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

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
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SMR/115 - 54

WINTER COLLEGE ON LASERS, ATOMIC AND MOLECULAR PHYSICS

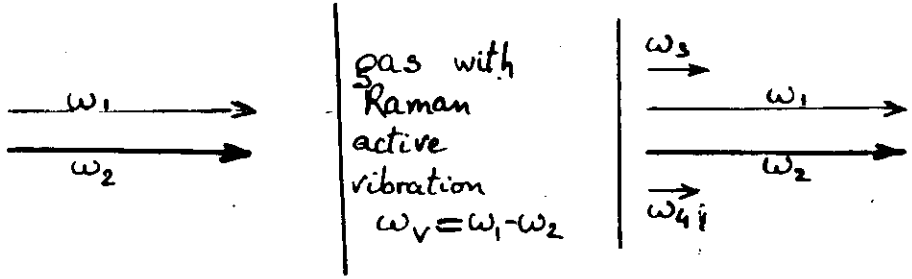
(21 January - 22 March 1985)

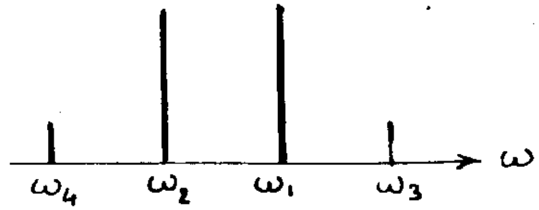
LASER RAMAN SPECTRA
(Lectures III & IV)

J.P. TARAN
Office National d'Etudes et de Recherches Aérospatiales
Chatillon
France

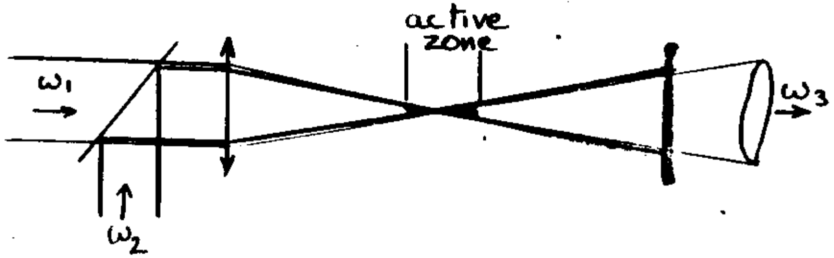
LECTURE III

CARS





CARS with focused beams



BASIC EQUATIONS

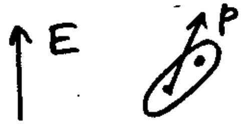
material equation

$$\left[\frac{\partial^2}{\partial t^2} + \gamma \frac{\partial}{\partial t} + \omega_v^2\right] q = F/m$$

wave equation

$$\left[\frac{\partial^2}{\partial z^2} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right] E_3 = \frac{4\pi}{c^2}\frac{\partial^2}{\partial t^2} P$$

Plackzek's presentation of molecular polarizabilities



$$P = N\alpha E$$

with

$$\alpha = \alpha_0 + \frac{\partial \alpha}{\partial q} q$$

potential energy of a molecule

$$W = -\frac{1}{2}\alpha E^2$$

hence, driving force

$$F = -\frac{\partial W}{\partial q}$$

take

$$E = \mathcal{E}_1 + \mathcal{E}_2$$

$$\mathcal{E}_1 = \frac{1}{2}\left[E_1 e^{-i(\omega_1 t - k_1 z)} + cc\right]$$

$$\mathcal{E}_2 = \frac{1}{2}\left[E_2 e^{-i(\omega_2 t - k_2 z)} + cc\right]$$

problem

1 Torr CO

$P_1 = P_2 = 100$ kW

Solution

CARS — Spontaneous Raman

P_s (signal) ~ 1 mW — ~ 10^{-12} W/sr ↓P_s

cost ~ 10^{-11} $/photon — ~ 10^{-2} $/photon

Schreiber	Wright Patterson AFB
Harvey	NRL
Eckbreth	United Technologies
Chang	Yale
Byer	Stanford
Rahn	Sandia
Hoppe	Nasa
	US army - Dover

ANTI STOKES SIGNAL

Parallel beams

$$I_3 \approx \left(\frac{4\pi^2\omega_1}{c^2}\right)^2 |\chi|^2 z^2 I_1^2 I_2$$

Focused beams

$$P_3 \approx \left(\frac{\omega_1}{\pi}\right)^2 \left(\frac{4\pi^2\omega_1}{c^2}\right)^2 |\chi|^2 \frac{1}{c^2} P_1^2 P_2$$

with

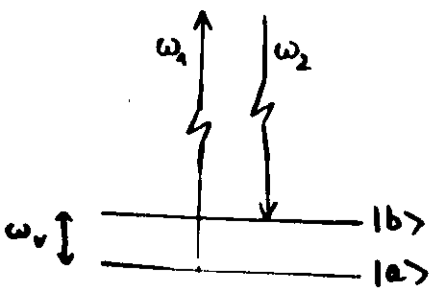
$$\chi \simeq \left(\frac{2c^4}{\hbar\omega_2^4}\right)\left(\frac{1}{\omega_v-(\omega_1-\omega_2)-i\Gamma}\right)$$

× N → concentration measurements

× Δ → temperature measurements

× $\left(\frac{d\sigma}{d\Omega}\right)$

+ χ^{NR} → problems

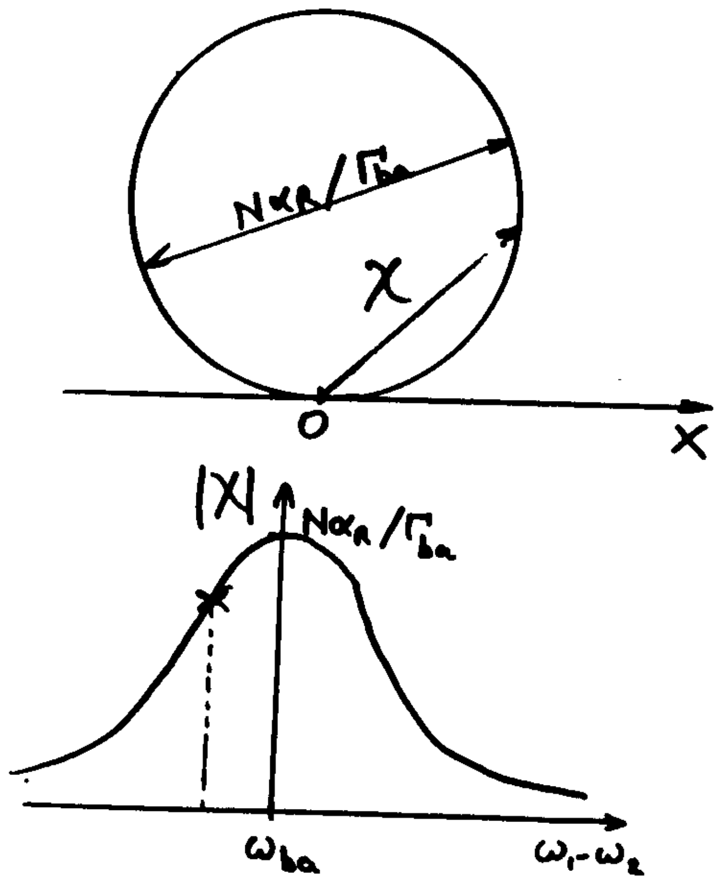


6 a

COLLISIONAL BROADENING

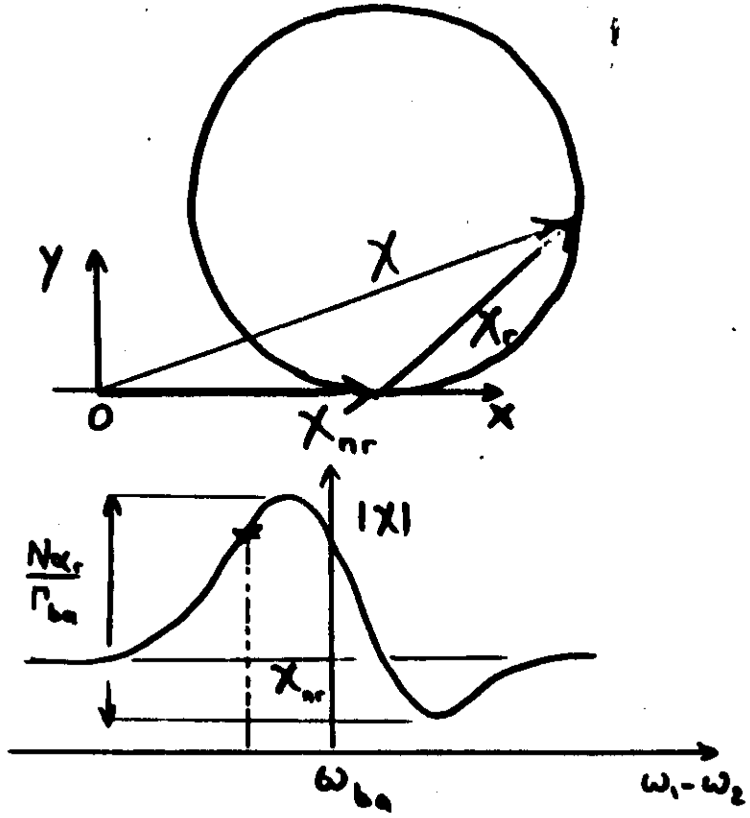
Isolated CARS line off resonance

$$\chi = \chi_R \simeq N\alpha_r/(\omega_{ba}-\omega_1+\omega_2-i\Gamma_{ba})$$



6 b

ISOLATED CARS LINE with BACKGROUND



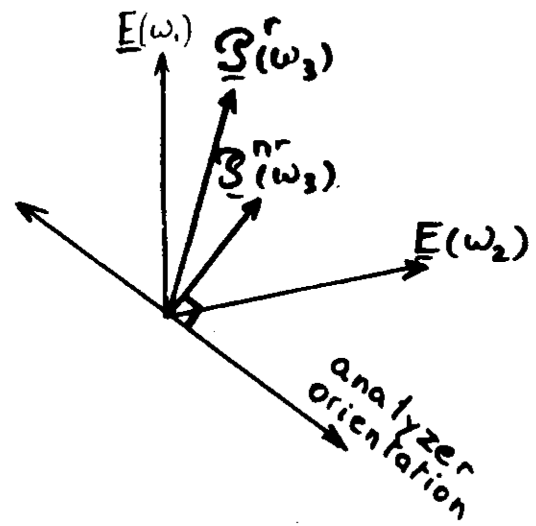
BACKGROUND SUPPRESSION

Source Polarization :

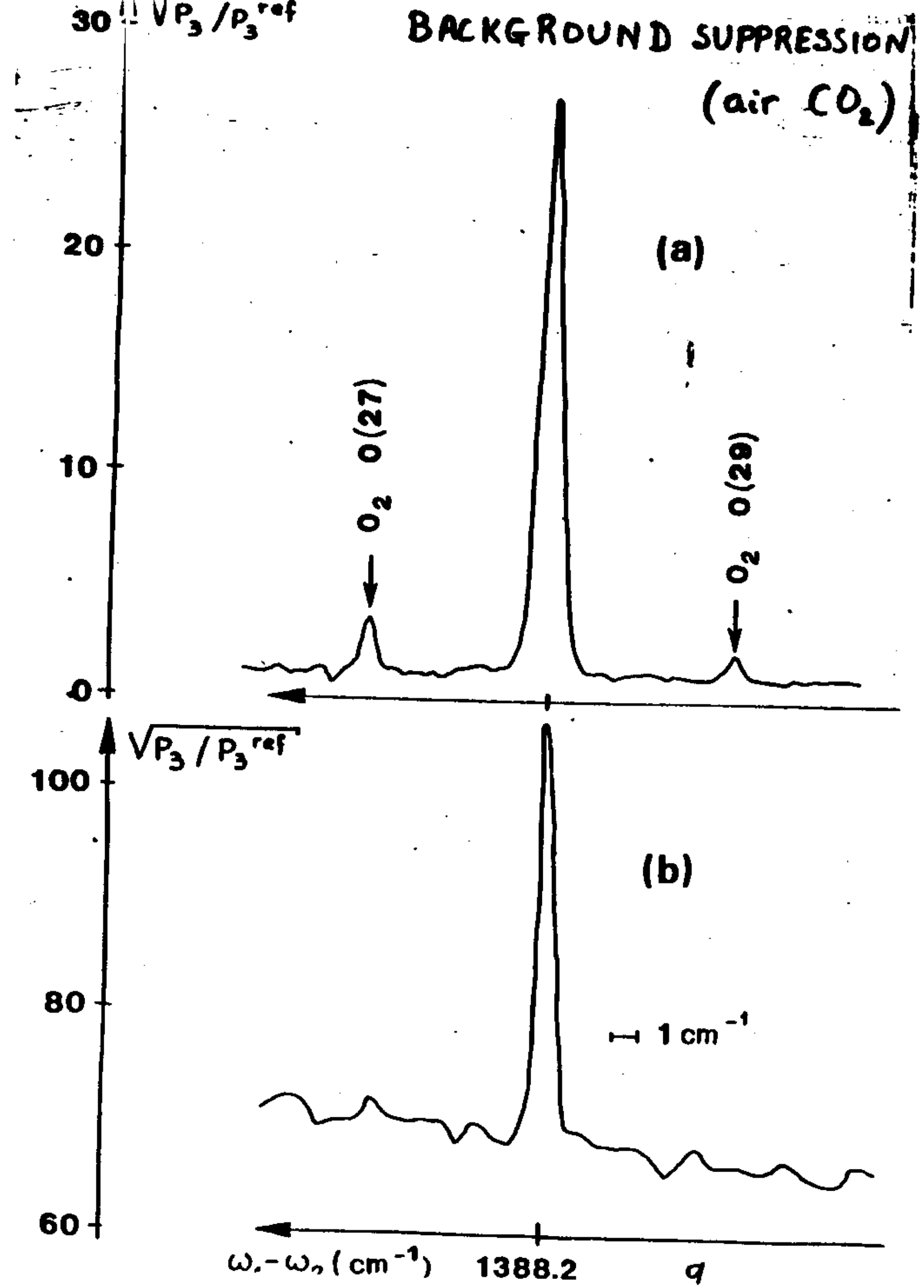
$$\underline{S}(\omega_3) = \underline{\underline{\underline{\chi}}}\ \underline{E}(\omega_1)\ \underline{E}(\omega_1)\ \underline{E}^*(\omega_2)$$

with

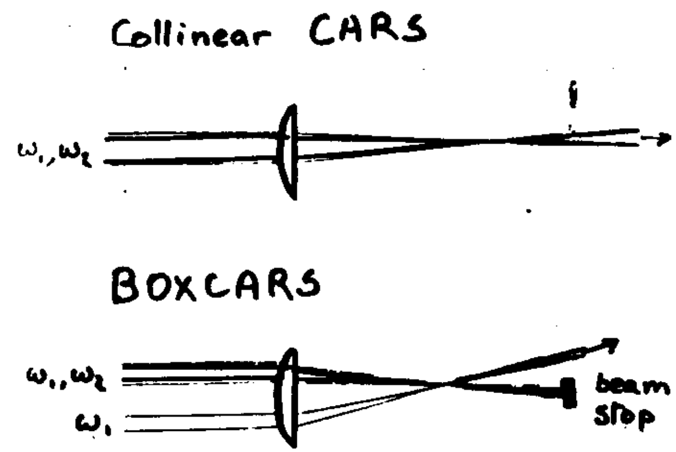
$$\underline{\underline{\underline{\chi}}} = \underline{\underline{\underline{\chi}}}^r + \underline{\underline{\underline{\chi}}}^{nr}$$



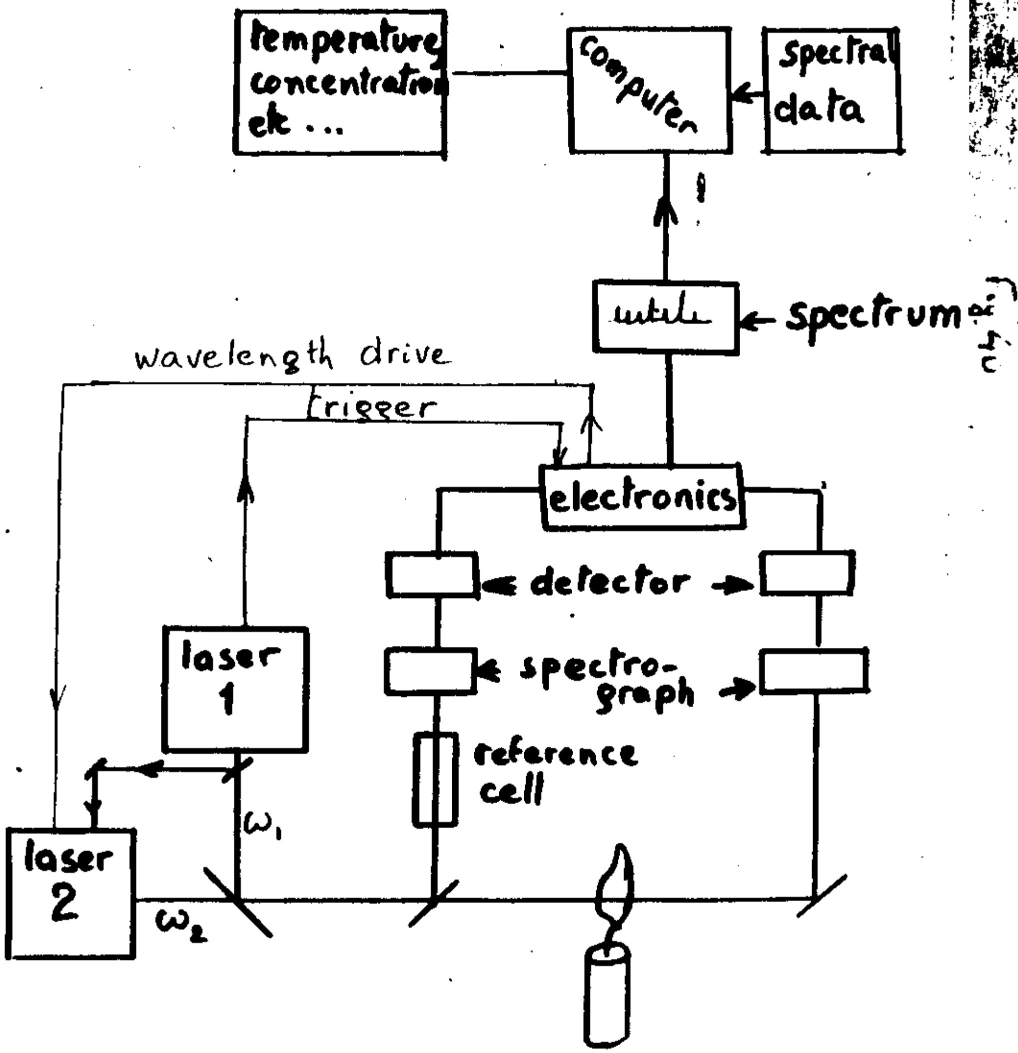
BACKGROUND SUPPRESSION (air CO_2)

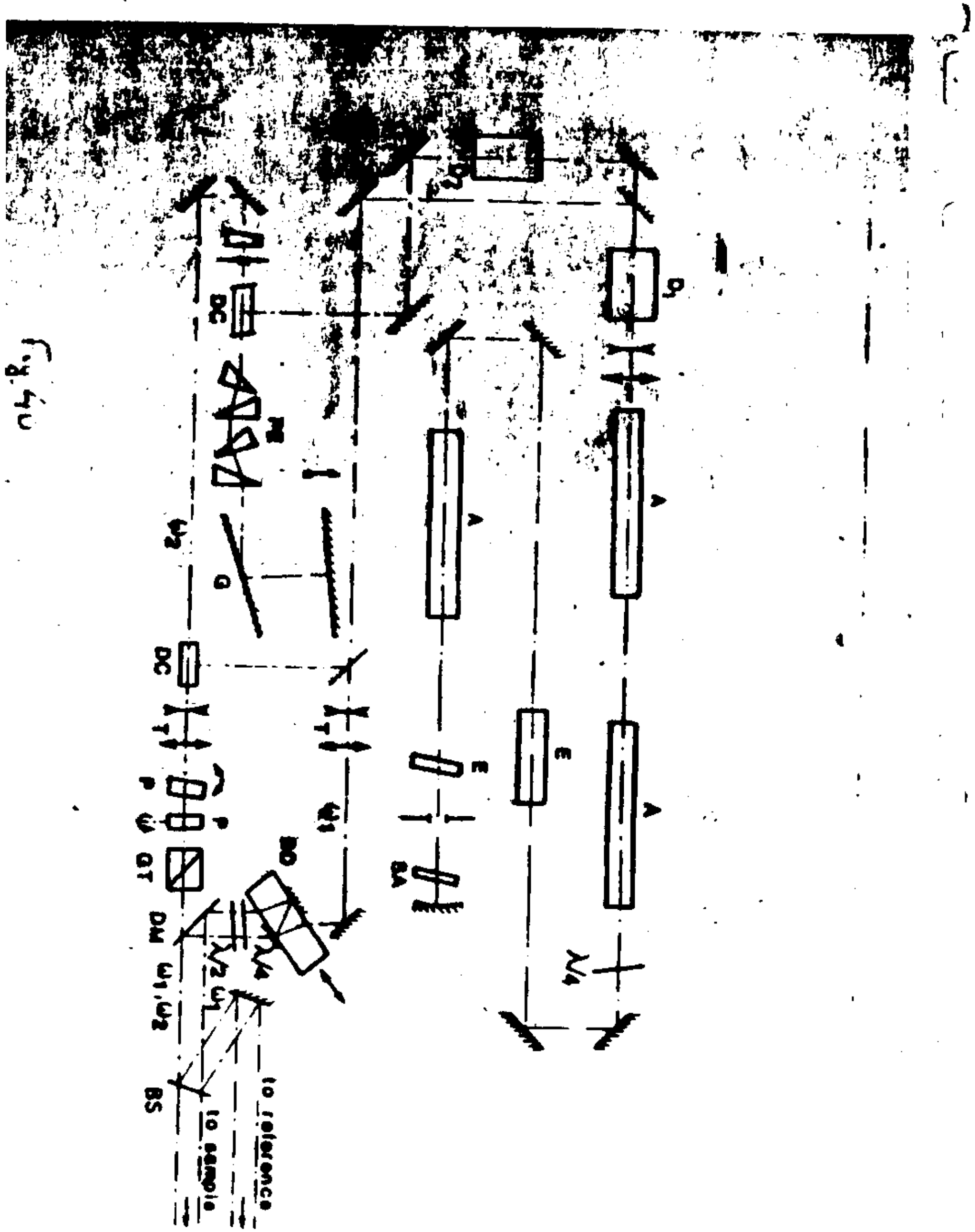


SPATIAL RESOLUTION



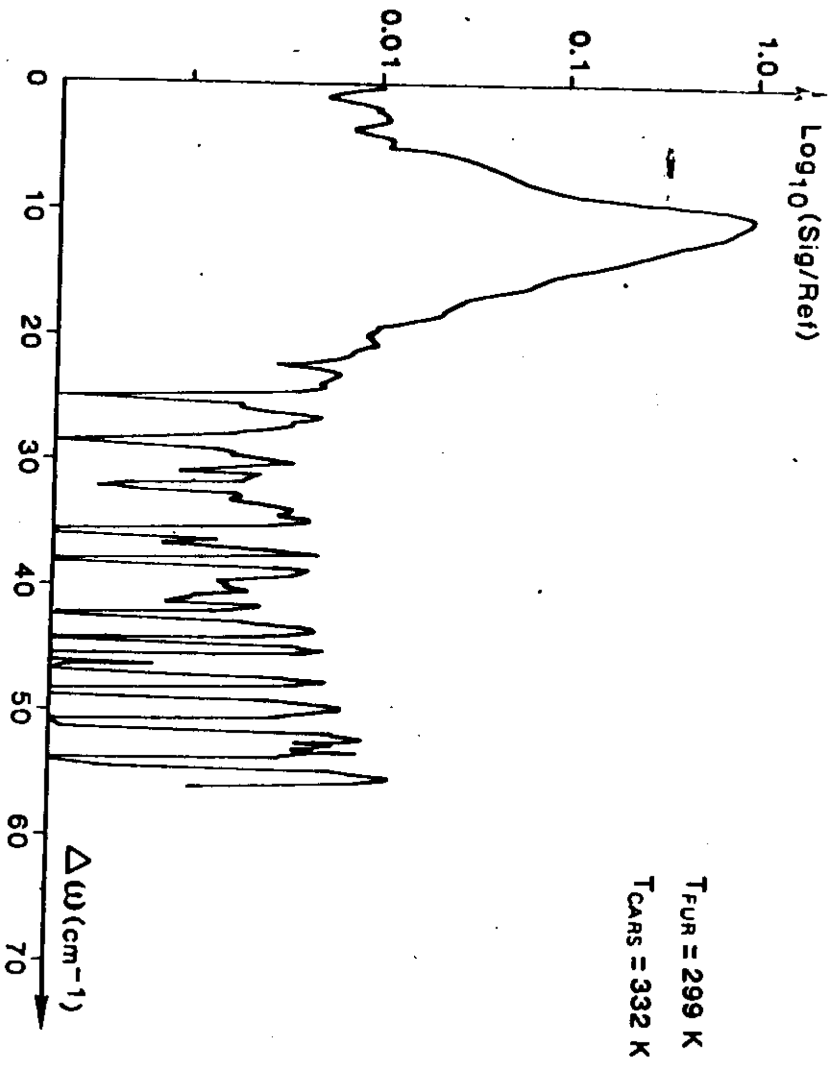
A conventional CARS setup

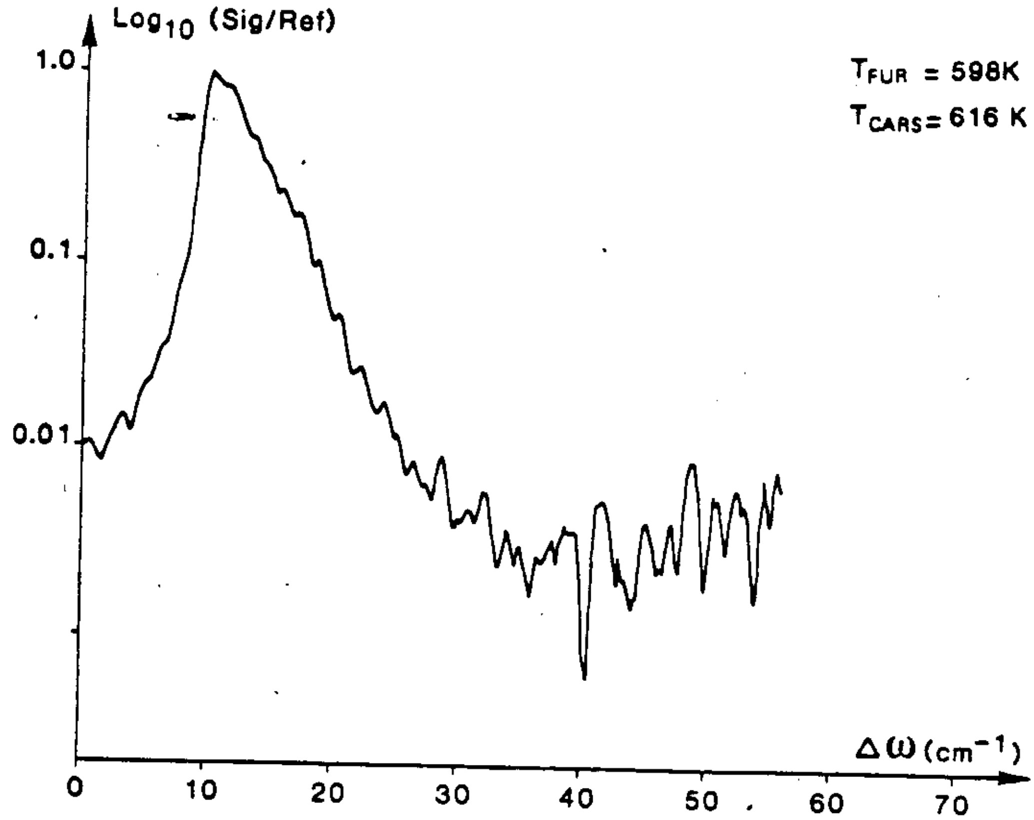




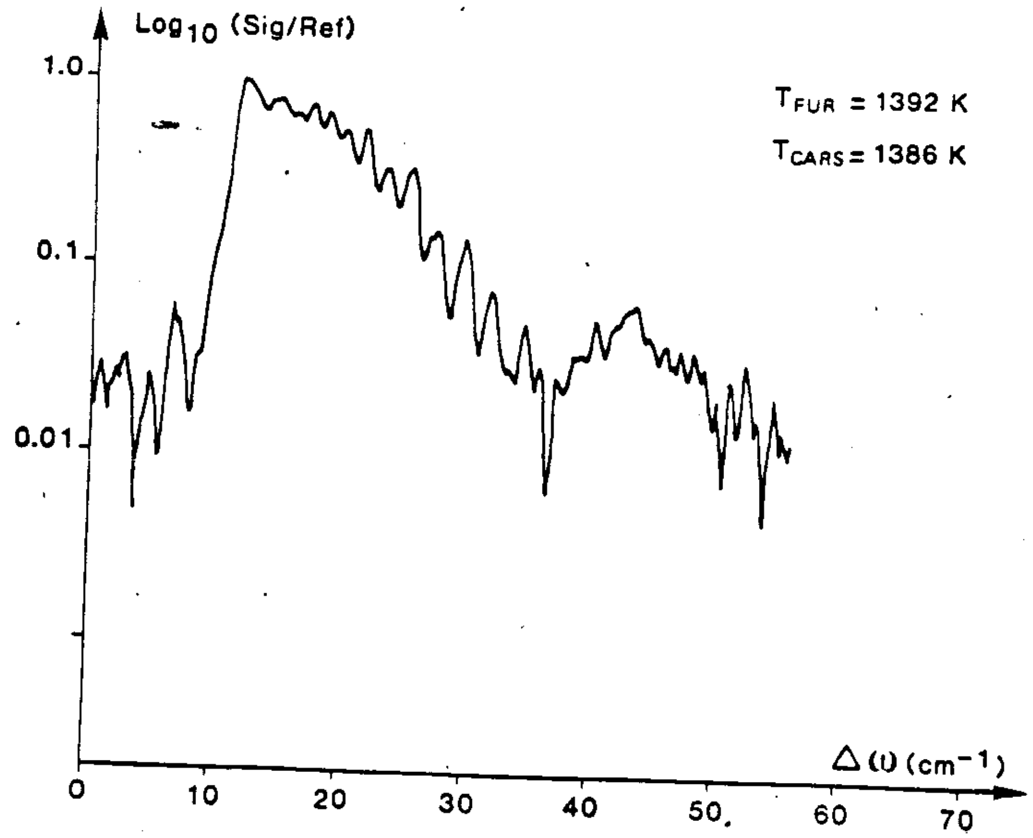
FLAME STUDIES

- multiplex CARS
- BOXCARS

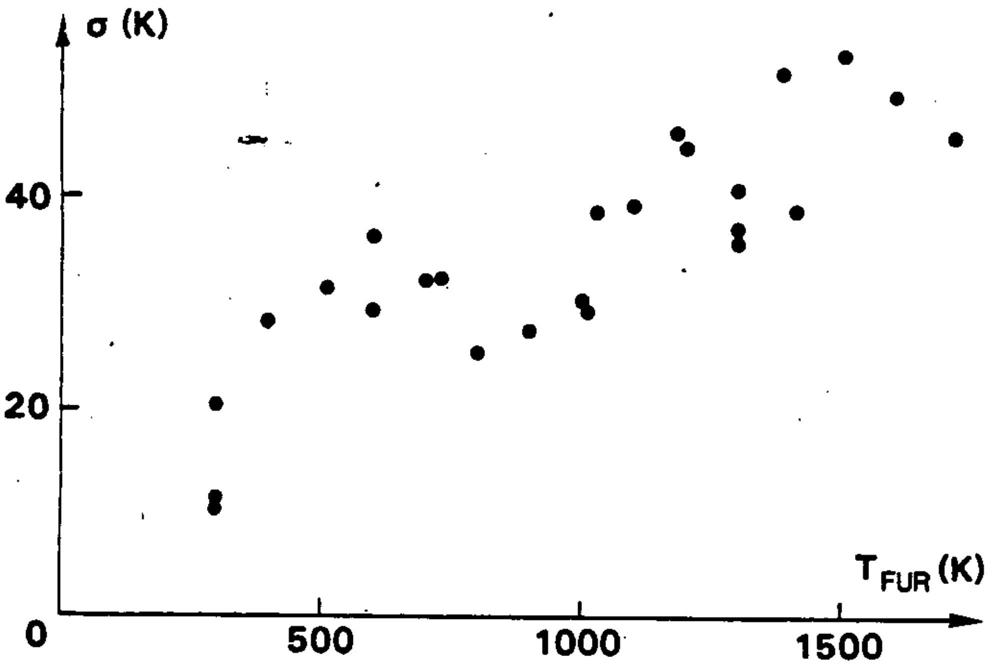



Log10 (Sig/Ref)
1.0
0.1
0.01
T_FUR = 598K
T_CARS= 616 K
Δω (cm⁻¹)
0
10
20
30
40
50
60
70

14

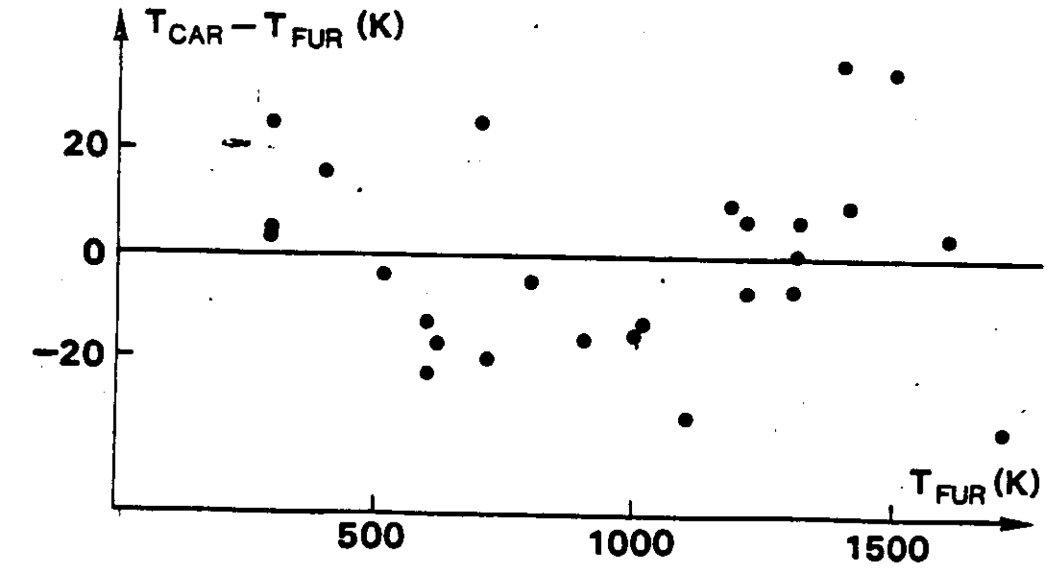

Log10 (Sig/Ref)
1.0
0.1
0.01
T_FUR = 1392 K
T_CARS= 1386 K
Δω (cm⁻¹)
0
10
20
30
40
50
60
70

15



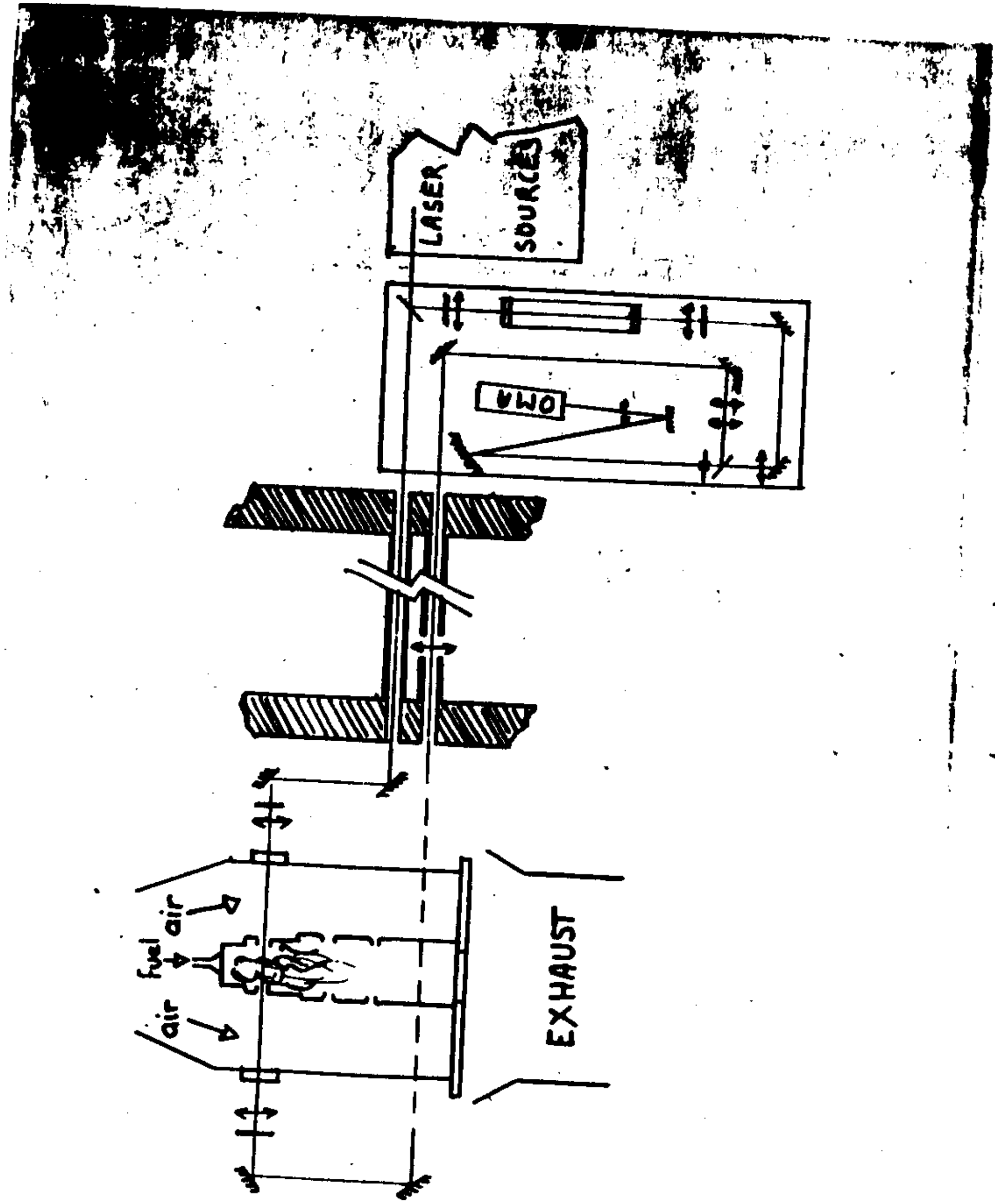
Standard deviation of repeated single shot CARS temperatures

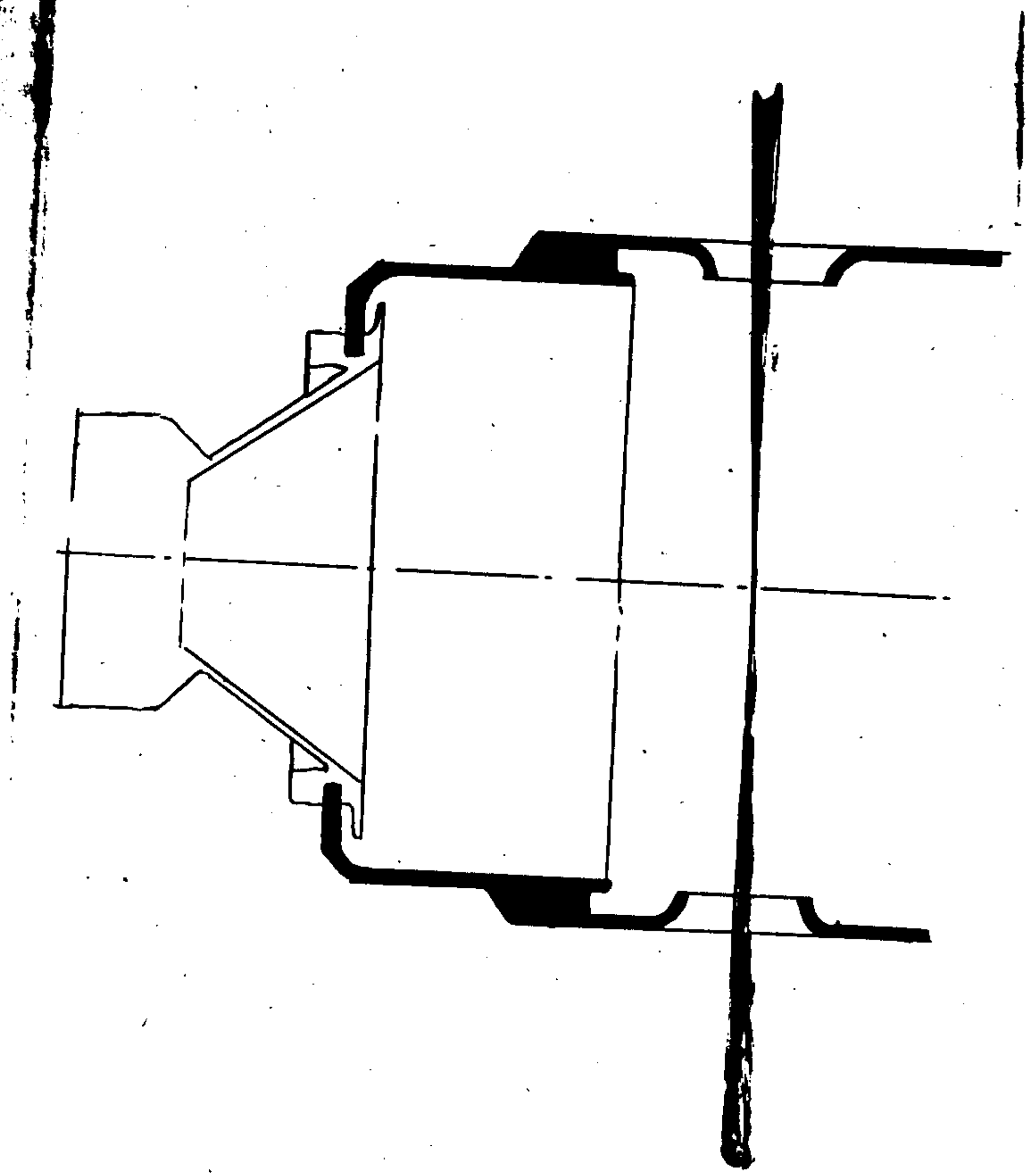
18



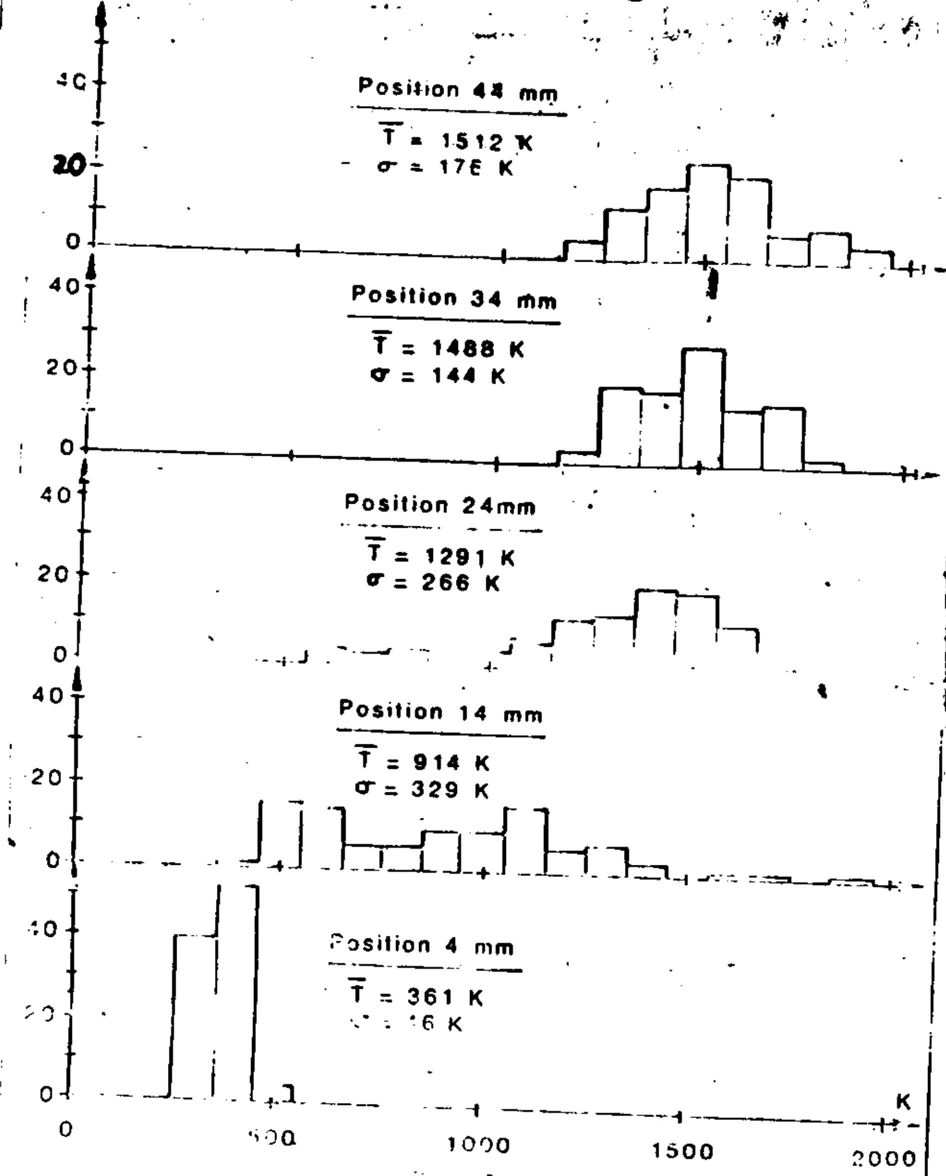
Deviation of mean CARS temperature from furnace temperature

17


LASER
SOURCES
OMA
fuel
air
air
EXHAUST



temperature histograms



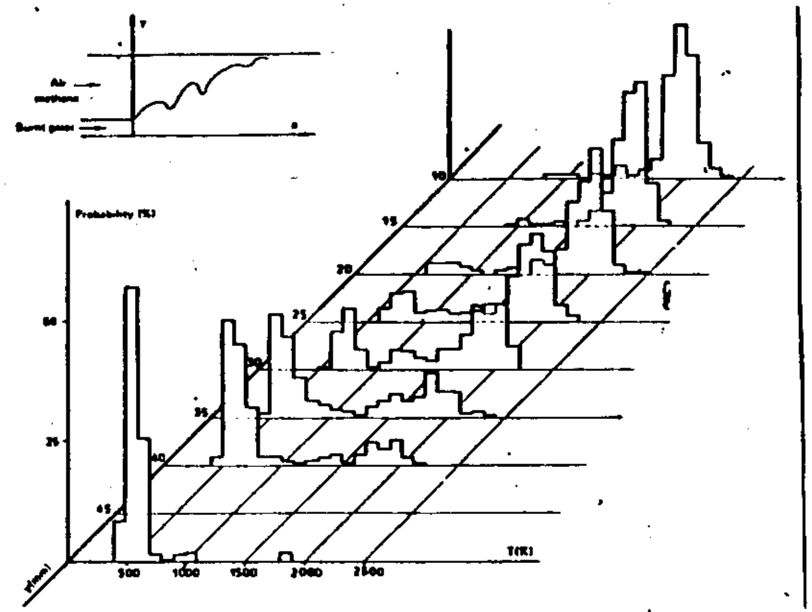


Fig. 2 – Temperature PDF with combustion (φ = 0.8, x = 122 mm).

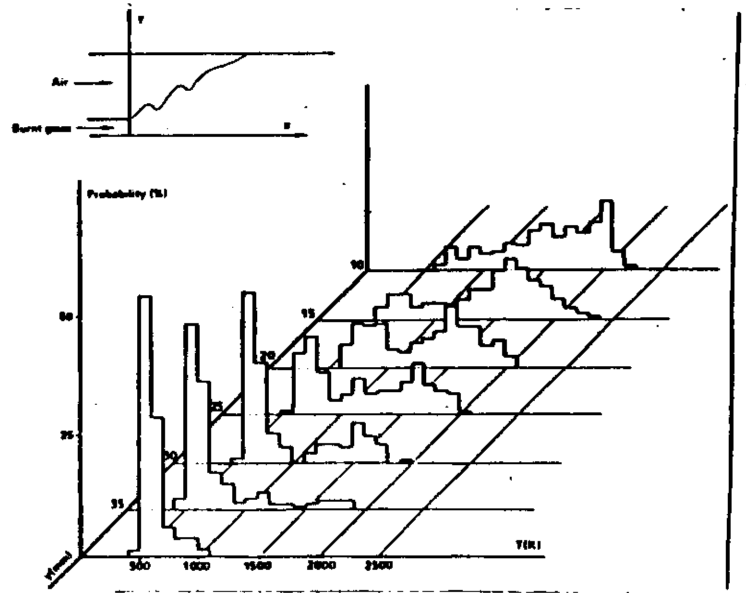
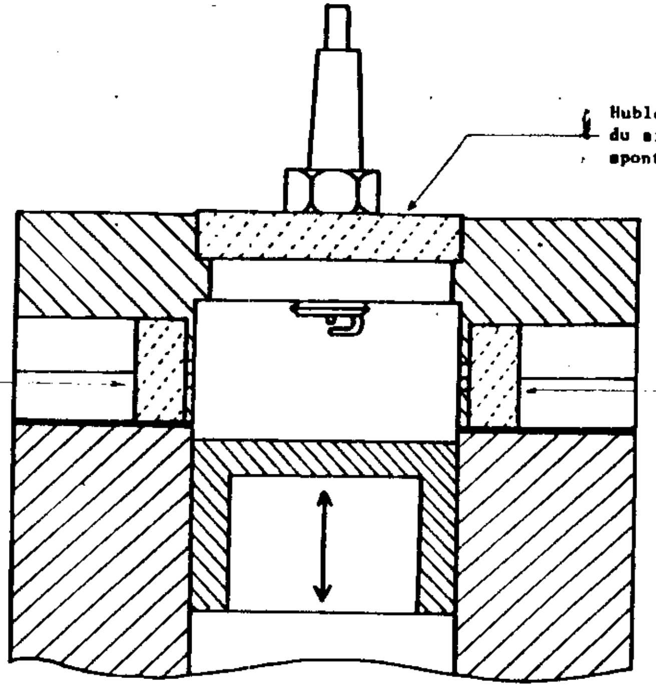
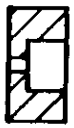


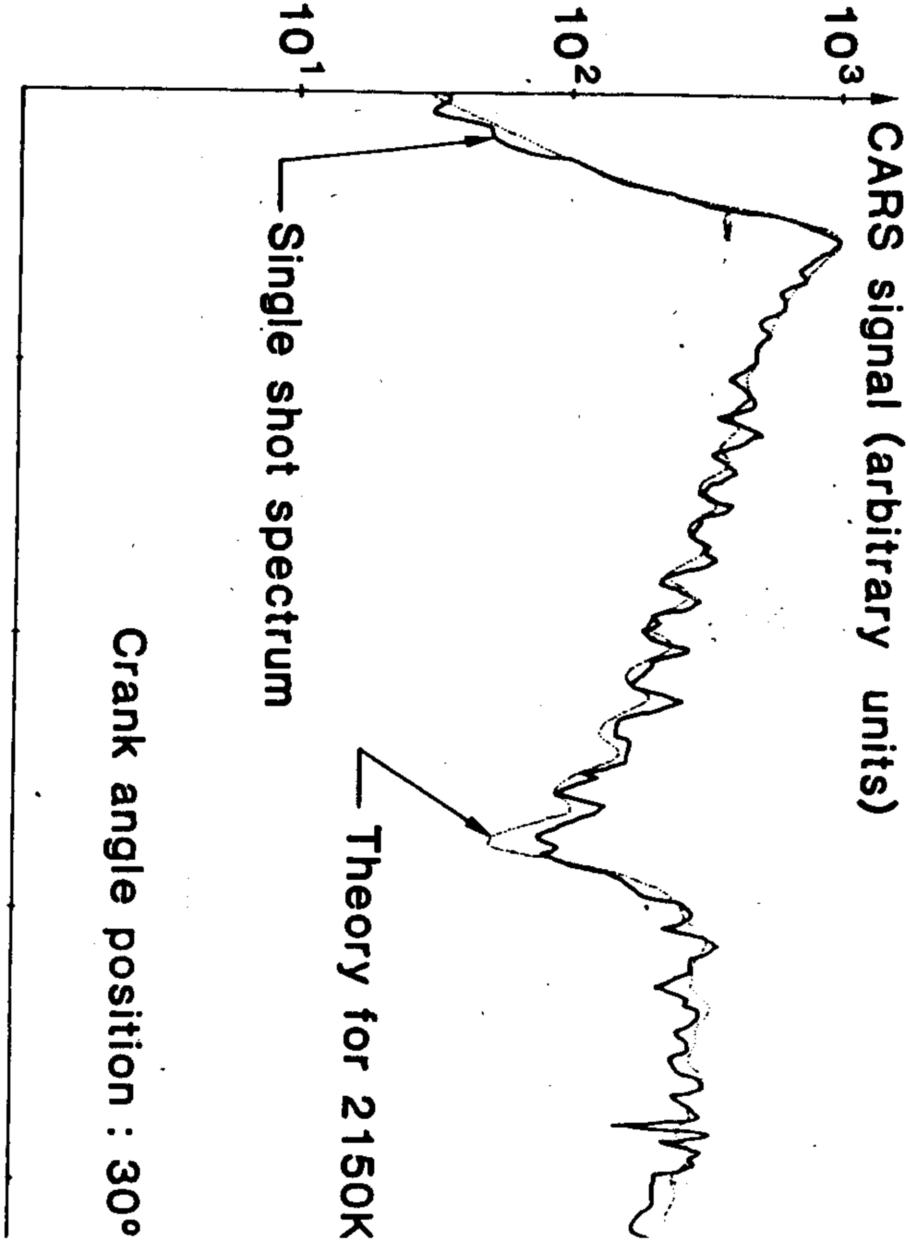
Fig 3 – Temperature PDF without combustion (φ = 0, x = 122 mm).

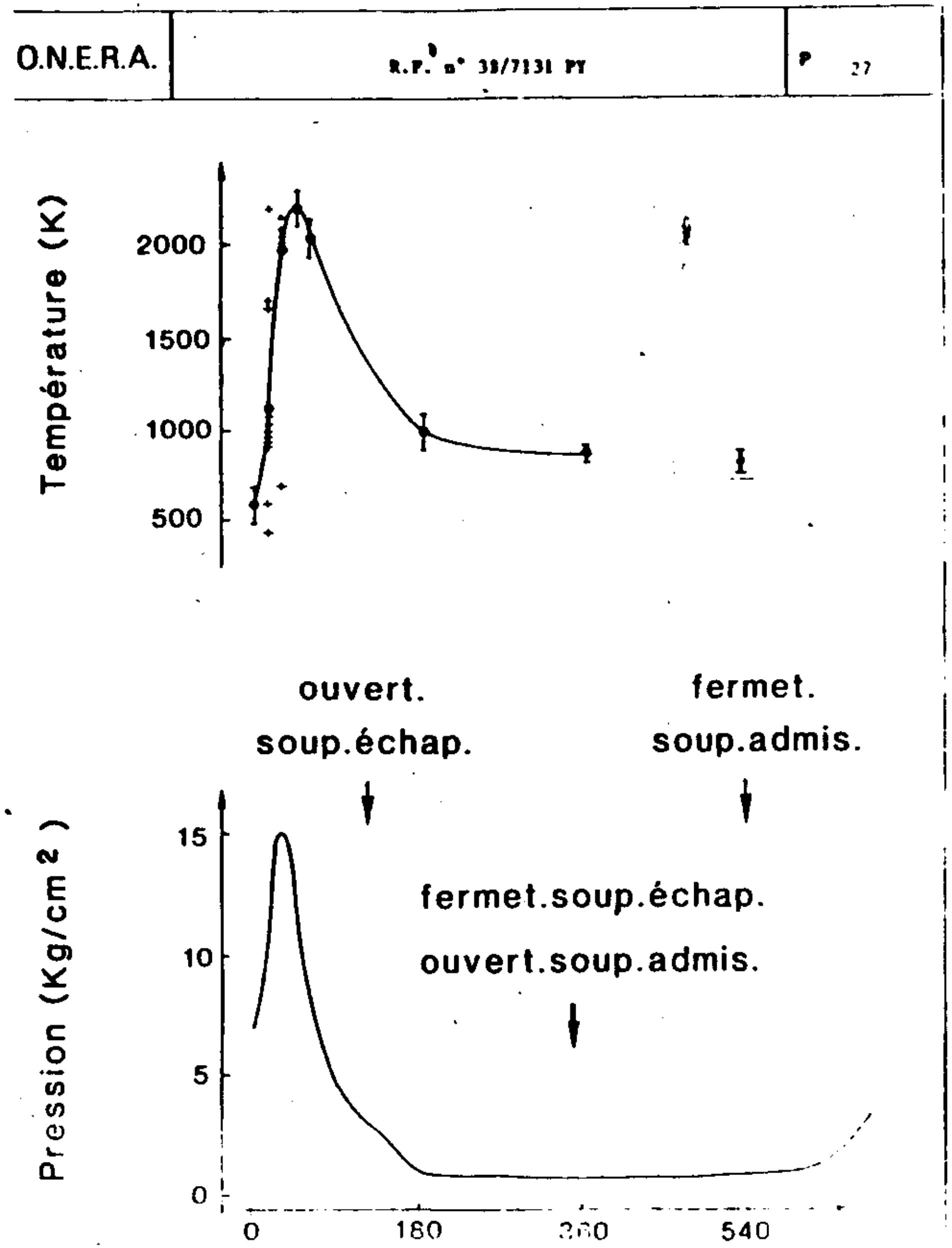




pièces métalliques
remplaçant les
hublots

Fig. 3 - Schéma des accès optiques dans le moteur.





PERFORMANCE
(flame studies)

spatial resolution:

1 - 3 mm

temporal resolution

10 - 20 ns

flame size

< 20cm at 3-4 bars

temperatures

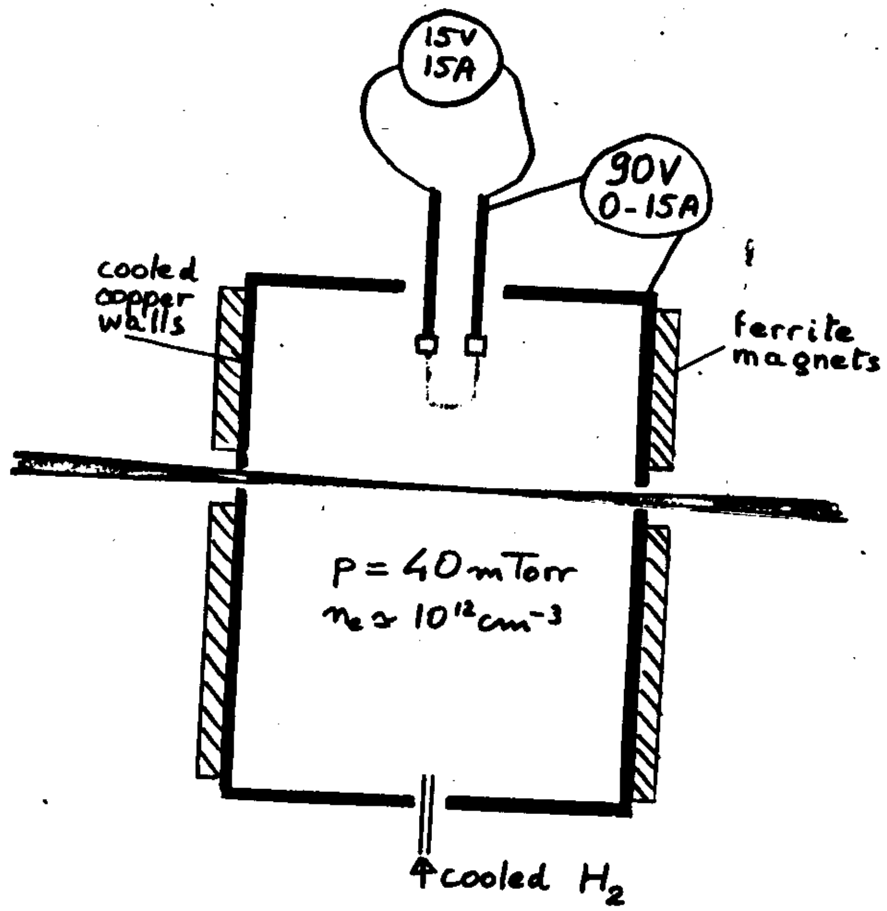
300 ... 2200 K
(accuracy 3 - 5% rms)

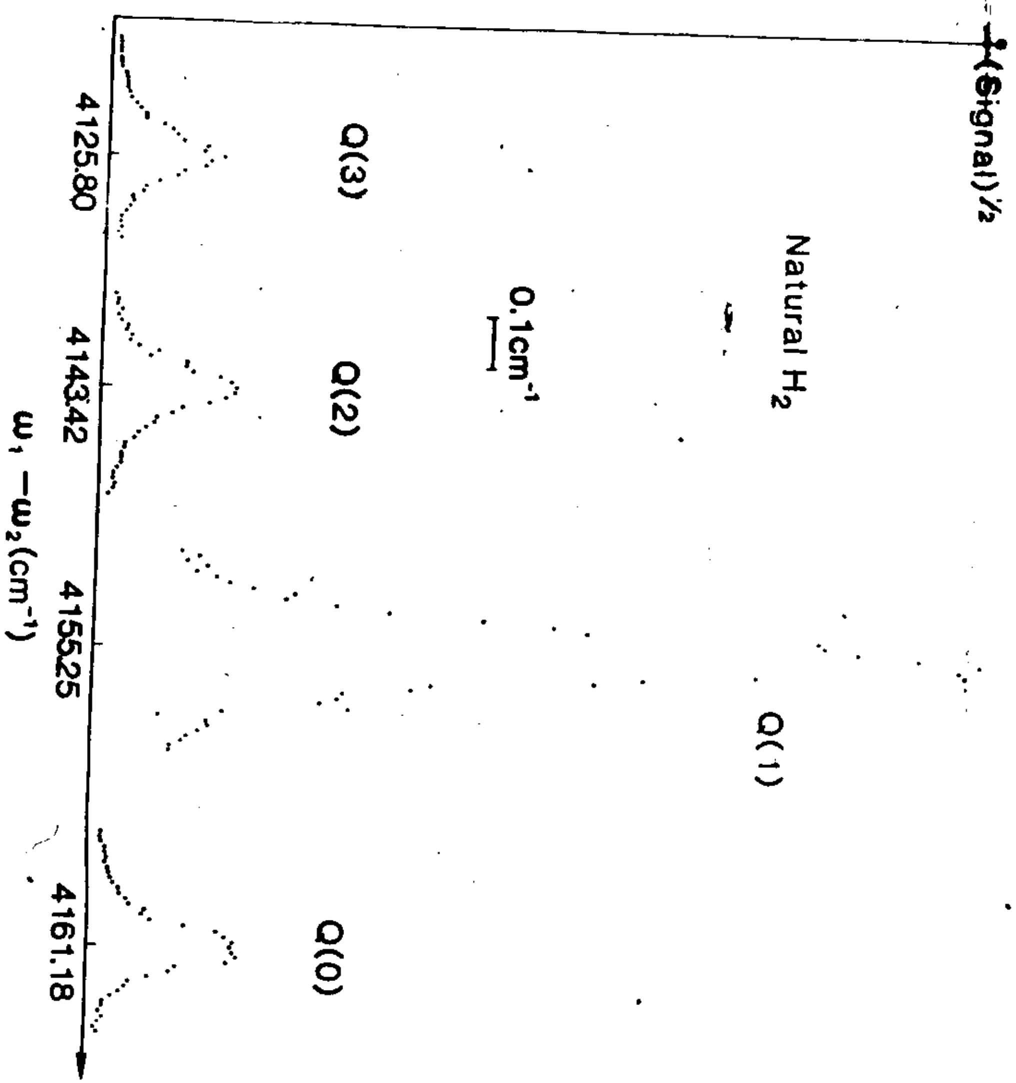
concentrations

100 ppm - 1% . at 1500K
(accuracy 10 - 20% rms)

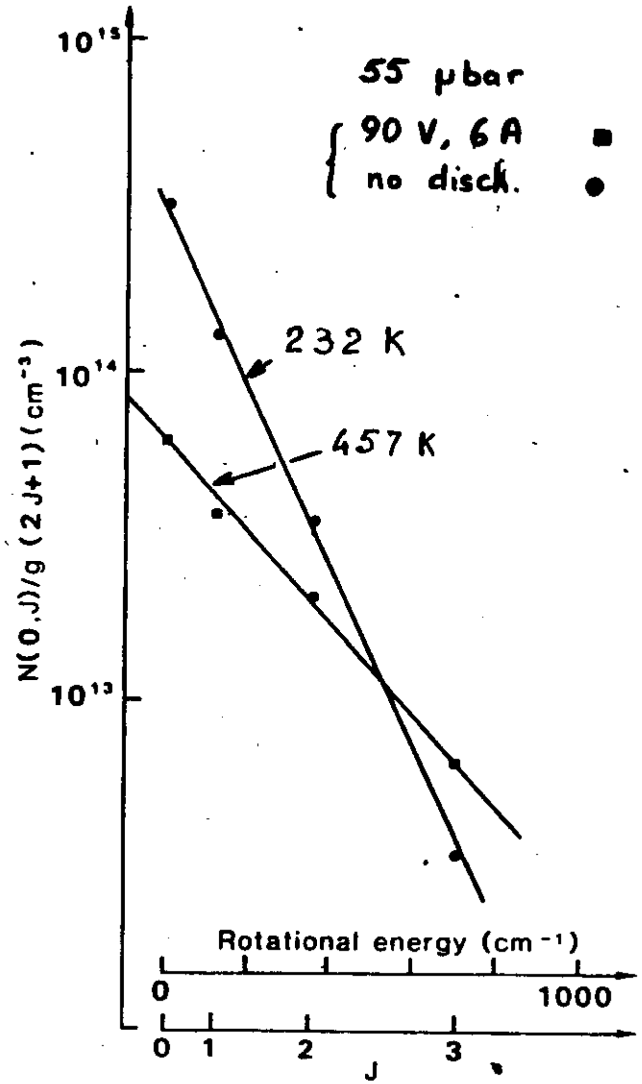
PHOTOCHEMISTRY & PLASMA STUDIES

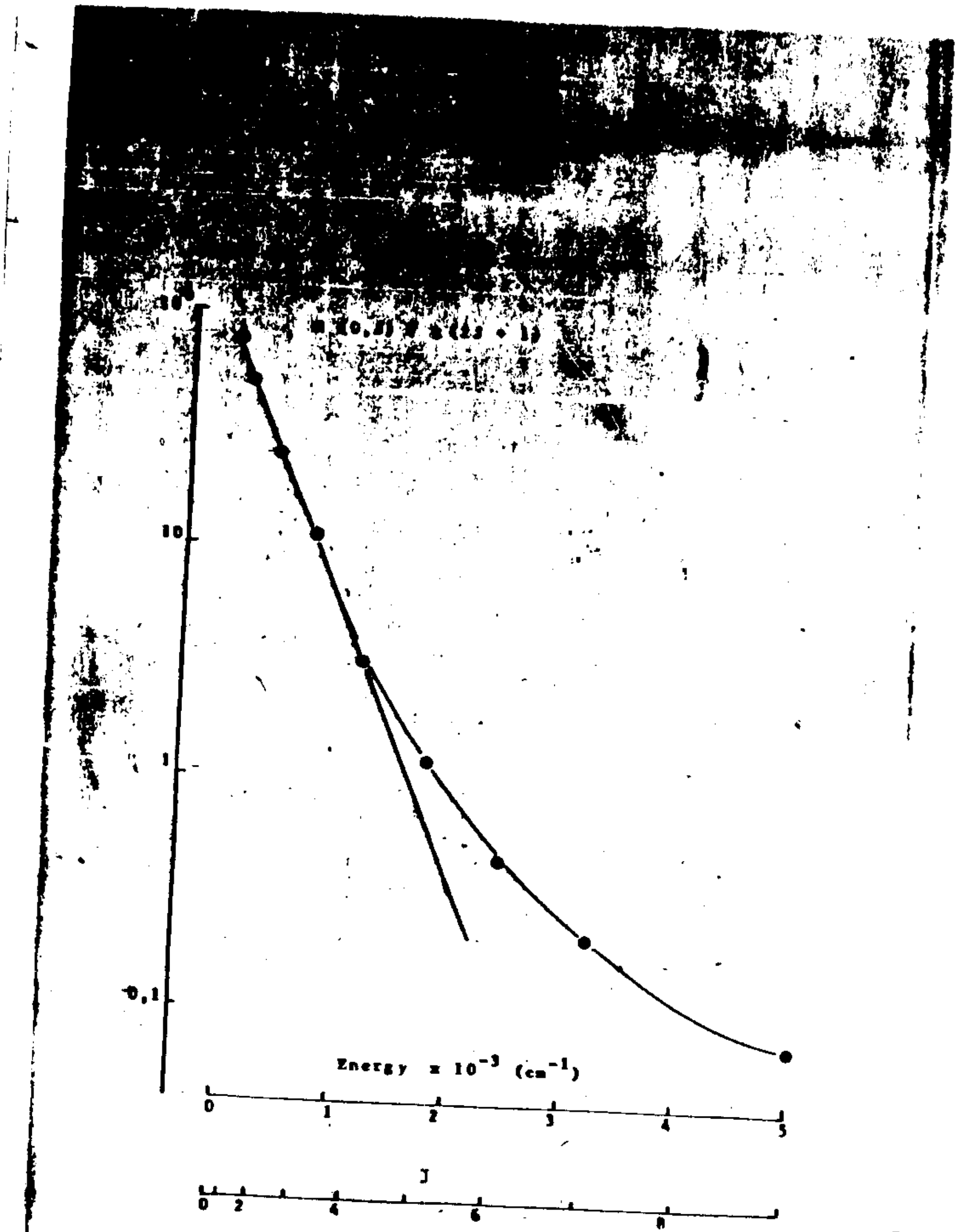
- scanning CARS
- BOXCARS or collinear CARS





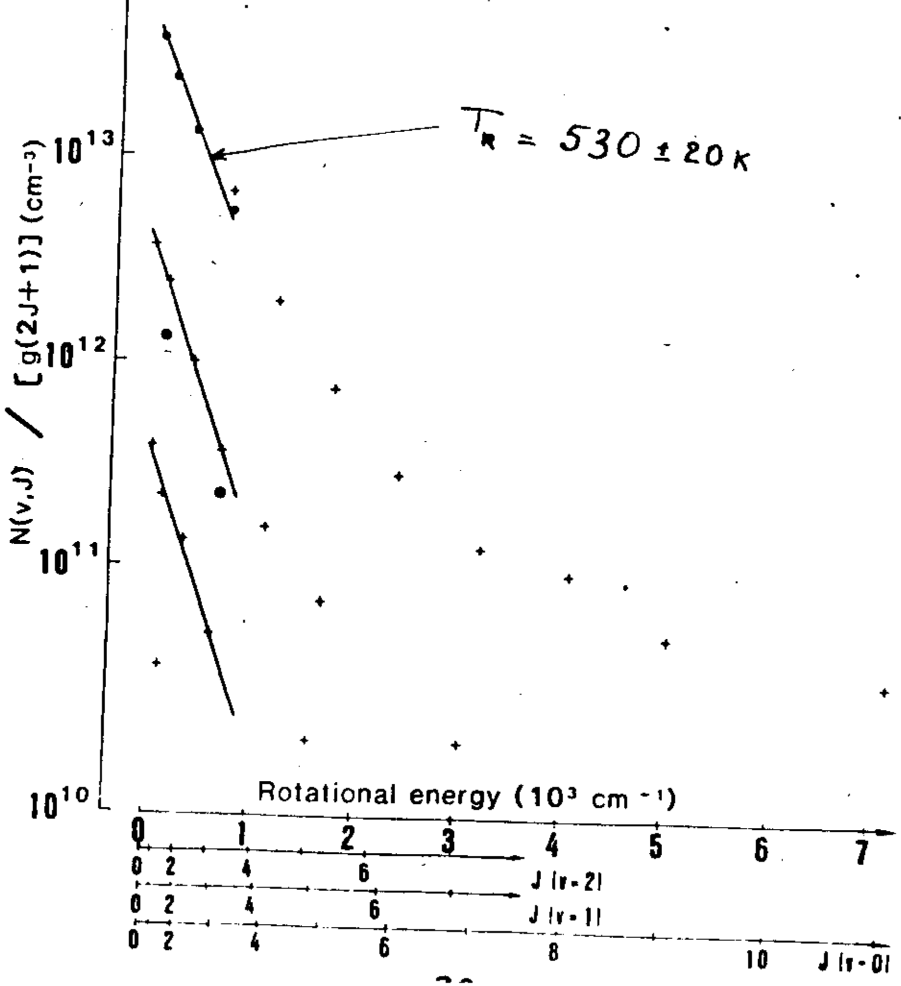
Rotational Temperatures



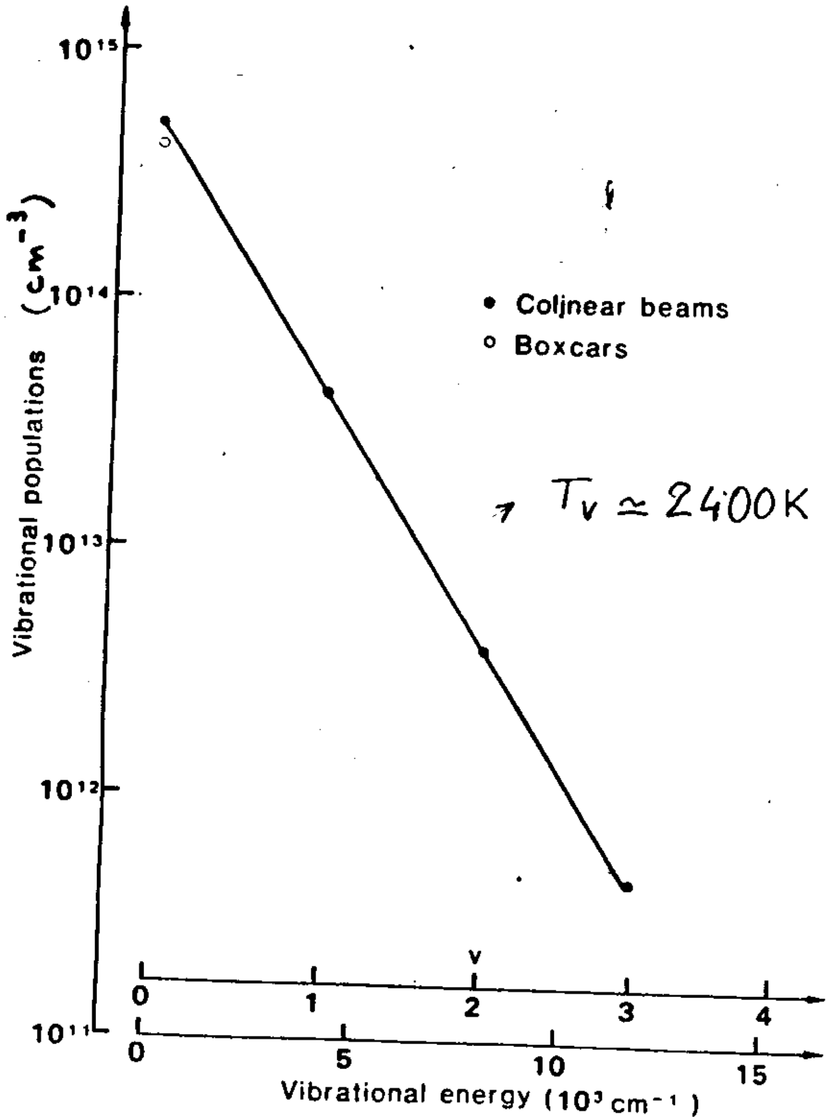


H_2 ROVIBRATIONAL POPULATIONS

90 V, 10 A
55 μbar
225 K anode



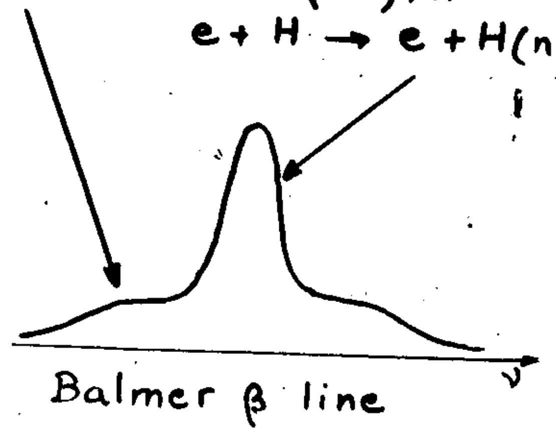
VIBRATIONAL POPULATIONS



H DENSITY MEASUREMENT *

$$e + H_2 \rightarrow e + H(n=4) + H \quad (1)$$

$$e + H \rightarrow e + H(n=4) \quad (2)$$



$n_H \simeq 4\ 10^{13}\ cm^{-3}$

$T_H \simeq 4500\ K$

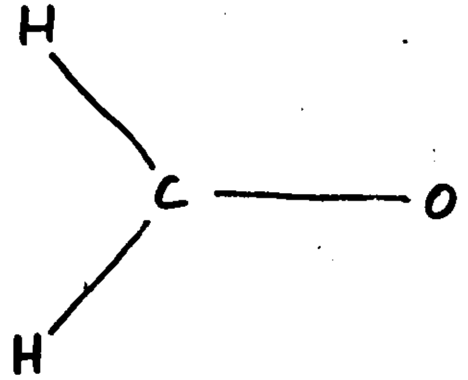
SUMMARY

	H_2	H	H_-	e
n (cm^{-3})	5.6 10^4	4.2 10^3	10^{10}	10^{12}
T(K)	530	4500K		10^4 (0.85eV)

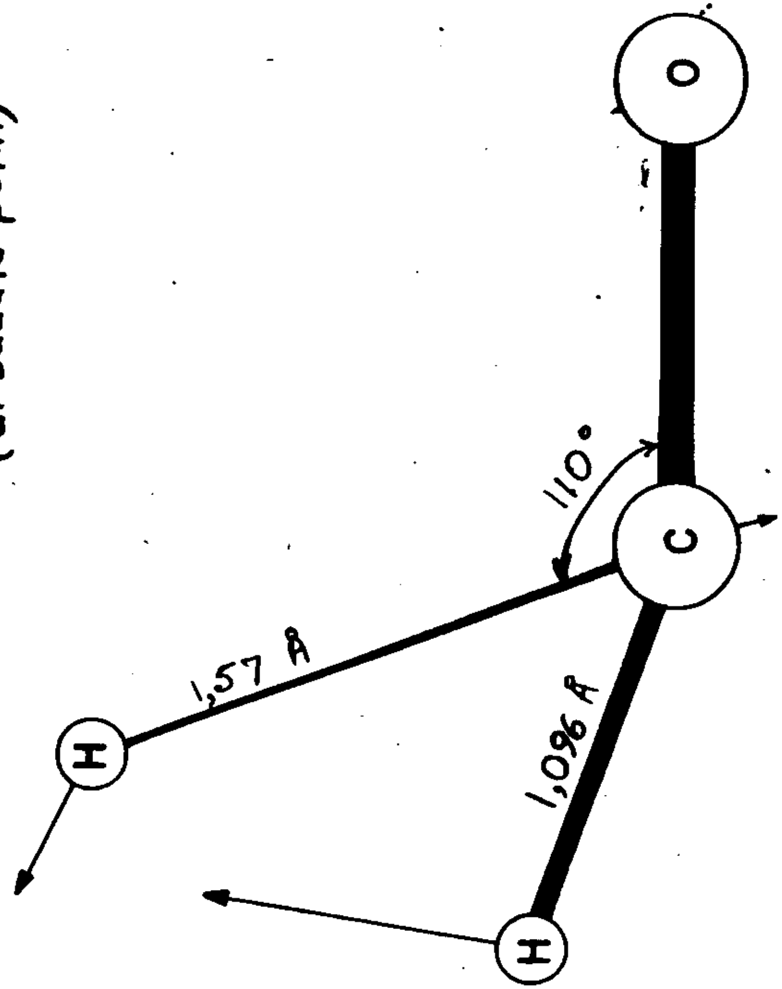
$$H_2CO + h\nu \xrightarrow{(335 < \lambda < 350nm)} H_2CO^*$$

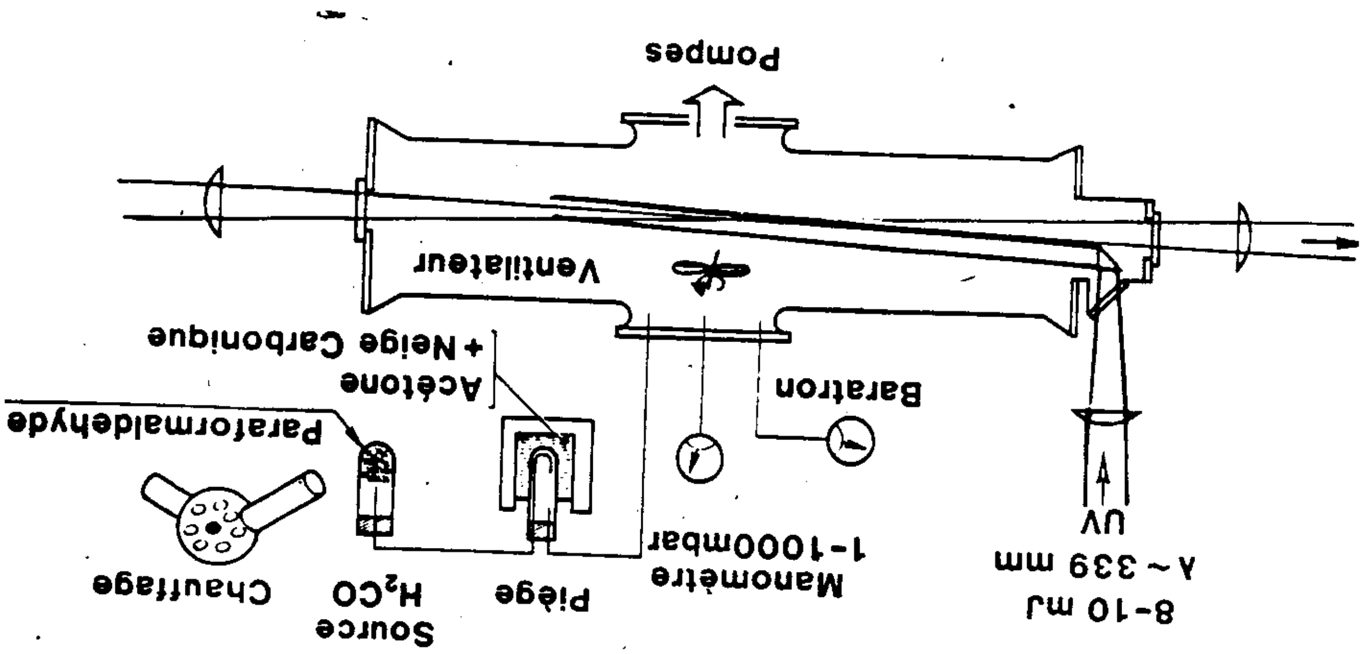
$$H_2CO^* \longrightarrow H_2 + CO$$

H_2CO at rest

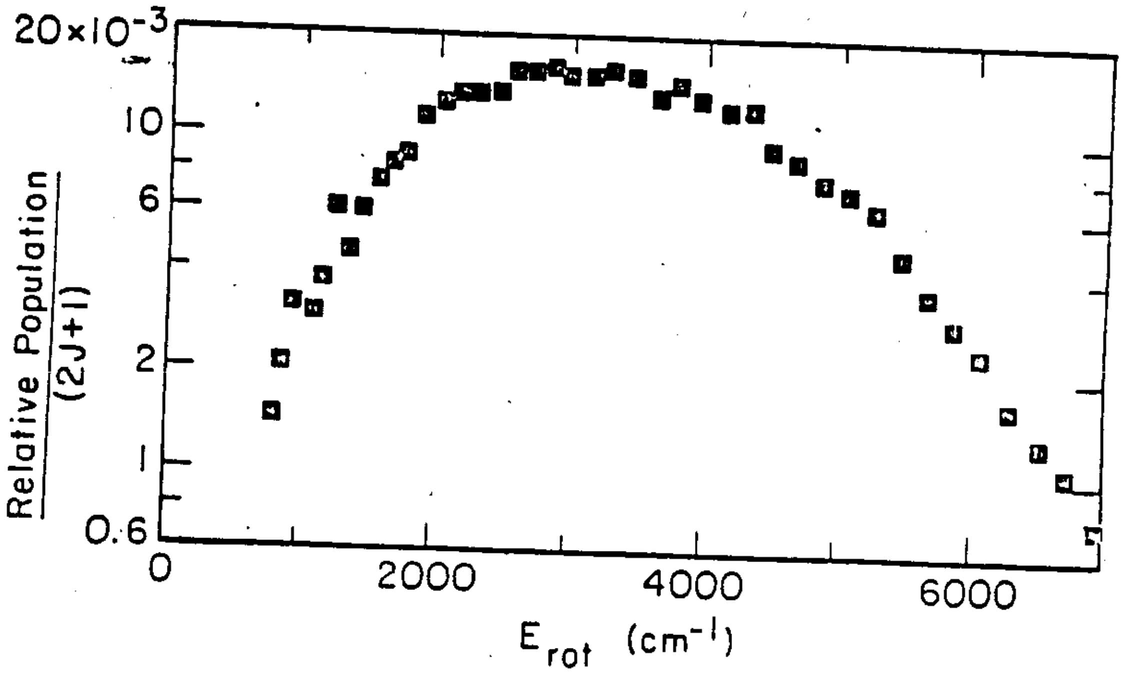


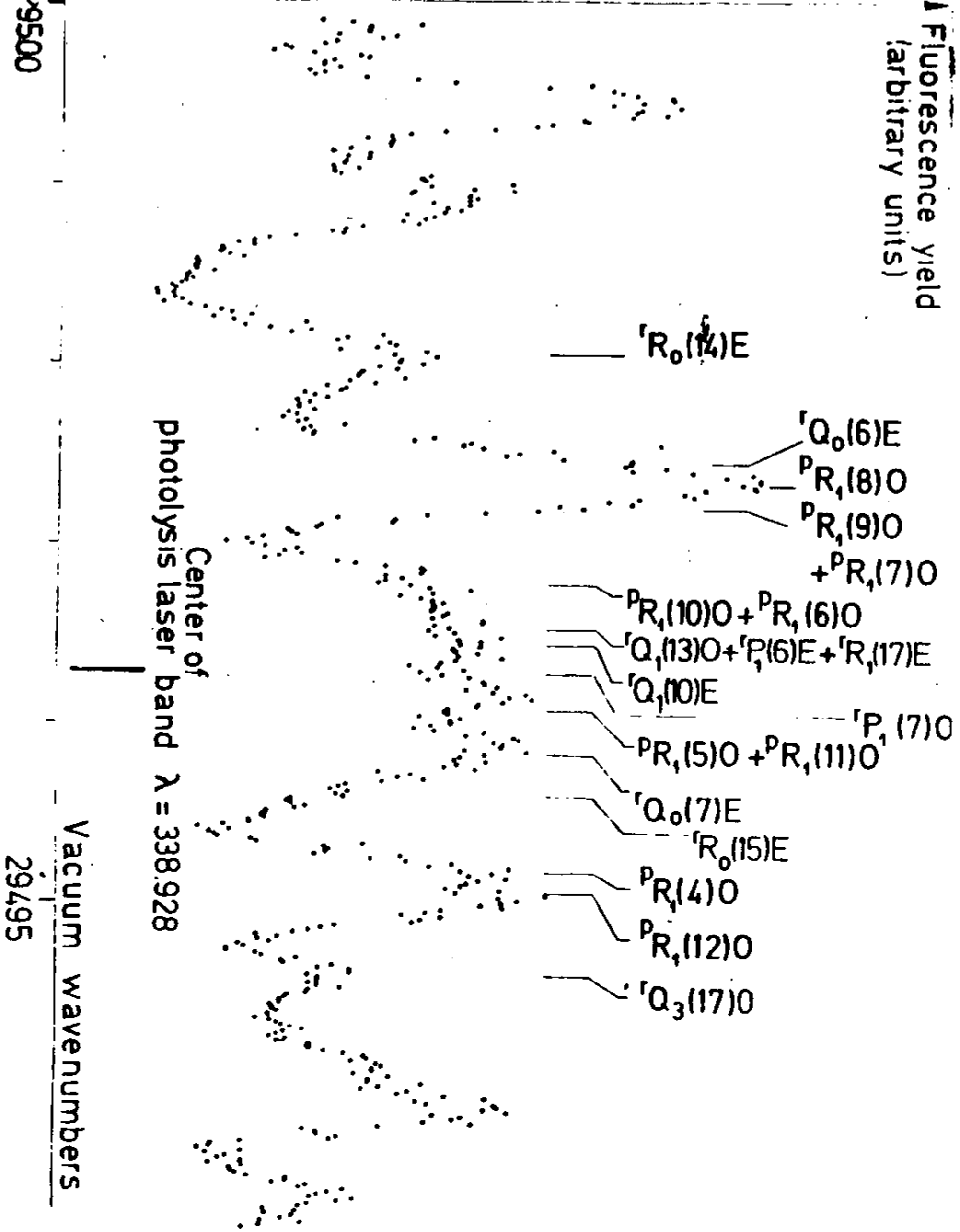
GEOMETRY
REACTION COORDINATE
(at saddle point)



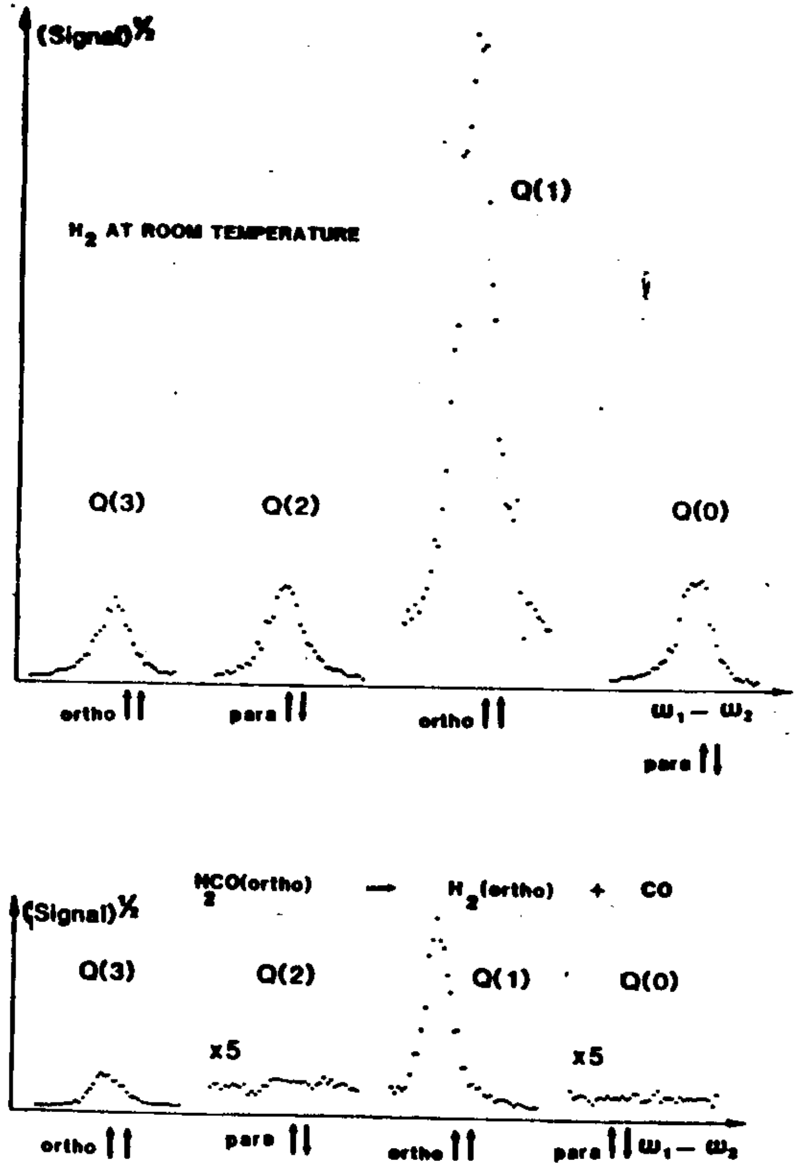


CO ROTATIONAL POPULATIONS

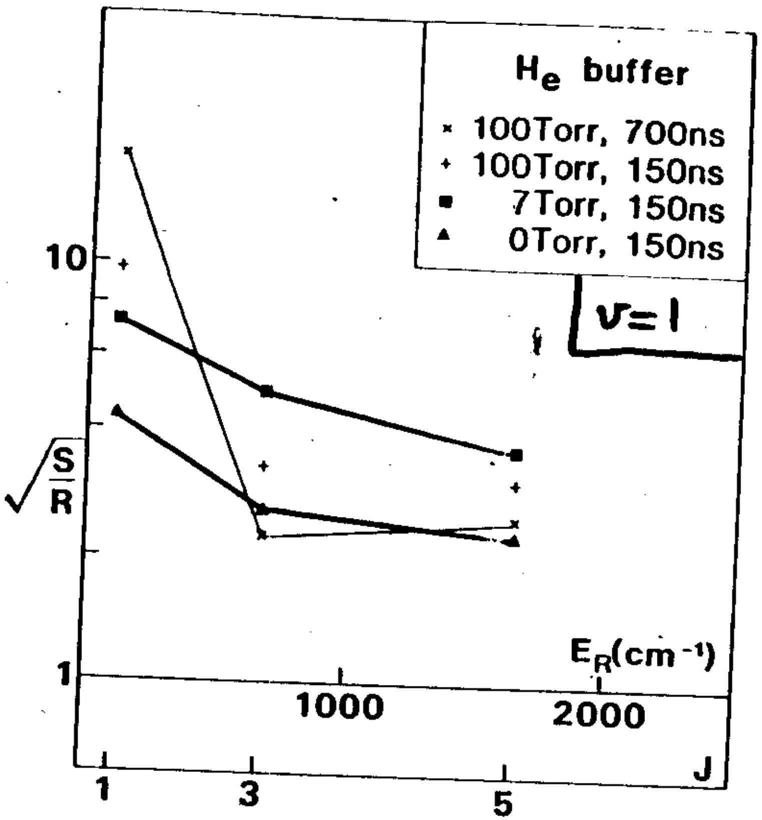



Fluorescence yield (arbitrary units)
29500
29495
Vacuum wavenumbers
Center of photolysis laser band λ = 338.928
rR0(14)E
rQ0(6)E
pR1(8)O
pR1(9)O
+pR1(7)O
pR1(10)O+pR1(6)O
rQ1(13)O+rP1(6)E+rR1(17)E
rQ1(10)E
rP1(7)O
pR1(5)O+pR1(11)O
rQ0(7)E
rR0(15)E
pR1(4)O
pR1(12)O
rQ3(17)O

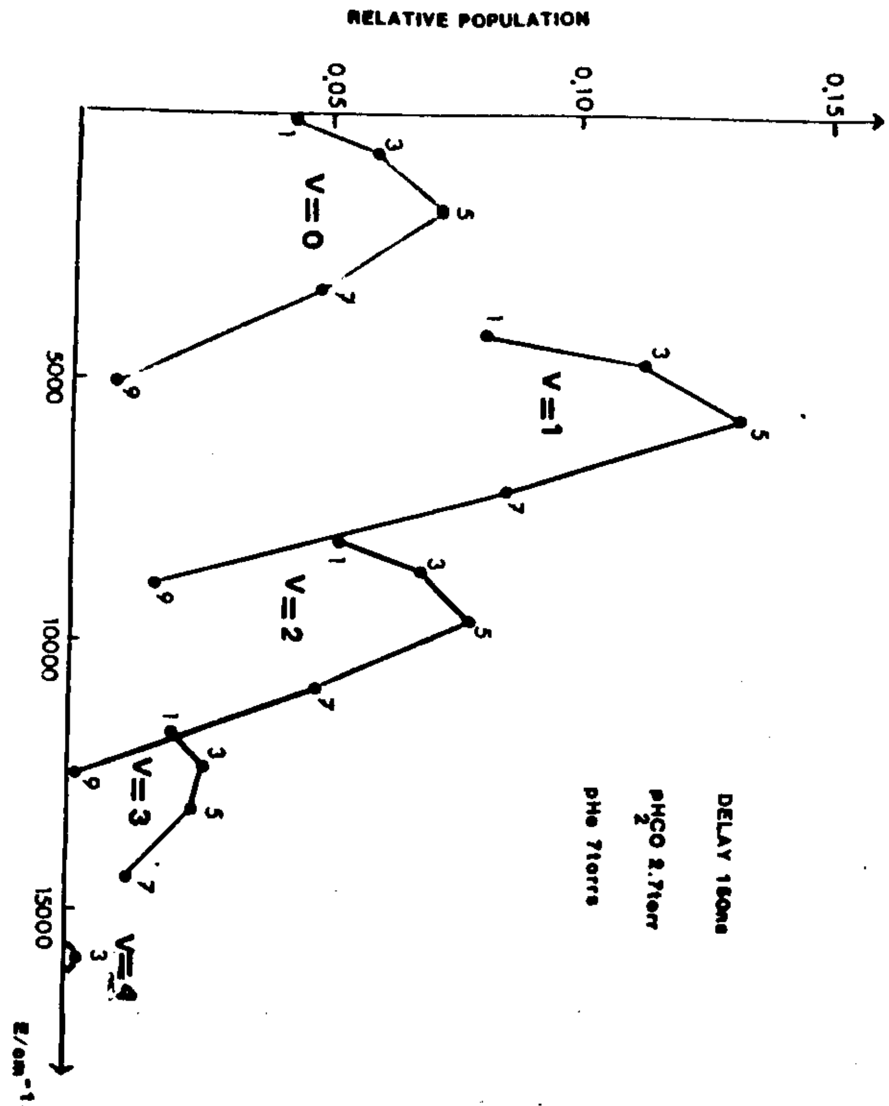
41

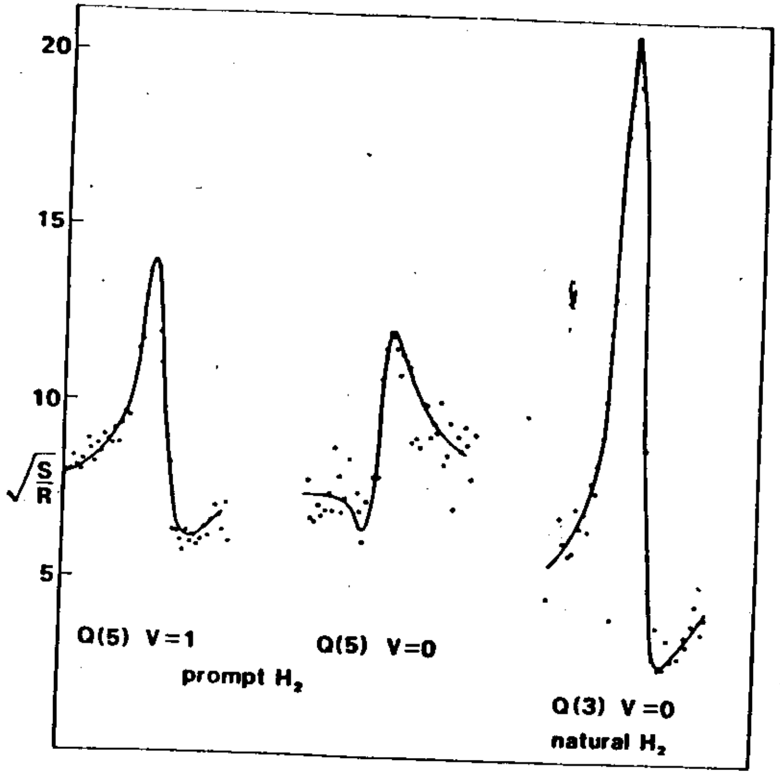

(Signal)½
H2 AT ROOM TEMPERATURE
Q(1)
Q(3)
Q(2)
Q(0)
ortho ↑↑
para ↑↓
ortho ↑↑
ω1 – ω2
para ↑↓
(Signal)½
H2CO(ortho) → H2(ortho) + CO
Q(3)
Q(2)
Q(1)
Q(0)
x5
x5
ortho ↑↑
para ↑↓
ortho ↑↑
para ↑↓ ω1 – ω2

42

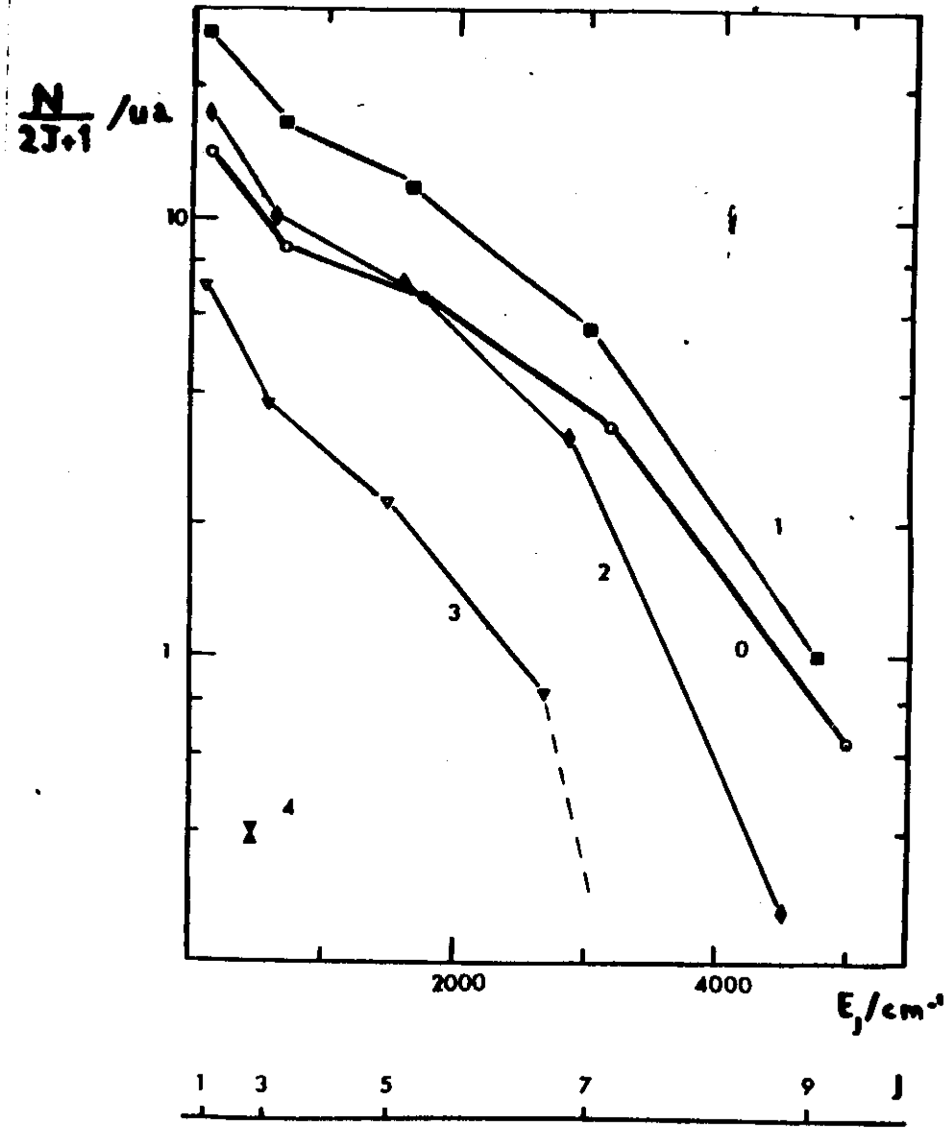


ROTATIONAL
RELAXATION
by
HELIUM

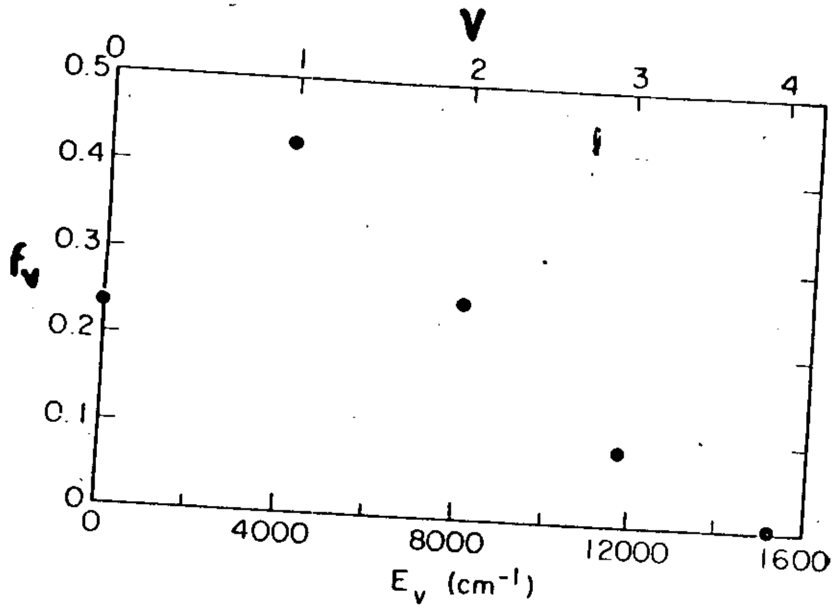




SIGN OF POPULATION DIFFERENCES



VIBRATIONAL POPULATIONS



COSTS

equipment

2 MF or 220 k$

personnel

2-3 scientists

100 - 200 kF or 10-20 k$ /month.

Detection sensitivity in conventional CARS

a – multiplex CARS with crossed beams

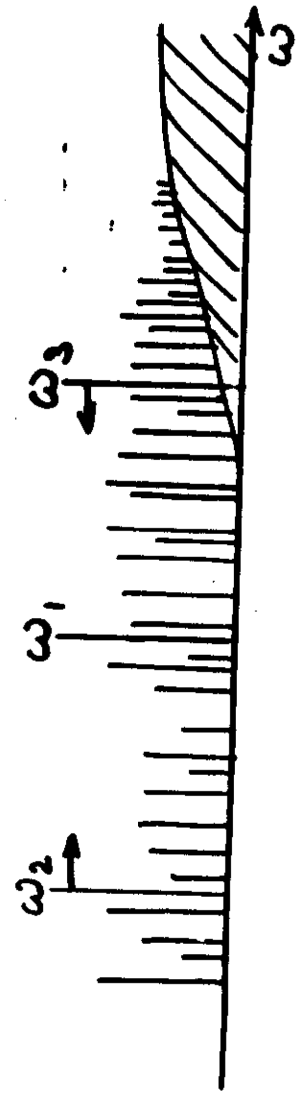
10^{-2} mole fraction at 1500K and 1bar
→ majority species

b – scanning CARS

10^{-3} – 10^{-5} mole fraction at 1500K and 1bar

10^{11} – 10^{12} cm^{-3} pure gas near 300 K
↓ per quantum state

Resonance-enhanced CARS should permit an improvement



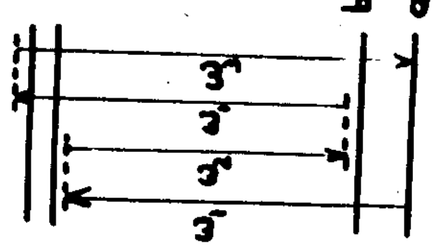
RESONANCE CARS SUSCEPTIBILITY

$$\chi = \chi_R + \chi_{NR} \quad , \text{ with}$$

$$\chi_R = \frac{N}{\hbar^3} \times \sum_{ba} \Big\{ \frac{1}{\omega_{ba} - (\omega_1 - \omega_2) - i\Gamma_{ba}}$$

$$\times \sum_n \Big(\rho_{aa}^{(0)} \frac{P_{an} P_{na}}{\omega_{na} - \omega_1 - i\Gamma_{na}} - \rho_{bb}^{(0)} \frac{P_{bn} P_{nb}}{\omega_{nb} - \omega_2 - i\Gamma_{nb}} \Big)$$

$$\times \sum_{n'} \frac{P_{an'} P_{n'b}}{\omega_{n'a} - \omega_3 - i\Gamma_{n'a}} \Big\}$$



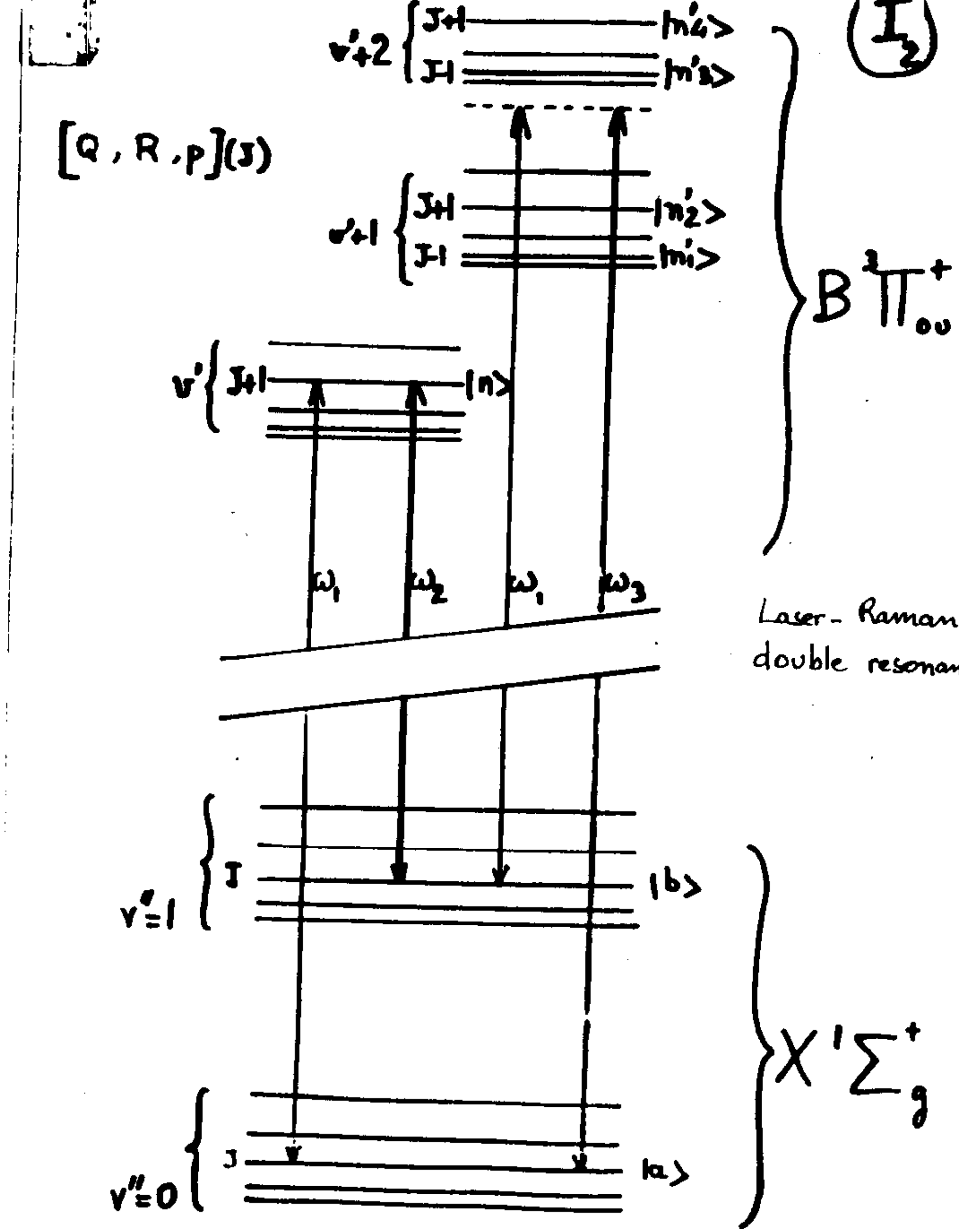
TWO BASIC PROBLEMS

I WHAT IS SPECTRAL CONTENT?

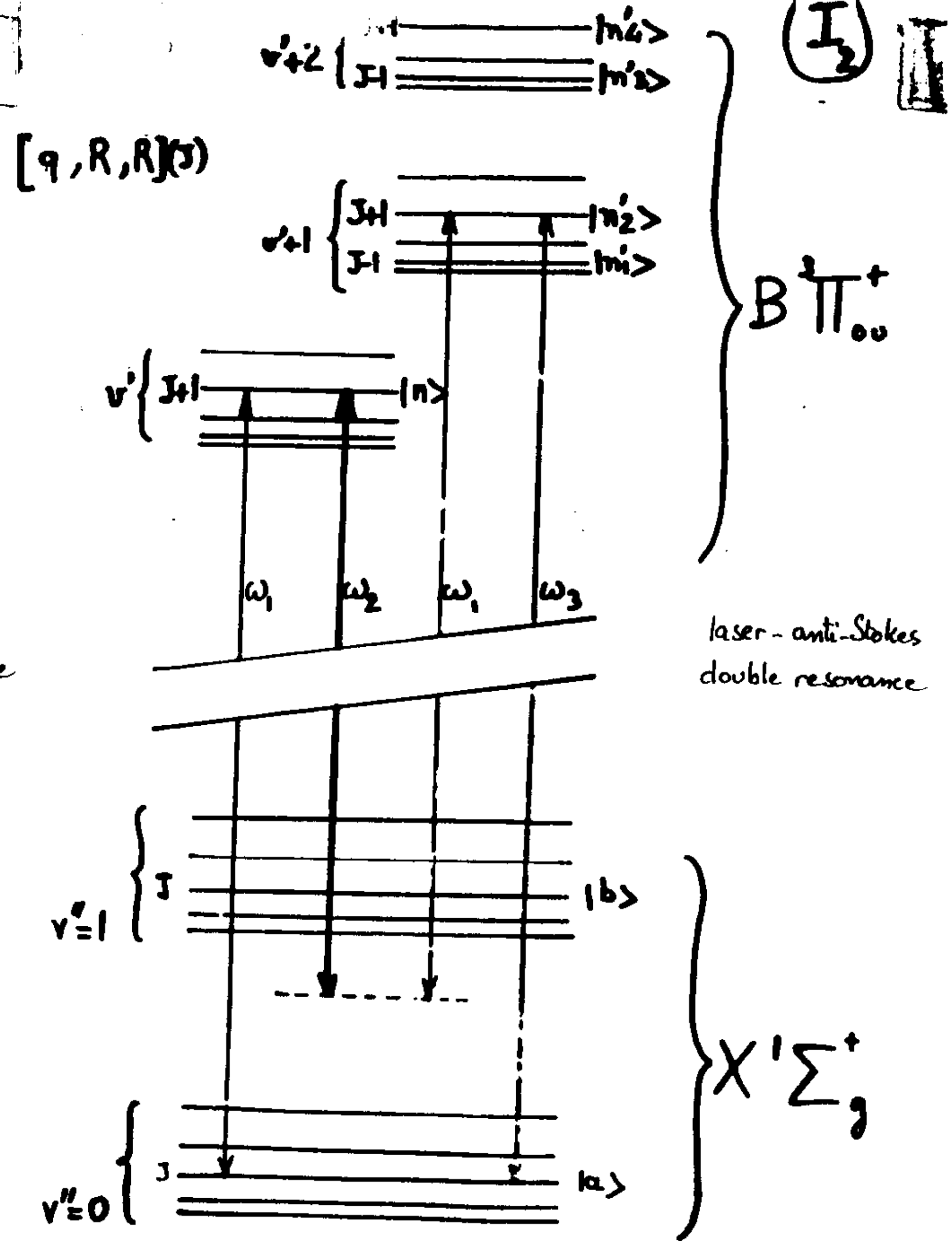
- ρ_{aa} , ρ_{bb}
- transition moments
- electronic resonances

II WHAT IS LINE CONTOUR?

- interference with χ_{nr}
- relative positions of exciting waves and absorption lines
- nature of broadening



Laser-Raman double resonance



laser-anti-Stokes double resonance

Positions of lines

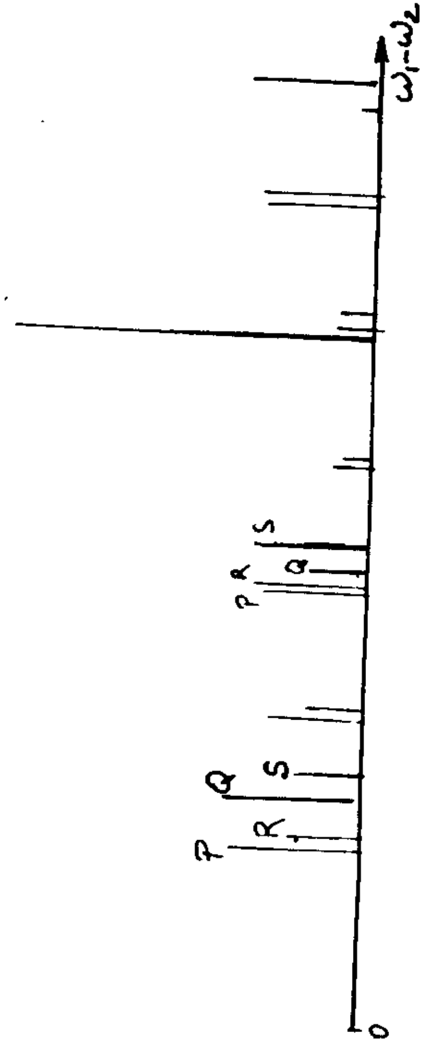
- Raman

$$\omega_1 - \omega_2 = \omega_{ba}$$

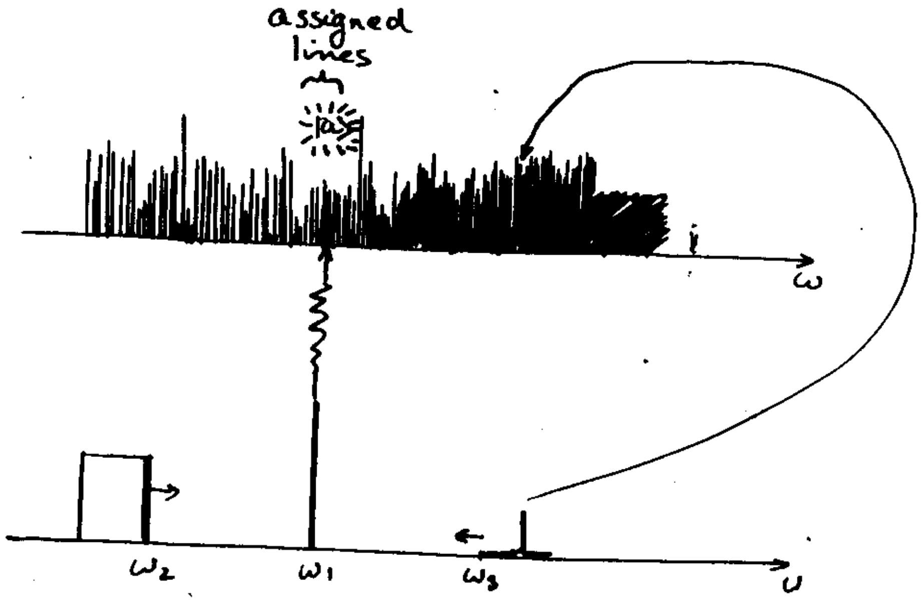
- electronic

$$\omega_3 = \omega_{n'a} \quad , \text{ hence}$$

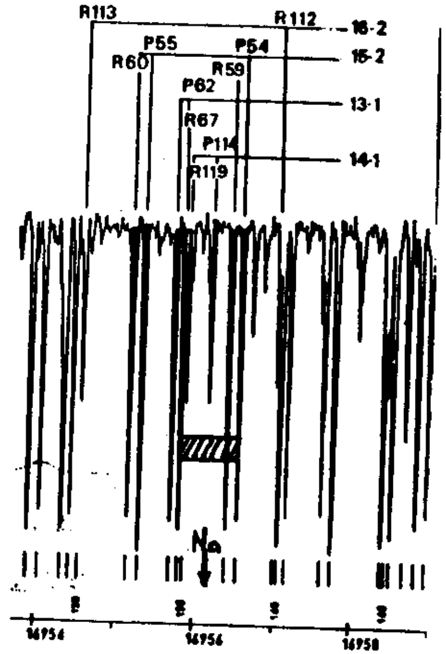
$$\omega_1 - \omega_2 = \omega_{n'a} - \omega_1$$

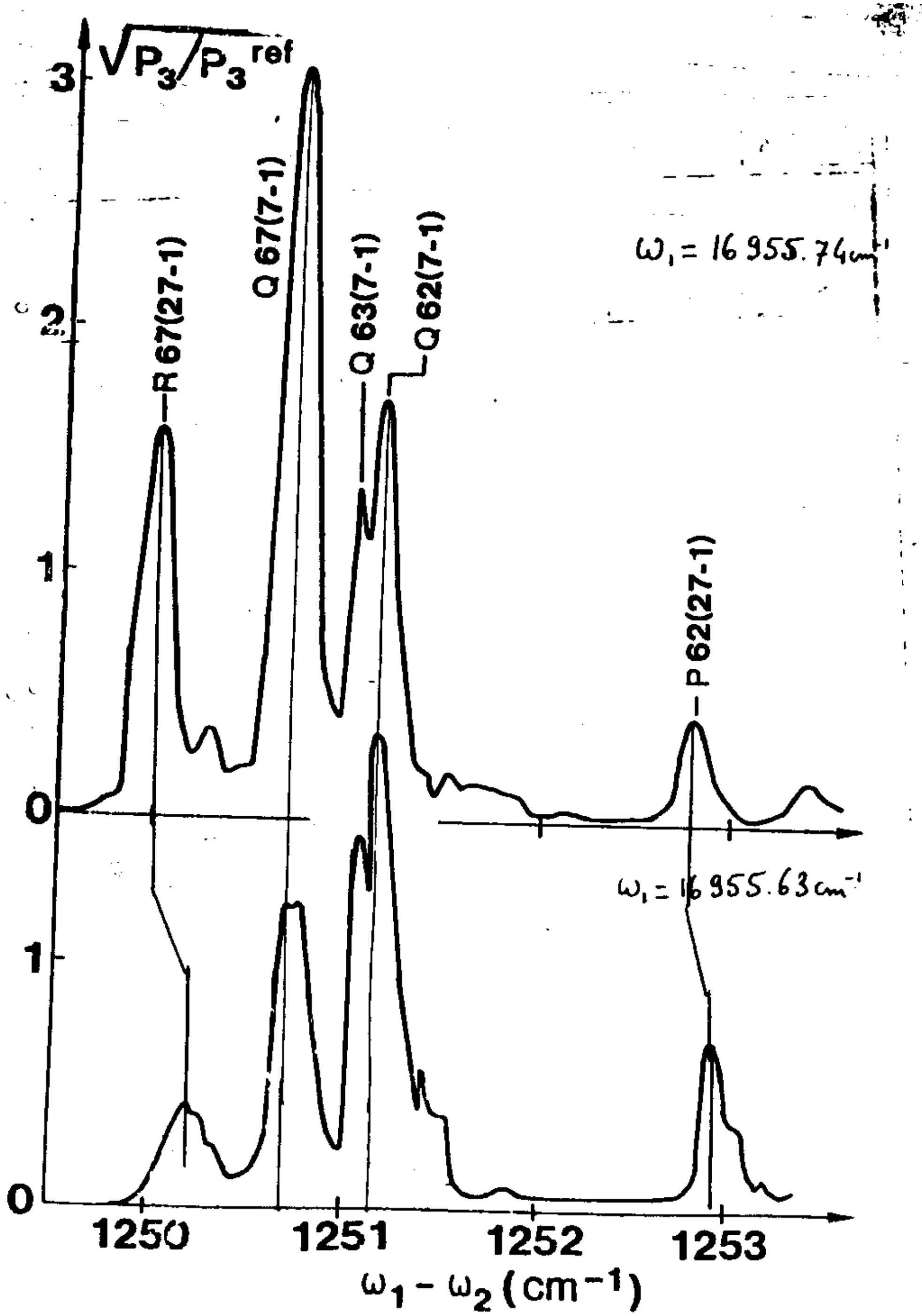


...sing resonance CARS



I_2 Fourier-transform spectrum near Na-D line





Line contours

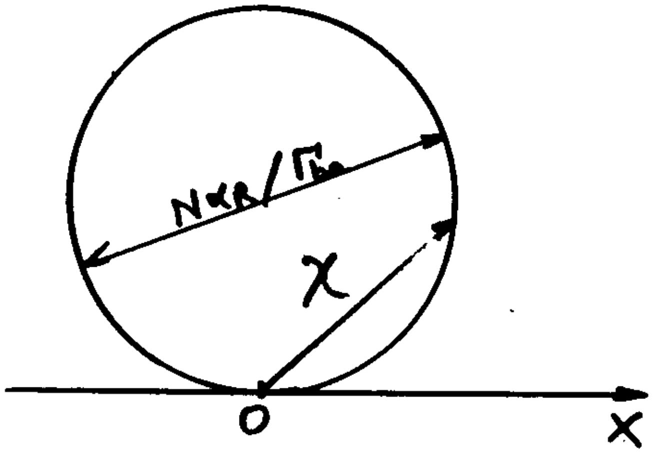
a – collisional broadening

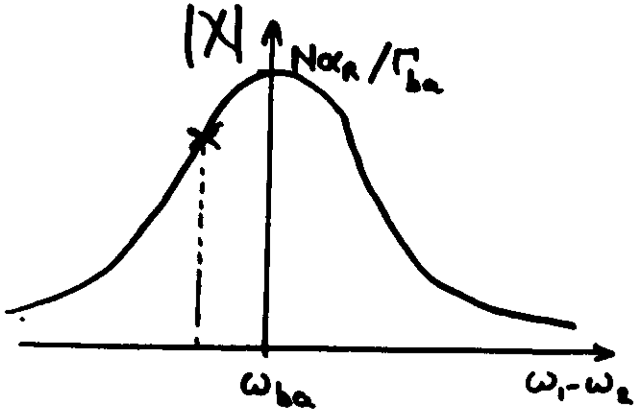
b – mixed broadening (collisional + Doppler)

COLLISIONAL BROADENING

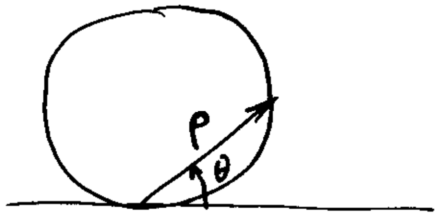
Isolated CARS line off resonance

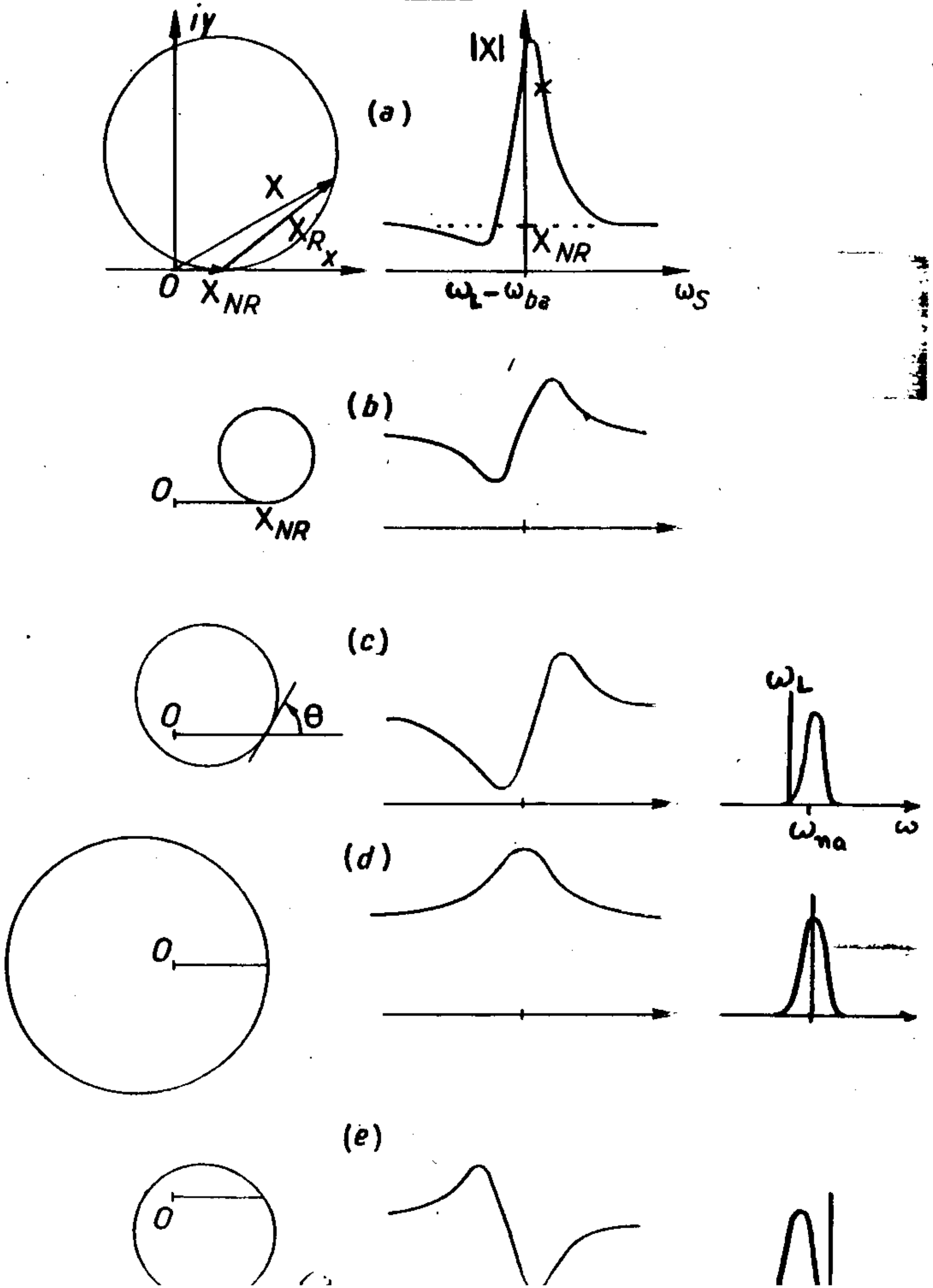
$$\chi = \chi_R \simeq N\alpha_r / (\omega_{ba} - \omega_1 + \omega_2 - i\Gamma_{ba})$$

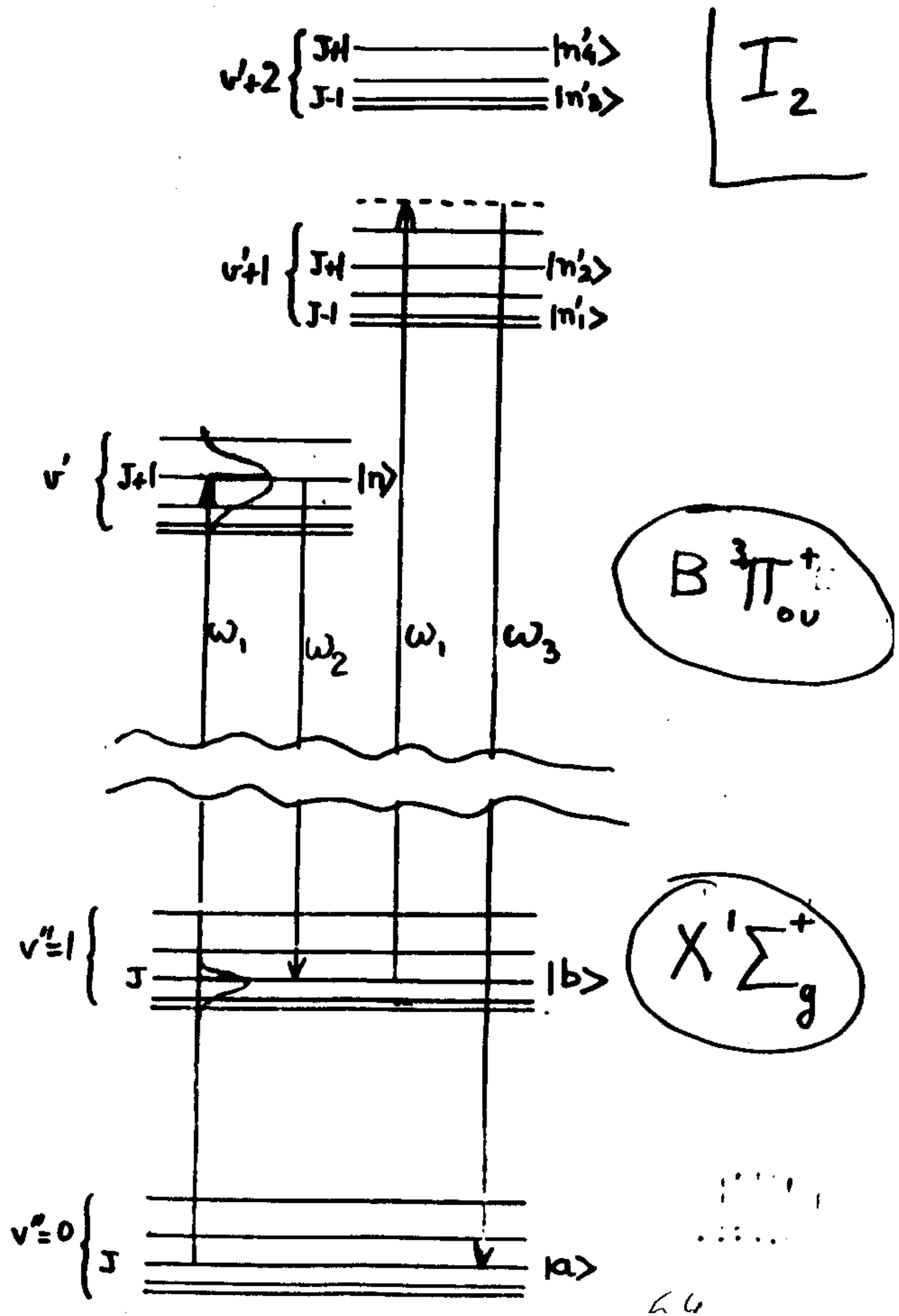


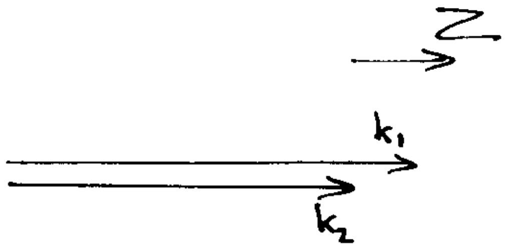


$$\alpha_R \propto \underbrace{\frac{1}{\omega_{na} - \omega_1 - i\gamma_{na}}}_{=\rho e^{i\theta}} \times \underbrace{\frac{1}{\omega_{n'a} - \omega_3 - i\gamma_{n'a}}}_{\simeq c^t}$$




iy
(a)
|X|
X
X_{R_X}
X_{NR}
O
$\omega_L - \omega_{ba}$
ω_S
(b)
O
X_{NR}
(c)
O
θ
ω_L
ω_{na}
ω
(d)
O
(e)
O


I₂
v'+2
J+1
J-1
|n'₄>
|n'₃>
v'+1
|n'₂>
|n'₁>
v'
|n>
$B\,^3\Pi^+_{0u}$
ω_1
ω_2
ω_1
ω_3
v"=1
J
|b>
$X\,^1\Sigma^+_g$
v"=0
|a>



Doppler shift on vibrational driving frequency

$(k_1 - k_2) v_z$

Resonance CARS lines in gases with mixed broadening

$$\chi_R \propto \int (\omega_{ba} - \omega_1 + \omega_2 + (k_1 - k_2) v - i\Gamma_{ba})^{-1}$$

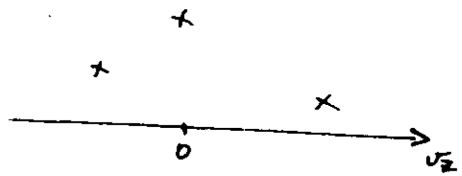
$$\times (\omega_{na} - \omega_1 + k_1 v - i\Gamma_{na})^{-1}$$

$$\times (\omega_{n'a} - \omega_3 + (2k_1 - k_2) v - i\Gamma_{n'a})^{-1}$$

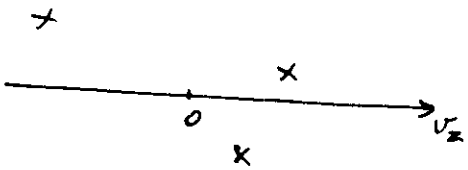
$$\times F(v)\, dv$$

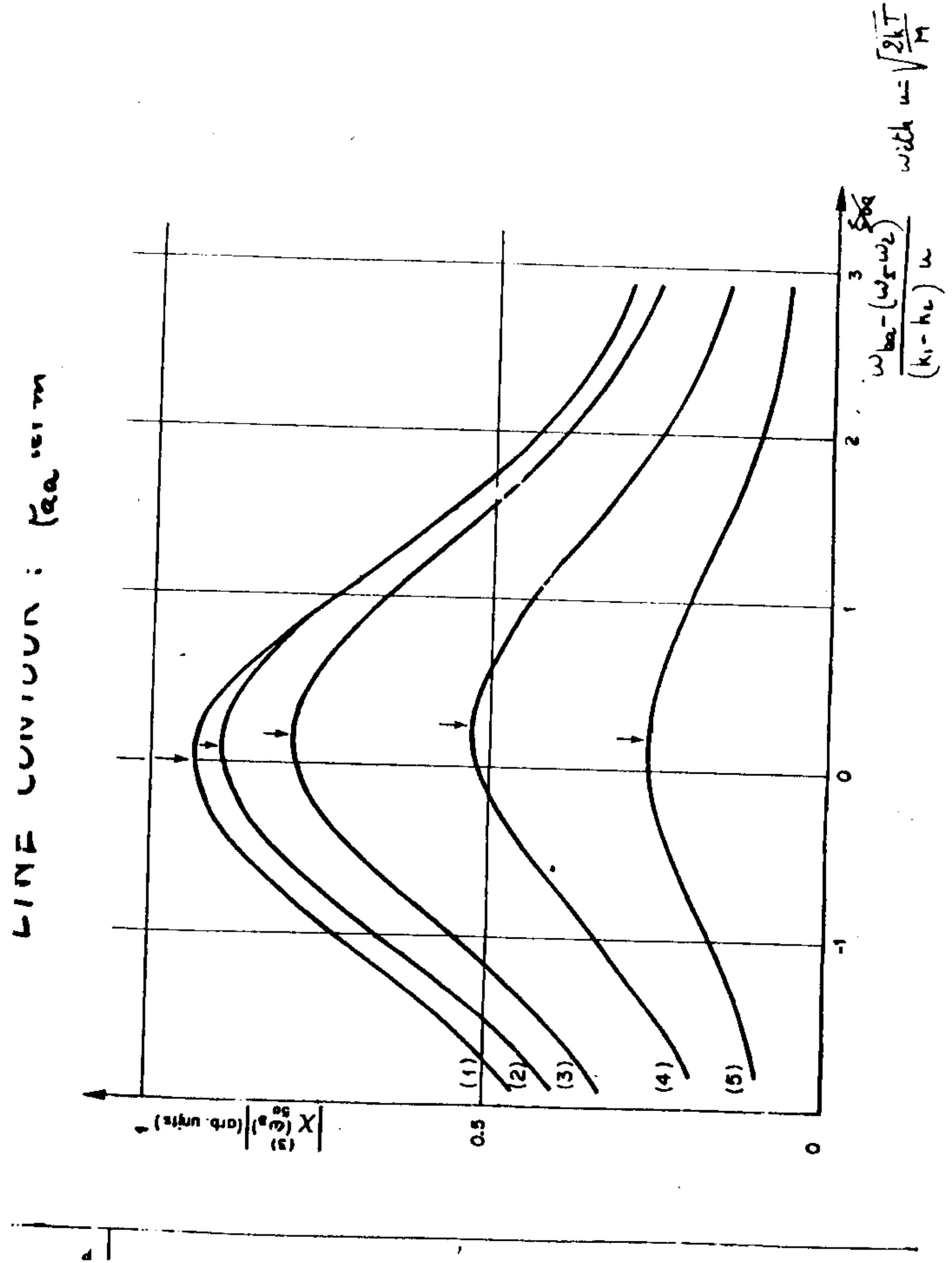
S. Druet, C. Bordé, J.P. Taran

poles of ρ_{aa} term



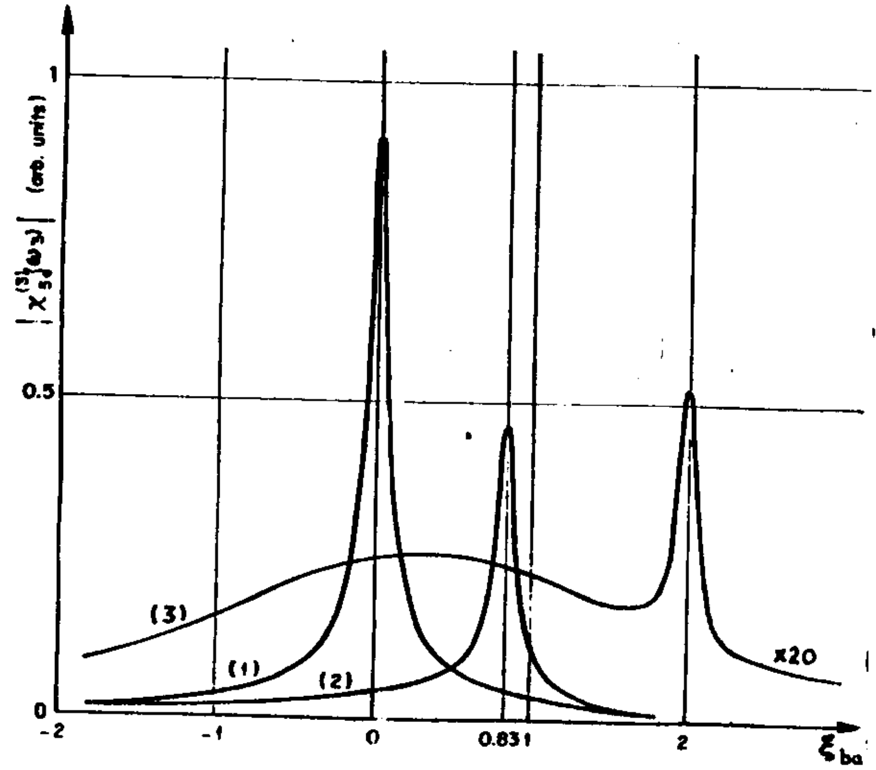
poles of main ρ_{bb} term





LINE CONTOUR :

ρ_{bb} term



WHY C_2 ?

- combustion interest
- electronic transitions in the visible
- large transition moments
- easy preparation

However:

- preparation actually not so easy
- emission spectrum not so well known
- concentrations in flames and discharges always low
- one photon and Raman saturation

Condition for triple resonance

$$\omega_{n'n} = \omega_{ba}$$

- hence three possibilities for $|a\rangle$:

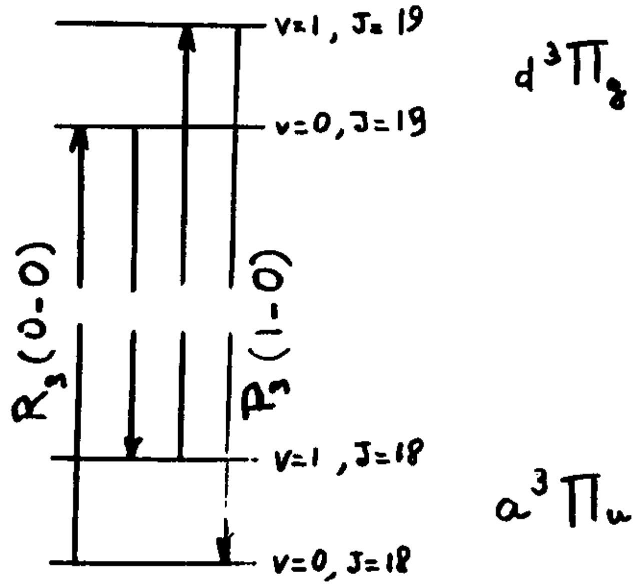
$$\begin{cases} v=0, & J=18, & \Omega=0, & i=3 \\ v=0, & J=19, & \Omega=1, & i=2 \\ v=0, & J=20, & \Omega=2, & i=1 \end{cases}$$

- for each of which there are two frequency arrangements:

① [Q_i (1-0), R_i (0-0), P_i (1-0)] J

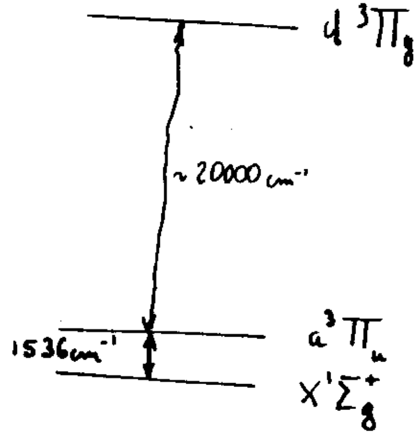
② [S_i (1-0), R_i (0-0), R_i (1-0)] J

- best choice is nb ①



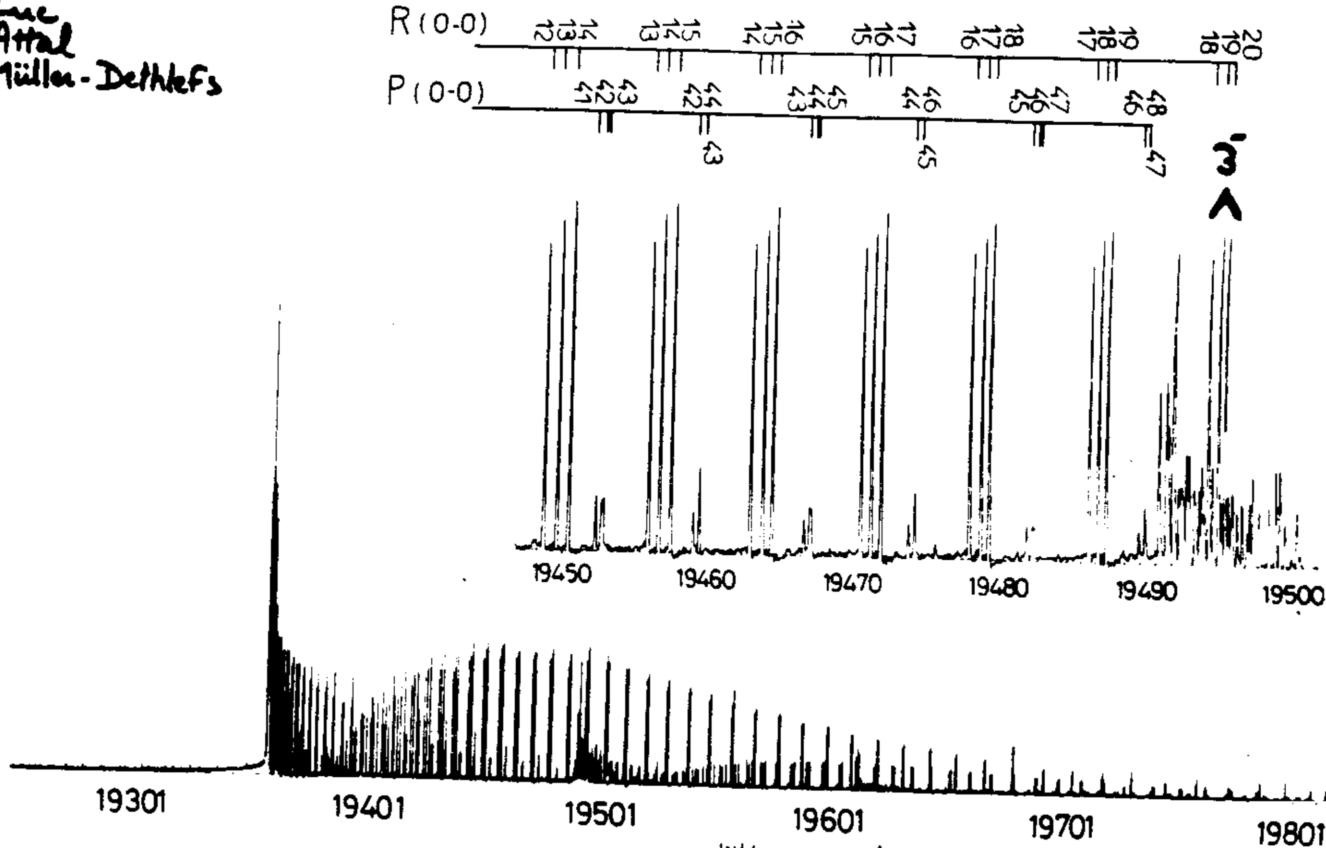
C_2 Swan system

$$d^3\Pi_g \leftarrow a^3\Pi_u$$

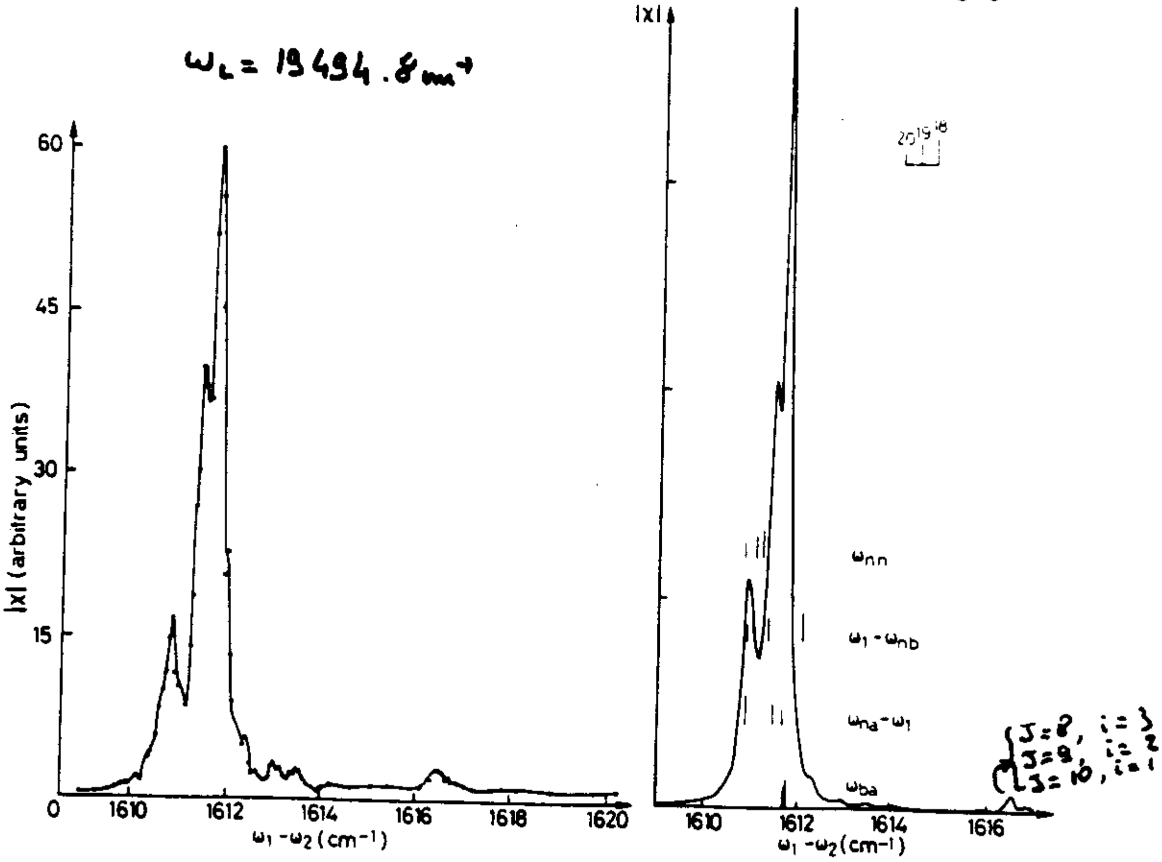


C_2 SWAN SYSTEM

Delbarre
Amiot
Luc
Attal
Müller-Dethlefs



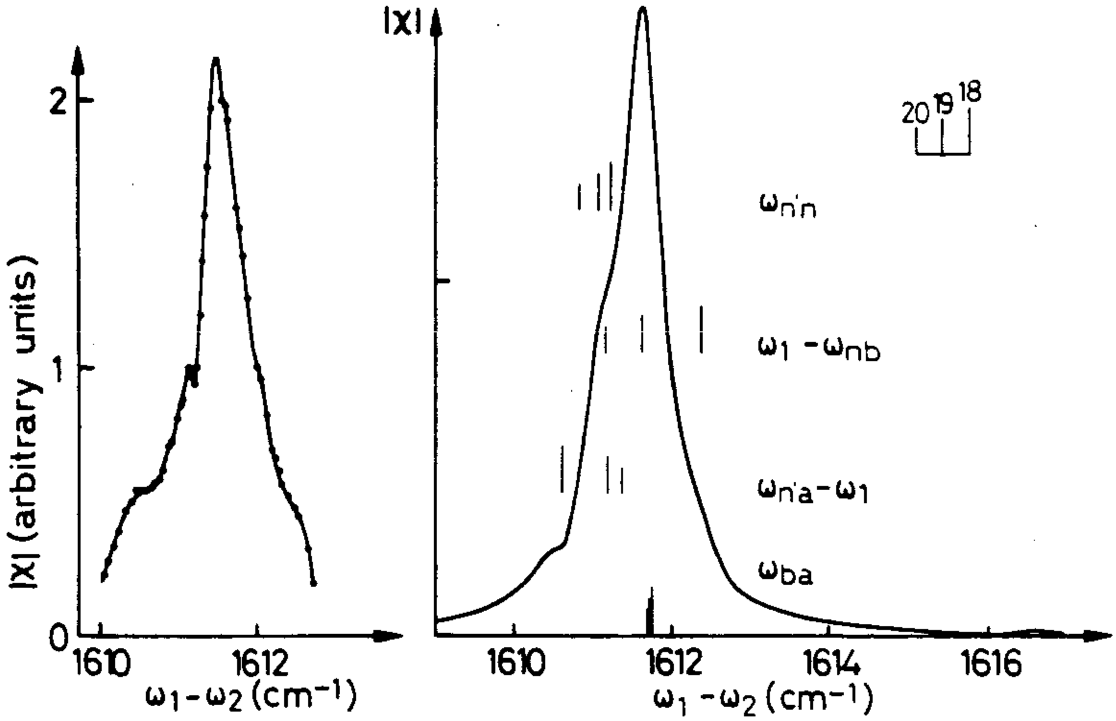
$\omega_L = 19494.8\ cm^{-1}$



C_2 in microwave discharge

73

74



C_2 in welding torch