatus

- **KrF Excimer laser (248 nm)**
- **UV photolysis laser 248 nm**
- **n-H₂ buffer gas + F₂ precursor**
- **double-jacketed reservoir and Laval nozzle cooled to 77 K**
- **collection optics (MgF₂)**
- **solar blind photomultiplier tube with 121.6 nm filter**
- **BBO f.d.u.**
- **Kr/Ar tripling cell ~365 nm**
- **dye laser (~730 nm)**
- **VUV LIF laser 121.6 nm**
- **Nd:YAG (532 nm)**
- **Computer-controlled delay**
$F^{(2P)} + H_2 \rightarrow HF + H$  Experimental measurement 295 K
$F(^2P) + H_2 \rightarrow HF + H$  Experimental measurement 295 K

$k = (2.5 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$

$T = 295 \text{ K}$
$F(2P) + nH_2 \rightarrow HF + H$ results

Temperature (K)

$\kappa$ (cm$^3$ molecule$^{-1}$ s$^{-1}$)
\[ F(2P) + nH_2 \rightarrow HF + H \] results

\[ k \ (\text{cm}^3\text{ molecule}^{-1} \text{s}^{-1}) \]

- Stevens et al. experimental results
- Zhu et al. quantum scattering on SW surface
- CRESU results
- Lique and Alexander B-O
- Lique and Alexander non B-O
- Persky and Kornweitz Arrhenius extrapolation

Temperature (K)
F(2P) + H₂ → HF + H  Experimental measurement 77 K

\[ I_{\text{LIF}} = I_0 \exp(-k_1 t) + A\left(\exp(-k_1 t) - \exp(-k_2 t)\right) \]
$F(^2P) + H_2 \rightarrow HF + H$  Experimental measurement 77 K

$k = (2.5 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
\[ \text{F}^{(2P)} + n\text{H}_2 \rightarrow \text{HF} + \text{H} \] results

\[
\begin{align*}
\text{Stevens et al.} \\
\text{experimental results}
\end{align*}
\]

\[
\begin{align*}
\text{Zhu et al quantum} \\
\text{scattering on SW surface}
\end{align*}
\]

\[
\begin{align*}
\text{CRESU results}
\end{align*}
\]

\[
\begin{align*}
\text{Lique and Alexander B-O} \\
\text{Lique and Alexander non B-O}
\end{align*}
\]

\[
\begin{align*}
\text{Aq I} \\
\text{Aq II} \\
\text{Aq III}
\end{align*}
\]

\[
\text{Persky and Kornweitz} \\
\text{Arrhenius extrapolation}
\]
F(2P) + nH₂ → HF + H results

Stevens et al. experimental results
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k (cm³ molecule⁻¹ s⁻¹)

Temperature (K)
H-atom LIF growth curve at 20.4 K

F + H₂ 20.4 K

H atom VUV LIF signal

VUV LIF

F + H₂ 20.4 K
H-atom LIF growth curve at 20.4 K

\[ I_{LIF} = I_0 \exp(-k_1 t) + A(\exp(-k_2 t) - \exp(-k_2 t)) \]

\[ k = (2.0 \pm 0.7) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1} \]

F + H\_2 20.4 K
H-atom LIF growth curve at 11.3 K

![Graph showing H atom VUV LIF signal against time (t) at 11.3 K]

F + H₂ 11.3 K
H-atom LIF growth curve at 11.3 K

$k = (2.6 \pm 1.7) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$

$F + H_2 \ 11.3 \ K$
H-atom LIF growth curve at 5 K

\[ F + H_2 \]
Short (50 ns) and long (222 µs) line profiles

Doppler width corresponds to $T = \text{ca. } 2000$ K
Possible causes of ‘prompt’ H-atom signal

Facts
- signal is real H-atoms
- appears to be initially hot
- increases in amplitude versus reactive H-atom signal as $T$ drops

Possible explanations
- photolysis of hydrocarbon impurities generates prompt, hot H – but why does this increase in importance at low $T$ – no
- small concentration of $\text{H}_2\text{F}_2$ complexes produced in flow give immediate reaction on photolysis, possibly enhanced absorption cross-section for photolysis also
- CCSD(T) calculations by F. Lique show $\text{F}_2\text{H}_2$ complex bound by 100 cm$^{-1}$
$F(^2P) + nH_2 \rightarrow HF + H$ results

![Graph showing results for the reaction $F(^2P) + nH_2 \rightarrow HF + H$.](image)
$F^{(2P)} + nH_2 \rightarrow HF + H$ results

![Graph showing reaction rate constant ($k$ in cm$^3$ molecule$^{-1}$ s$^{-1}$) versus temperature (K) for various studies and models. Notable data points and lines include Stevens et al. experimental results, Zhu et al. quantum scattering on SW surface, CRESU results, Lique and Alexander B-O, Lique and Alexander non B-O, Aq I, Aq II, Aq III, and Persky and Kornweitz Arrhenius extrapolation.]
F(2P) + H₂ → HF + H: Discussion

Ian:
“Our experimental results confirm the accuracy of the new non-B-O calculations of Lique and Alexander”

Millard:
“Our new non-B-O calculations confirm the accuracy of the experimental results of Tizniti et al”

The calculations
- can be used to predict the rate constant of F + H₂ down to 10 K and below (H₂ in LTE)
$F^{(2P)} + H_2 \rightarrow HF + H: k(T) \text{ at LTE}$
$F(^{2}P) + H_{2} \rightarrow HF + H: k(T)$ at LTE
$F(^2P) + H_2 \rightarrow HF + H: k(T)$ at LTE
\[ \text{F}{}^{(2P)} + \text{H}_2 \rightarrow \text{HF} + \text{H} \: \text{Discussion} \]

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The calculations
- can be used to predict the rate constant of F + H\(_2\) down to 10 K and below (H\(_2\) in LTE)
- and then inserted into predictions of H\(_2\) density from HF observations by Herschel
F(2P) + H₂ → HF + H: Discussion

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The calculations

- can be used to predict the rate constant of F + H₂ down to 10 K and below (H₂ in LTE)
- and then inserted into predictions of H₂ density from HF observations by Herschel
- a factor two change in prediction of total mass ensues under certain circumstances

Summary

Introduction: Radical reactivity at low temperatures

Low temperature environments

Experimental techniques

Polyynes and cyanopolyynes

\[ F + H_2 \rightarrow HF + H \]
Some Future Directions in Rennes

**CRESUSOL**
- implementation of SPIMS detection of products in a pulsed CRESU capable of attaining interstellar cloud temperatures
- PI Sébastien Le Picard

**HYDRIDES**
- state to state rotational energy transfer in CO, OH and CH – H₂ collisions at 5—20 K for astrophysics
- pulsed mid-IR (V)UV double resonance techniques

**Chirped Pulse Microwaves**
- collaboration with Arthur Suits’ and Bob Field’s groups - chirped-pulse Fourier-transform microwave/pulsed uniform flow spectrometer
- product detection
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