united nations educational, scientific and cultural organization

international atomic energy agency

the
abdus salam
international centre for theoretical physics

SMR/1238-30

ADRIATICO RESEARCH CONFERENCE on

LASERS IN SURFACE SCIENCE

11–15 September 2000

Miramare - Trieste, Italy

Infrared laser-induced desorption after resonant excitation of small molecules condensed on insulator surfaces using the Free Electron Laser "FELIX"

B. Redlich
FOM Institute for Plasmaphysics Rijnhuizen
Nieuwegein, The Netherlands

Infrared laser-induced desorption after resonant excitation of small molecules condensed on insulator surfaces using the Free Electron Laser 'FELIX"

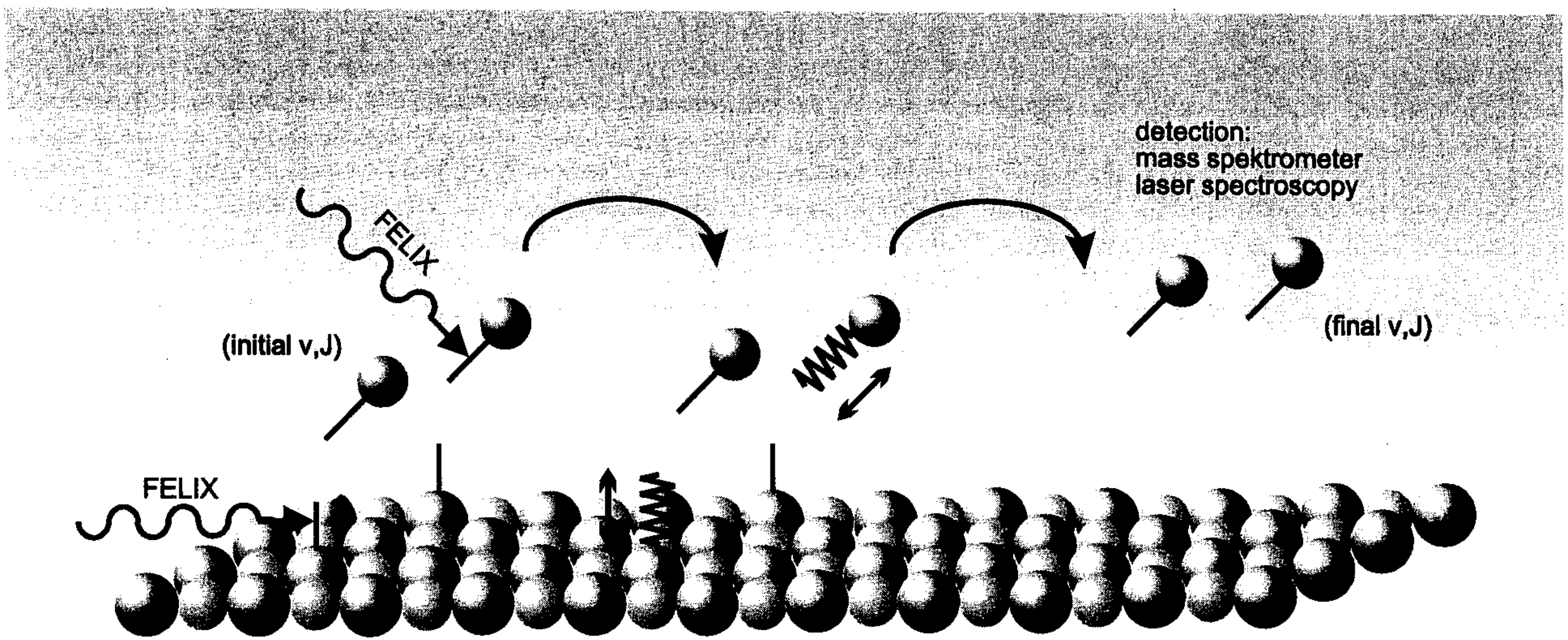
B. Redlich[1], H. Zacharias[2], G. von Helden[1], G. Meijer[1]

[1] FOM Institute for Plasma Physics Rijnhuizen, Edisonbaan 14, 3439 MN Nieuwegein, The Netherlands
[2] Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany

---

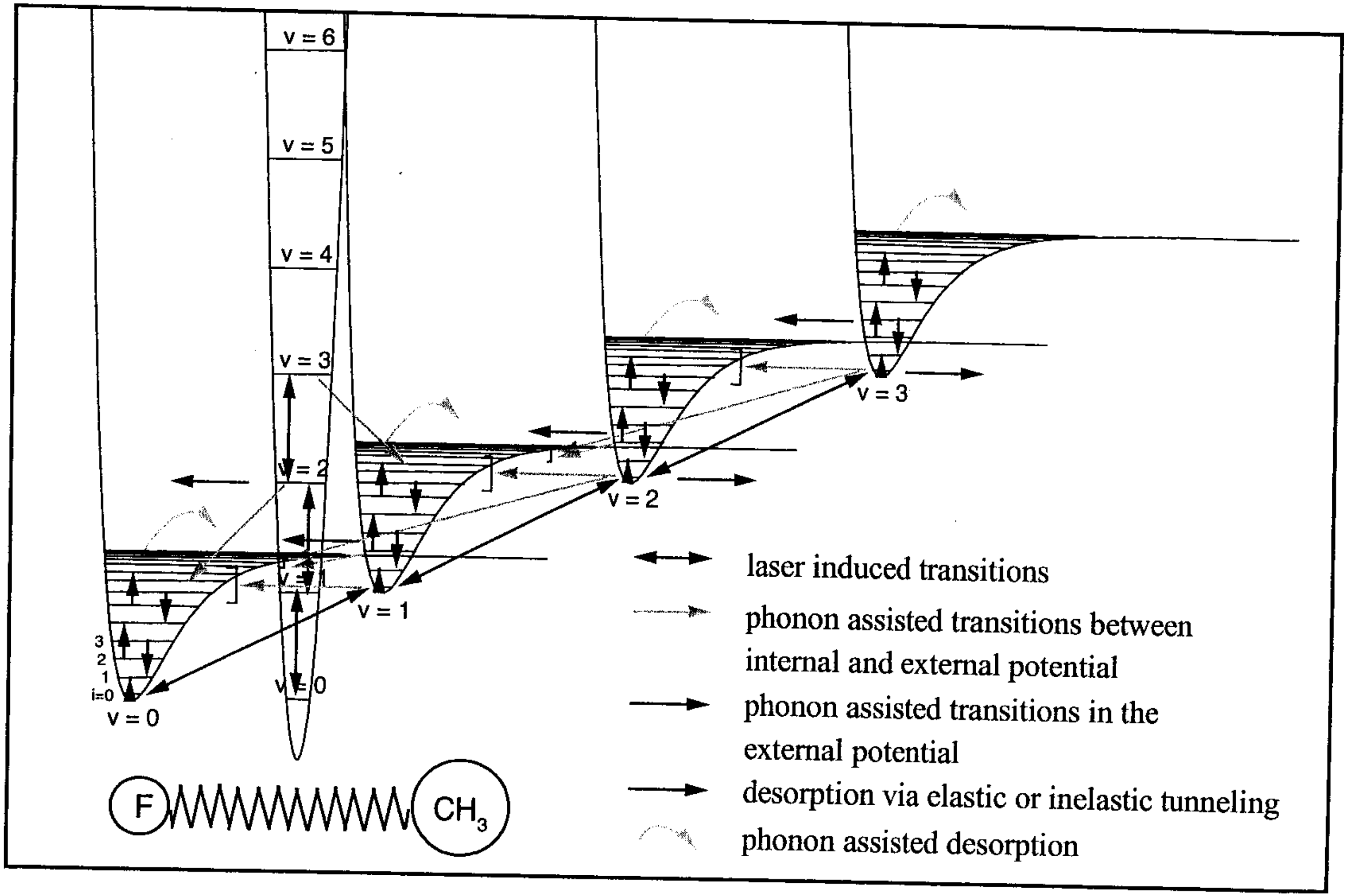
- Motivation
- The Free Electron Laser 'FELIX'
- Experimental setup
- Results: CD_3F, methane and N_2O condensed on NaCl(100)
- Conclusions
- Outlook

Motivation



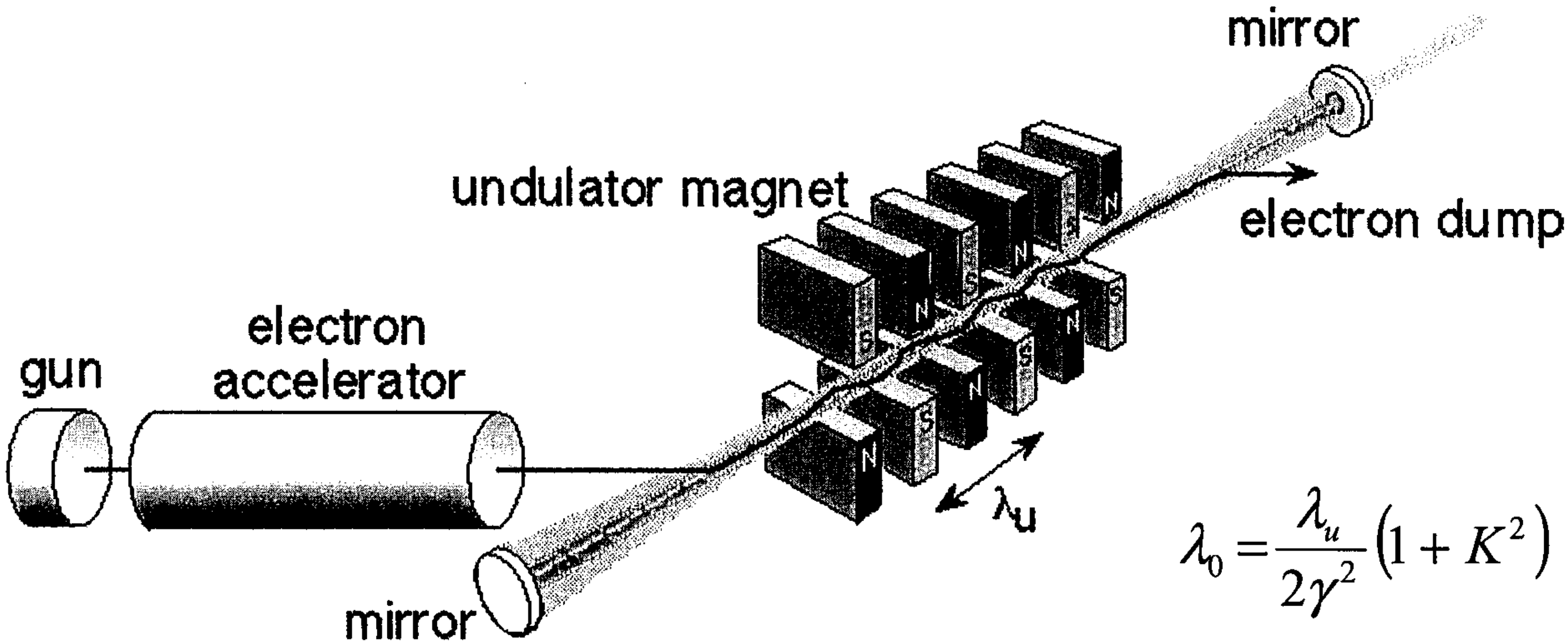
- energy flow in vibrationally excited adsorbates: desorption or relaxation ?
- isotope selective excitation ⇒ isotope selective desorption ?

Excitation and relaxation channels



Gortel et al., Phys. Rev. B 27 (1983) 5066

Scheme of the Free Electron Laser



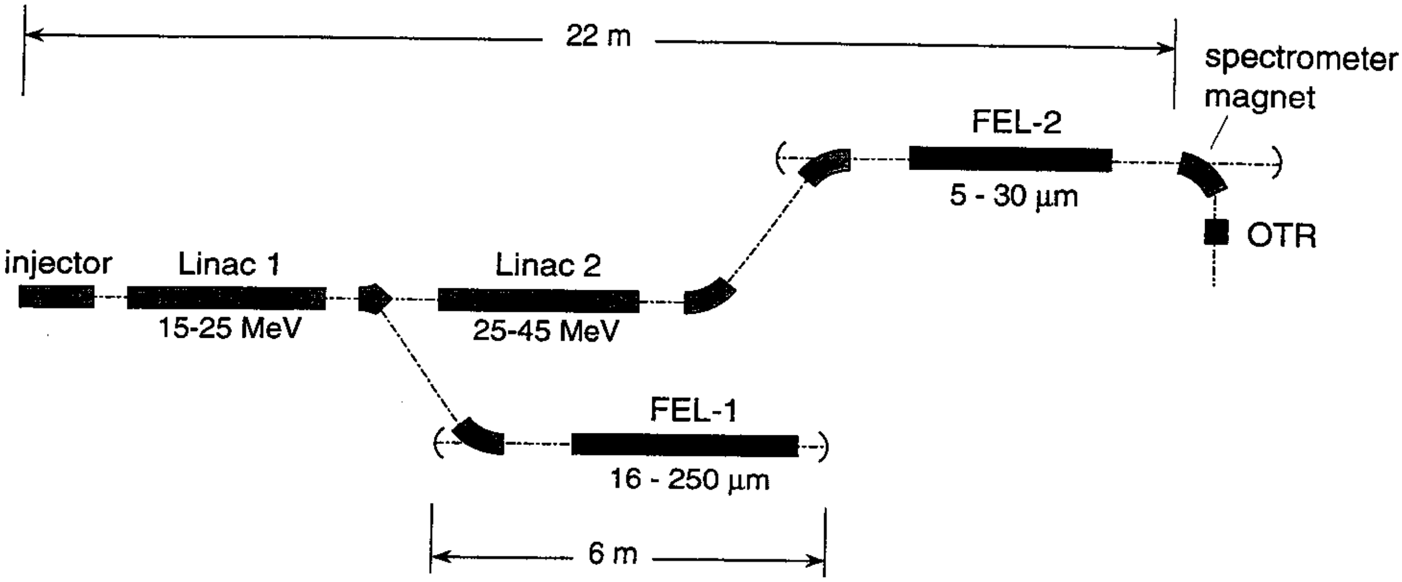
$$\lambda_0 = \frac{\lambda_u}{2\gamma^2}\left(1 + K^2\right)$$

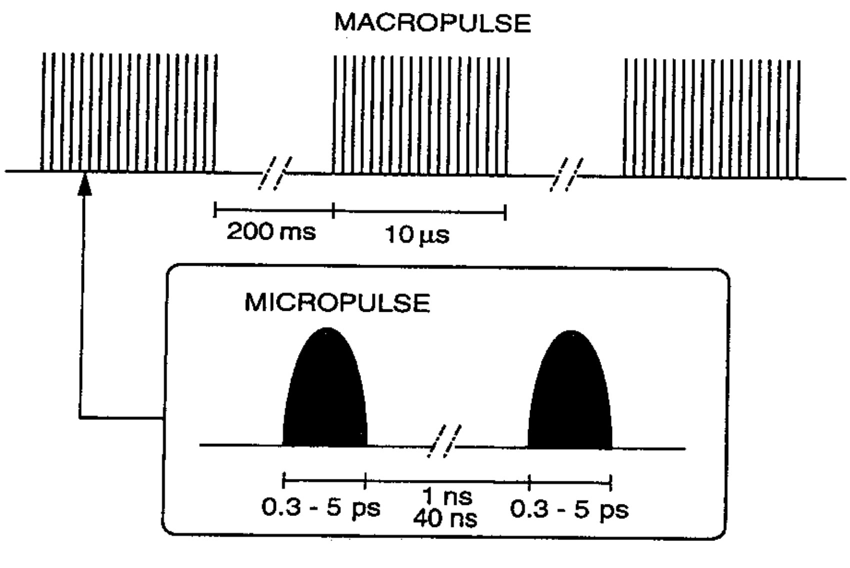
λ_0 = wavelength of the radiation λ_u = periodicity of the undulator field

K = dimensionsless constant proportional to the amplitude of the magnetic field

γ = relativistic factor ($\gamma^2 >> 1$)

Free Electron Laser for Infrared eXperiments 'FELIX'

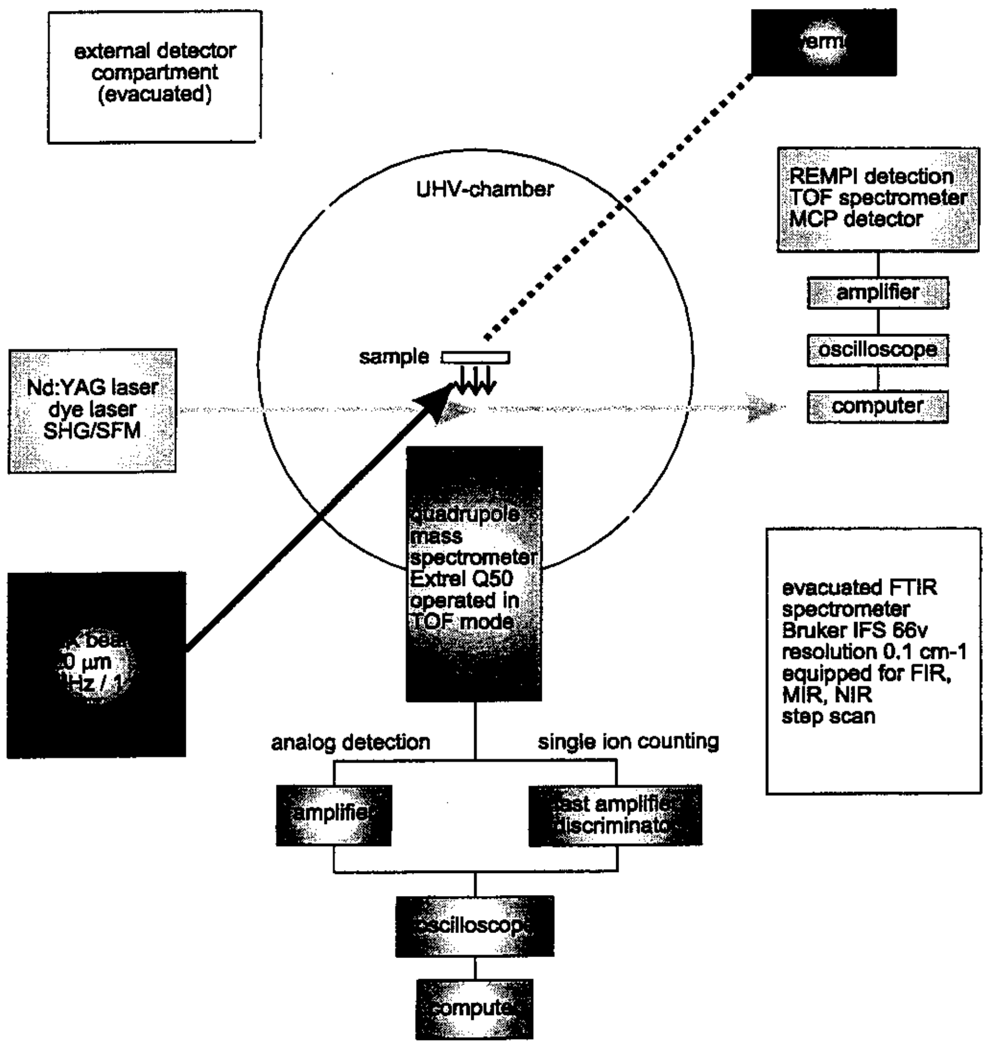




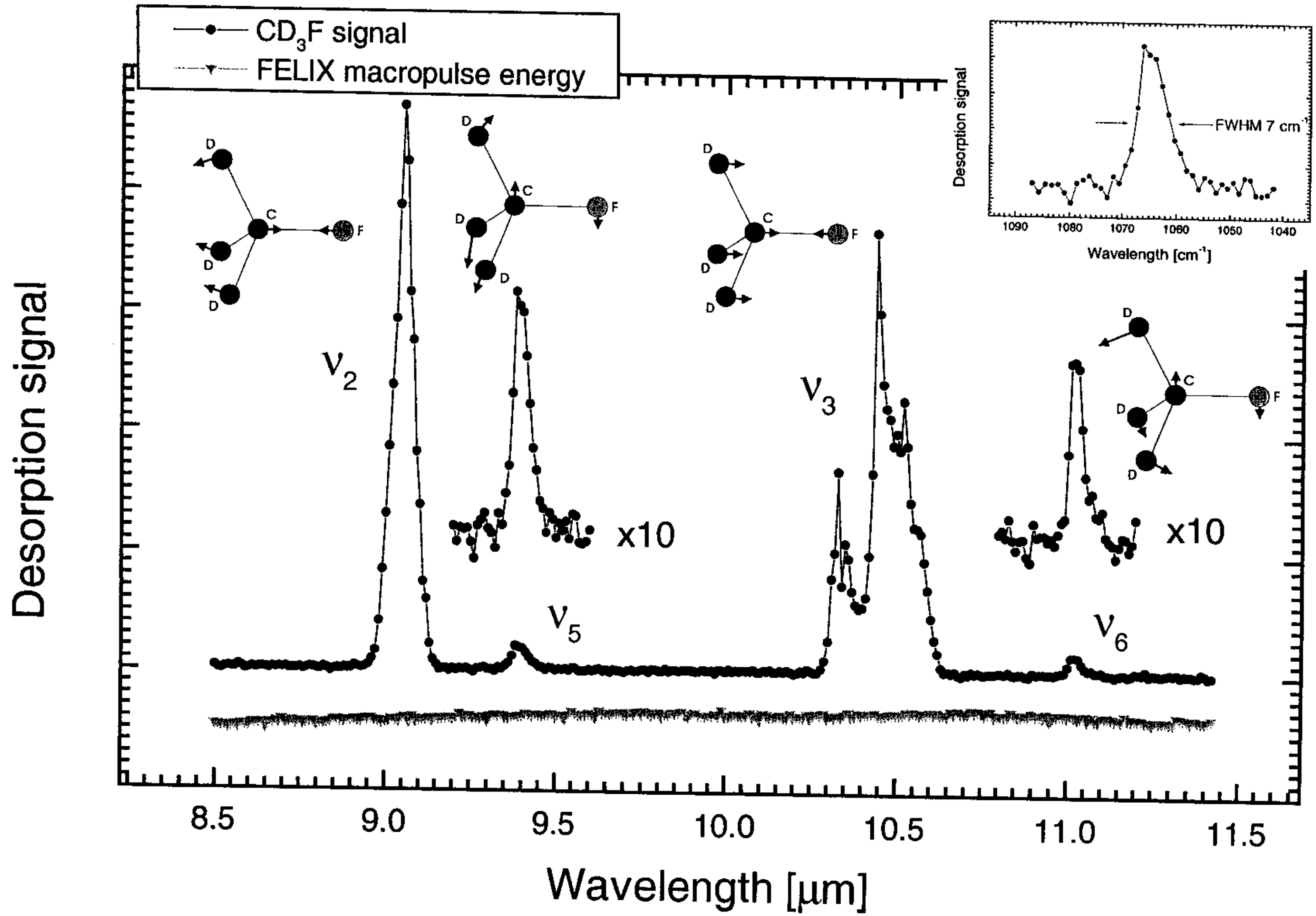
tuning range: 40 - 2000 cm^{-1}
macropulse energy: 20-100 mJ
bandwidth: transform limited

Experimental Setup

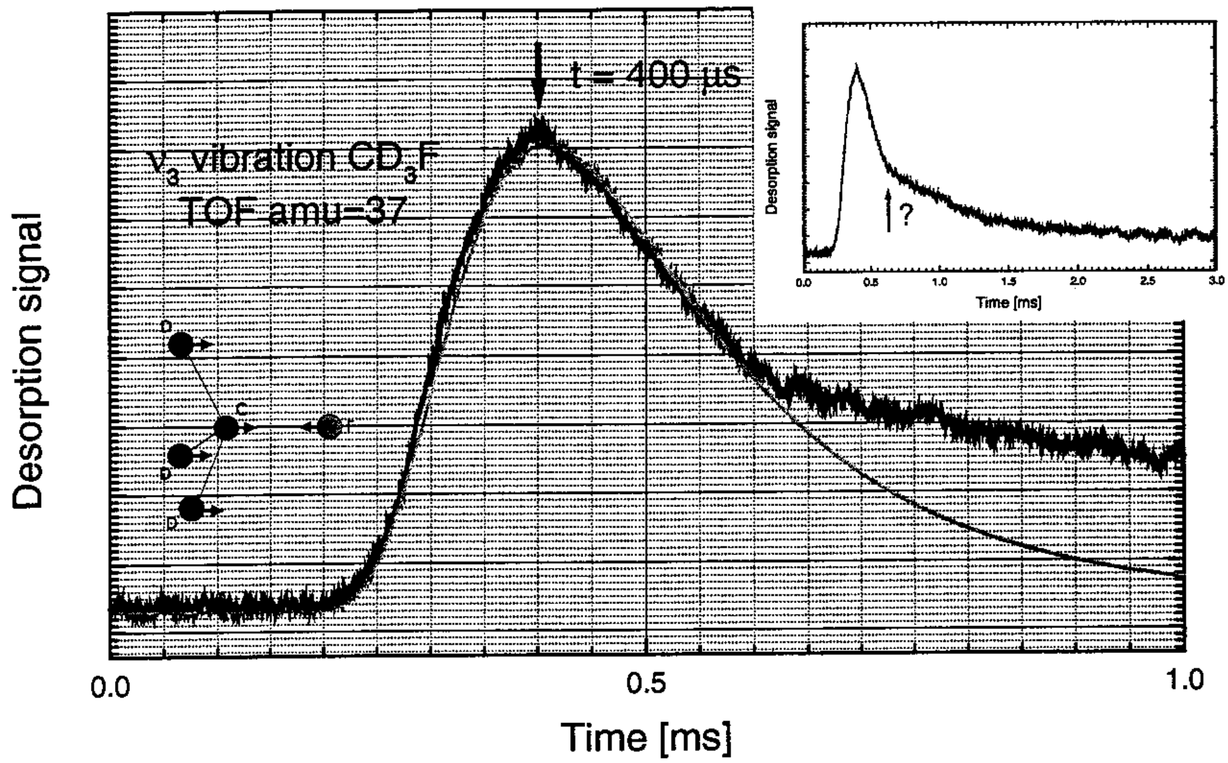
- UHV chamber
- substrate: NaCl(100) single crystal, cleaved under nitrogen atmosphere
- sample coolable down to 20 K, annealing of the sample up to 700 K
- detection of the desorbing species:
  - time resolved with a quadrupole mass spectrometer (analog or single ion detection)
  - state resolved with a REMPI scheme and TOF detection
- detection and characterization of the adsorbates using FTIR spectroscopy
- condensation of the multilayers at low temperatures, no significant desorption observable



Laser-induced desorption of CD_3F condensed on NaCl(100)



TOF spectra of multilayers $CD_3F/NaCl(100)$



- estimation of the translational temperature of the desorbing molecules via a Maxwell-Boltzmann distribution

most probable velocity:* $$v = \sqrt{\frac{2kT}{m}}$$

Translational temperature: 217.4 K

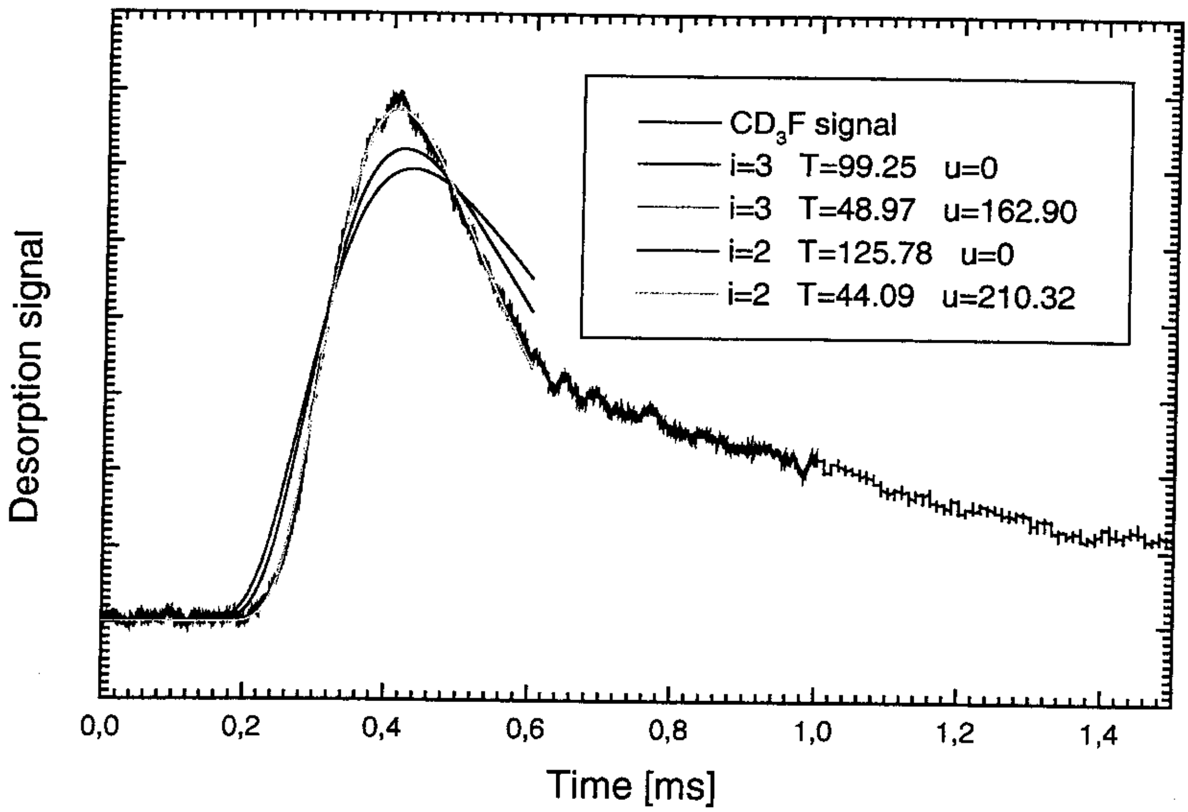
(* after correction for the drift time of ~5 µs)

- calculated desorption temperatures are well above the measured sample temperature of about 30 K

Determination of translational temperature

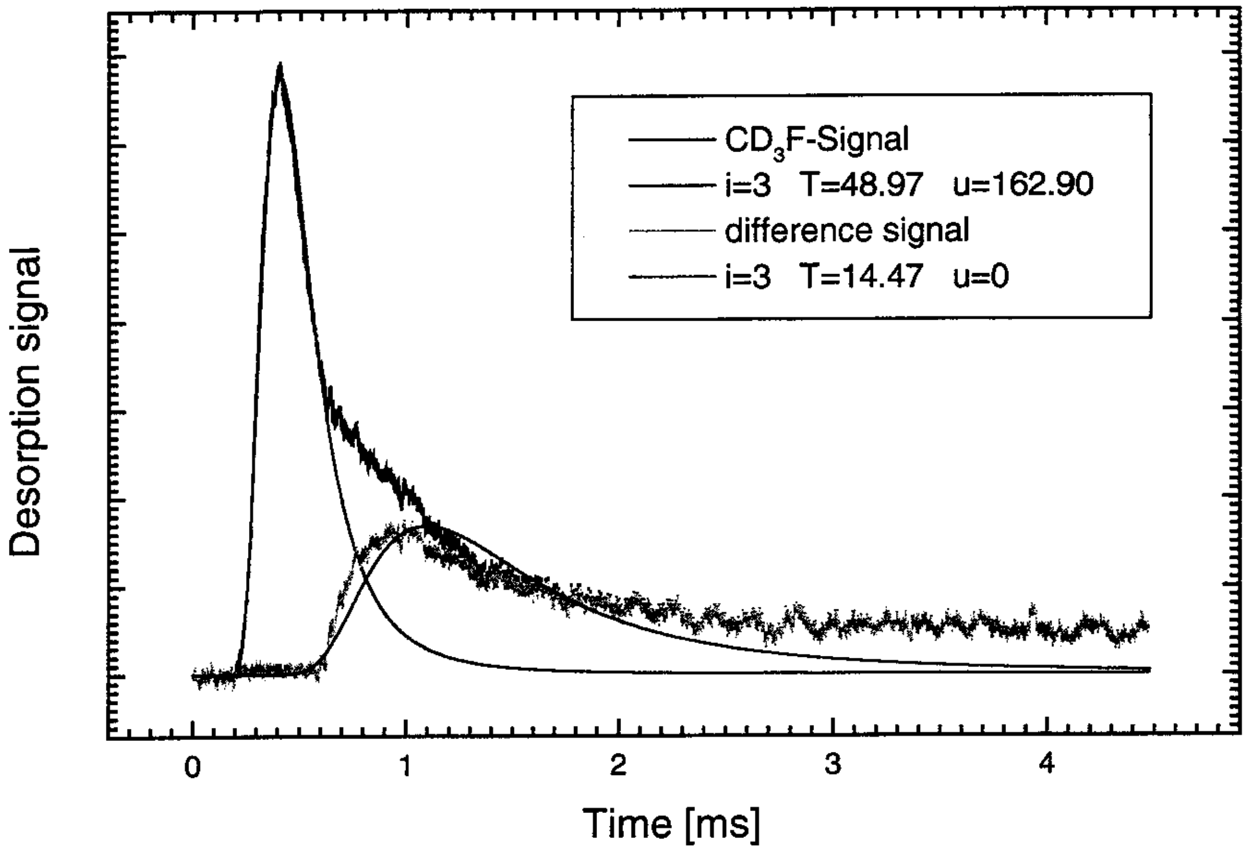
$$f(t) \propto \frac{d^i}{\left(t - t_{drift}\right)^{i+1}} \cdot e^{\frac{-m \cdot \left(\frac{d}{(t-t_{drift})} - u\right)^2}{2kT}} dt$$

d	distance sample-ionizer	t_{drift}	flight time ionizer - SEV
i=2	Maxwell-Boltzmann distribution	u	stream velocity
i=3	flux density distribution		



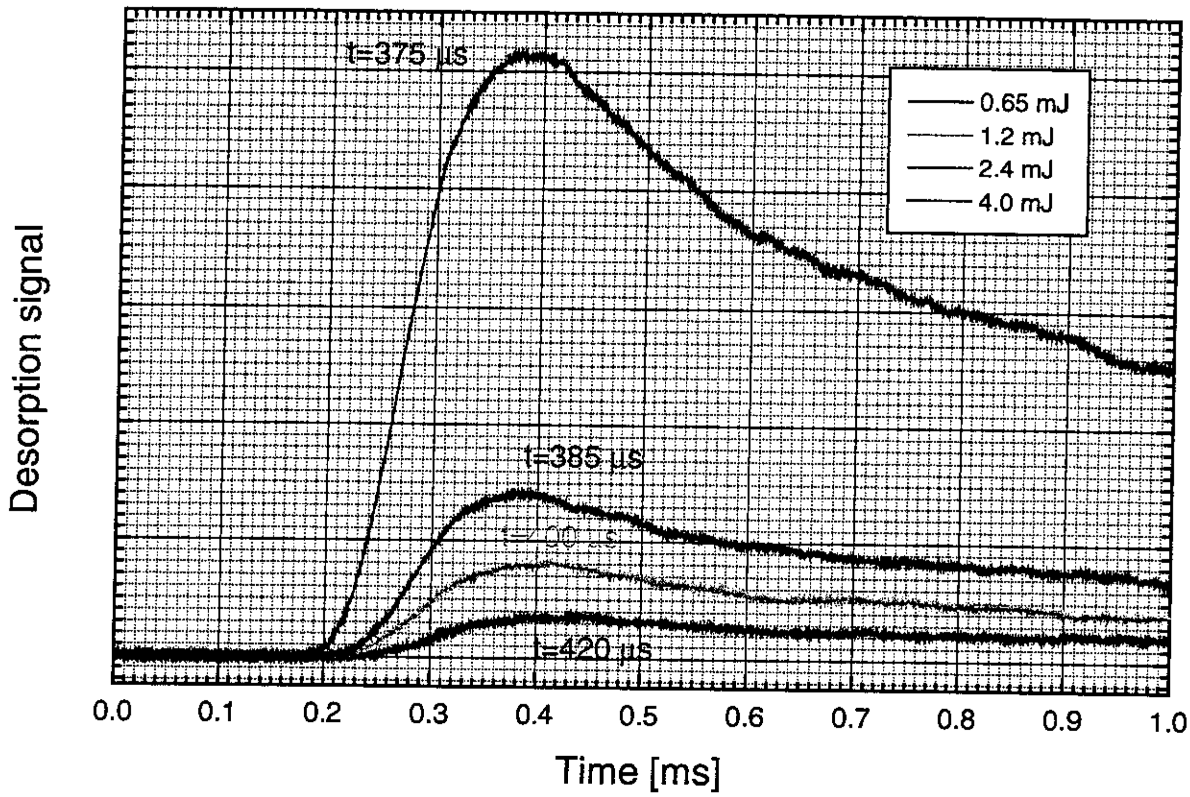
- reasonable fit to the experimental TOF spectra in the first part of the distribution
- better agreement for flux density distribution
- better agreement with overlapping stream velocity

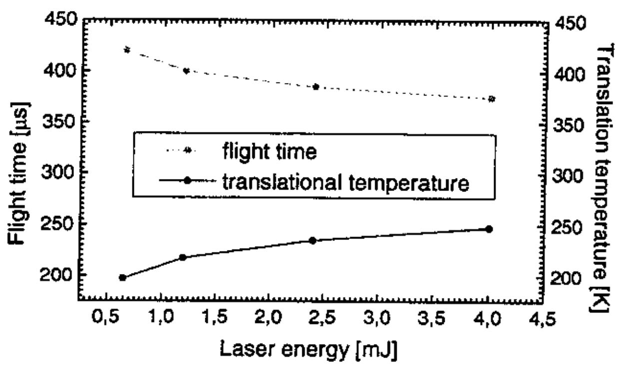
Determination of translational temperature

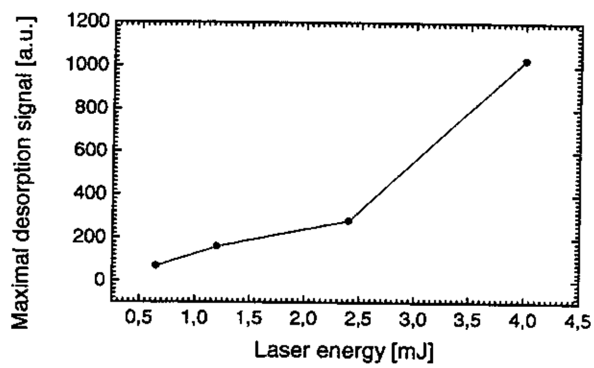


- bimodal velocity distribution ?
- two desorption channels ?

Dependence of the flight time on the laser energy







- flight time in the TOF spectra depends weakly on the applied laser fluence
- indication for a resonant heating process ?

Desorption mechanism:
Dependence of the desorption yield Y on the laser fluence F

Desorption via a direct process

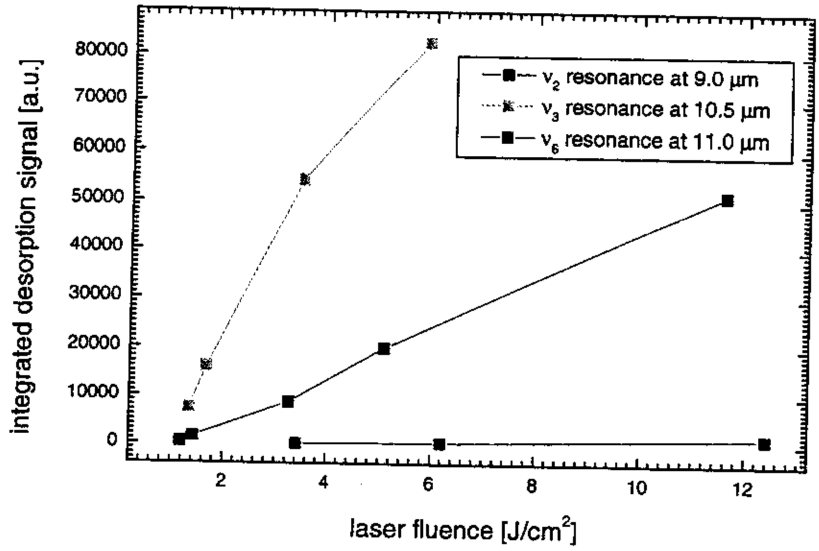
$$Y \propto F^n$$
$$\ln Y = n \cdot \ln F + \text{const.}$$

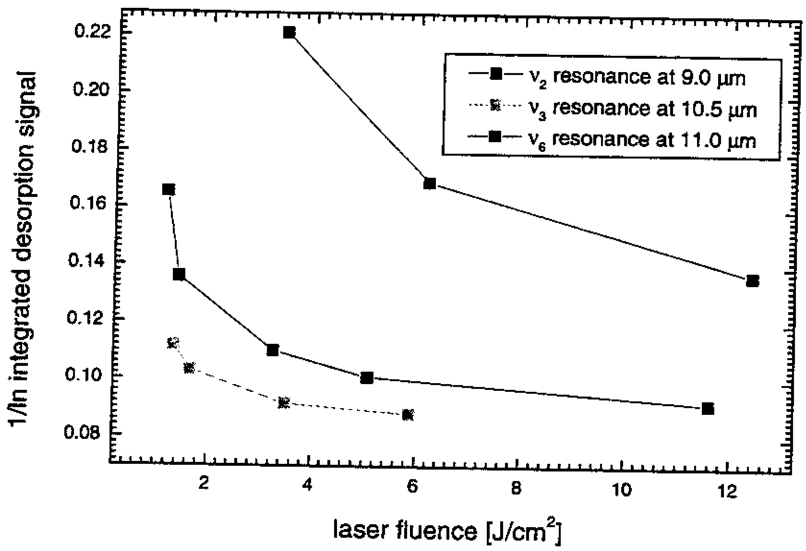
Desorption via resonant heating

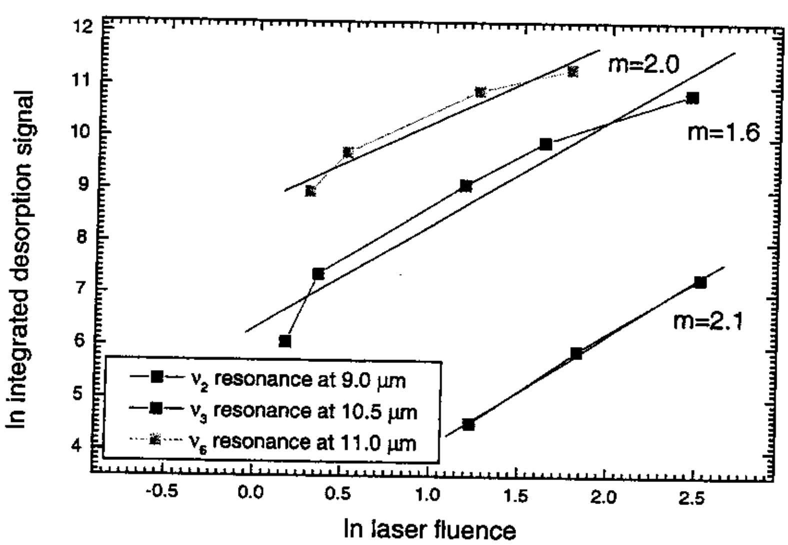
$$Y = k' \cdot e^{-E_{des}/k \cdot T}$$
$$k' \propto \nu_{des} \cdot \theta$$
$$T = T_0 + \Delta T$$
$$\Delta T = c \cdot F$$
$$Y = k' \cdot e^{-E_{des}/k \cdot (T_0 + c \cdot F)}$$
$$\frac{1}{\ln Y - \ln k'} = -\frac{k}{E_{des}} \cdot T_0 - \frac{k \cdot c}{E_{des}} \cdot F$$

$$\frac{1}{\ln Y - \ln k'} = a + b \cdot F$$

Desorption signal as a function of the laser fluence: Thermal versus direct desorption mechanism

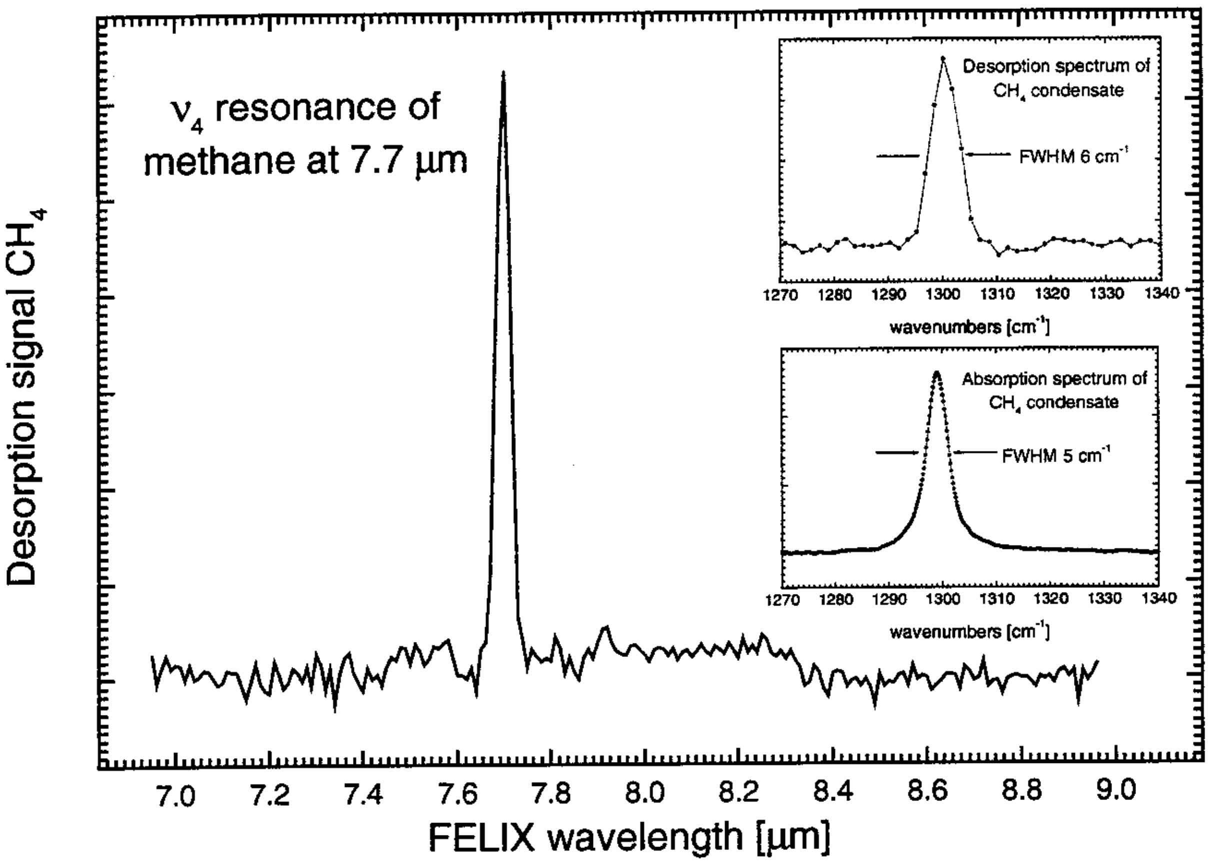


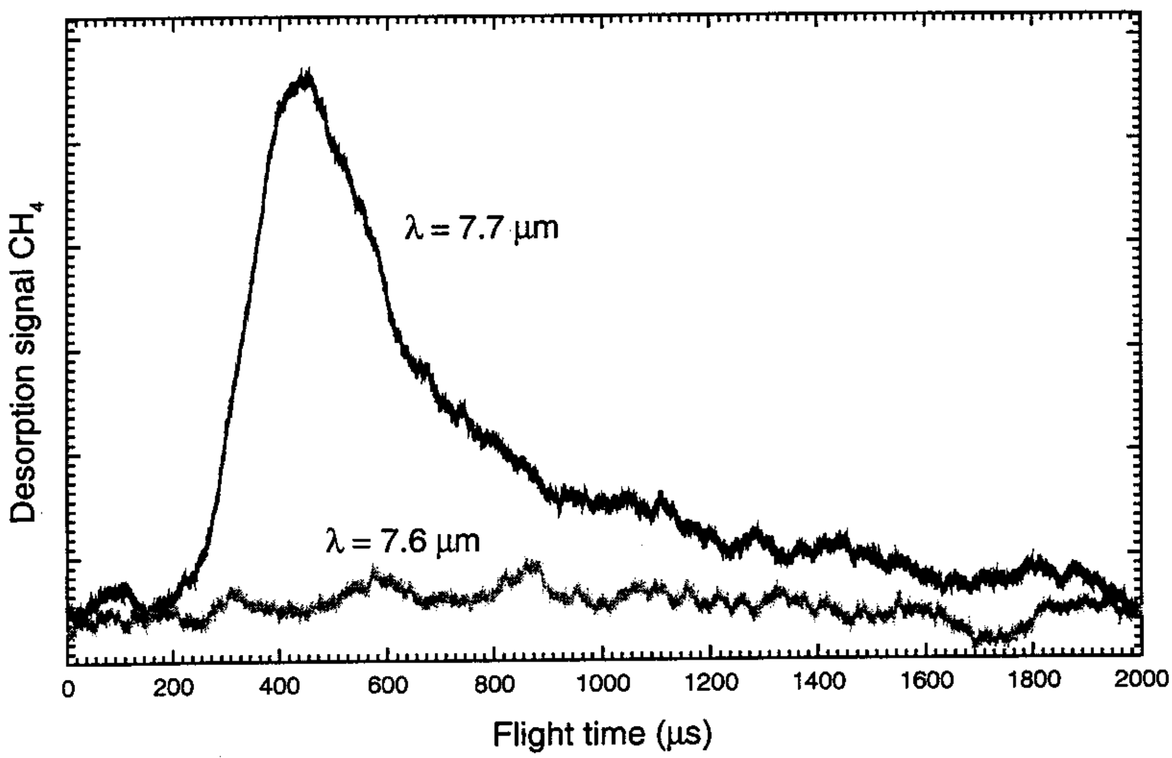




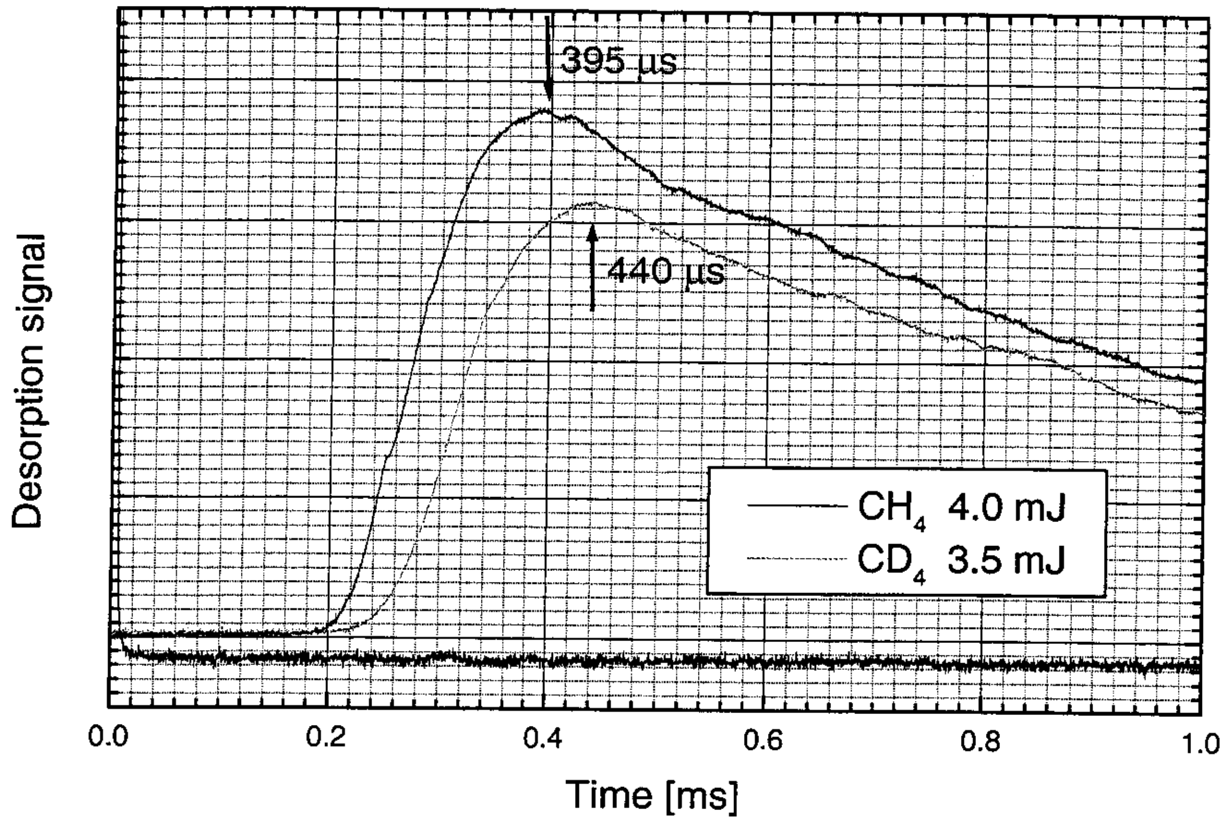
- Indication for a direct desorption mechanism ?

Laser-induced desorption of CH_4 condensed on NaCl(100)





TOF spectra for multilayers CH_4/NaCl(100)



- flight times of CH_4 and CD_4 scale by the squareroot of the mass ⇒ comparable kinetic energy and desorption mechanism?

- estimation of the translational temperature of the desorbing molecules via a Maxwell-Boltzmann distribution

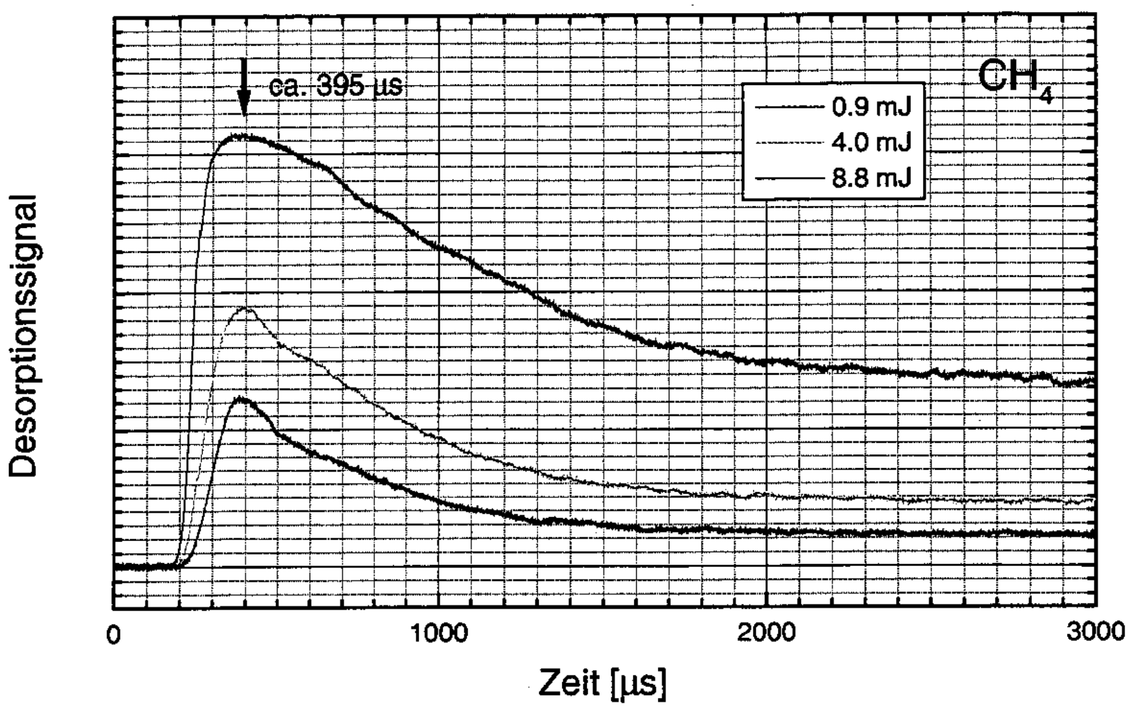
most probable velocity:* $v = \sqrt{\frac{2kT}{m}}$

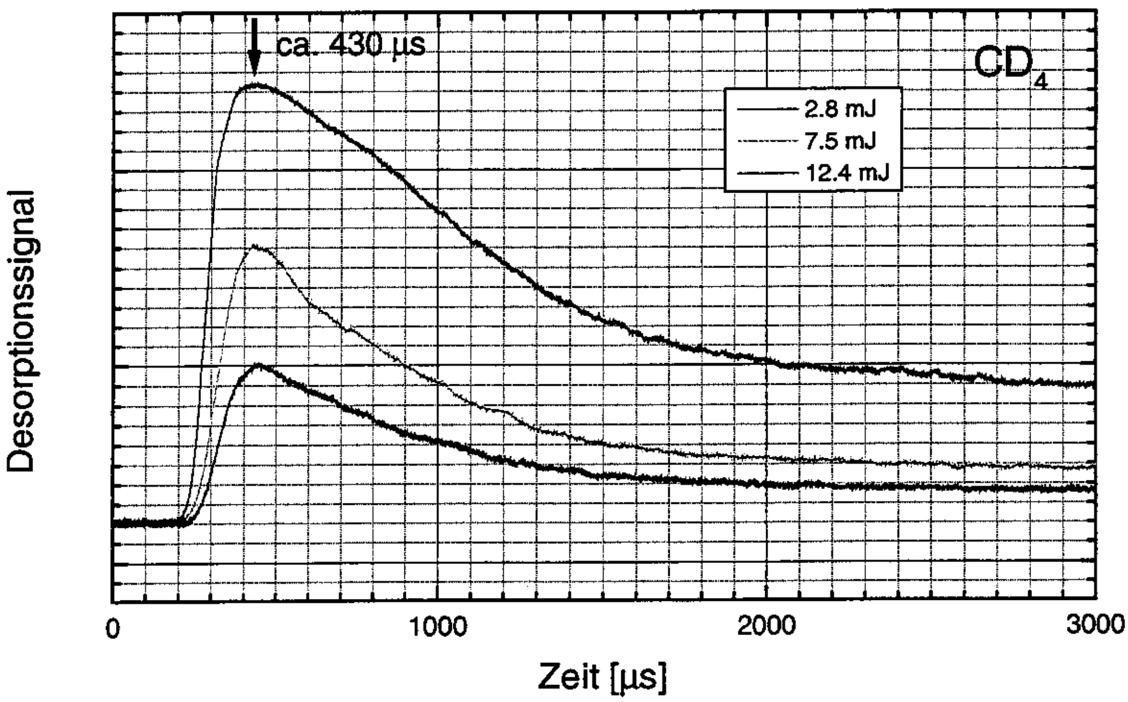
Translational temperature:	CH_4	96.5 K	99.0 K*
	CD_4	97.1 K	99.3 K*

(* after correction for the drift time of 5 µs)

- calculated desorption temperatures well above the measured sample temperature of ~30 K

Dependence of the flight time on the laser energy





- flight time in the desorption spectra of CH_4 and CD_4 is independent on the applied laser energy
- indication for a direct mechanism ?

Determination of translational temperature

$$f(t) \propto \frac{d^i}{\left(t - t_{drift}\right)^{i+1}} \cdot e^{\frac{-m \cdot \left(\frac{d}{\left(t - t_{drift}\right)} - u\right)^2}{2kT}} dt$$

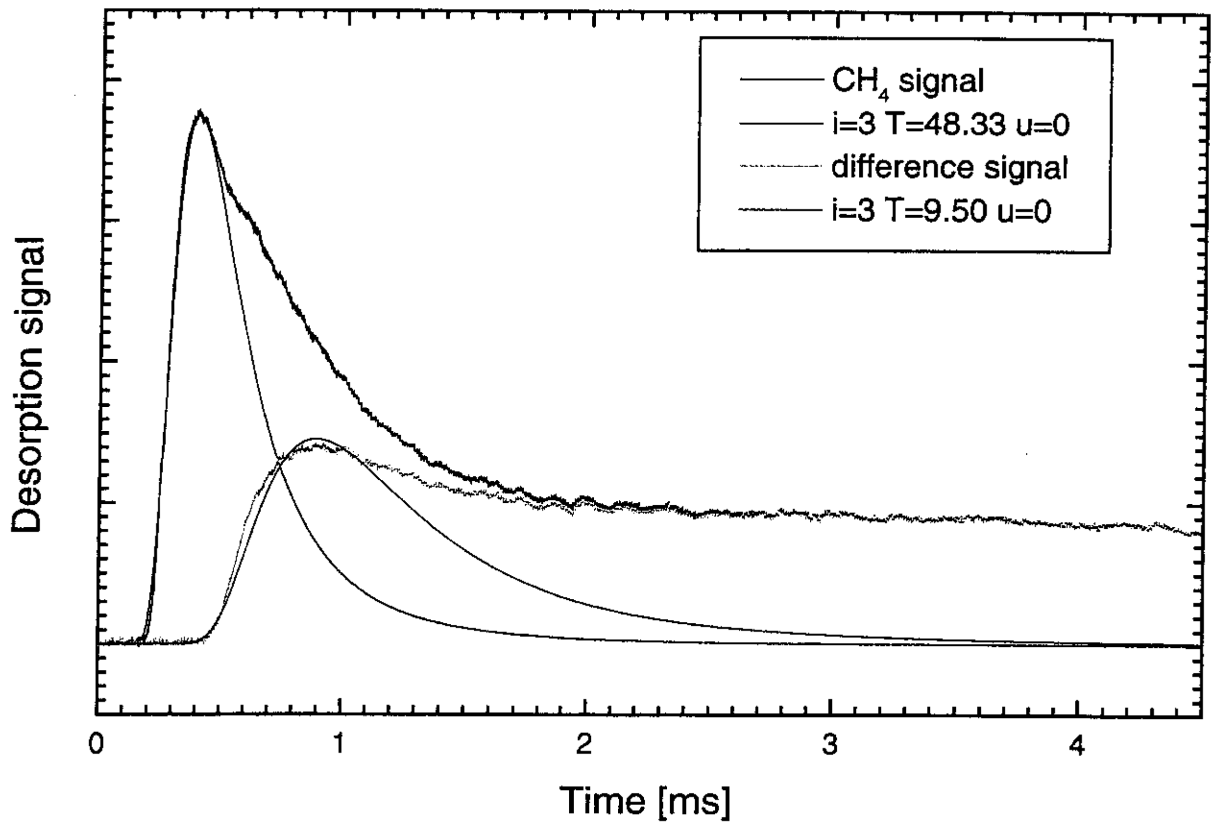
d distance sample-ionizer

i=2 Maxwell-Boltzmann distribution

i=3 flux density distribution

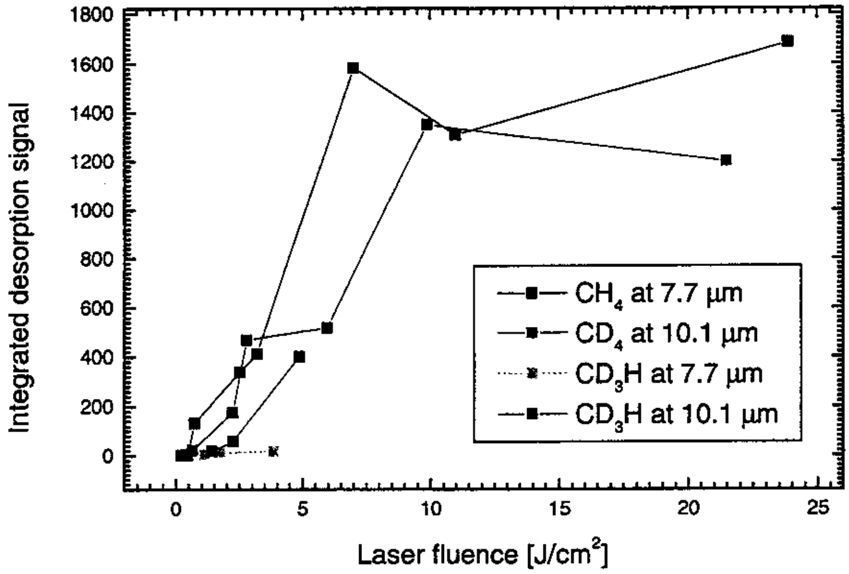
t_{drift} flight time ionizer - SEV

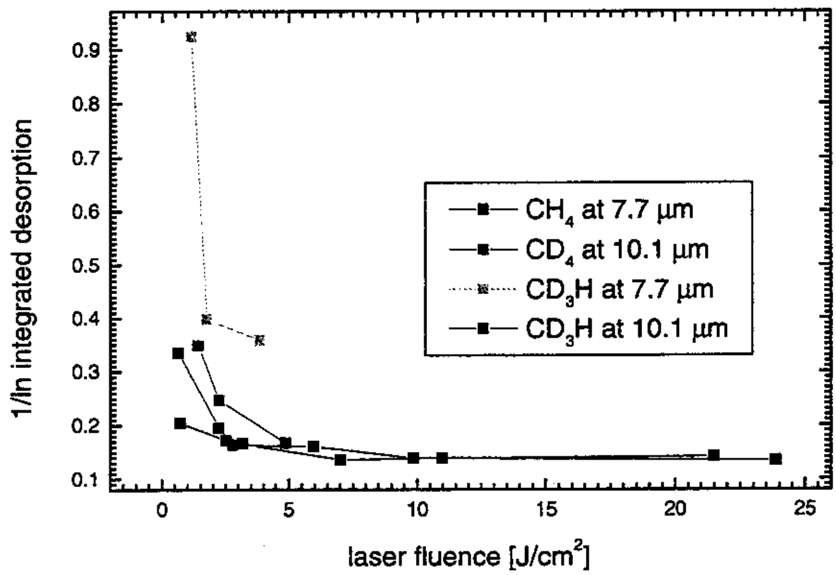
u stream velocity

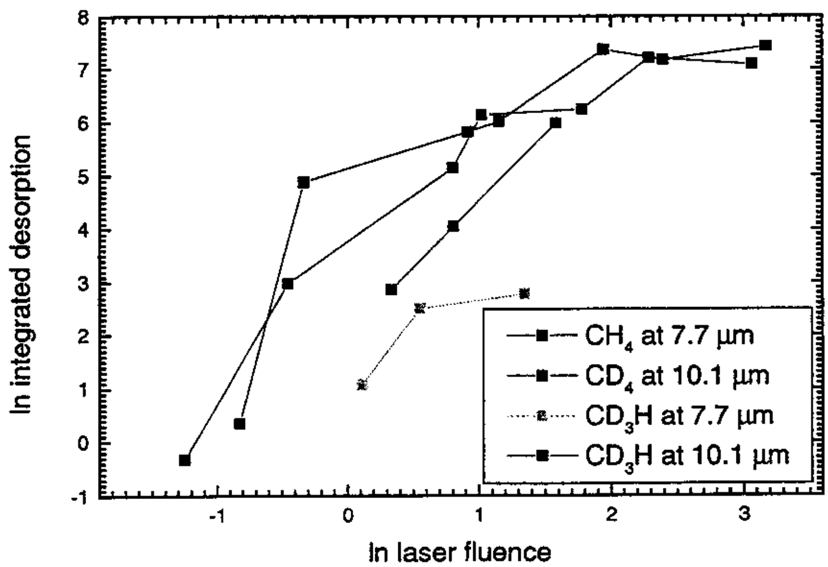


- reasonable fit to the experimental TOF spectra using two functions
- two desorption channels open ?

Desorption signal as a function of the laser fluence

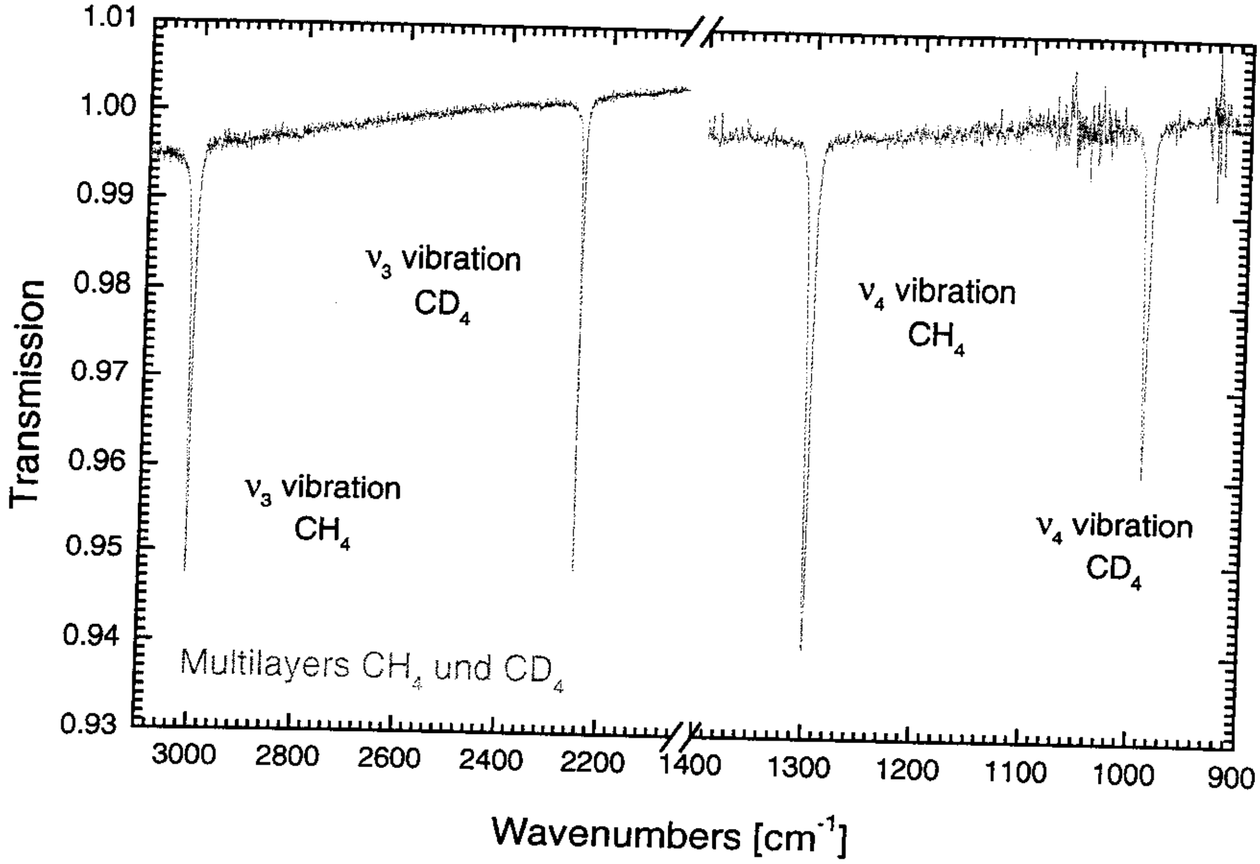


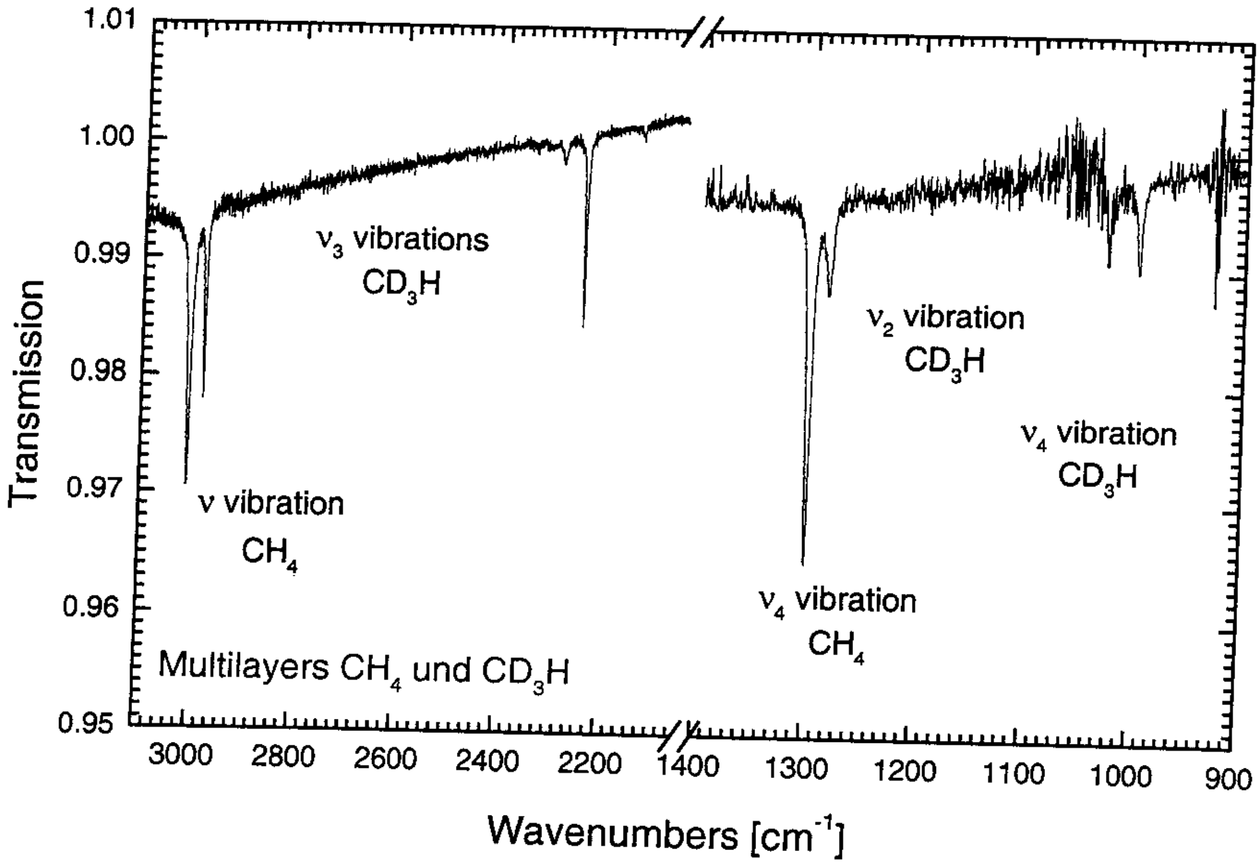




- Indication for a direct desorption mechanism ?

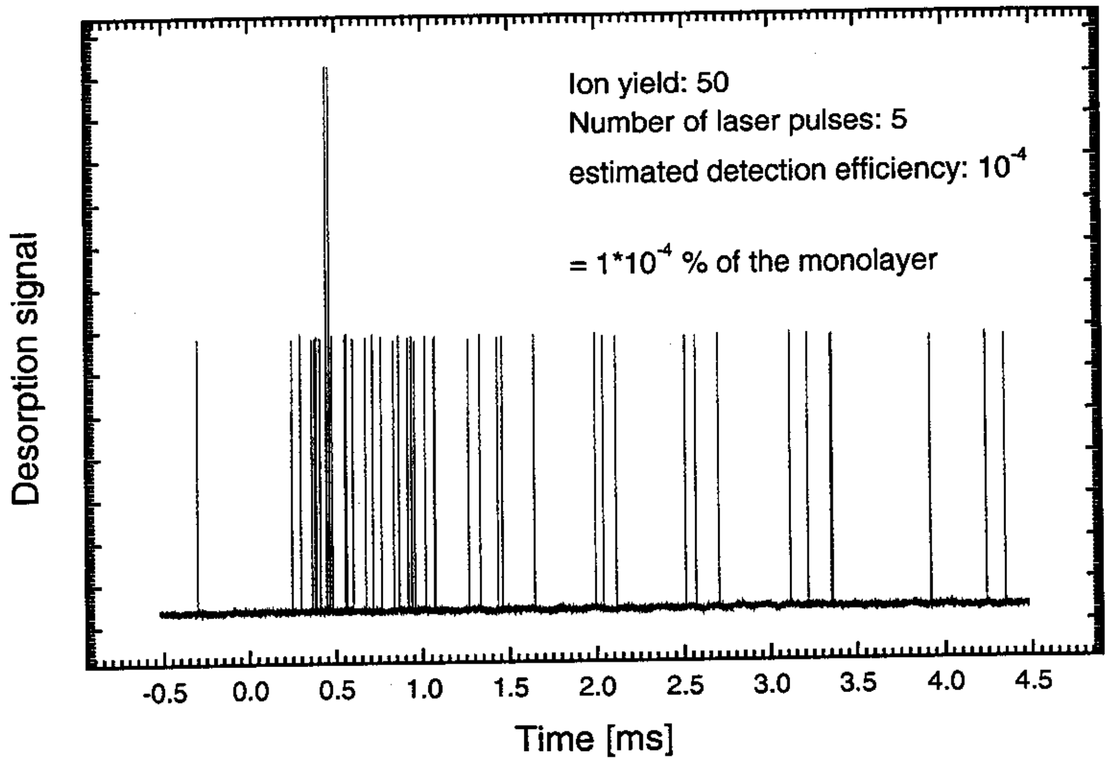
FTIR spectra of the isotope mixtures of methane





Outlook

- resonant monolayer desorption for CD_3F/NaCl(100) detected with single ion detection



- continuation of the studies on multilayer systems
- experiments on monolayers, isotopic mixtures and coadsorbates
- desorption after resonant excitation of external modes of the molecule to the surface
- two color experiments with ultrashort IR laser pulses

Acknowledgements:
B. Redlich thanks the Deutschen Forschungsgemeinschaft for a research fellowship in the "Emmy-Noether-Programm".