INTERNATIONAL ATOMIC ENERGY AGENCY
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WINTER COLLEGE ON

ATOMIC AND MOLECULAR PHYSICS

(9 March - 3 April 1987)

PHOTOTHERMAL LASER SPECTROSCOPY

(TRANSPARENCIES)

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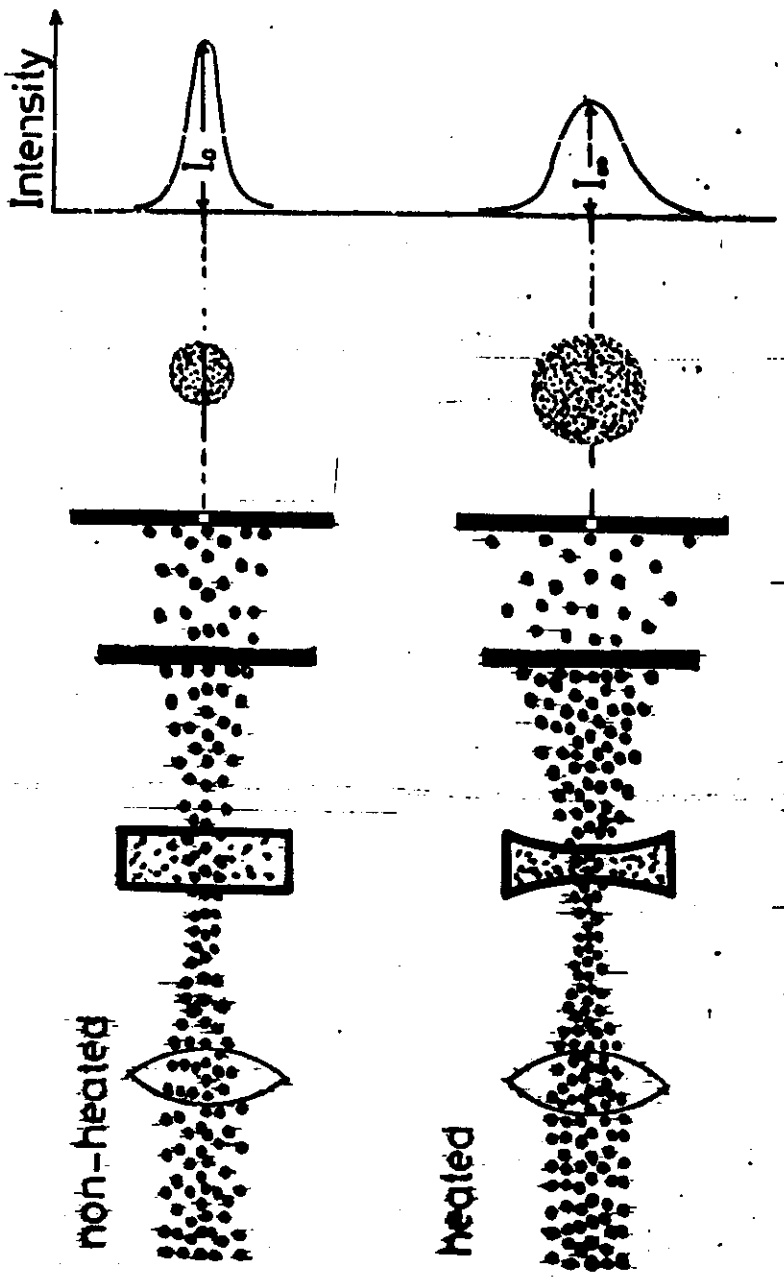
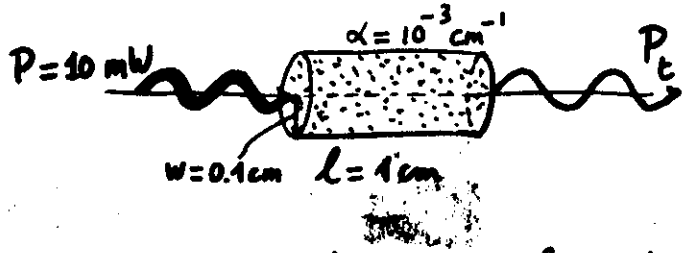
IX.

☆ Photothermal Laser Spectroscopy



Schematic of thermal lens effect

PHOTOTHERMAL EFFECT



$P_{abs} \cong P\alpha l$

- Energy Deposited $\Rightarrow P\alpha l$ $\quad Js^{-1}cm^{-1}cm \Rightarrow \frac{Js^{-1}}{4.18\ J/cal} \rightarrow \frac{cal}{s}$

$$\frac{dQ_{in}}{dt} = 2.39 \times 10^{-6}\ cal\,s^{-1}$$

- $\dfrac{dQ_{in}}{dT} = m C_p = \rho V C_p = \rho \pi w^2 l C_p$ — assuming all energy absorbed is given up as heat

(C_p: specific heat, $cal\,g^{-1}K^{-1}$; ρ: density, g/cm^3)

$$\Downarrow$$

$$\frac{dT}{dt} = \frac{dQ_{in}}{4.18\,\pi w^2 l \rho C_p} \Rightarrow K s^{-1}$$

- Example : BENZENE $\Rightarrow$ $\rho = 0.88\ g\,cm^{-3}$, $C_p = 0.41\ cal\,g^{-1}K^{-1}$ $\Rightarrow \frac{dT}{dt} = 2.1 \times 10^{-4}\ K s^{-1}$

- $\dfrac{dQ_{out}}{dt} = (k)(2\pi w l)(\Delta T)/b$ — heat dissipation by conduction

(k: thermal conductivity, $cal\,s^{-1}cm^{-1}K^{-1}$ (benzene : $3.41 \times 10^{-4}\ cal\,s^{-1}cm^{-1}K^{-1}$); b: thickness of material, cm)

At equilibrium

$$\frac{dQ_{in}}{dt} = \frac{dQ_{out}}{dt}$$

$$\Downarrow$$

$$\frac{dQ_{in}}{dt} = (k)(2\pi w l)\frac{\Delta T}{b}$$

$$\Downarrow$$

$$\frac{\Delta T}{b} = 1.11 \times 10^{-2}\ K\ cm^{-1}$$

if beam is gaussian, then $b \approx w$

$$\Downarrow$$

Difference in T between sample illuminated and non illuminated $\Delta T \simeq 1.11 \times 10^{-3}\ K$

- $\Delta T = \frac{dT}{dt} \cdot \Delta t \Rightarrow \Delta t = \frac{w^2 \rho C_p}{2k}$

Response Time of the system → time necessary to reach equilibrium

→ For benzene, using values given above, equilibrium should be reached after ~ 5 seconds.

- $k/\rho C_p \equiv D$ = coefficient of thermal diffusion $(cm^2 s^{-1})$

HOW IS THE EFFECT MEASURED ?

In our case, by creating a distribution of values of index of refraction in the medium, which is then interrogated optically.

$$\downarrow$$

$$\frac{dn}{dT} = \left(\frac{\partial n}{\partial \rho}\right)\left(\frac{\partial \rho}{\partial T}\right) + \left(\frac{\partial n}{\partial T}\right)_{\rho}$$

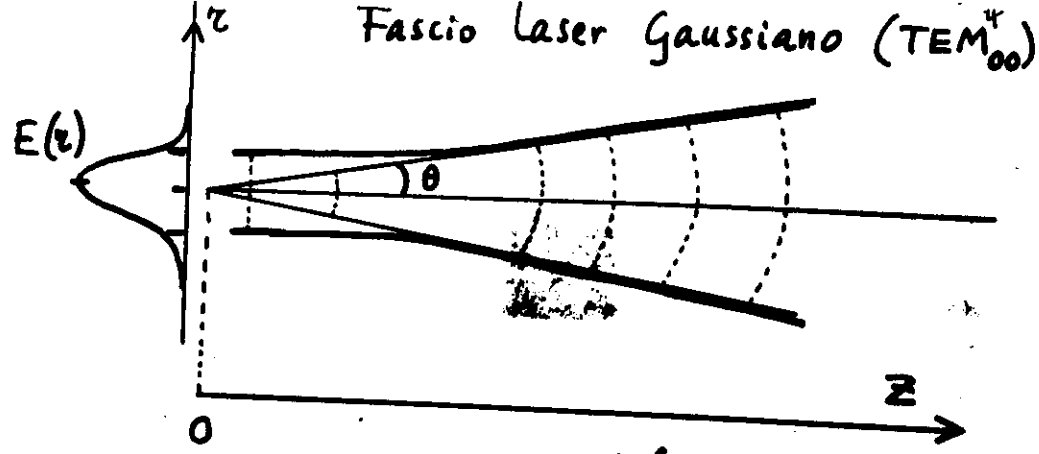
The variation of n is mainly due to density variations. Since the majority of liquids expand when heated, $\frac{\partial n}{\partial T}$ is negative.

- For benzene $\frac{dn}{dT} = -3.9 \times 10^{-4}\ K^{-1}$

$$\Downarrow$$

$$\Delta n = \left(\frac{dn}{dT}\right)\Delta T = -4.3 \times 10^{-7}$$

Fascio Laser Gaussiano (TEM_{00}^{*})

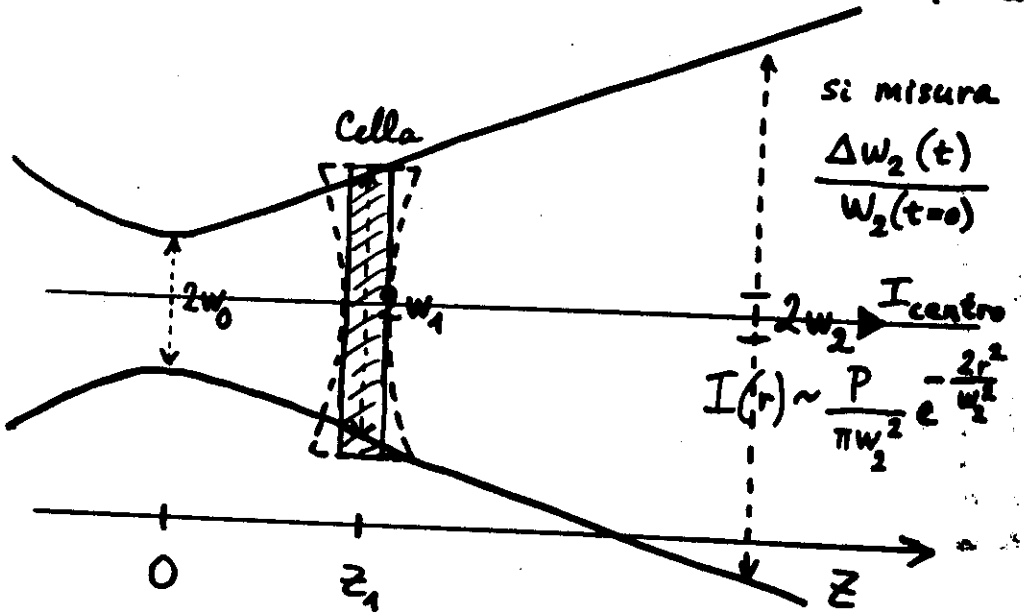


$$E(r,z) = \frac{E_0 w_0}{w} \exp\left\{-i\left(\frac{2\pi z}{\lambda} - \phi\right) - \frac{i\pi r^2}{\lambda R} - \frac{r^2}{w^2}\right\}$$

- $E(r,z)$: ampiezza del campo elettrico lungo l'asse z
- $\frac{E_0 w_0}{w}$: ampiezza
- $-i\left(\frac{2\pi z}{\lambda} - \phi\right)$: variazione di fase longitudinale e trasv.
- $-\frac{r^2}{w^2}$: profilo radiale ampiezza

$$w^2 = w_0^2\left(1 + \frac{z}{z_c}\right) \qquad z_c \equiv \frac{\pi w_0^2}{\lambda}$$

z_c: distanza confocale



- FOCAL LENGTH OF LENS FORMED

$$F(t) = \frac{\pi k w_1^2}{\alpha P \ell (dn/dT)}\left(1 + \frac{t_c}{2t}\right)$$

t_c: response time

P_{abs}

$F(t)$ when $t = \infty$

- MEASURE AT BEAM CENTRE

$$I_c \propto \frac{P}{\pi w_2^2} \rightarrow \frac{I_c(t=0) - I_c(t=\infty)}{I_c(t=\infty)} = \frac{\Delta I_c}{I_c} =$$

$$= \frac{w_2^2(t=\infty) - w_2^2(t=0)}{w_2^2(t=0)} = \frac{\Delta w_2^2}{w_2^2}$$

- COMPARISON WITH CONVENTIONAL SPECTROPHOTOMETER

$$\text{TL}: \quad \frac{\Delta I}{I} = \frac{P_{abs}(dn/dT)}{\lambda k} = \frac{P(2.3)A(dn/dT)}{\lambda k}$$

$$\text{CS}: \quad \frac{\Delta I}{I} = 2.3A \qquad A = \varepsilon b C$$

$$\Downarrow$$

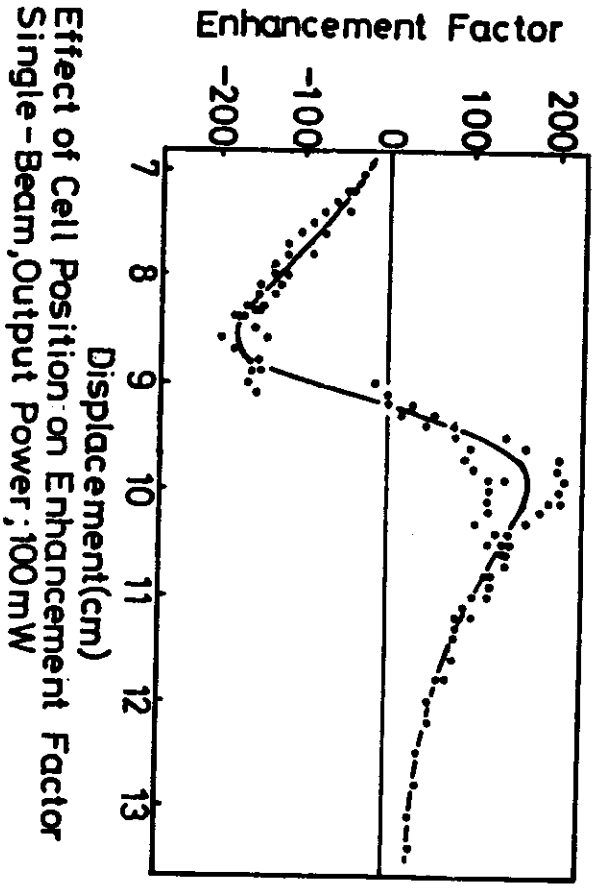
$$\text{Enhancement Factor}: \quad \frac{P(dn/dT)}{\lambda k}$$

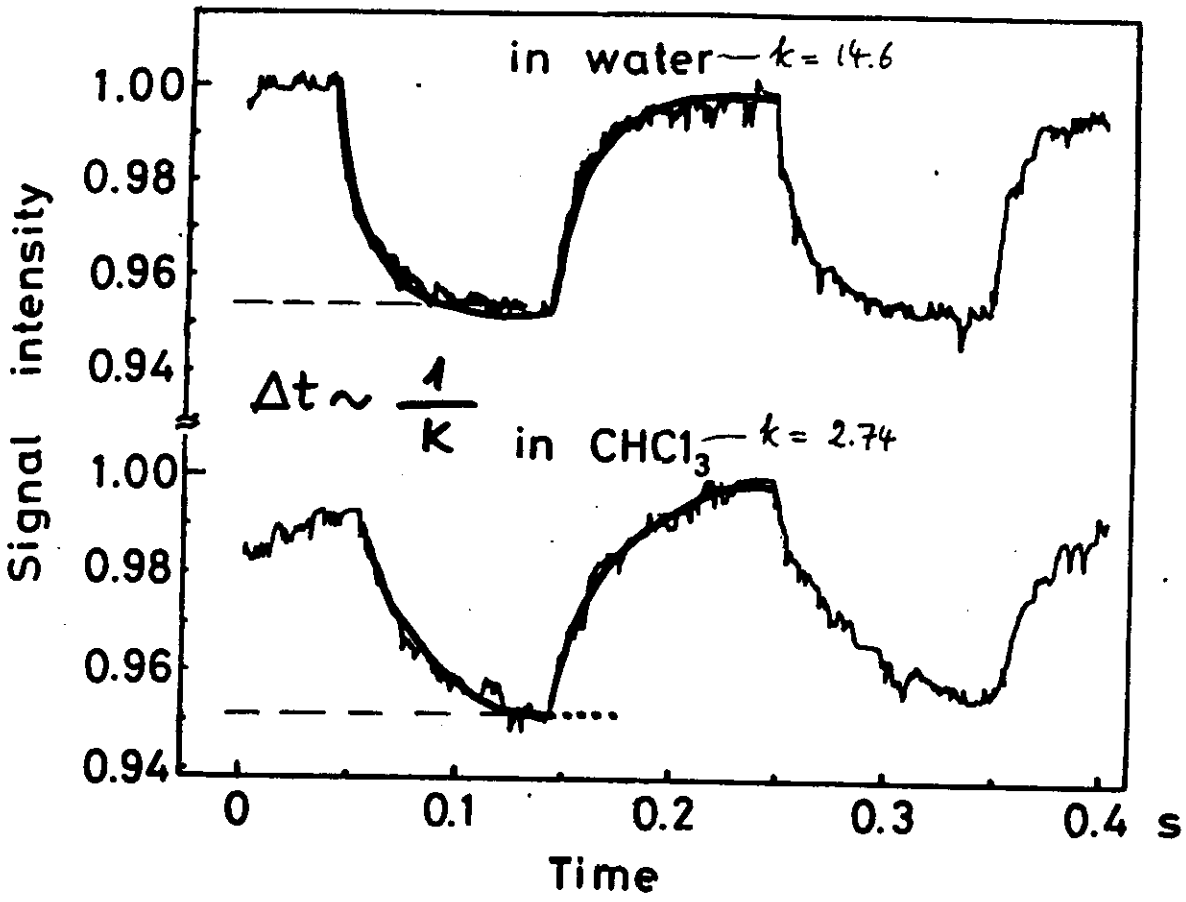
$$E = \left(\frac{P}{\lambda k}\right) \cdot \left(\frac{dn}{dT}\right)$$

Calculated enhancement factors under the exciting power of 1W

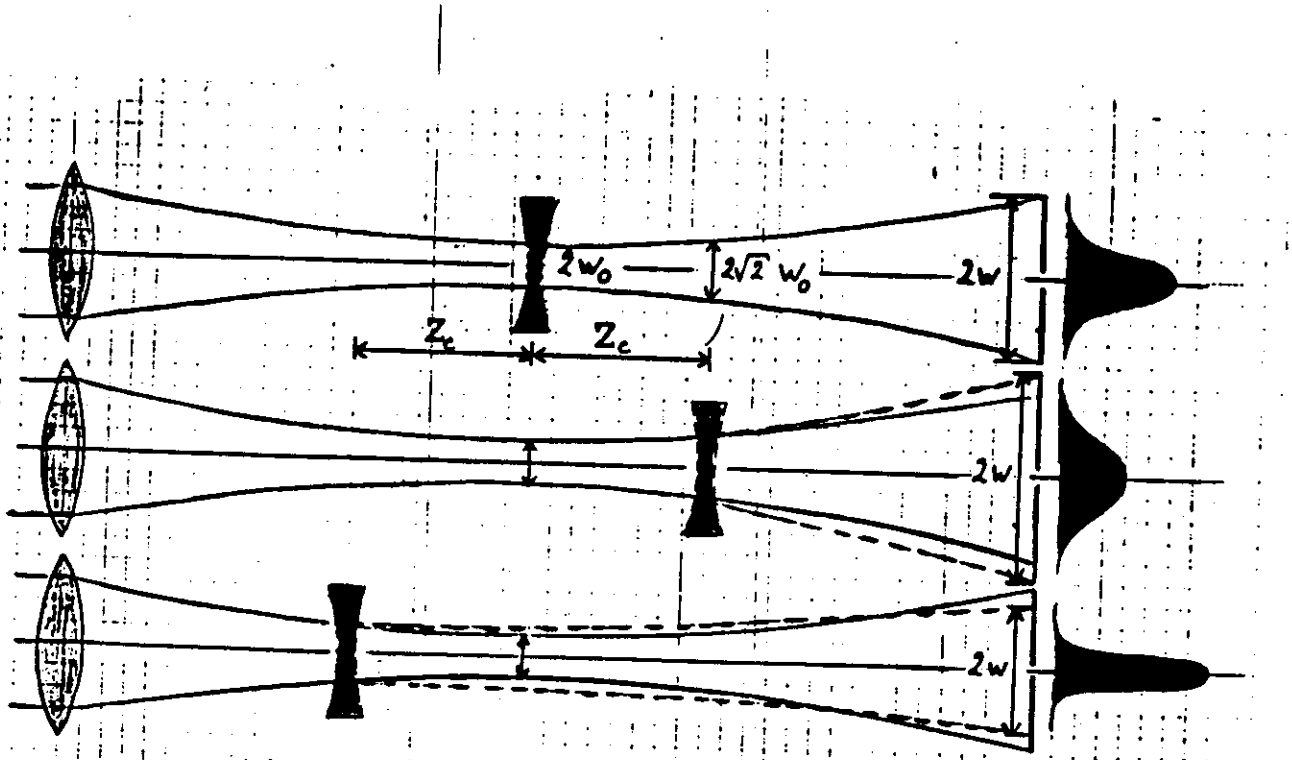
Solvent	E	k	(dn/dT)	ε
Heptane	6300	3.00	5.0	1.924
Cyclohexane	6920	2.95	5.4	2.015
Ethanol	3680	4.00	3.9	24.30
Toluene	6650	3.18	5.6	2.4
Nitrobenzene	4830	3.60	4.6	34.82
Chloroform	8000	2.74	5.8	4.806
→ CCl_4	8940	2.45	5.8	2.2
Acetone	4970	3.80	5.0	20.7
→ Water	207	14.6	0.8	78.54

E: enhancement factor
k: heat conductivity [10^{-4}cal/sec·cm·°C]
(dn/dT): variation in refractive index with temperature [10^{-4}·°C]
ε: dielectric constant





Waveform of thermal lens signal

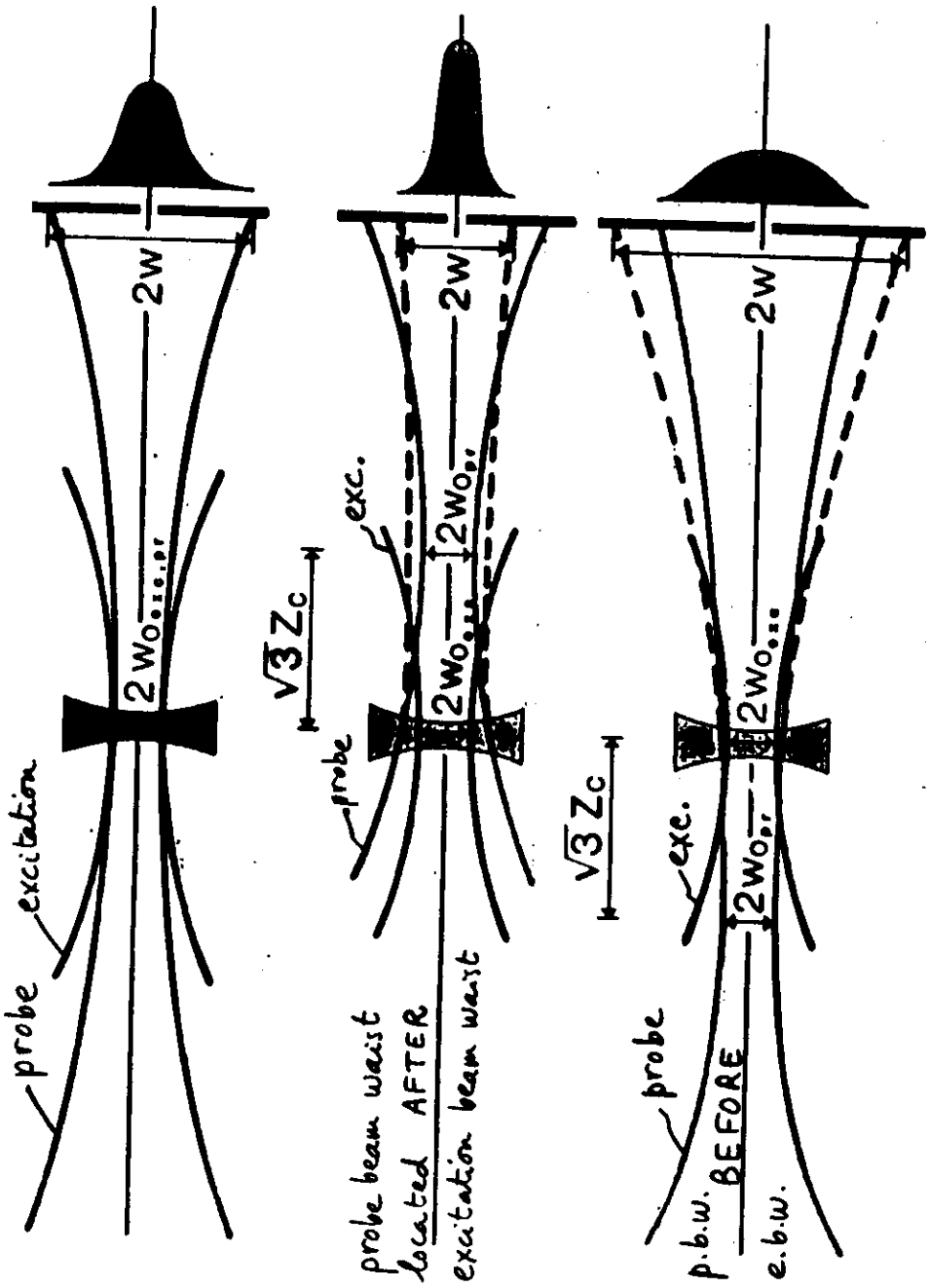


w_0 = minimum waist of gaussian beam at $Z = 0$

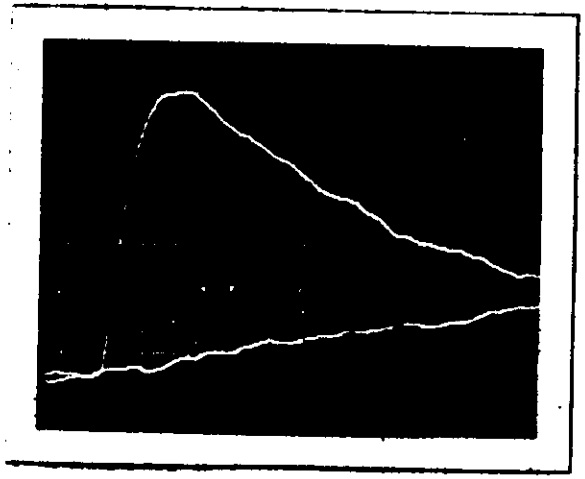
$w^2 = w_0^2 [1 + (Z/Z_c)^2]$

Z_c = confocal distance $= \pi w_0^2 / \lambda$

I_{bc} = Intensity of the beam center sampled in the far field $= 2P/\pi w^2$ where P is the total laser power.



Typical TLS pulse



Sensitivity Considerations :

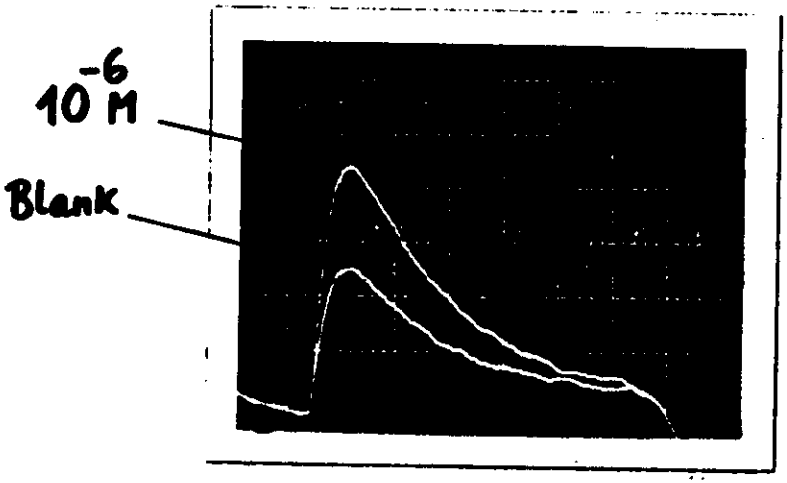
$$A = \varepsilon\, b\, C$$

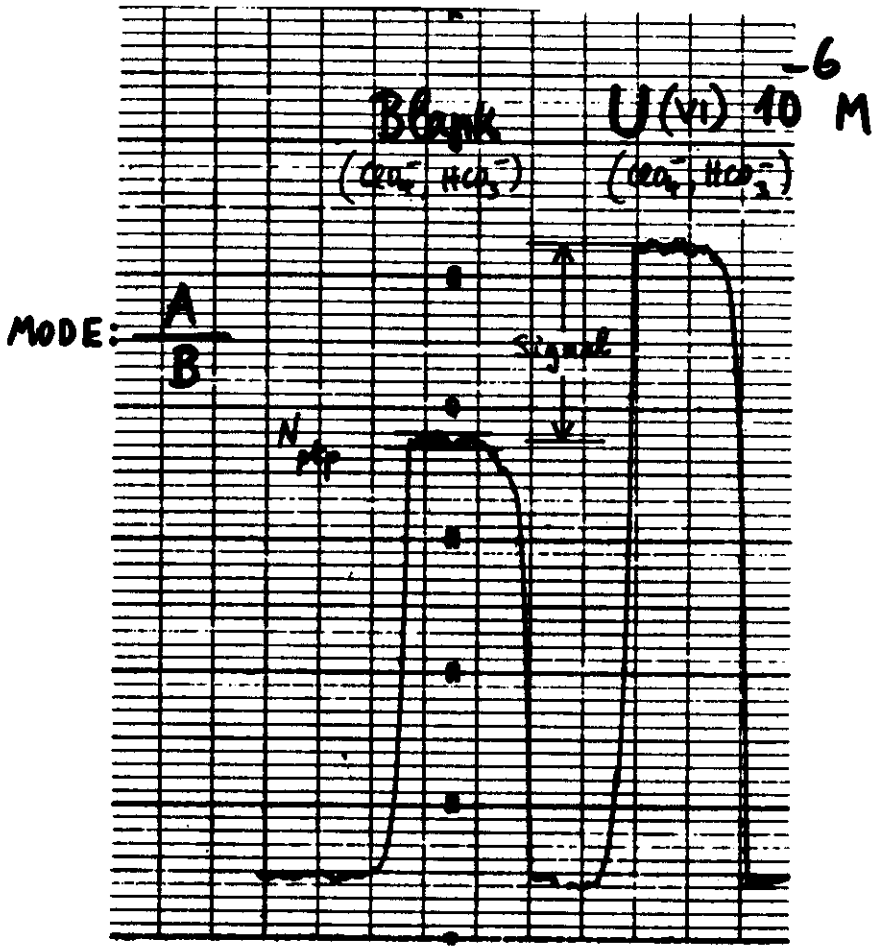
(ε: L mole^{-1}, b: cm, C: moles L^{-1})

- $b = 1$ cm
- minimum $A \sim 10^{-8}$ cm^{-1} (claimed) $\Rightarrow 10^{-7}$ cm^{-1}
- ε for strongly absorbing complexes : $\sim 10^{5}$ L mole^{-1}

$$C_{min} \sim 10^{-12} \div 10^{-13}\ M$$

U (VI)
(ClO_4^-, HCO_3^-)





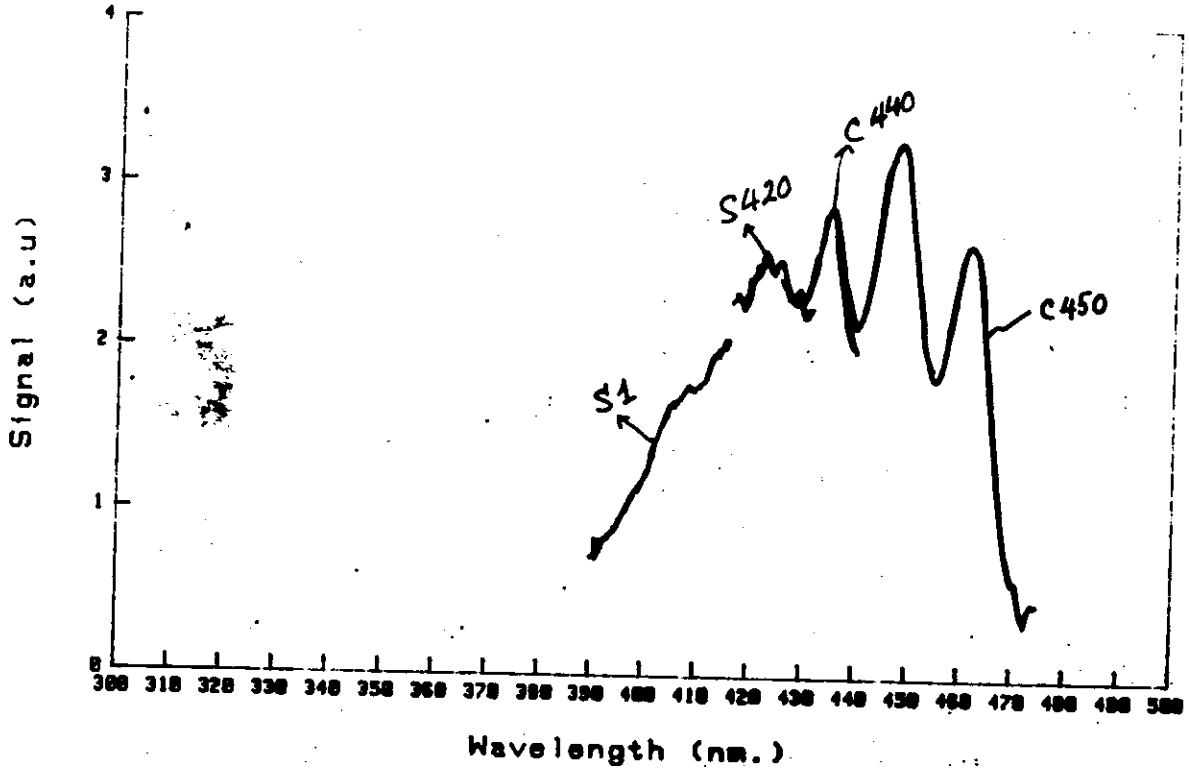
$\frac{S}{N_{rms}} = 73.5$

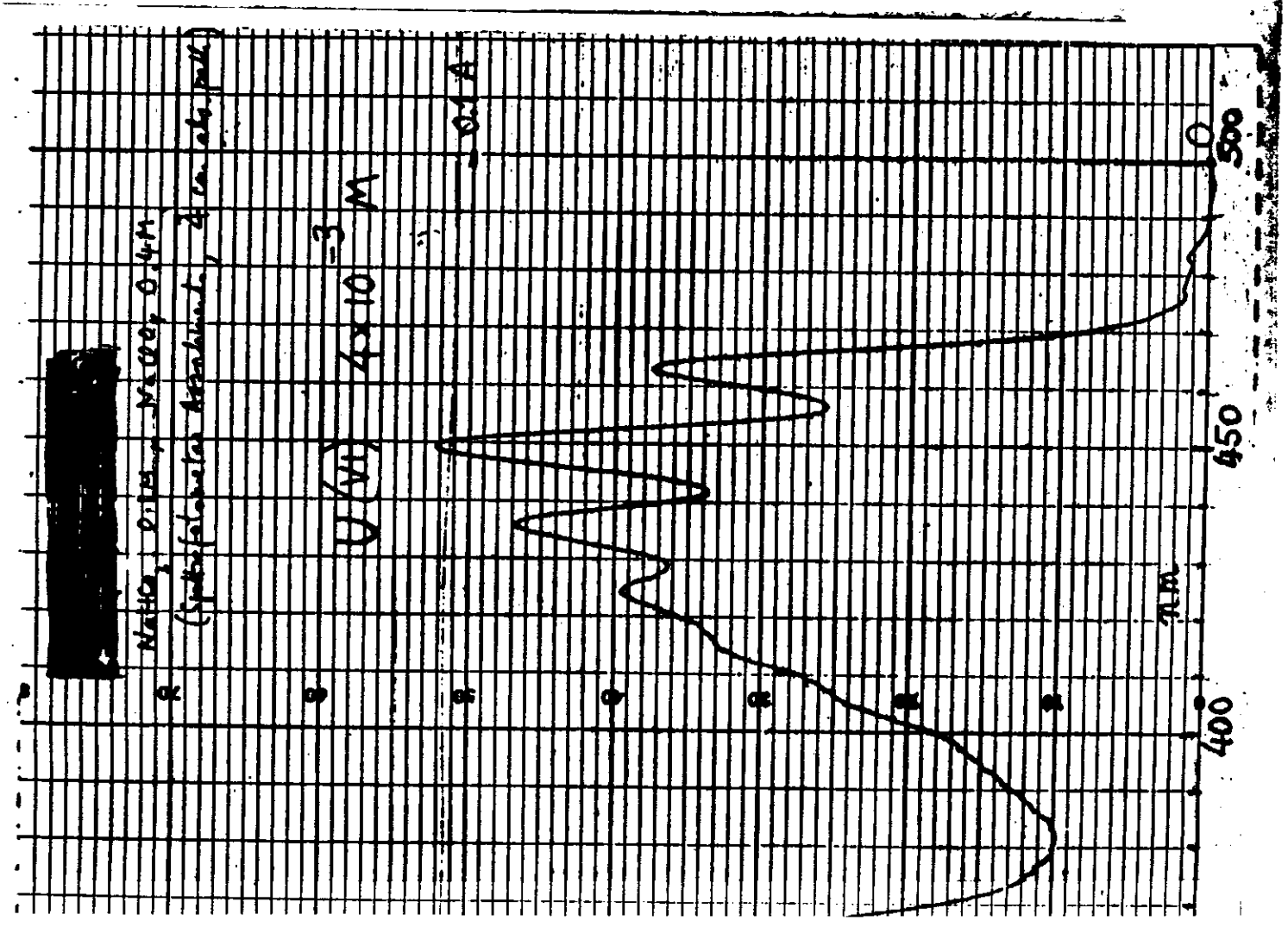
DL = 2.76×10^{-8} M
(S/N = 2)

$\varepsilon = 25 \Rightarrow A \equiv 7 \times 10^{-7}$ cm^{-1}

UE4 CARBONATE $U(VI)\ 10^{-4}$ M

MULTI-DYE LASER





TAKING A SPECTRUM IS MUCH DIFFERENT FROM OBTAINING A DETECTION LIMIT!

- Ratioing unsuitable → many dyes needed
  pyroelectric detector preferable
- Achromatic lens needed
- Divergence lower in the UV, so source is smaller
- Polarization effects need control