Modelling and Diagnostics of Combustion Processes: 40 years of Collaboration with Jürgen Warnatz

Jürgen Wolfrum

Heidelberg University

FOUNDING DIRECTOR BioQuant

Capri

September 14-19, 2008

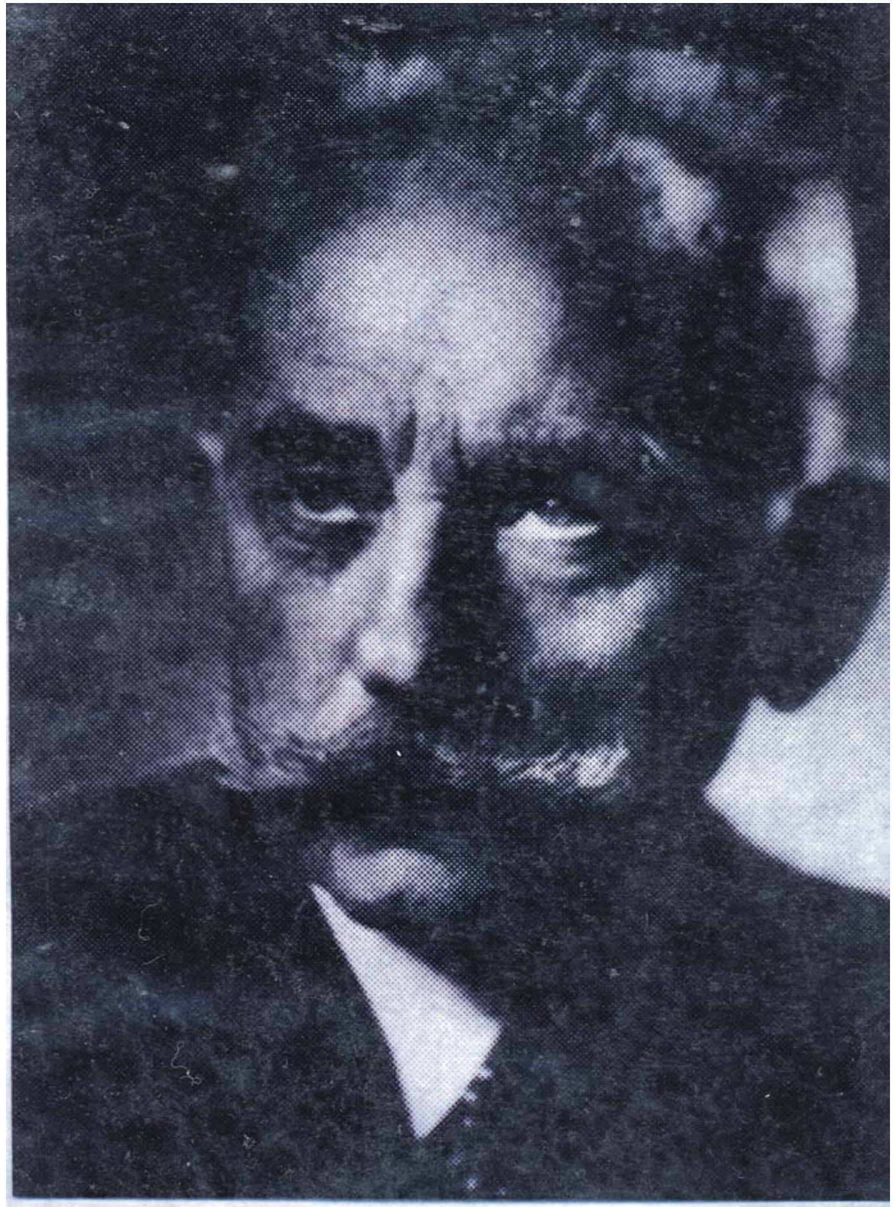

ARNOLD
EUCKEN
1929 - 1950


WALTHER
NERNST
1896 - 1905


GUSTAV
TAMMANN
1908-1930


ARNOLD
EUCKEN
1929 - 1950


WILHELM
JOST
1953 - 1968



Max Bodenstein

MAX BODENSTEIN
1923 successor of W.Nernst in Berlin
1899 Habilitation Heidelberg

Eighteenth Symposium (International) on Combustion

1980

THE STRUCTURE OF LAMINAR ALKANE-, ALKENE-, AND ACETYLENE FLAMES

JÜRGEN WARNATZ

Institut für Physikalische Chemie der Technischen Hochschule 6100 Darmstadt, W. Germany

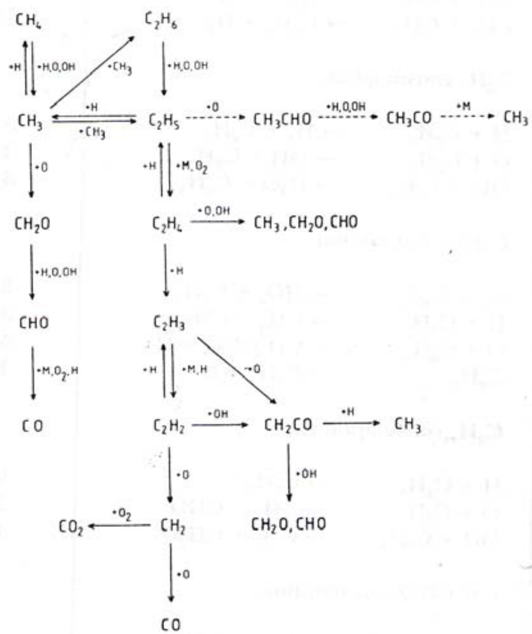


FIG. 2. Mechanism of CH_3 and C_2H_5 oxidation (see text).

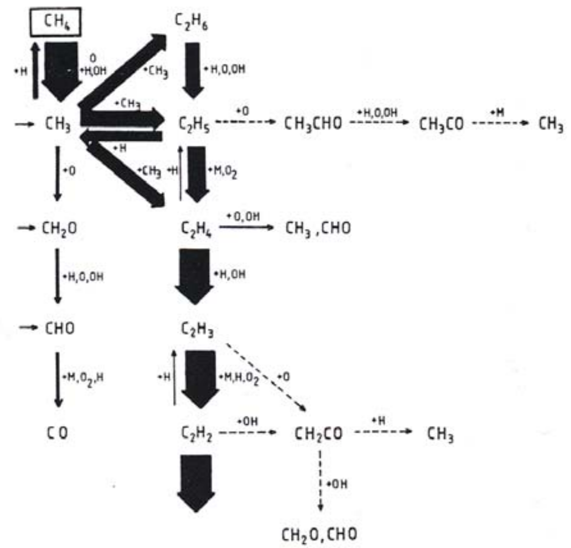
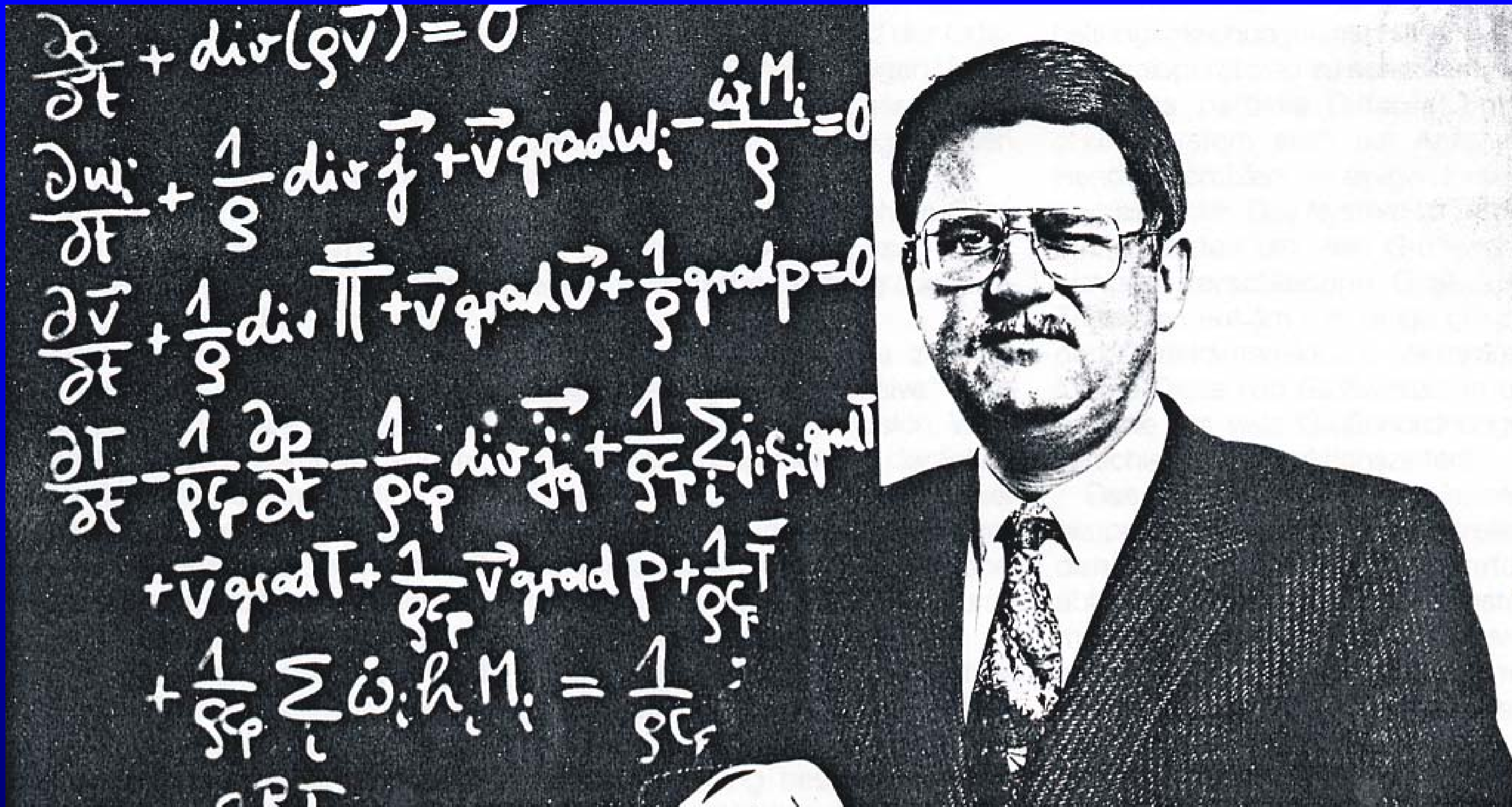
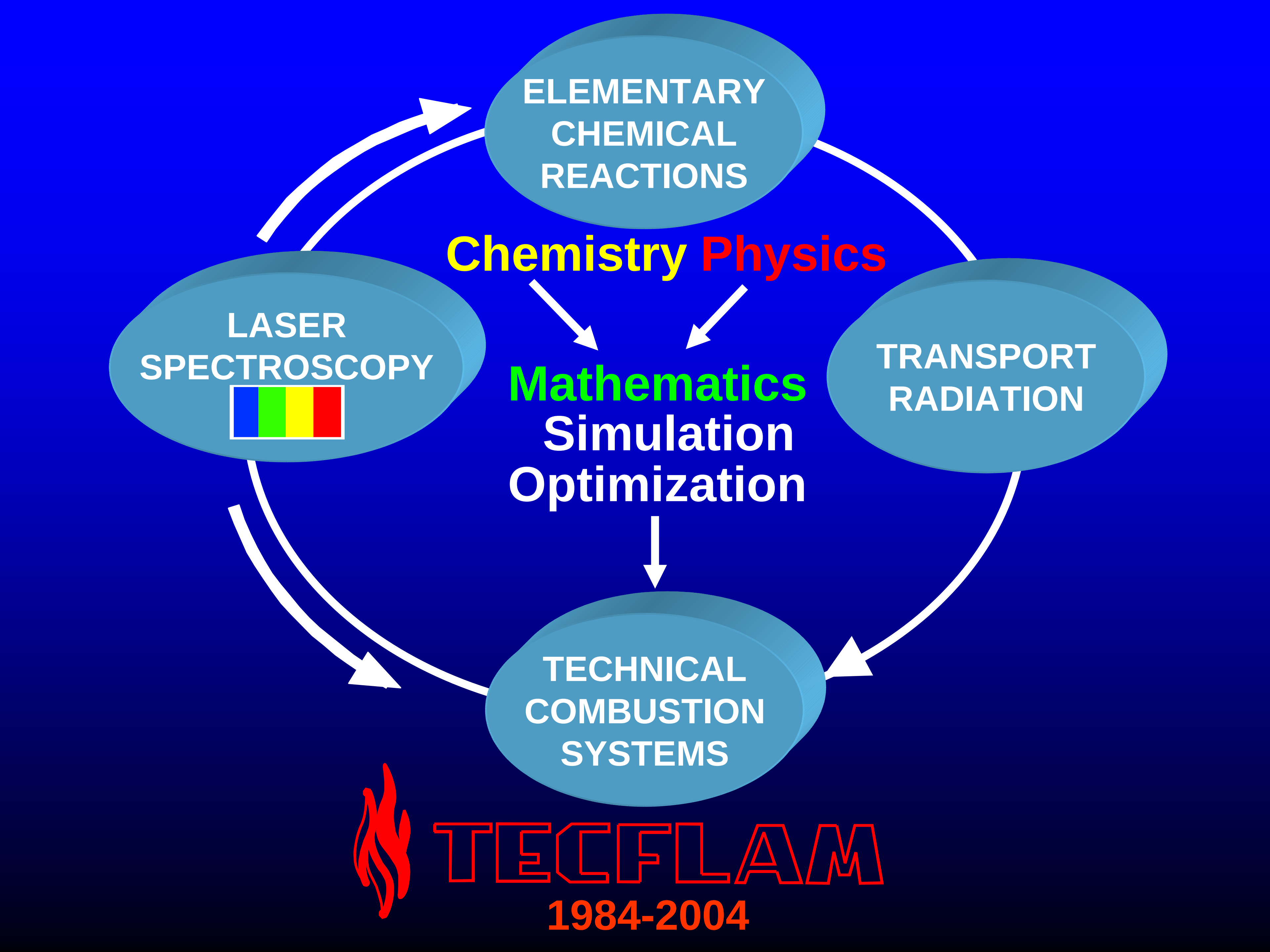


Fig. 10

Molar chemical fluxes in a stoichiometric C_2H_6 – air (upper drawing), a stoichiometric CH_4 – air (central drawing) and a rich CH_4 – air flame (x_{CH_4} = 0.15, lower drawing). All flames are calculated for P = 1 bar, T_u = 298 K

The „Warnatz Mechanism“


$\frac{\partial \rho}{\partial t} + div(\rho\vec{v}) = 0$
$\frac{\partial w_i}{\partial t} + \frac{1}{\rho} div\,\vec{j} + \vec{v}\,grad\,w_i - \frac{\dot{\omega}_i M_i}{\rho} = 0$
$\frac{\partial \vec{v}}{\partial t} + \frac{1}{\rho} div\,\bar{\bar{\Pi}} + \vec{v}\,grad\,\vec{v} + \frac{1}{\rho} grad\,p = 0$
$\frac{\partial T}{\partial t} - \frac{1}{\rho c_p}\frac{\partial p}{\partial t} - \frac{1}{\rho c_p} div\,\vec{j}_q + \frac{1}{\rho c_p}\sum_i j_i c_{pi}\,grad\,T$
$+ \vec{v}\,grad\,T + \frac{1}{\rho c_p}\vec{v}\,grad\,p + \frac{1}{\rho c_p}\bar{\bar{T}}$
$+ \frac{1}{\rho c_p}\sum_i \dot{\omega}_i h_i M_i = \frac{1}{\rho c_p}$


ELEMENTARY CHEMICAL REACTIONS
Chemistry Physics
LASER SPECTROSCOPY
TRANSPORT RADIATION
Mathematics
Simulation
Optimization
TECHNICAL COMBUSTION SYSTEMS
TECFLAM
1984-2004

1. **Formation and Destruction of Nitric Oxide**

2. **Explosion and Ignition Phenomena**

3. **Heterogeneous Catalysis**

Thermal NO (Zeldovich,1946)

$O+N_2 \rightarrow NO+N$

$N+O_2 \rightarrow NO+O$

Prompt NO (Fenimore, 1971)

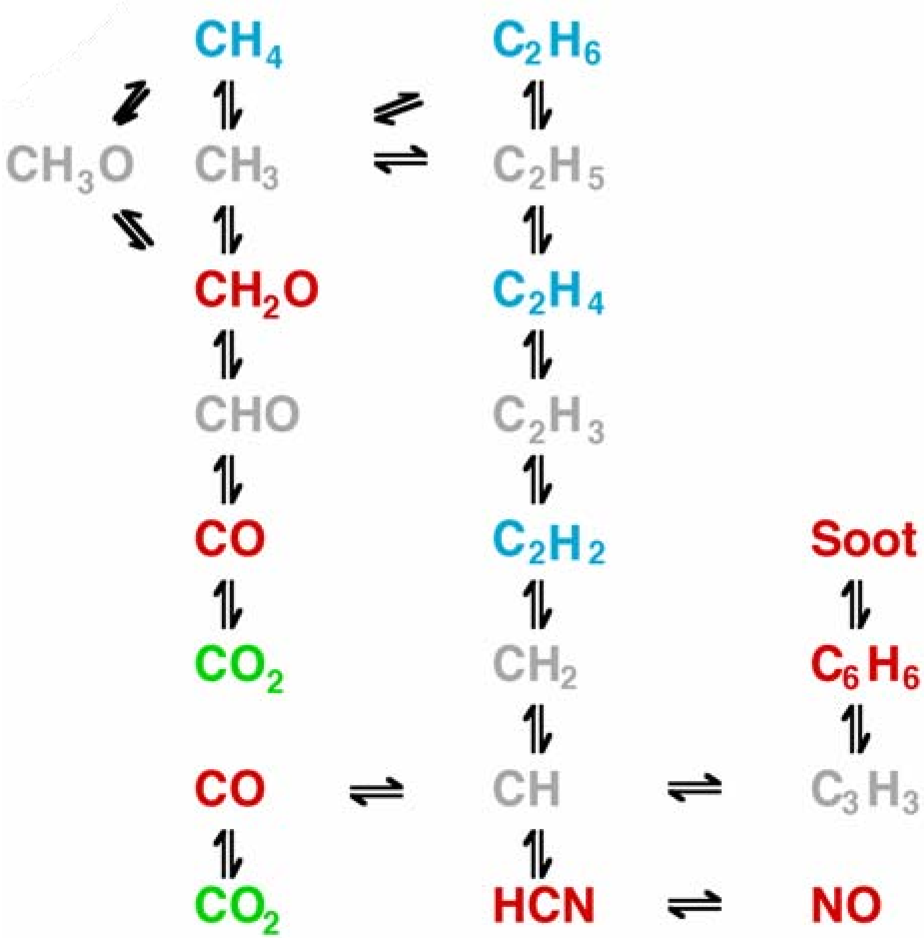
$CH+N_2 \rightarrow NCN+H \dashrightarrow NO$

Nitrous NO (Wolfrum, 1972)

$O+N_2+M \rightarrow N_2O+M$

$O+N_2O \rightarrow 2NO$

Reaction Mechanism for CH_4 Oxidation



red: pollutants,
blue: hydrocarbons,
grey: intermediates,
green: desired products

J. WARNATZ: Resolution of Gas Phase and Surface Chemistry into Elementary Reactions. Plenary Lecture, 24th Symposium (International) on Combustion, S. 553-579. The Combustion Institute, Pittsburgh (1992)

THE COMBUSTION INSTITUTE

University Park, Pennsylvania

August 20–25, 1972

DIRECT STUDIES OF SOME ELEMENTARY STEPS FOR THE FORMATION AND DESTRUCTION OF NITRIC OXIDE IN THE H–N–O SYSTEM

M. GEHRING, K. HOYERMANN, H. SCHACKE, AND J. WOLFRUM

Institut für Physikalische Chemie der Universität Göttingen, Max-Planck-Institut für Strömungsforschung, Göttingen, W.-Germany

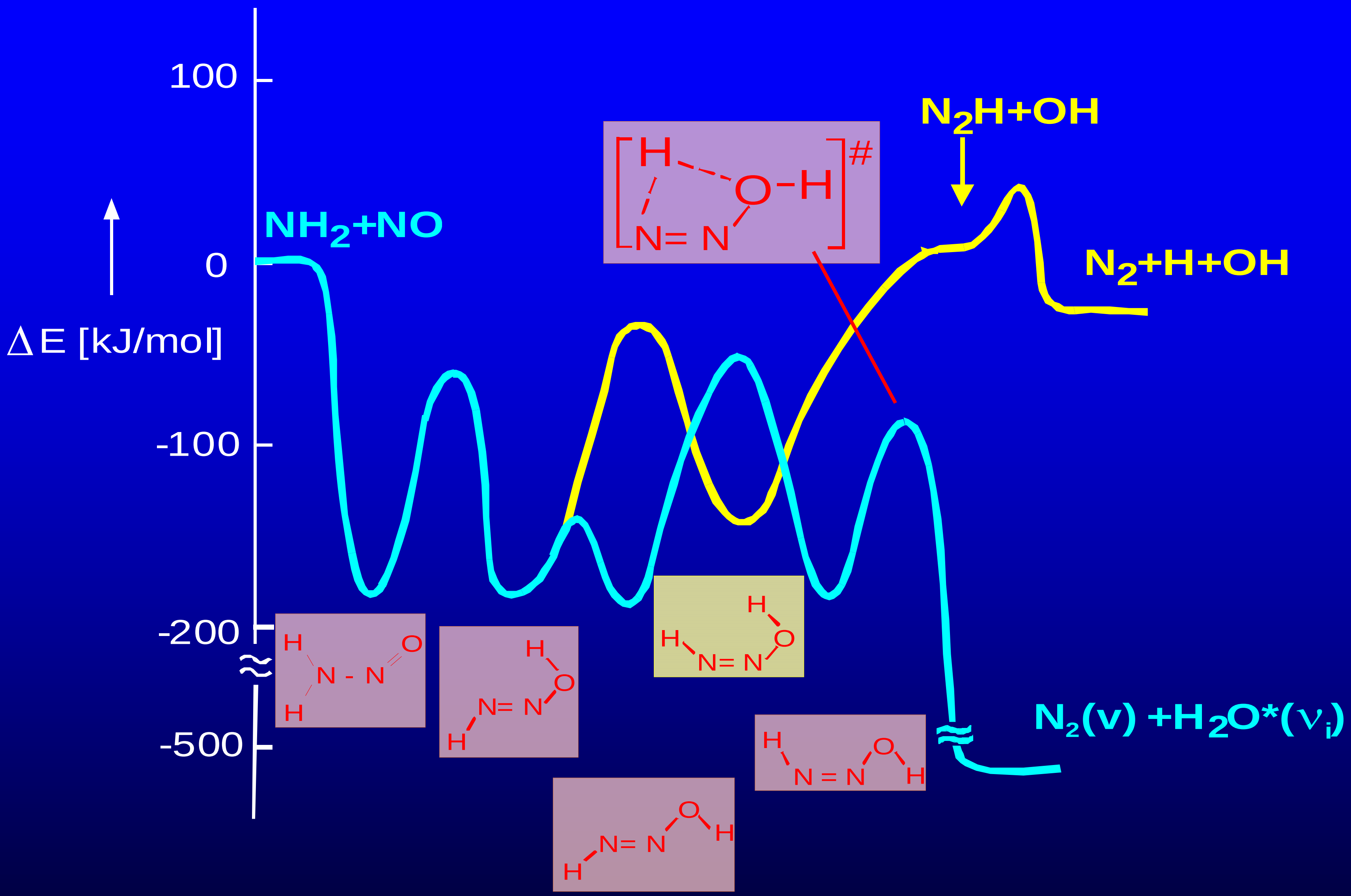
When NH_2 radicals were generated by

$$H+NO_2 \rightarrow NO+OH,$$
$$OH+NH_3 \rightarrow NH_2+H_2O, \qquad (11)$$

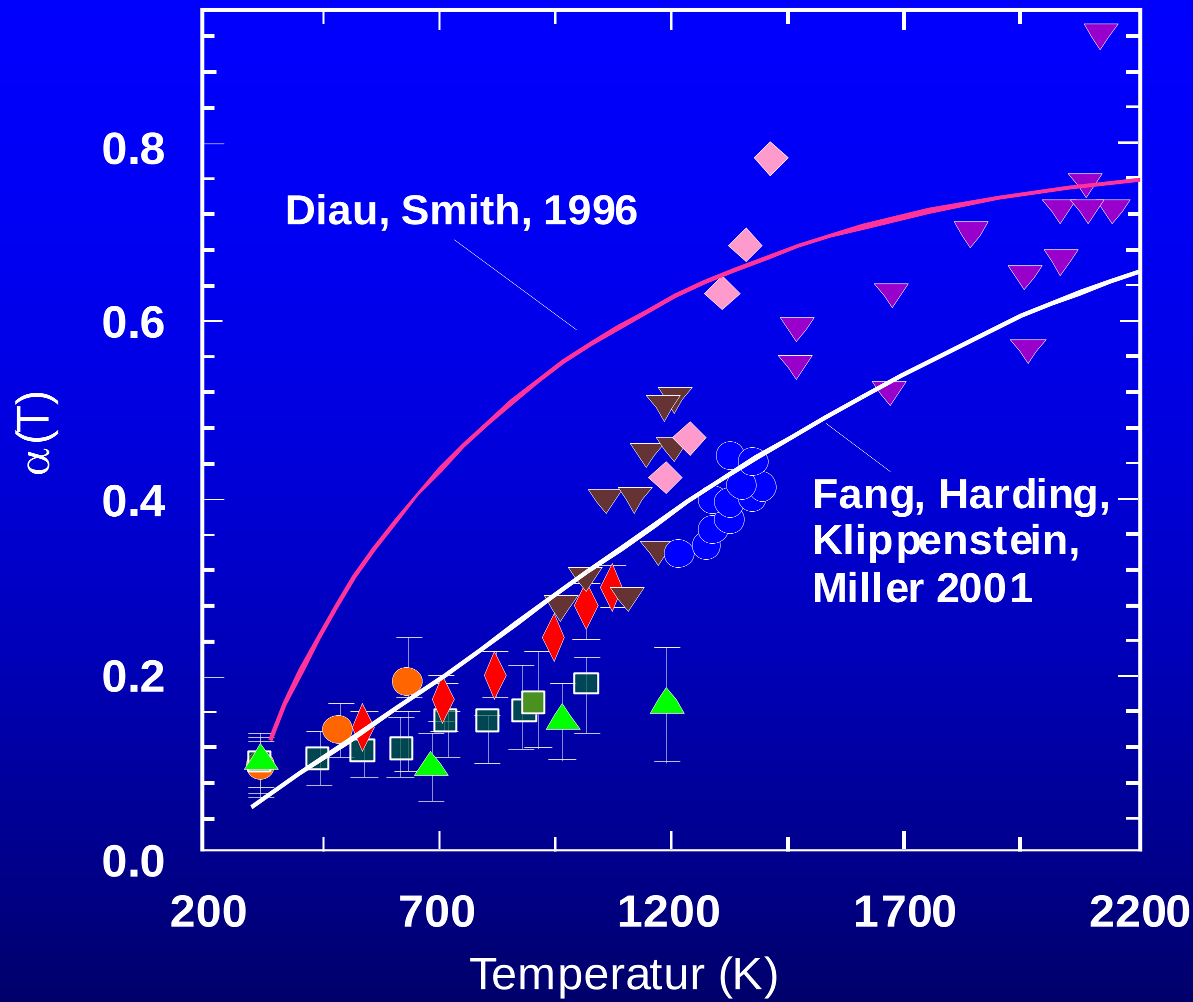
$k_{11}=1.7\times10^{11}$ cm³/mole sec at 298°K, in a discharge-flow system coupled to a TOF mass spectrometer with nozzle-beam sampling, the rate of the reaction

$$\boxed{NO+NH_2 \rightarrow N_2+H_2O^*,} \qquad (4)$$

$\boxed{k_4=5(\pm1)\times10^{12}\text{ cm}^3\text{/mole sec at 298°K,}}$ could be directly measured. Using a gold-coated Pyrex reaction vessel and monitoring the infrared chemiluminescence from Reaction (4), strong vibrational excitation of the H_2O formed was observed. In addition to N_2 and H_2O^*, a small amount of NH_2NO is produced in (4).

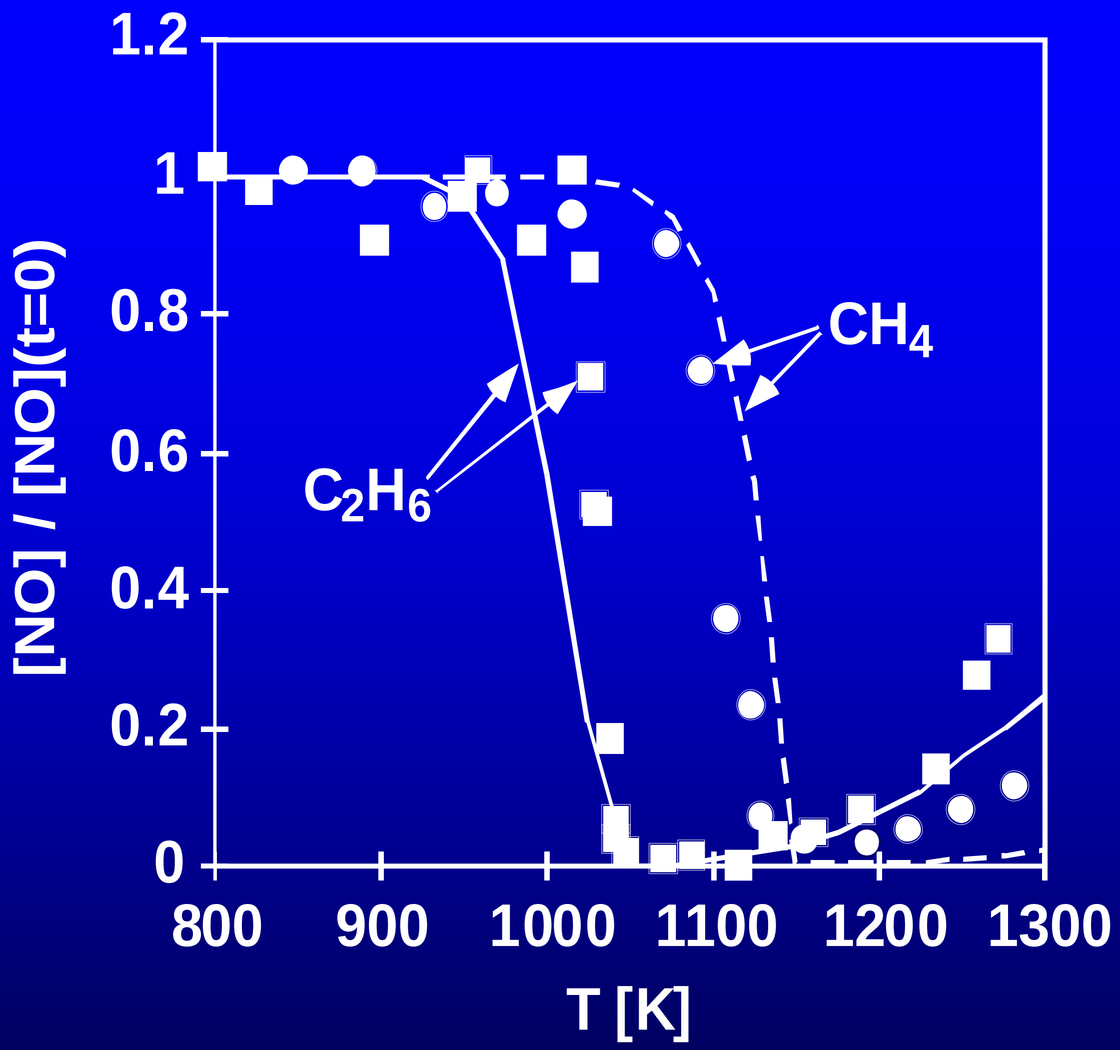


Potential energy diagram NH_2+NO

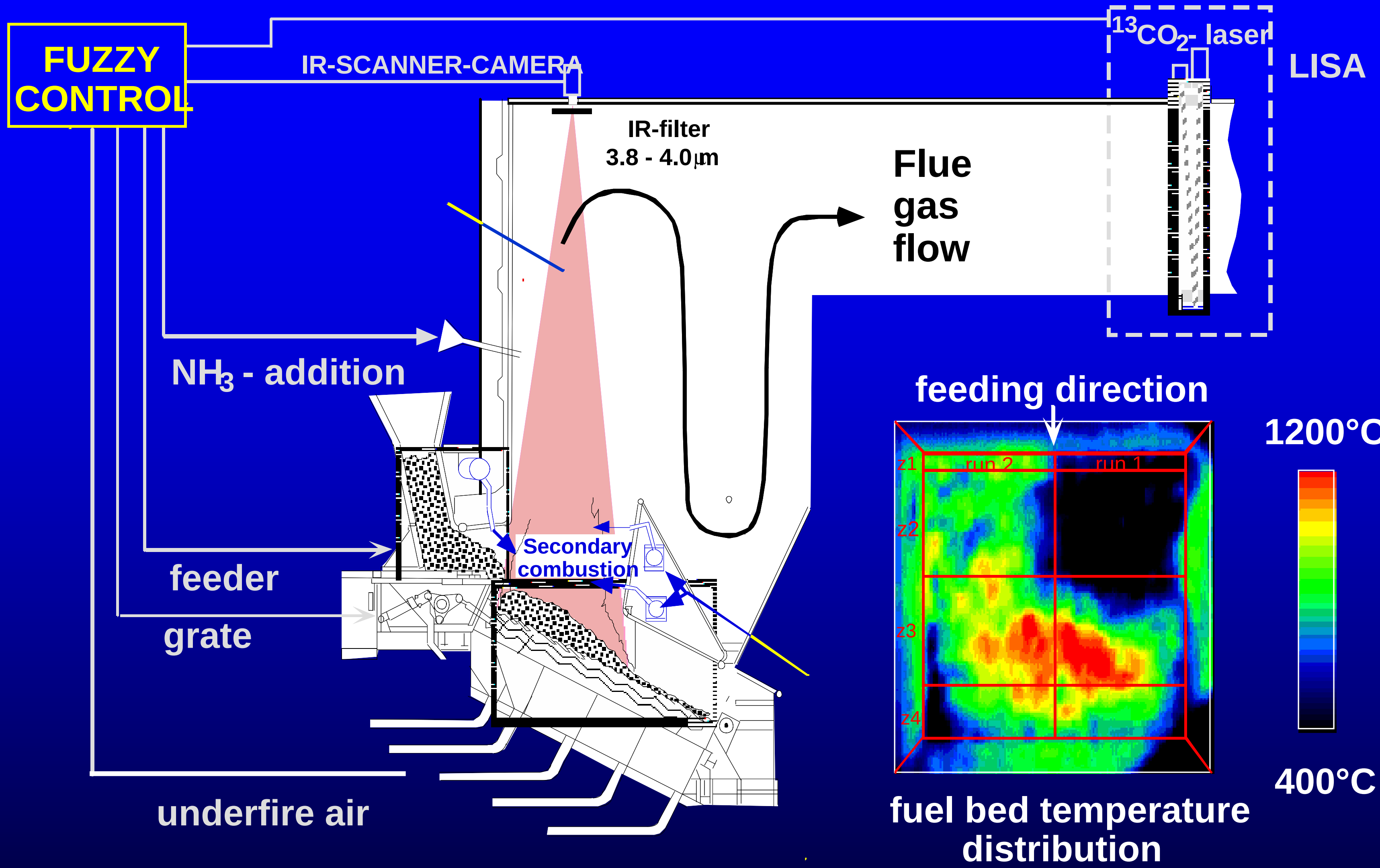


$$NO + NH_2 \xrightarrow{\alpha} N_2H + OH$$

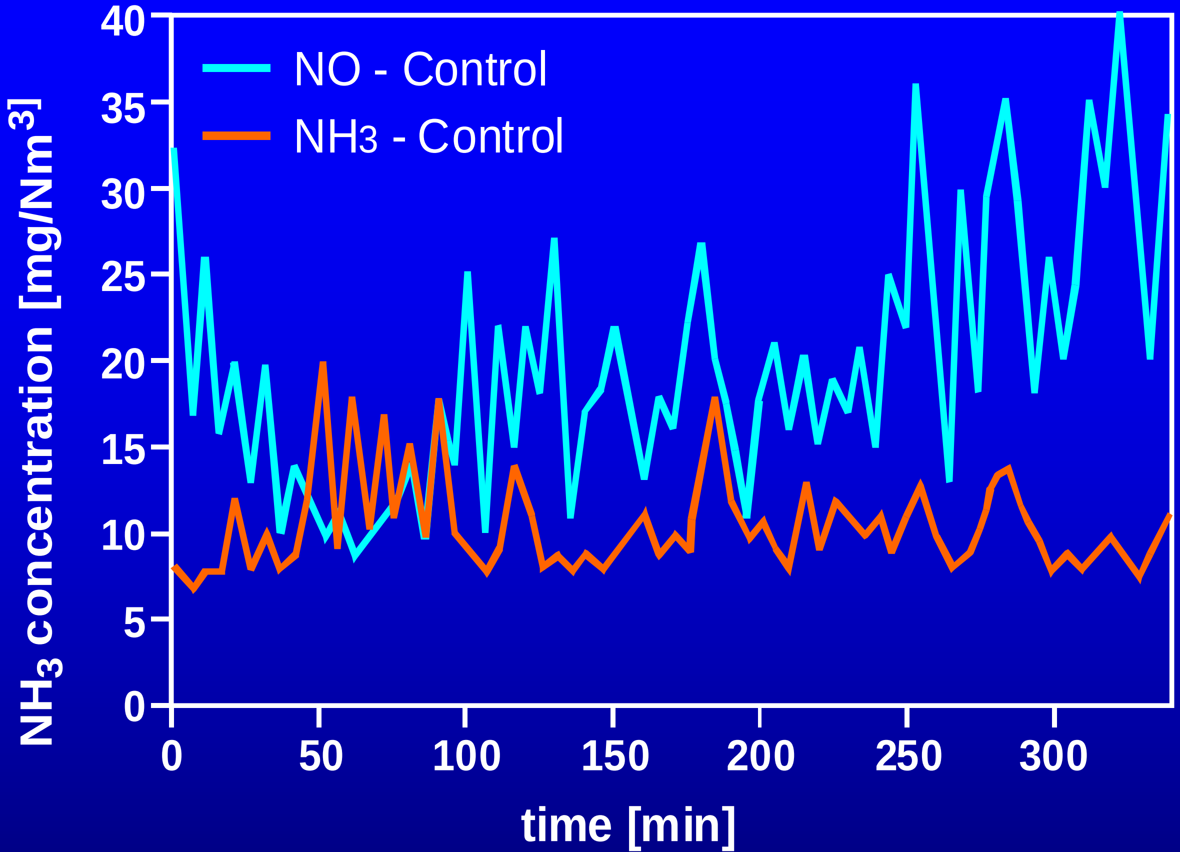
$$\xrightarrow{1-\alpha} N_2 + H_2O$$



Influence of hydrocarbons on the temperature window of the NO-NH_3-O_2 SNCR-process



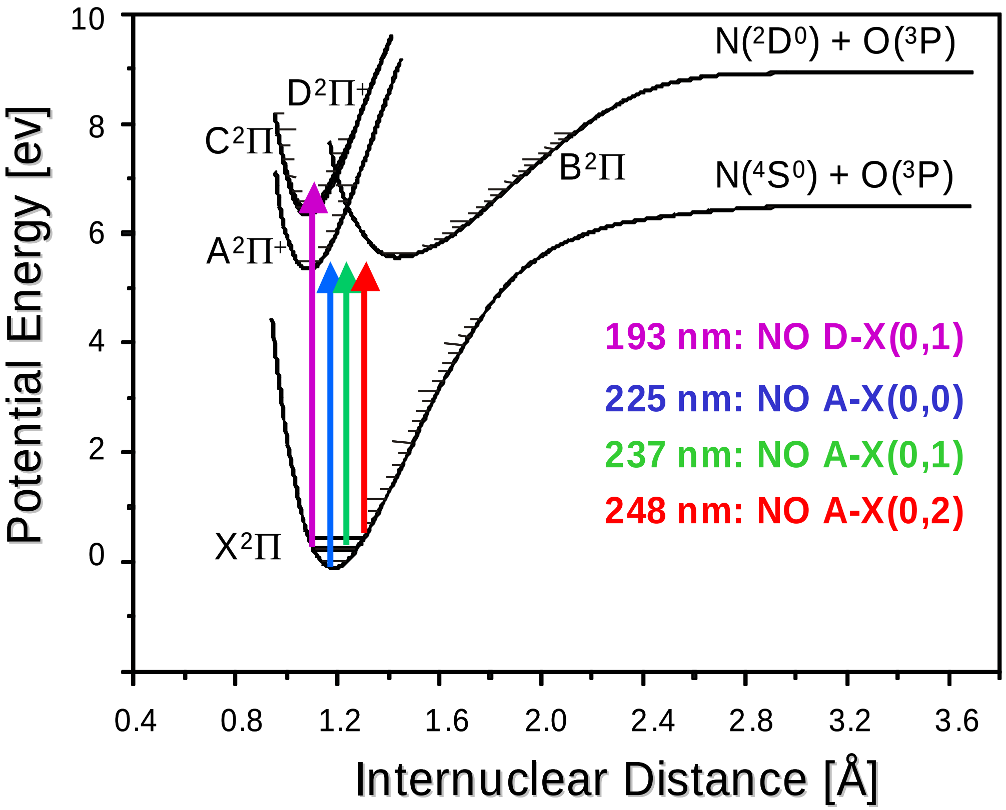
OPTIMIZATION OF WASTE COMBUSTION



Selective non-catalytic reduction of nitric oxide in a waste incinerator by laser-based active combustion control

NO_X final concentration: 40 mg/Nm^3

Efficiency of reduction: 90%



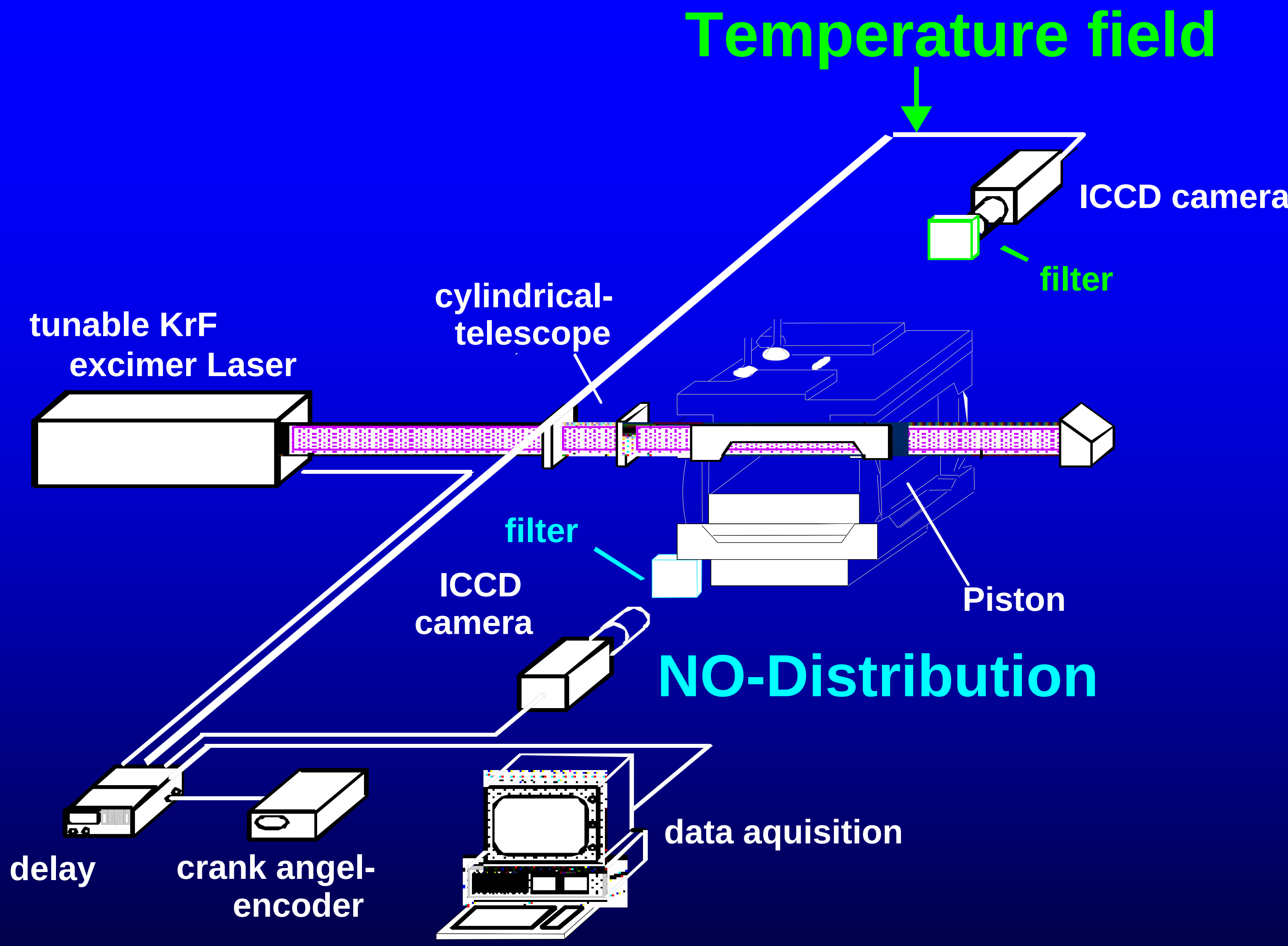
193 nm: ArF
- Ketterle et al
- Andresen et al
- Ter Meulen et al.

225 nm: Dye / OPO / shifted KrF
- Sick et al.
- DiRosa et al.
- Laurendeau et al.

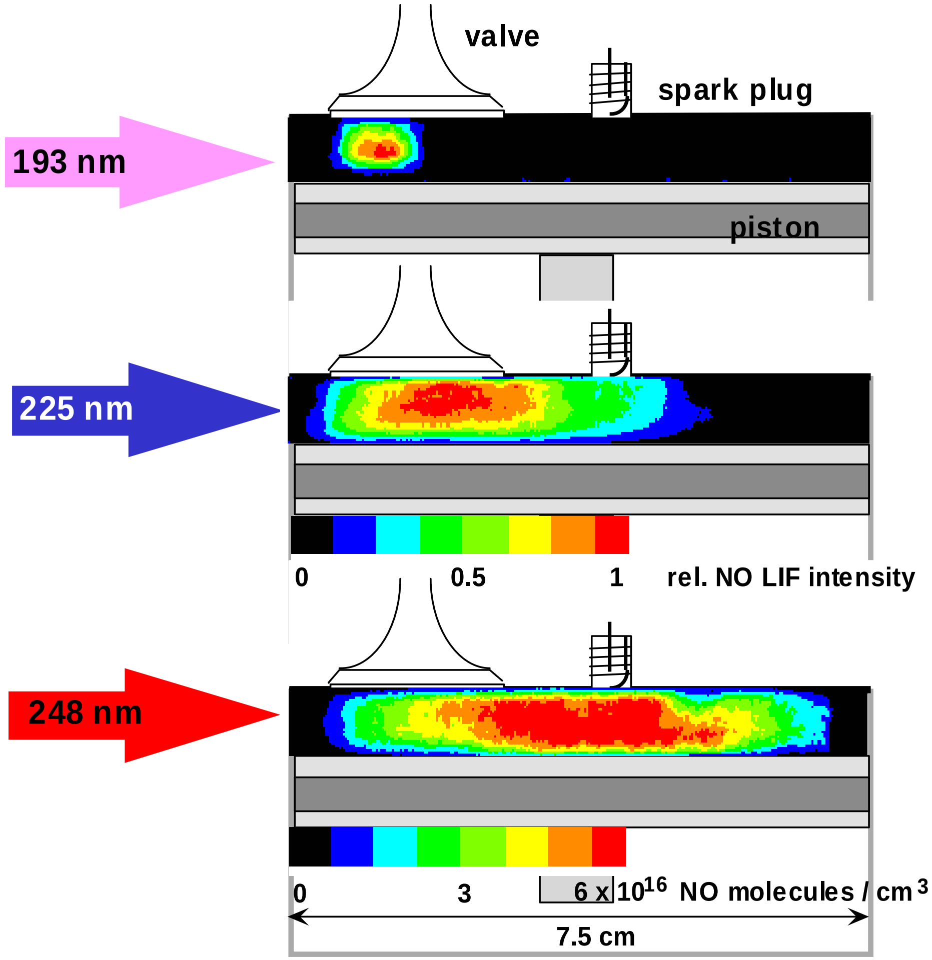
237 nm: Dye / OPO
- Jamette et al.
- Bessler et al.

248 nm: KrF Laser
- Schulz et al.

NO potential energy diagram

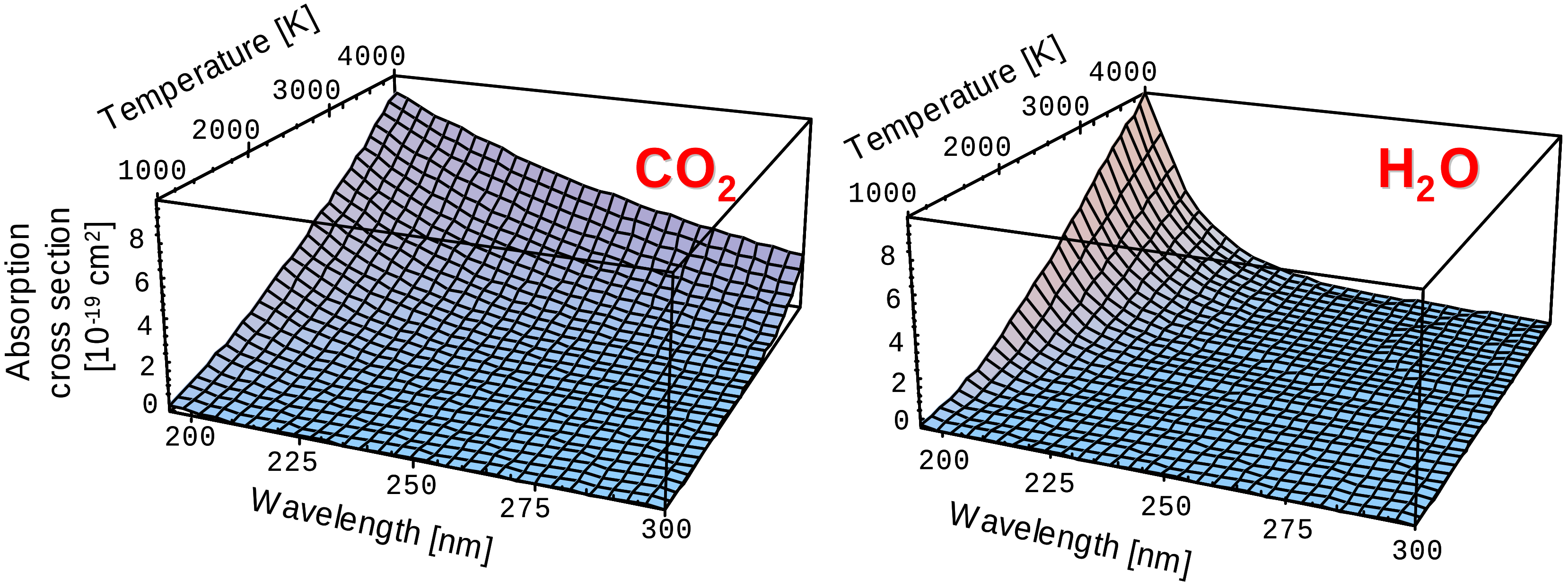


Simultaneous quantitative measurement of
NO concentrations and temperature fields
in a spark ignition engine



SI engine, fueled with propane / air, $\phi = 1.0$, 13 bar, 7°ca after TDC

Choice of excitation wavelength



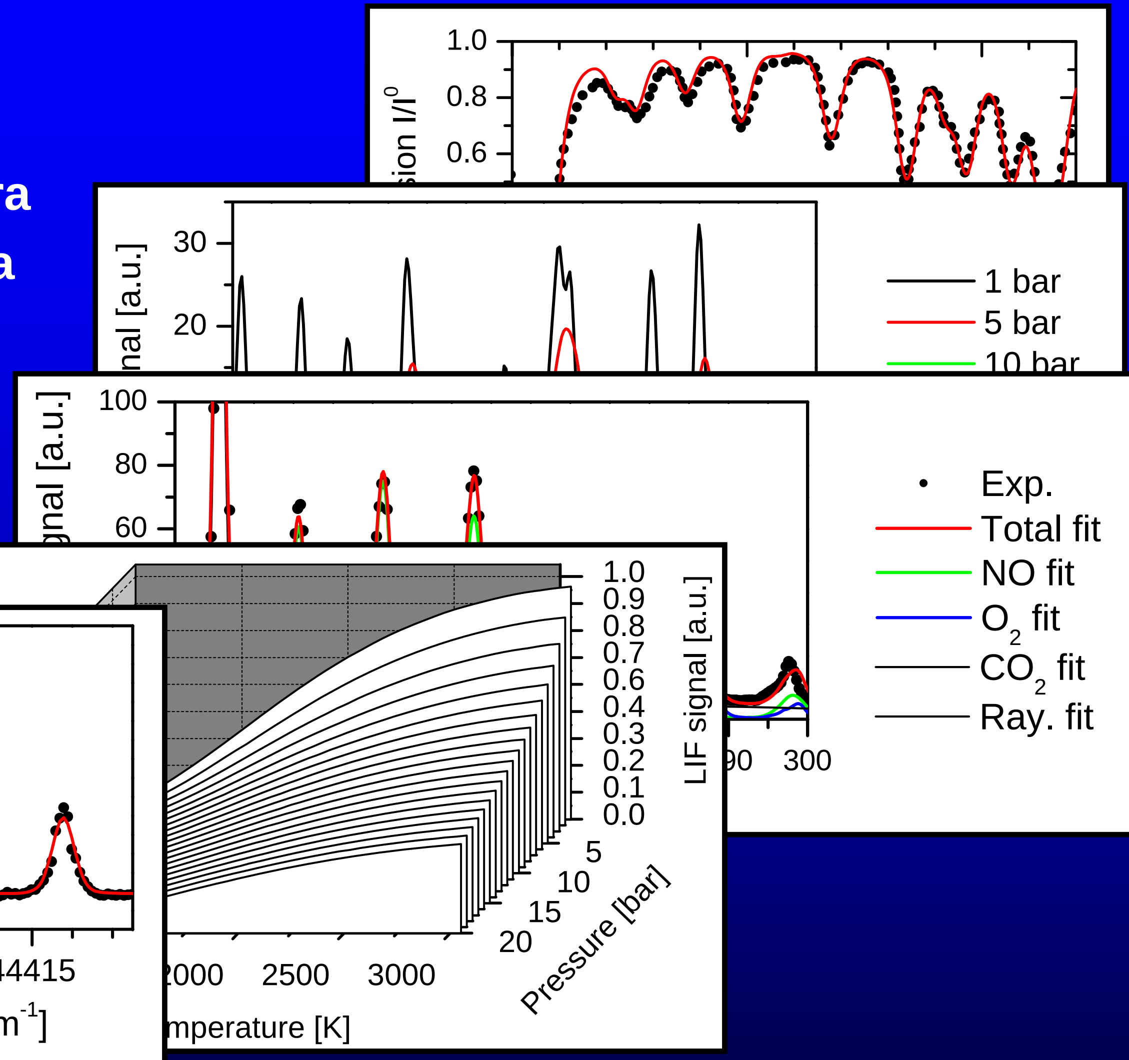
Dependence of absorption cross-sections on temperature and wavelength

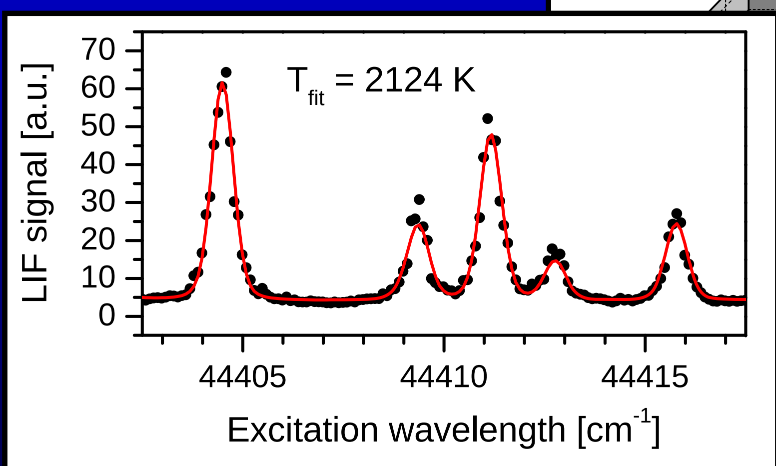
- H_2O: Minor importance at $\lambda > 230$ nm
- CO_2: Absorption relevant up to 300 nm

CO_2 and H_2O absorption cross-sections

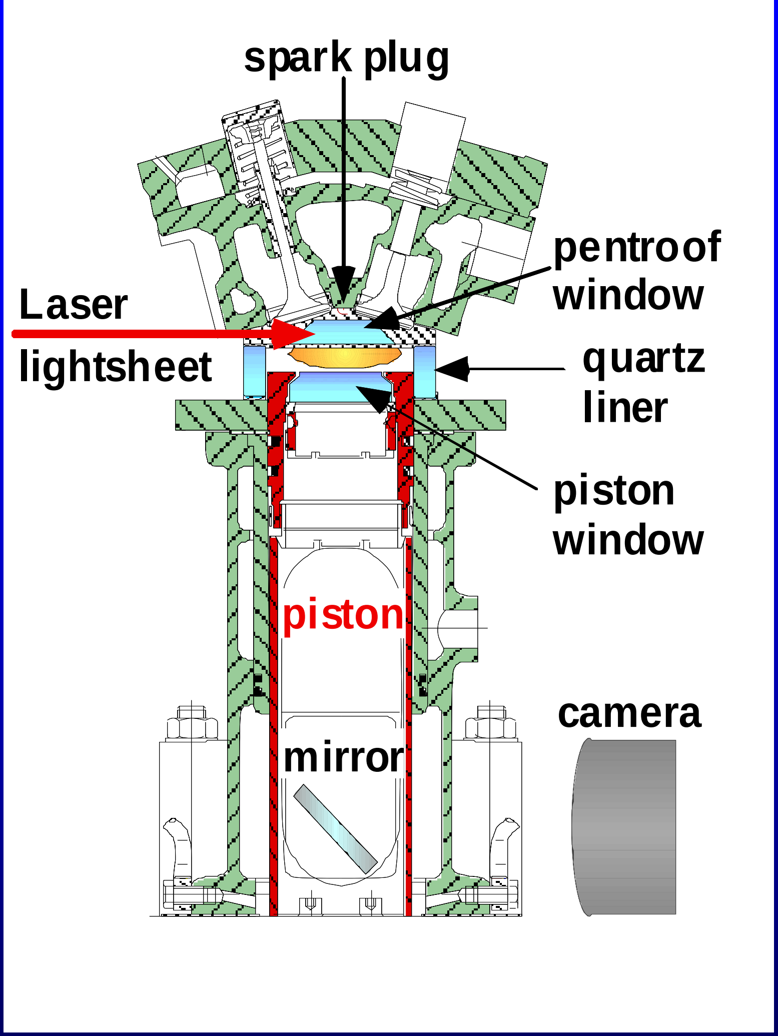
http://www.pci.uni-heidelberg.de/pci/lifsim

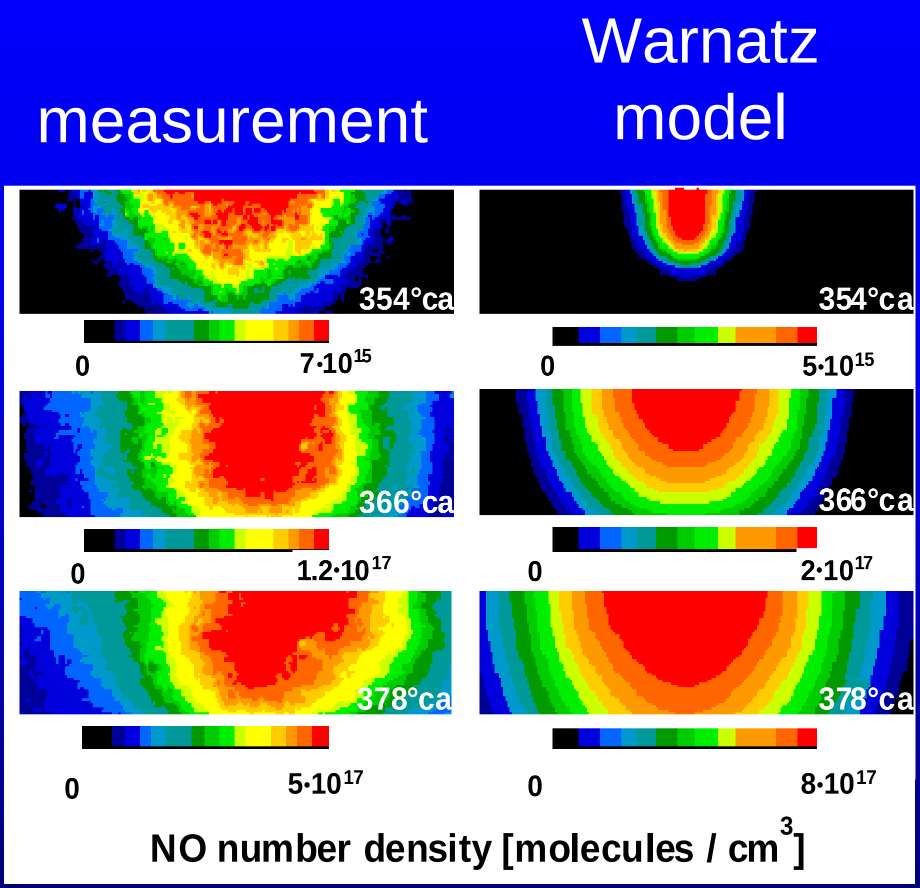
- Absorption spectra
- LIF excitation spectra
- LIF emission spectra
- p/T-dependence of LIF signal
- Spectrum fitting





LIFSim: Implementation of literature spectroscopy data into a numerical simulation program





NO-formation in a SI engine:
NO-LIF measurements compared to CFD-based simulation

1. **Formation and Destruction of Nitric Oxide**

2. **Explosion and Ignition Phenomena**

3. **Heterogeneous Catalysis**

Explosion Phenomena

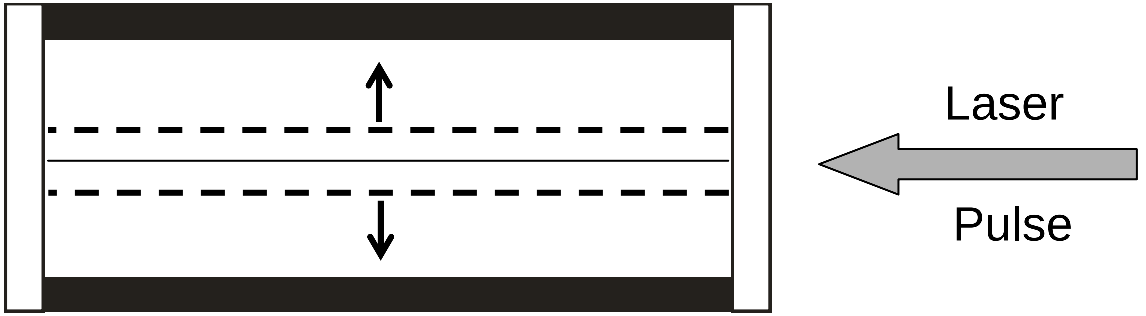
SIMPLE CHEMISTRY: Ozone Decomposition Flame

$$O_3 \longrightarrow O_2 + O$$

$$O + O_3 \longrightarrow O_2 + O_2$$

SIMPLE GEOMETRY:

SIMPLE TIMING:



Proc. 6th Annual Meeting IEA Committee on Conservation in Combustion (1984)

LASER-INDUCED THERMAL IGNITION IN O_2/O_3 MIXTURES

AND SIMULATION OF IGNITION PROCESSES

B. Raffel, J. Warnatz, H. Wolff, J. Wolfrum
Physikalisch-Chemisches Institut, Universitat Heidelberg
6300 Heidelberg, West Germany

To allow for evaluation by one-dimensional calculations, a method has been developed to study laser-induced ignition in a constant volume bomb of cylindrical shape. To avoid experimental (due to participation of a suitable absorbing species) and calculational (due to participation of many species) difficulties, this method has been tested studying the ignition of O_2/O_3 mixtures[1].

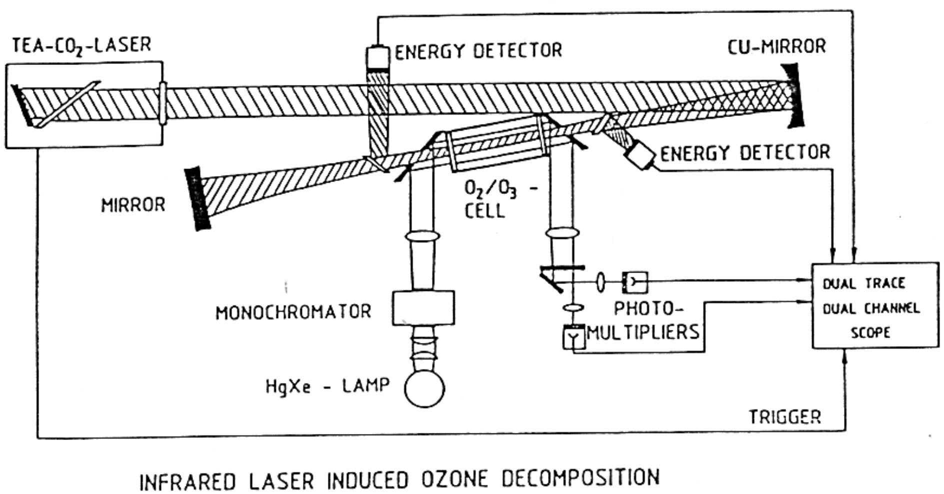


Fig. 1 - Experimental set-up for laser-induced ignition

COMBUSTION AND FLAME 78: 13–41 (1989)

How to Attack Complex Gas Phase Combustion Systems

JÜRGEN WOLFRUM

Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität, 6900 Heidelberg, West Germany

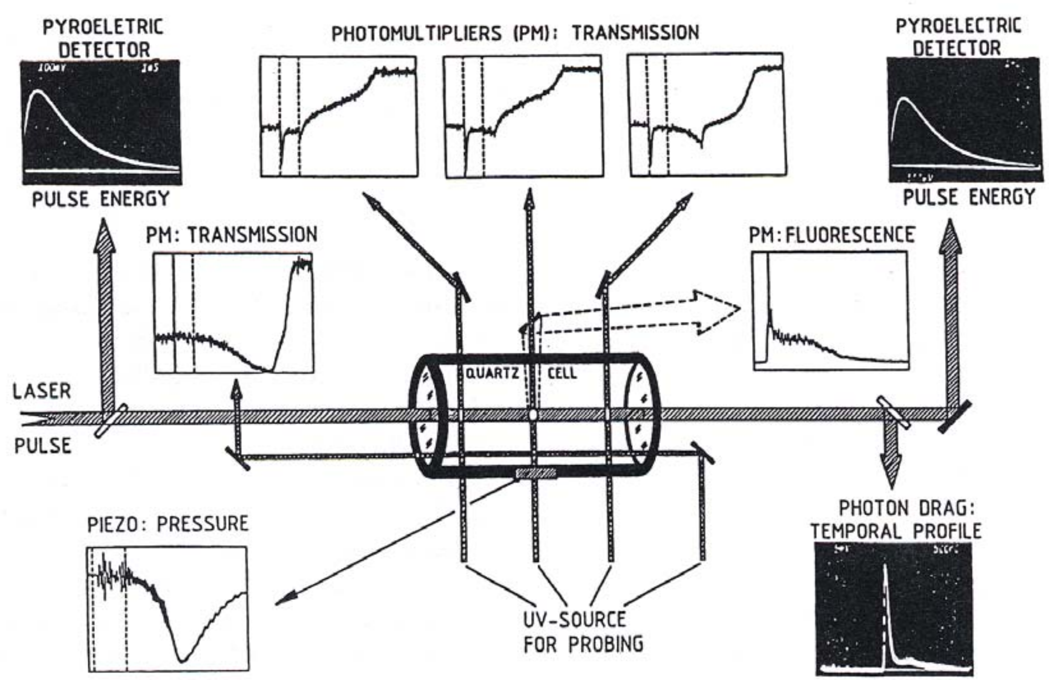


Fig. 19. Experimental setup for the investigation of CO_2 laser-induced ignition of O_3–O_2 mixtures.

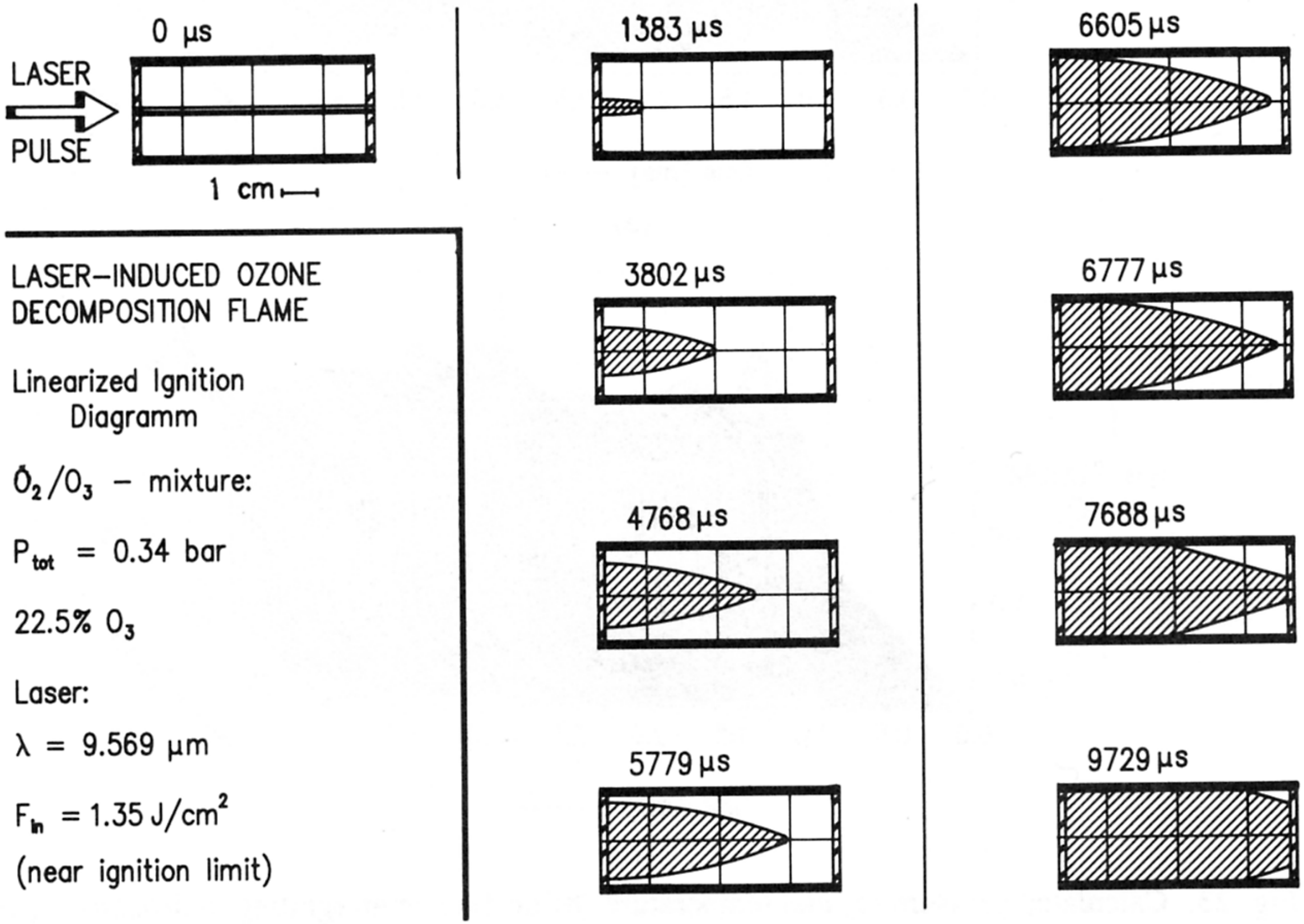
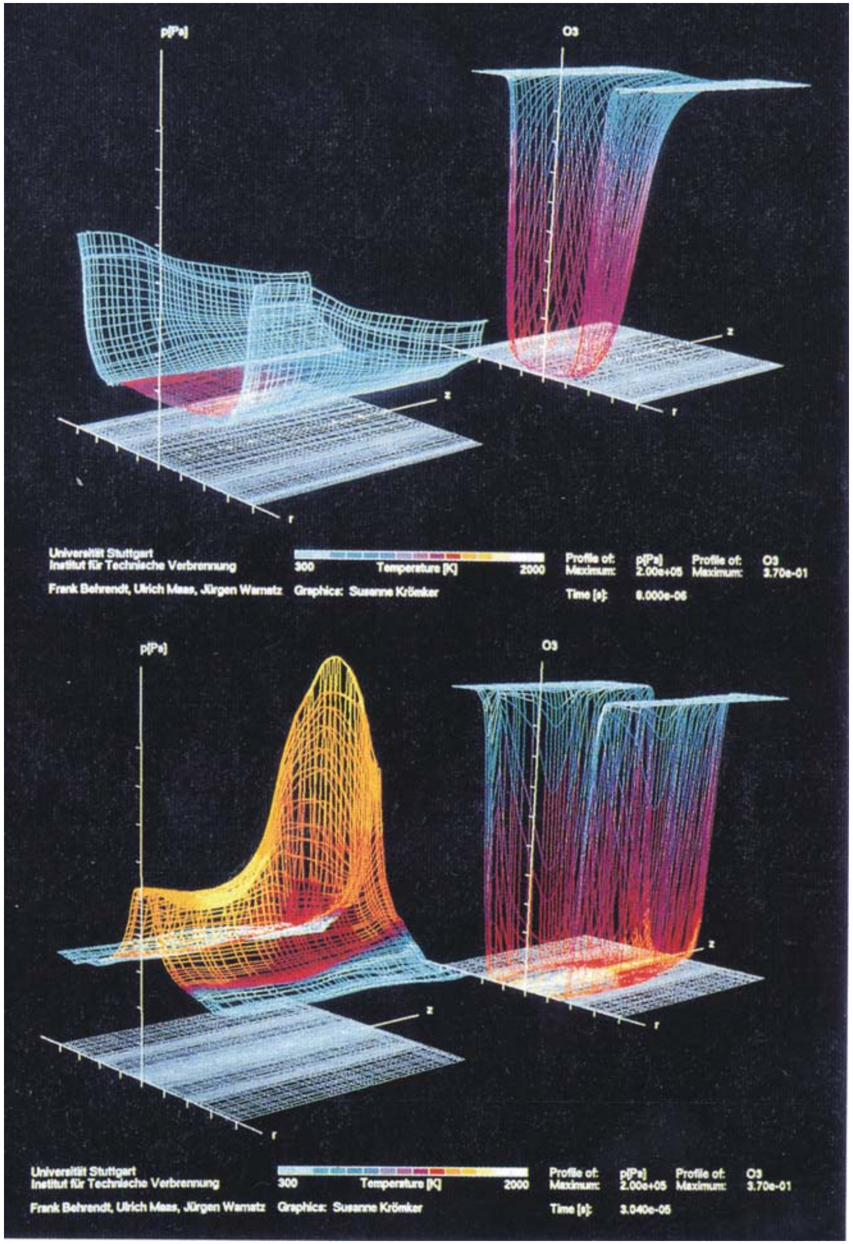


Fig. 22. Evolution of the CO_2 laser–induced ozone decomposition flame near to ignition limit (hatched region = burned gas) [80].



F. Behrendt
U. Maas
J. Warnatz

Modelling of CO_2-laser-induced ignition of O_3/O_2 mixtures

LASER STIMULATION AND OBSERVATION OF IGNITION PROCESSES IN CH_3OH/O_2—MIXTURES

A. ARNOLD, R. HEMBERGER, R. HERDEN, W. KETTERLE, AND J. WOLFRUM

Physikalisch-Chemisches Institut der Universität
Im Neuenheimer Feld 253, D-6900 Heidelberg
Fed. Rep. Germany

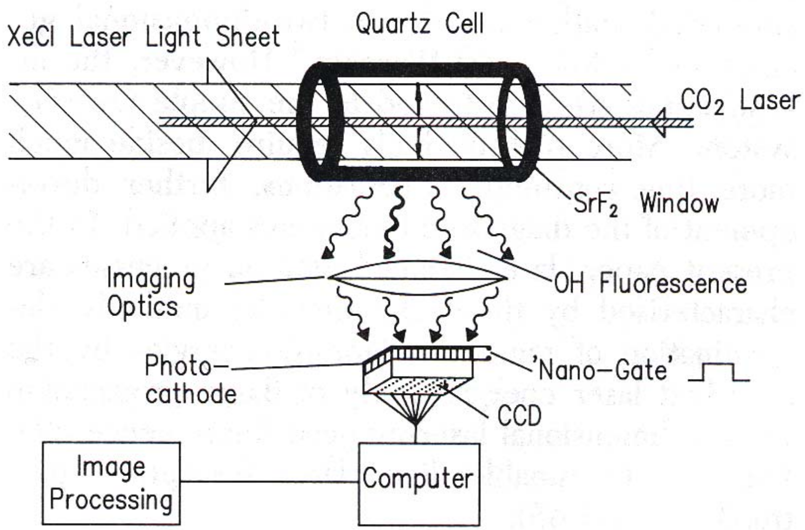


FIG. 2. Experimental arrangement for 2D-LIF detection of OH radicals formed in CO_2 laser induced ignition

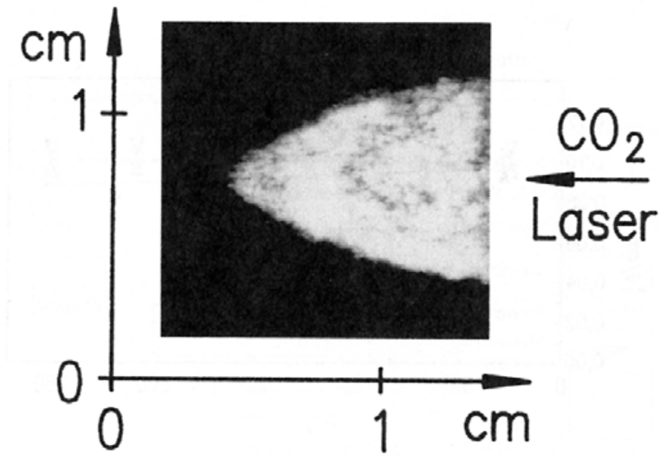
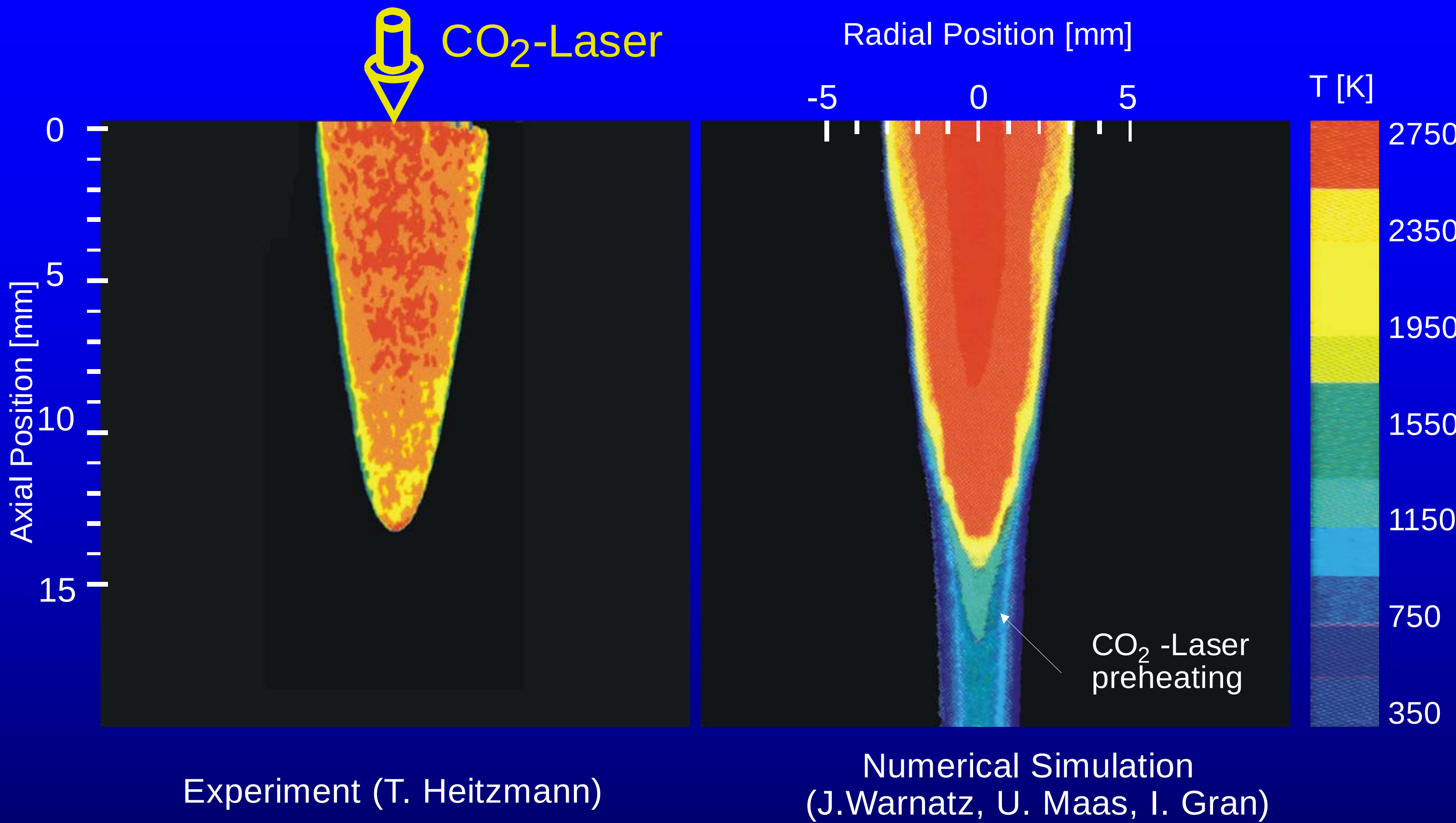


FIG. 6. 2D-LIF image of OH showing the flame propagation in laser ignited mixture of methanol (100 Torr) and oxygen (400 Torr)



CO_2 Laser induced ignition of a CH_3OH/O_2 mixture (Φ=0,9,p=300mbar)

J. Warnatz, J. Wolfrum

Umweltschutz mit Laserlicht

Laserspektroskopische Analyse und mathematische Modellierung von Verbrennungsprozessen

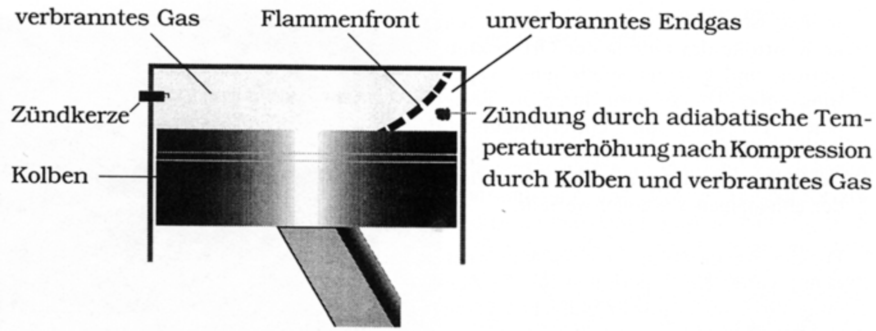


Abb. 8: Auftreten von Selbstzündungsprozessen aufgrund der Kompression des Endgases im Otto-Motor durch das verbrannte Gas und durch die Kolbenbewegung.

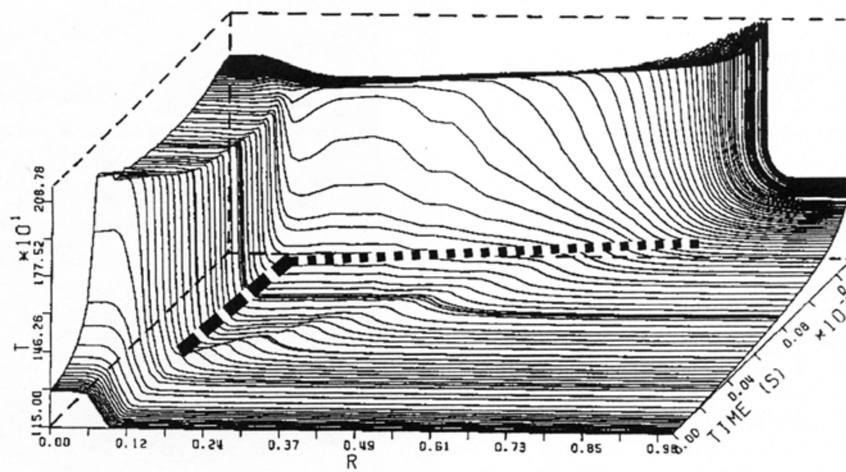
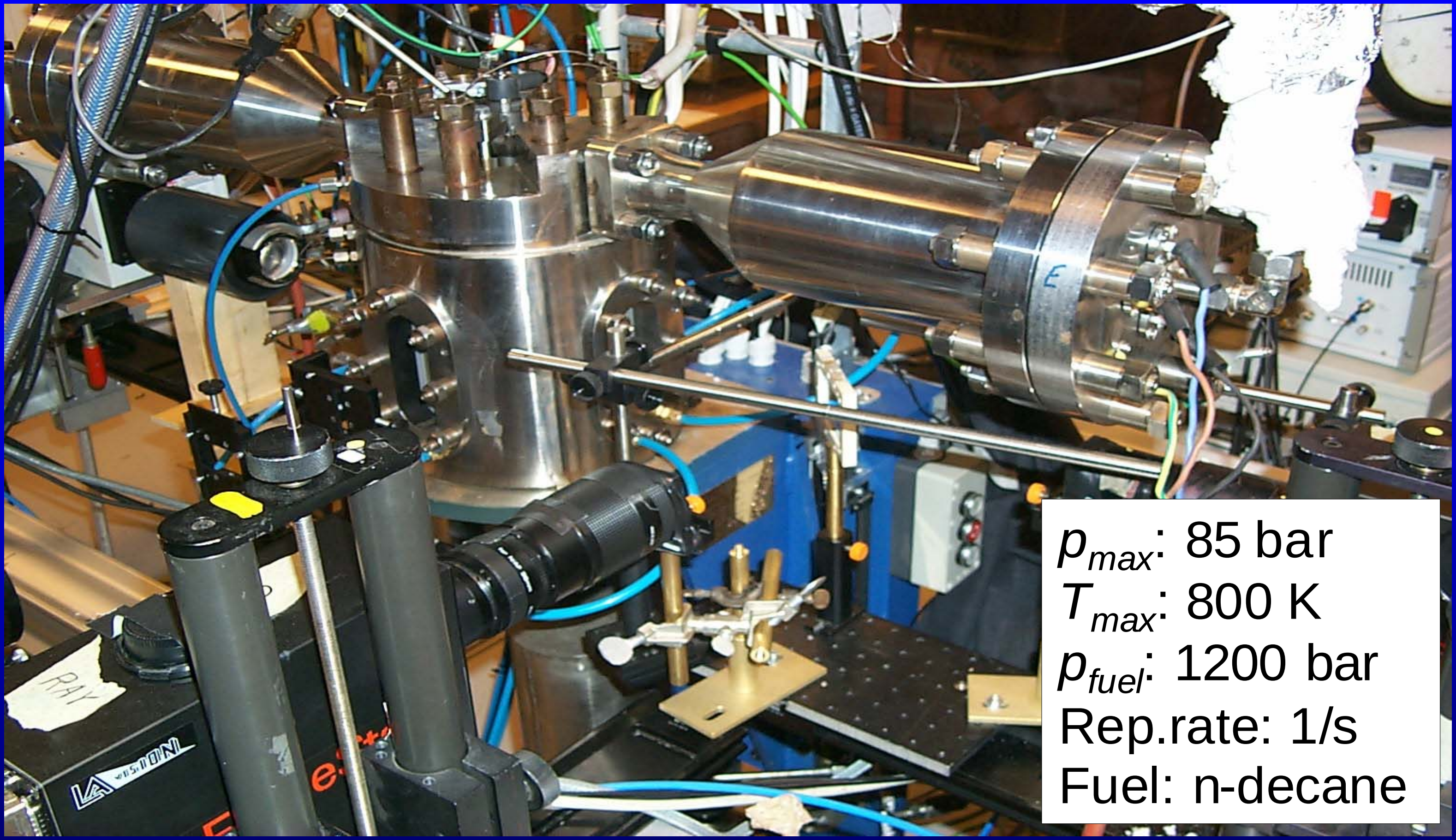
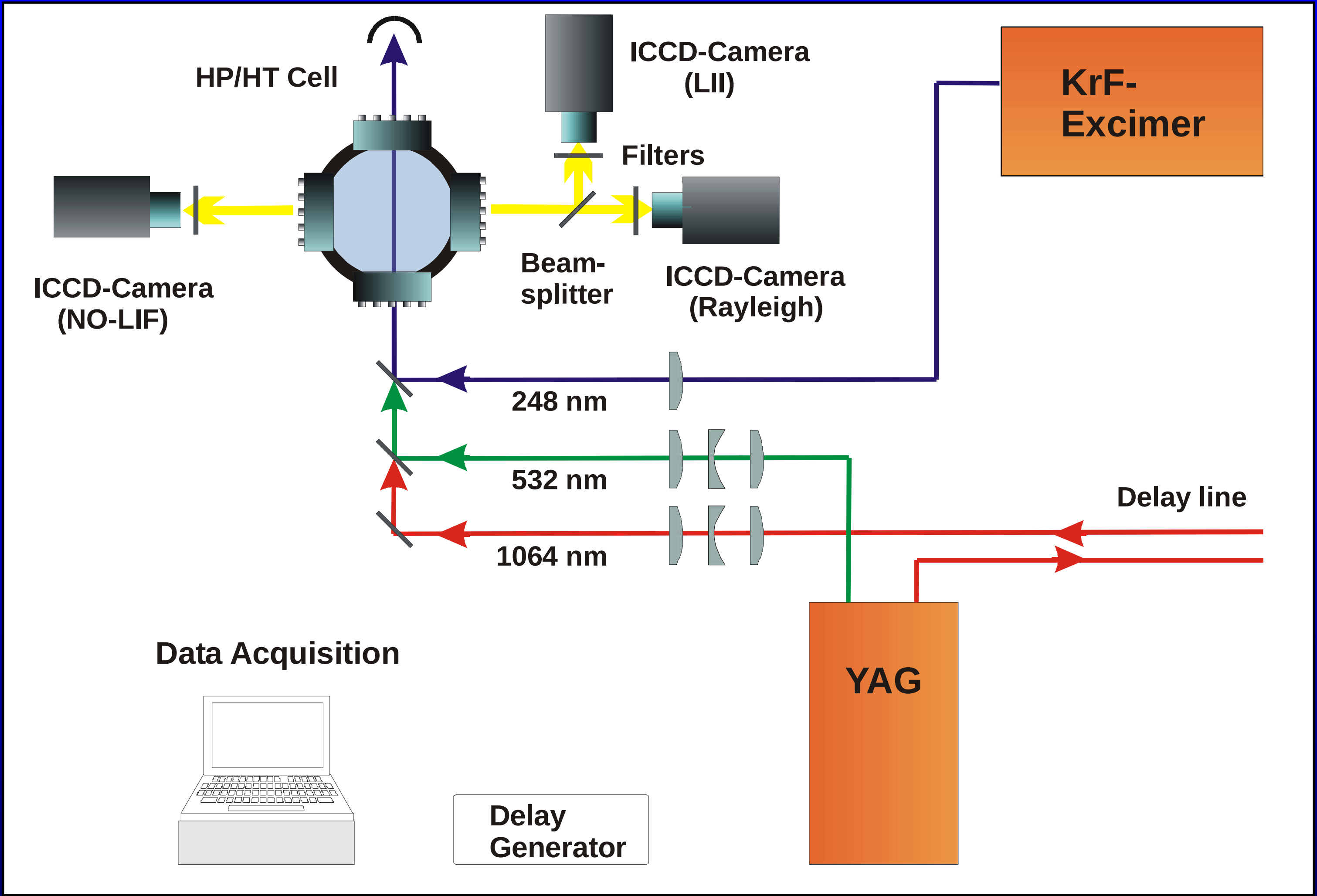


Abb. 9: Auftreten von normaler (gestrichelt) und von schneller (scheinbarer) Flammenfortpflanzung (punktiert) durch stoßwelleninduzierte Selbstzündung im Endgas eines Otto-Motors.



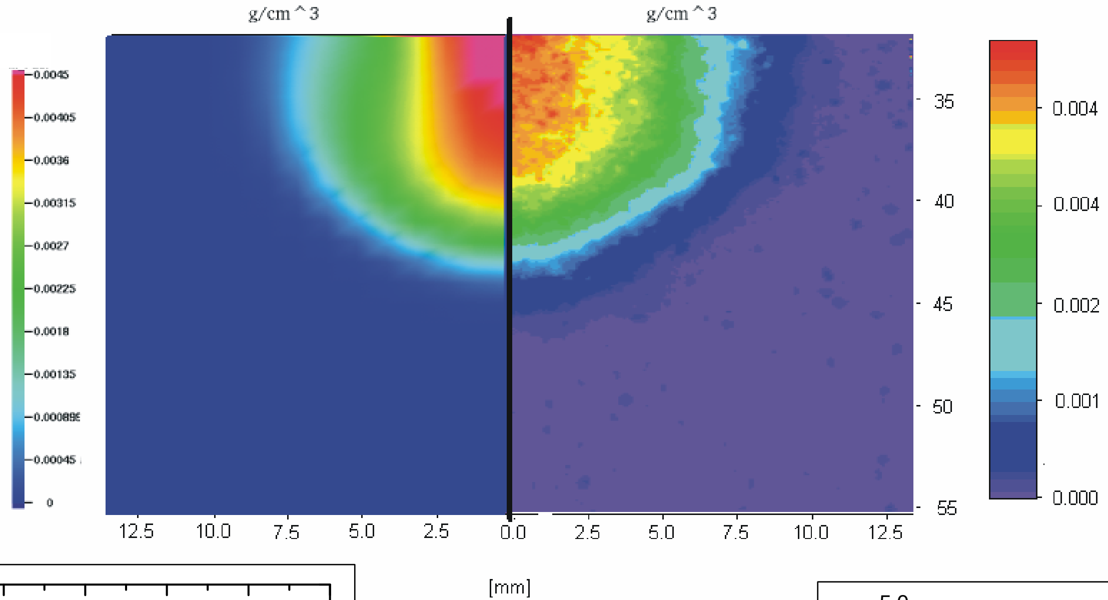
Simultaneous measurement of Diesel fuel vapor density by Rayleigh scattering and soot volume fraction by LII in a high temperature and high pressure chamber

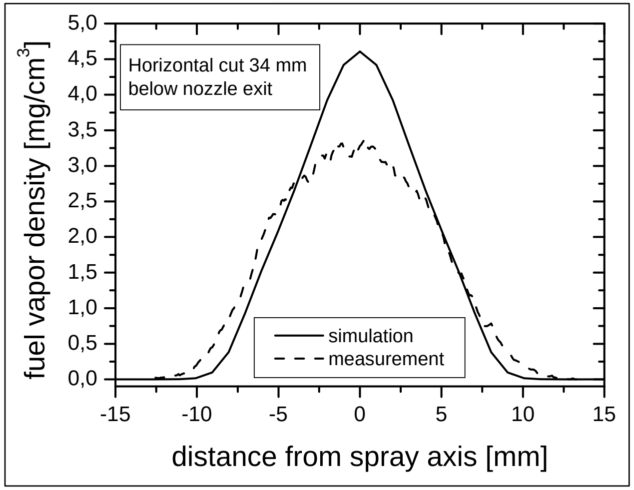


Simultaneous measurement of Diesel fuel vapor density by Rayleigh scattering and soot volume fraction by LII in a high temperature and high pressure chamber

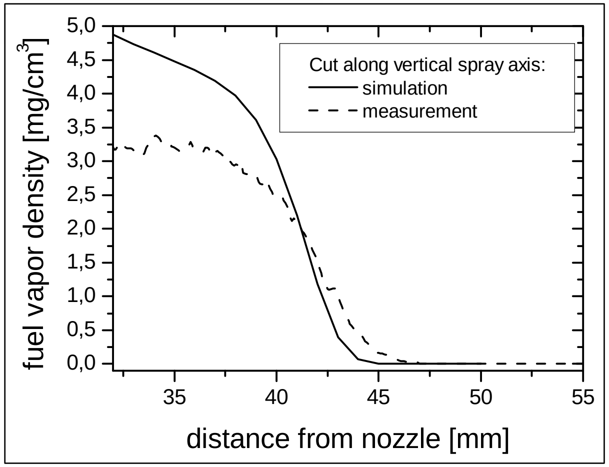
Numerical simulation

Experiment





Fuel vapor density



Measurement of Diesel fuel vapor density by Rayleigh scattering in a high temperature and high pressure chamber

$$RH + O_2 \longrightarrow R + HO_2$$

$$R + O_2 \rightleftharpoons RO_2$$

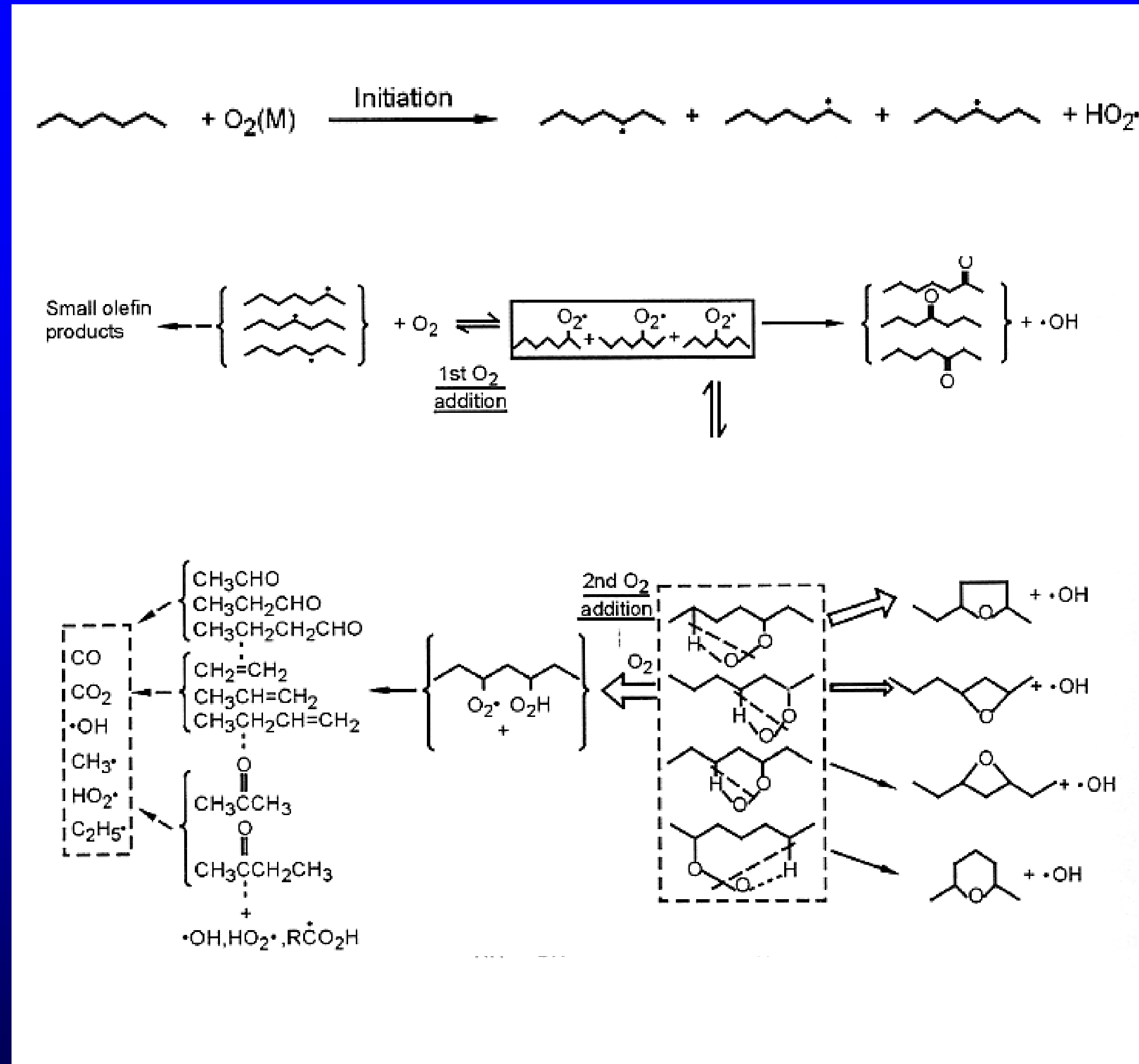
$$RO_2 \longrightarrow QO + OH$$

$$RO_2 \longrightarrow QOOH$$

$$QOOH \longrightarrow QO_C + OH$$

$$QOOH \xrightarrow{+O_2} O_2QOOH$$

$$RH + OH \longrightarrow R + H_2O$$



Reaction mechanism for the thermal oxidation of n-heptane in the cool flame region

Twenty-Sixth Symposium (International) on Combustion/The Combustion Institute, 1996/pp. 773–780

KINETIC MODELING OF THE OXIDATION OF LARGE ALIPHATIC HYDROCARBONS

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Because of the complexity of low-temperature oxidation, a detailed reaction scheme of higher hydrocarbons (which are components of practical fuels) typically involves several hundred chemical species taking part in thousands of elementary reactions. Nevertheless, only a very limited number of different reaction types is appearing, for example, alkane thermal decomposition, H-atom abstraction to form an alkyl radical, alkyl radical isomerization, and β decomposition of the alkyl radical for the high-temperature range and a few additional reaction types at low temperature. A LISP program developed for the automatic generation of reaction mechanisms is able to produce mechanisms for the oxidation of aliphatic hydrocarbons. In contrast to earlier attempts described in the literature, a rather complete description of the reaction paths for the decomposition of the intermediate dihydroperoxyalkyl radicals and a description of the aldehyde oxidation is included. The transition between low- and high-temperature range with a negative temperature dependence is well reproduced. With the help of newly available experiments for *n*-decane, the reaction mechanisms for *n*-heptane and *n*-decane are validated for a wide range of pressures, temperatures, and equivalence ratios, covering conditions dictated by potential applications. This is a severe test case, because calculated ignition-delay times are very sensitive with respect to the quality of the reaction mechanism used. Additional sensitivity analysis based on the OH concentration shows the principal rate-determining reactions. However, more kinetic data for high hydrocarbons and oxygenated species are necessary to validate the reaction mechanism, especially with respect to chain-length dependencies of rate coefficients and the behavior of fuels with multiple C–C bonds. Furthermore, some results on flame velocity are given for *n*-heptane.

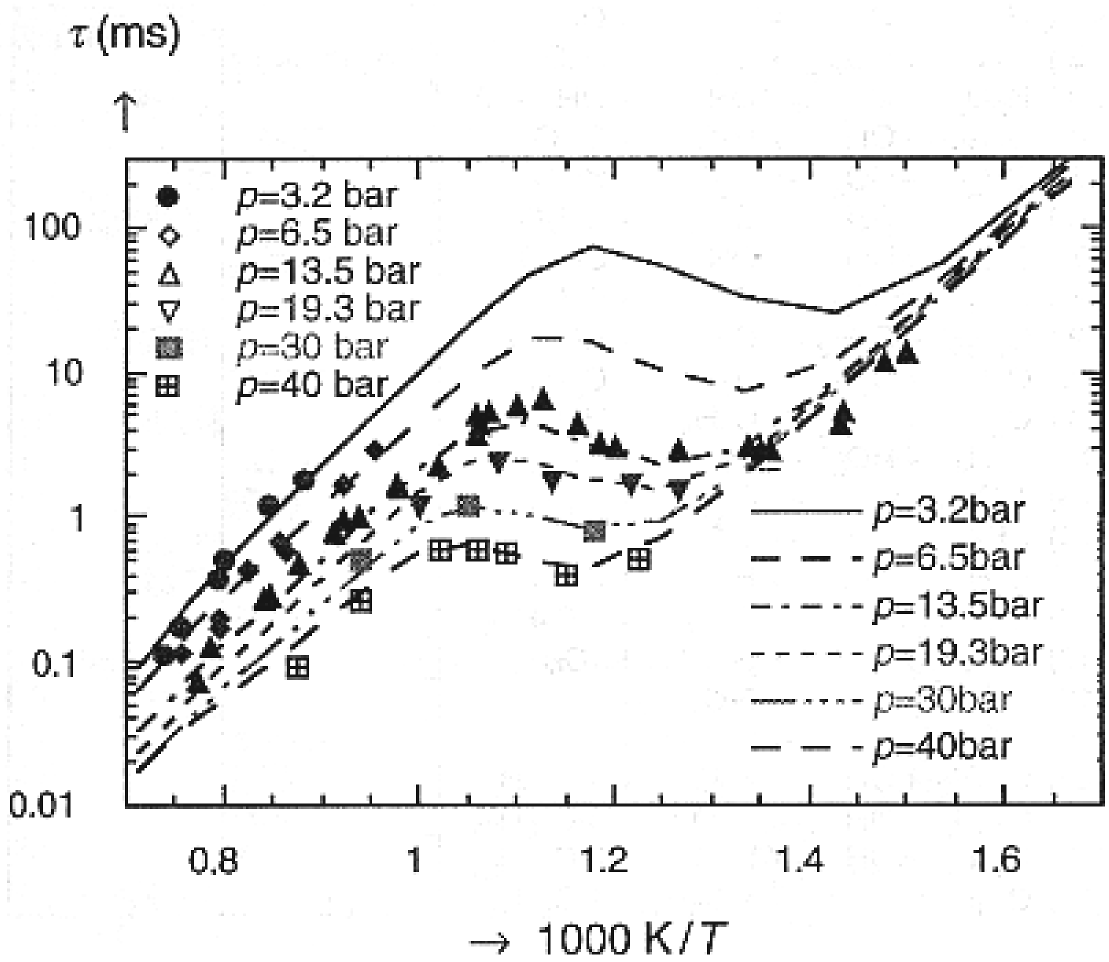
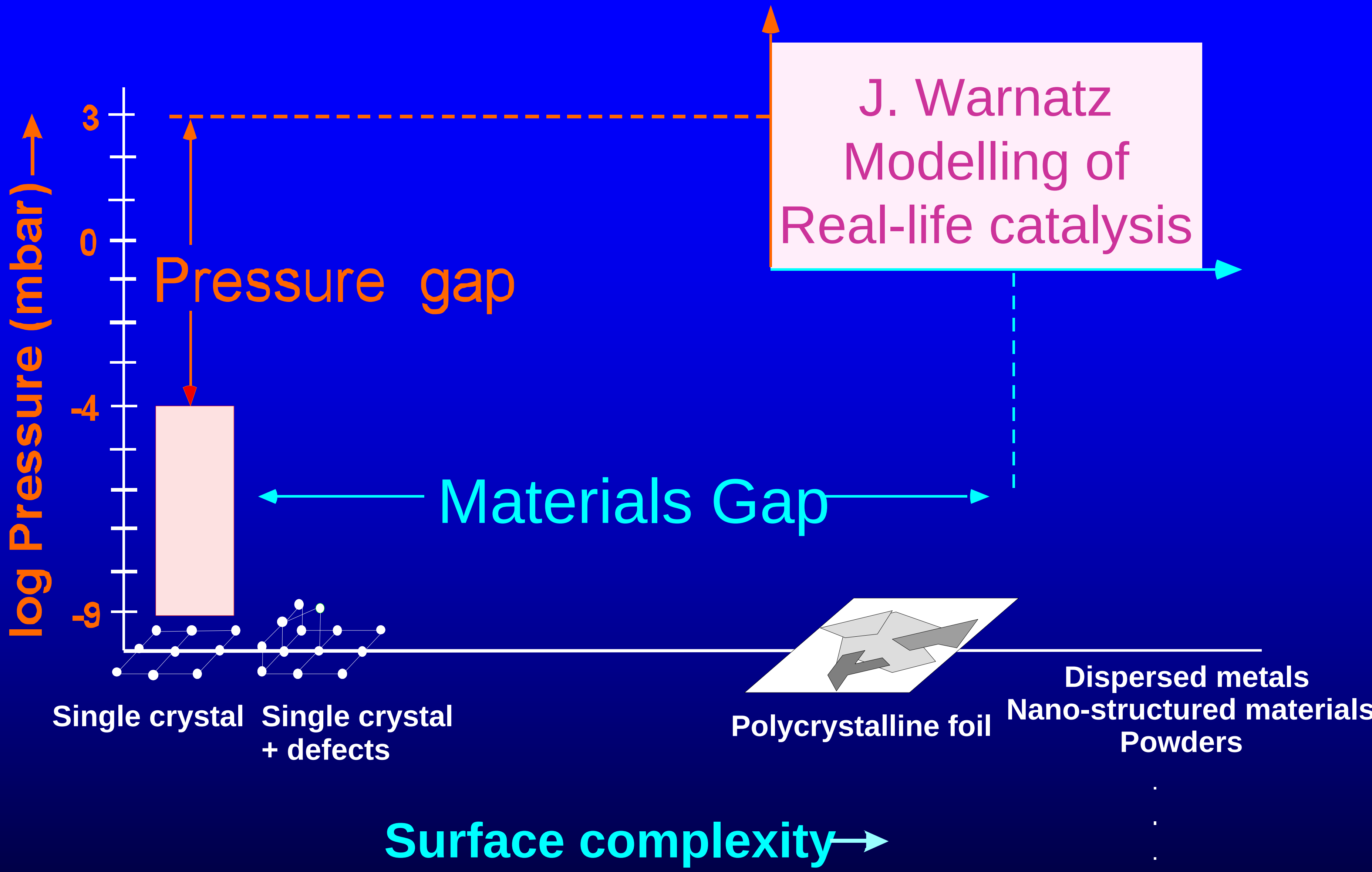
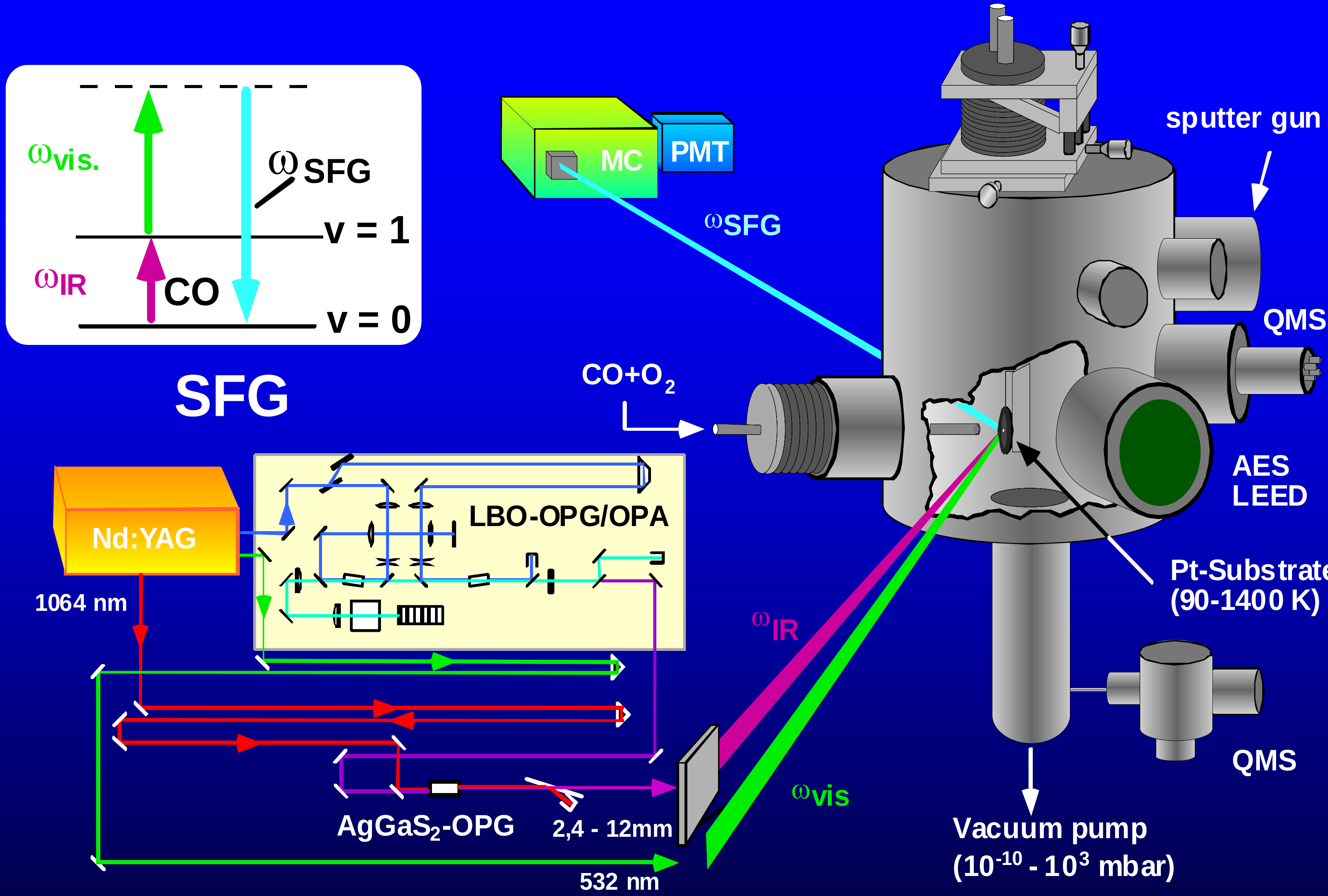


FIG. 3. Ignition-delay times τ in stoichiometric n-heptane–air mixtures as a function of the initial temperature T for different pressures p; lines, simulations (this work); symbols, experiments [26].

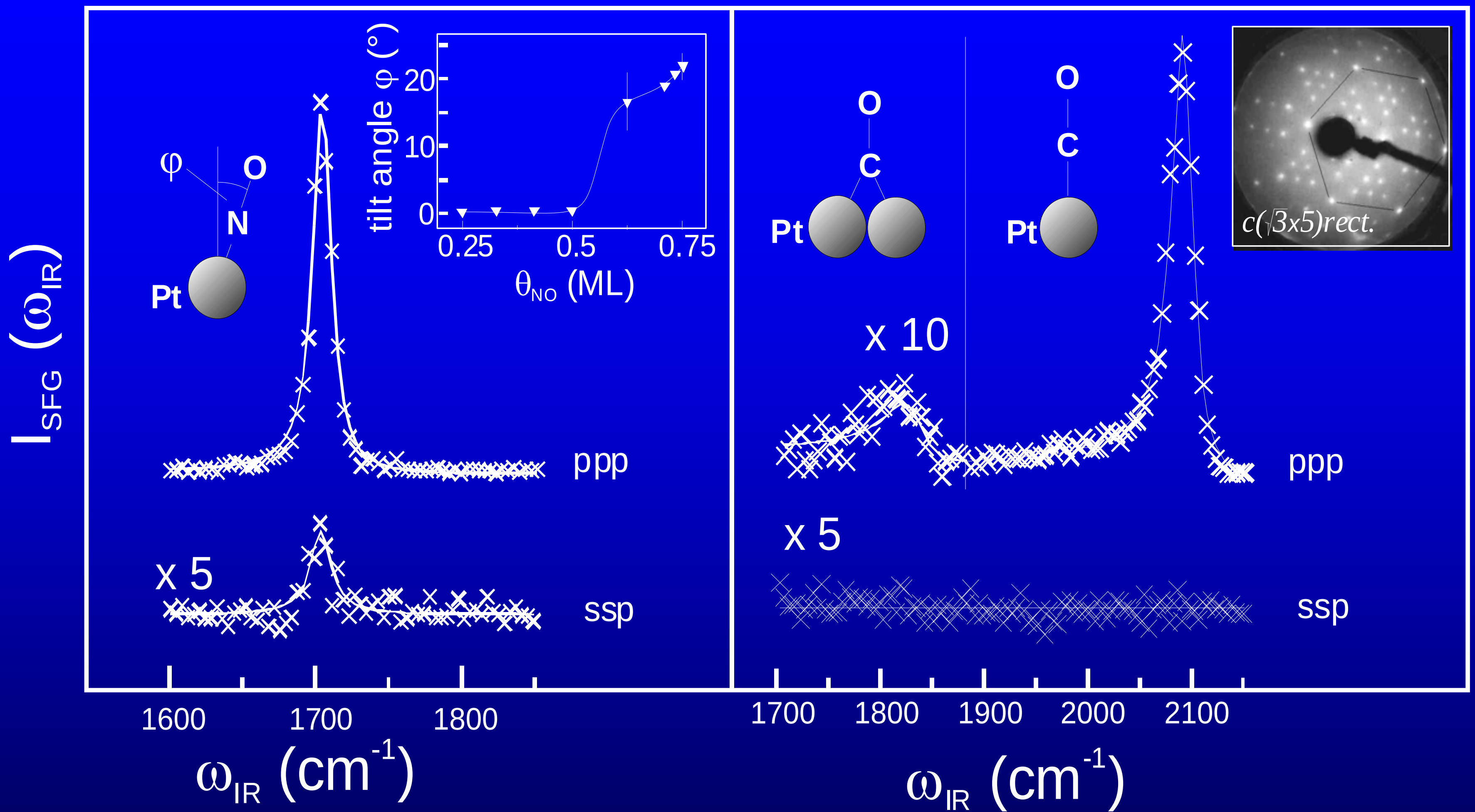
1. **Formation and Destruction of Nitric Oxide**
2. **Explosion and Ignition Phenomena**
3. **Heterogeneous Catalysis**



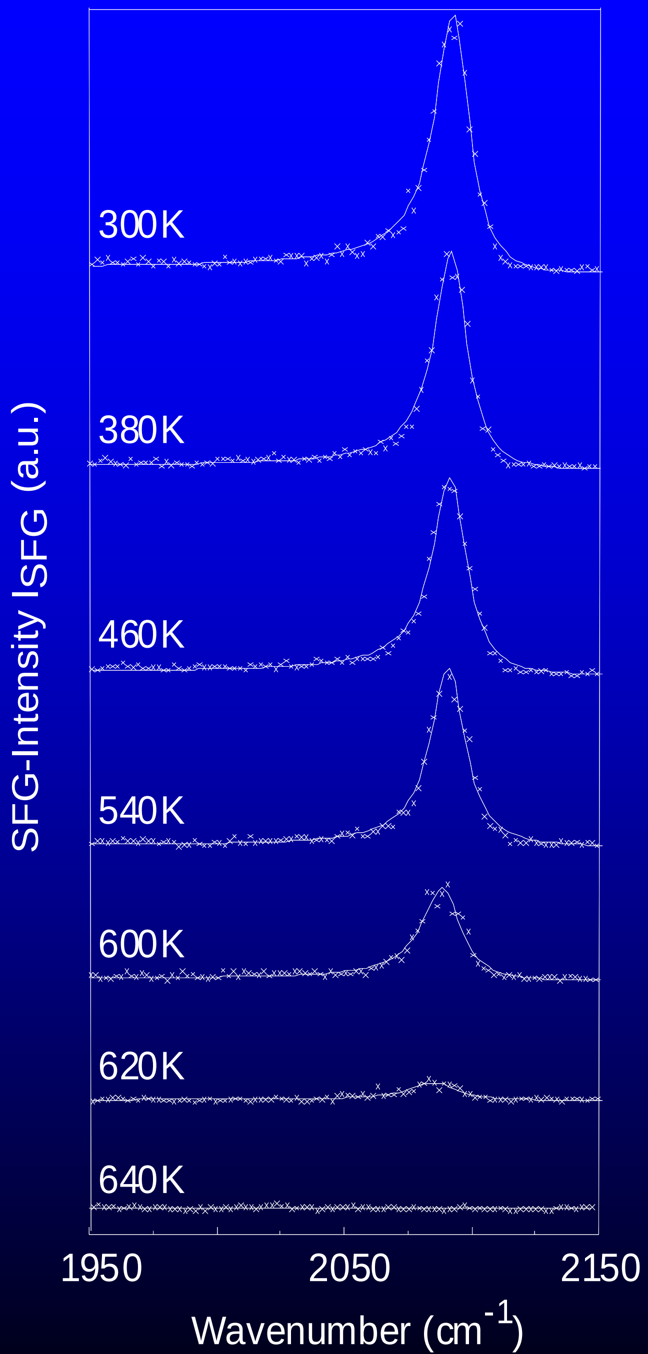
Investigation of Elementary Surface Reactions

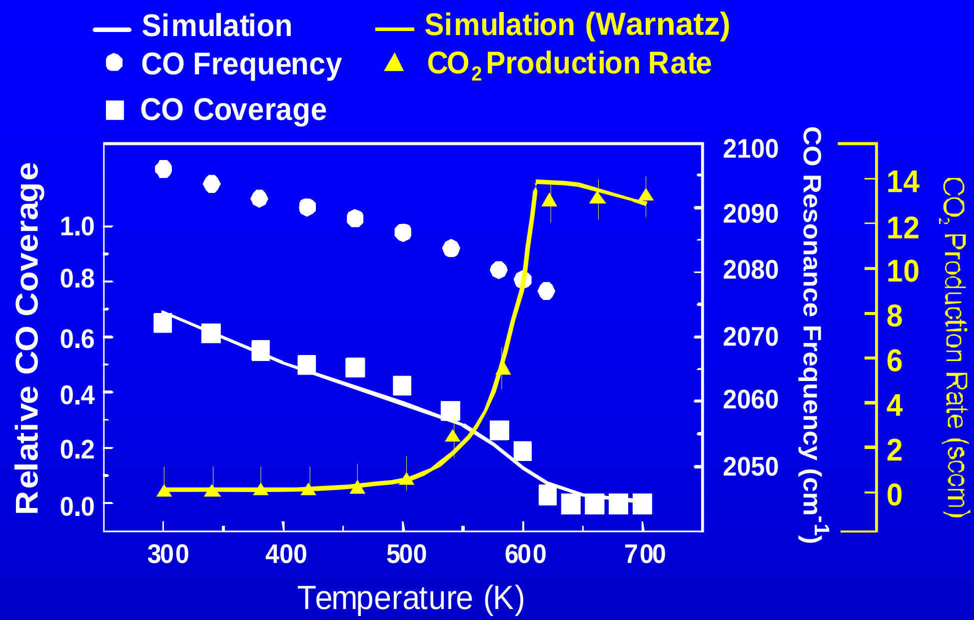


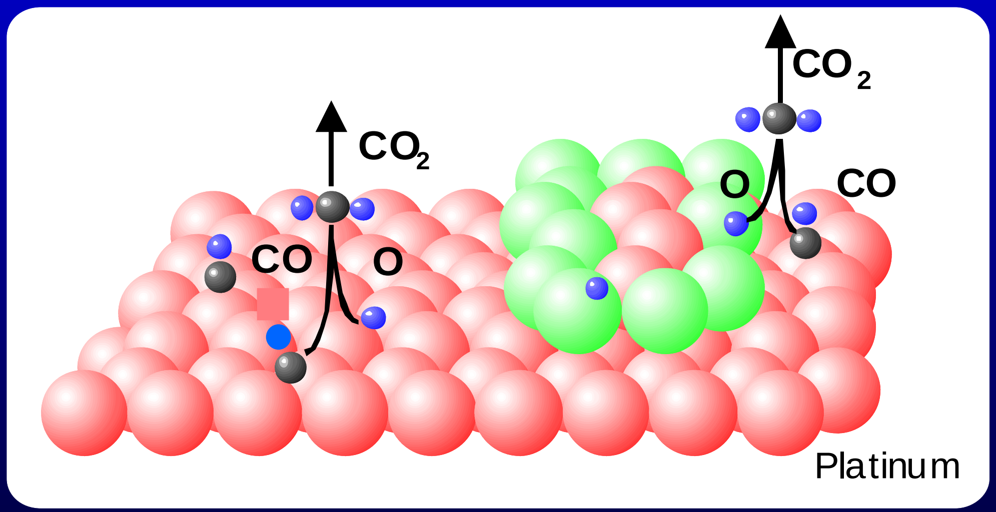
In-situ detection of chemisorbed CO during oxidation on a polycrystalline platinum foil using infrared-visible sum-frequency generation (SFG)



SFG spectra of NO and CO on Pt(111) single crystal







CO Oxidation on a Platinum Foil

p = 20 mbar, : 30 sccm CO, 15 sccm O_2, 105 sccm Ar

The deep pain that is felt at the death of every friendly soul arises
from the feeling that there is in every individual something
which is inexpressible, peculiar to him alone,
and is, therefore, absolutely and irretrievably lost.

A. Schopenhauer, 1851