INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
34100 TRIESTE (ITALY) - P.O.B. 586 - MIRAMARE - STRADA COSTIERA 11 - TELEPHONES: 224281/2/3/4/5 6
CABLE: CENTRATOM - TELEX 460392-1

SMR/100 - 65

WINTER COLLEGE ON LASERS, ATOMIC AND MOLECULAR PHYSICS

(24 January - 25 March 1983)

Lasers in Chemistry

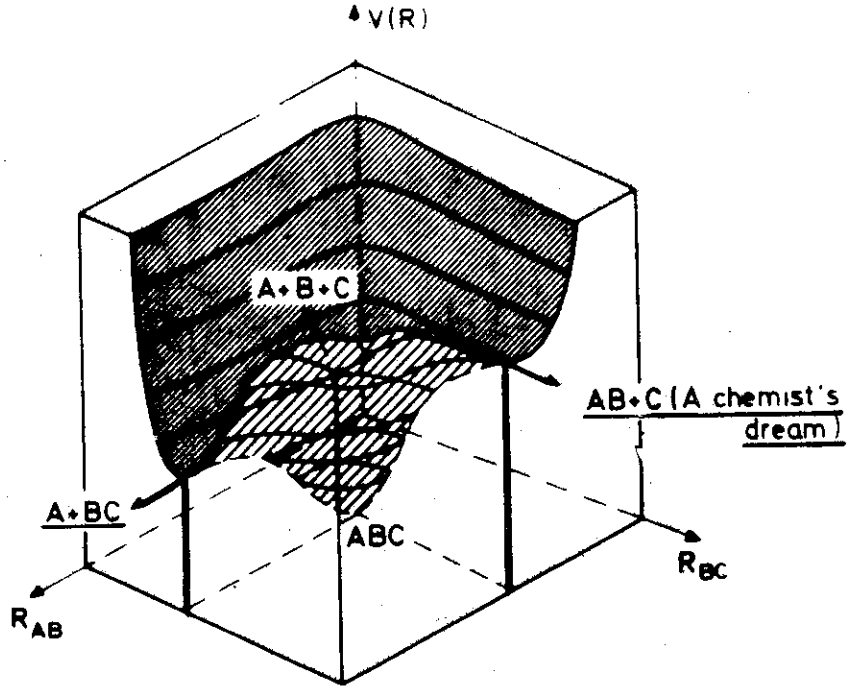
H. SCHRÖDER

Max-Planck-Institut für Quantenoptik
8046 Garching bei München
Fed. Rep. Germany

Outline

1) Laser chemistry - philosophical
2) fixed frequency UV & IR Laser sources
3) tunable "
4) vitamin-D synthesis
   chemical activation with I_2^*
5) mechanisms of IR-multiphoton excitation
6) scaling of Laser-isotope separation
7) Kinetic spectroscopy of
   multiphoton excitation in benzene
8) multiphoton dissociation of OsO_4
   - visualized
9) gain measurements in electronical
   chemi-luminescence

Routes of dissociation of a triatomic molecule ABC



techniques to activate molecules

(1) photons

(2) electrons (plasmachemistry
electro-chemistry)

(3) heat bath

(4) collisional activation
with certain groups

⋮

(i) catalysers (... hot surfaces ...
... Me-organics ...
... biological ...) .

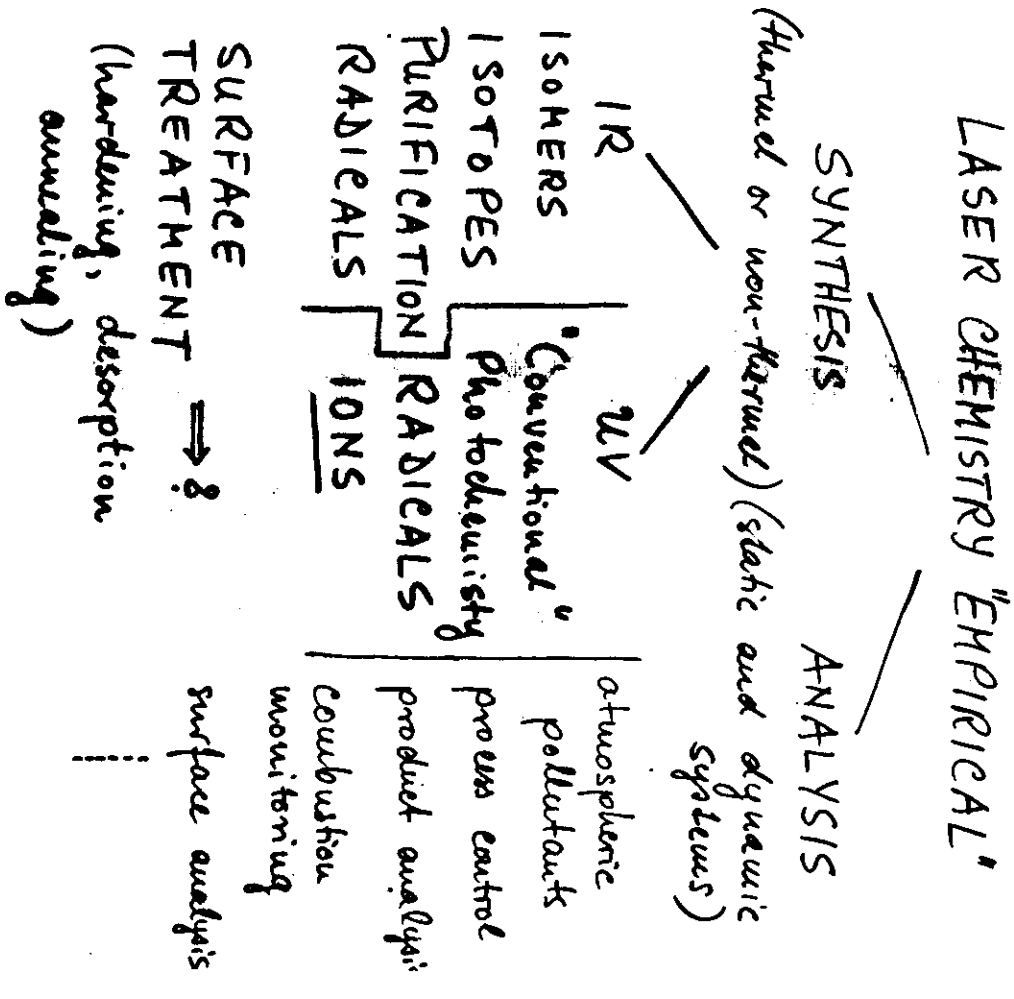
3 topics in Laser-chemistry

(1) selective activation of molecules

(2) new chemical processes

(3) diagnostic with lasers

LASER SOURCE PROPERTY	TYPES OF APPLICATIONS	TYPICAL EXAMPLES
MONOCHROMATICITY/ TUNABILITY	STATE SELECTIVE EXCITATION/PROBING	BASIC CHEMICAL DYNAMICS (SMALL MOLECULES; BEAMS/JETS) LASER ASSISTED COLLISIONAL INTERACTION
HIGH POWER/ENERGY	MULTIPHOTON EXCITATION; HIGH EXCITATION RATES	SEPARATION/PURIFICATION (ISOTOPES); CONTROLLED RADICAL FORMATION; PHOTOIONIZATION;
SHORT PULSES	HIGH TEMPORAL RESOLUTION	psec PHENOMENA (CONDENSED PHASES; BIOPHYSICS)
DIRECTIONALITY/ FOCUSABILITY	HIGH SPATIAL RESOLUTION; REMOTE HEAT TRANSFER	HIGH TEMPERATURE CHEMISTRY and THERMAL PROCESS CONTROL; MICROCHEMISTRY



LASER CHEMISTRY "SYSTEMATIC"

Laser Synthesis
(= Preparation of Reagents)

Vib-Rotational State Selection
Small molecules, beams
no preparative scale

Electronic State Selection
Gases and condensed phases, Ionization

Vibrational Mode (Group) Selection
In Gases (?) and on surfaces (?)

Species (Compound) Selective Excitation in Mixture
Isotope Separation, Isomers, Purification

Laser thermal chemistry
Special Gradients in Temp., Space, Time

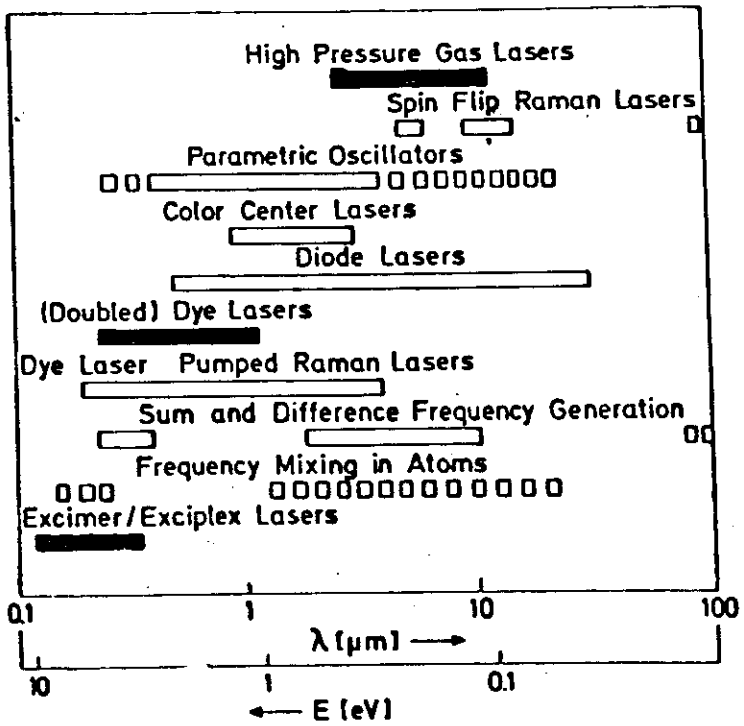
Laser Analysis
(= Probing of Molecules)

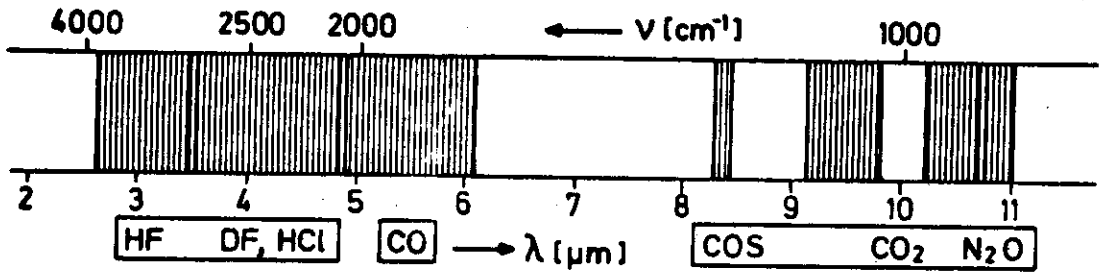
Light scattering
Mie, Rayleigh, Raman, Identity and Concentration

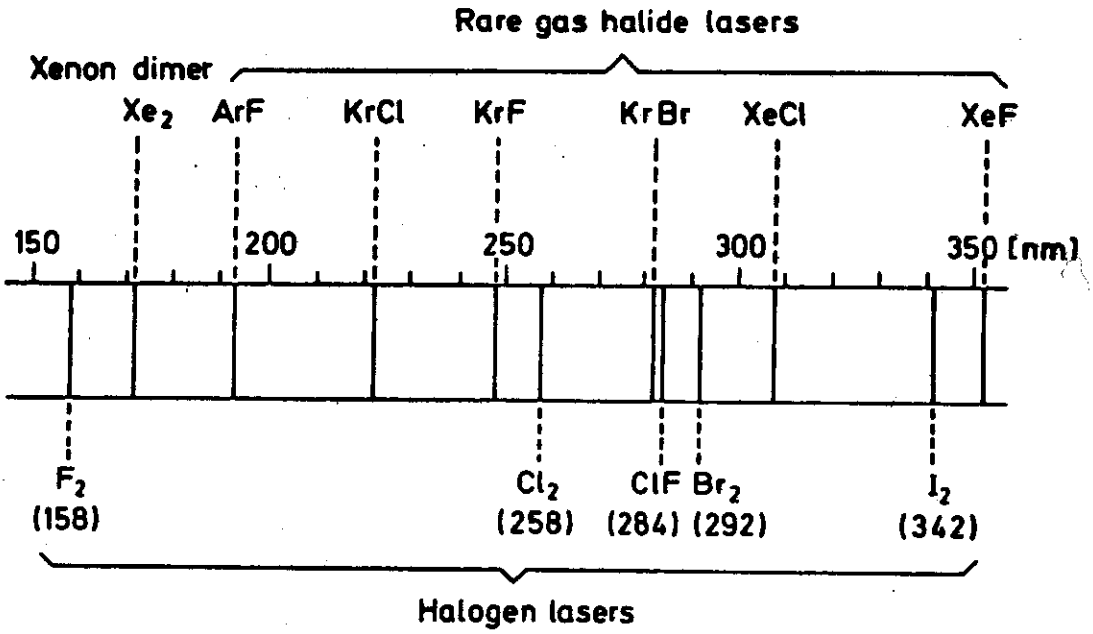
Absorption / Fluorescence
Differential Abs.
LIF, Identity, Conc.,
Temperature

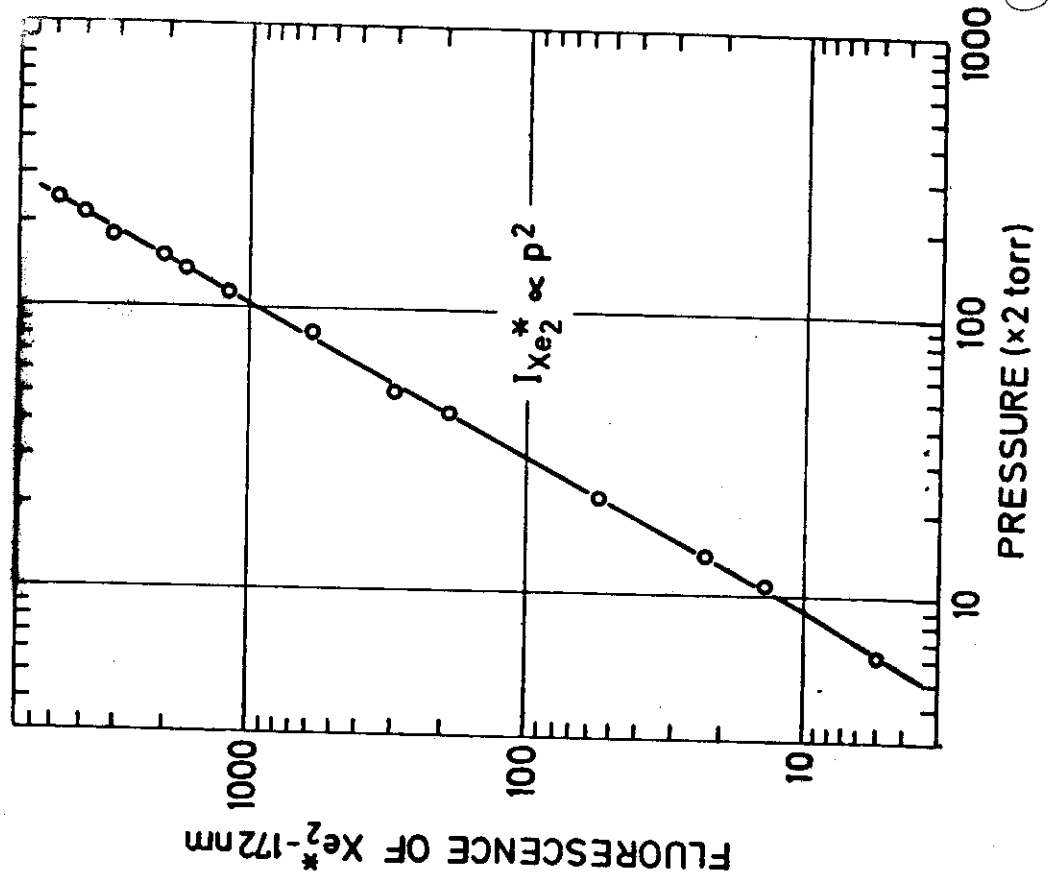
Velocimetry
Transport and Motion, Temperature

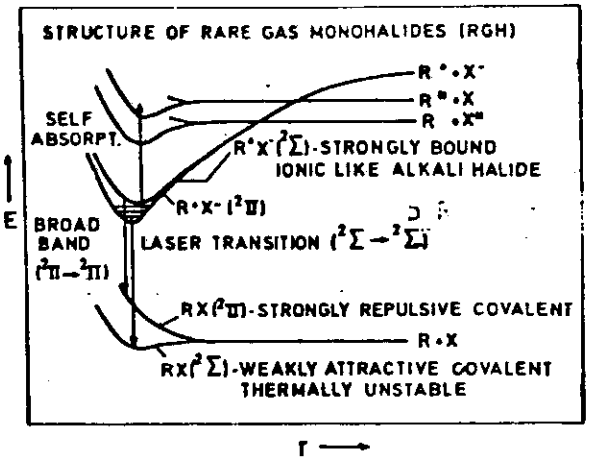
Ionization
Mass Spectrometry
Identification

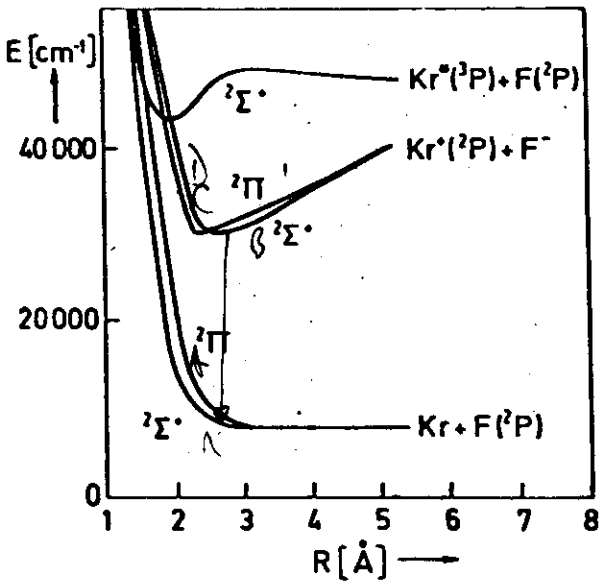


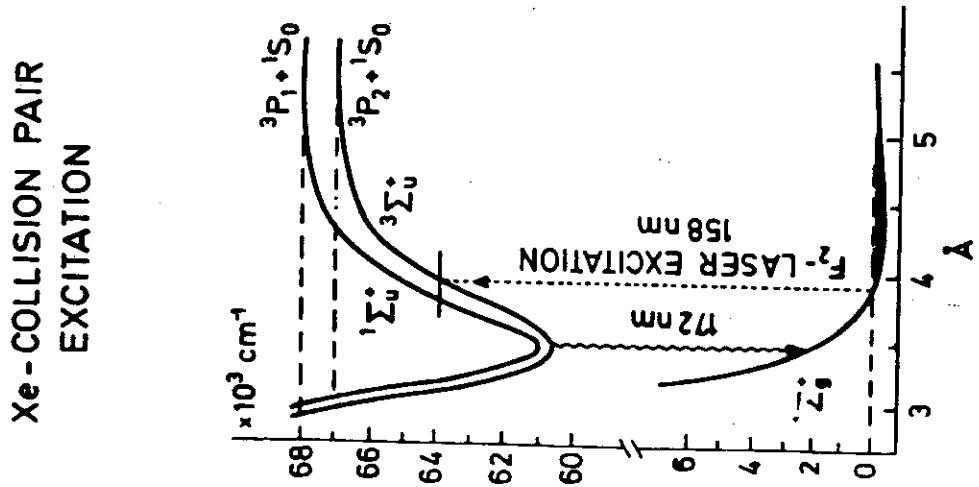

4000
2500
2000
ν [cm⁻¹]
1000
2
3
4
5
6
7
8
9
10
11
HF
DF, HCl
CO
λ [μm]
COS
CO2
N2O

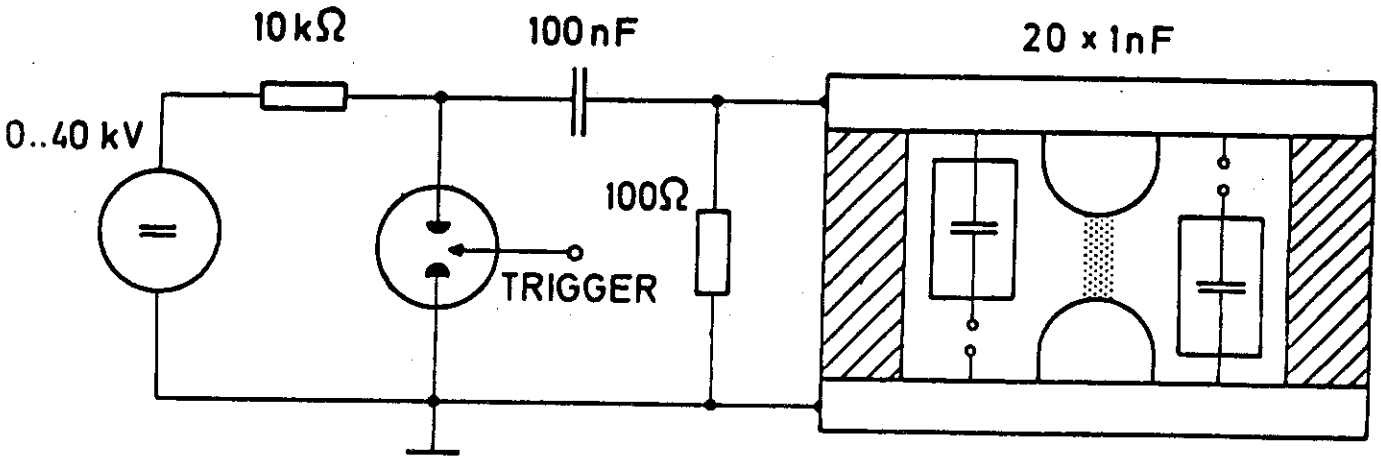

Rare gas halide lasers
Xenon dimer
Xe2
ArF
KrCl
KrF
KrBr
XeCl
XeF
150
200
250
300
350 [nm]
F2
(158)
Cl2
(258)
ClF
(284)
Br2
(292)
I2
(342)
Halogen lasers


FLUORESCENCE OF Xe_2^*-172 nm
$I_{Xe_2^*} \propto p^2$
PRESSURE (x2 torr)
1000
100
10


STRUCTURE OF RARE GAS MONOHALIDES (RGH)
SELF ABSORPT.
BROAD BAND
LASER TRANSITION
IONIC LIKE ALKALI HALIDE
E
r


E [cm⁻¹]
40000
20000
0
R [Å]
1 2 3 4 5 6 7 8

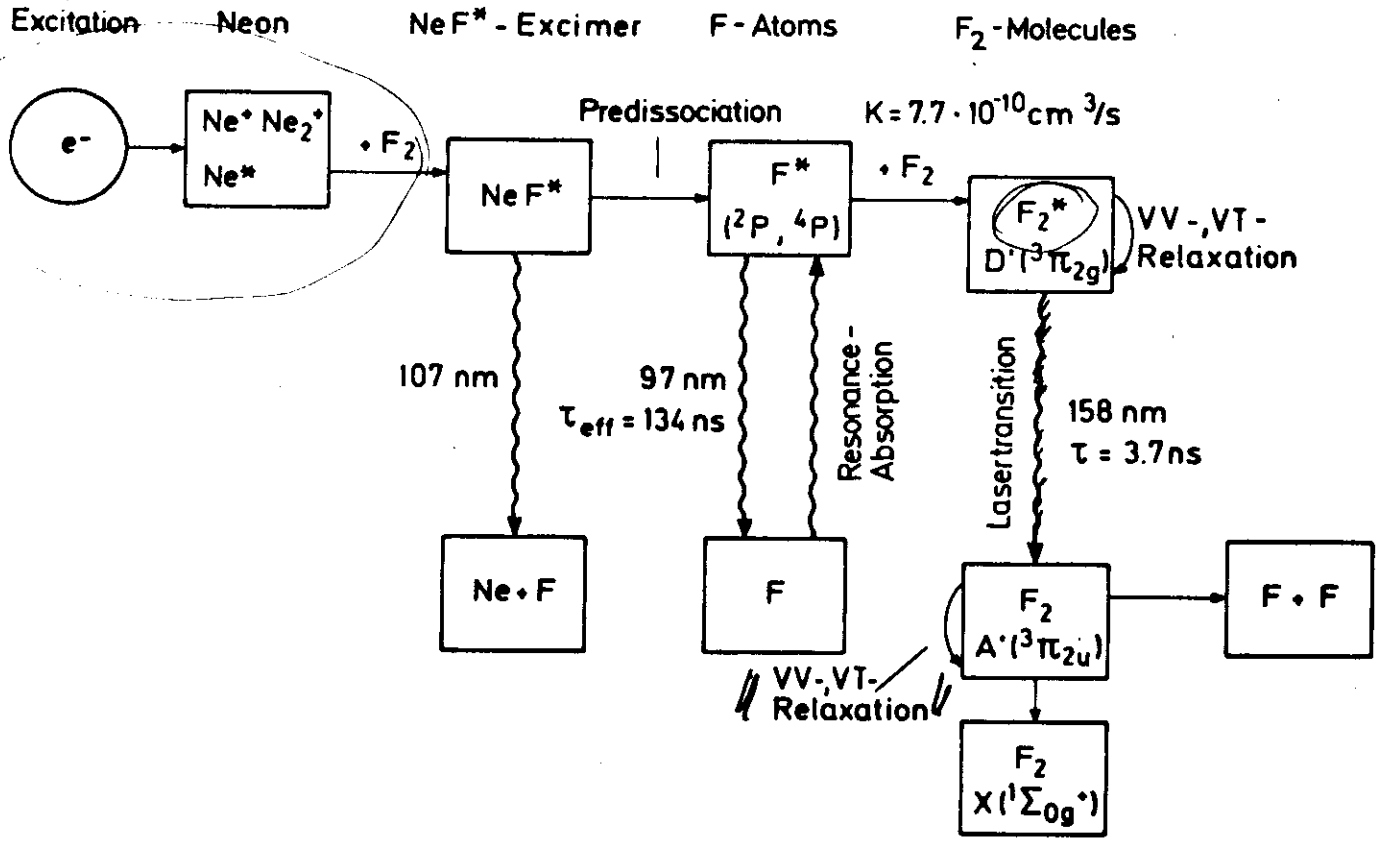

Xe - COLLISION PAIR EXCITATION
F_2- LASER EXCITATION
158 nm
172 nm
Å
$\times 10^3$ cm^{-1}



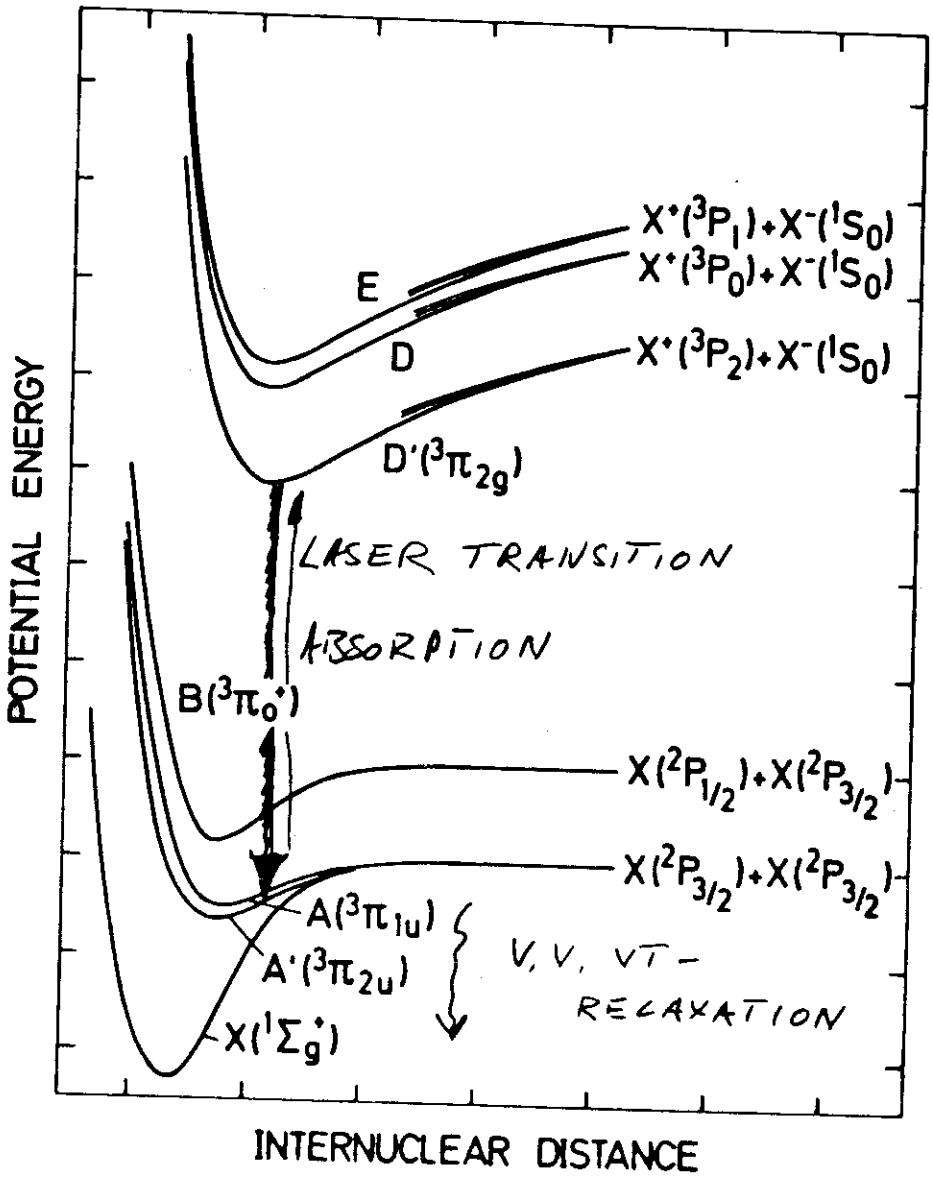
PULSE CHARGING CIRCUIT

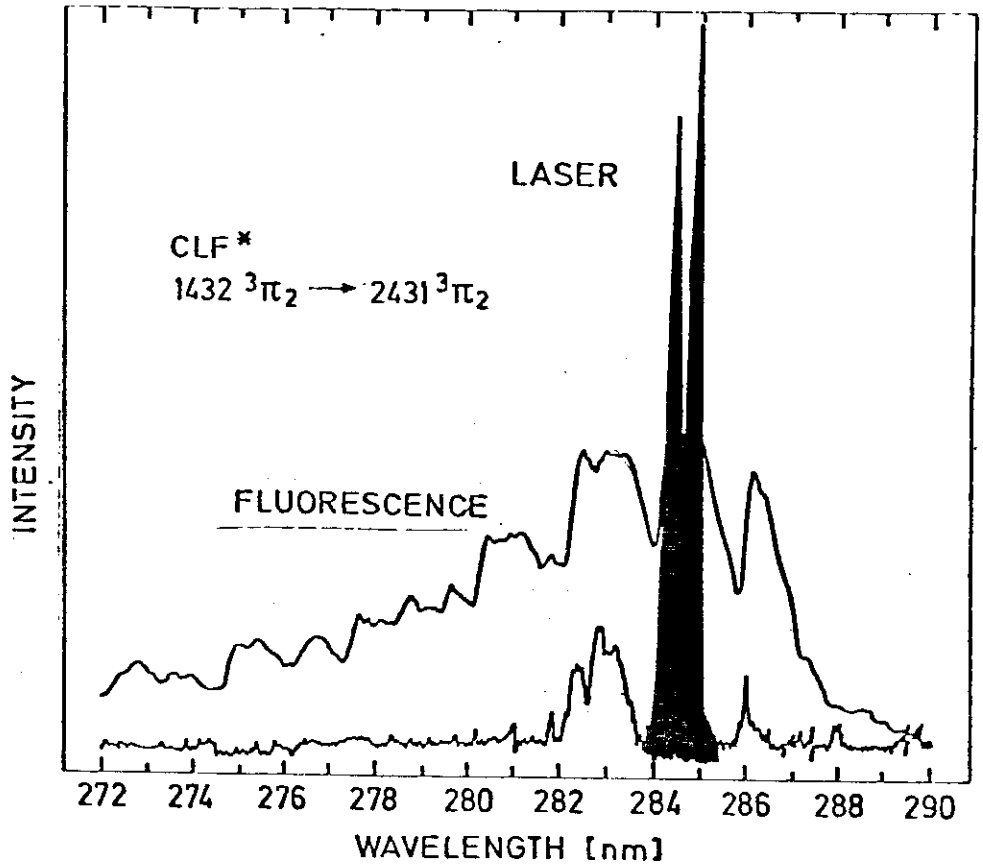
TEA-LASER-CHAMBER

TRANSIENTS



F_2 potential surface





	F	Cl	Br	I
I	~~490.8 nm~~ F*, ~~L*~~	431.3 nm F	385.7 nm F*	~~342.4 nm~~ F, ~~K~~, L
Br	~~351.5 nm~~ F*, ~~L*~~	314.2 nm F*	~~292.0 nm~~ F, ~~L~~	← 292 nm
Cl	~~284.4 nm~~ F*, ~~L*~~	~~257.7 nm~~ (F), K, L		
F	~~157.6 nm~~ (F), K, L			

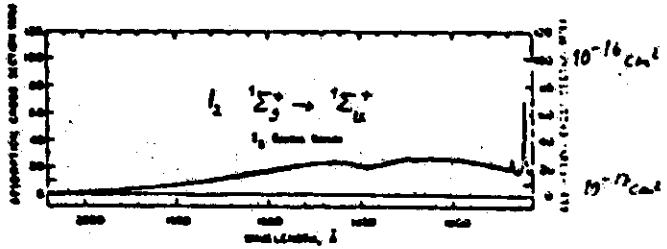
F = Fluoreszenzspektrum bekannt

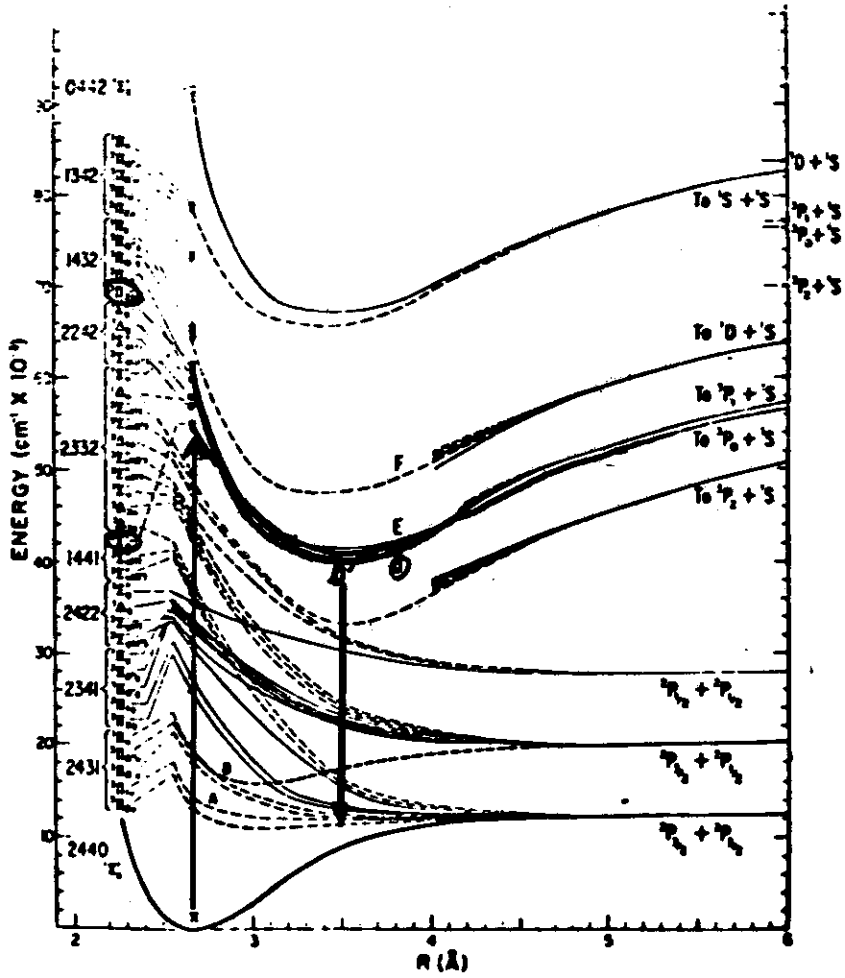
F* = Fluoreszenzspektrum in dieser Arbeit erstmalig aufgenommen

K = Kinetik in dieser Arbeit untersucht

L = Laser bekannt

L* = Laser in dieser Arbeit erstmalig demonstriert





$$CH_4 + I_2^* \longrightarrow [\, CH_3 + HI + I \xrightarrow{I_2} \,] \quad CH_3I + HI$$

$$CF_3H + I_2^* \longrightarrow \cdots\cdots \longrightarrow \begin{matrix} CF_3I\,, \\ CF_2HI\,, \\ (C_2F_5I\,,\ CF_4) \end{matrix}$$

clean reaction

$$CF_3H + I_2^*\ (620\ kJ/mol) \longrightarrow CF_3H\ (vib)$$

Pyralysis

$$CF_3H \longrightarrow CF_2 + HF - 235\ kJ/mol$$

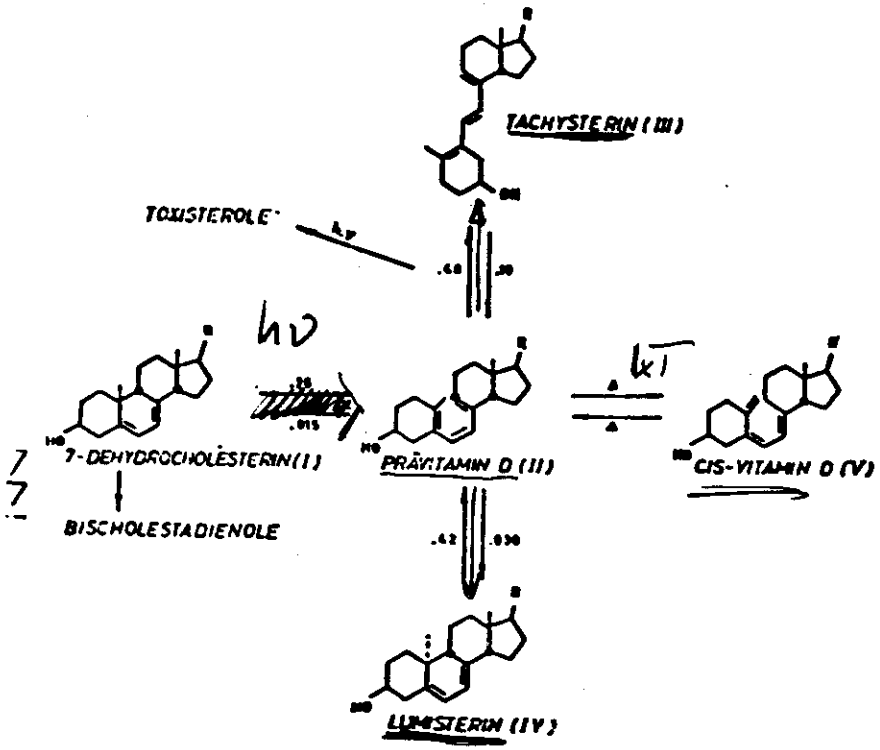
$$\longrightarrow CF_3 + H - 445\ kJ/mol$$

$$\longrightarrow CF_2H + F - 520\ kJ/mol$$

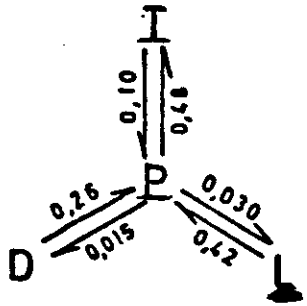
Problem in technical vitamin D synthesis:

The ideal frequency !

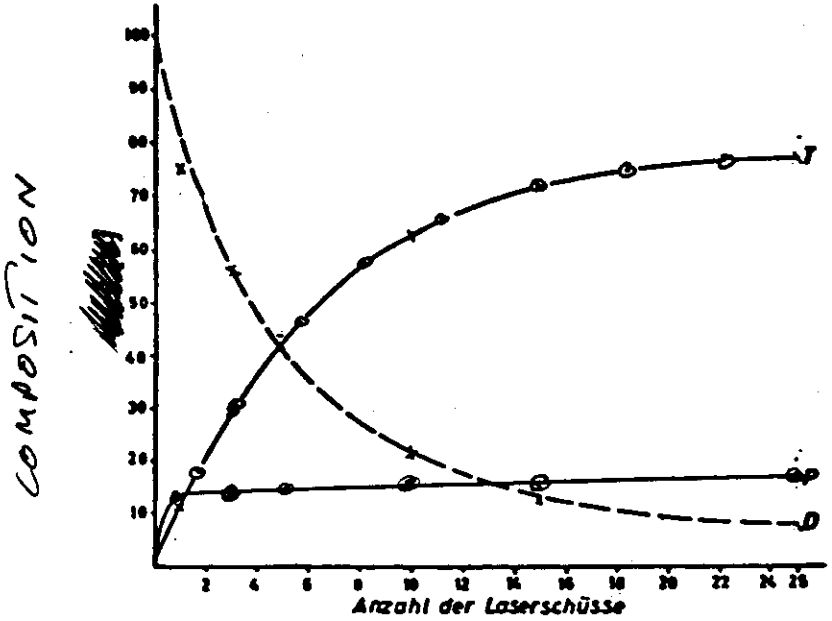
M. BRAUN et al.



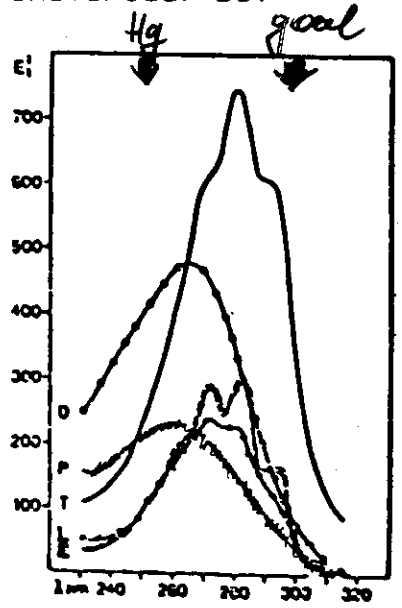
Photochemische Isomerisierungen von 7-DHC



Vereinfachtes Reaktionsscheme

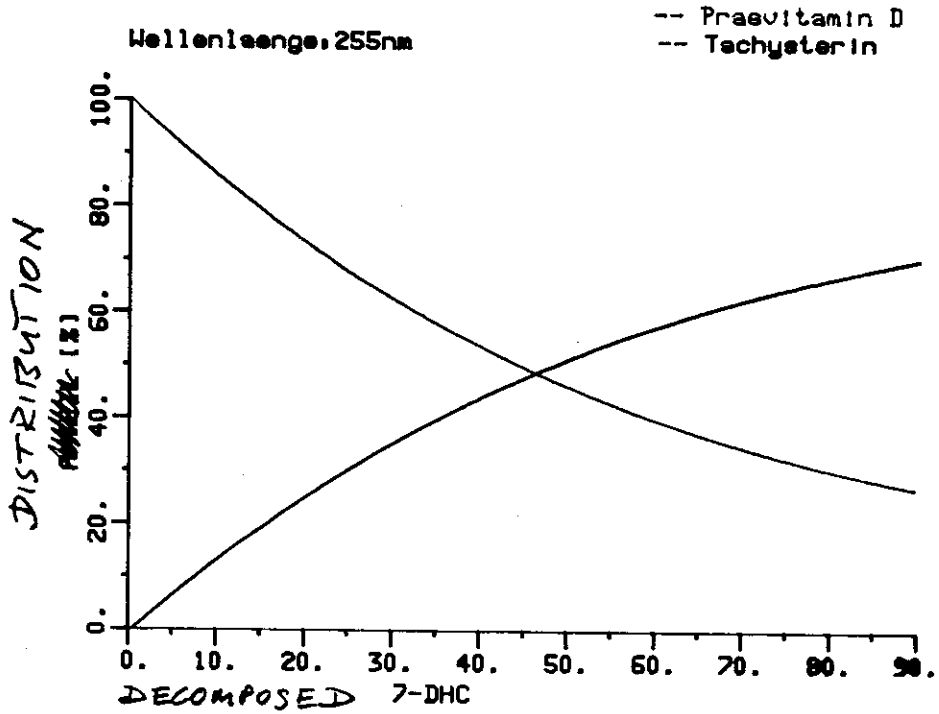


Reaktionsverlauf bei = 248 nm (kr, F-Cases)



Spektren in Ethanol von
E = Ergosterol bzw. 7-DHC
P = Prävitamin D
T = Tachysterol
L = Lumisterol
(nach K. Proertner, und J.P. Weber, Helv.Chim.Acta 55, 921 (1972

bad run



good run with a Laser

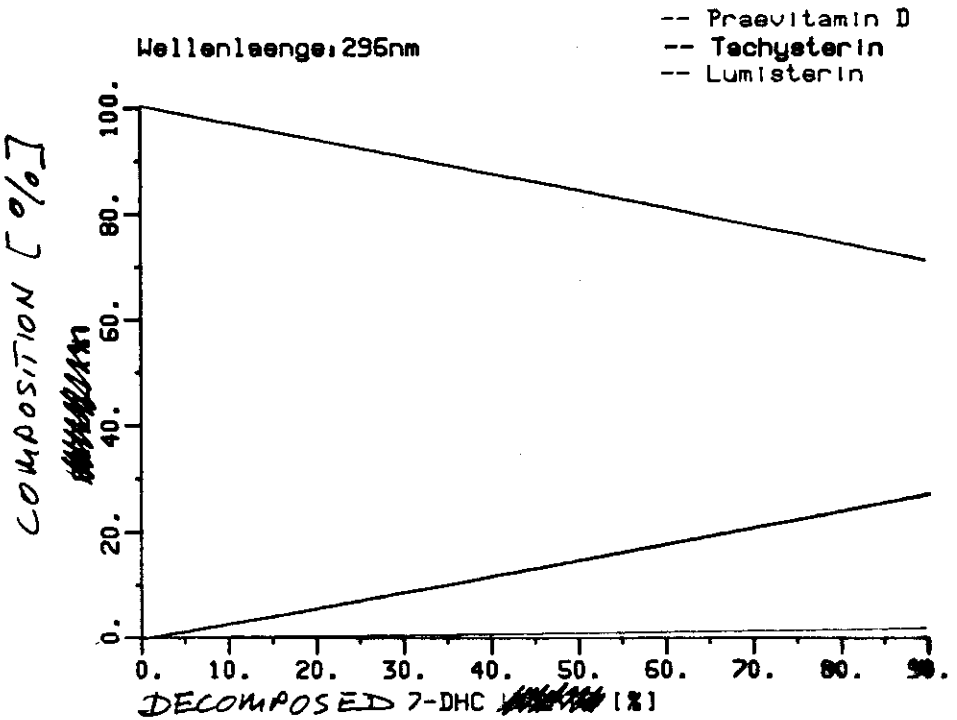


TABLE I; (Ref. 7)

Compound	Plant Capacity 10^6 kg/yr	% of Total Manufacturing Cost: Raw Materials	Operation	Costs Fixed	Energy*
Aniline	3.3	84.9	9.8	2.7	2.6
p-Phenylene-diamine	0.1	84.5	5.9	4.4	5.2
DDT	4.5	59.2	13.6	20.4	6.8
Sulfonated Dodecylbenzene	2.0	87.6	7.6	2.9	1.9
Phenol	22.7	85.6	7.6	4.2	2.6
Urea	40.8	70.0	11.1	13.4	5.5
HCN	10.4	71.3	8.7	14.1	5.9

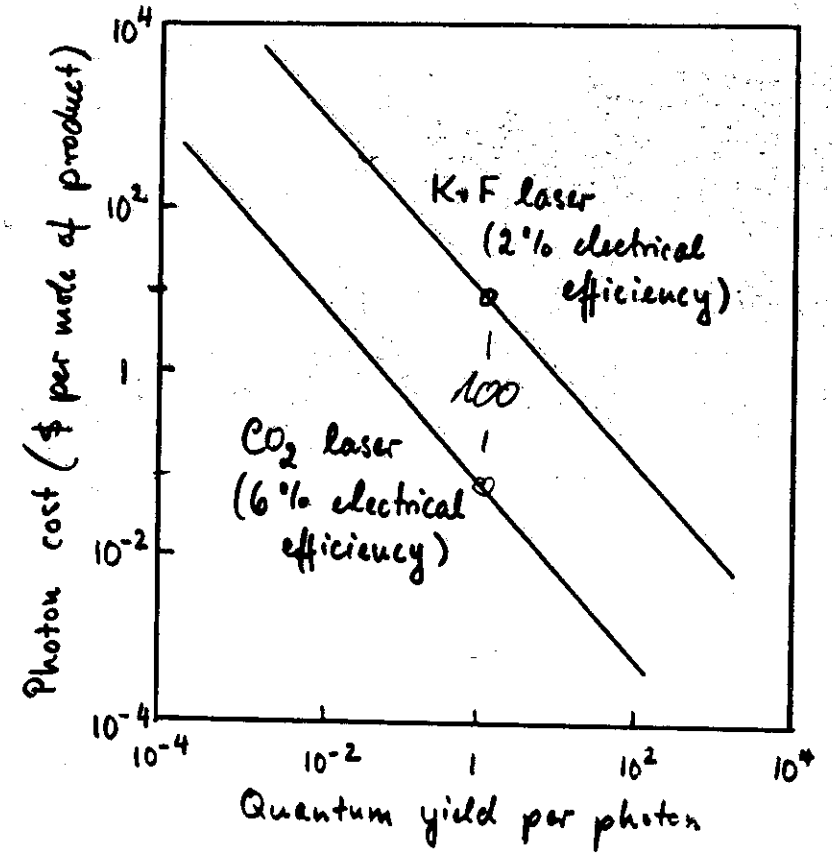
*Includes steam, electricity and cooling water.

TABLE II

Costs	w/o laser	w/laser (Single step case)
Raw materials	a	a
Energy	b	b + ß
Fixed & operations	c	c + γ
Overall yield	$A \equiv A_o\, \alpha$	$A + \Delta A \equiv A_o\, (\alpha + \Delta\alpha)$
Production cost-per unit	$\frac{(a+b+c)}{A_o \alpha}$	$\frac{(a+b+c) + (ß + \gamma)}{A_o\,(\alpha + \Delta\alpha)}$

$\| \Delta\alpha/\alpha \gg ß+\delta, \quad a+b+c \|$

Randbedingung: IR Laser i.a. nur in der Gasphase einsetzbar



Triatomic rare-gas halide
excimer lasers ?

broad continuum emission Xe_2Cl
→ tunable UV-lasers

Prof. Gu et al. Ar_2F

goal: discharge for
high repetition rates
& simplicity
(different kinetics)

tunable

THE GENERATION OF ULTRAVIOLET AND VACUUM-ULTRAVIOLET RADIATION

D. J. Brink

F. D. Proch

Max-Planck-Institut für Quantenoptik

D-8046 Garching

Experiments that we have in mind

- Photoionization
- Photofragmentation

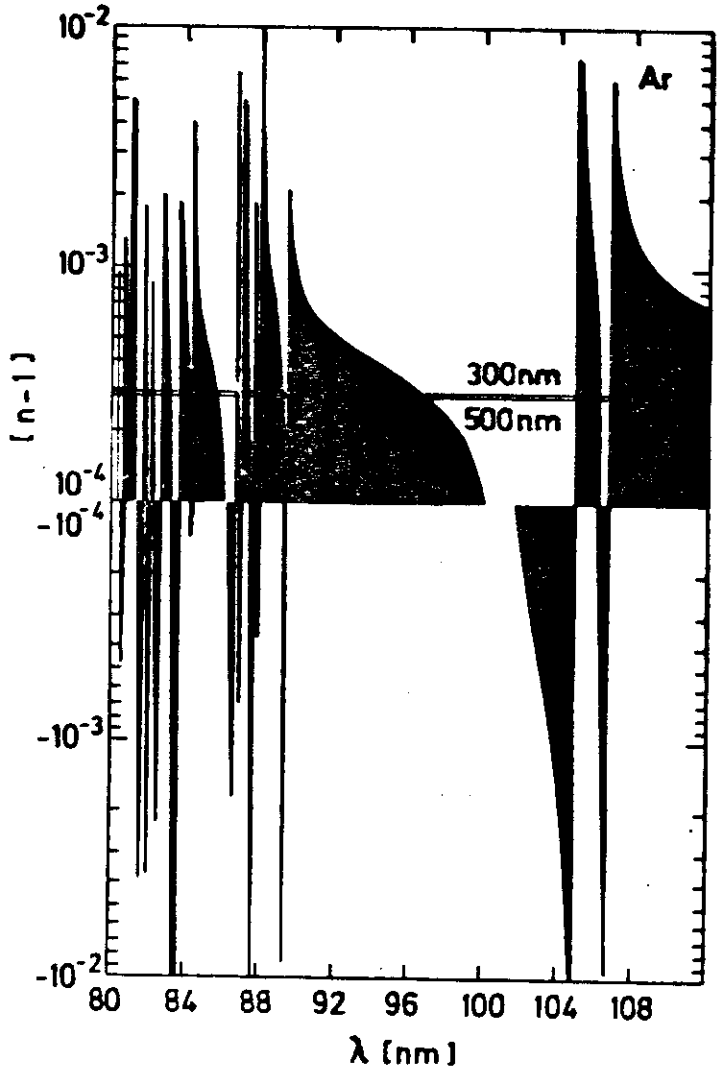
- Ion-Molecule Reactions
- Initiation of Photochemical Reactions

- Photon Stimulated Desorption

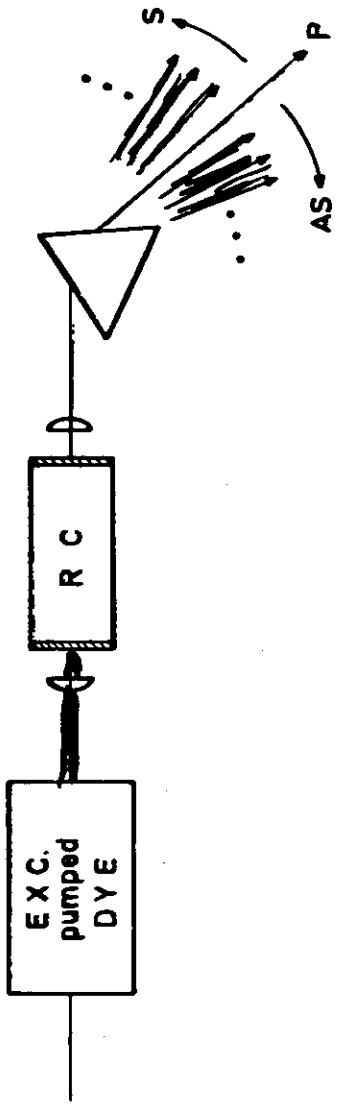
Properties the laser should have

- Continuous Tunability $\geq$ 100nm
- Output Power $\geq$ 1KW
- Good Spatial Quality
- Narrow Bandwidth

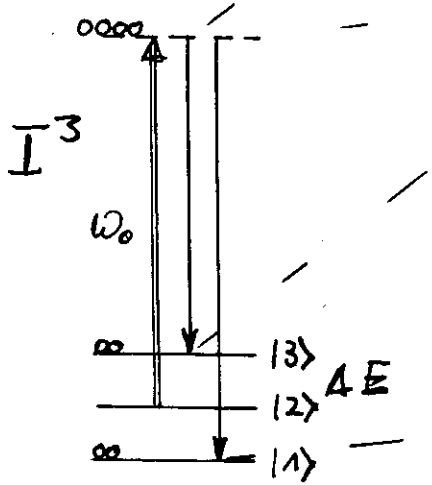
- Reliable Performance, Ease of Operation



STOKES LIGHT GENERATION

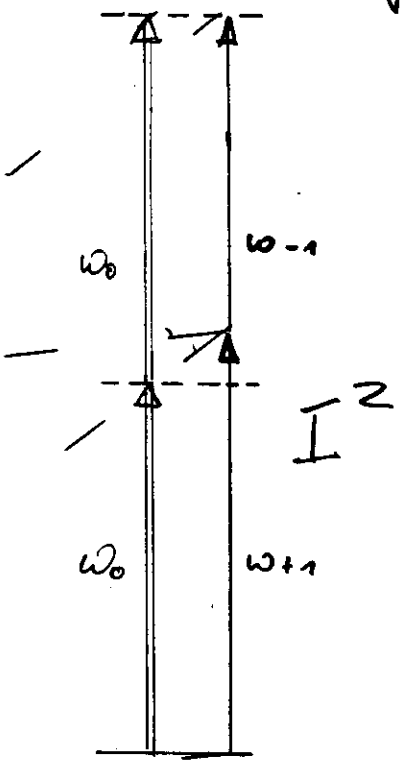


SRS



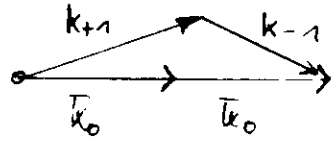
$$\omega_{\pm 1} = \omega_0 \pm \Delta E/\hbar$$

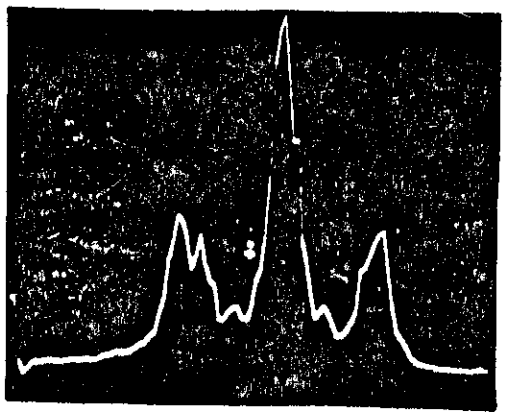
4 - wave mixing



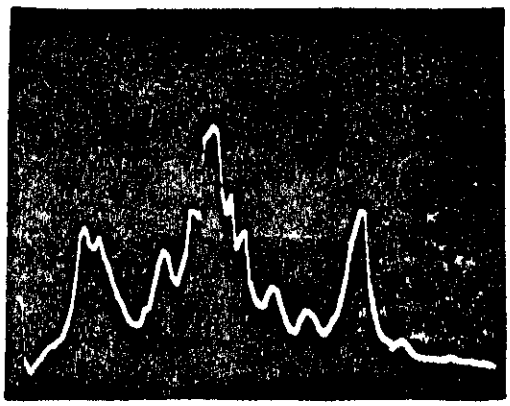
$$\omega_0 + \omega_0 = \omega_{+1} + \omega_{-1}$$

$$\omega_{+1} = \omega_0 + \Delta E/\hbar$$



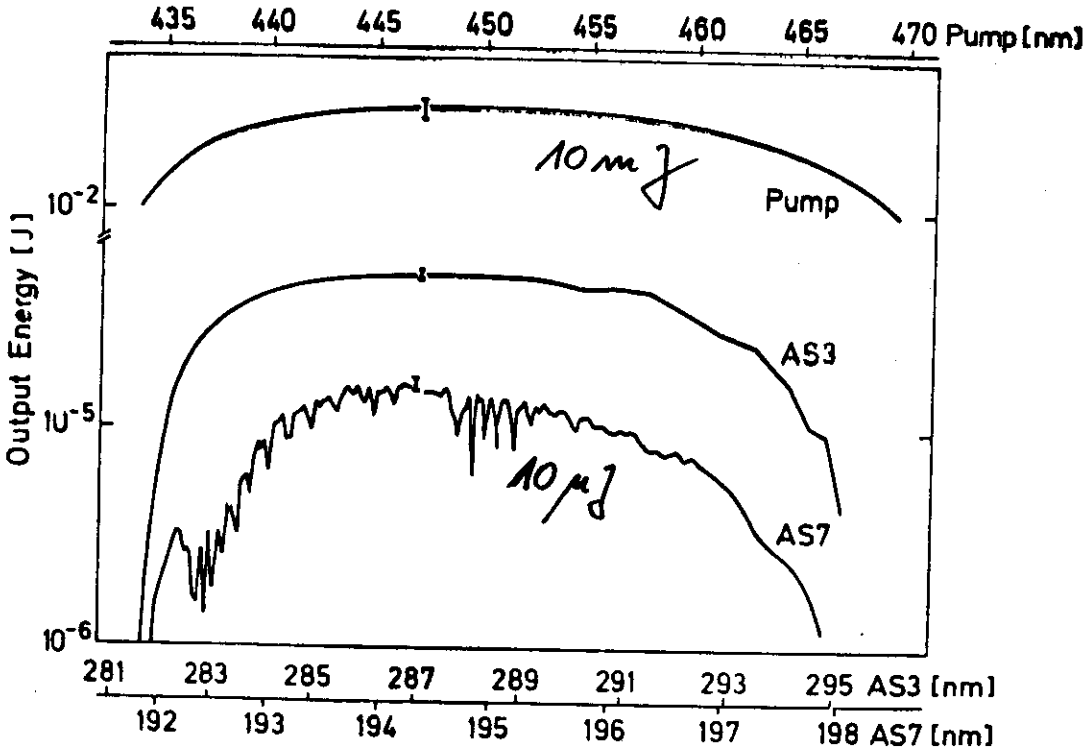


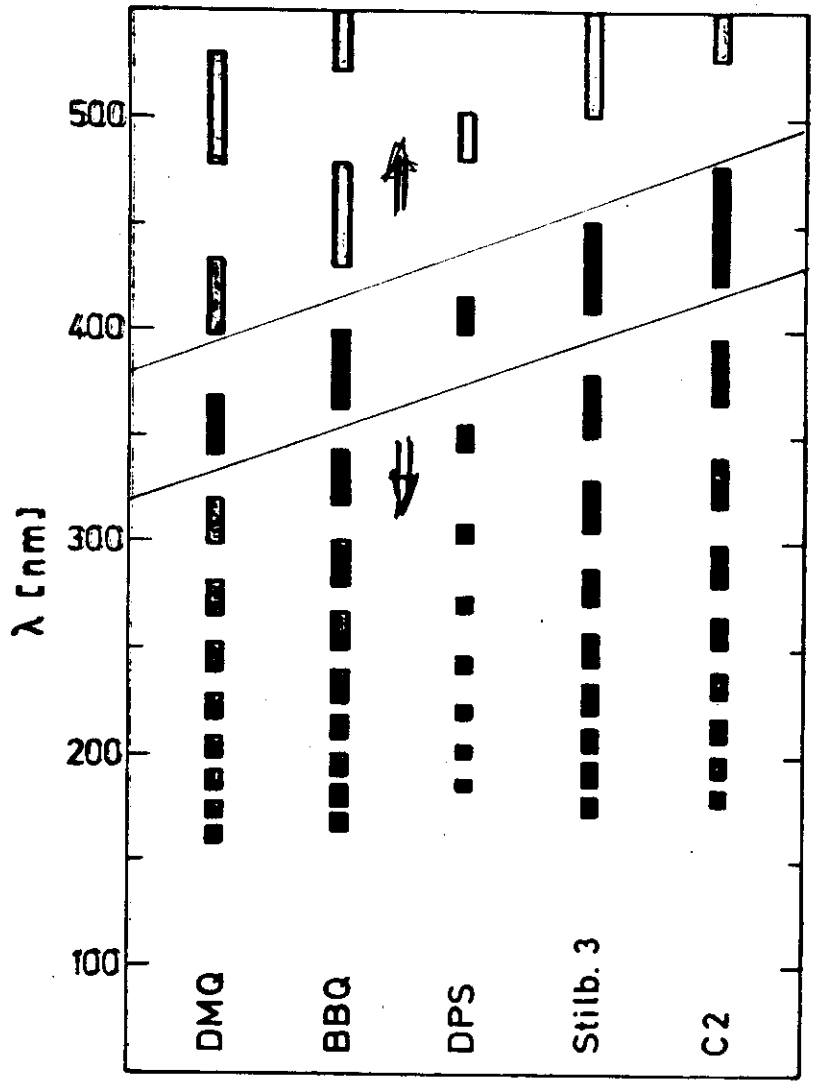
$\Gamma_L = 0.04\,cm^{-1}$



$\Gamma_L = 0.2\,cm^{-1}$

S_1





$$g_{-,} = \omega_{-} / (2 \varepsilon_0^2 c^2 \hbar n_{-} n_0) |\bar{\alpha}|^2 (N/\gamma)$$

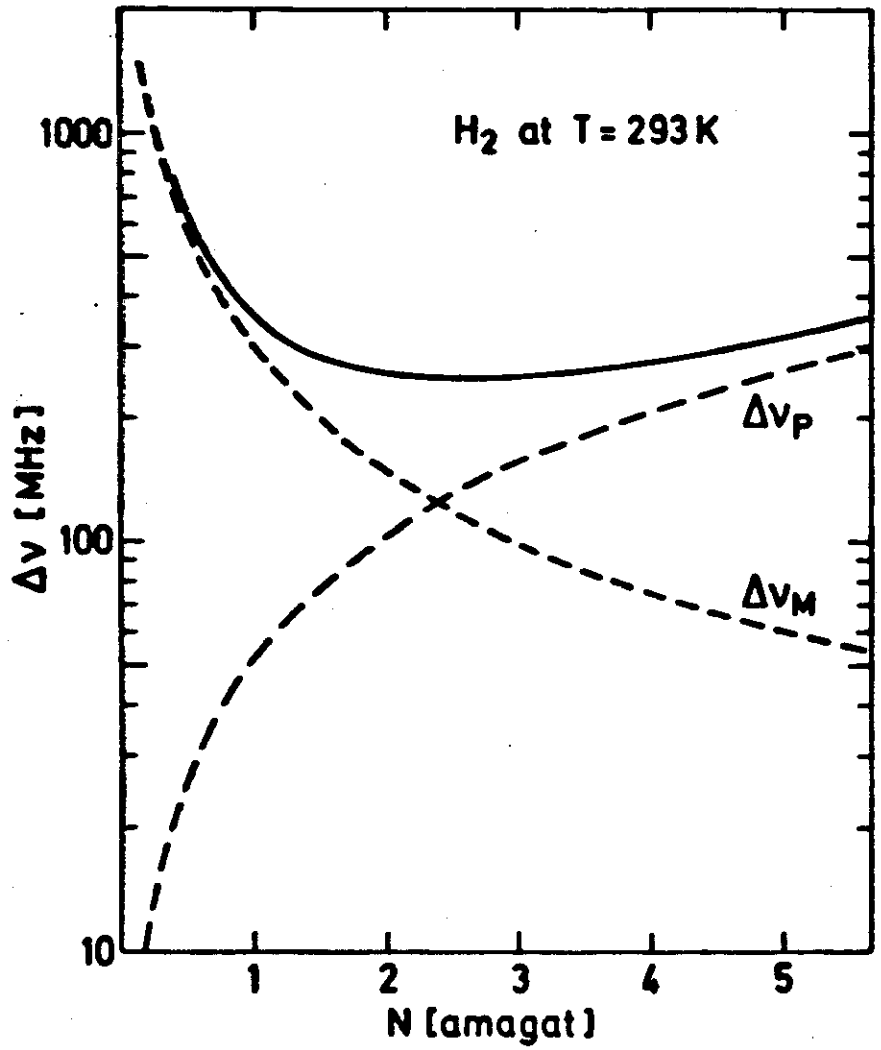
$$\gamma \propto \Delta\nu = D_0 K^2 / (\pi N) + \chi N = \Delta\nu_M + \Delta\nu_p$$

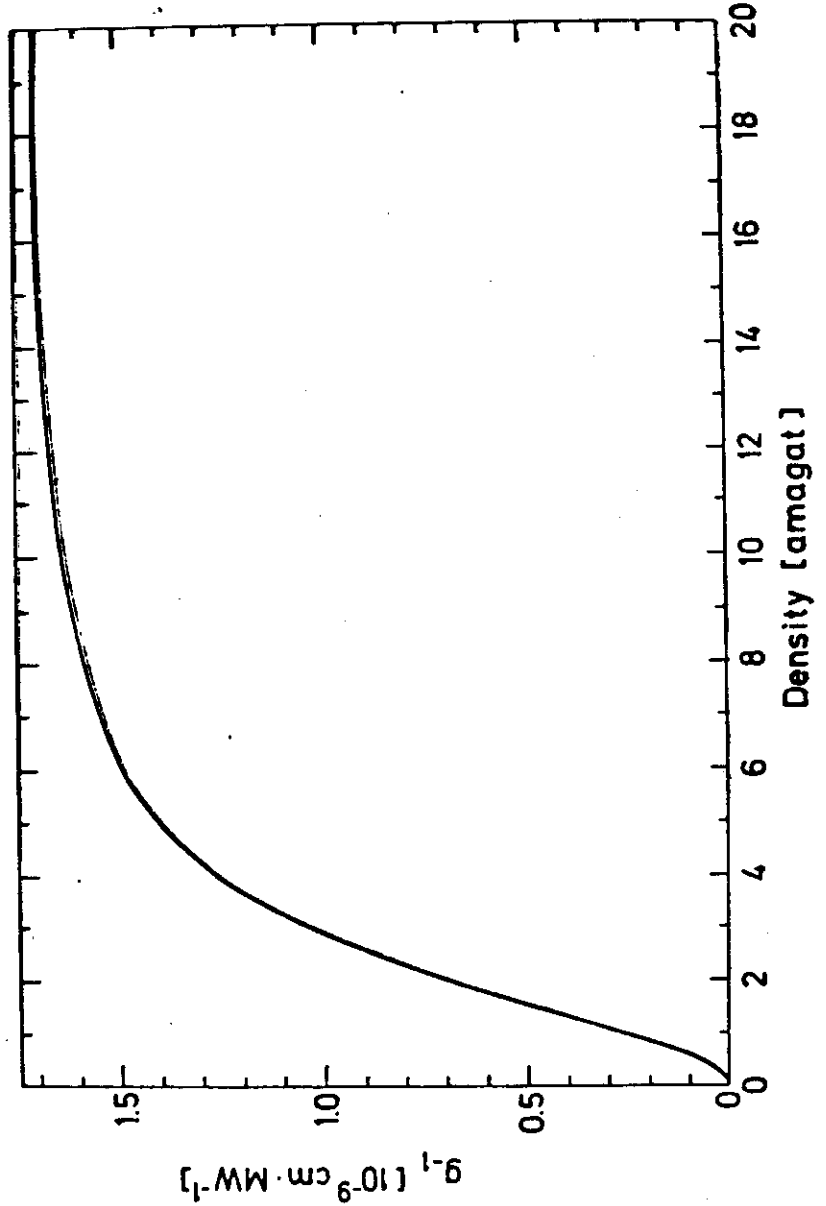
Motional narrowing — PRESSURE Broadening

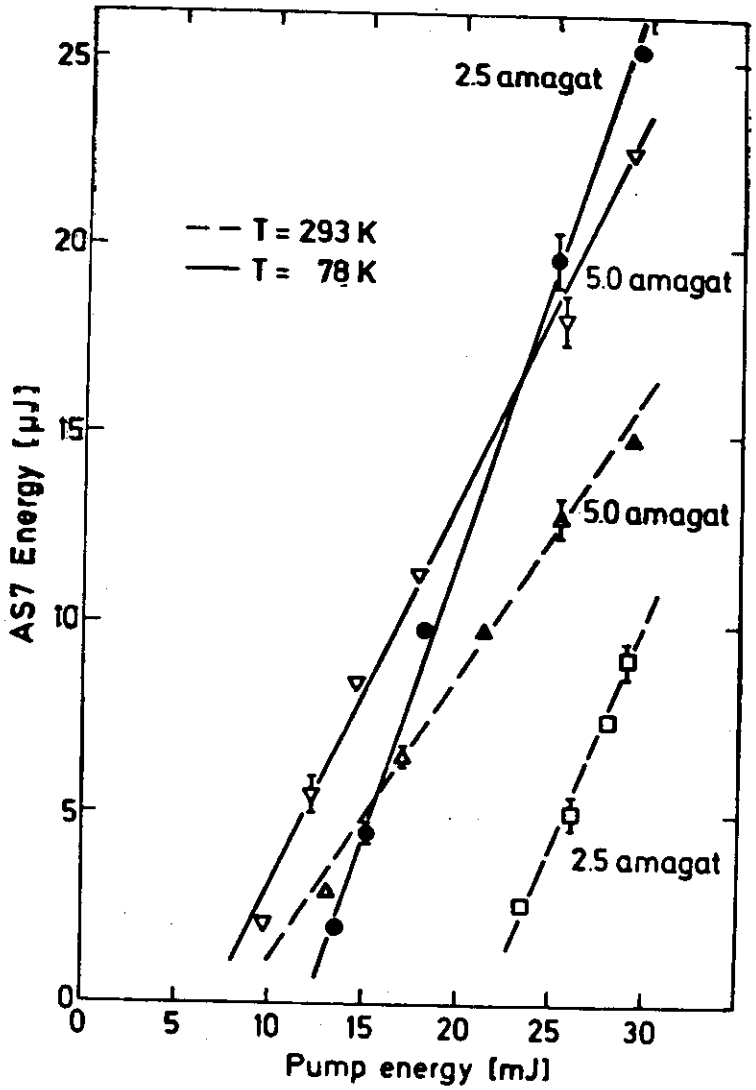
$$D_0 \propto \bar{v} = (3kT/m)^{1/2}$$

$$\Delta\nu_p = 2N\sigma\bar{v} \propto T^{1/2}$$

$$\Rightarrow g_{-,} \propto T^{-1/2}$$


H_2 at T = 293 K
$\Delta\nu_P$
$\Delta\nu_M$
Δν [MHz]
1000
100
10
1
2
3
4
5
N [amagat]


Density [amagat]
0
2
4
6
8
10
12
14
16
18
20
0
0.5
1.0
1.5
g_{-1} [10^{-9} cm · MW^{-1}]



ACHIEVEMENTS, ... so far

$\lambda_{min} = 163\ nm$

($\triangleq AS_8$ of 356 nm)

$E_{163} \gtrsim 1\mu J$ @ $\tau = 1.5\ ns$

$\Rightarrow \sim 1\ kW$

Focusability: $\phi\ 100\ \mu m$

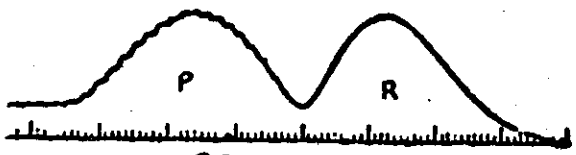
$\Rightarrow > 10\ MW/cm^2$

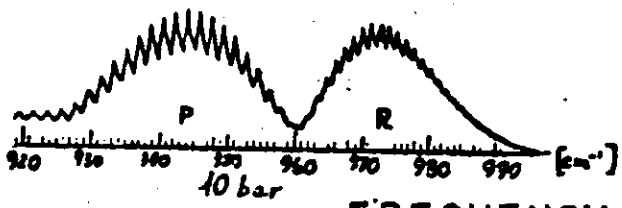
! These figures for T=293K !

HOCHDRUCK. HOCHLEISTUNG CO_2 LASER

MIT ELEKTRONENSTRAHL VORIONISIERUNG

ANWENDUNG: LR. Vielfotonenanregung → Spektroskopie
                                    → Chemie

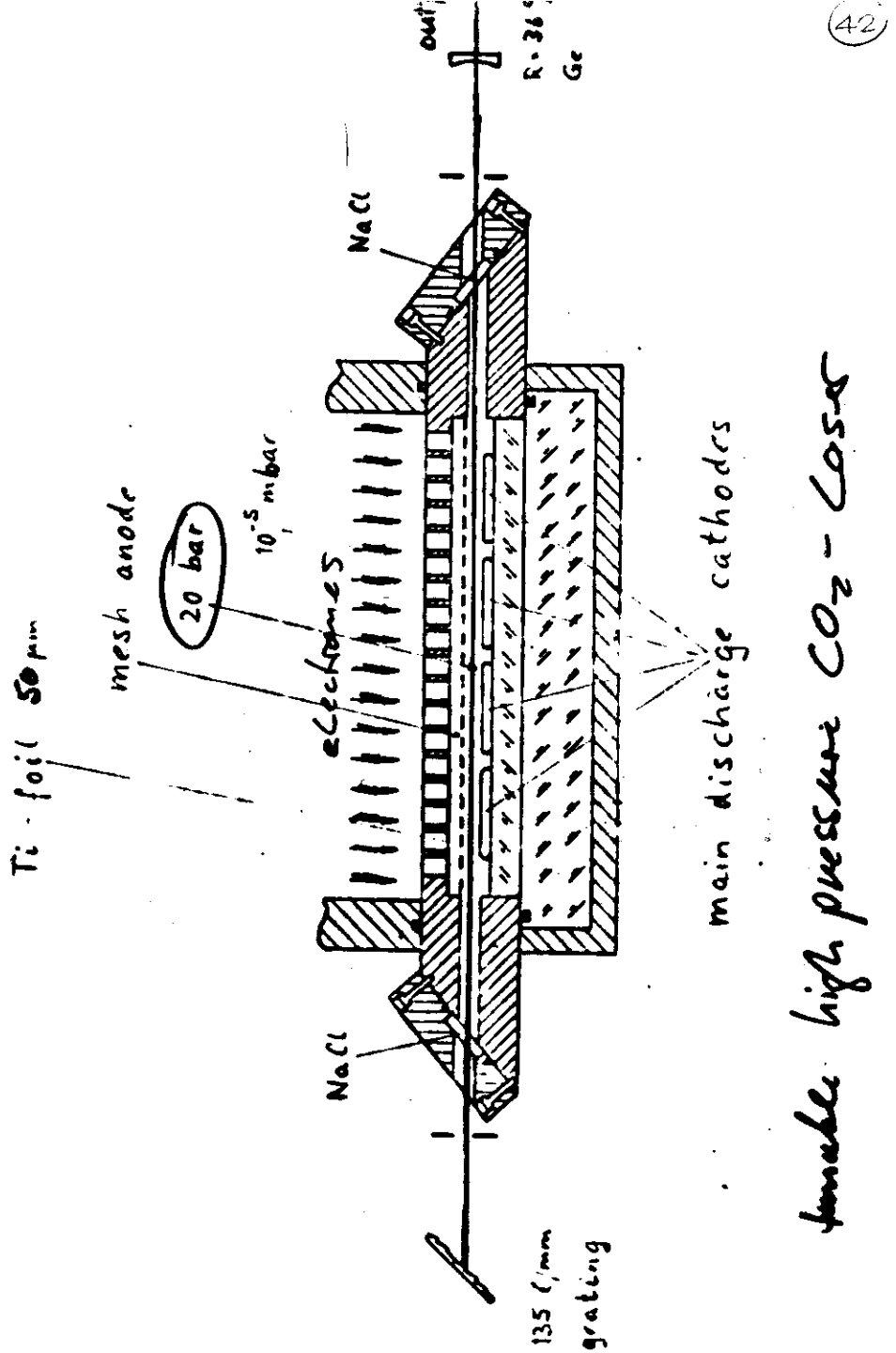




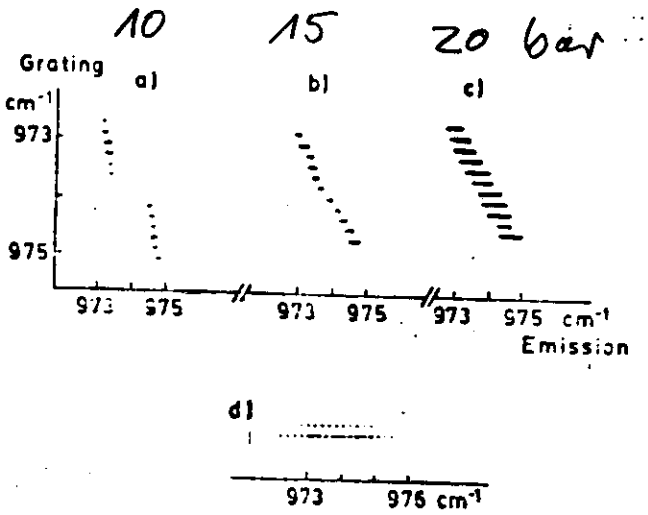
ENTFERNUNG ZWISCHEN LINIEN → 1.8 cm⁻¹ (P)
                           → 1.2 cm⁻¹ (R)

LINIENBREITE MIT 20 bar: ~ 2.6 cm⁻¹

↳ Stetigabstimmbarkeit
  Vielefrequenzoperation



tunable high pressure CO_2-Laser



HeNe Flux = 50 mW

Energy ~ 1 J