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WINTER COLLEGE ON LASERS, ATOMIC AND MOLECULAR PHYSICS

(21 January - 22 March 1985)

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# LASER RAMAN SPECTRA

(Lectures I & II)

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LECTURE 1

# OPTICAL PROCESSES

## # SPONTANEOUS EMISSION

| | $\frac{d\sigma}{d\Omega}$ ($cm^2/sr$) |
|---|---|
| * MIE SCATTERING | $10^{-8}$ |
| * (ABSORPTION) | |
| FLUORESCENCE (LIF) | $10^{-20}$ |
| * RAYLEIGH SCATTERING | $10^{-27}$ |
| * RAMAN SCATTERING (SRS) | $10^{-30}$ |

## # NONLIEAR INTERACTION

- COHERENT ANTI-STOKES RAMAN SCATTERING (CARS)
- RAMAN INDUCED KERR EFFECT (RIKE)
- STIMULATED RAMAN GAIN SPECTROSCOPY (SRGS)
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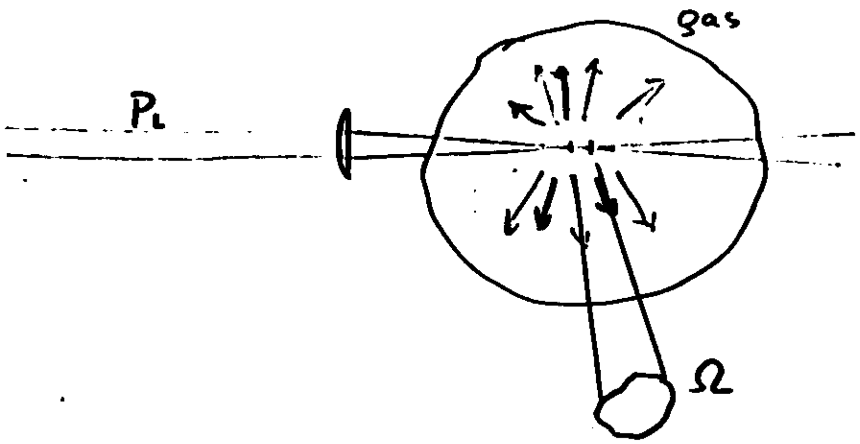
# SCATTERING OF LIGHT
# by
# MOLECULES



$$P_{scattered} = P_L \times N \times dz \times \Omega \times \frac{d\sigma}{d\Omega}$$

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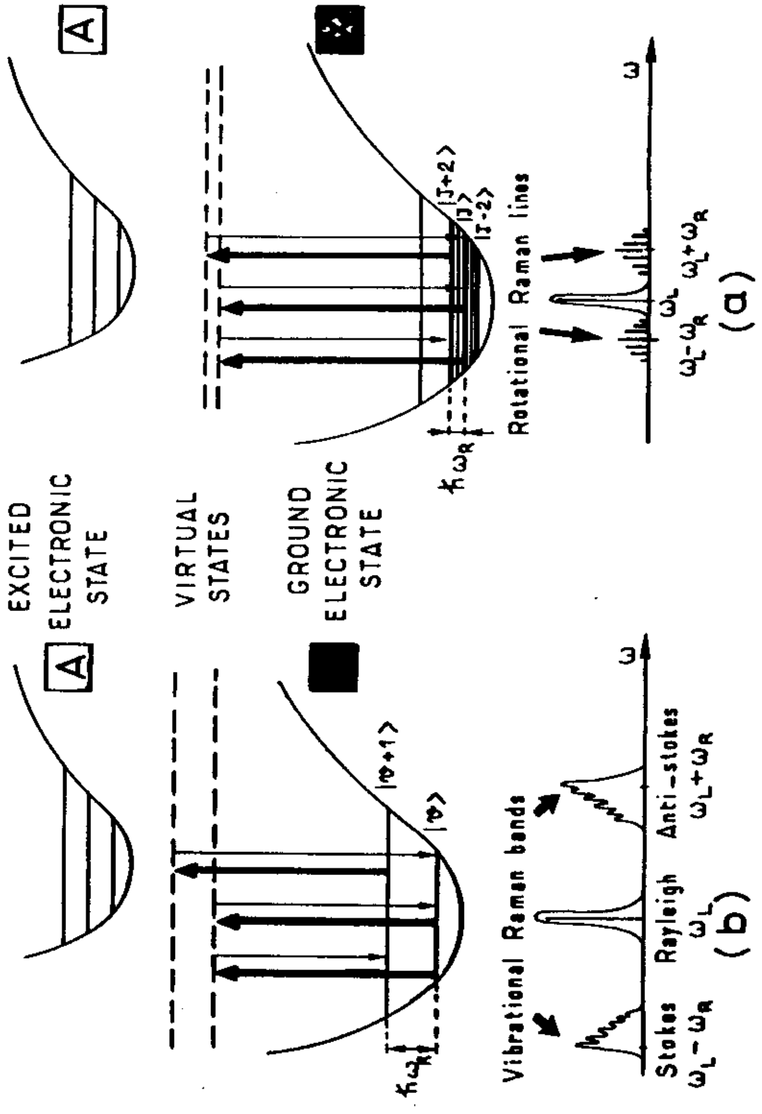
# SPONTANEOUS RAMAN PROCESS

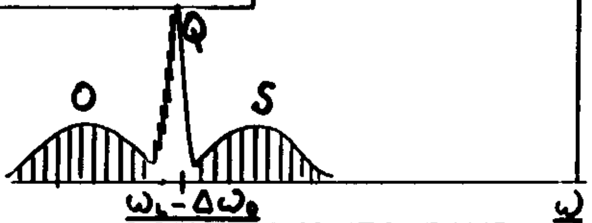


# SPONTANEOUS RAMAN SCATTERING

# $$P_{scatt.} = P_L \cdot N \cdot \frac{d\sigma}{d\Omega} \cdot l \cdot \Omega$$

# **SELECTION RULE**

$$v' - v = \Delta v = \pm 1$$
$$J' - J = \Delta J = 0, \pm 2$$



VIBRATIONAL STOKES BAND

# **TERM VALUE**

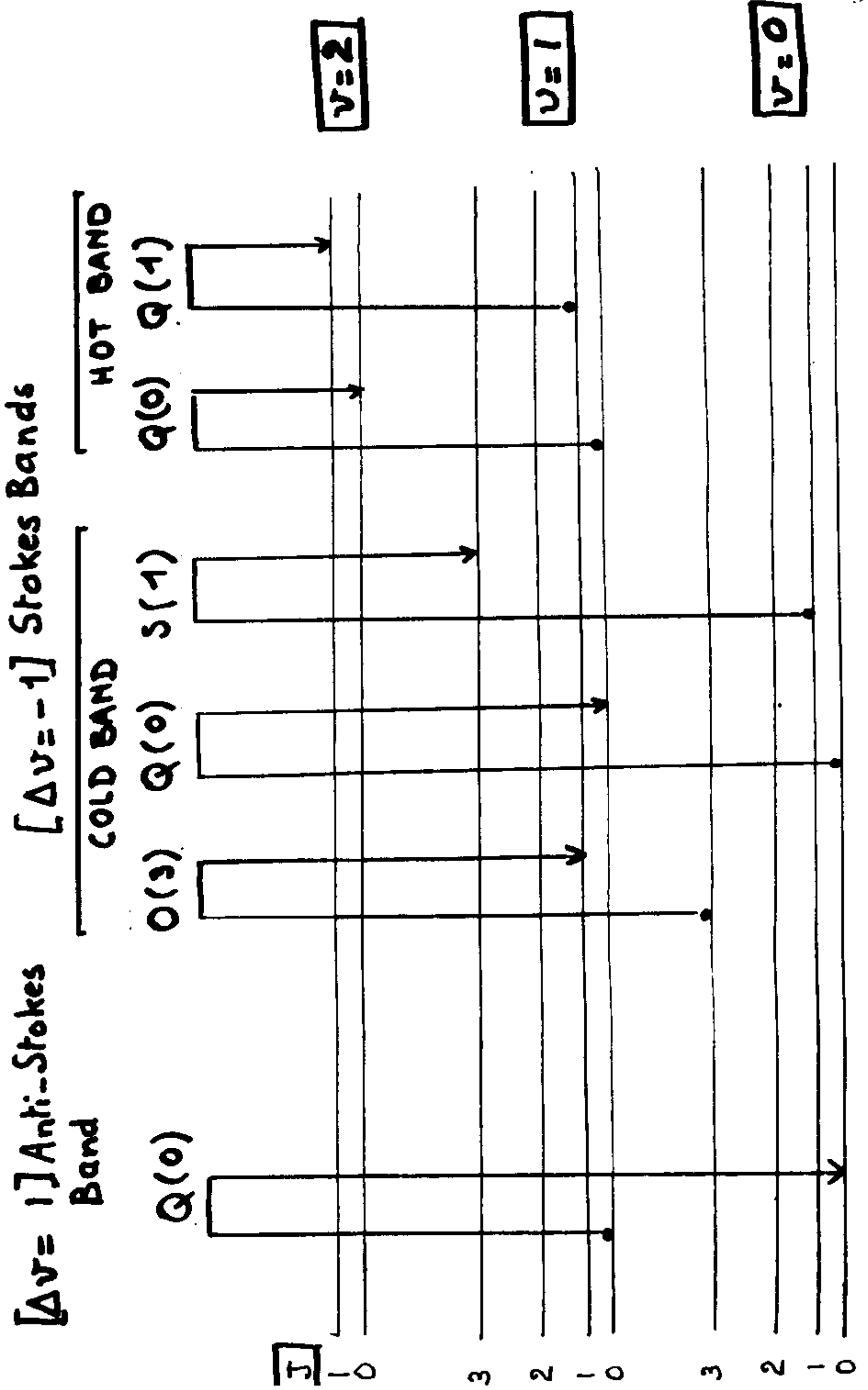
$$\frac{E}{hc} = G(v) + F(J) = \omega_e(v+\tfrac{1}{2}) - \omega_e x_e(v+\tfrac{1}{2})^2 + B_v J(J+1)$$

# **RAMAN SHIFT**

$$\hbar\omega_R = \underbrace{\Delta\omega_0}_{\text{vibrat.}} + \underbrace{F(J') - F(J)}_{\text{rotational}}$$

$$\Delta O : 2B_v' - (3B_v' + B_v'')J + (B_v' - B_v'')J^2$$
$$\Delta Q : (B_v' - B_v'')(J+1)J$$
$$\Delta S : 6B_v' + (5B_v' - B_v'')J + (B_v' - B_v'')J^2$$

# RAMAN TRANSITIONS



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# POPULATION DISTRIBUTION

$$N_{v,J} = N \times \underbrace{\frac{(2J+1)\, g_J \exp\left(-\frac{[G(v)+F(J)]hc}{kT}\right)}{Q_R\, Q_v}}_{f(T)}$$

*

# RAMAN INTENSITY

**Stokes:** $P_S(\underline{v}, J \longrightarrow v+1, J) = N \times P_L \times \left(\frac{d\sigma}{d\Omega}\right)_S \times f_v(T) \times \Omega \times \ell$

**Anti-Stokes:** $P_{A.S}(\underline{v+1}, J \longrightarrow v, J) = N \times P_L \times \left(\frac{d\sigma}{d\Omega}\right)_{A.S} \times f_{v+1}(T) \times \Omega \times \ell$

$$\frac{P_S}{P_{A.S}} \propto \frac{f_v(T)}{f_{v+1}(T)}$$

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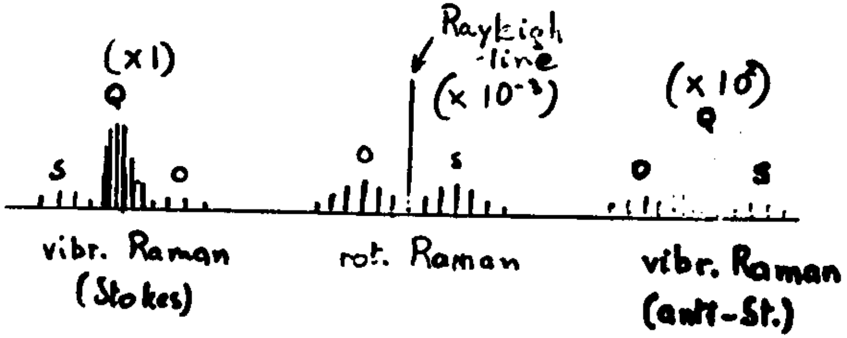
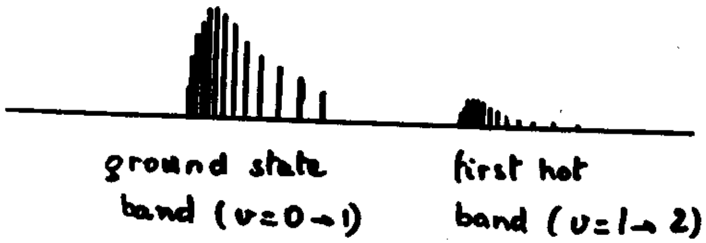
# ANEOUS RAMAN SPECTRA

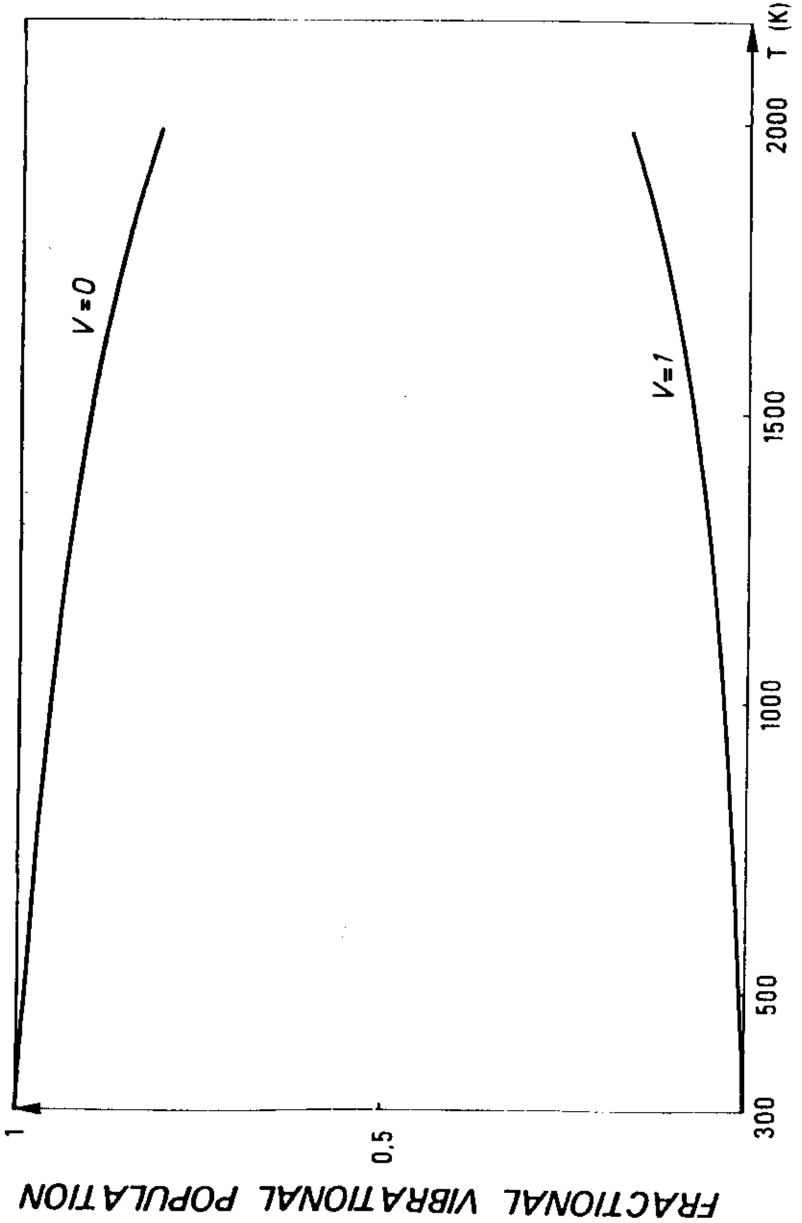
1- total spectrum at moderate temperatures



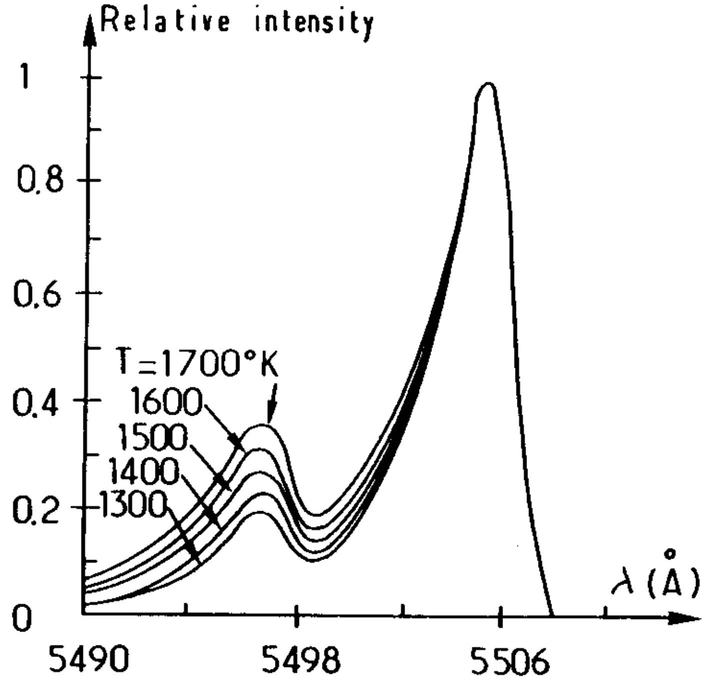
2_ Stokes Q branch at high temperatures



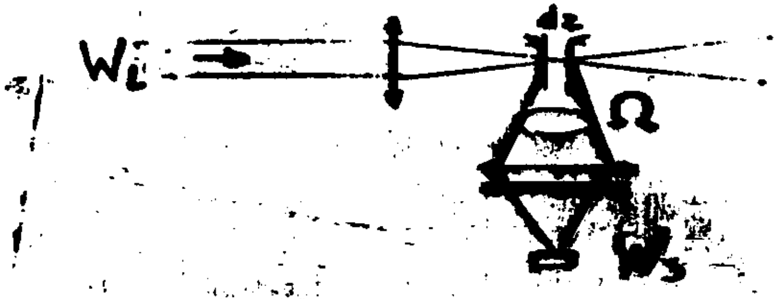
## VIBRATIONAL DISTRIBUTION IN N2



## VIBRATIONAL BANDS OF $N_2$



$$\frac{P_{S1}}{P_{S0}} = \left(\frac{\omega_{S1}}{\omega_{S0}}\right)^4 \exp\left(\frac{\hbar\omega_R}{kT}\right) \times \frac{v+2}{v+1}$$

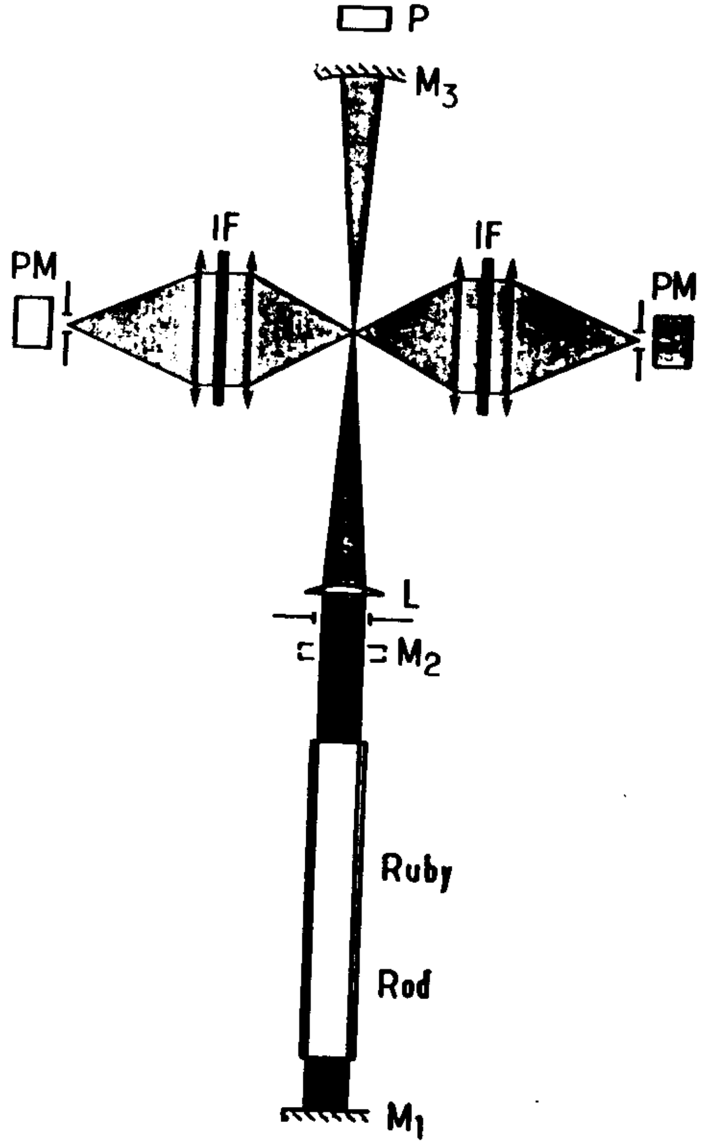


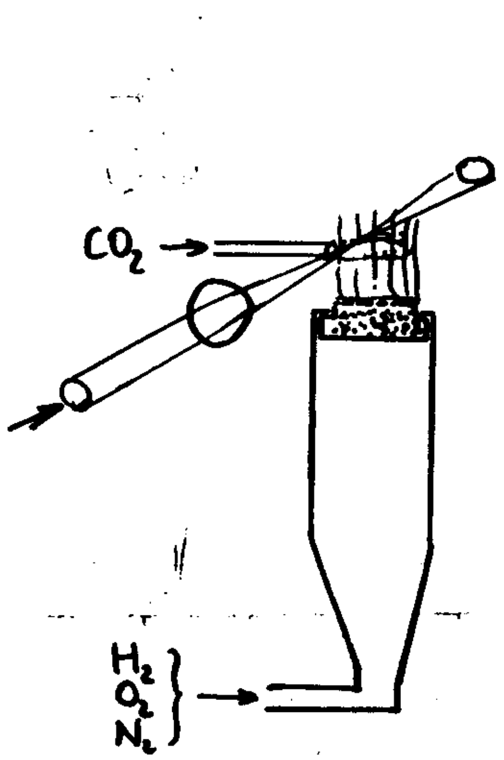
$$W_s = W_i \, N \, \Omega \, dz \, \frac{d\sigma}{d\Omega}$$

example : $N_2$ at STP

$\Omega = 1$ sr
$dz = 1$ mm
$W_i = 1$ J

$W_s \simeq 10^4$ photoelectrons





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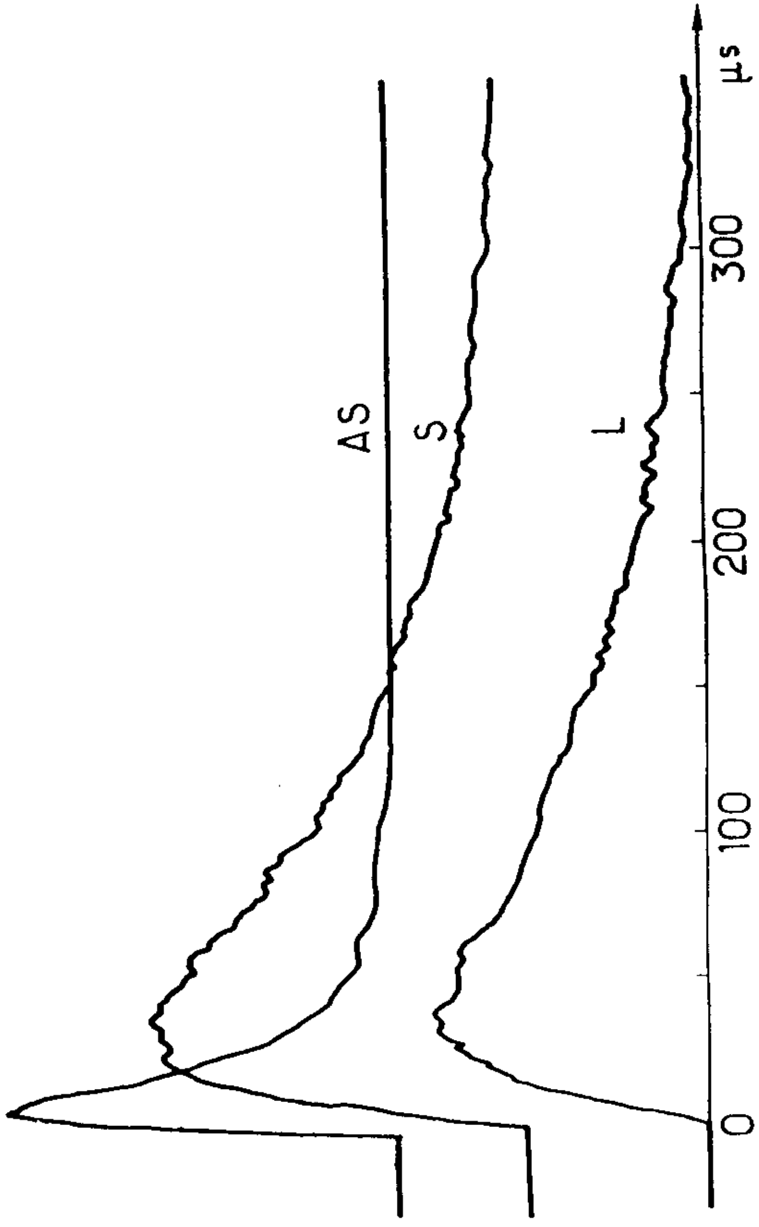
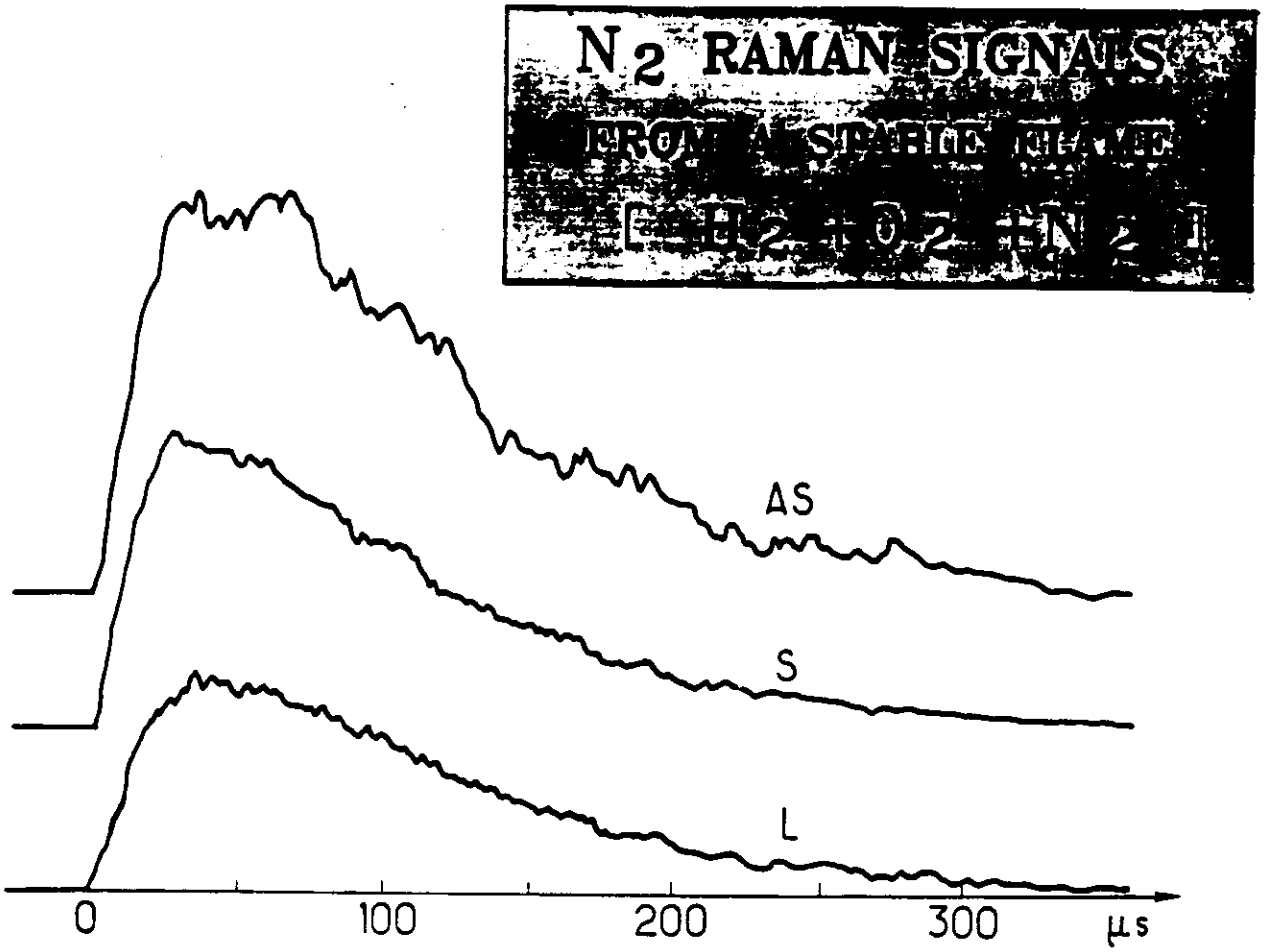
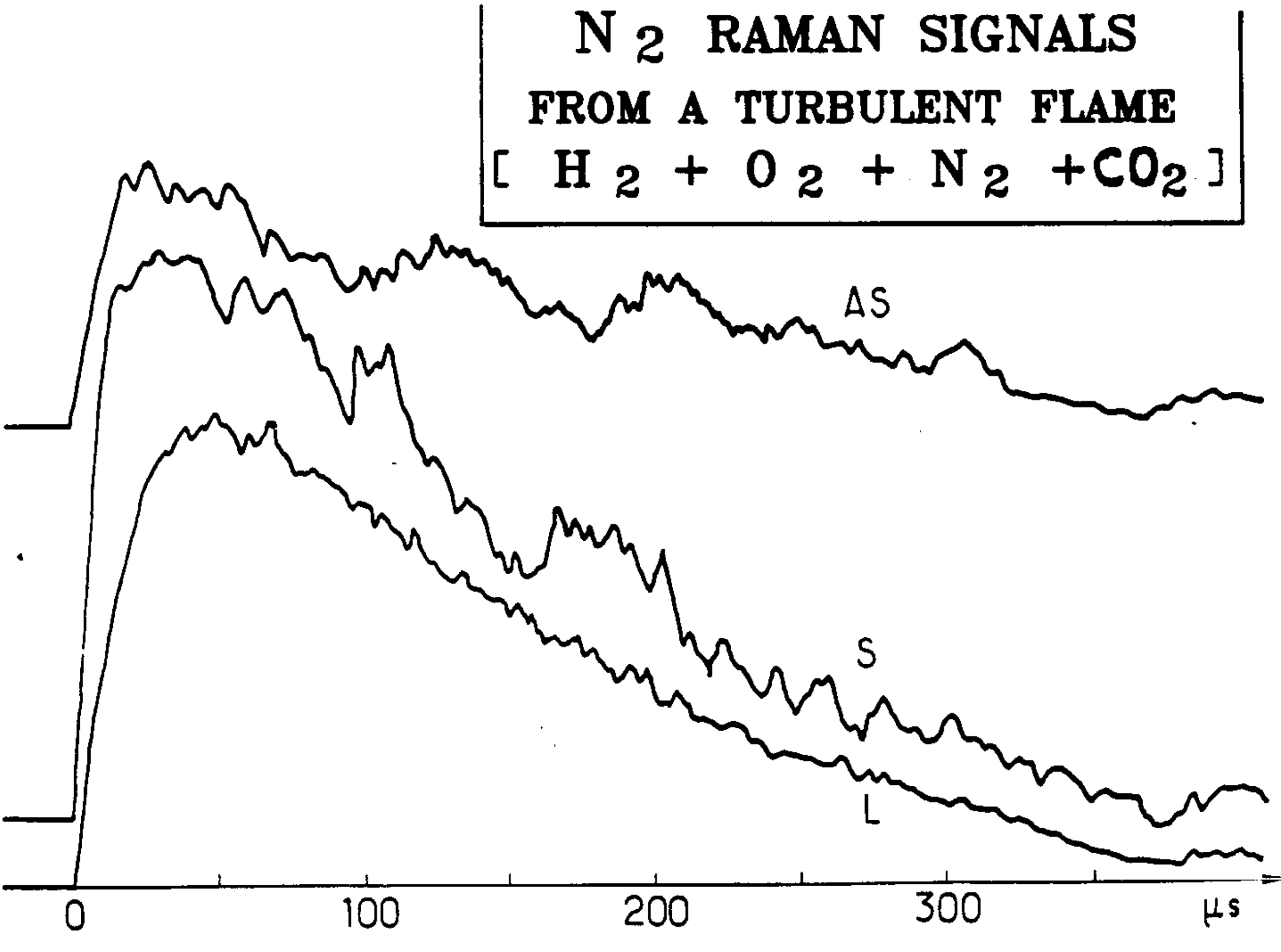


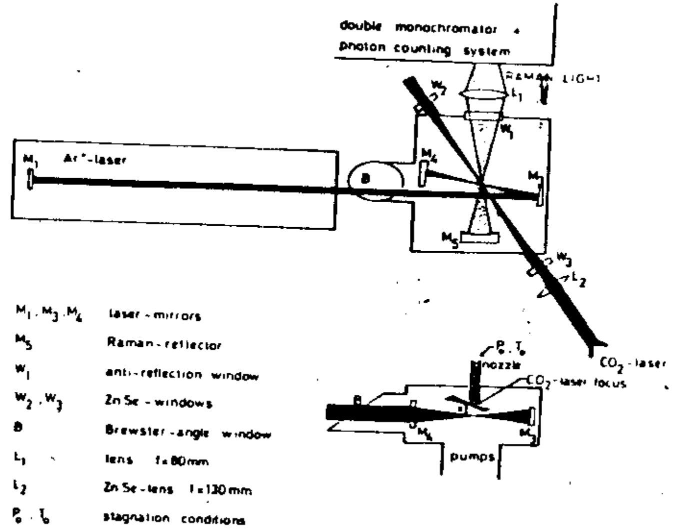


**$N_2$ RAMAN SIGNALS**
**FROM A STABLE FLAME**
**[ $H_2$ + $O_2$ + $N_2$ ]**



**$N_2$ RAMAN SIGNALS**
**FROM A TURBULENT FLAME**
**[ $H_2$ + $O_2$ + $N_2$ + $CO_2$ ]**

# MOLECULAR JET STUDIES



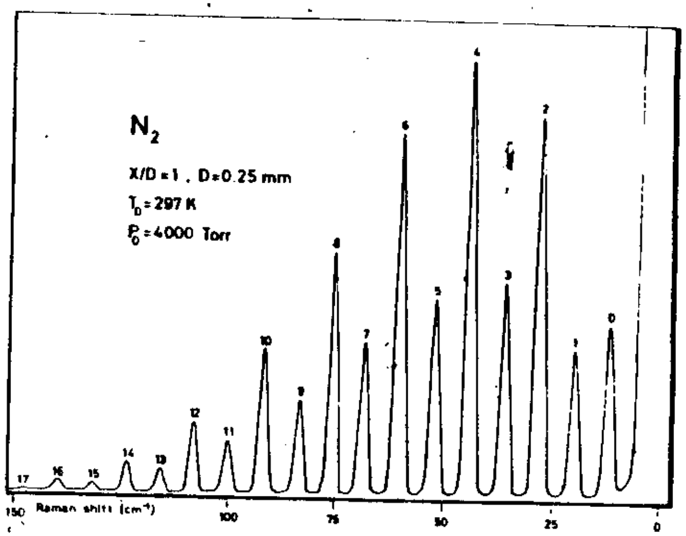


*Fig. 2.4. The pure rotational Raman spectrum of $N_2$ in a beam. For each peak the quantum number of the initial J state is indicated. The alternation of the peaks is due to nuclear spin degeneracy ($g_n$=2 for J even, $g_n$=1 for J odd).*

G. Luijks – Univ. Nijmegen

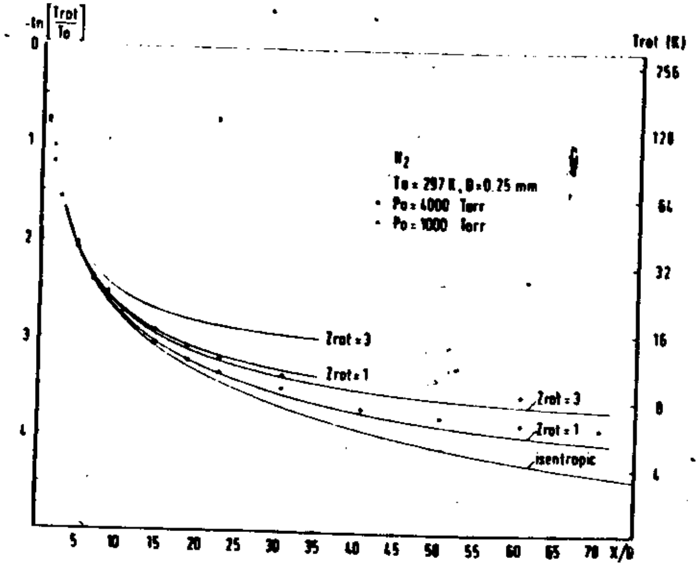


Fig. 2.5. The rotational temperature $T_{rot}$ versus x/D for $N_2$. The lower curve corresponds to the isentropic expansion. The other curves are calculated according to Quah et al.(9), with $Z_{rot}$=1 and 3 for two stagnation pressures. The measurement (■) at x/D=60 has been taken downstream the Mach disc ($P_{background}$=0.6 Torr).

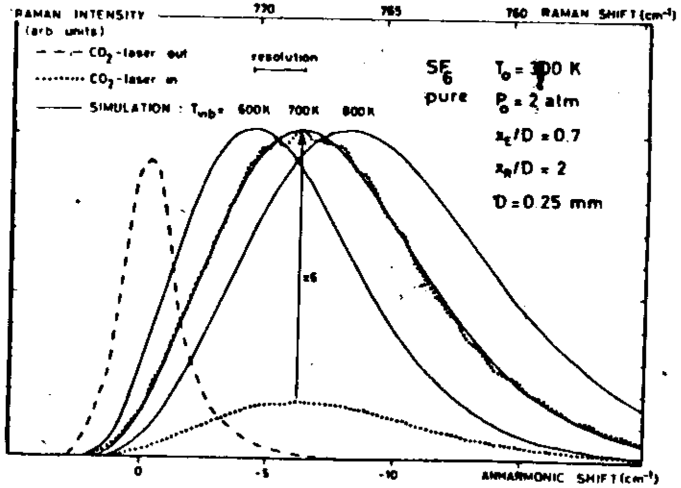
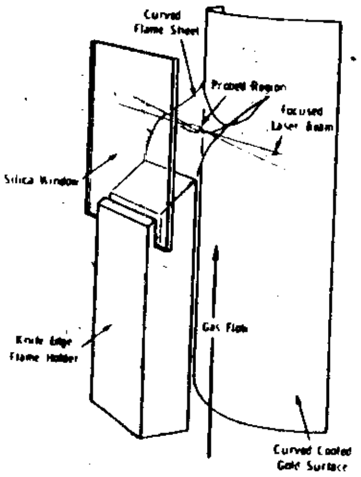


Fig. 4.6. The $\nu_1$ Raman spectrum of $SF_6$ in a pure beam with (...) and without (- - -) $CO_2$-laser excitation [70 W at 10P(16)] at $x_E/D$=0.7 as observed at $x_R/D$=2 (type 1 configuration). The $CO_2$-laser beam is focused to a waist $2w_0$=0.4 mm; completely overlapping the molecular beam at the nozzle exit. Three computer simulations are drawn corresponding to thermalized distributions with $T_{vib}$=600, 700 and 800 K indicating that, for the excited spectrum, the best fit is obtained for $T_{vib}$=700 K ($\langle n \rangle$=4). For reasons of clarity a magnification factor six has been introduced.

# STABLE FLAME FRONTS



Applied Optics

*Figure 1. Schematic of the slot burner used in this experiment (13)*

J. BECHTEL

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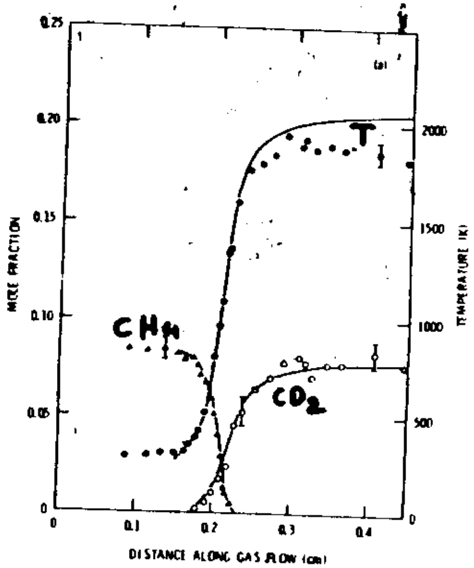

*Figure 5. Temperature, $CH_4$, and $CO_2$ profiles for a fuel-lean (φ = 0.86) atmospheric-pressure, premixed, laminar $CH_4$– air flame. The experimental data are from laser Raman scattering and the theoretical predictions are from the computer code of Ref. 1 (——), theory; (●), temperature ($N_2$); (○), $CO_2$; (▲), $CH_4$.*

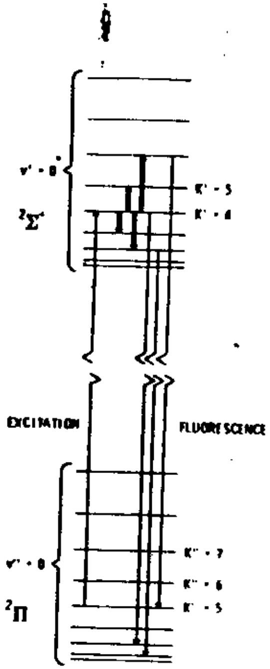

*Figure 2. Schematic of the energy levels for the OH molecule. The collision-induced energy-transfer transitions are denoted by double-line arrows. The rotational quantum number is denoted by K' or K''. Both spin doubling and lambda doubling have been suppressed for clarity.*

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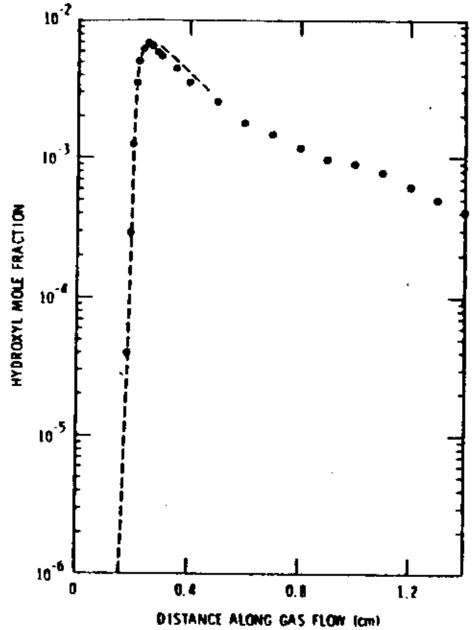
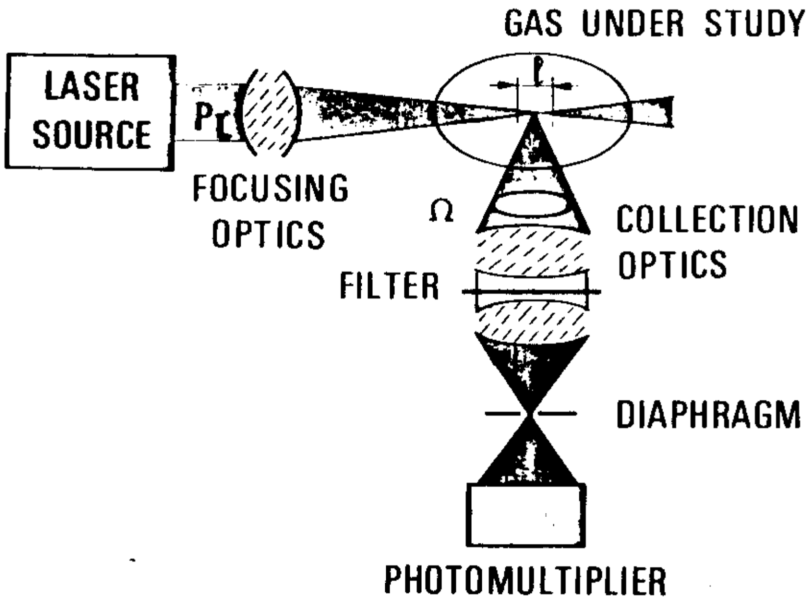
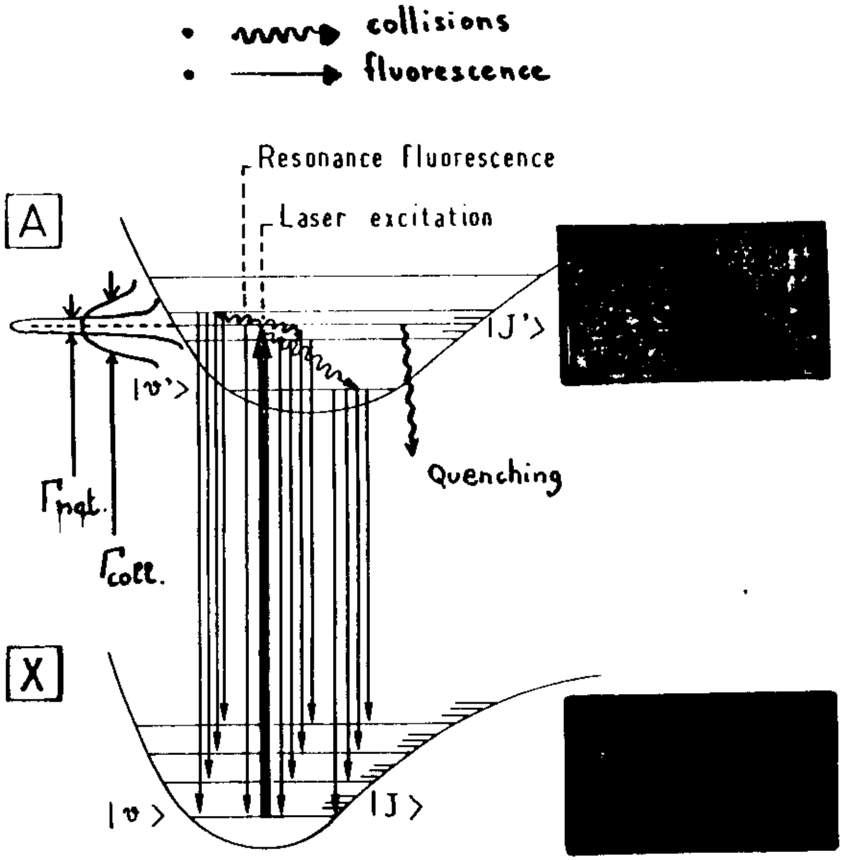


*Figure 8. Comparison of hydroxyl concentration as measured by laser-induced fluorescence and the theoretical predictions of Ref. 1. The hydroxyl concentration uncertainty is ±30%. Stoichiometric $CH_4$–air flame. (●), Experiment; (– – –), theory.*

# EXPERIMENTAL SET-UP FOR L I F AND S R S





## LASER INDUCED FLUORESCENCE

## SOME MOLECULES & RADICALS DETECTED by FLUORESCENCE

CH
$C_2$
CN

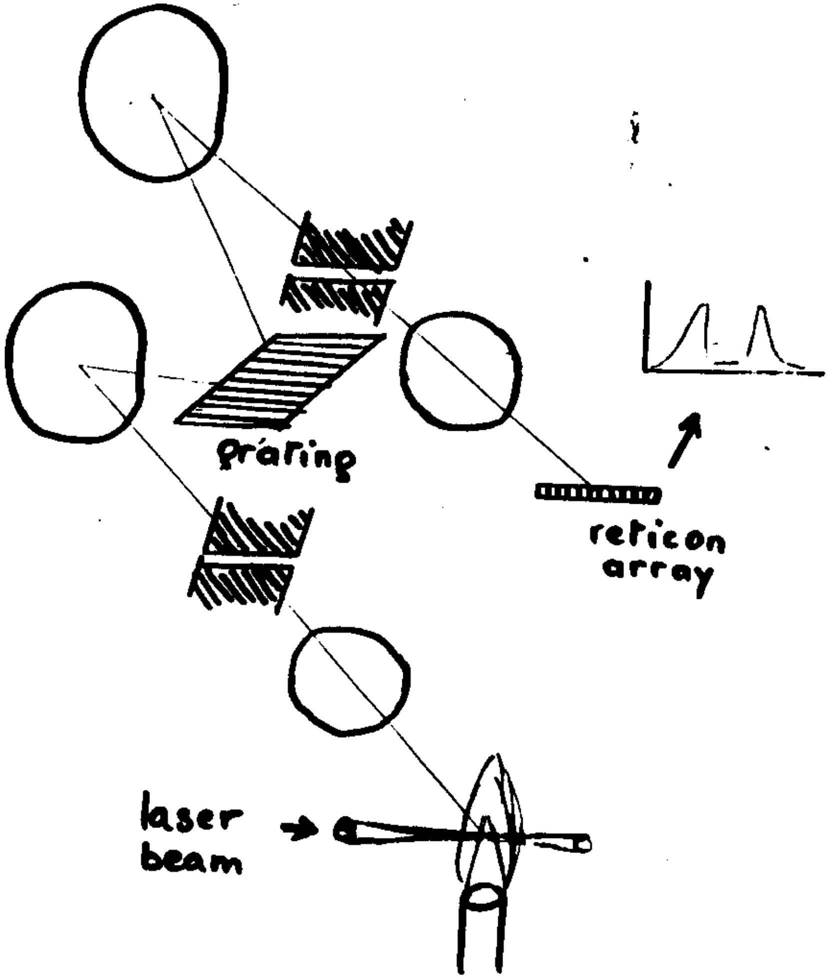
$S_2$
SH
$SO_2$
SO

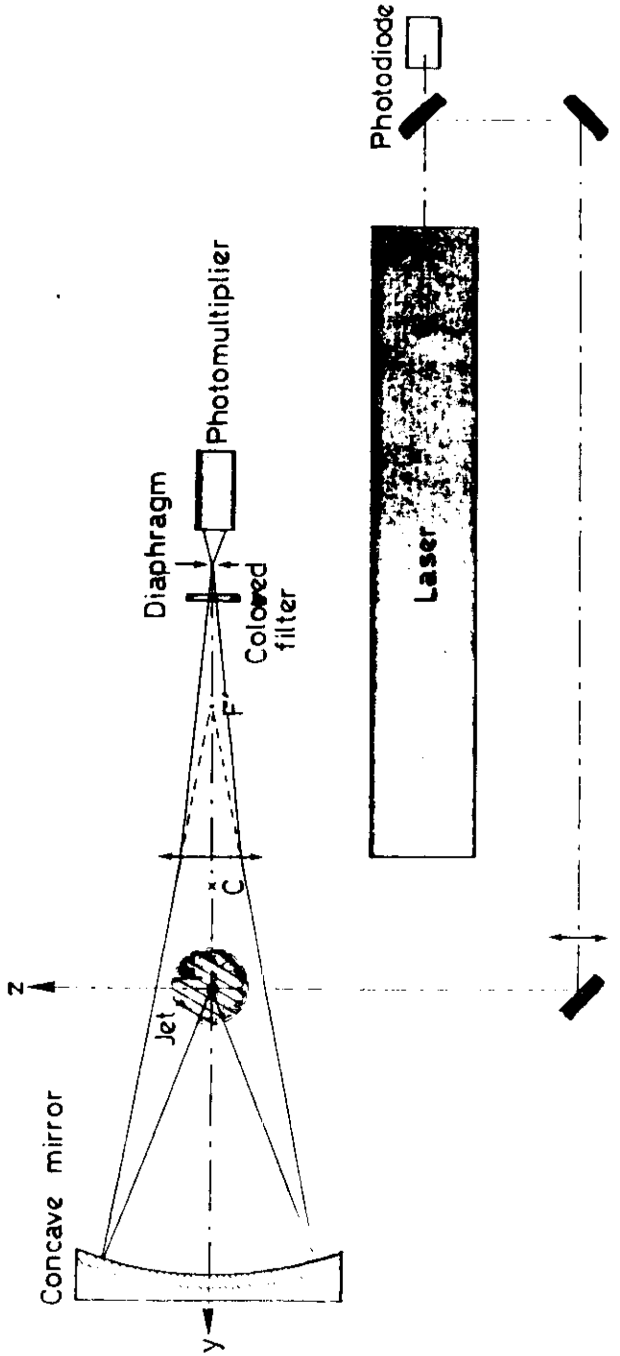
NO
NH

→ OH
→ $H_2$

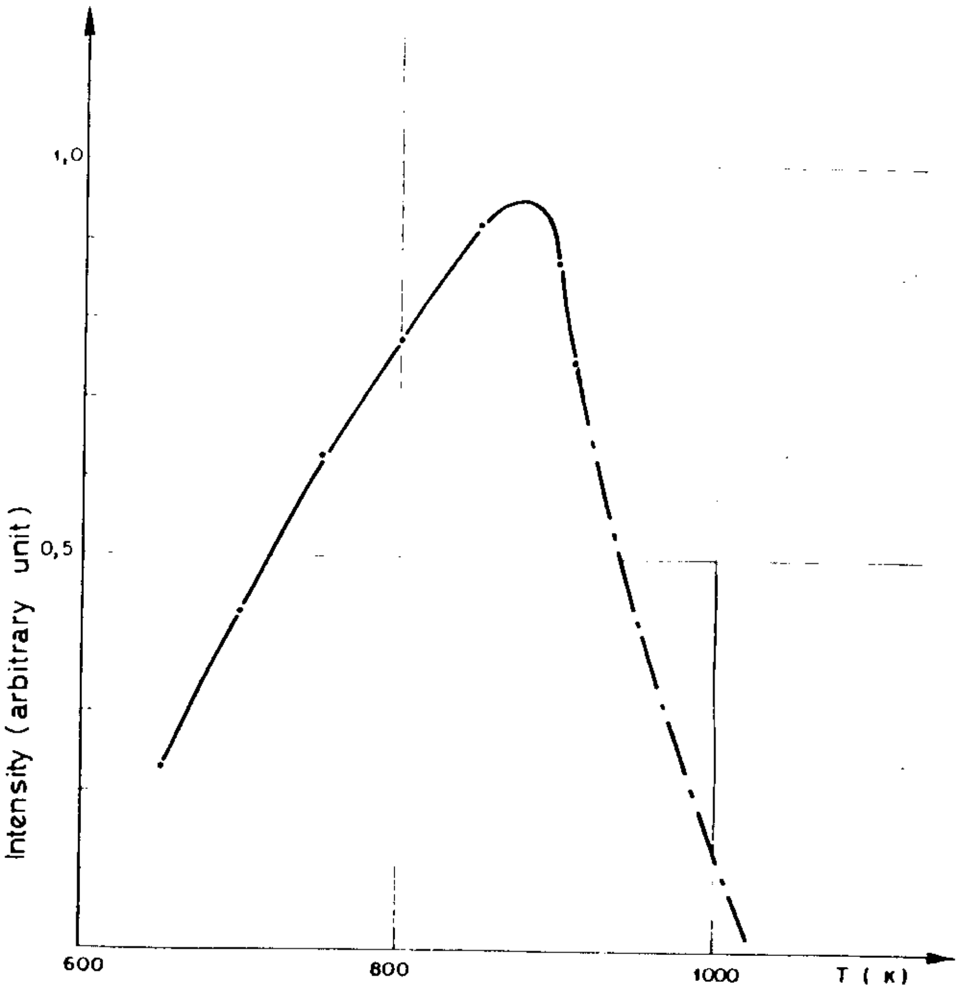
etc ...

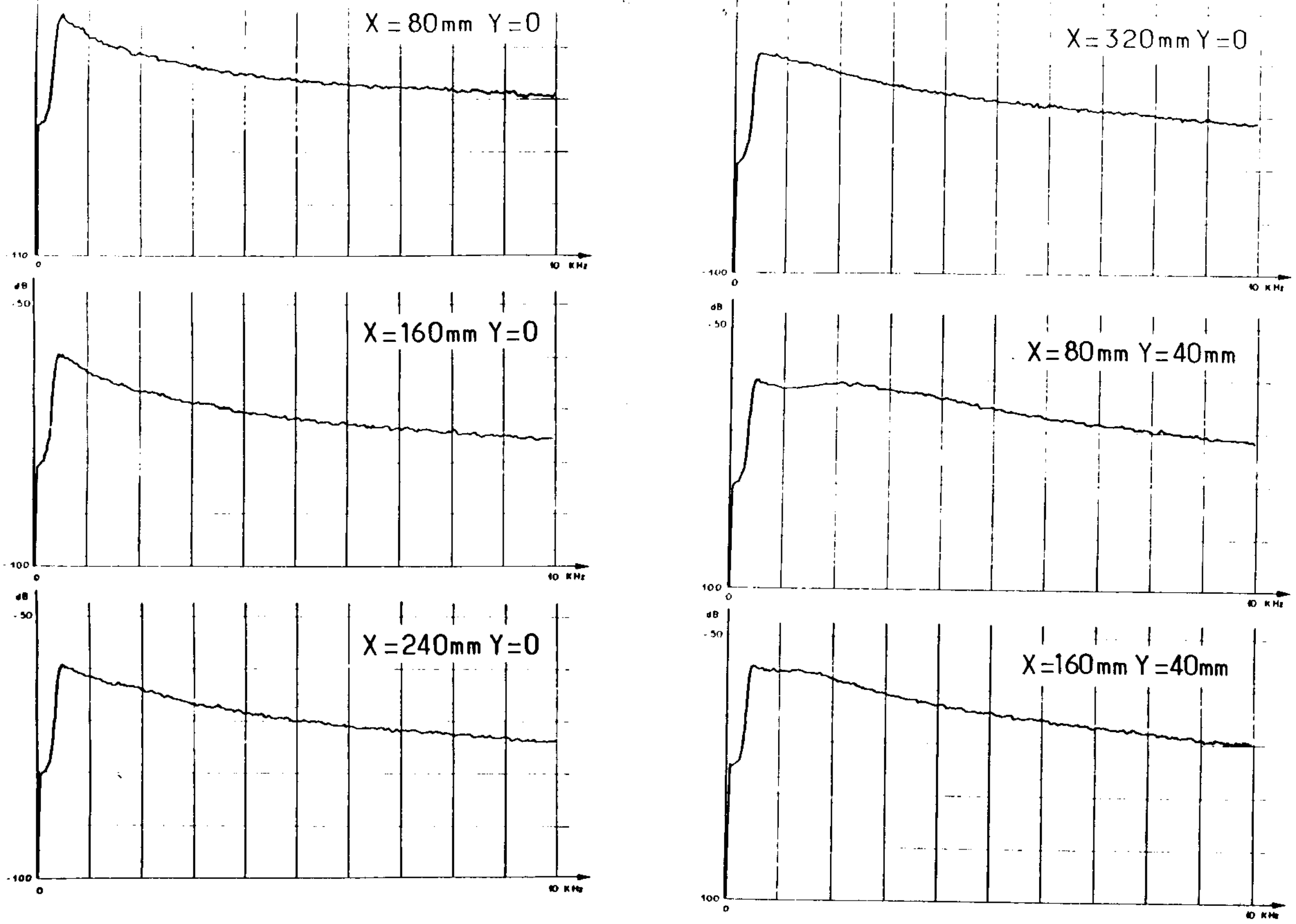
## IMAGING by FLUORESC





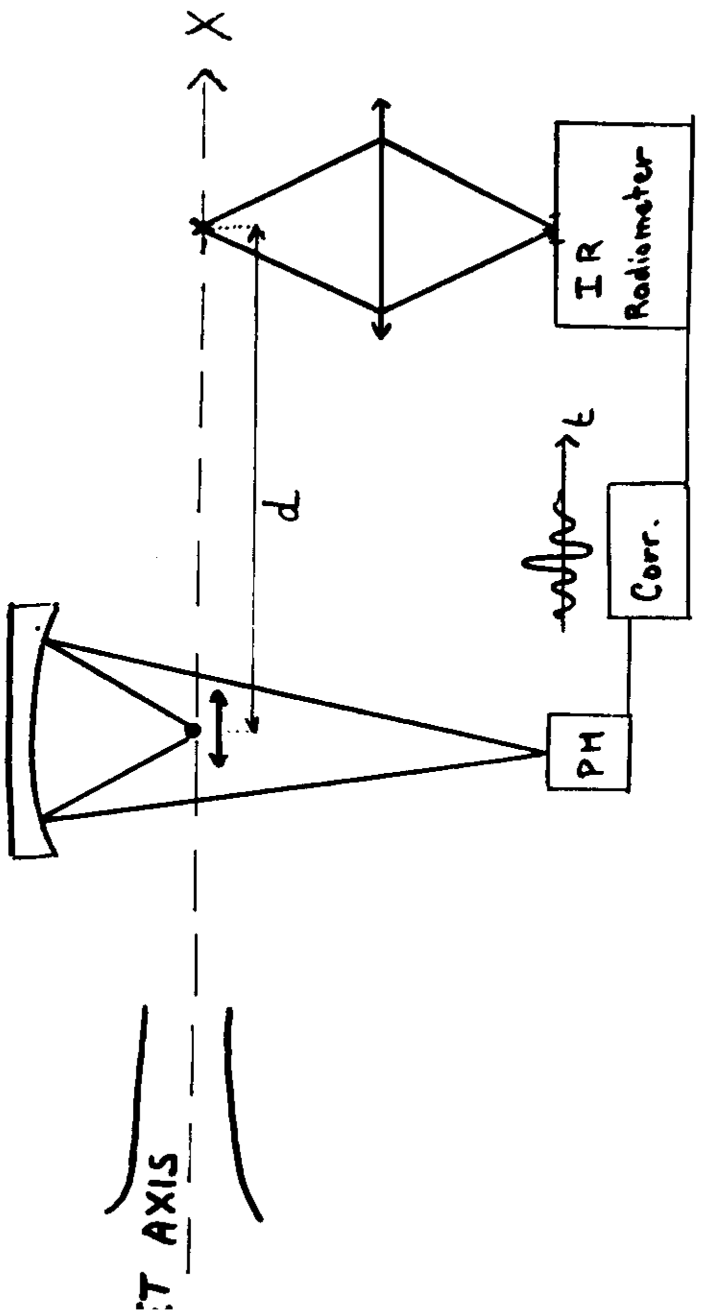
# FLUORESCENCE INTENSITY VERSUS TEMPERATURE



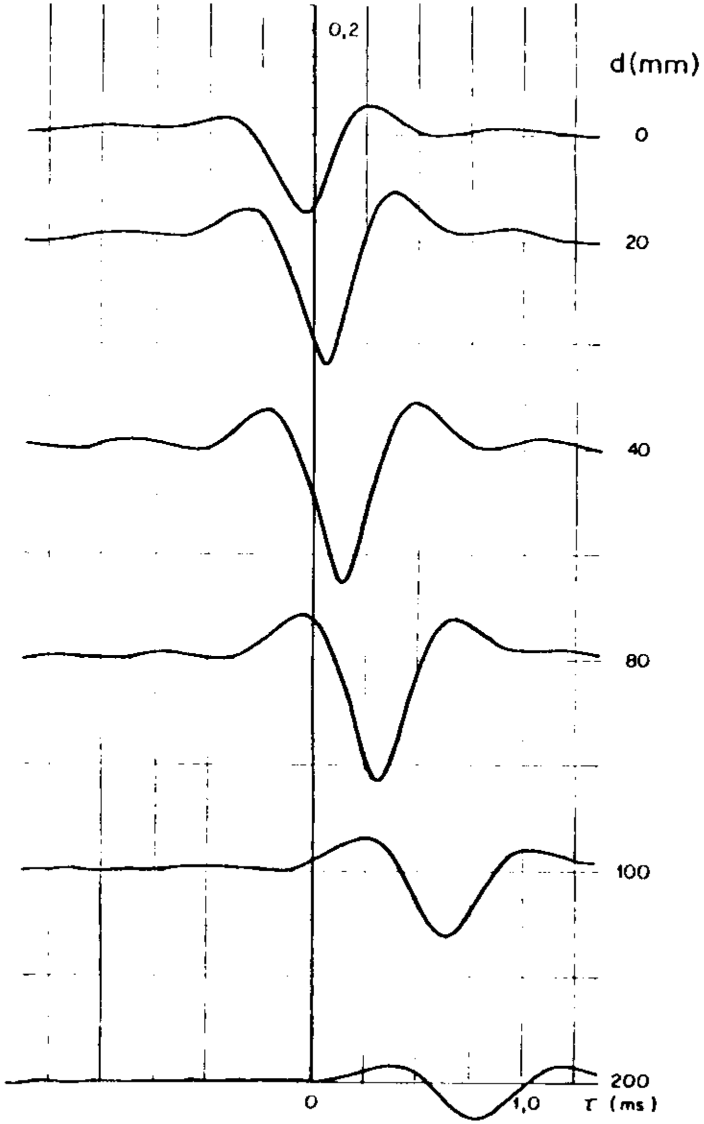


**FLUCTUATION SPECTRA**

# CORRELATION MEASUREMENTS



# CORRELATION PROFILES



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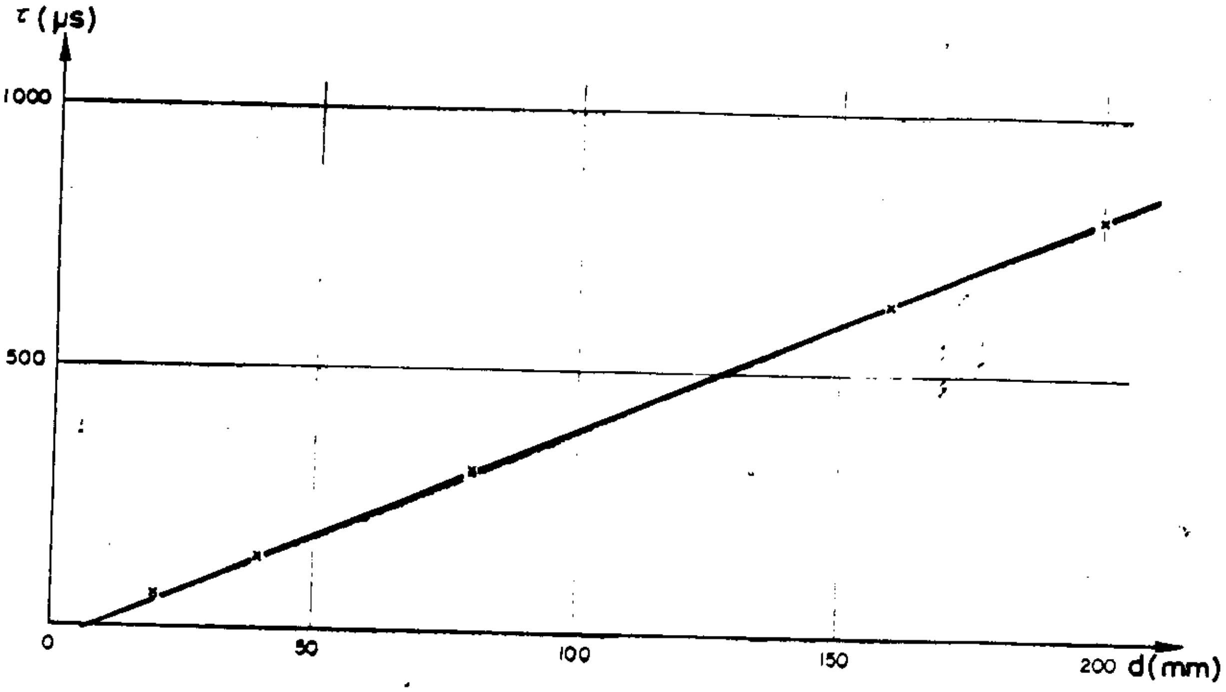

|  | RAMAN SCATTERING | FLUORESCENCE |
|---|---|---|
| Time dependence | Instantaneous | Relatively slow exponential decay $e^{-\frac{t}{\tau}}$ |
| Dependence on density of gas under study | Linear | linear |
| Dependence on density of buffer gas | insignificant | Strong dependence in time and intensity (QUENCHING) |
| Signal strength | Very weak | strong |
| Dependence on the spectral distribution of incident light | Relatively insensitive | very sensitive |
| Polarization | polarized | Unpolarized |