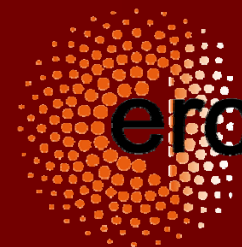


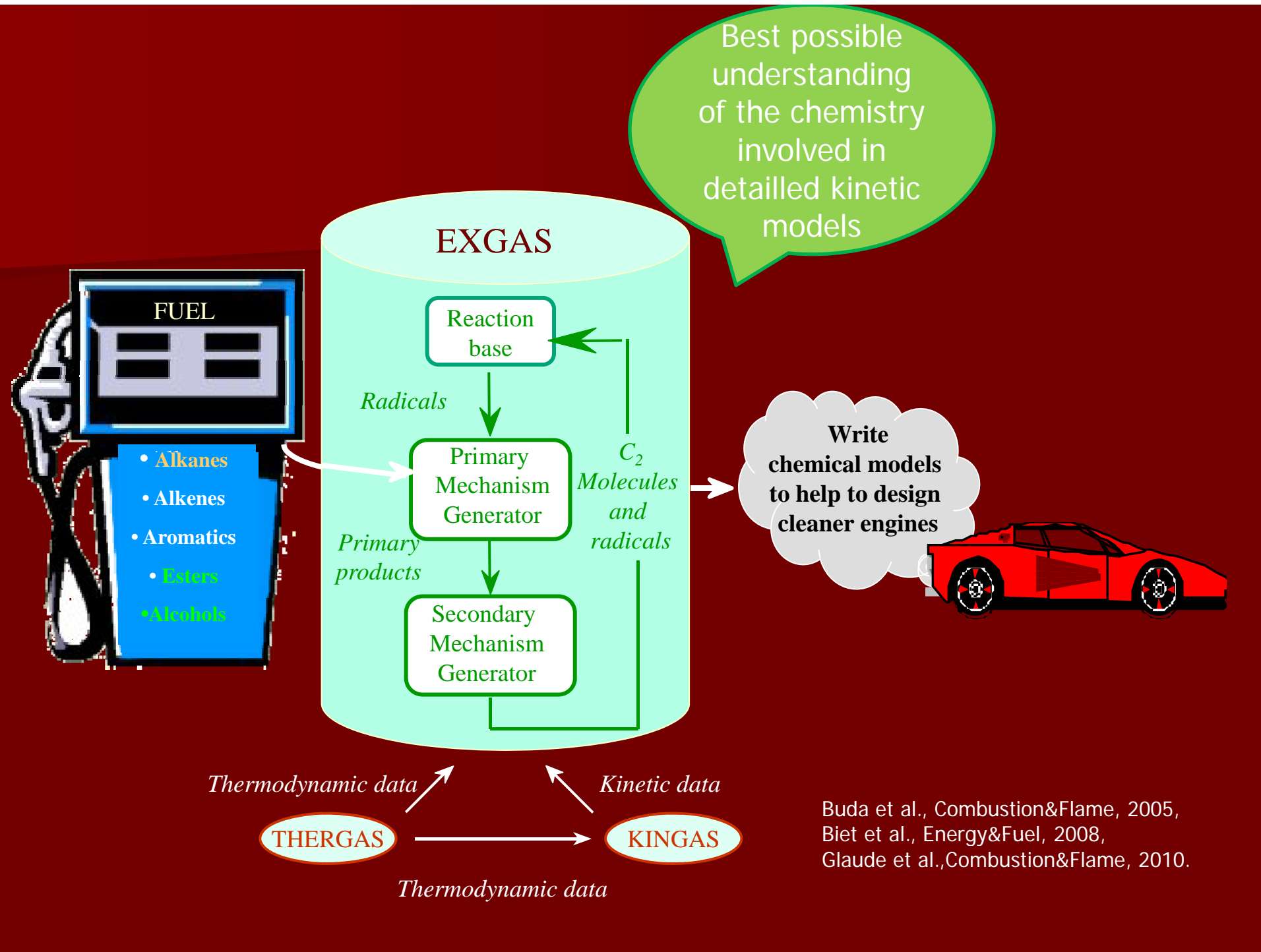


The 7th International Conference
on Chemical kinetics
July 10-14, 2011
MIT, Cambridge (USA)

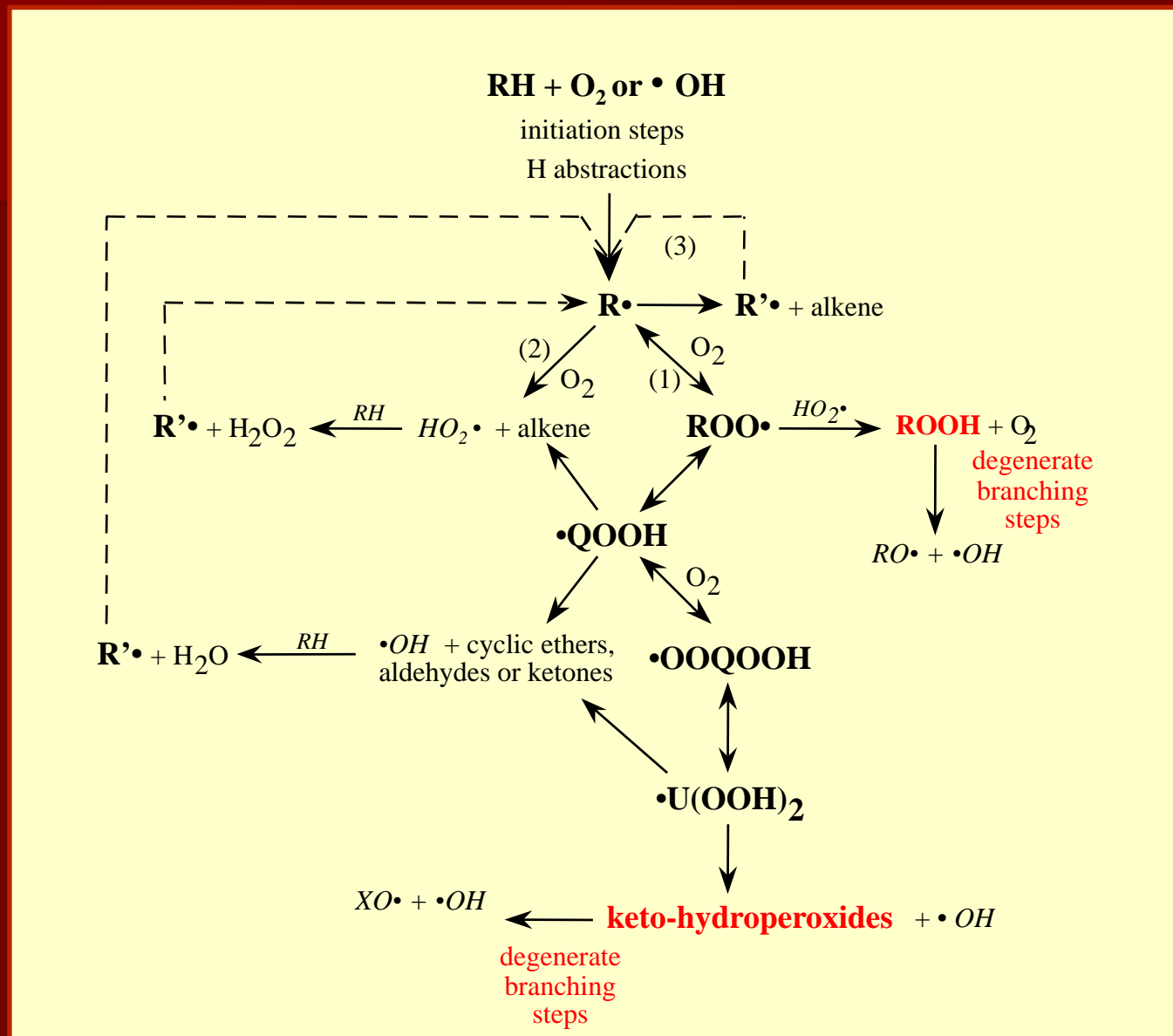


MINOR PRODUCTS ANALYSIS DURING THE LOW-TEMPERATURE OXIDATION OF ALKANES

F. Battin-Leclerc, O. Herbinet, B. Husson, P.A. Glaude, R. Fournet,
Z. Wang, Mingfeng Xie and F. Qi



Mechanism usually proposed for the gas-phase oxidation of alkanes



Experimental evidences of the formation of hydroperoxides during autoignition

Links between the concentration of hydroperoxides and the appearance of cool flame
shown using iodometric method,
but the structure of the involved species could not be determined by this way
(Burgess and Laughlin, 1967)

Ketohydroperoxides detected
after trapping at the outlet of a CFR engine
(experiments never repeated)
and of a flow reactor
(very low temperatures (498-518 K) and with very large excess in oxygen
(oxygen/hydrocarbon ratio was 1176
while the stoichiometric ratio for a complete combustion is 18.5)
(Sahetchian et al., 1991-2001)

***A new method to detect hydroperoxides
under conditions close to those observed prior autoignition***

Hydroperoxides
are very reactive species:

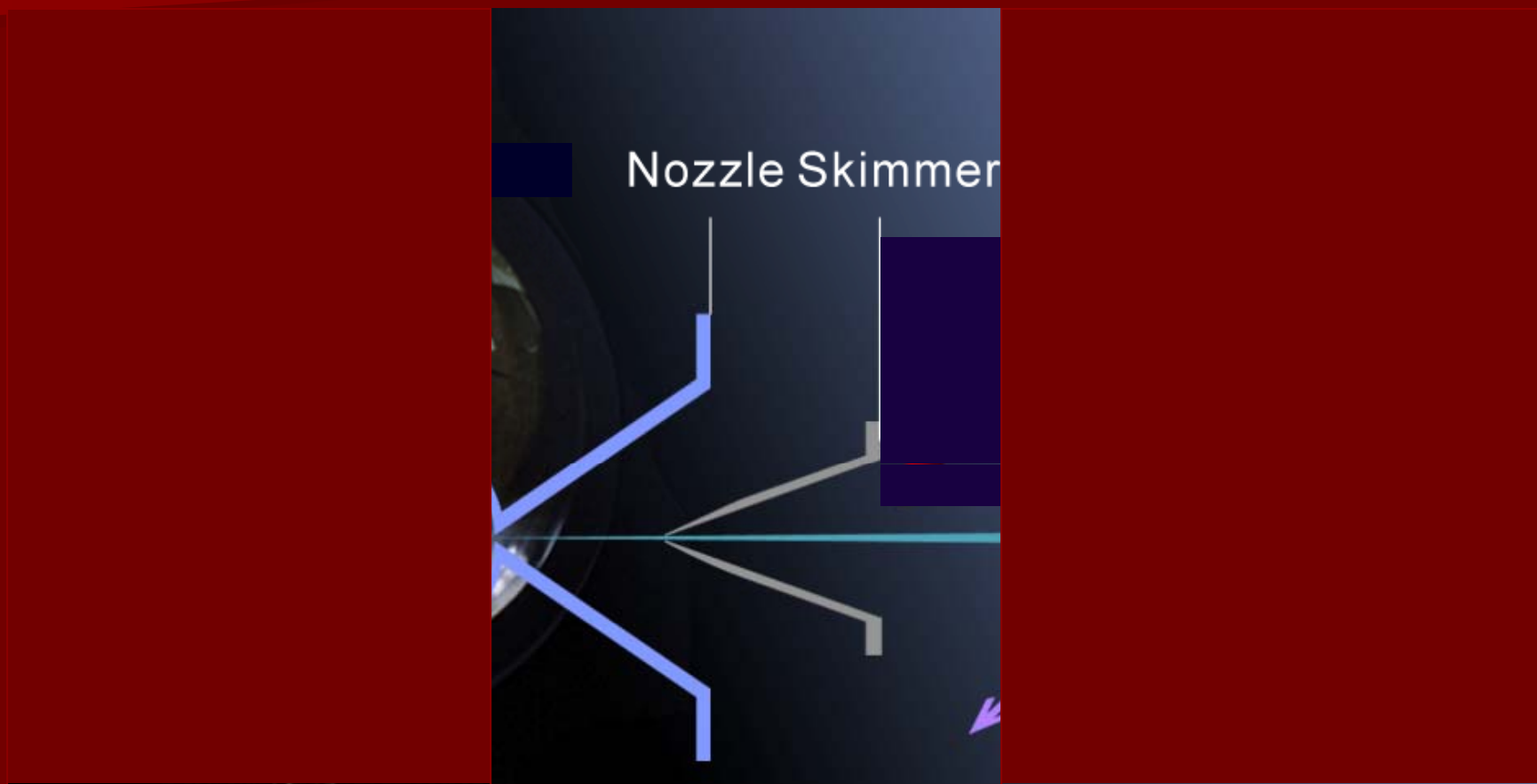
need to minimize
possible reactions
between their formation
and their detection.



**Use a
molecular beam**

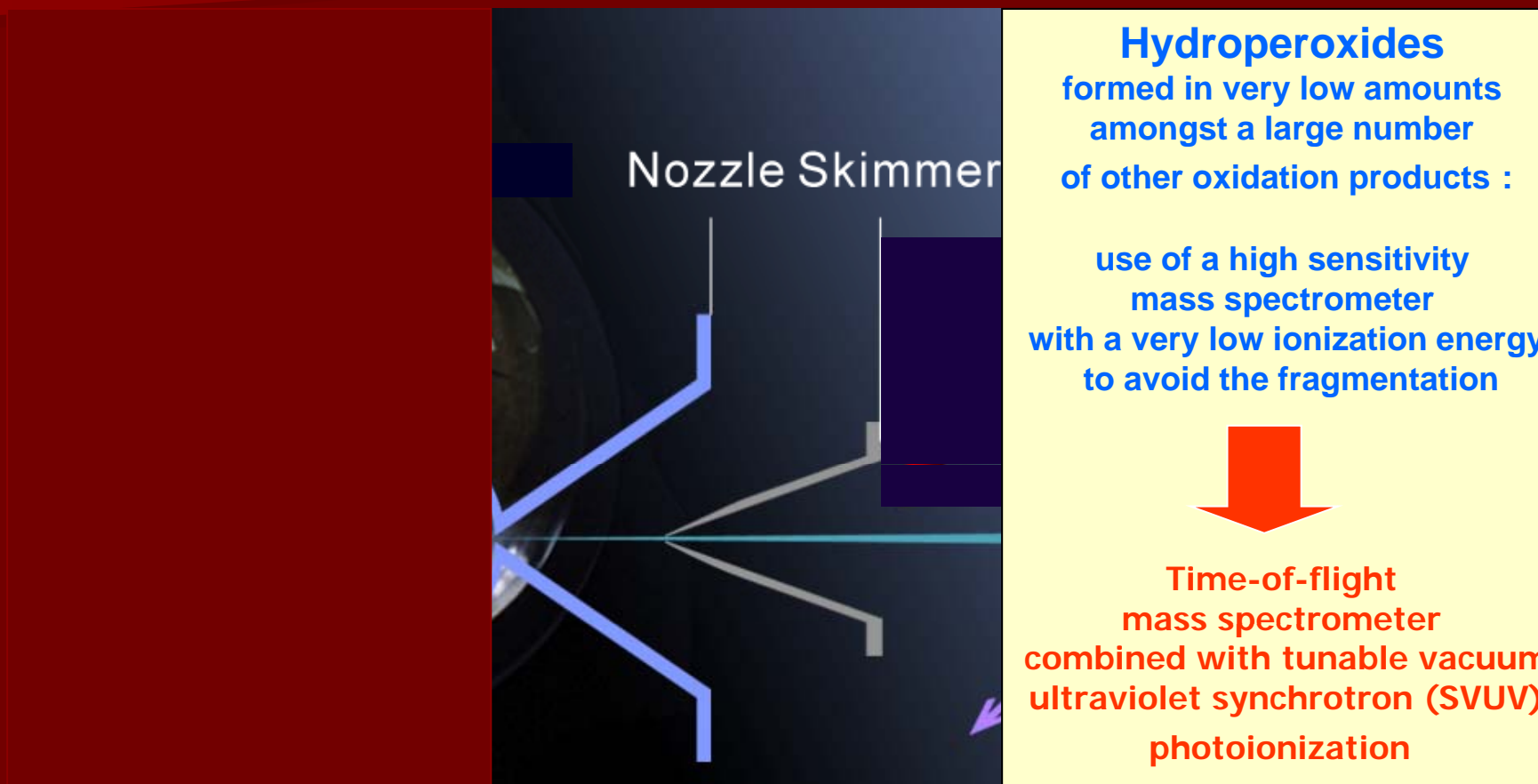
***A new method to detect hydroperoxides
under conditions close to those observed prior autoignition***

Molecular beam



***A new method to detect hydroperoxides
under conditions close to those observed prior autoignition***

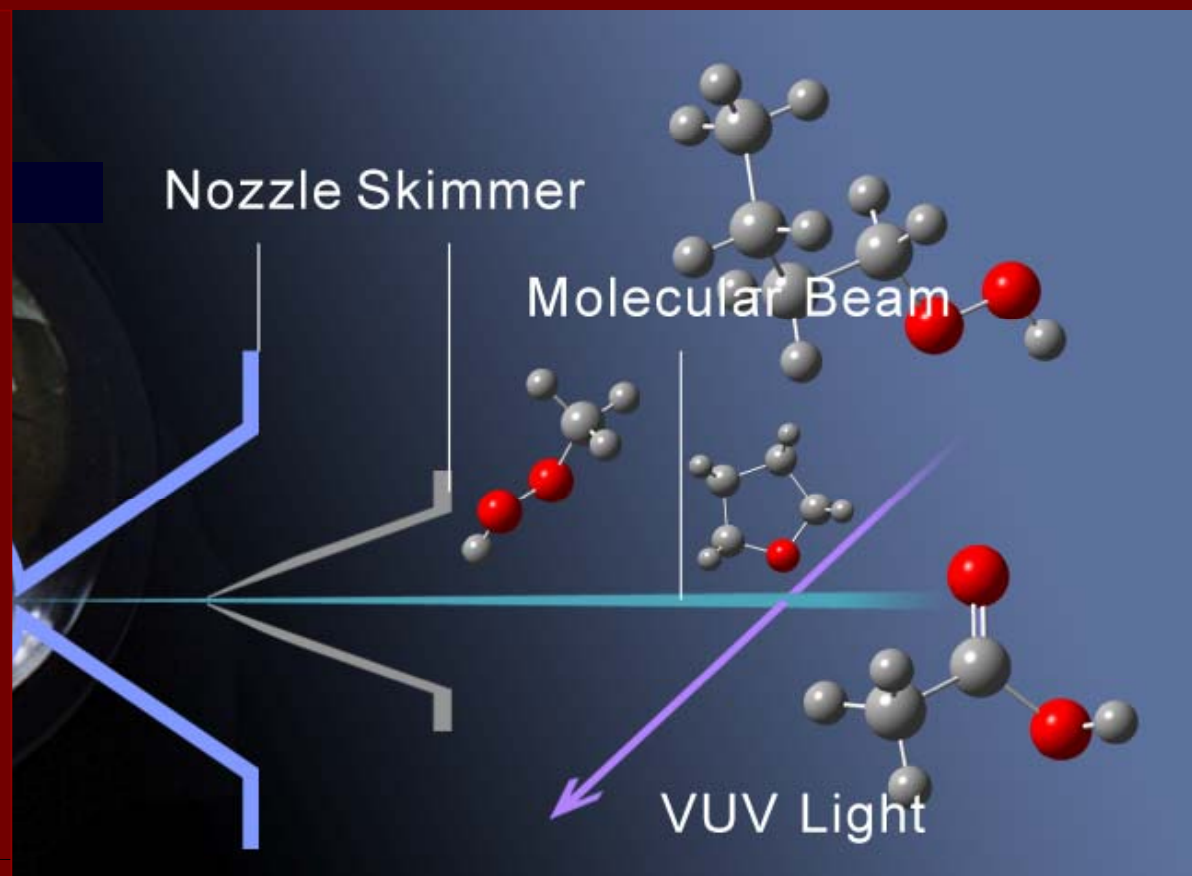
Molecular beam



*A new method to detect hydroperoxides
under conditions close to those observed prior autoignition*

Molecular beam

TOF-MS with SVUV
photoionization



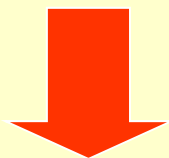
*A new method to detect hydroperoxides
under conditions close to those observed prior autoignition*

Molecular beam

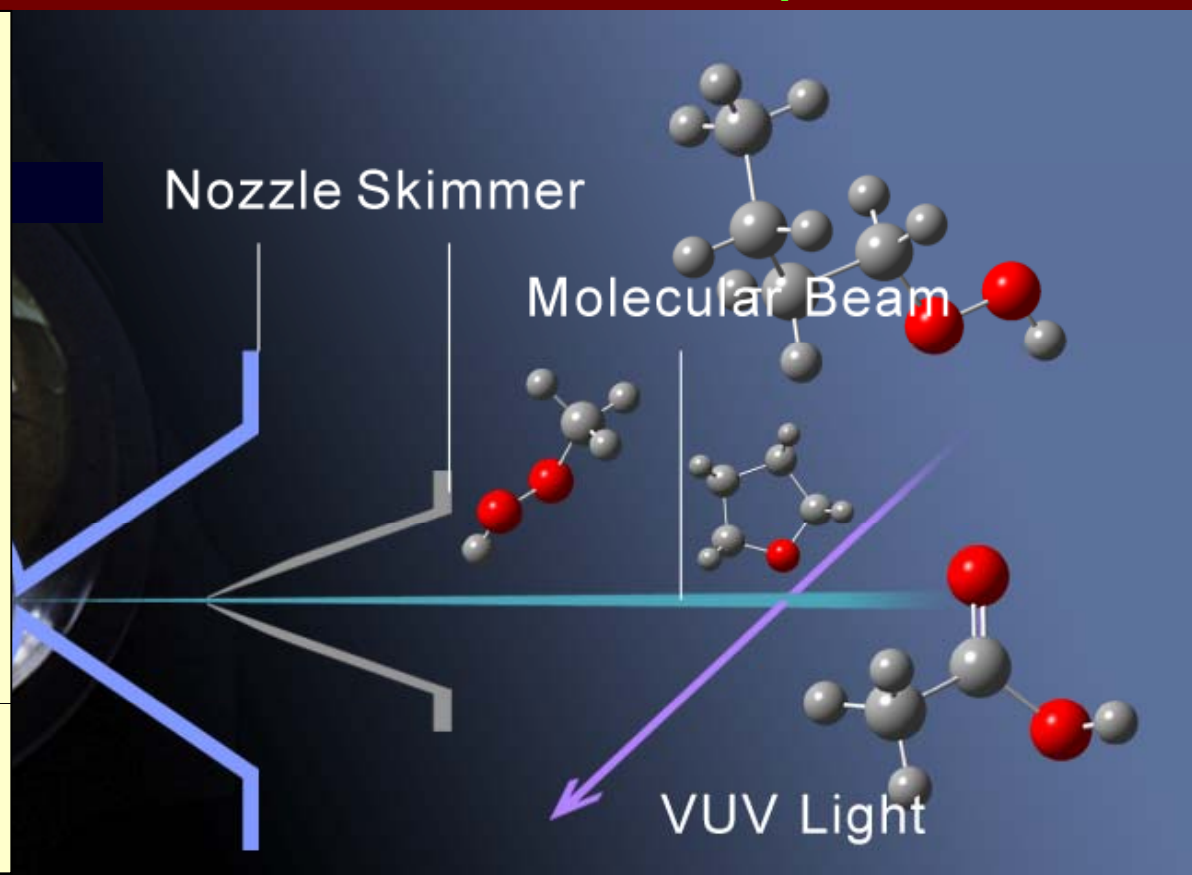
**TOF-MS with SVUV
photoionization**

Need of accumulating
several scans to obtain
a **good sensitivity**

Coupling with
a reacting system
working
under steady conditions



**Spherical quartz
jet-stirred reactor**

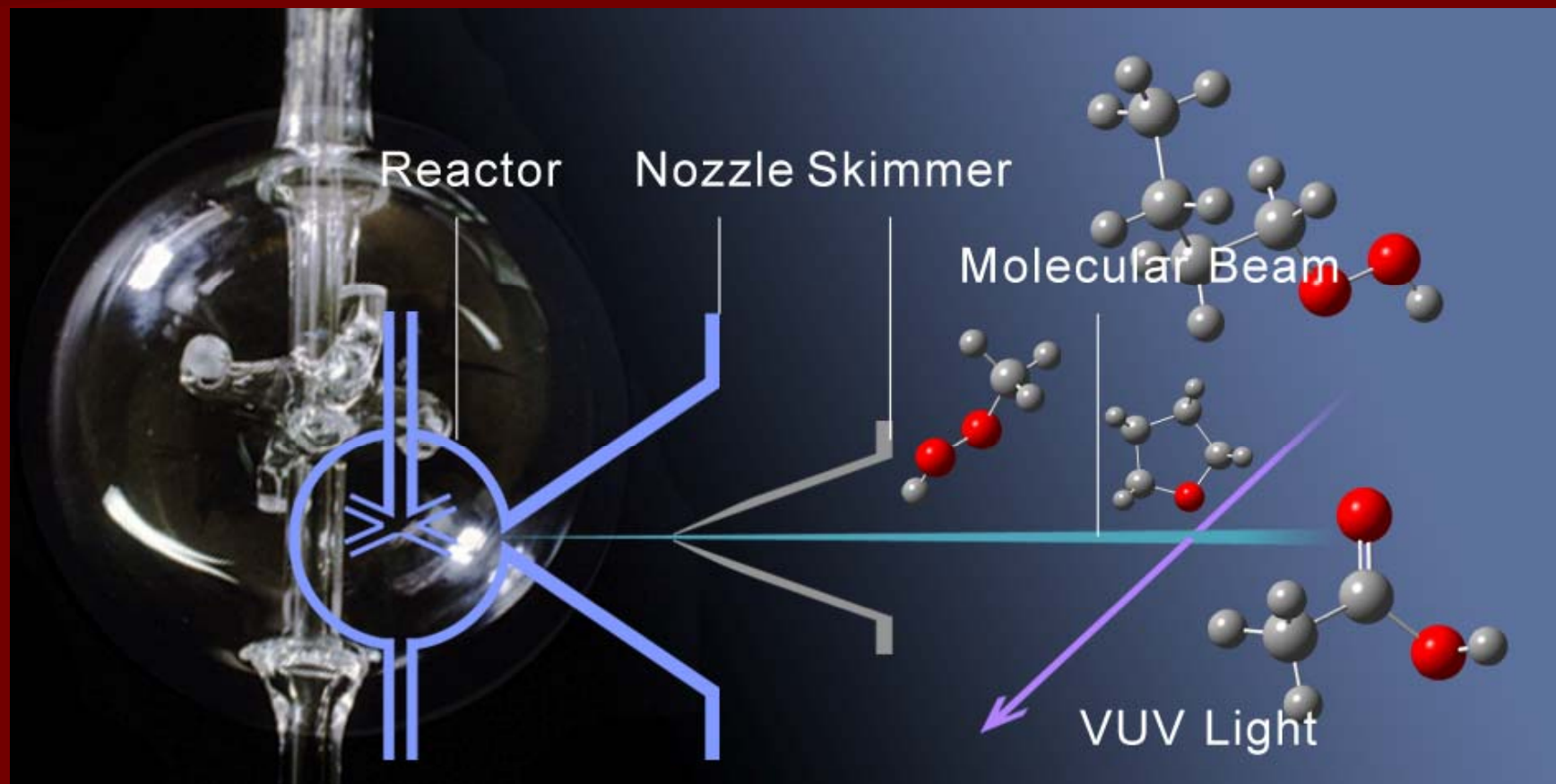


*A new method to detect hydroperoxides
under conditions close to those observed prior autoignition*

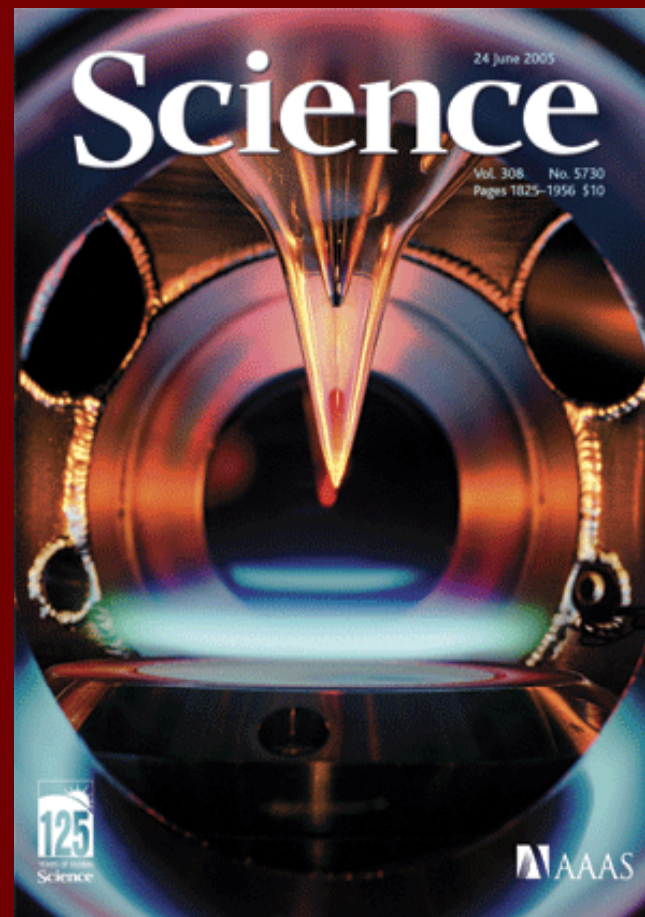
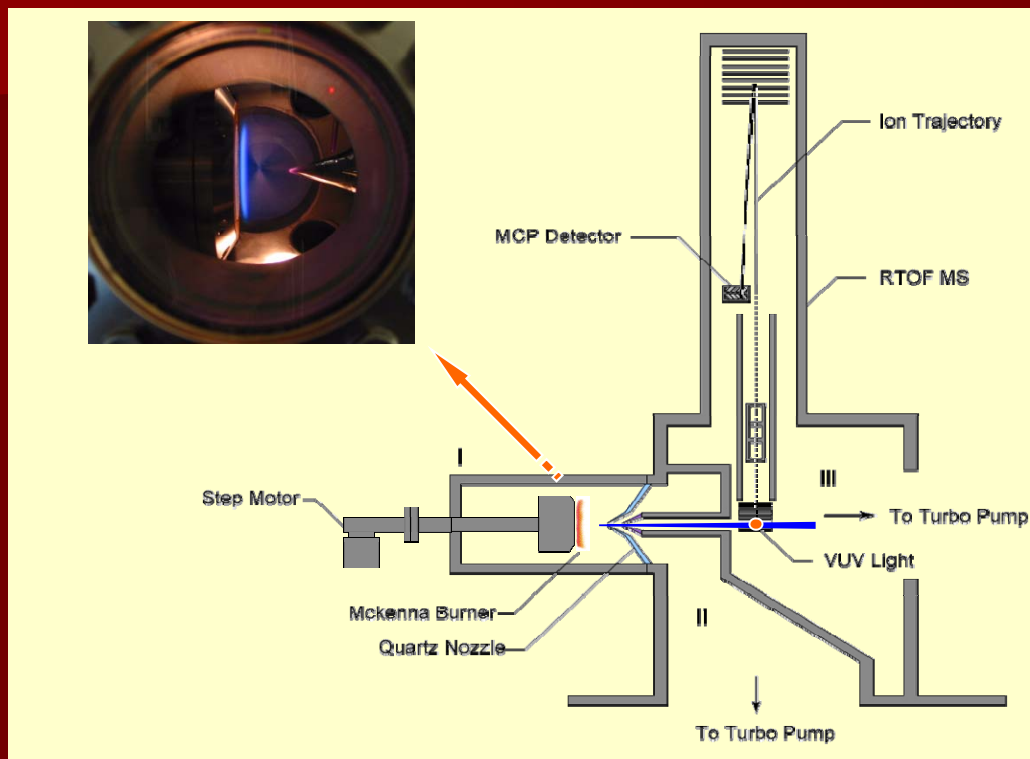
Spherical quartz
jet-stirred reactor (JSR)

Molecular beam

TOF-MS with SVUV
photoionization



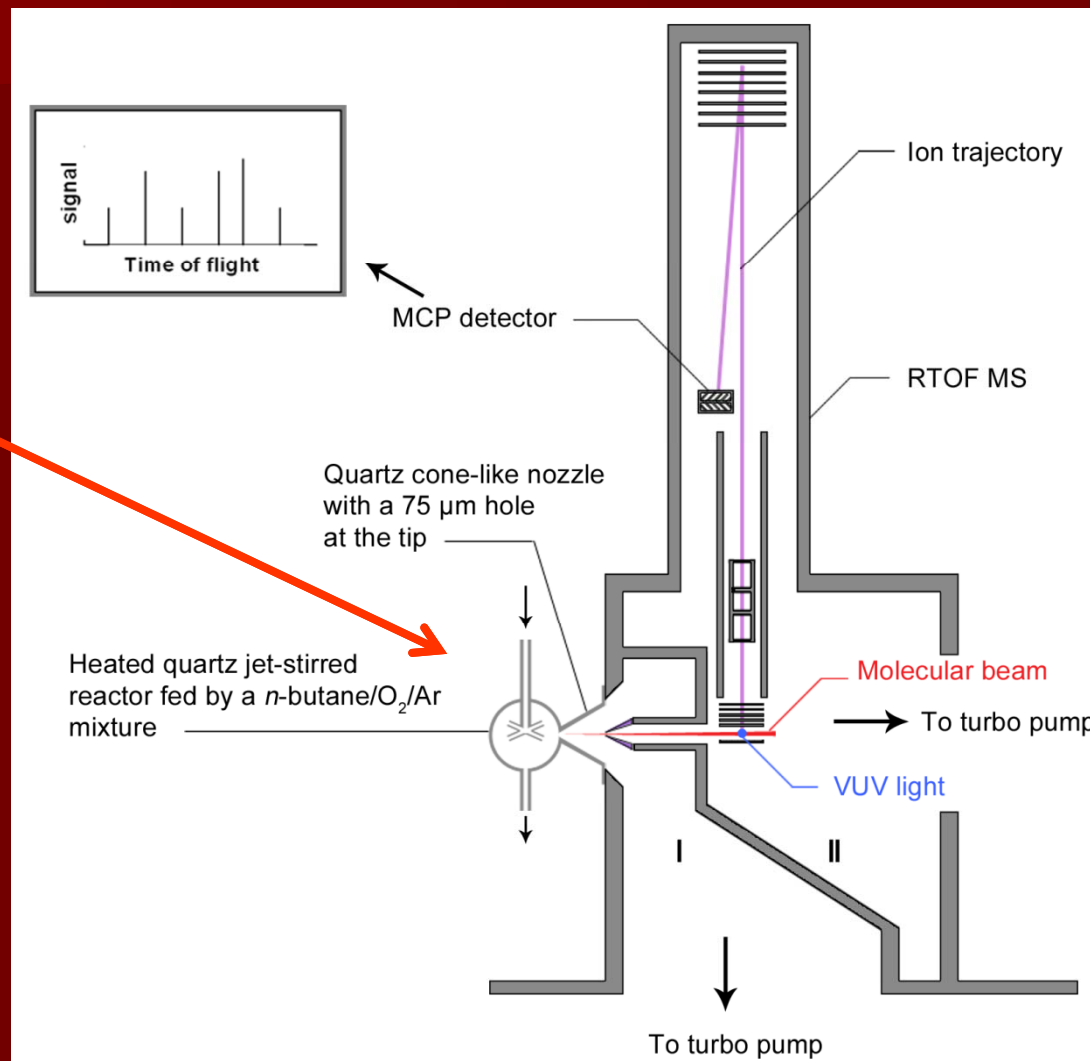
Recent applications of mass spectrometry with SVUV photoionisation



C.A. Taatjes, N. Hansen, A. McIlroy, J.A. Miller, J.P. Senosiain, S.J. Klippenstein, F. Qi, L. Sheng, Y. Zhang, T.A. Cool, J. Wang, P.R. Westmoreland, M.E. Law, T. Kasper, K. Kohse-Höinghaus, **Chemistry: Enols are common intermediates in hydrocarbon oxidation** *Science*, 308, 1887 (2005).

Coupling of a mass spectrometer combined with tunable synchrotron vacuum ultraviolet photoionization to a JSR through a molecular-beam sampling system

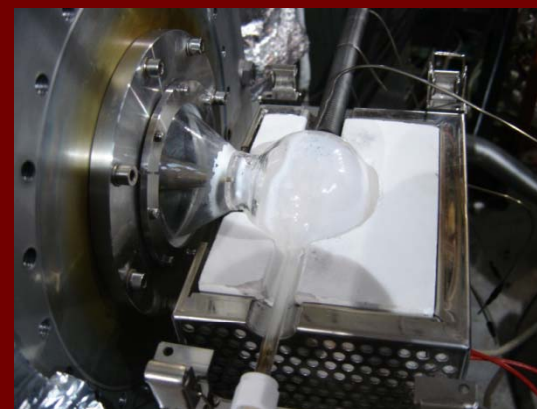
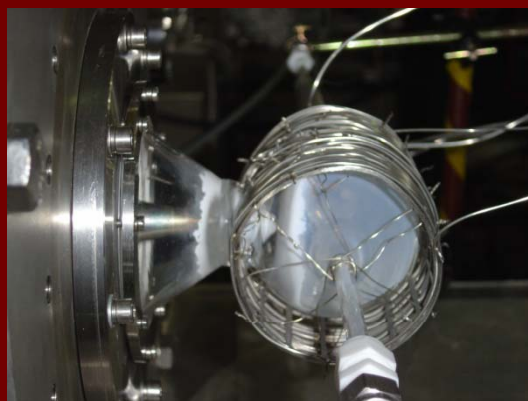
**Isotherm
quartz
jet-stirred
reactor
at atmospheric pressure
(JSR)**



The coupling through a molecular-beam sampling system between a JSR and a mass spectrometer combined with tunable synchrotron vacuum ultraviolet photoionization made in Hefei



A cone, the tip of which is pierced with a 75 μm hole has been inserted in the reactor (made in France)



The cone, with the reactor and its heating system has been connected to the MS chamber

***Study of the low-temperature
oxidation of *n*-butane
in a jet-stirred reactor under
conditions
close to that observed prior
ignition***

Study of the low-temperature oxidation of *n*-butane in a jet-stirred reactor under conditions close to that observed prior ignition

Conversion of *n*-butane

$P = 1 \text{ bar}$, $\Phi = 1$, $\tau = 6 \text{ s}$, 4% *n*-butane
(3.1 % for a stoichiometric *n*-butane/air mixture)

In Hefei:

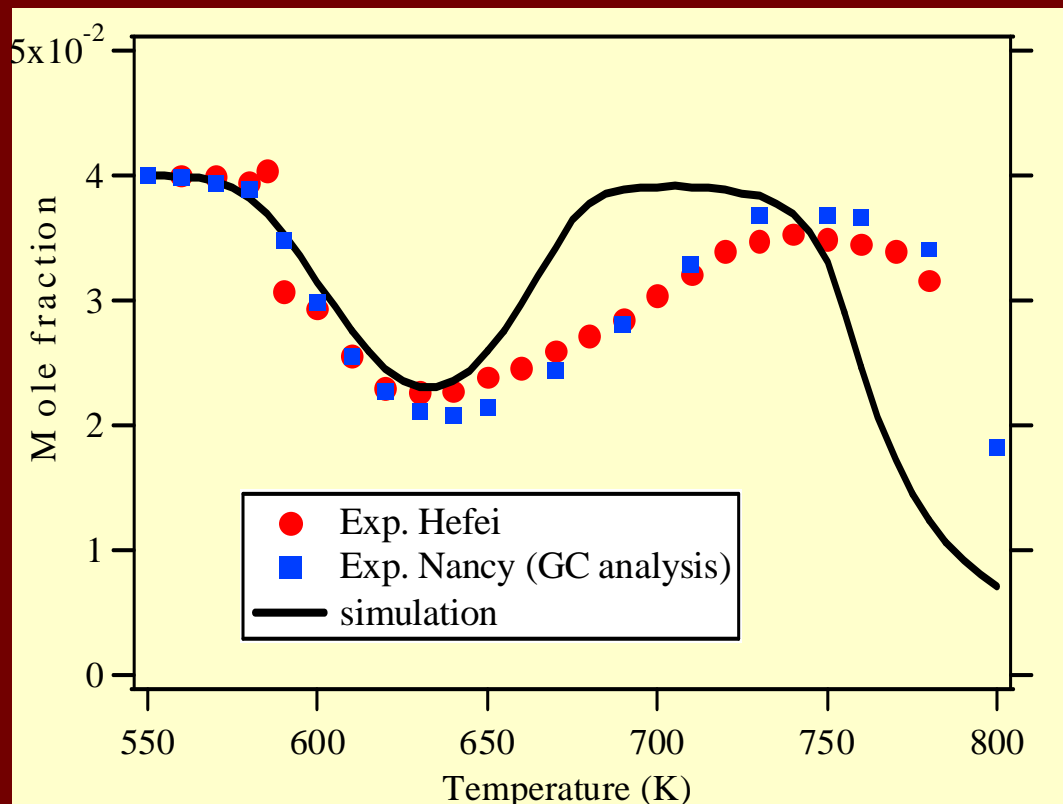
Quantification by assuming no reaction below 580K

In Nancy:

on-line gas chromatographic analysis of outlet gas

Simulation:

Using a model generated using EXGAS software



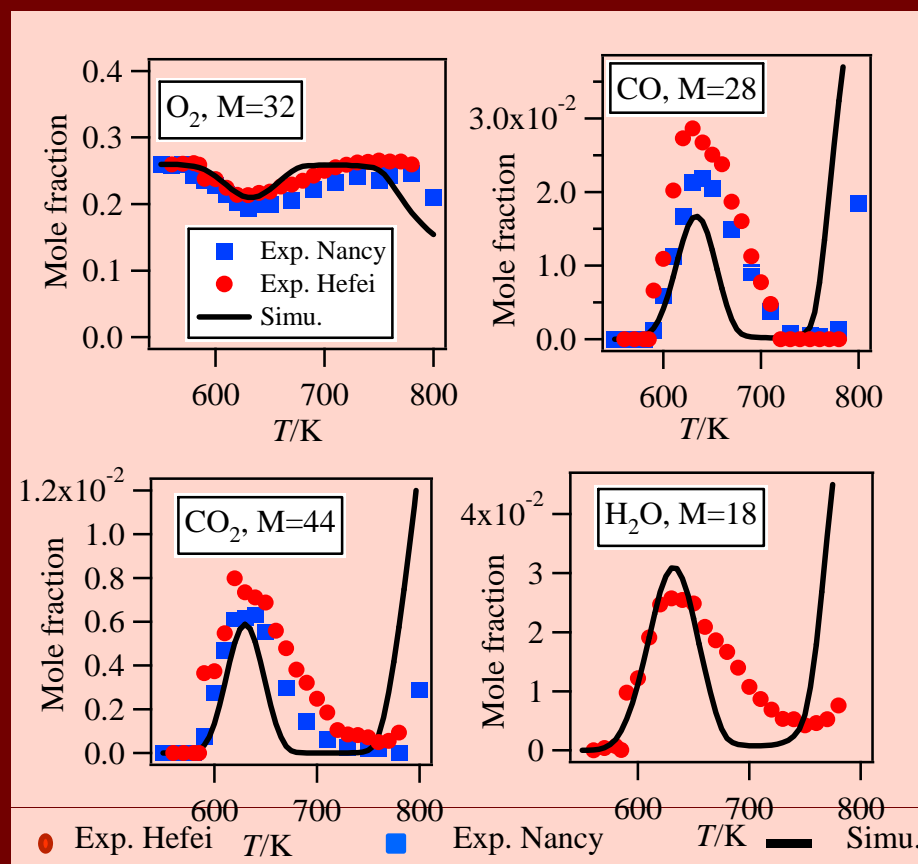
Study of the low-temperature oxidation of *n*-butane in a jet-stirred reactor under conditions close to that observed prior ignition

Main combustion products

$P = 1 \text{ bar}$, $\Phi = 1$, $\tau = 6 \text{ s}$, , 4% *n*-butane

$$\frac{S_i(T)}{S_{\text{ref}}(T)} = \frac{X_i(T)}{X_{\text{ref}}(T)} \cdot \frac{\sigma_i(T)}{\sigma_{\text{ref}}(T)} \cdot \frac{D_i(T)}{D_{\text{ref}}(T)}$$

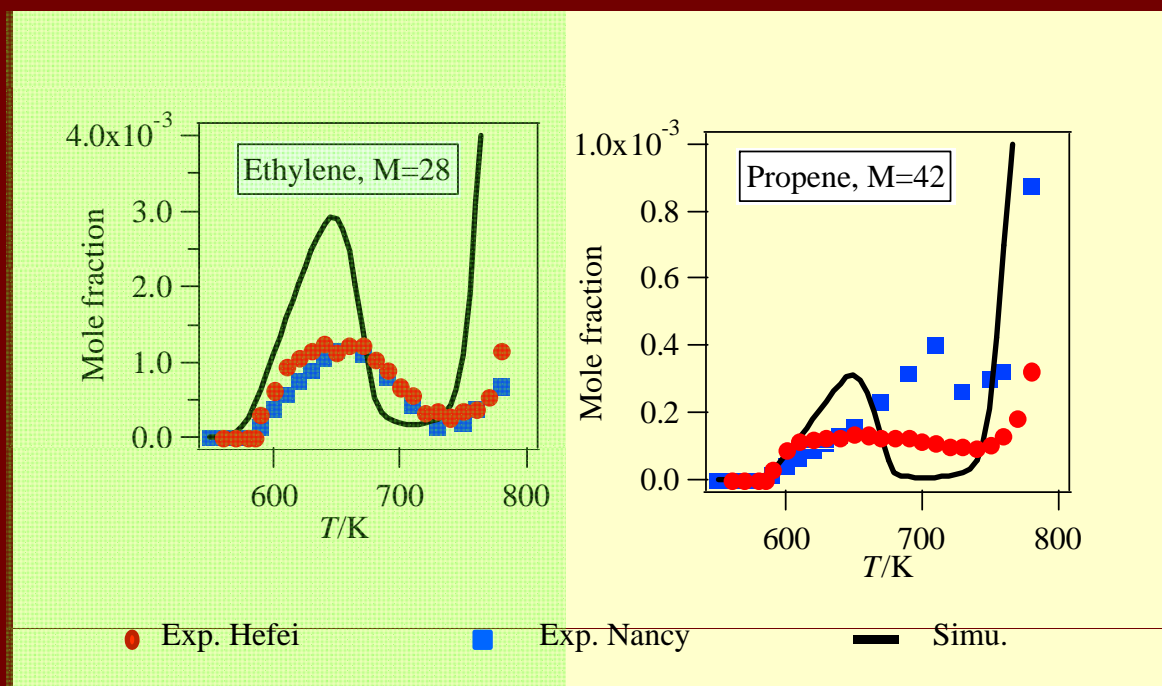
Reference is argon (16.2 eV)



Study of the low-temperature oxidation of *n*-butane in a jet-stirred reactor under conditions close to that observed prior ignition

Main combustion products

$P = 1 \text{ bar}$, $\Phi = 1$, $\tau = 6 \text{ s}$, , 4% *n*-butane



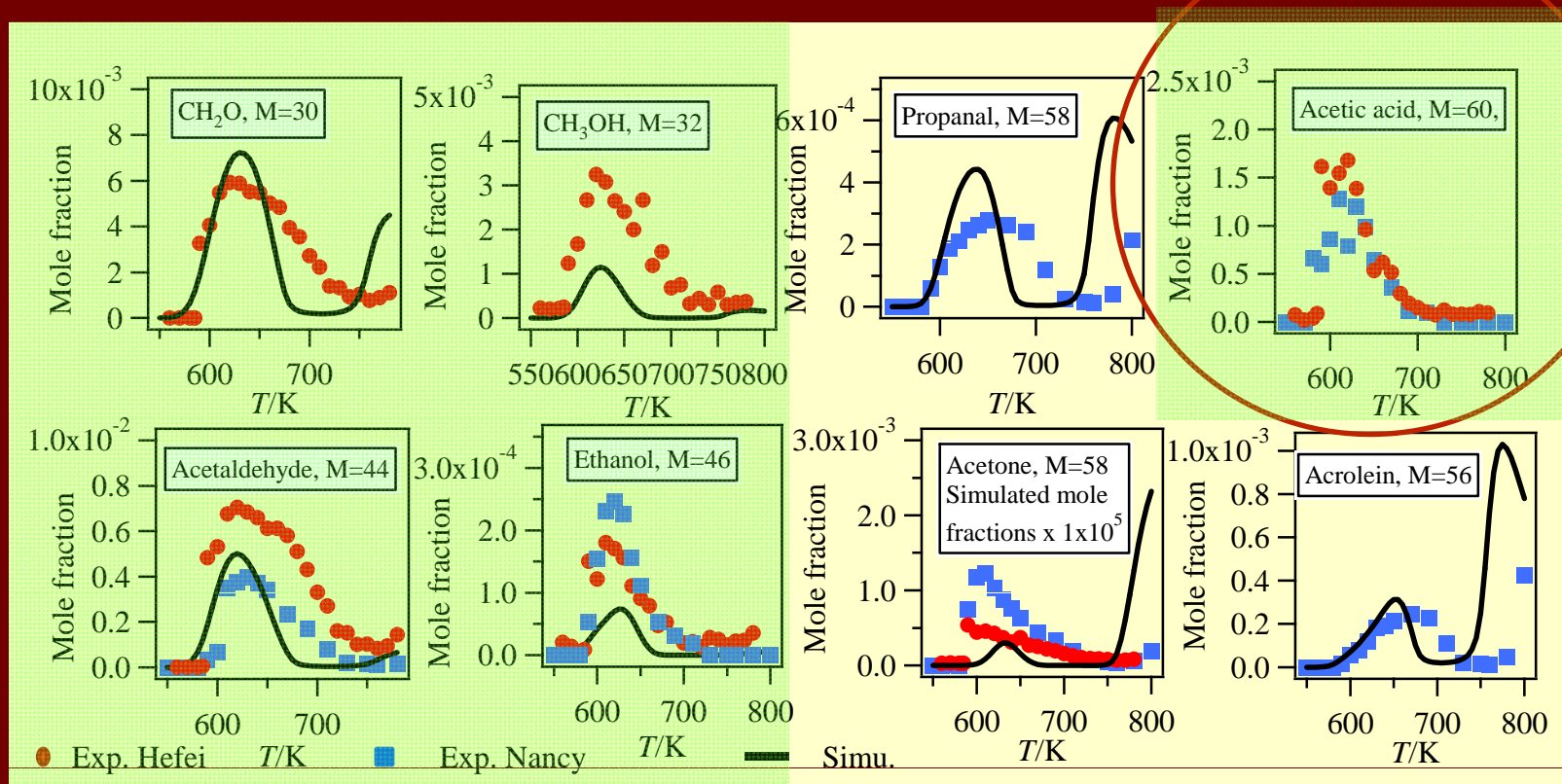
For the measurements made in Hefei, reference is **ethylene (11 eV)** and **butene (10 eV)** measured at 650 K in Nancy

Study of the low-temperature oxidation of *n*-butane in a jet-stirred reactor under conditions close to that observed prior ignition

Not usually considered in models

Light oxygenated products

$P = 1 \text{ bar}$, $\Phi = 1$, $\tau = 6 \text{ s}$, 4% *n*-butane

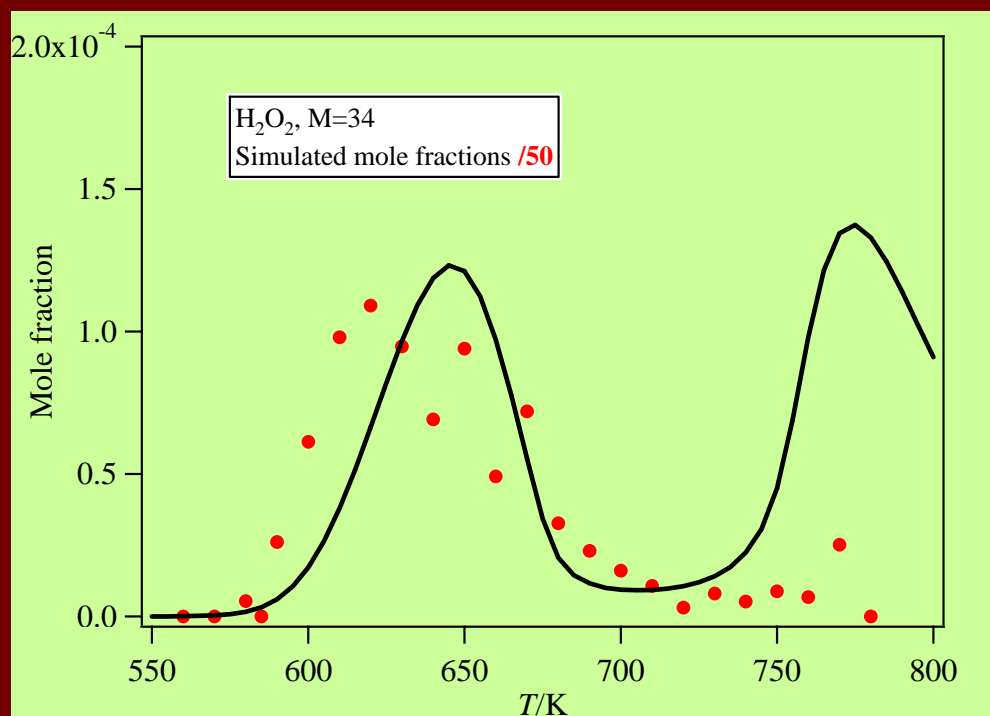


Reference is ethylene (11 eV) and butene (10 eV)

**Study of the low-temperature oxidation of *n*-butane
in a jet-stirred reactor under conditions
close to that observed prior ignition**

Hydrogen peroxide

$P = 1 \text{ bar}$, $\Phi = 1$, $\tau = 6 \text{ s}$, , 4% *n*-butane



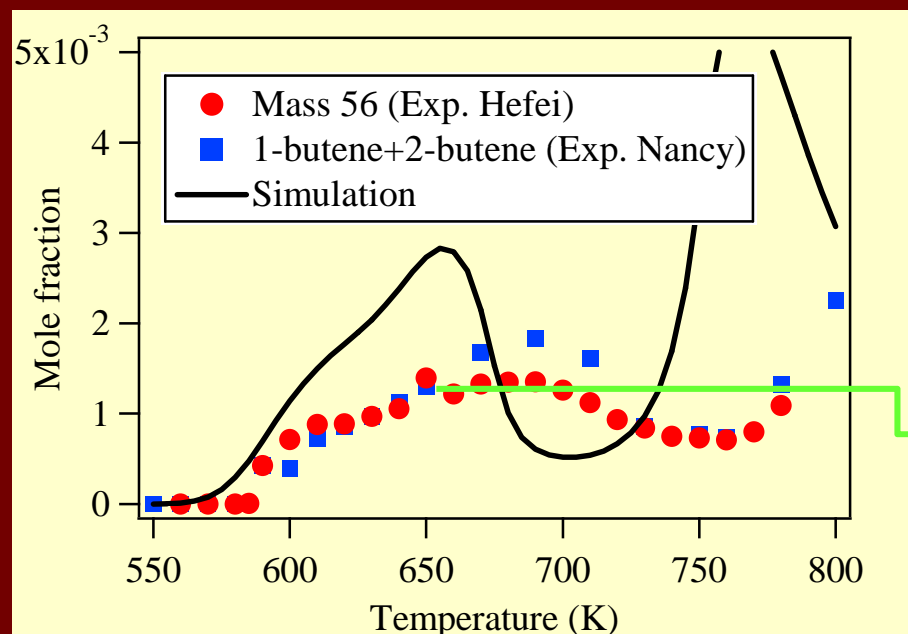
**PIE (10.65 eV) in good agreement with literature
Reference is ethylene (11 eV), σ is estimated**

Study of the low-temperature oxidation of *n*-butane in a jet-stirred reactor under conditions close to that observed prior ignition

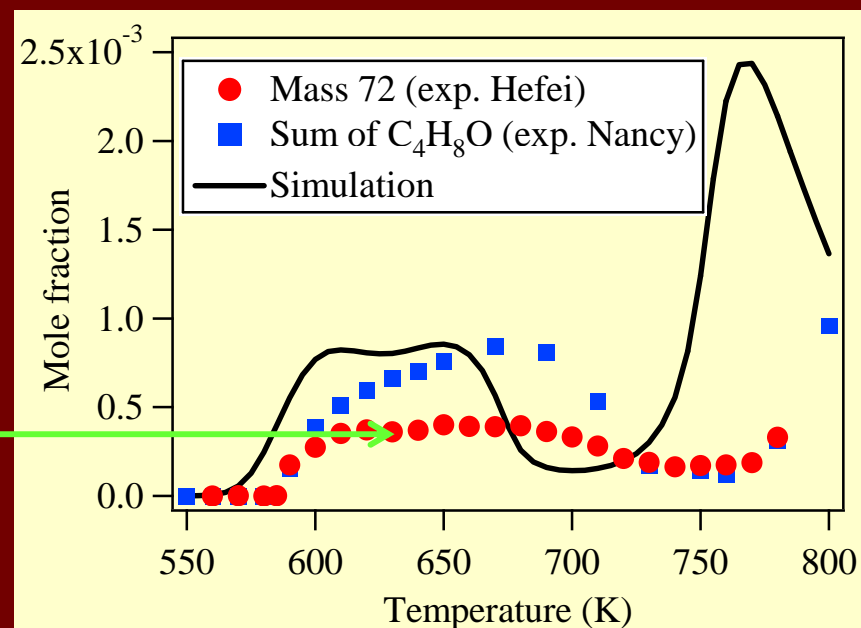
Main C₄ products

$P = 1 \text{ bar}$, $\Phi = 1$, $\tau = 6 \text{ s}$, 4% *n*-butane

Butenes



Oxygenated compounds

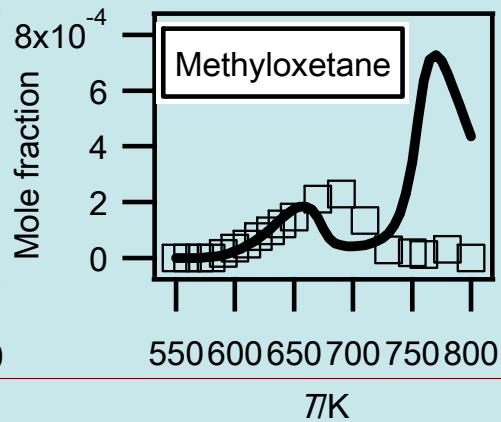
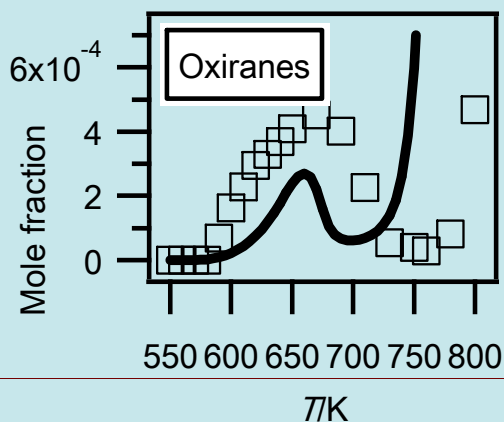
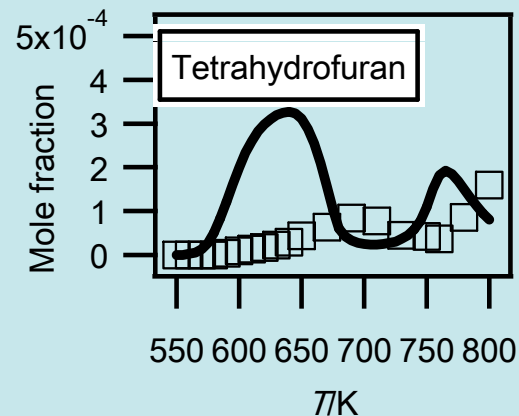
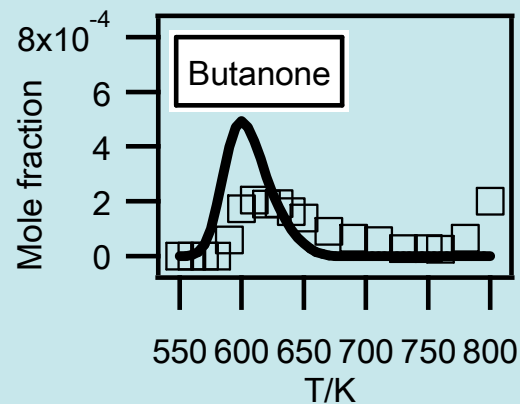
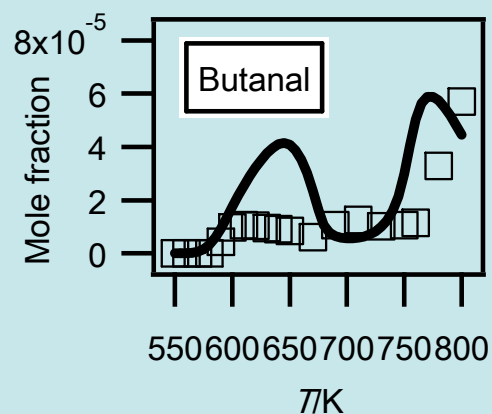


Reference is butene (10 eV, 650 K),
 σ_i of oxygenated compounds taken equal to that of tetrahydrofuran

Study of the low-temperature oxidation of *n*-butane in a jet-stirred reactor under conditions close to that observed prior ignition

Details of C_4H_8O products

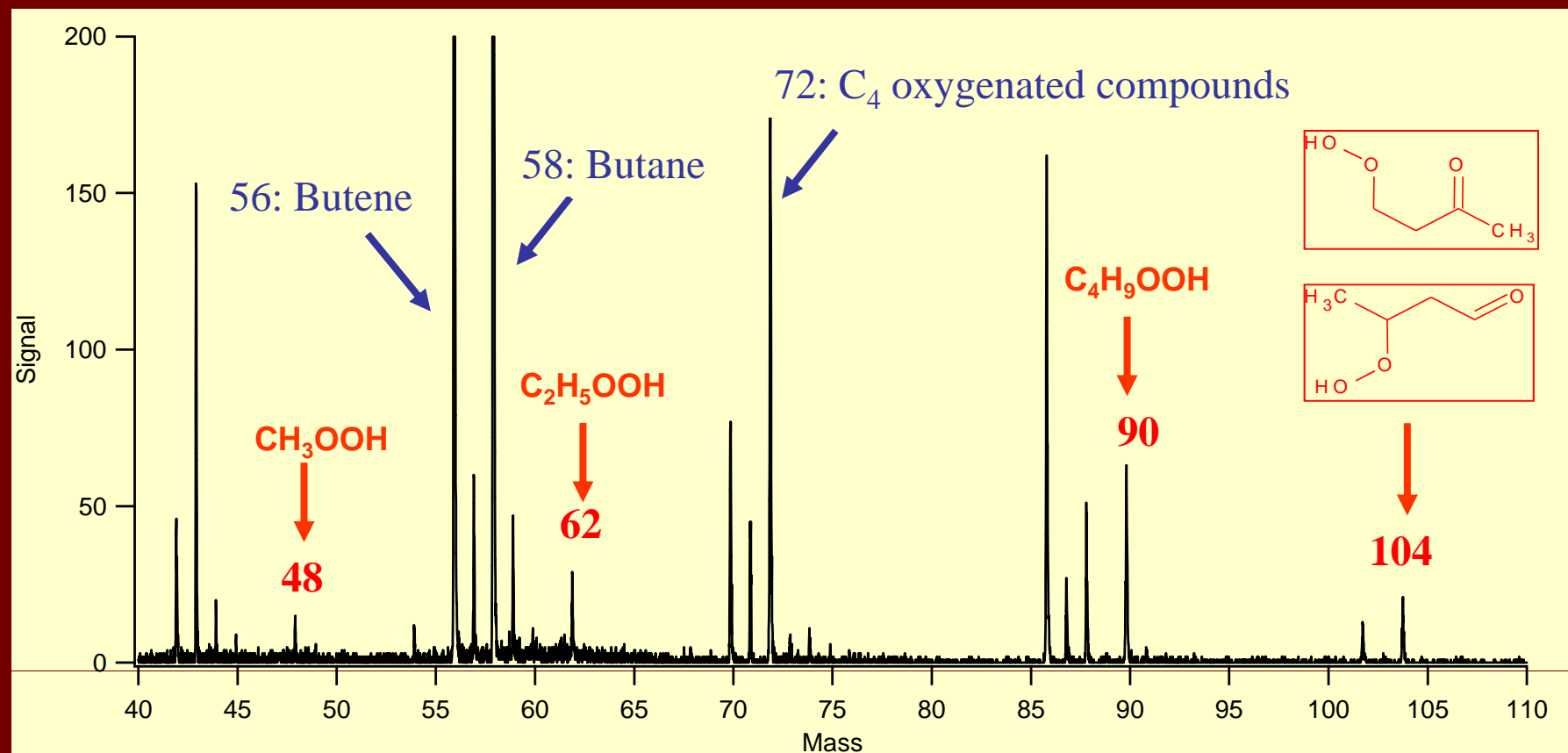
$P = 1 \text{ bar}$, $\Phi = 1$, $\tau = 6 \text{ s}$, 4% *n*-butane (GC Nancy)



**Study of the low-temperature oxidation of *n*-butane
in a jet-stirred reactor under conditions
close to that observed prior ignition**

Obtained mass spectrum

P = 1 bar, $\Phi = 1$, $\tau = 6$ s, 4% *n*-butane, 590 K, 10 eV

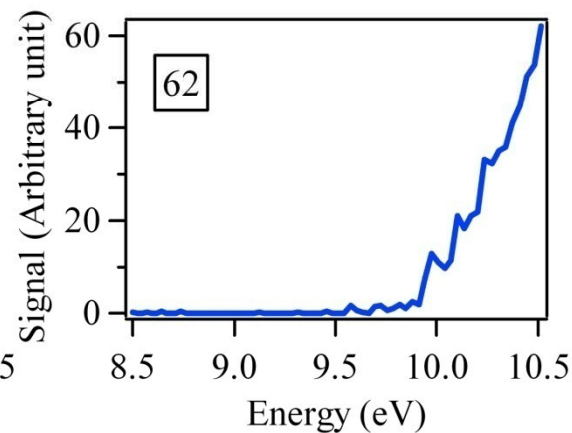
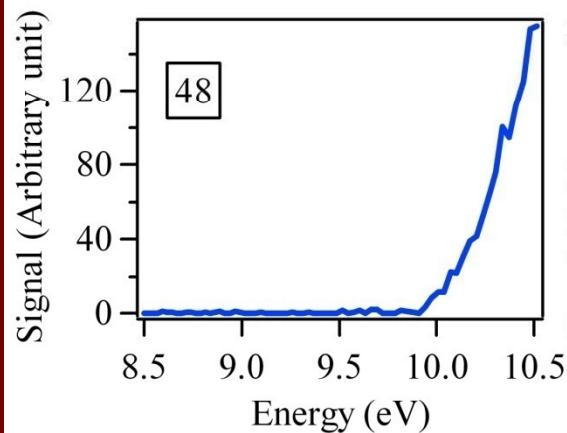


Study of the low-temperature oxidation of *n*-butane in a jet-stirred reactor under conditions close to that observed prior ignition

Ionization energy (IE) measurements

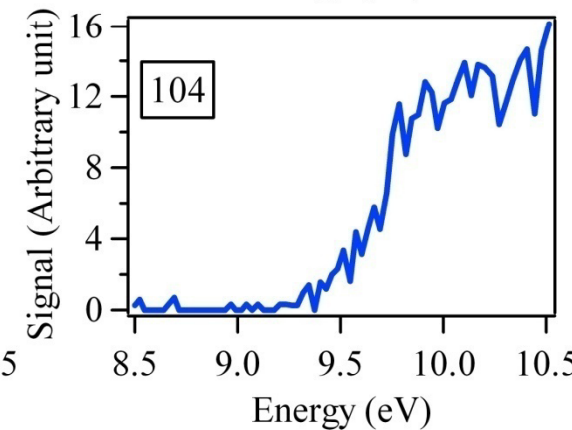
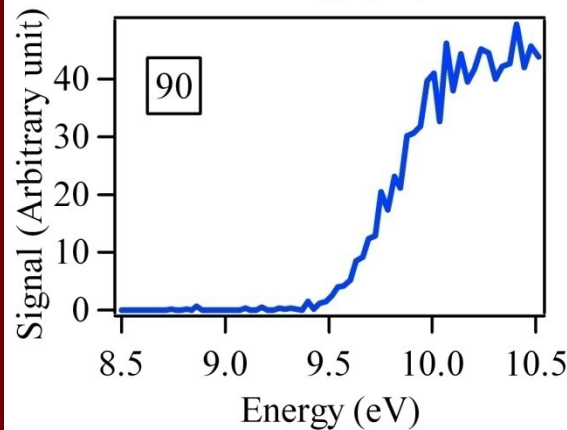
$P = 1$ bar, $\Phi = 1$, $\tau = 6$ s, 4% *n*-butane, 590 K

IE of CH_3OOH
=
9.83 eV



IE of $\text{C}_2\text{H}_5\text{OOH}$
=
9.61 eV

IE of $\text{C}_4\text{H}_9\text{OOH}$
=
9.33-9.36 eV



IE of ketohydroperoxides
=
9.34-9.39 eV

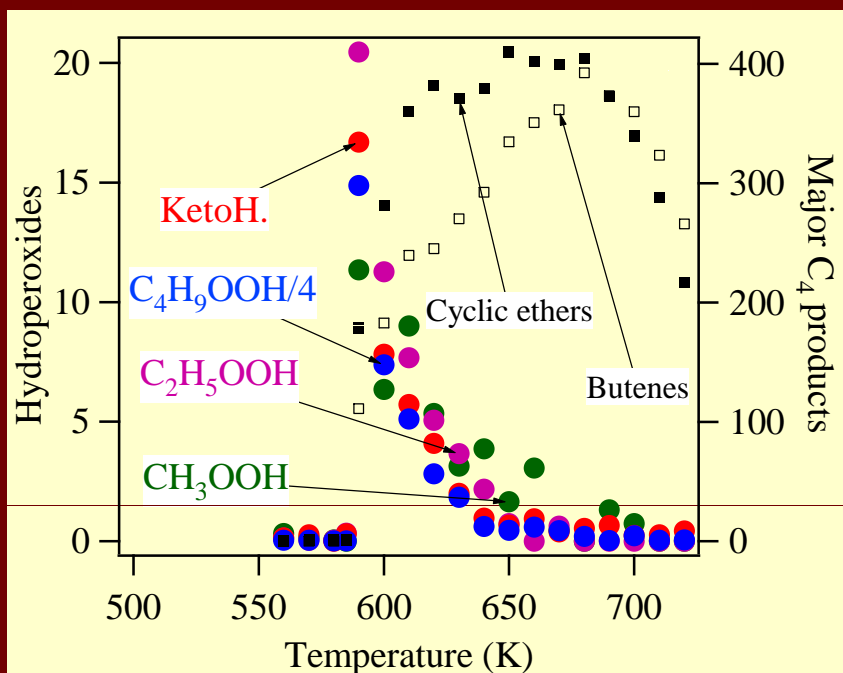
Zero-point energy corrected adiabatic IEs have been calculated from the CBS-QB3 method using Gaussian03.

Study of the low-temperature oxidation of *n*-butane in a jet-stirred reactor under conditions close to that observed prior ignition

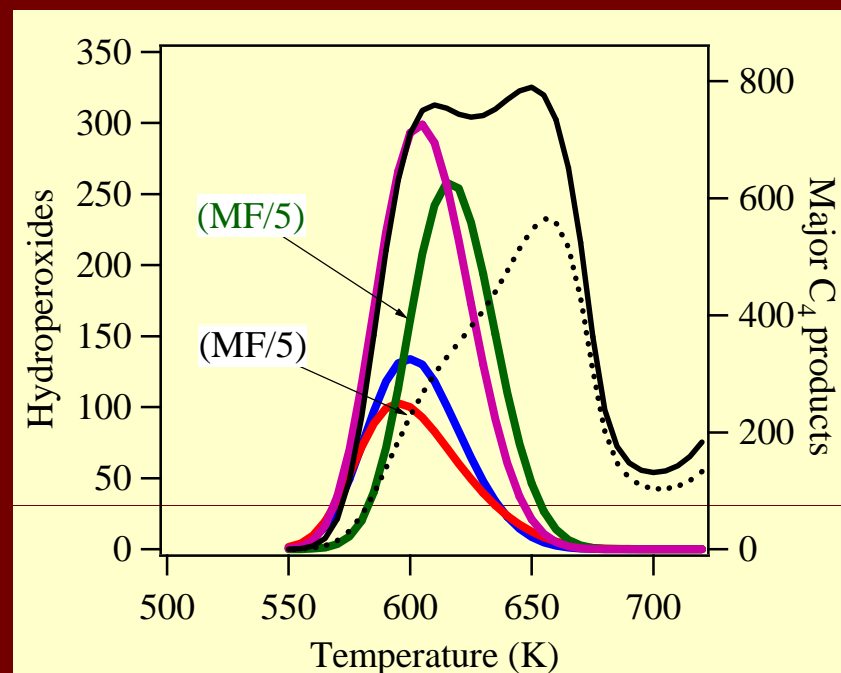
Evolution of hydroperoxides signal with temperature

$P = 1 \text{ bar}$, $\Phi = 1$, $\tau = 6 \text{ s}$, 4% *n*-butane, 10 eV

Experimental



Simulation

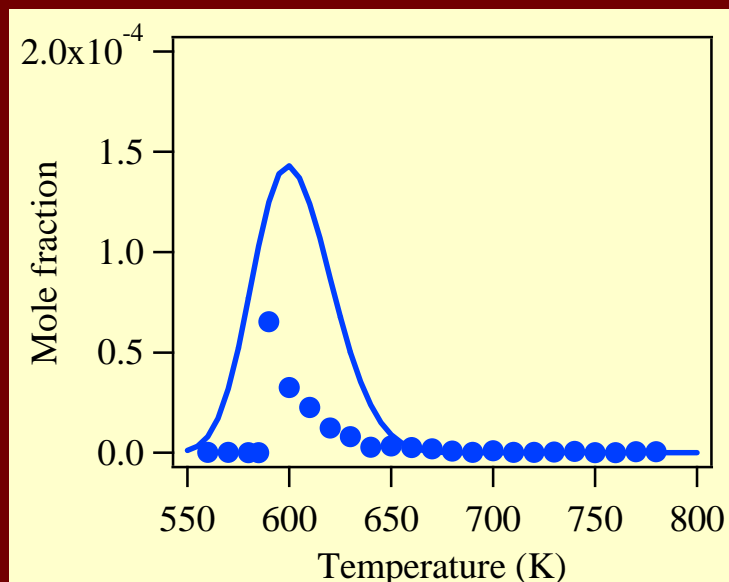


**Study of the low-temperature oxidation of *n*-butane
in a jet-stirred reactor under conditions
close to that observed prior ignition**

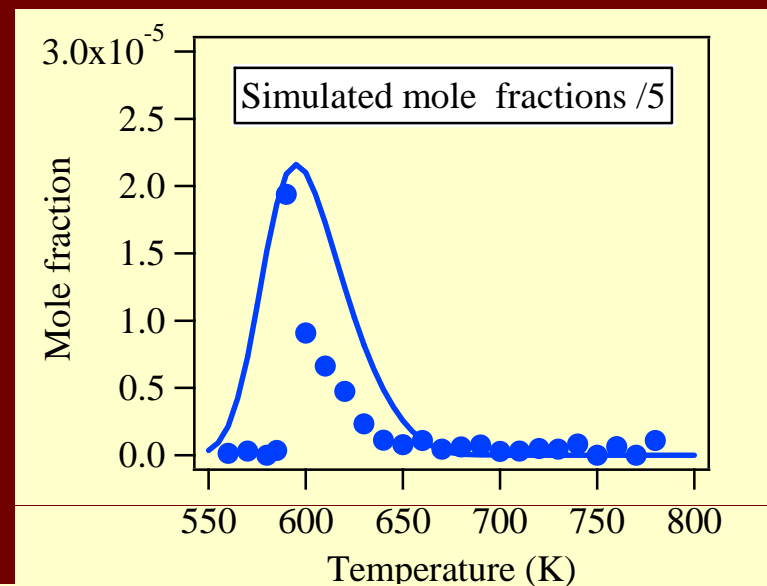
Quantification of C₄ hydroperoxides

P = 1 bar, Φ = 1, τ = 6 s, 4% *n*-butane

C₄H₉OOH



Ketohydroperoxides



● Exp. Hefei

■ Exp. Nancy

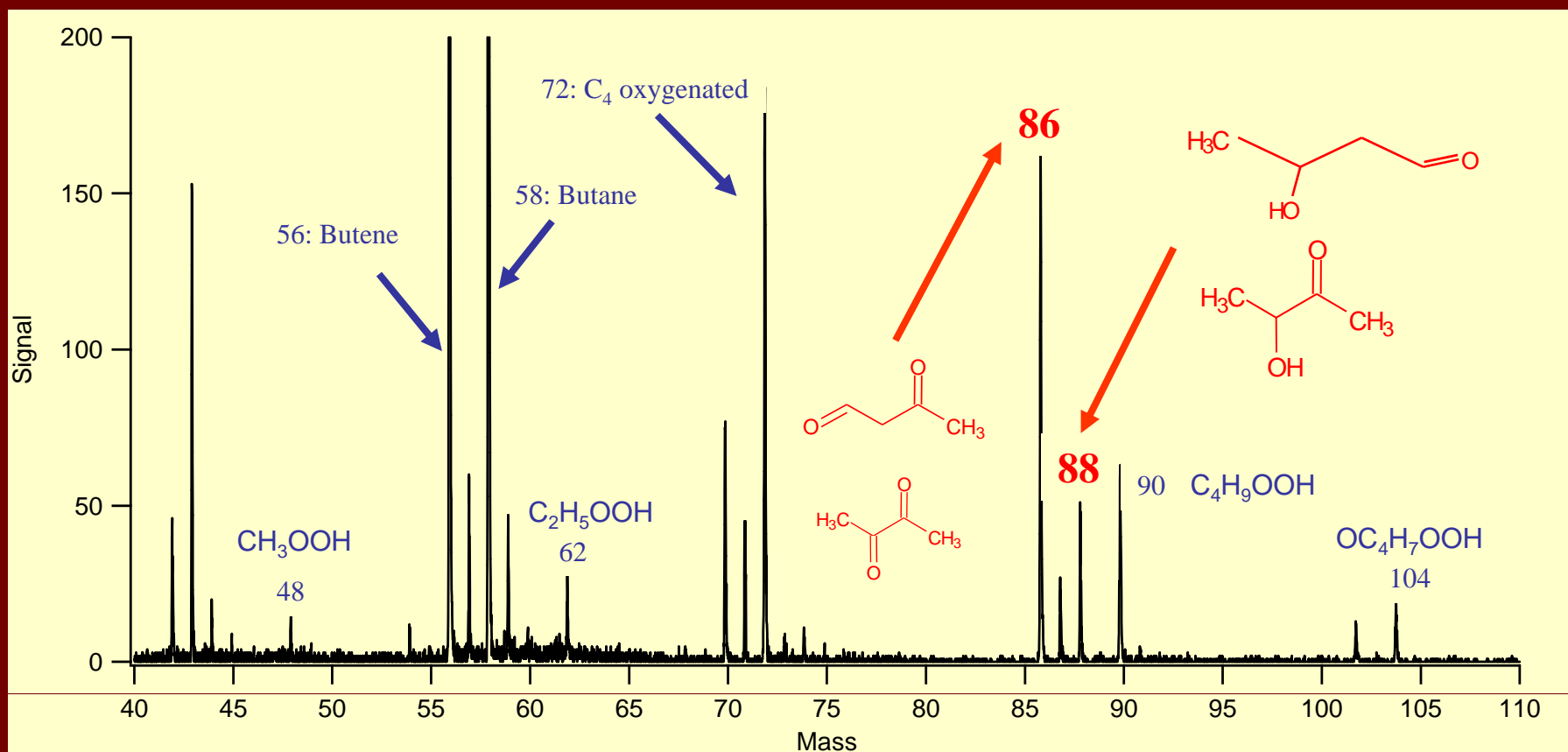
— Simu.

**Reference is butene (10 eV, 650 K),
σ_i taken equal to that of tetrahydrofuran**

Study of the low-temperature oxidation of *n*-butane in a jet-stirred reactor under conditions close to that observed prior ignition

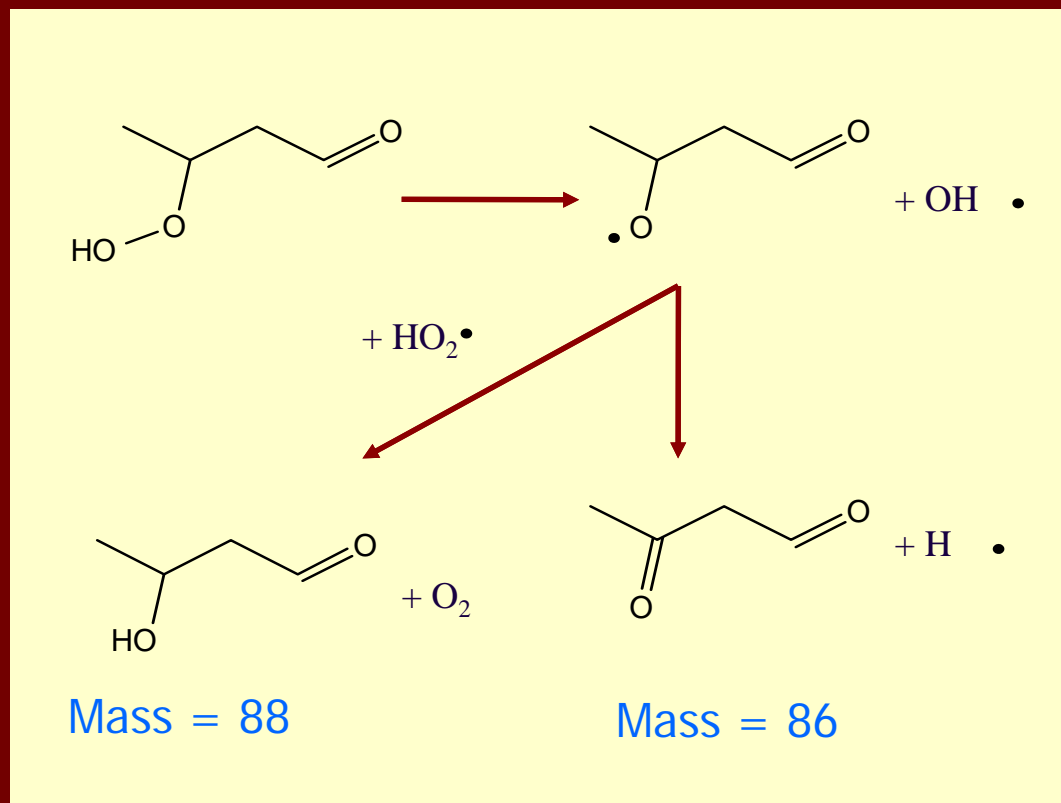
Other peaks on the obtained mass spectrum

P = 1 bar, $\Phi = 1$, $\tau = 6$ s, 4% *n*-butane, 590 K, 10 eV



*Study of the low-temperature oxidation of n-butane
in a jet-stirred reactor under conditions
close to that observed prior ignition*

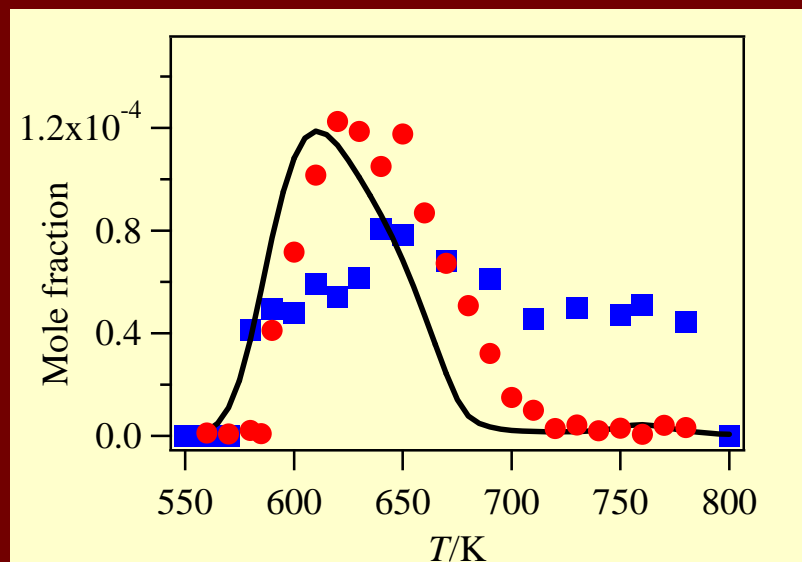
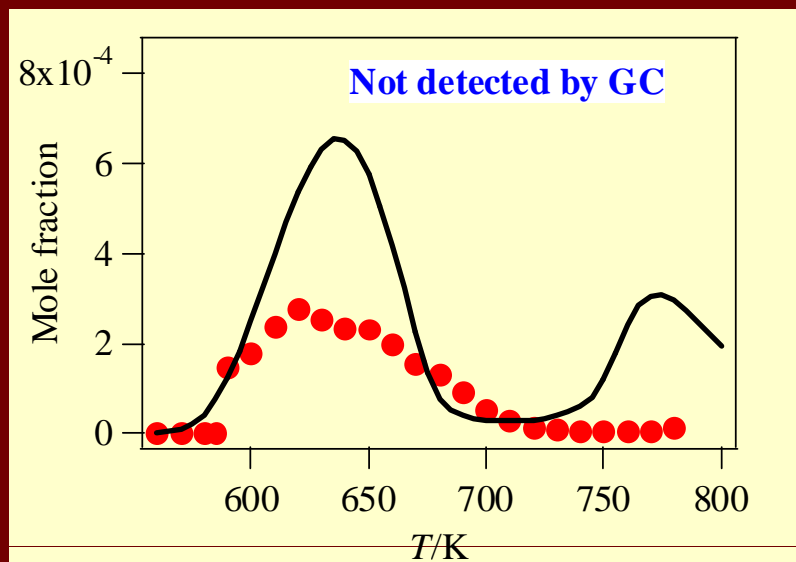
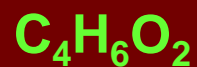
Possible ways of formation of C₄ dioxygenated compounds



**Study of the low-temperature oxidation of *n*-butane
in a jet-stirred reactor under conditions
close to that observed prior ignition**

Quantification of C₄ dioxygenated compounds

P = 1 bar, Φ = 1, τ = 6 s, 4% *n*-butane



● Exp. Hefei

■ Exp. Nancy

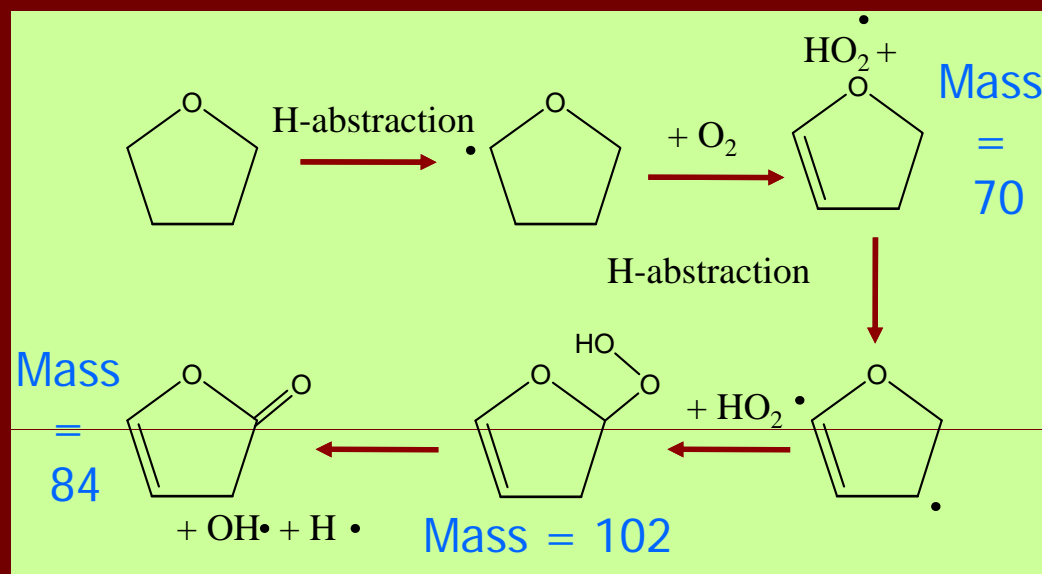
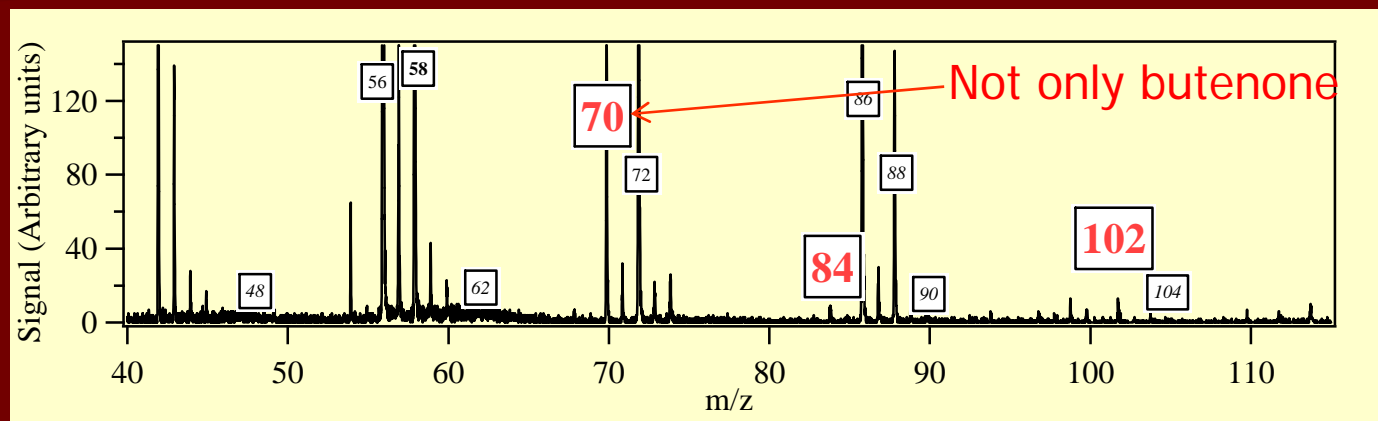
— Simu.

**Reference is butene (10 eV, 650 K),
σ_i taken equal to that of tetrahydrofuran**

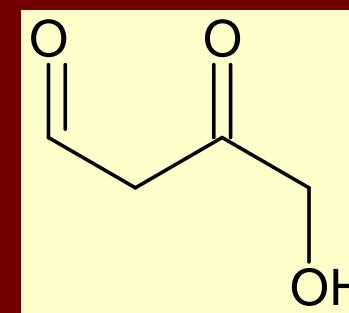
Study of the low-temperature oxidation of *n*-butane in a jet-stirred reactor under conditions close to that observed prior ignition

Minor peaks on the obtained mass spectrum

$P = 1 \text{ bar}$, $\Phi = 1$, $\tau = 6 \text{ s}$, 4% *n*-butane, 630 K, 10 eV



$M = 102$ is mainly:

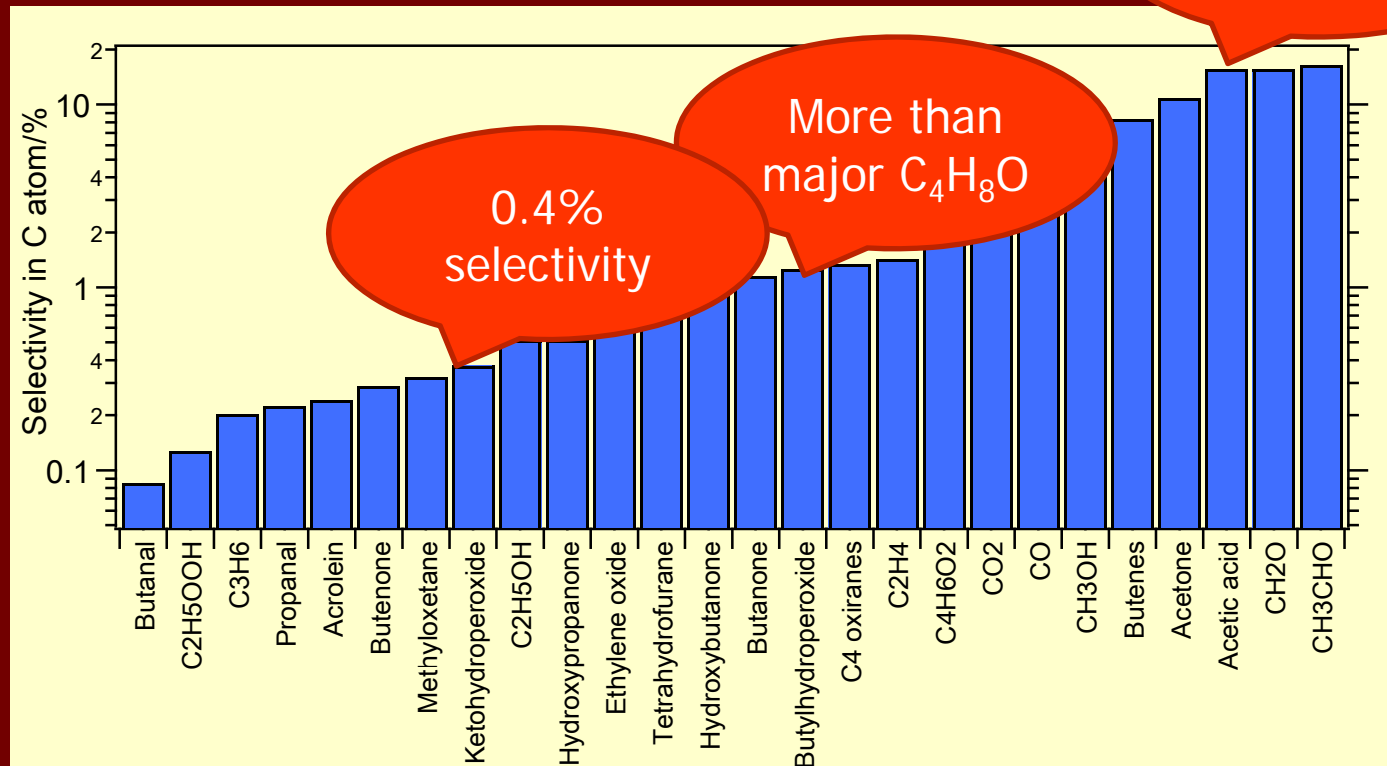


3rd addition on oxygen ?

**Study of the low-temperature oxidation of *n*-butane
in a jet-stirred reactor under conditions
close to that observed prior ignition**

Selectivity of products at 590 K (13% conversion)

P = 1 bar, $\Phi = 1$, $\tau = 6$ s, 4% *n*-butane



***Study of the low-temperature
oxidation of *n*-heptane
in a jet-stirred reactor under
conditions
close to that observed prior
ignition***

*Study of the low-temperature oxidation of n-heptane
in a jet-stirred reactor under conditions
close to that observed prior ignition*

Conversion of n-heptane

$P = 1 \text{ bar}, \Phi = 1, \tau = 2 \text{ s}, 0.5\% \text{ n-heptane}$

In Hefei:

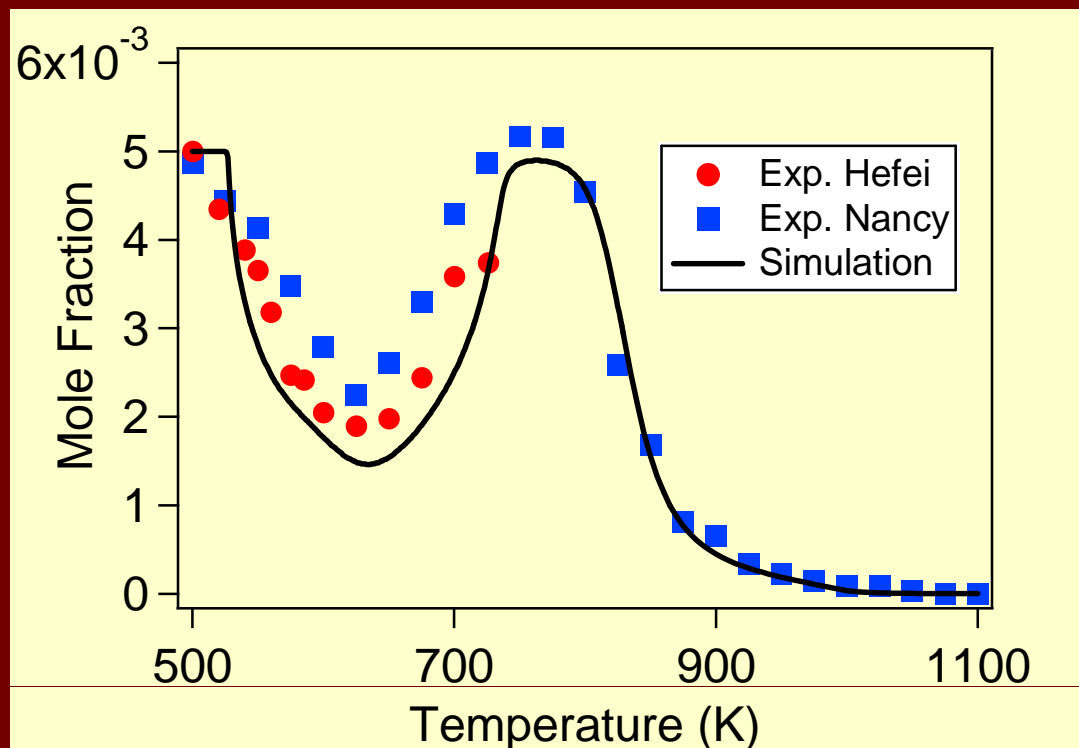
Quantification by
assuming no reaction
below 580K

In Nancy:

on-line
gas chromatographic
analysis of outlet gas

Simulation:

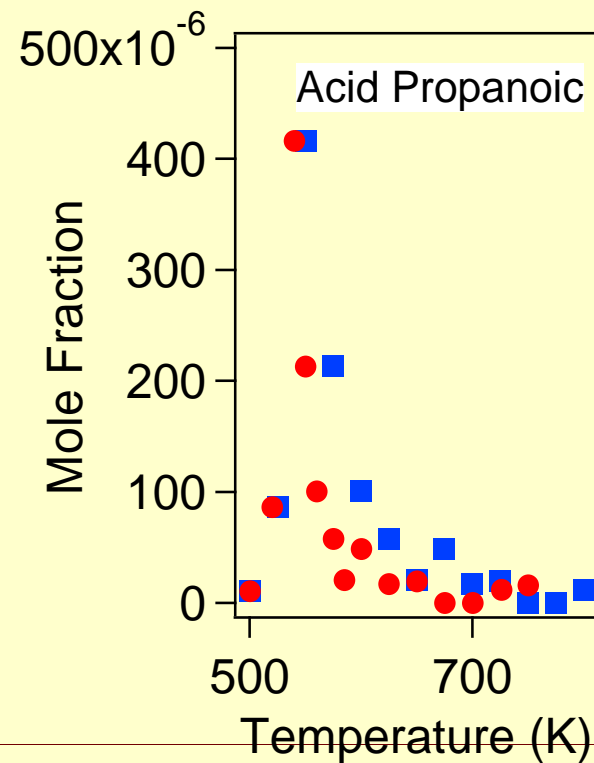
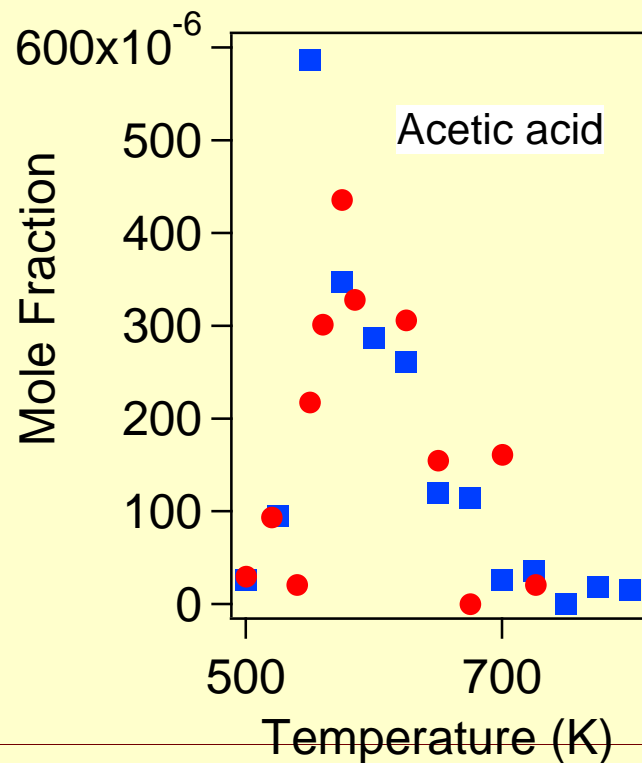
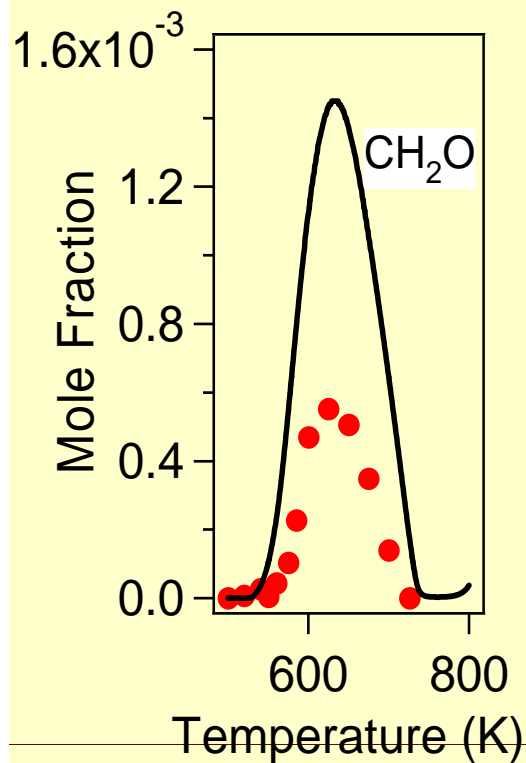
Using a model generated
using EXGAS software



Study of the low-temperature oxidation of *n*-heptane in a jet-stirred reactor under conditions close to that observed prior ignition

Light oxygenated products

$P = 1 \text{ bar}$, $\Phi = 1$, $\tau = 2 \text{ s}$, 0.5% *n*-heptane



○ Exp. Hefei

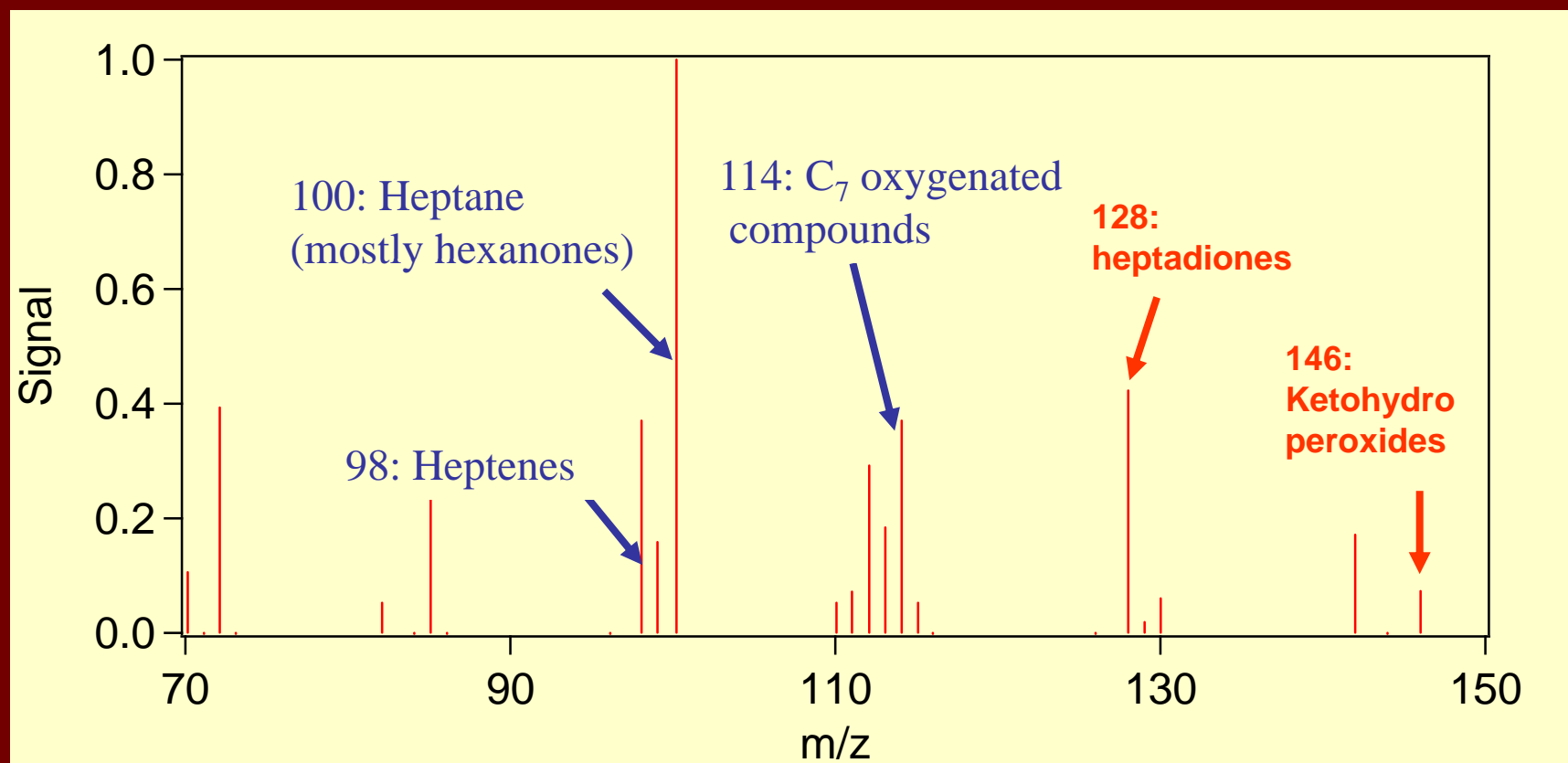
□ Exp. Nancy

— Simu.

**Study of the low-temperature oxidation of *n*-heptane
in a jet-stirred reactor under conditions
close to that observed prior ignition**

Obtained mass spectrum

$P = 1 \text{ bar}$, $\Phi = 1$, $\tau = 2 \text{ s}$, $0.5\% \text{ } n\text{-heptane}$, 530 K , 9.5 eV



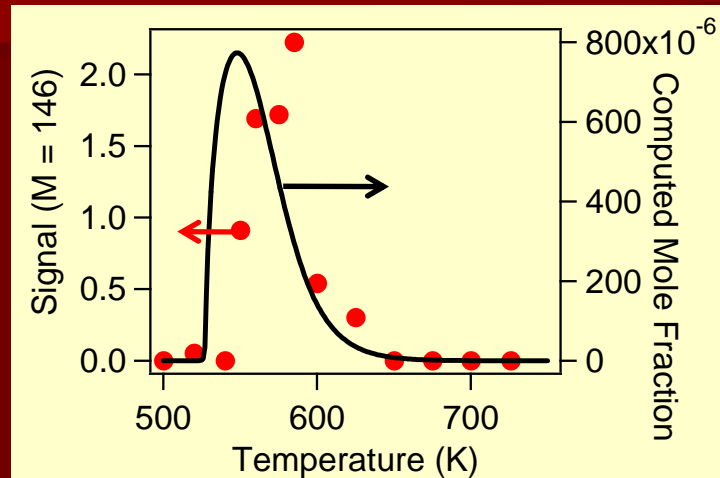
No hydroperoxide smaller than ketohydroperoxides

Study of the low-temperature oxidation of *n*-heptane in a jet-stirred reactor

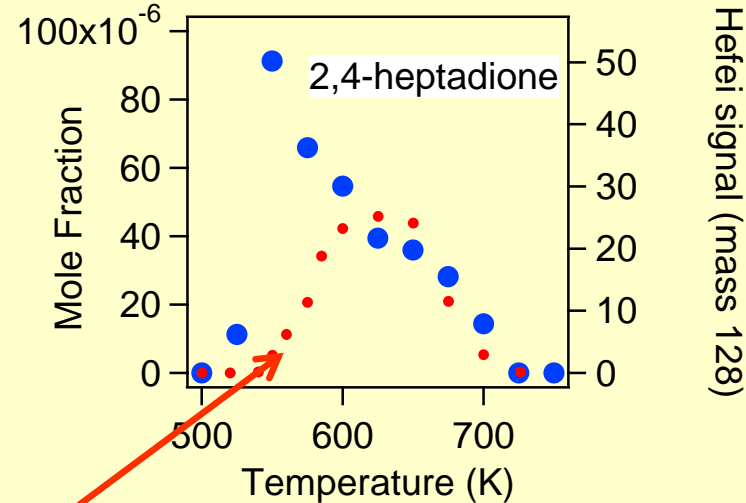
Analysis of diones and hydroperoxides

$P = 1 \text{ bar}$, $\Phi = 1$, $\tau = 2 \text{ s}$, 0.5% *n*-heptane

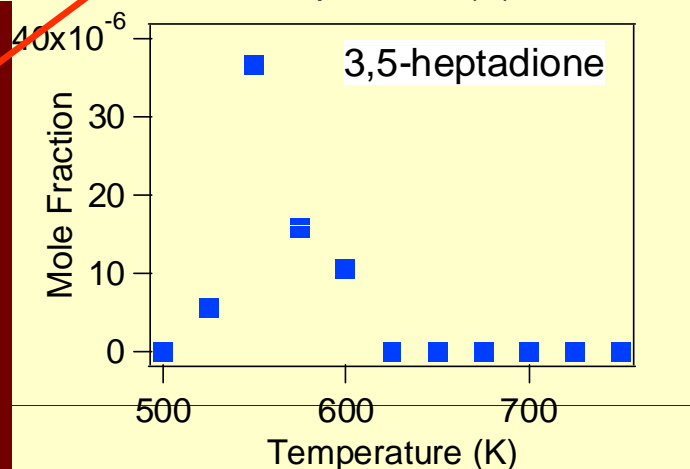
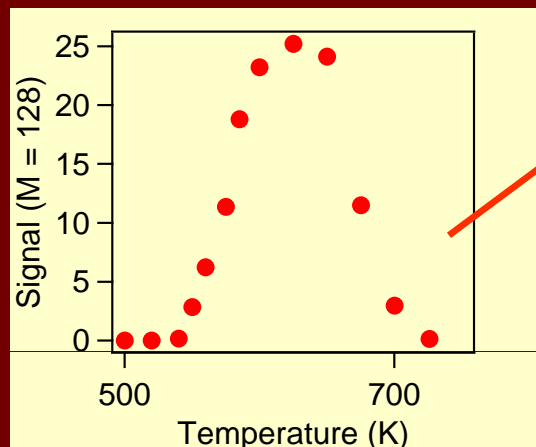
HEFEI



NANCY (on-line GC)



Ketohydroperoxides



Diones (Mass = 128, good PIE)

Are diones seen in Nancy partly due to ketohydroperoxides decomposed in GC ?

***Study of the low-temperature
oxidation of propane
in a jet-stirred reactor under
conditions
close to that observed prior
ignition***

**Study of the low-temperature oxidation of propane
in a jet-stirred reactor under conditions
close to that observed prior ignition**

Conversion of propane

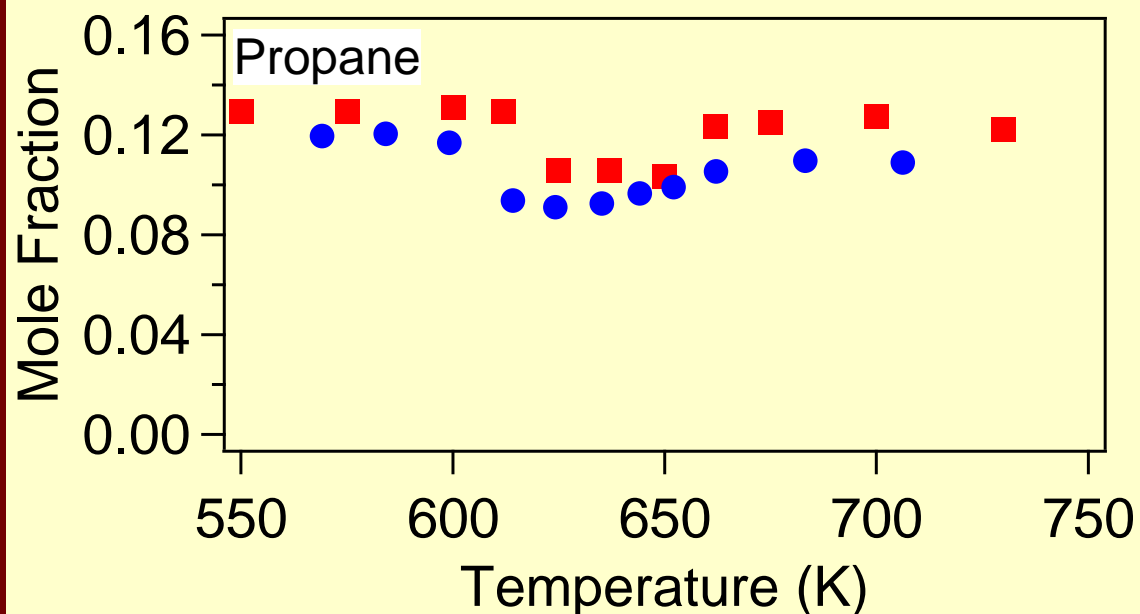
$P = 1 \text{ bar}, \Phi = 1, \tau = 6 \text{ s}, 12\% \text{ propane}$

In Hefei:

Quantification by
assuming no reaction
below 580K

In Nancy:

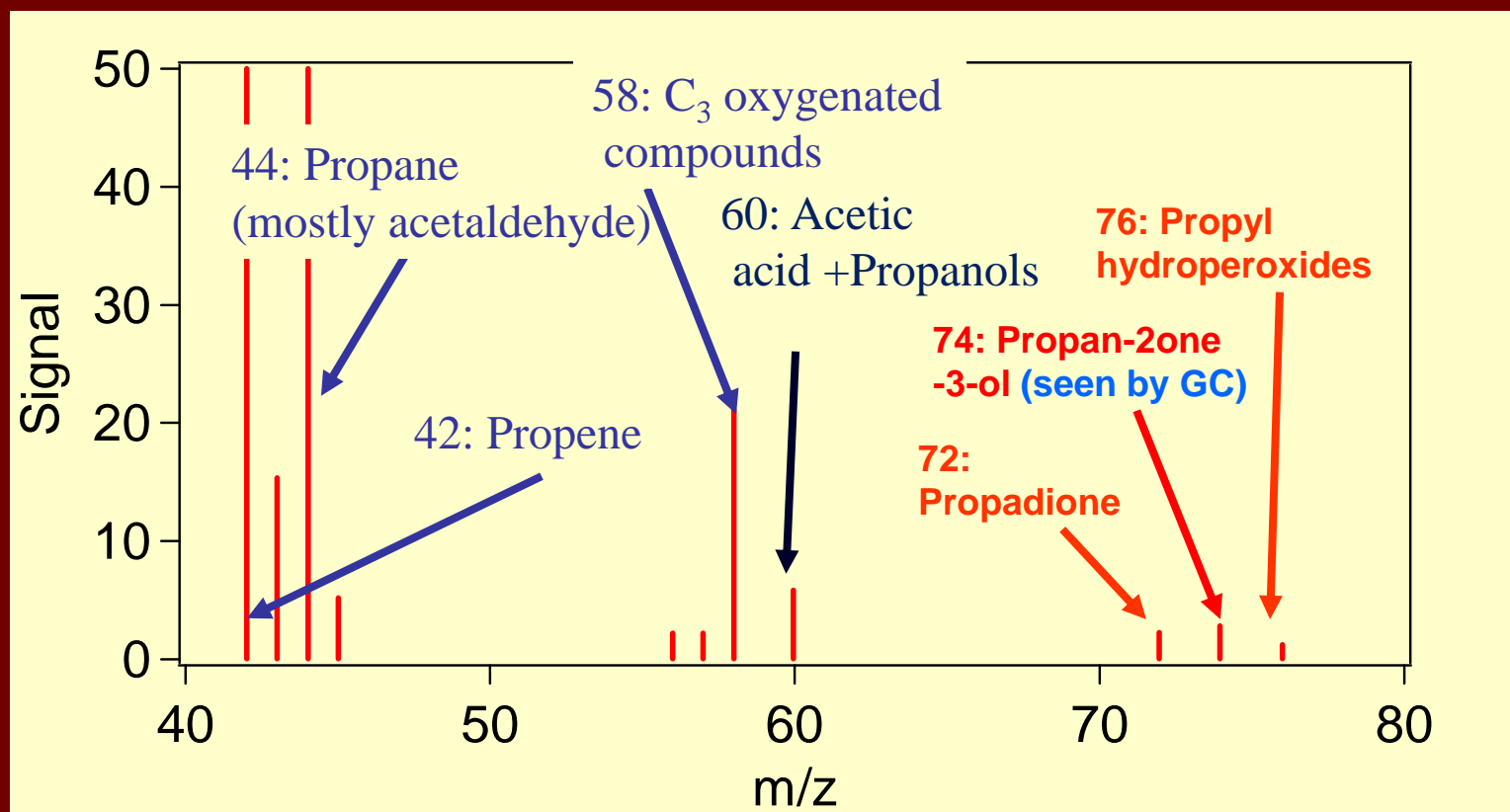
on-line
gas chromatographic
analysis of outlet gas



**Study of the low-temperature oxidation of propane
in a jet-stirred reactor under conditions
close to that observed prior ignition**

Obtained mass spectrum

$P = 1 \text{ bar}$, $\Phi = 1$, $\tau = 6 \text{ s}$, 12% propane, 635 K, 11 eV



No hydroperoxide other than propylhydroperoxides

Conclusion

Use of a new type of apparatus coupling through a molecular beam a jet stirred reactor and a tunable synchrotron vacuum ultraviolet photoionization mass spectrometer

Evidence of the formation of hydroperoxides compounds, especially ketohydroperoxides during the low-temperature oxidation of n-butane and n-heptane: mainly 2,4 and 3,5-ketohydroperoxides formed from n-heptane

Evidence of the formation of products deriving from ketohydroperoxides: diones

Next work

Study of the low-temperature oxidation of a series of branched alkanes to better understand the influence of the structure of the molecule on the formation of hydroperoxide compounds



Thank you for your attention