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 - 68

WINTER COLLEGE ON LASERS, ATOMIC AND MOLECULAR PHYSICS

(24 January - 25 March 1983)

I. Multiphoton Dissociation of O_sO_4- visualized.

II. Gain Measurements in Chemi-Luminescence.

H. SCHRÖDER

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

ELECTRONIC EMISSION FROM LASER PHOTOLYSIS

THE STUDY OF THE VISIBLE LUMINESCENCE OF CrO_2Cl_2 OsO_4 VAPORS AFTER PULSED IR- AND UV-LASER EXCITATION

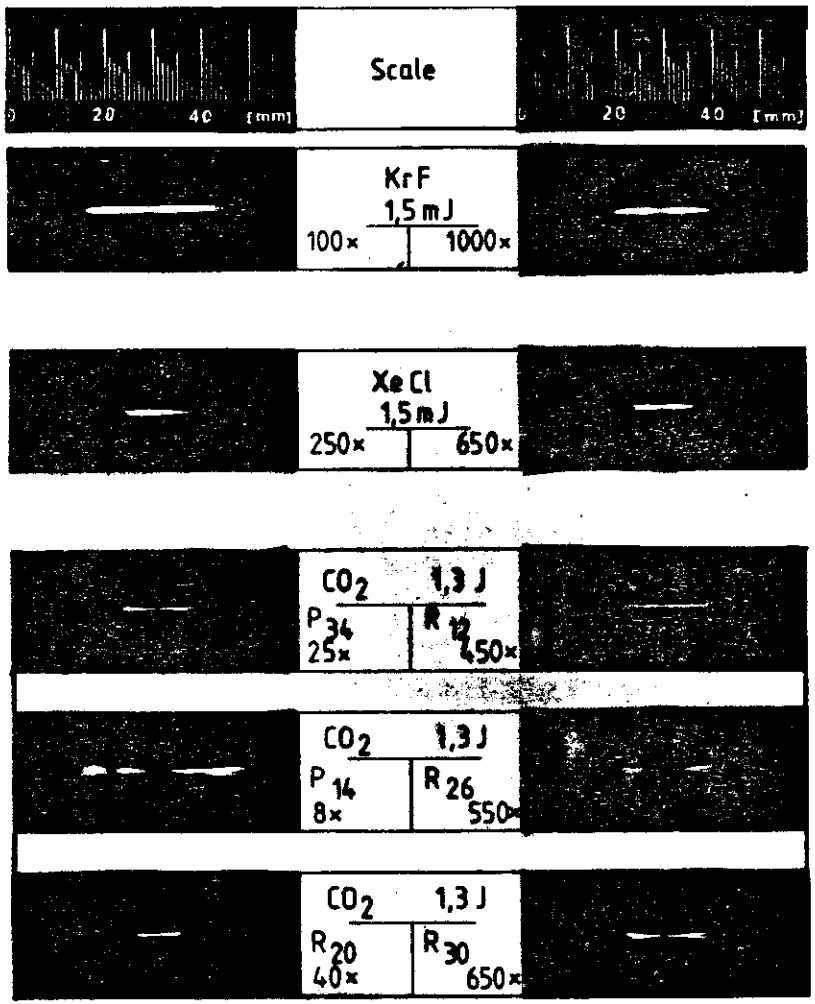
MOTIVATION

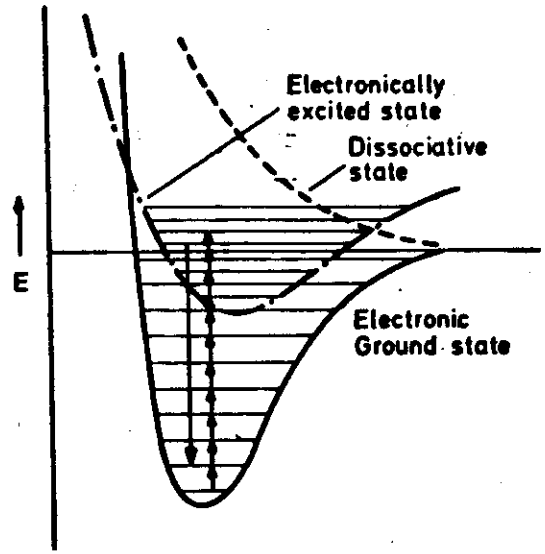
NEW PROCESSES IN ISOLATED MOLECULES
e.g. INVERSE ELECTRONIC RELAXATION

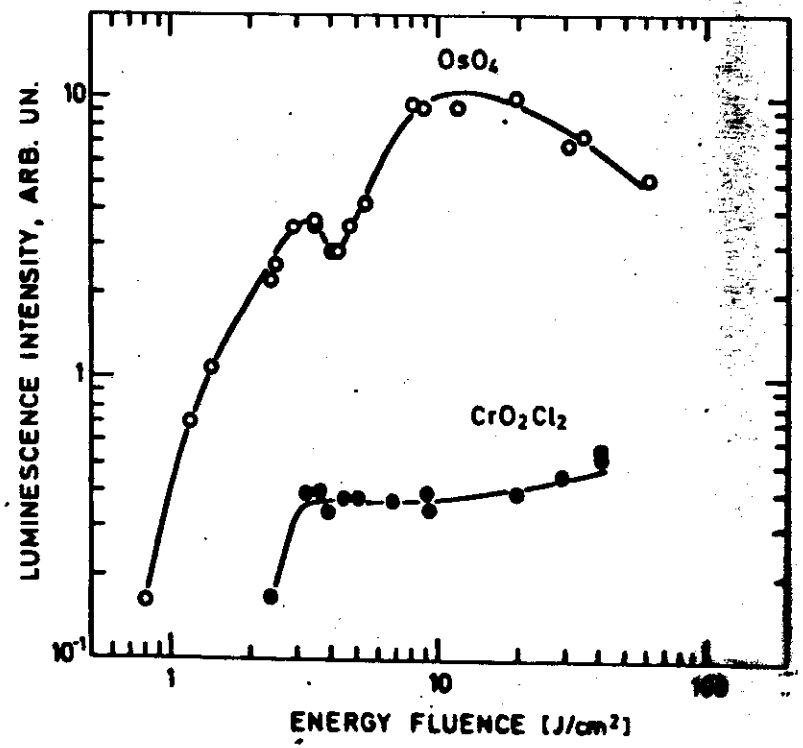
NEW EXPERIMENTAL TECHNIQUES FOR INFRARED MULTIPHOTON EXCITATION

NEW DYNAMICAL PROCESSES AND CHEMICAL REACTIONS OF EXCITED MOLECULES AT HIGH CONCENTRATIONS

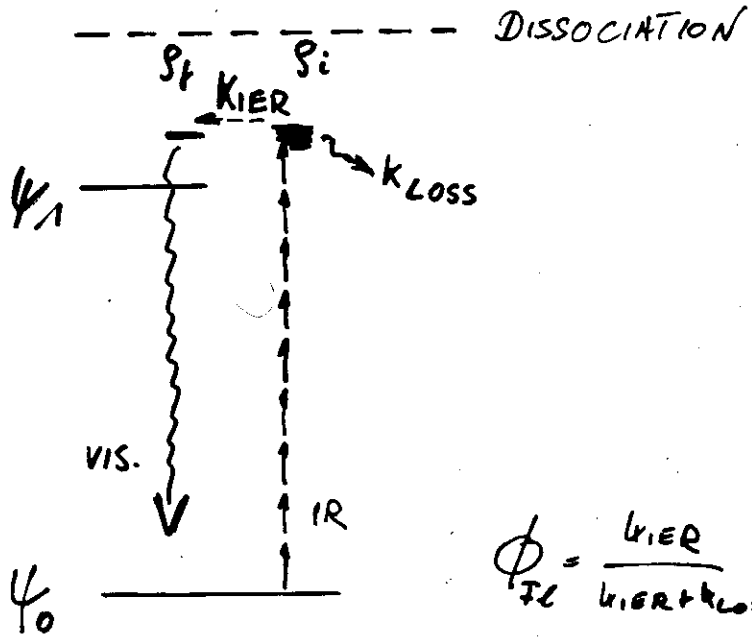
SURFACE LASER CHEMISTRY
VAPOR DEPOSITION
ETCHING
DOPING







Inverse Electronic Relaxation

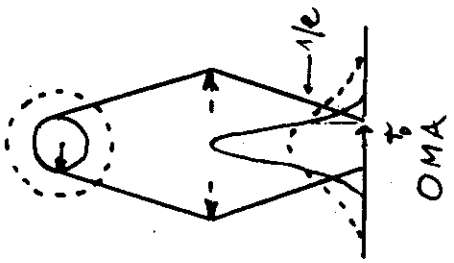


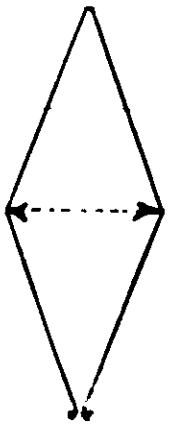
$$\Phi_{IC} = \frac{k_{IER}}{k_{IER}+k_{LOSS}} \ll 10^{-3}$$

$$\tau = \frac{1}{k_{LOSS}} \approx 1\,ms$$

$$k_{IER} \propto |\langle \psi_1 | T_n | \psi_0 \rangle|^2 \varphi_f/\varphi_i$$

$$\ll 1 \qquad 10^{-6}$$

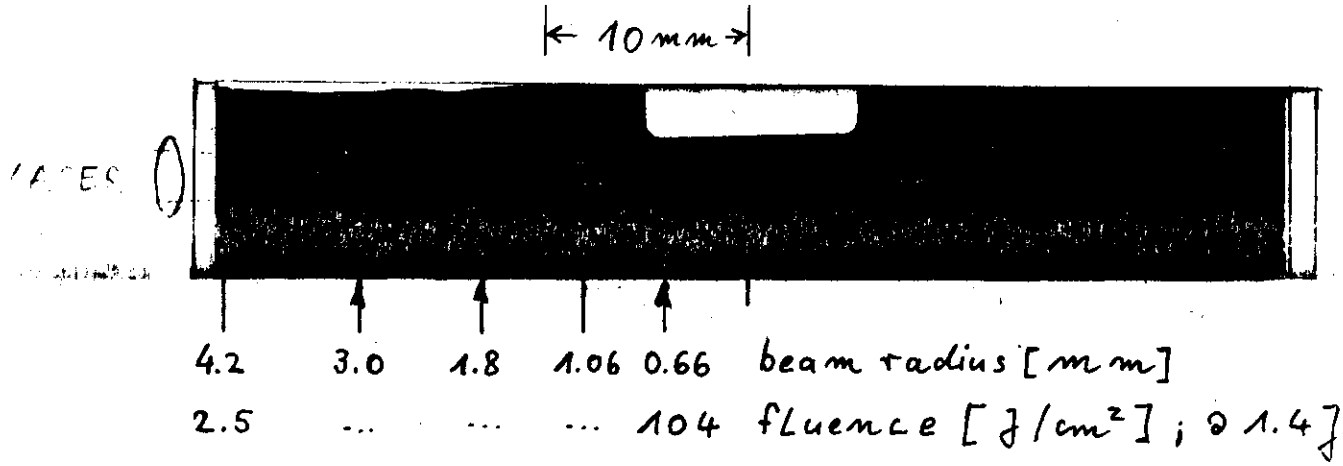




SPECTROMETER, OMA

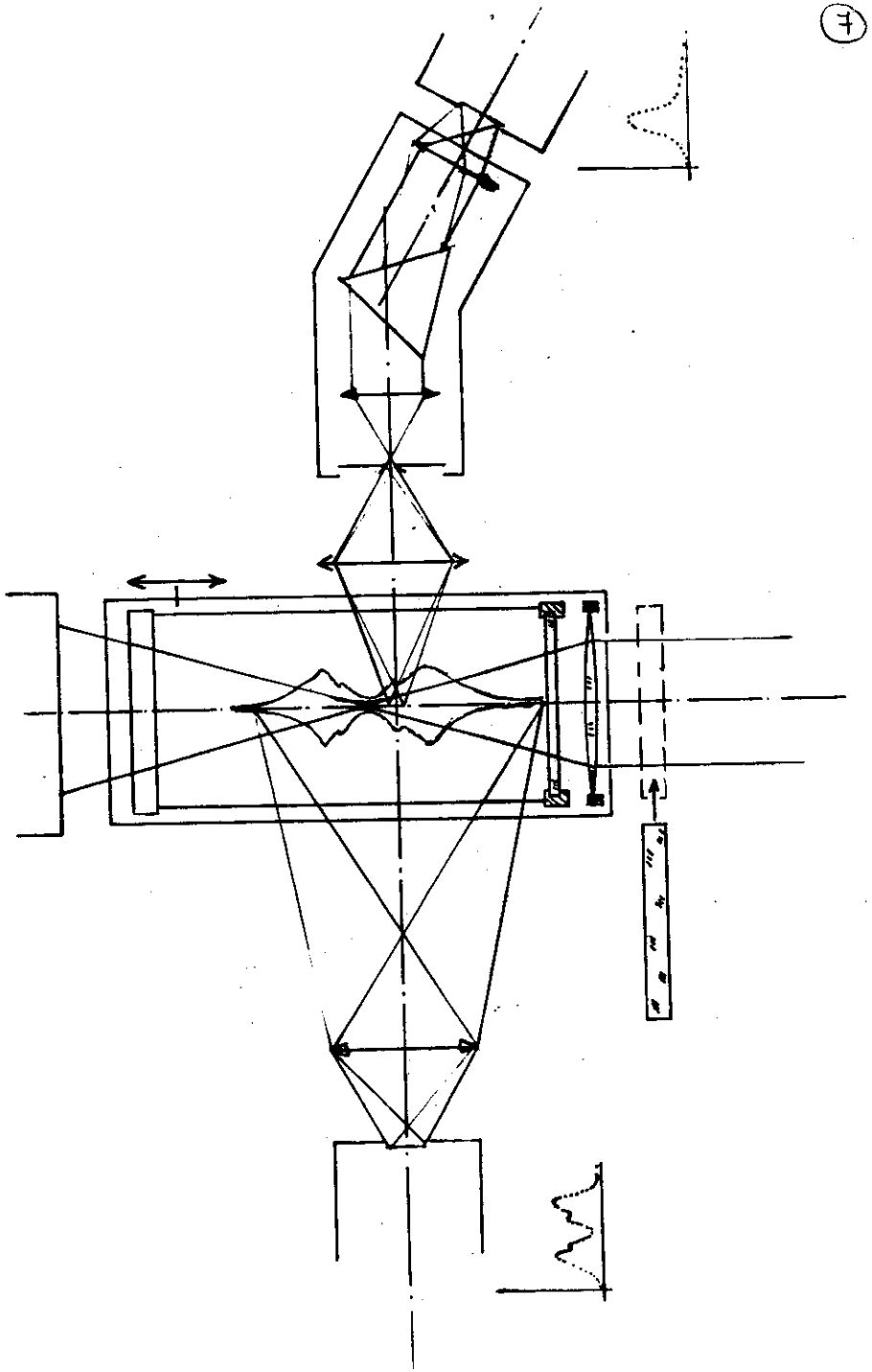
(5)

OsO_4

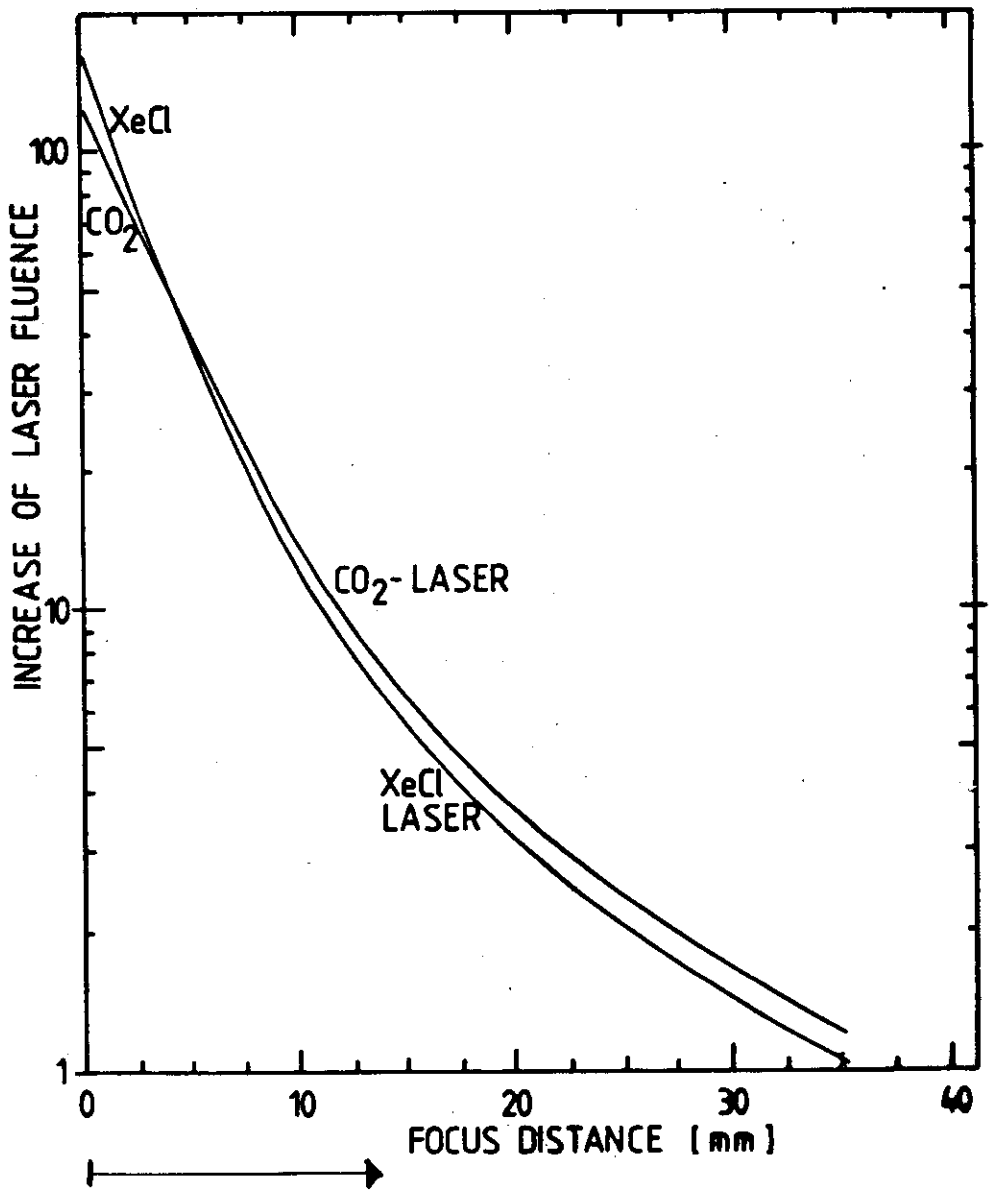


(6)

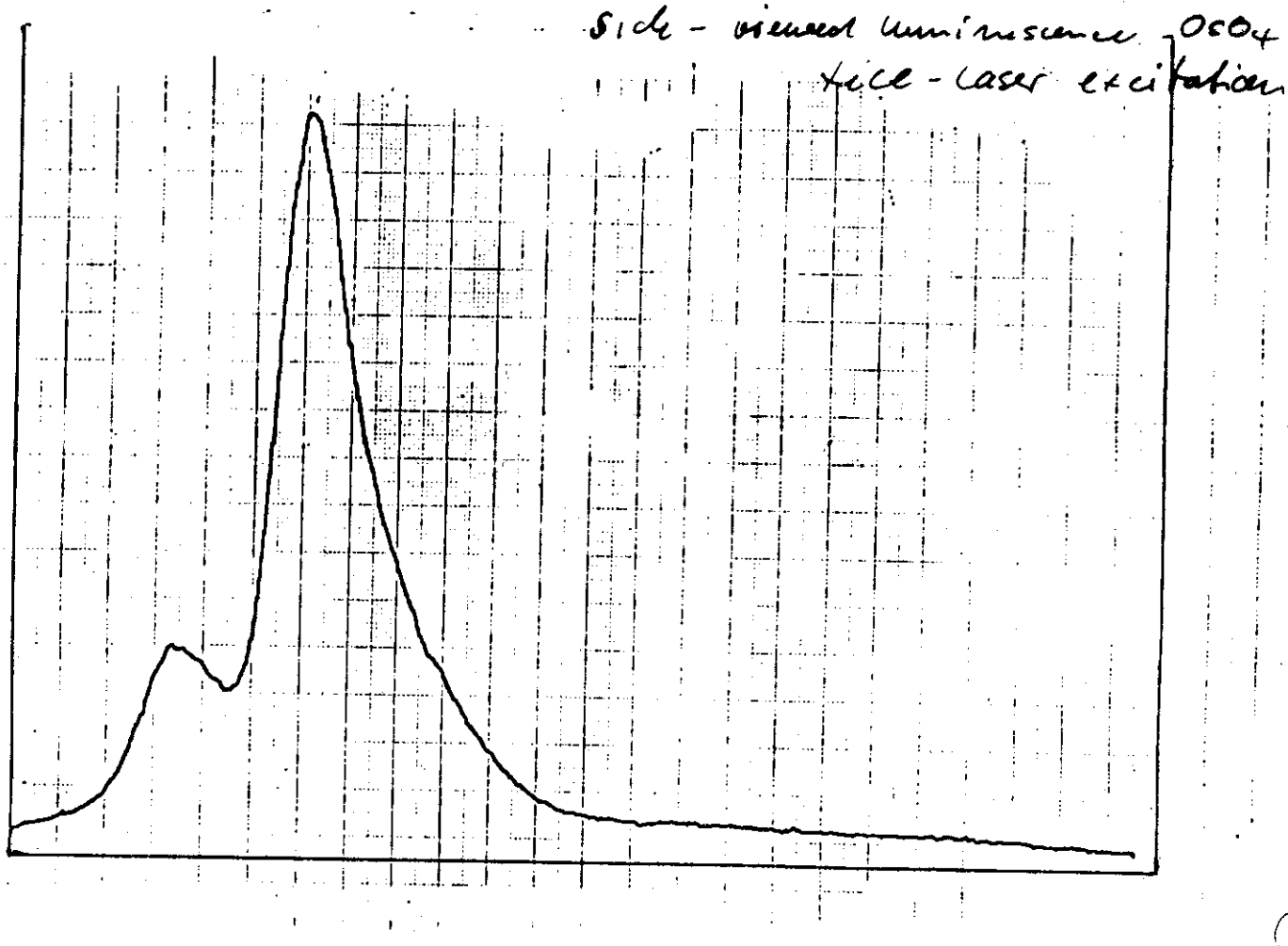
⑦



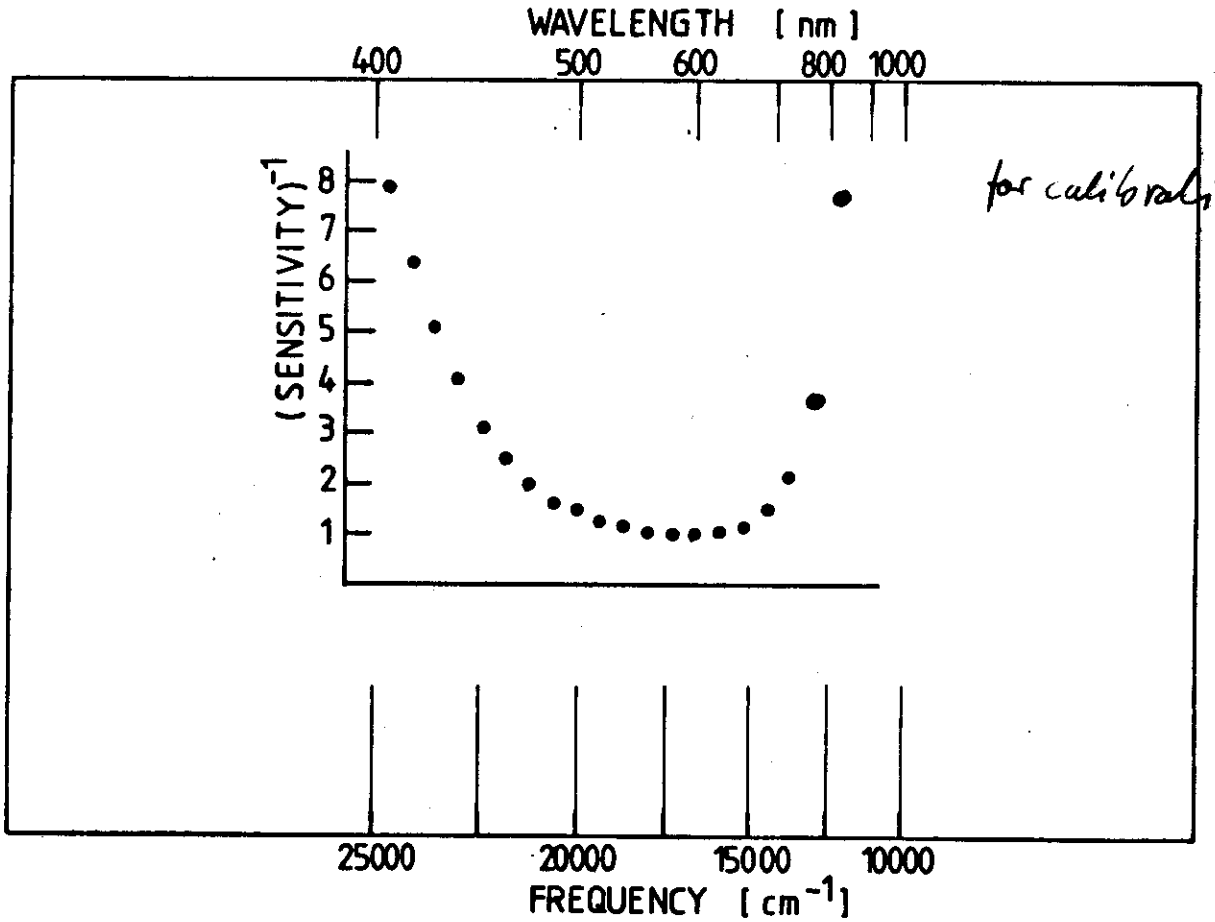
⑧


XeCl
CO_2
CO_2- LASER
XeCl
LASER
INCREASE OF LASER FLUENCE
100
10
1
0
10
20
30
40
FOCUS DISTANCE [mm]

Side-viewed luminescence OsO_4
Face-laser excitation

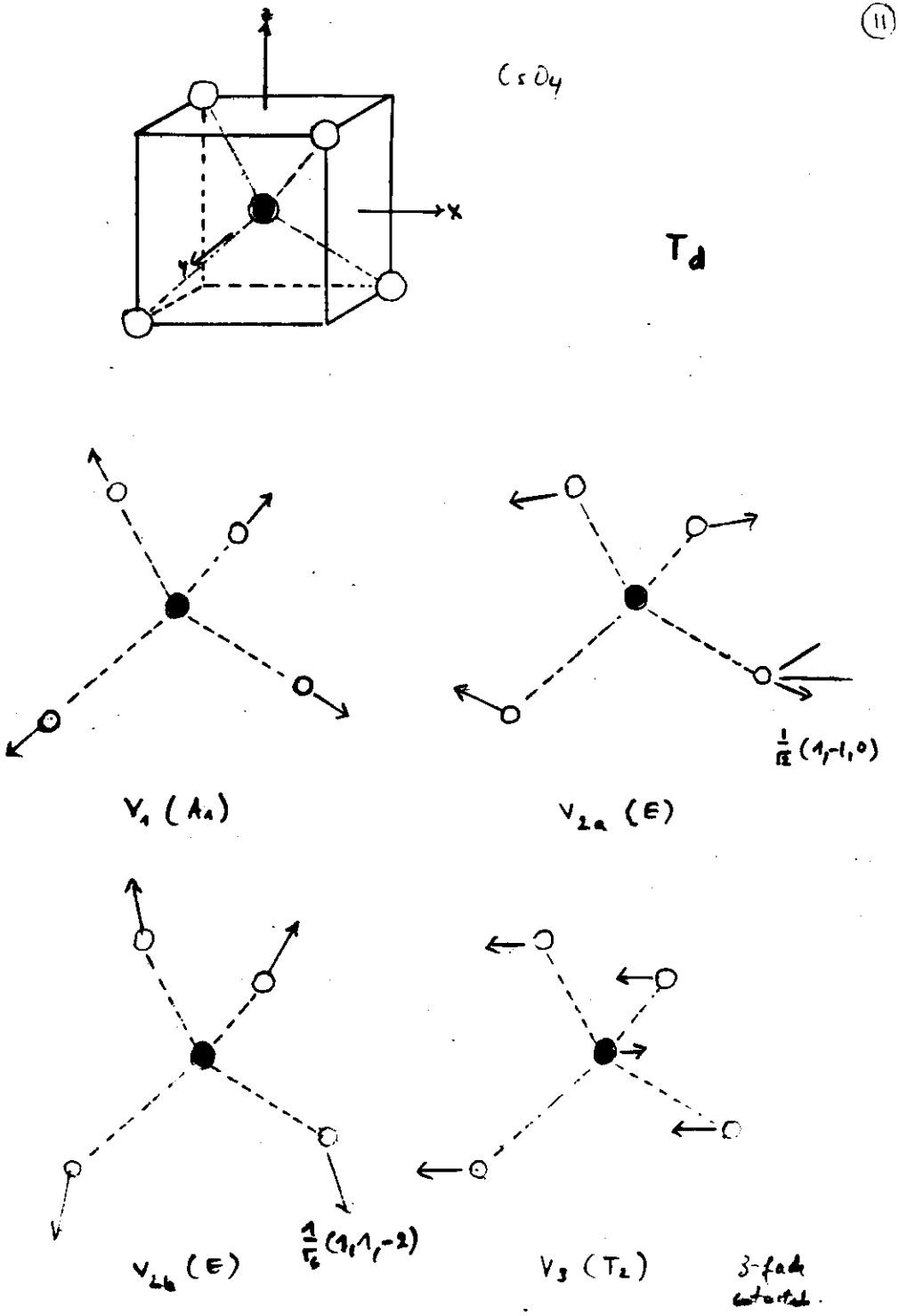


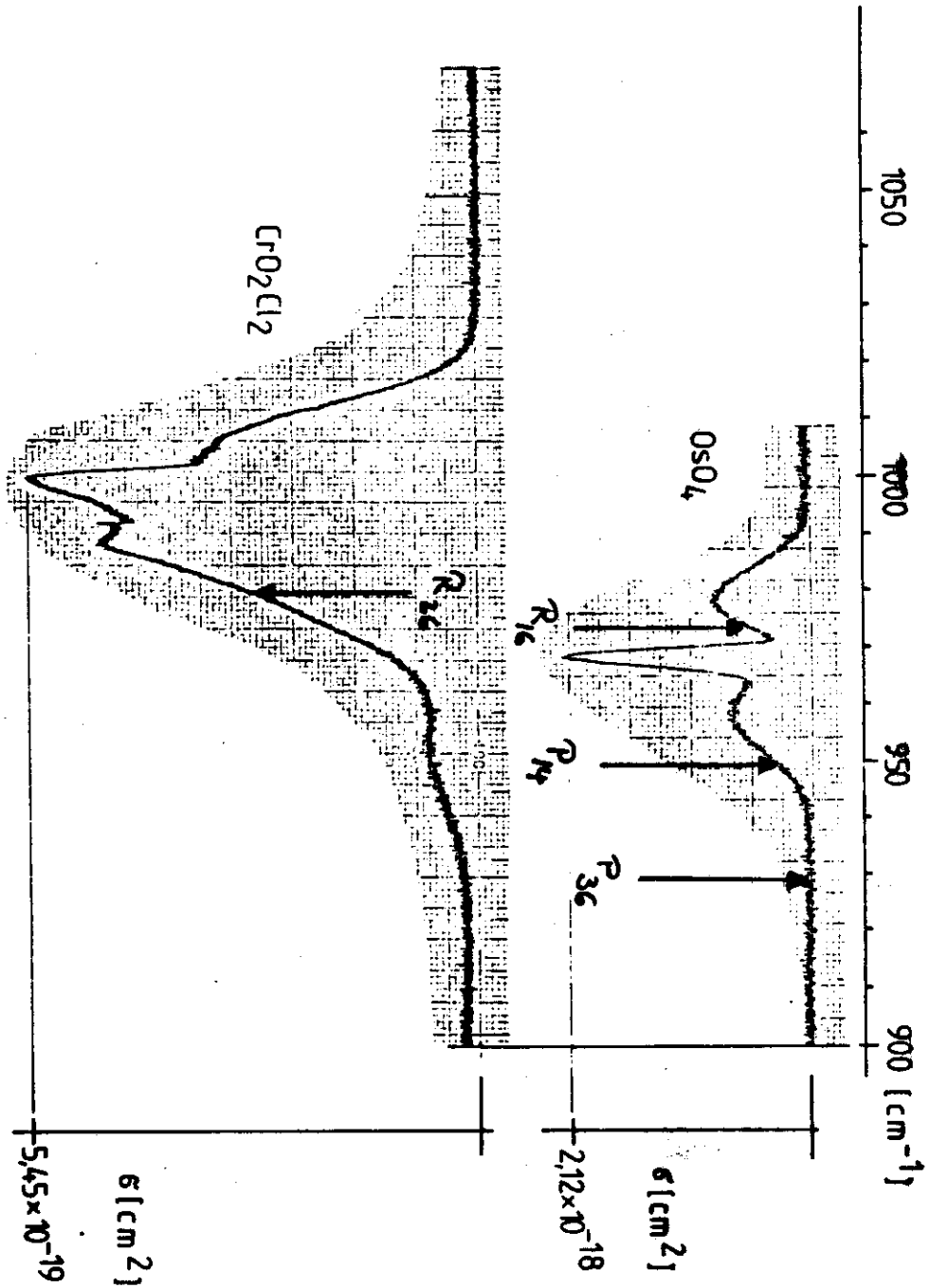
(9)

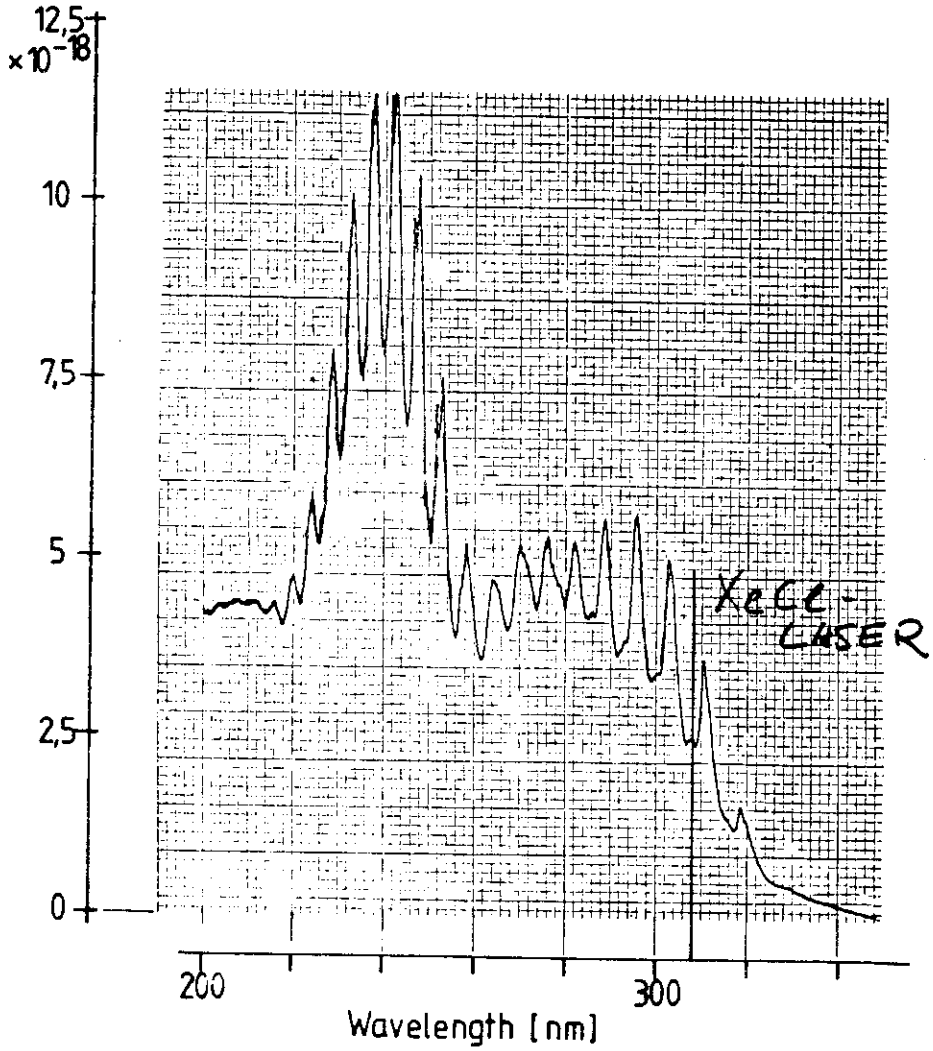


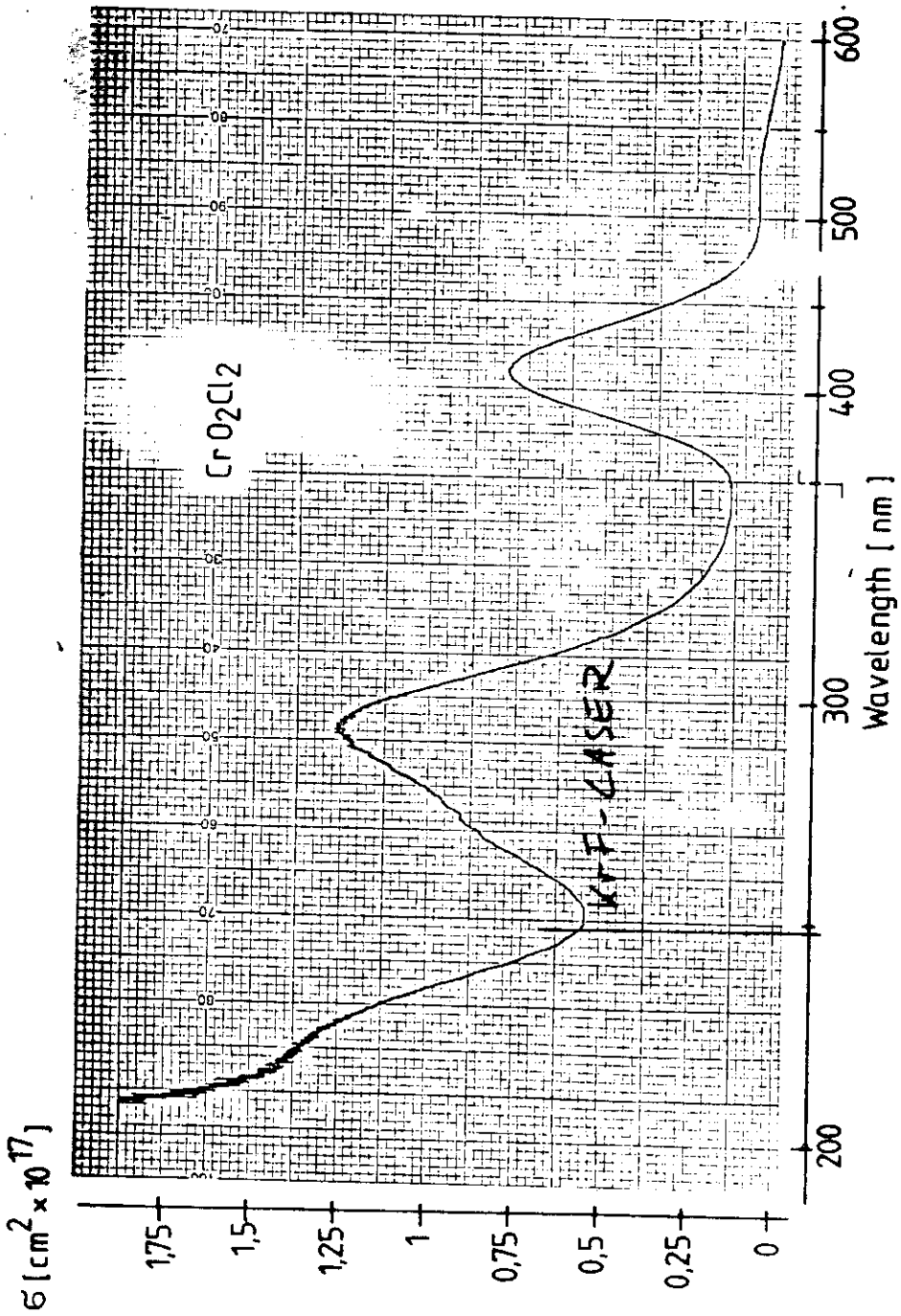
for calibration

(10)


CrO_4
T_d
V_1 (A_1)
V_{2a} (E)
$\frac{1}{\sqrt{2}}(1,-1,0)$
V_{2b} (E)
$\frac{1}{\sqrt{6}}(1,1,-2)$
V_3 (T_2)
3-fach entartet


CrO_2Cl_2
OsO_4
R_{26}
R_{16}
P_{14}
P_{36}
σ [cm^2]
$5{,}45\times10^{-19}$
$2{,}12\times10^{-18}$
1050
1000
950
900 [cm^{-1}]


σ [cm²]
OsO4
12,5
×10⁻¹⁸
10
7,5
5
2,5
0
200
300
Wavelength [nm]
XeCl-LASER


CrO2Cl2
KrF-LASER
σ [cm² × 10¹⁷]
1,75
1,5
1,25
1
0,75
0,5
0,25
0
200
300
400
500
600
Wavelength [nm]

OsO_4

Rise time of OsO_4 luminescence

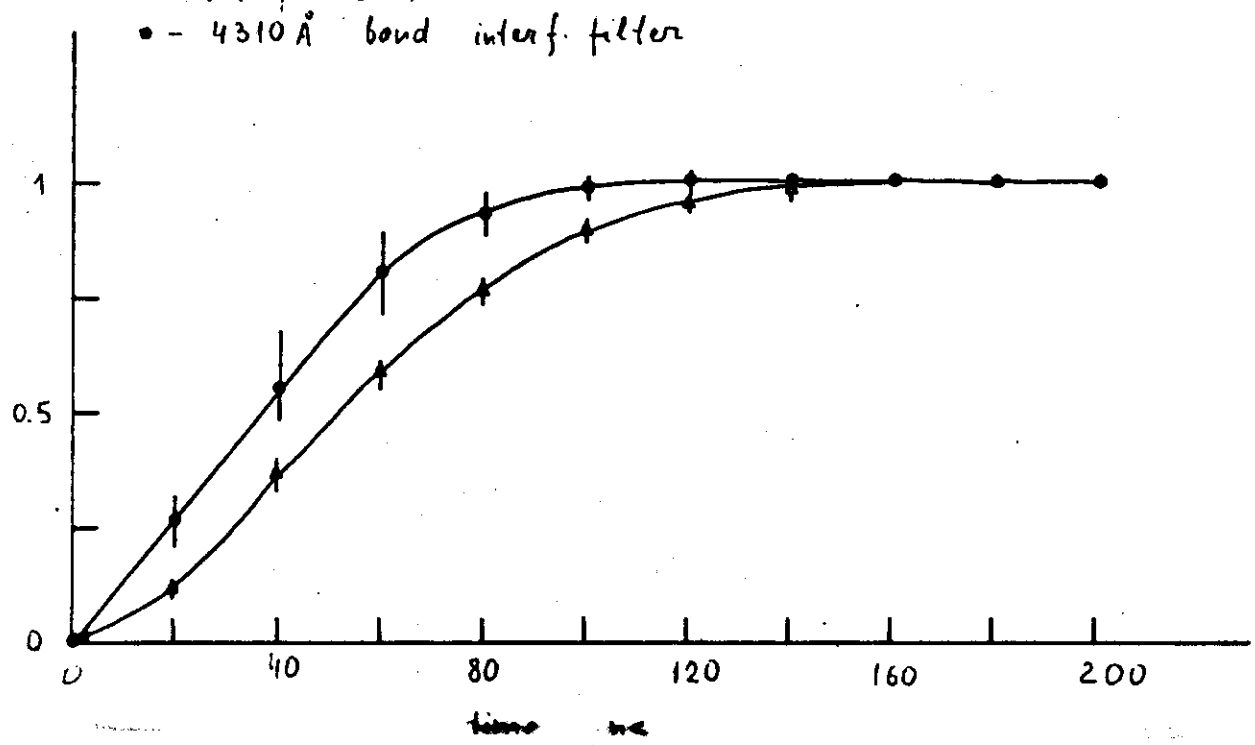
$\nu = 949.5\ cm^{-1}$, P(14) ω_2 - laser line

$p = 90\ \mu bar$

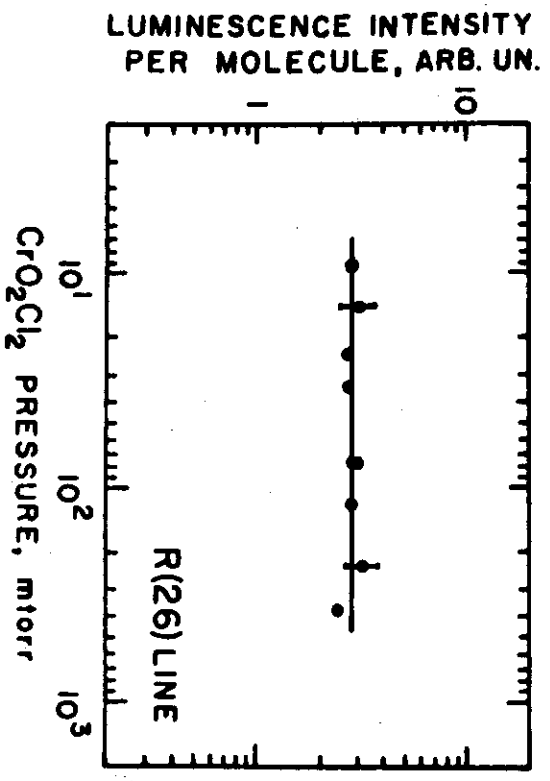
$\phi \sim 6\ J/cm^2$

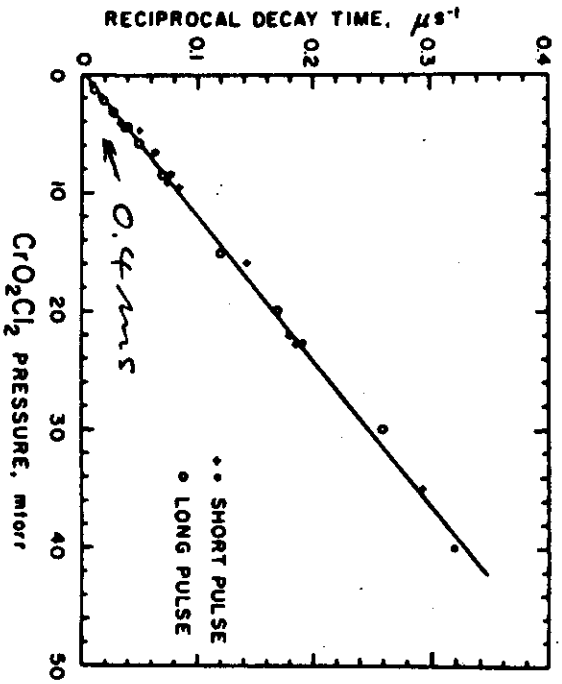
▲ - Red filter $\gtrsim 760$ nm

● - 4310 Å band interf. filter

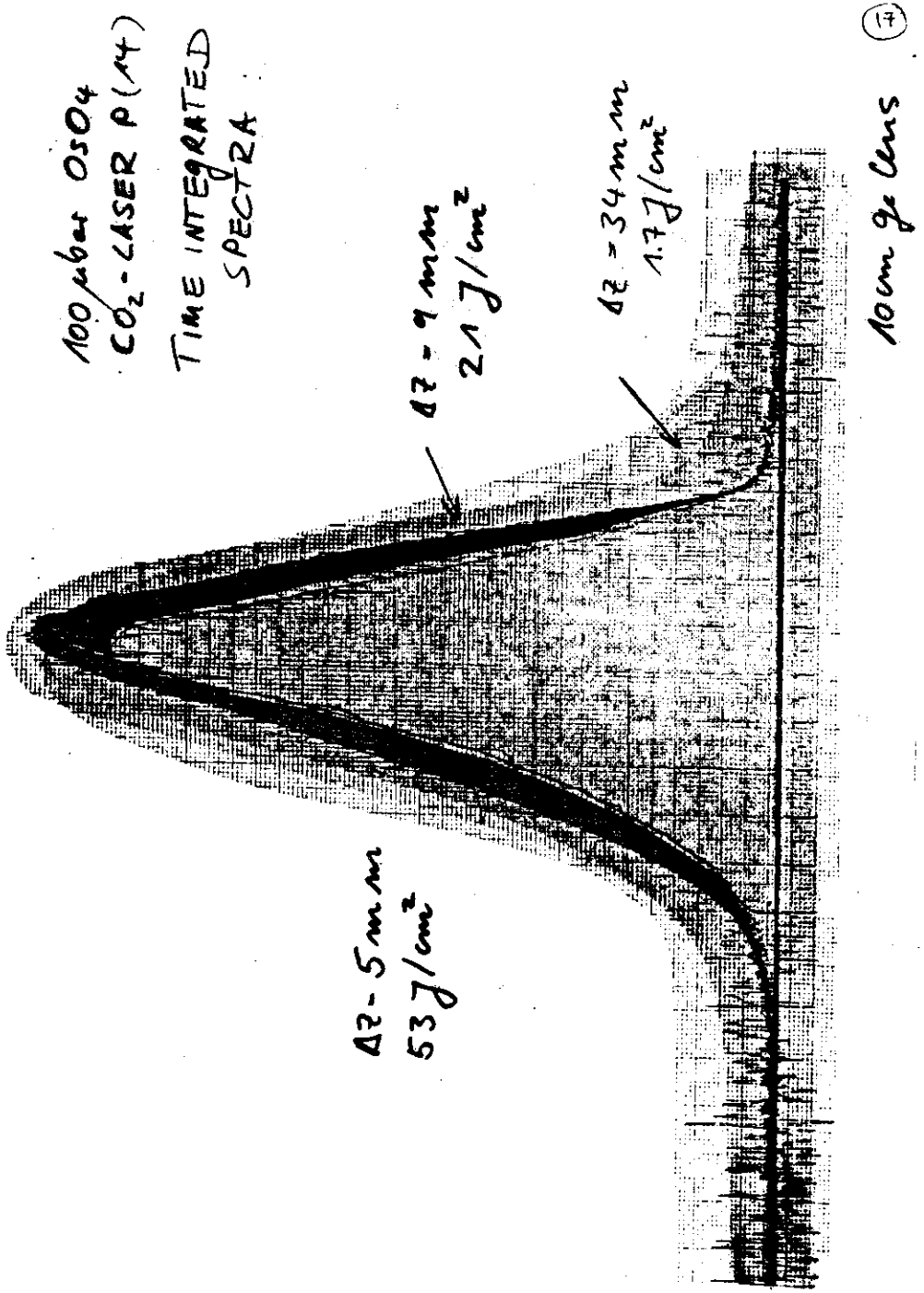


(15)

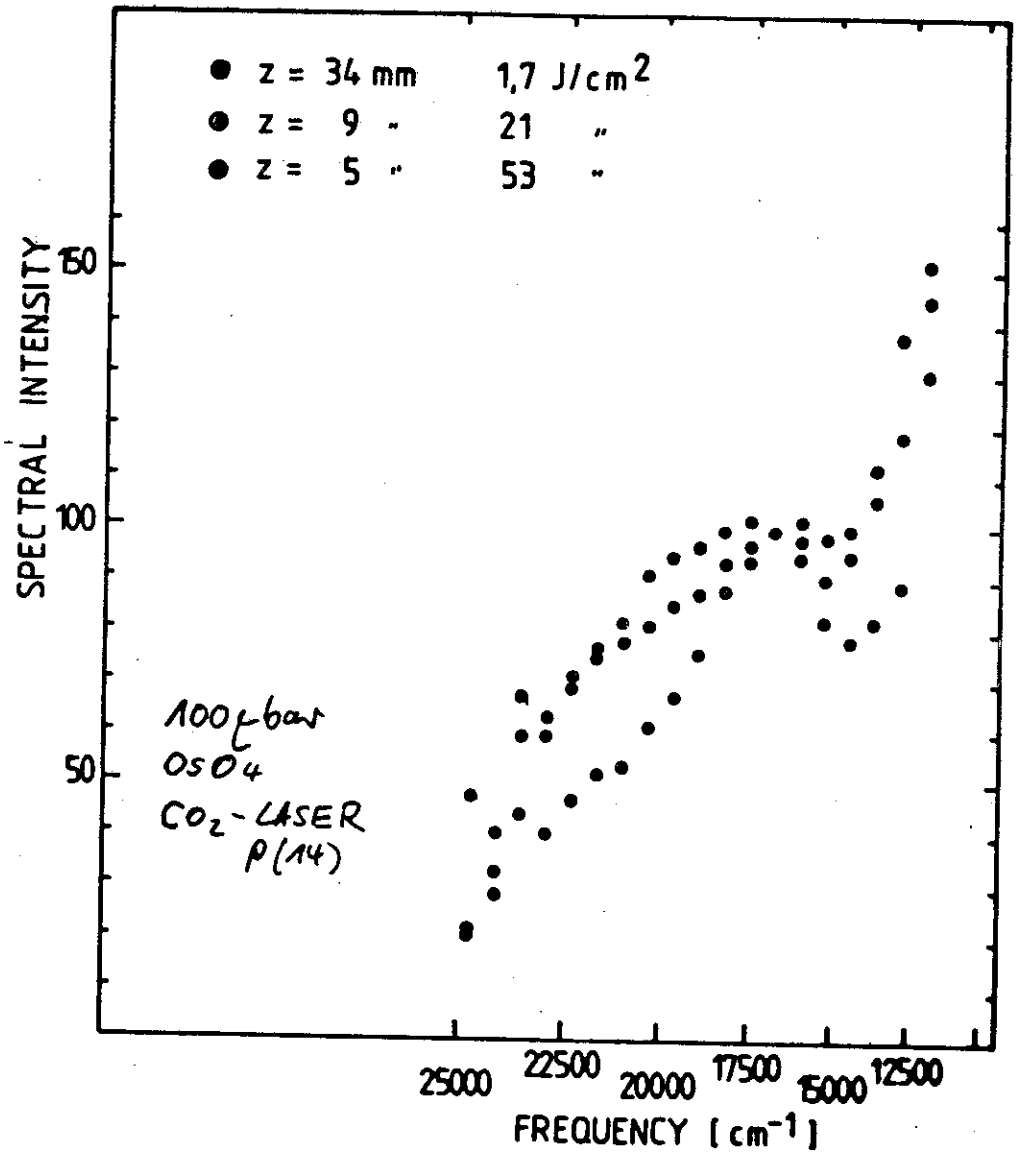




(16)

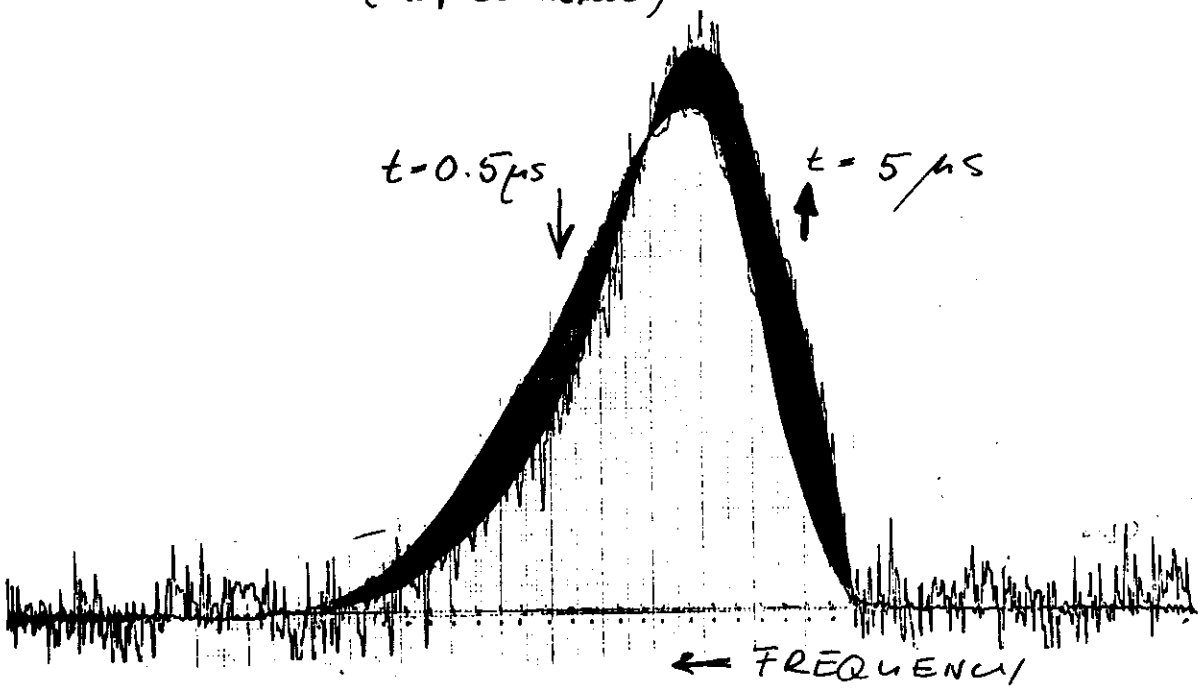


TIME INTEGRATED SPECTRA

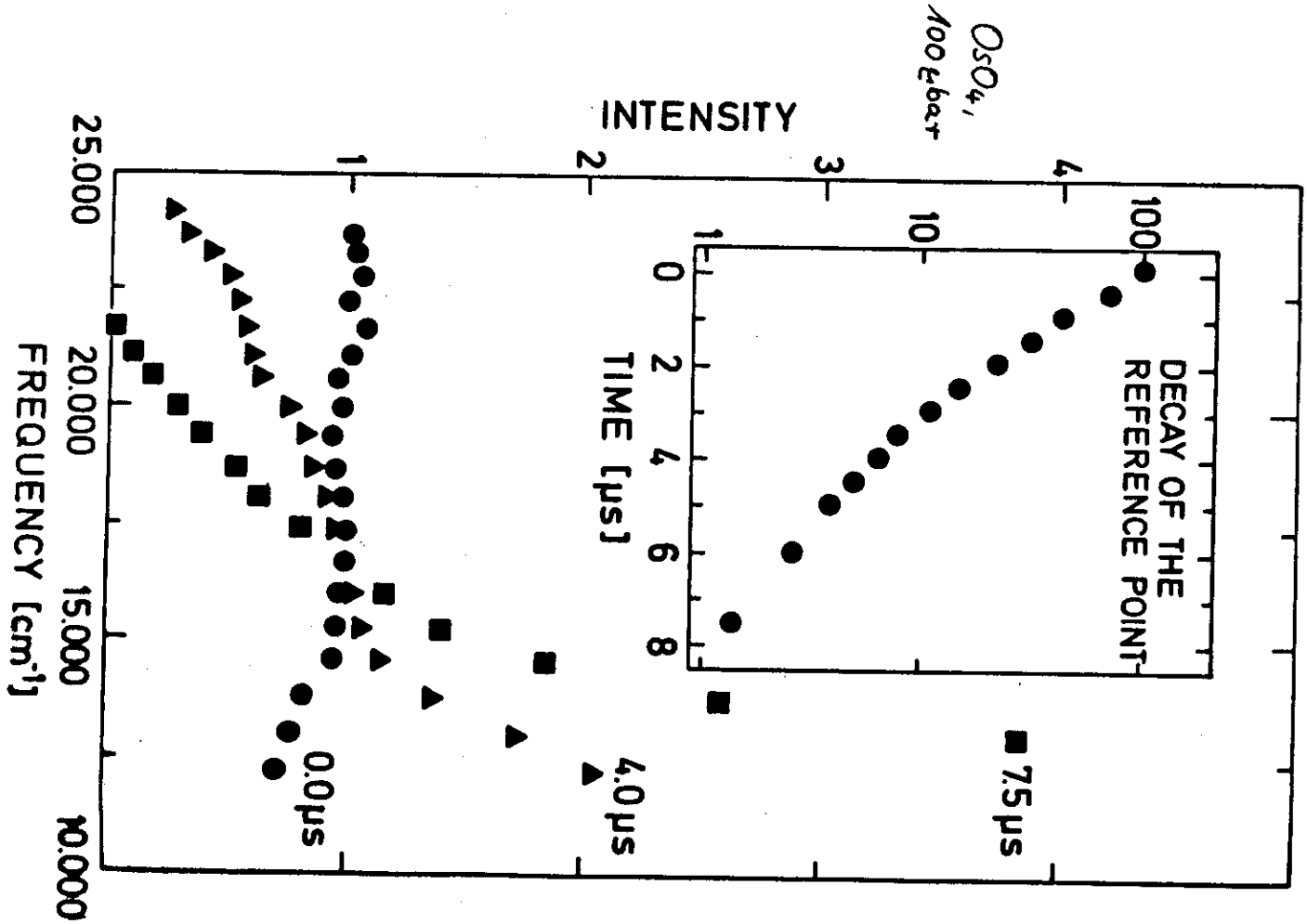


TIME EVOLUTION OF
EMISSION SPECTRA
IN THE FOCAL REGION
(not corrected)

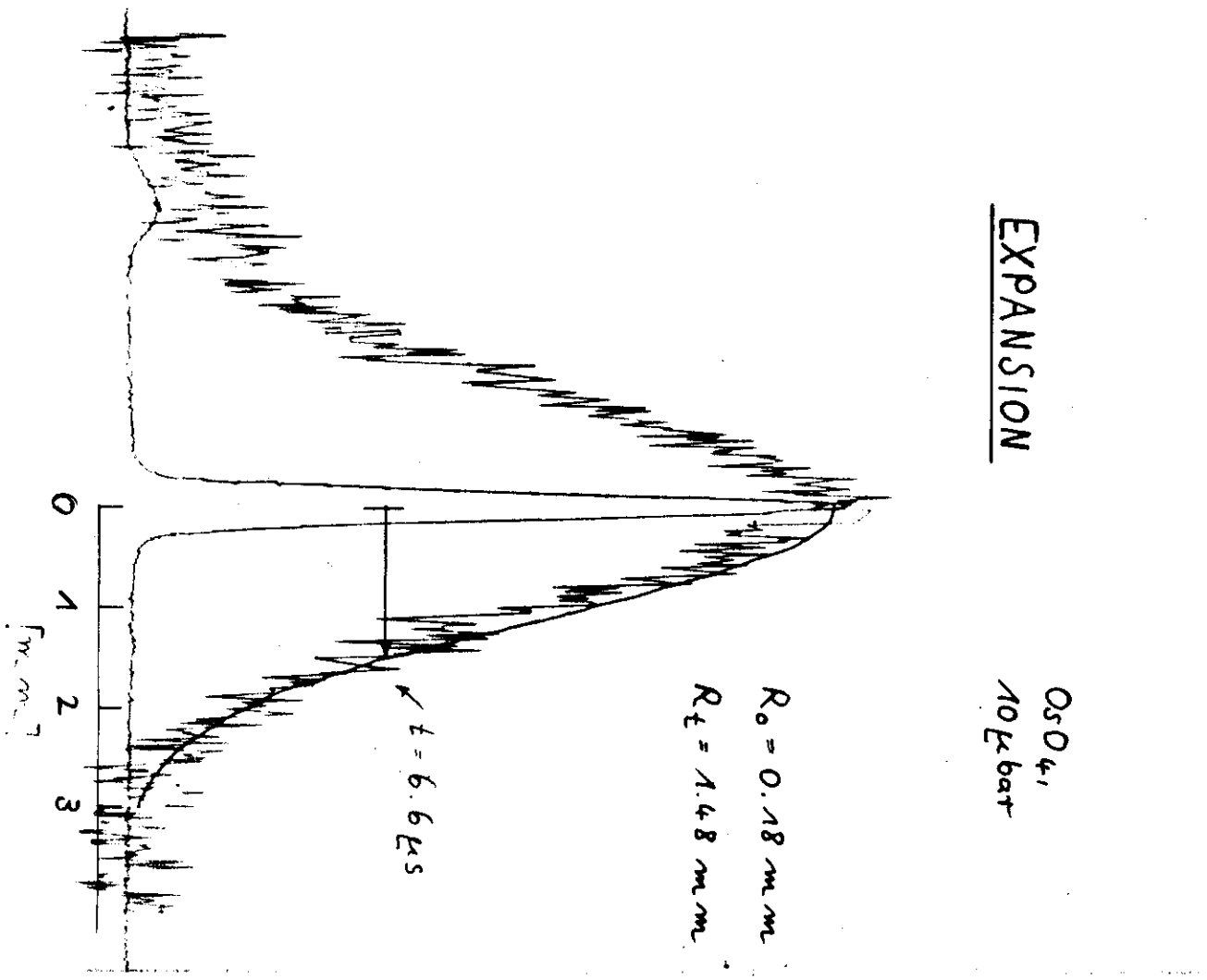
XeCl-LASER
2 mJ
100 μbar OsO_4



(19)

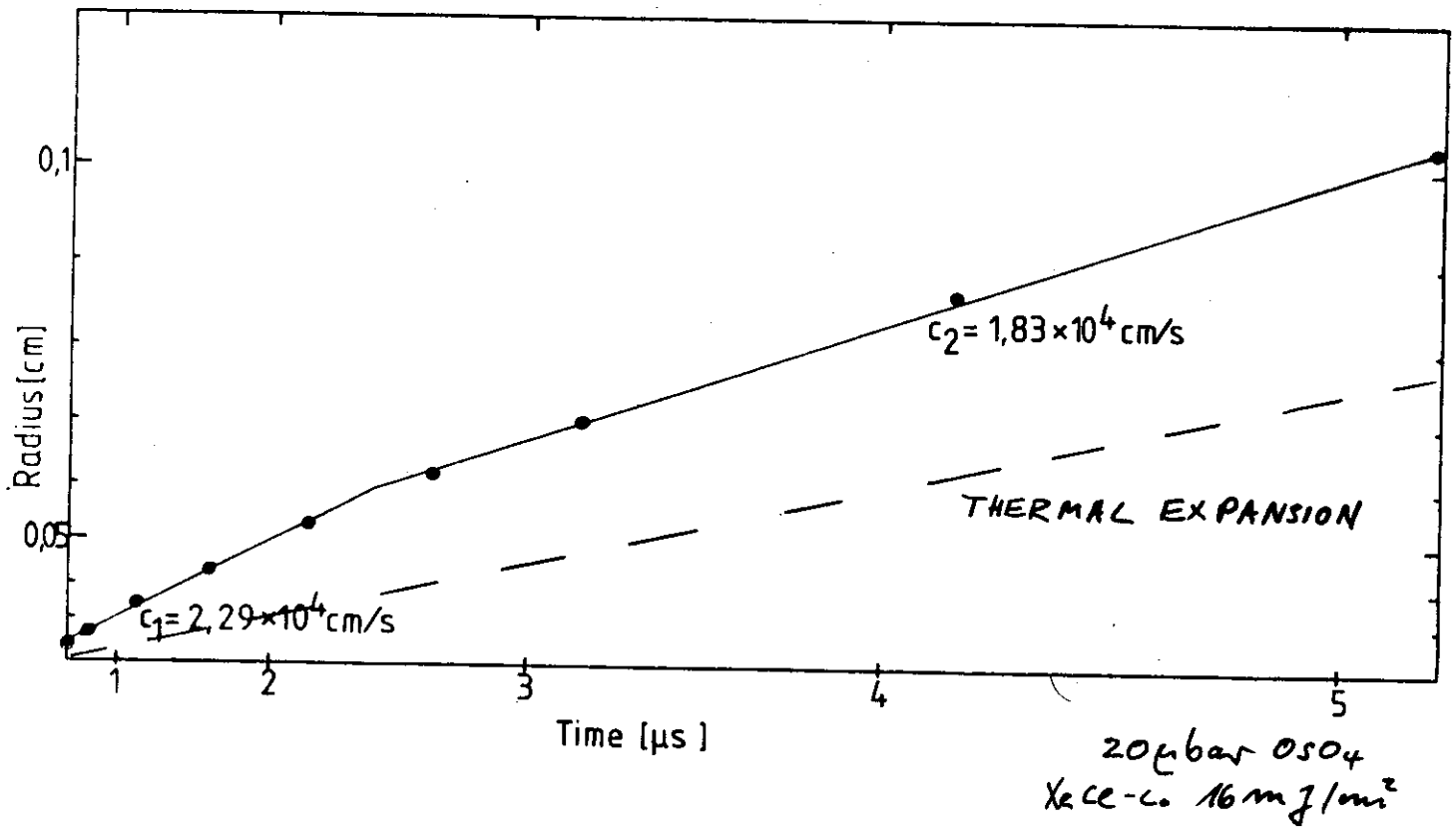


(20)

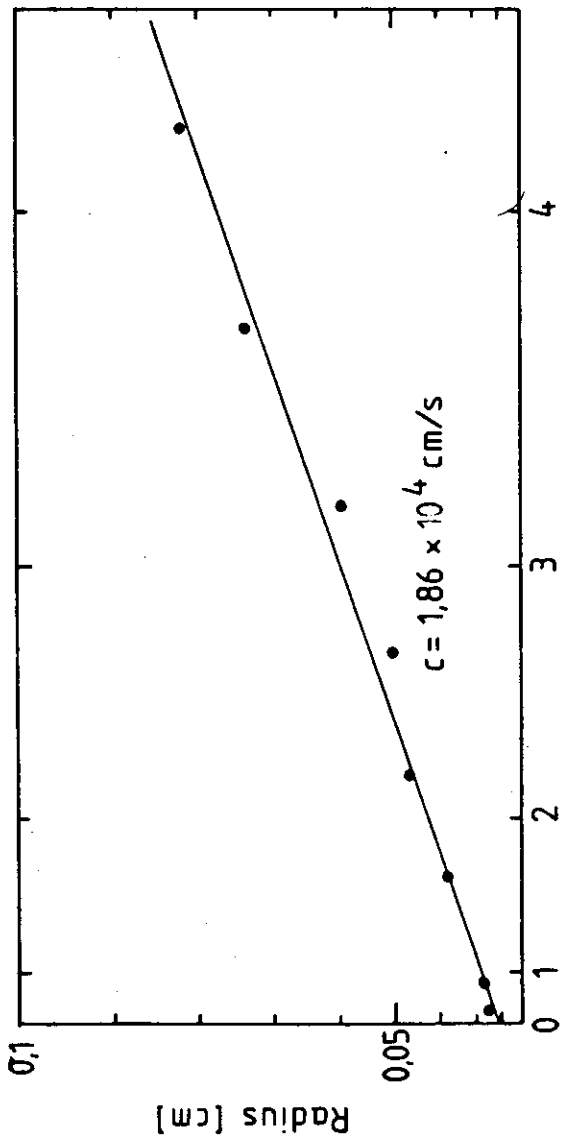


(21)

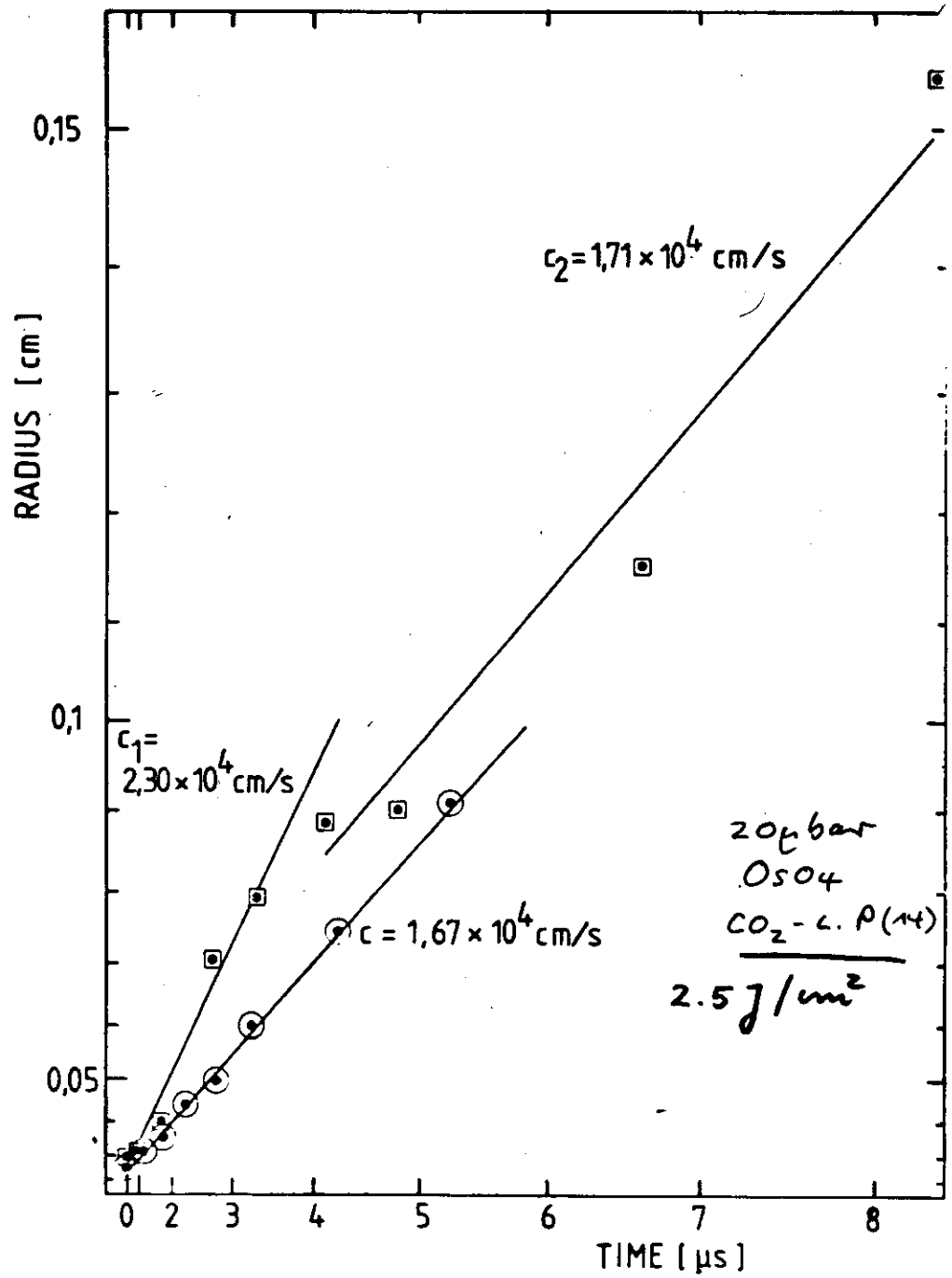
EXPANSION : $R(t)^2 = R_0^2 + c^2 t^2$; $c^2 = 2kT/m$



(22)

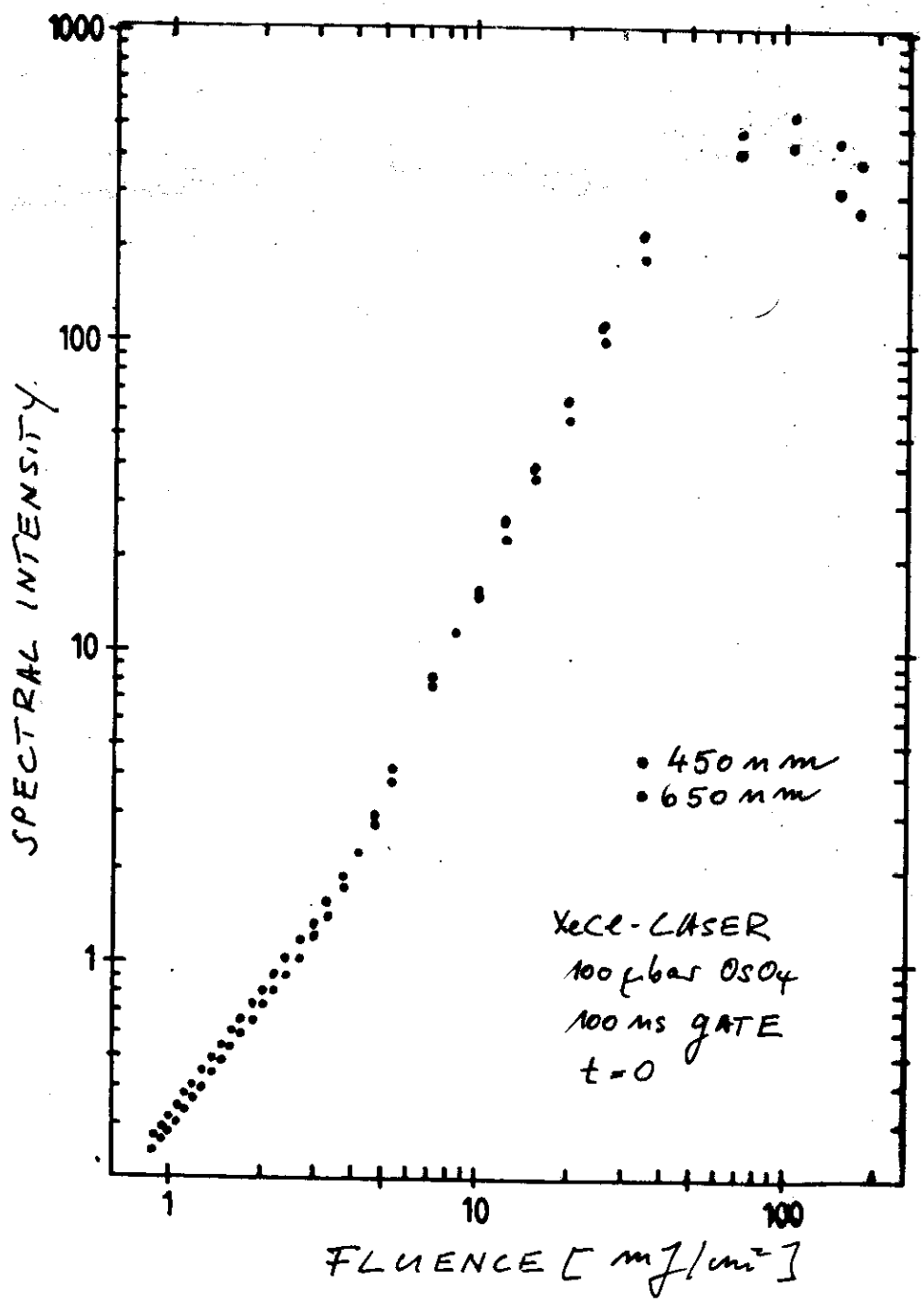


20 µbar OsO4
Xe Cl-L. 1 mJ/cm²

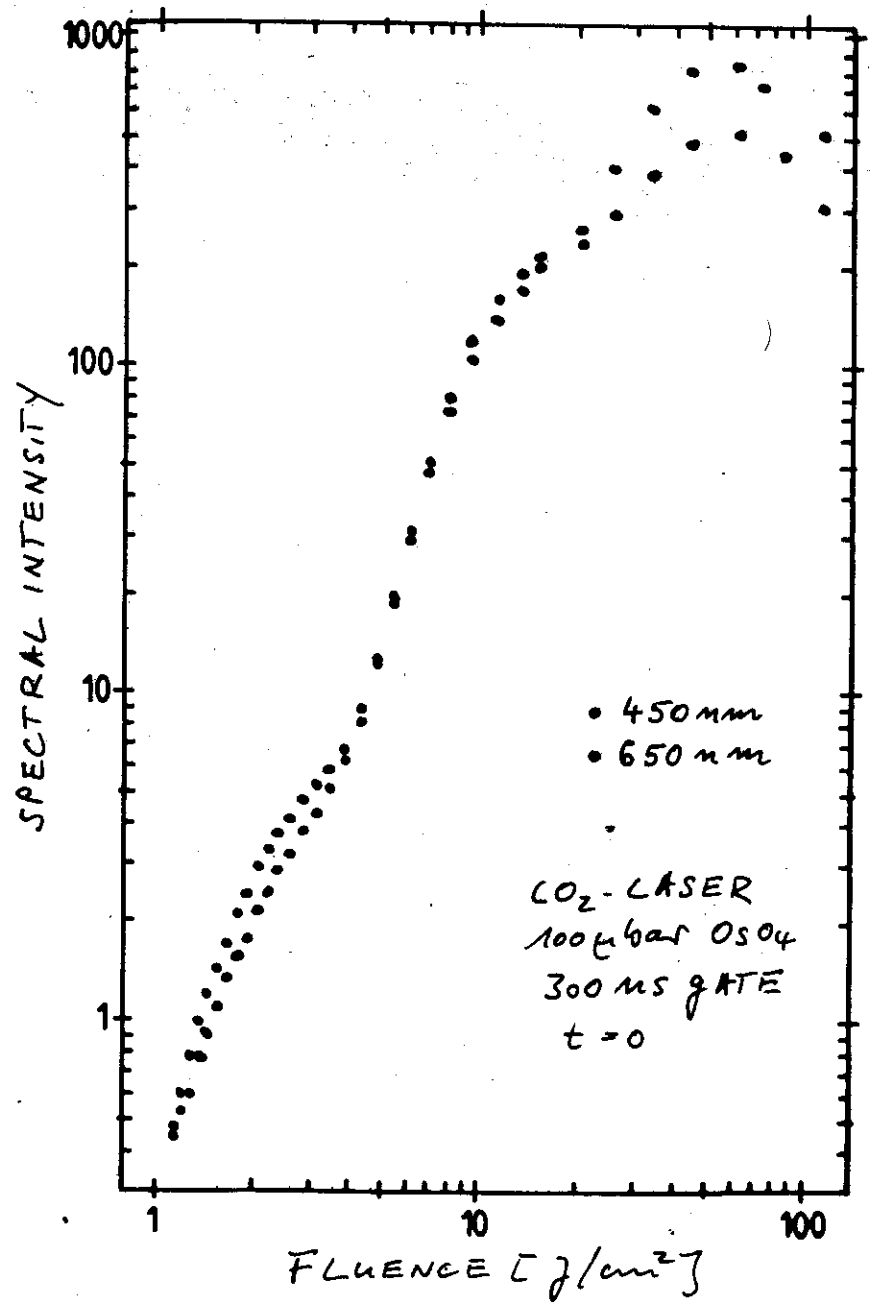


20 µbar
OsO4
CO₂ - L. P(14)
2.5 J/cm²

INITIAL FLUENCE DEPENDENCE

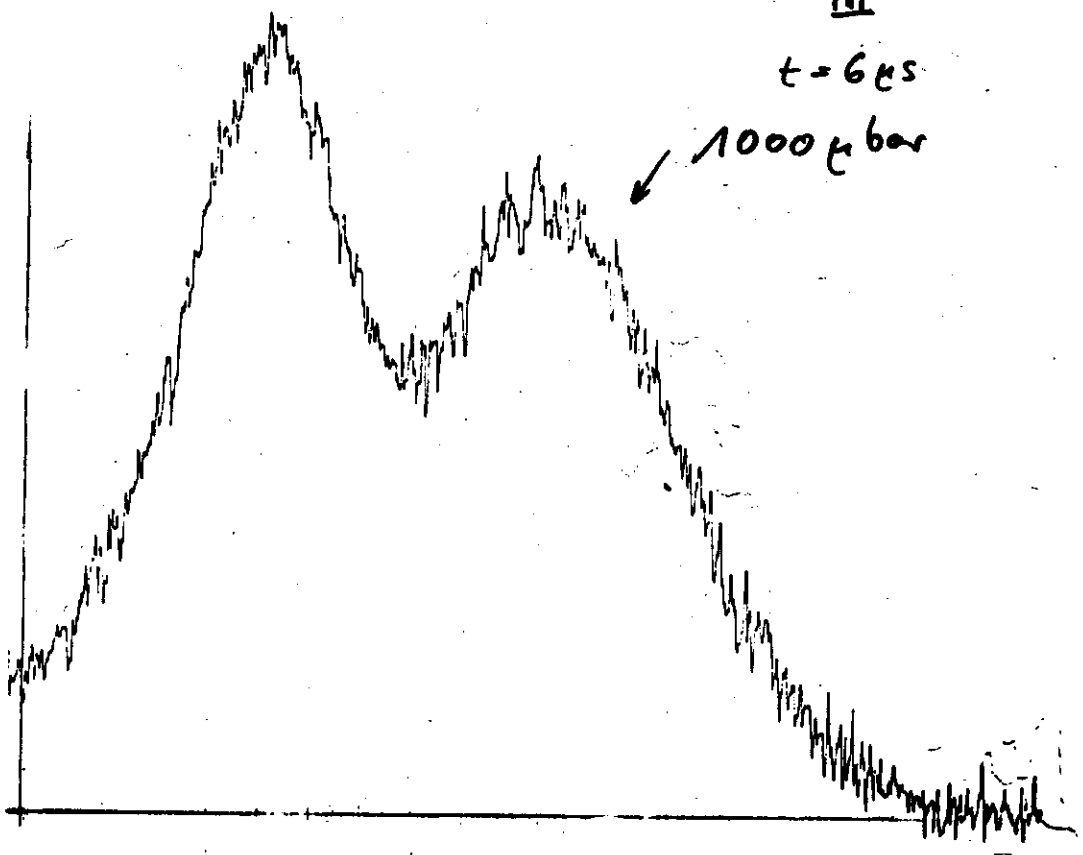


INITIAL FLUENCE DEPENDENCE



OsO4
CO2-Laser
P(14)
Ein ~ 1.2 J

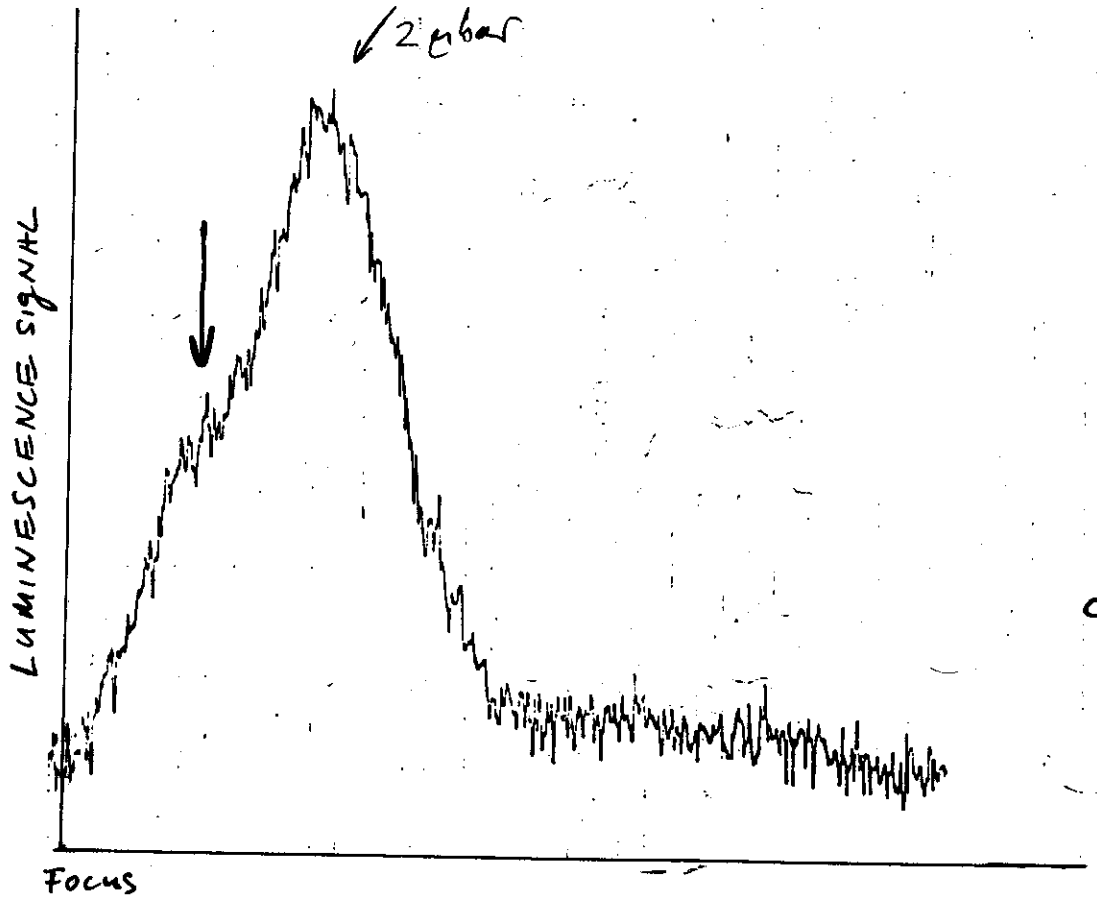
III
t = 6 µs
1000 µbar



OsO4
CO2-Laser
P(14)
Ein ~ 1.2 J

(27)

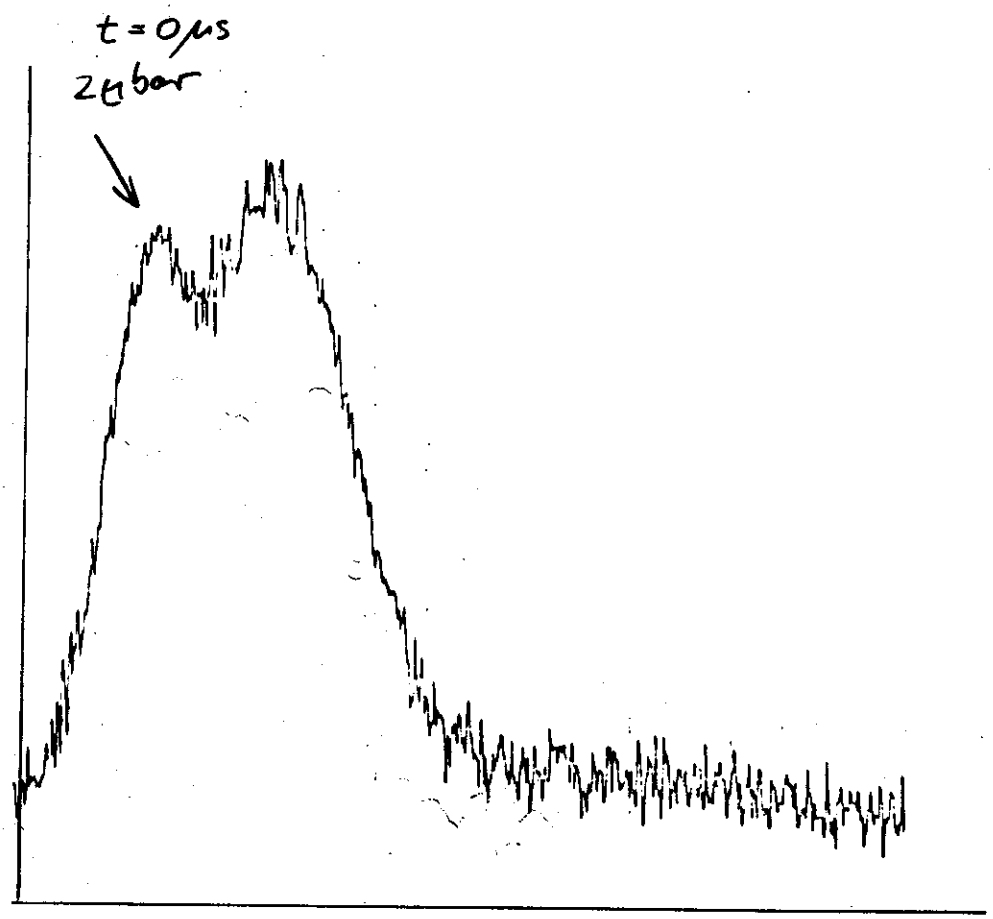
I
II
t = 5 µs
2 µbar



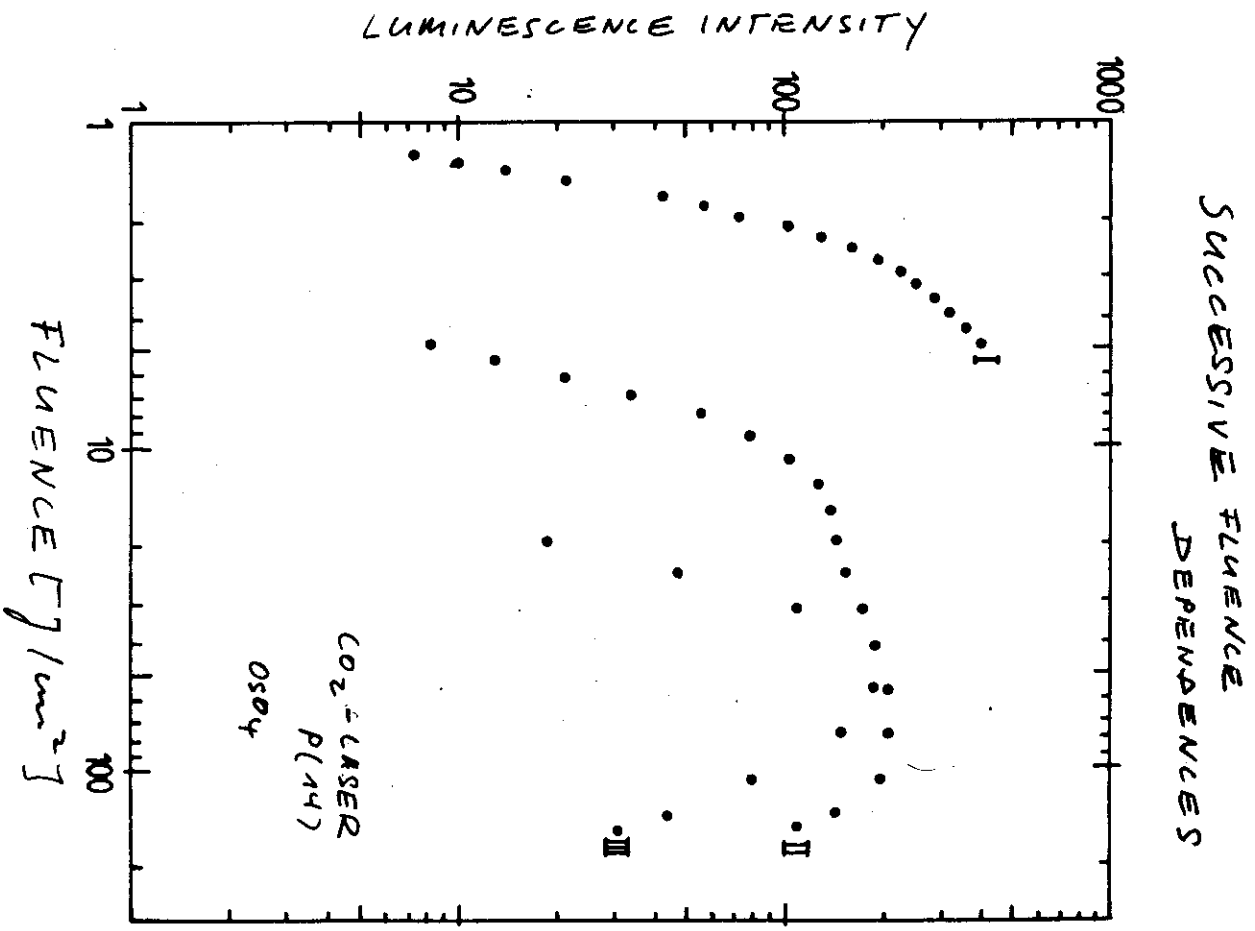
CO2-LASER

(28)

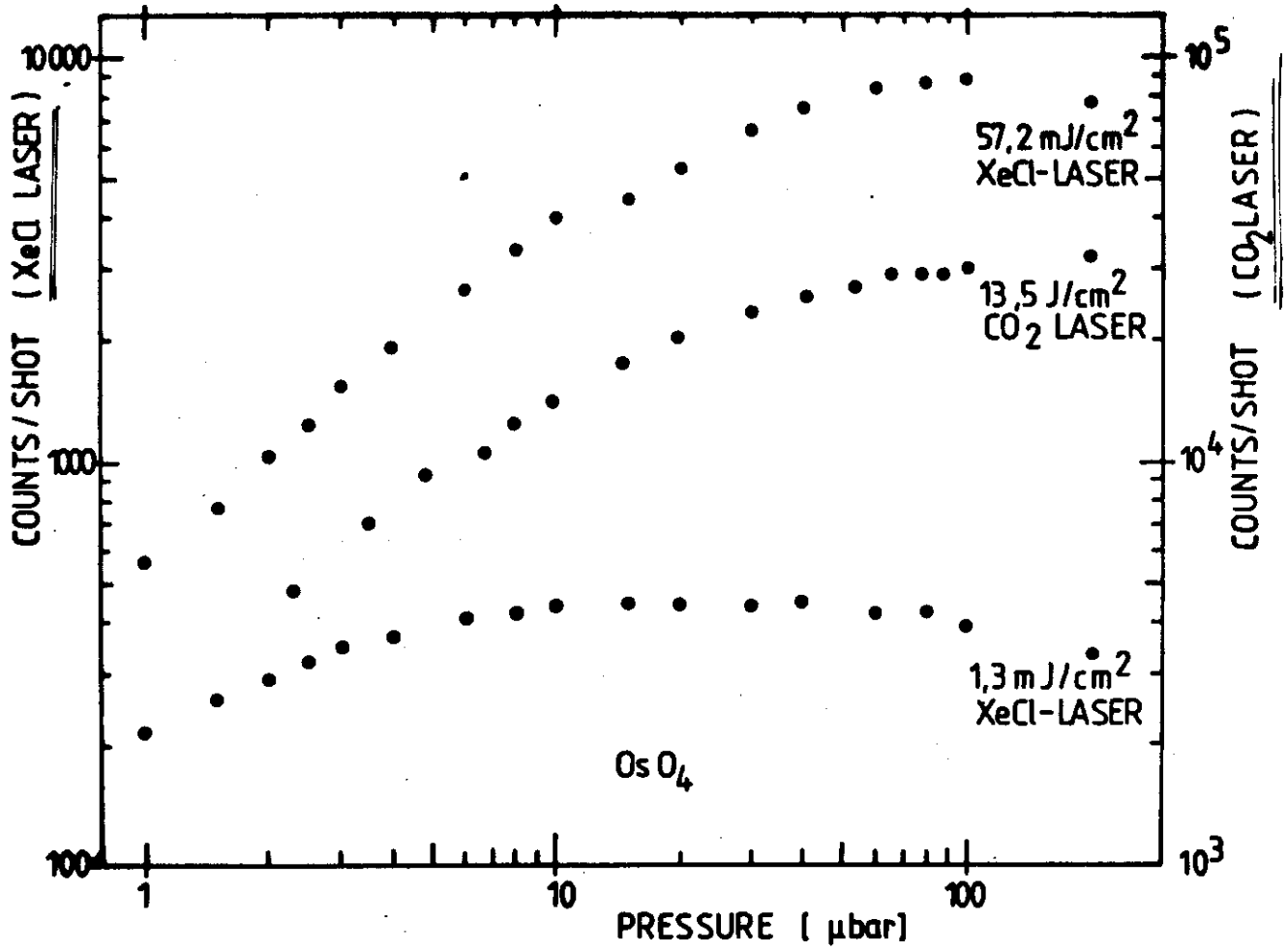
CO_2 - LASER P(14)
E ~ 1.2 J
OsO_4



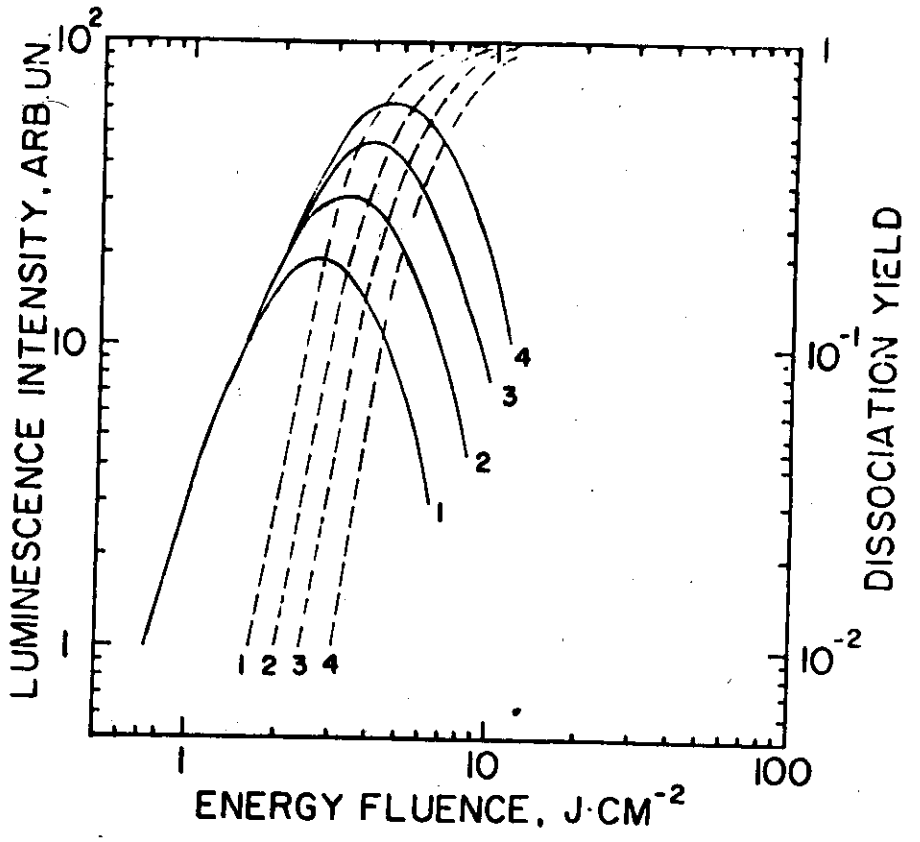
CO_2 - LASER



(32)


COUNTS/SHOT (XeCl LASER)
COUNTS/SHOT (CO2LASER)
10000
1000
100
10^5
10^4
10^3
1
10
100
PRESSURE [µbar]
57,2 mJ/cm2
XeCl-LASER
13,5 J/cm2
CO2 LASER
1,3 mJ/cm2
XeCl-LASER
OsO4

(31)


LUMINESCENCE INTENSITY, ARB.UN.
DISSOCIATION YIELD
10^2
10
1
10^-1
10^-2
1
10
100
ENERGY FLUENCE, J·CM^-2
1 2 3 4

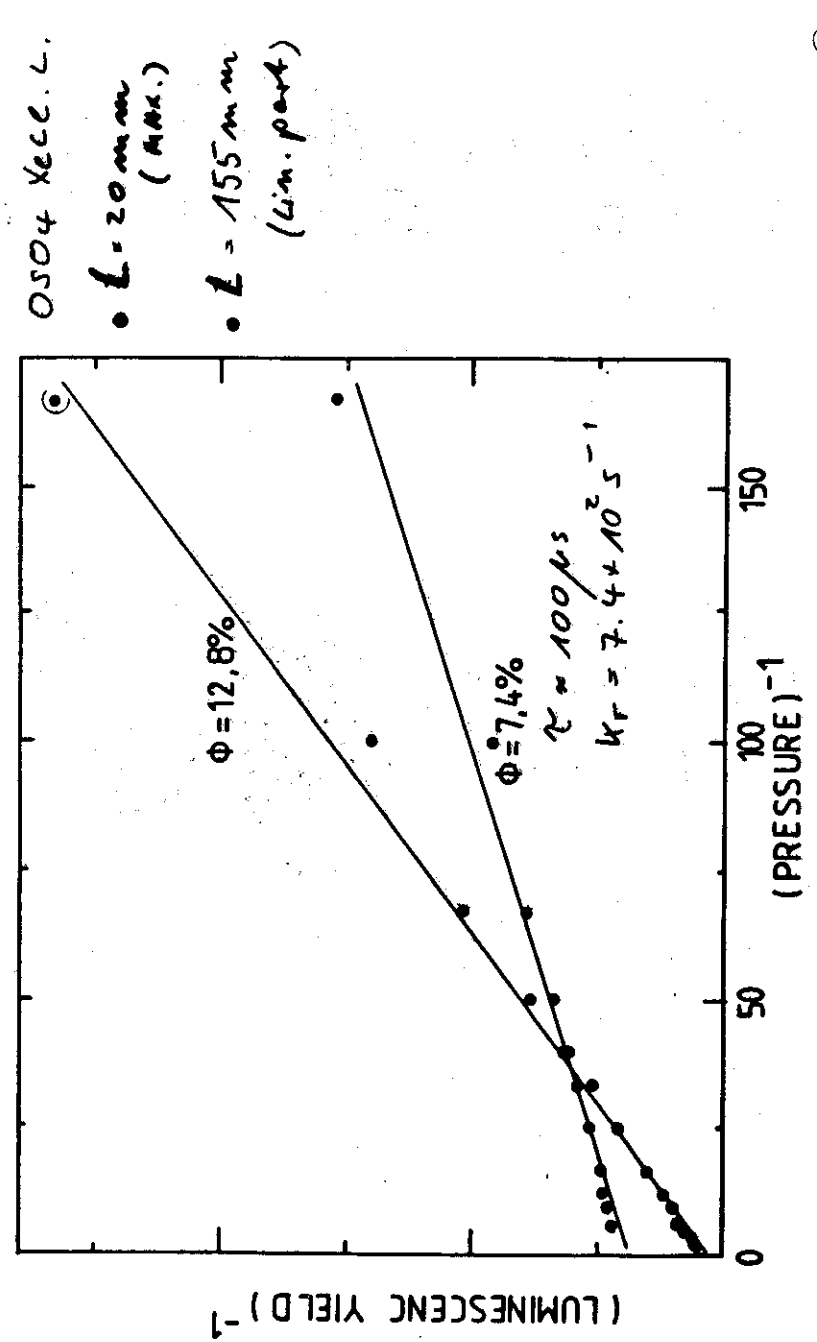
THE QUANTUM-YIELD

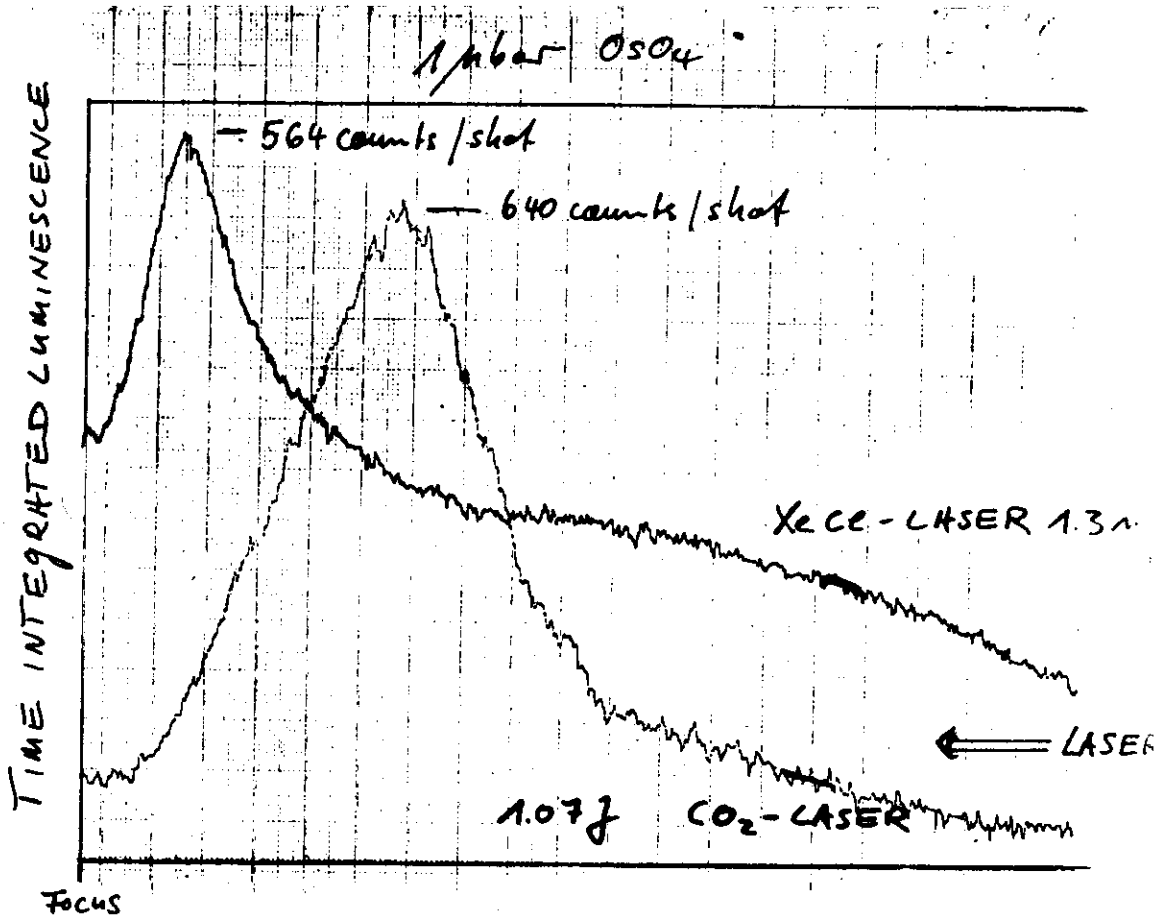
$$\frac{dF}{dt} = \left(\frac{\Omega}{\alpha}\right) k_R E_{IN} \sigma_{ax} N e^{-(k_R + k_{NR} + k_c N)t}$$

$$F = \left(\frac{\Omega}{\alpha}\right) E_{IN} \frac{\sigma_{ax} N \phi}{1 + \frac{k_c}{k_R}\phi N} \qquad \left| \begin{array}{l} \frac{1}{\tau} = k_R + k_{NR} \\ \phi = \frac{k_R}{k_R + k_{NR}} \; ; \; k_R = \phi/\tau \end{array} \right.$$

$$E_{obs.} = \left(\frac{\alpha}{\Omega}\right) F$$

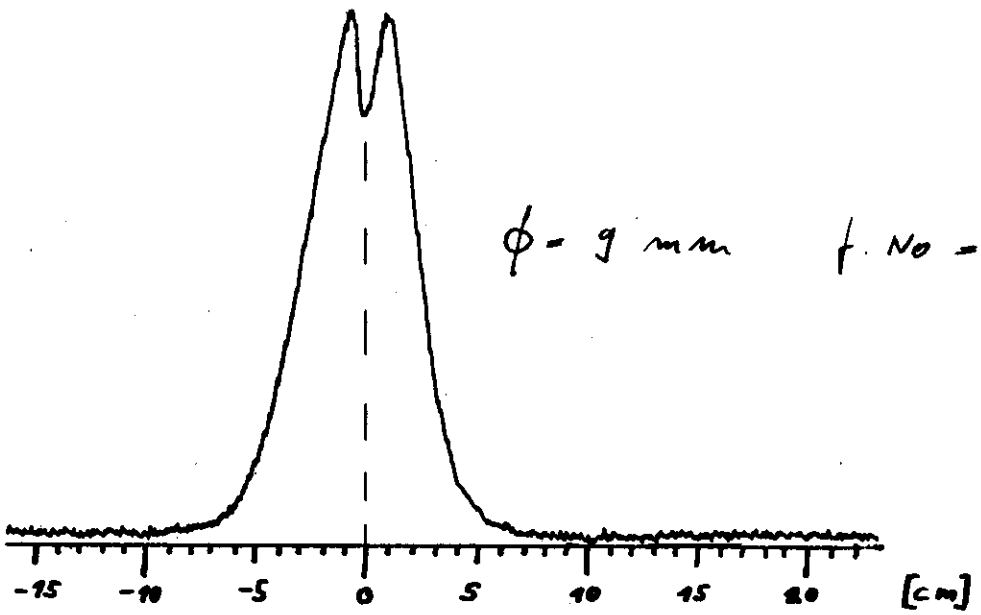
$$\frac{1}{E_{obs.}} = \left(\frac{k_c}{k_R}\right) \frac{1}{\sigma_{ax} E_{IN}} + \left(\frac{1}{\phi}\right) \frac{1}{\sigma_{ax} E_{IN}} \; \frac{1}{N}$$





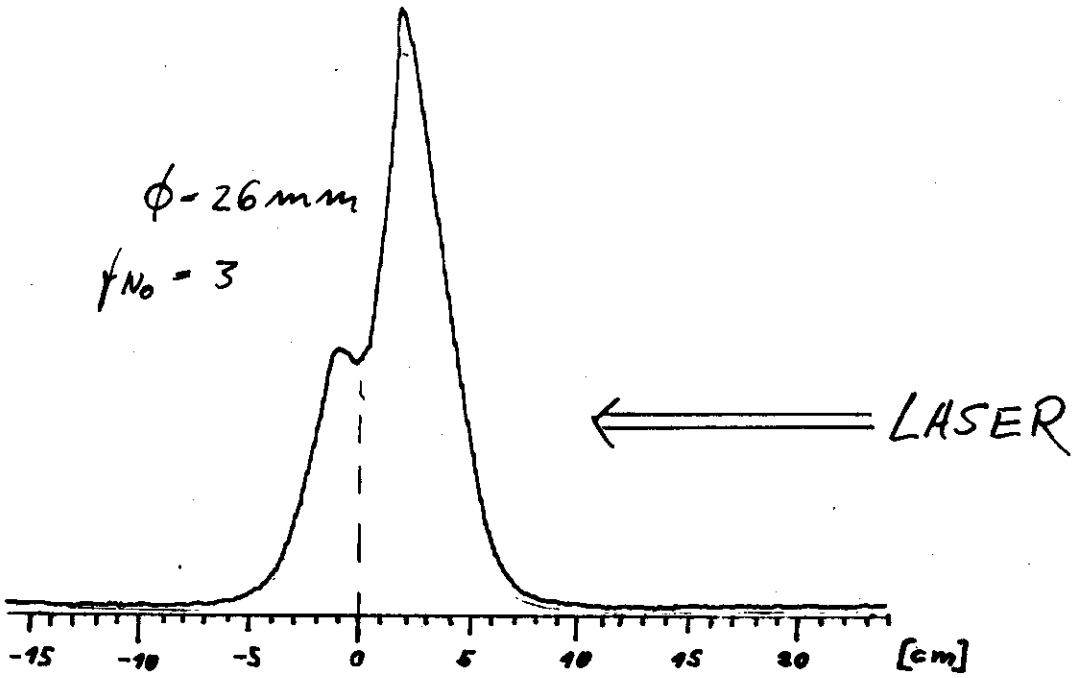
(35)

Xe Cl - Laser
100 µbar OsO_4
f_{lens} = 80 mm



(36)

Xe Cl - Laser
100 µbar OSO_4
f_{lens} = 80 mm



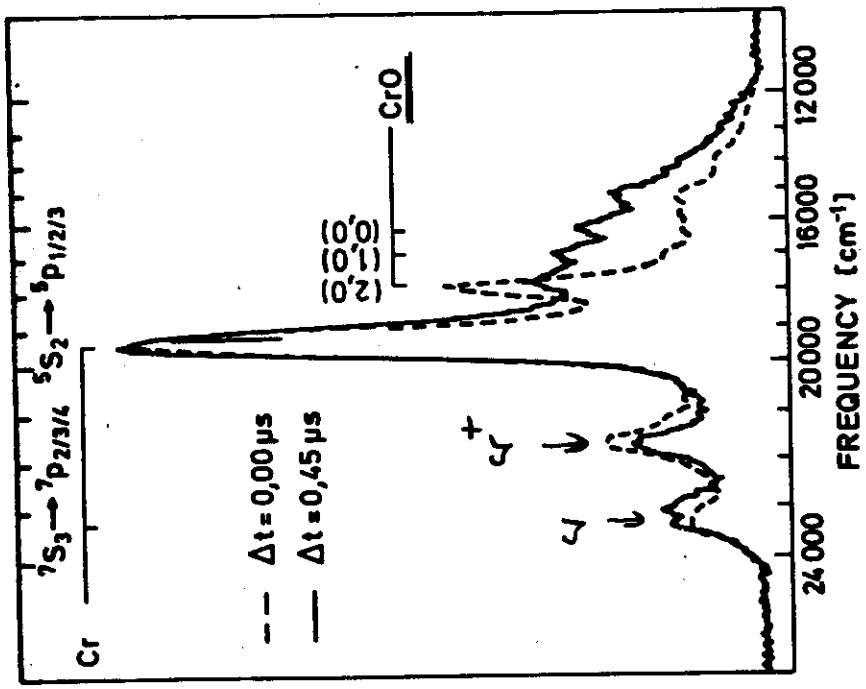
CrO_2Cl_2 / CHROMYL CHLORIDE

KrF-LASER EXCITATION

Cr - ATOMS IN EMISSION

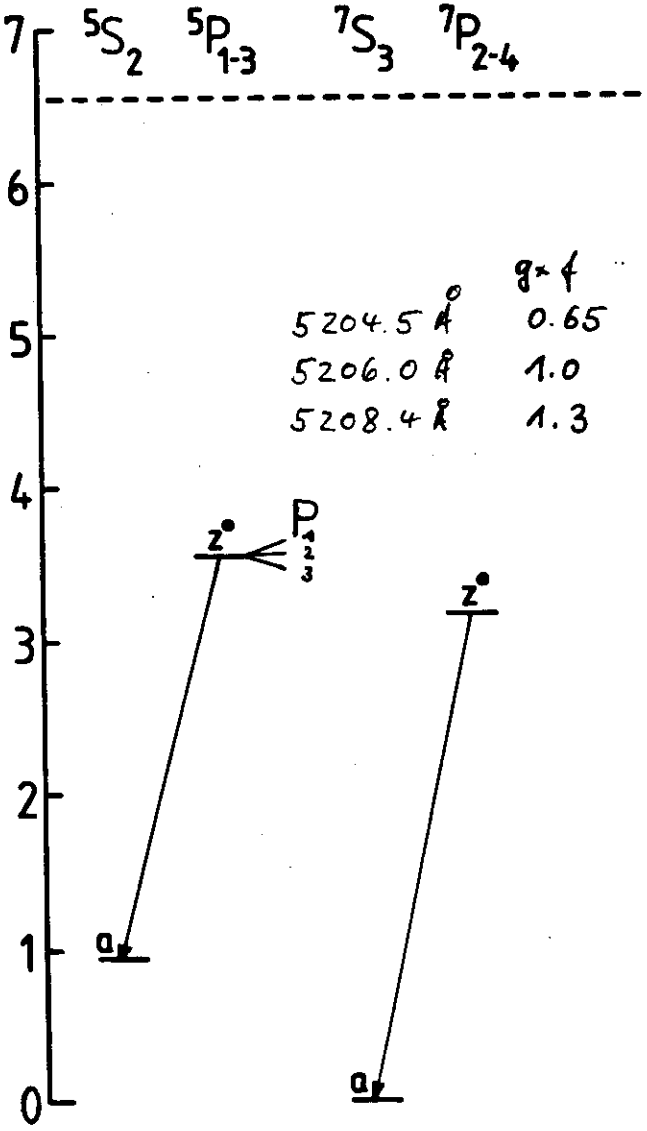
CrO_2Cl_2
100 µbar

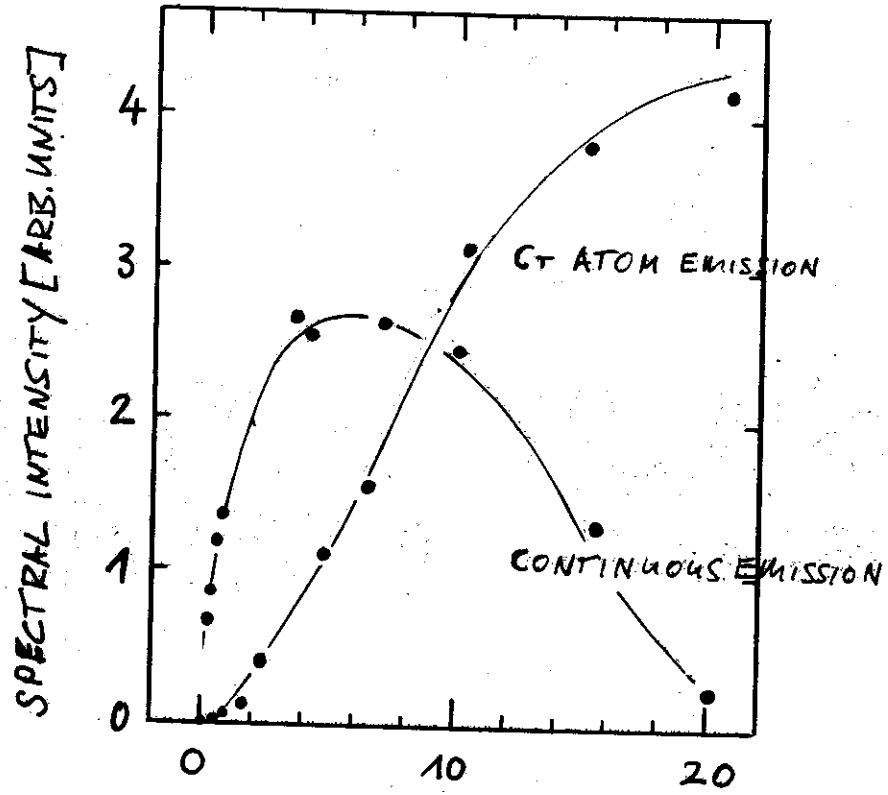
krF- LASER



SPECTRUM / CHROMIUM

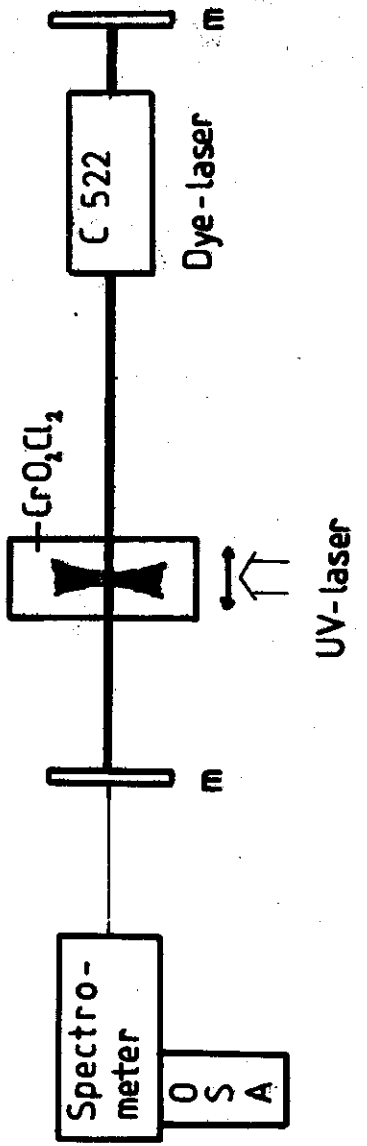
[VOLTS]

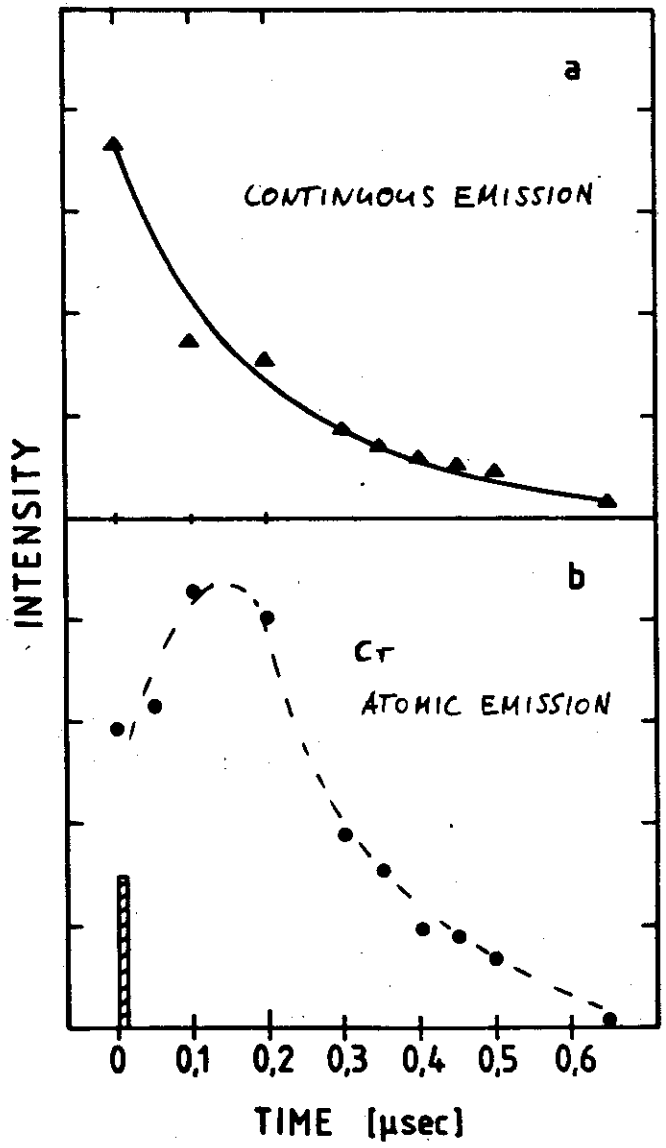




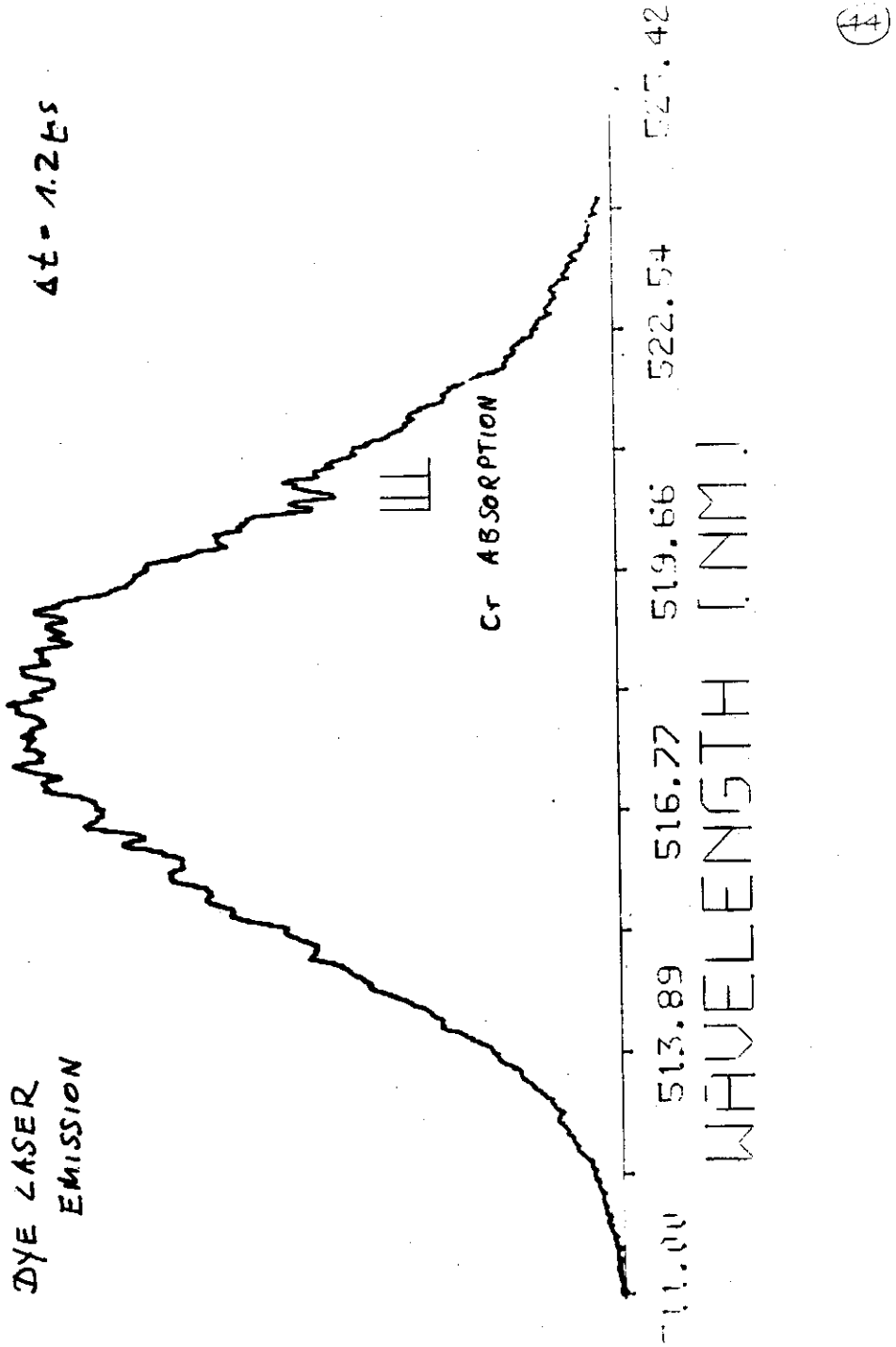
@ 100 µbar CrO_2Cl_2
TIME INTEGRATED

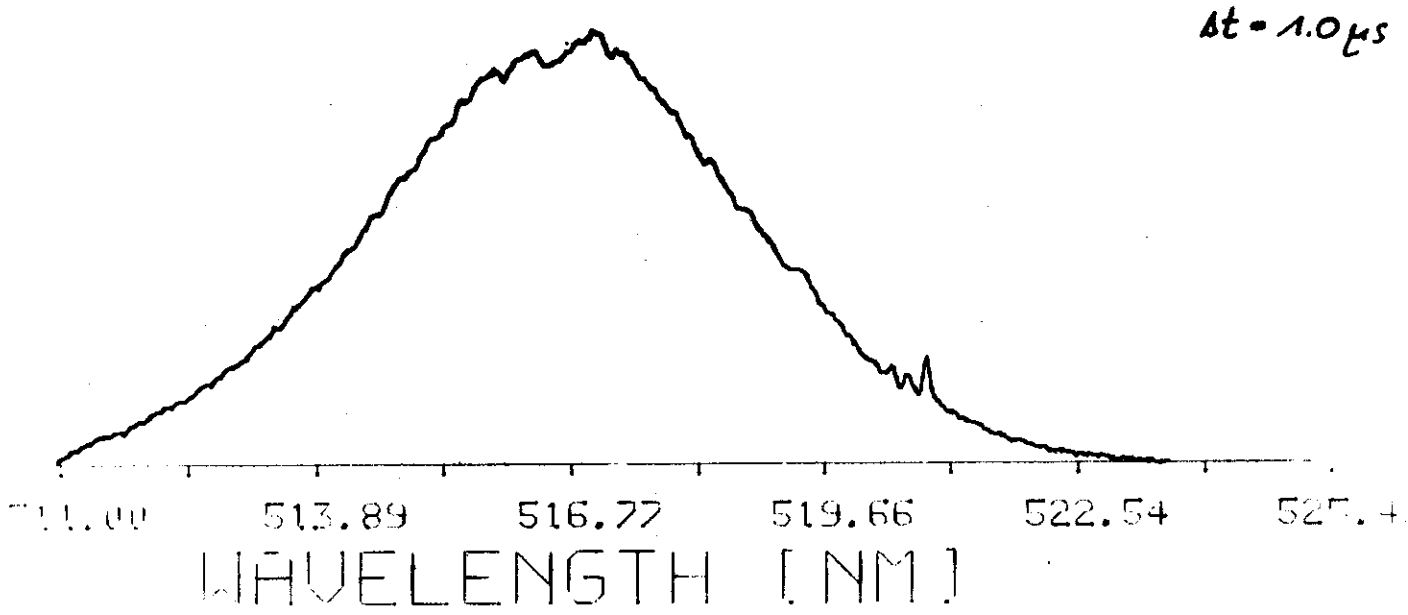
INTRACAVITY-EXPERIMENT

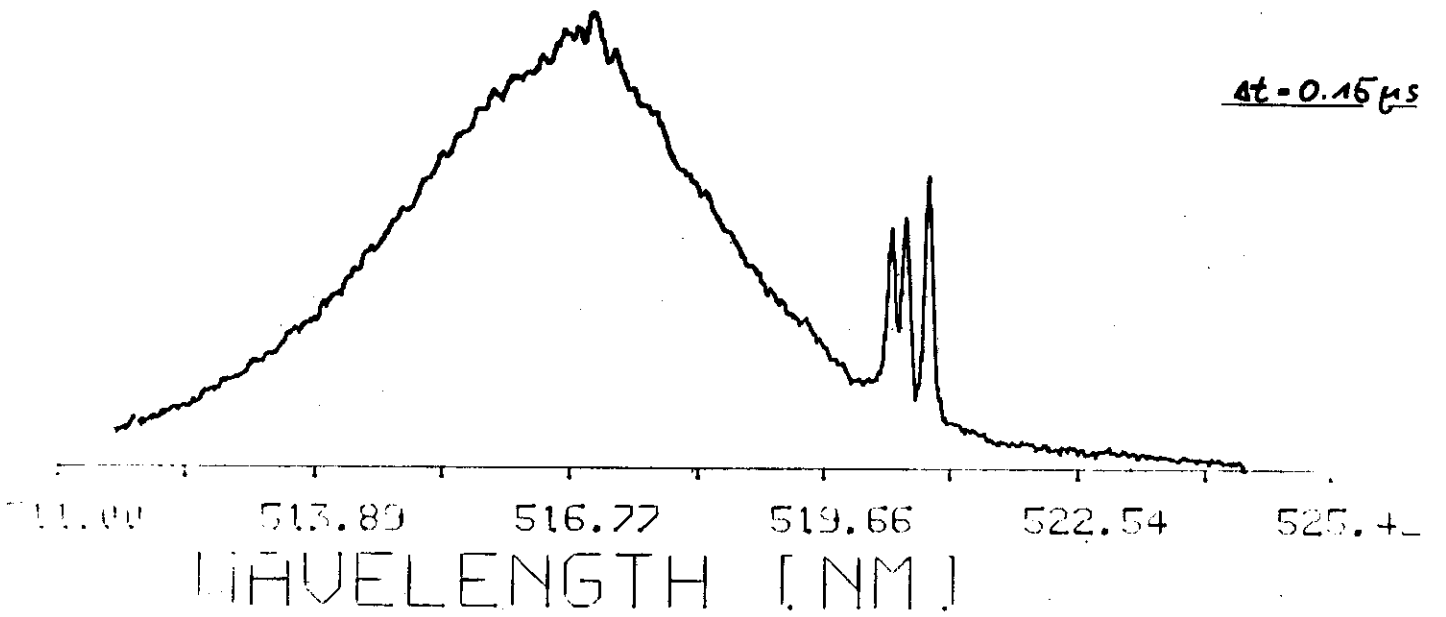


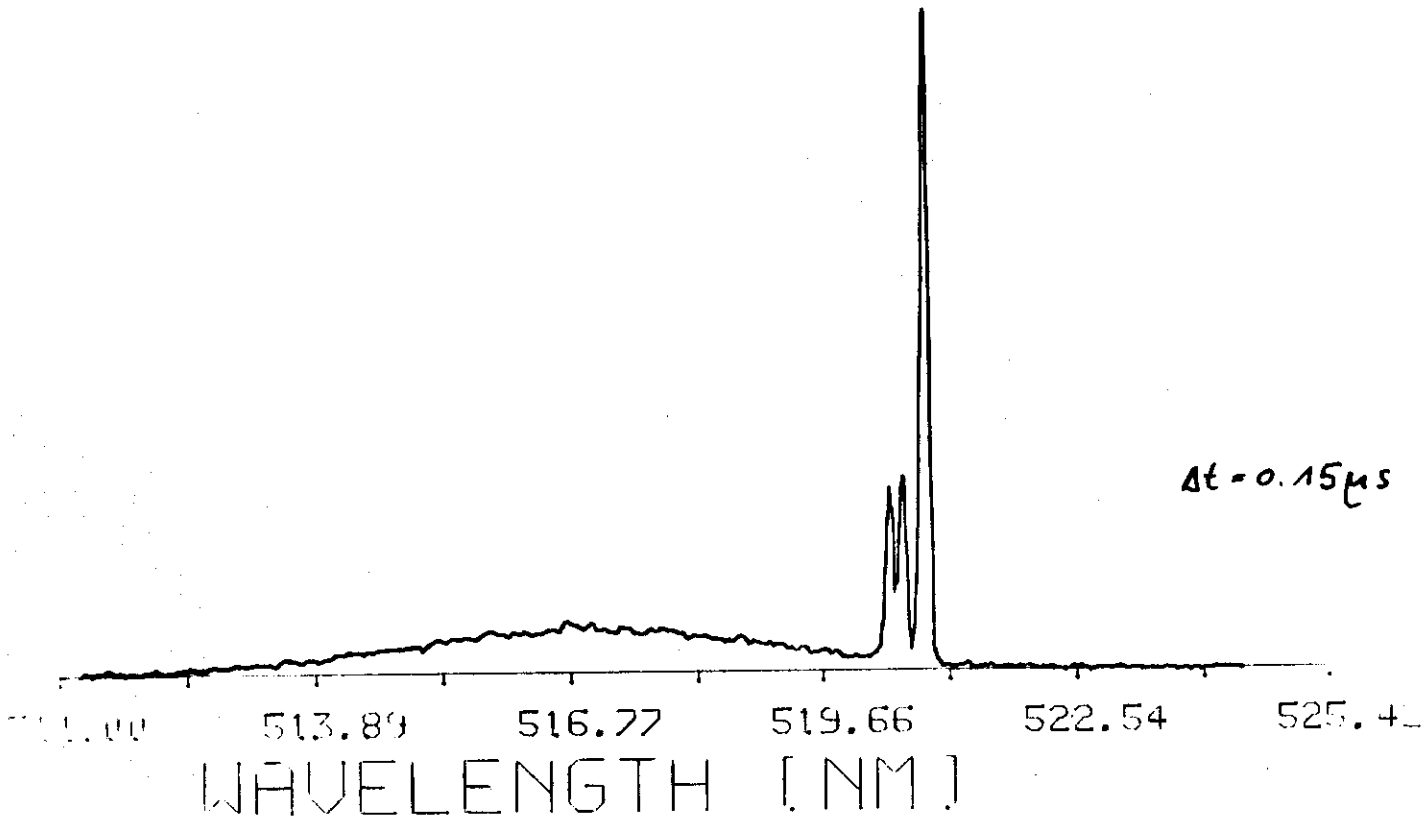


CrO_2Cl_2
100 µbar
krF-LASER

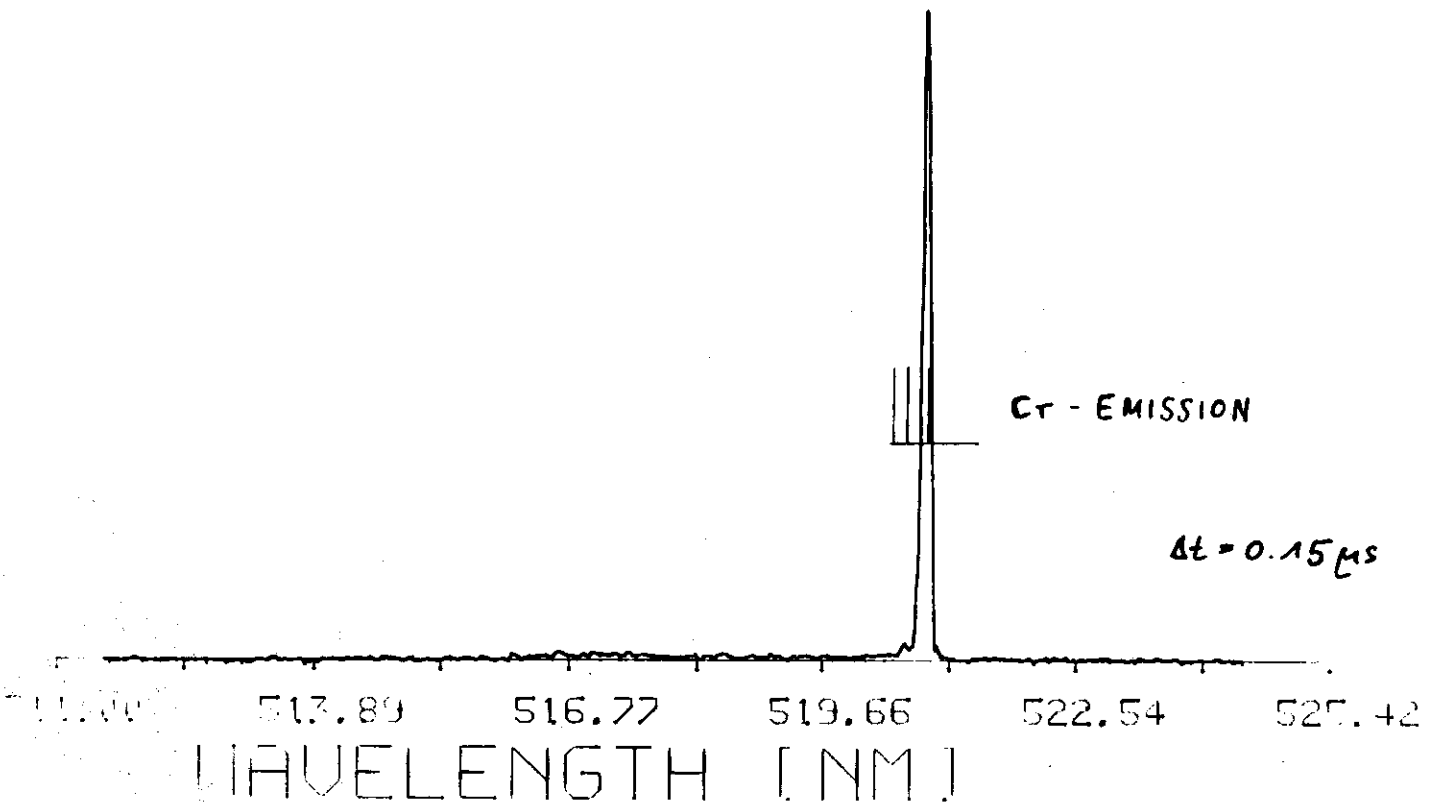



Δt = 1.0 μs
513.89
516.77
519.66
522.54
WAVELENGTH [NM]

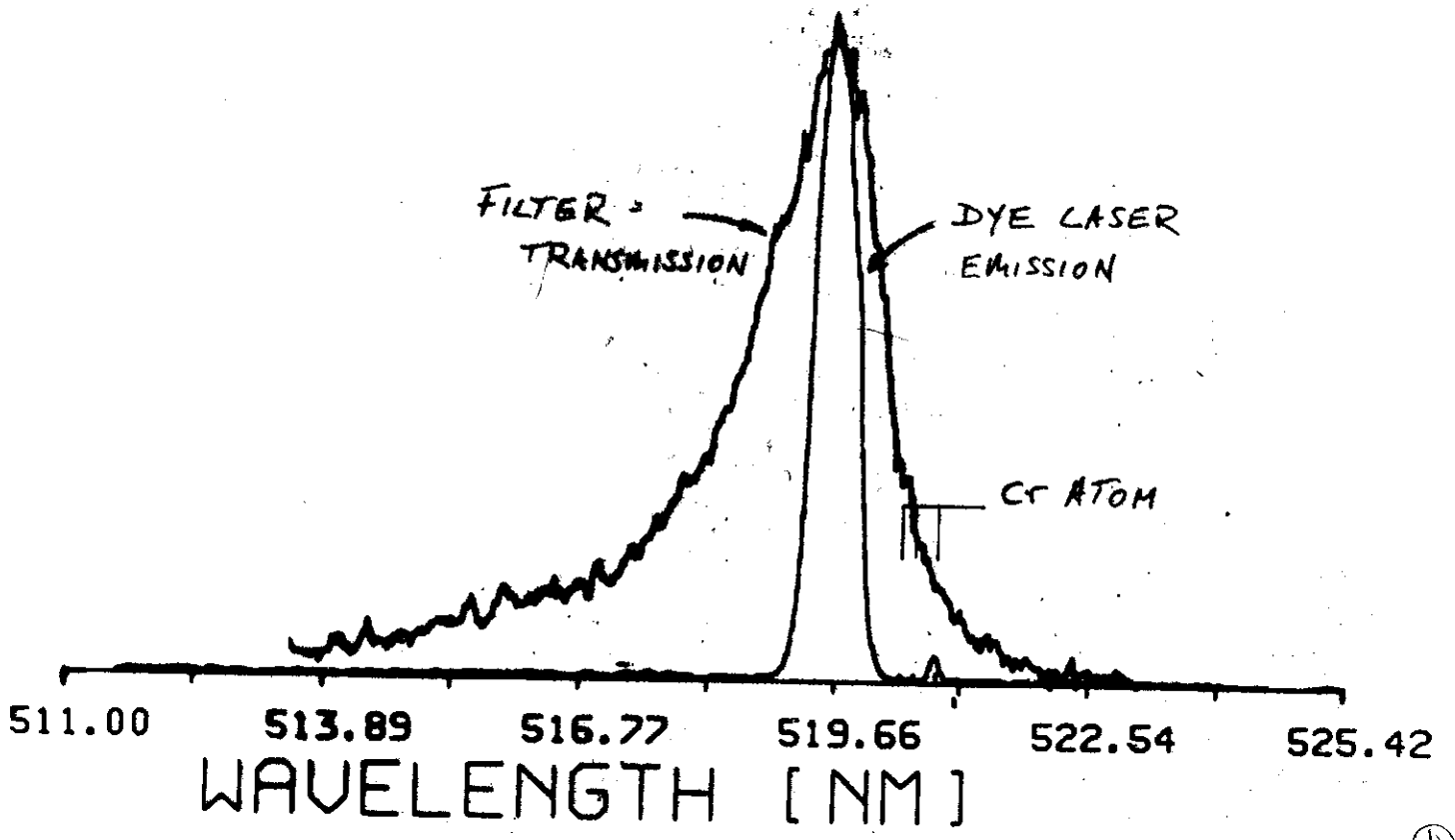

Δt = 0.15 μs
513.89
516.77
519.66
522.54
WAVELENGTH [NM]


Δt = 0.15 μs
513.89
516.77
519.66
522.54
WAVELENGTH [NM]

47


Cr - EMISSION
Δt = 0.15 μs
513.89
516.77
519.66
522.54
WAVELENGTH [NM]

48



Possible mechanisms:

I $CrO_2Cl_2 + h\nu \rightarrow CrO_2^+ + Cl_2$

II $CrO_2^+ + CrO_2^+ \rightarrow Cr^* + O_2 + CrO_2$

$\rightarrow CrO^* + O + CrO_2$

new electronically excited states

UV, VIS, IR multiphoton excitation
dissociation, ionization
yields at different light frequencies

- - — — —

collisional deactivation
mass transport in diluent gases

electronic chemiluminescence
chemi-ionization

- - - - — - - — --

in general all flame reactions
are a very fast time-scale