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WINTER COLLEGE ON LASERS, ATOMIC AND MOLECULAR PHYSICS

(21 January - 22 March 1985)

IR-LASERS FOR SPECTROSCOPY OF PARAMAGNETIC MOLECULES

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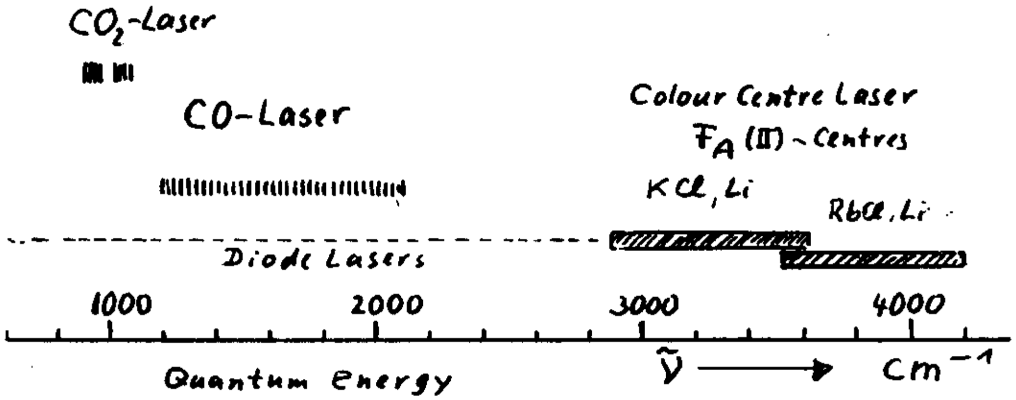
IR-Lasers for Spectroscopy of paramagnetic molecules

W. URBAN
University of Bonn



CO_2 and CO Lasers are stepwise tunable

Colour Centre Lasers are continuously tunable

Zeeman-tuning and modulation

Zeeman-modulation only

Topics of lectures

1.) Physics and technology of IR-Laser sources

2.) Techniques for sensitive spectroscopy of open shell systems

3.) Examples of Zeeman- and Faraday-modulation spectroscopy

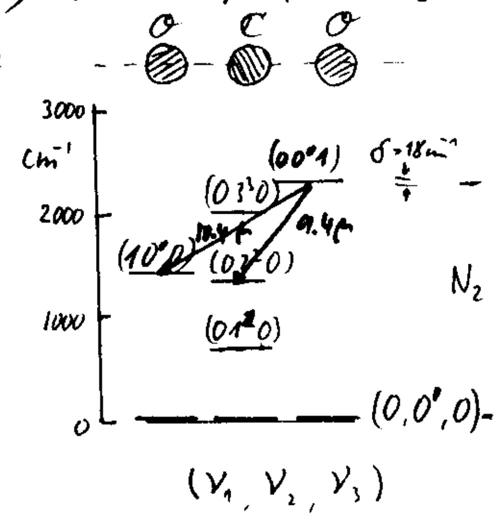
1. Physics and technology of IR-lasers

1.1 Molecular gas lasers

1.1.1 CO_2 – Laser

Builtup of gain in CO_2 by vib. transfer from N_2

Vibrational modes of CO_2
- symmetric stretch ν_1
- bending ν_2
- asymmetric stretch ν_3



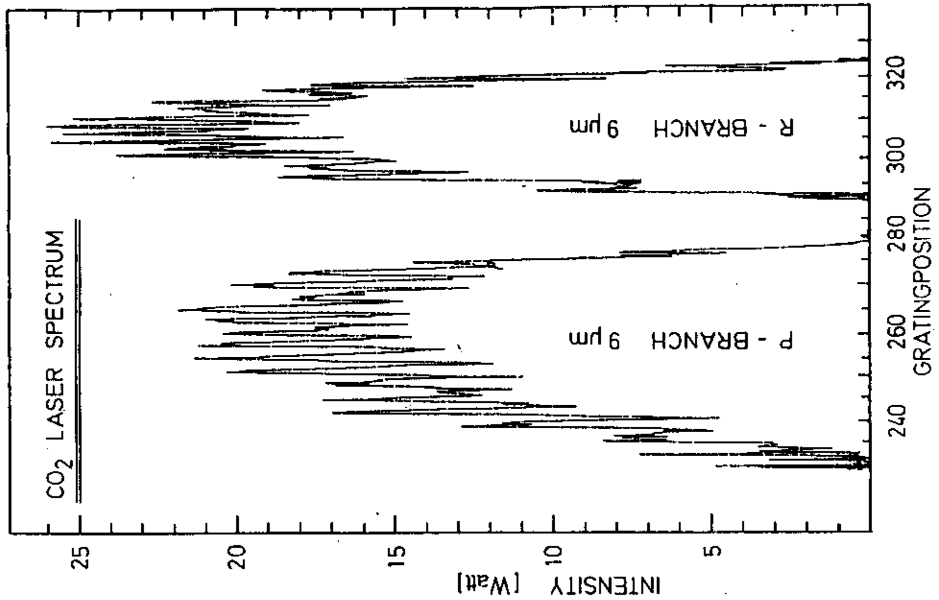
builtup of true inversion

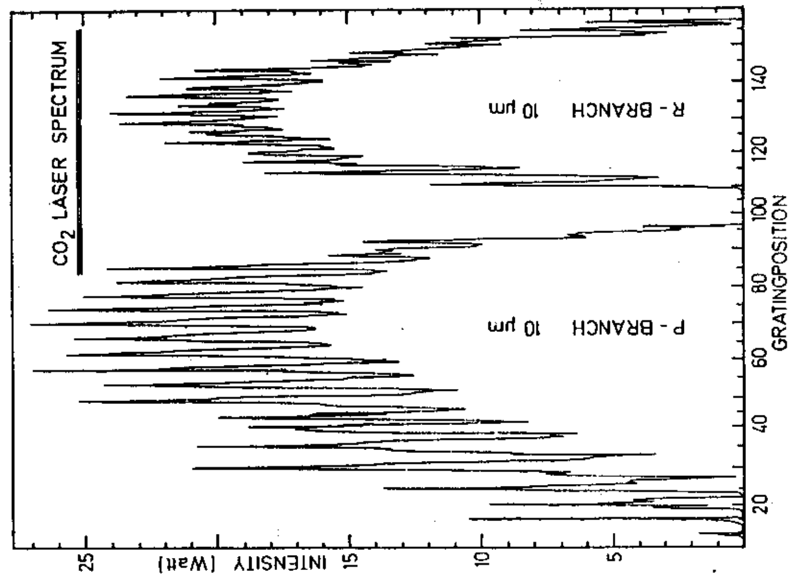
$(0\,0^0\,1) \xrightarrow{10.4\mu} (1\,0^0\,0)$

$(0\,0^0\,1) \xrightarrow{9.4\mu} (0\,2^2\,0)$

$\Delta J = \pm 1 \begin{cases} \text{R-branch} \\ \text{P-branch} \end{cases}$

~20 lines per branch → 80 different CO_2 laser lines.





1.1.2 CO – Laser

Complicated builtup of "partial inversion" via Vib.–Vib.–transfer (Treanor-pumping).

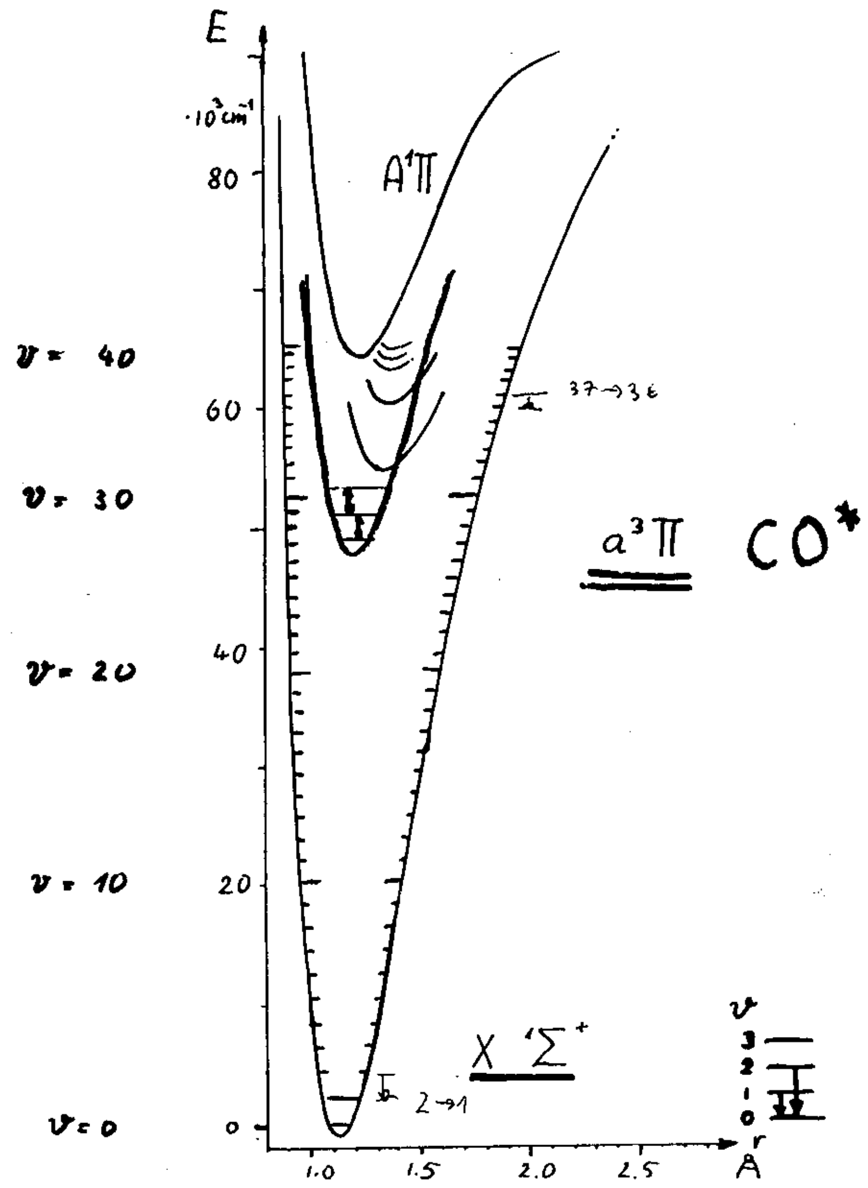
$$CO(v) + CO(w) \longrightarrow \begin{cases} CO(v-1) + CO(w+1) + \Delta E \\ CO(v+1) + CO(w-1) - \Delta E' \end{cases}$$

$v \leq w$

ΔE goes into $\Delta E'$ comes from thermal motion

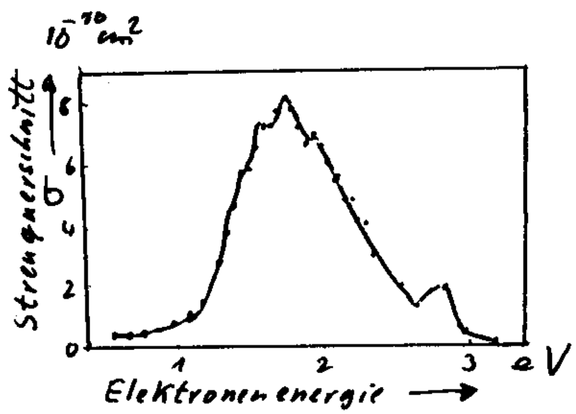
partial inversion only for some transitions in P-branch, but for many vibrational states.

450 CO laser lines between 1200 and 2050 cm⁻¹



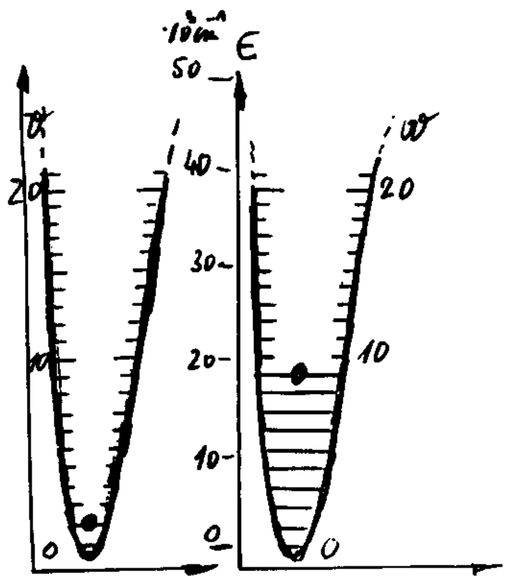
CO-molecule
potential of ground state and

cross section for vib. excitation of CO



exchange of vib.-excitation in collision

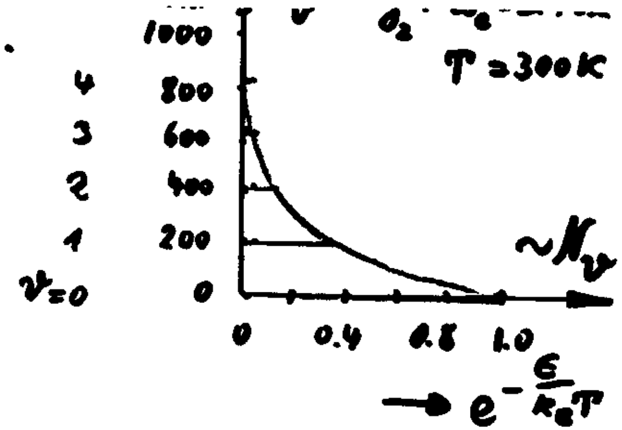
$$A(v=1) + B(w=9) \rightarrow \begin{cases} A(v=0) + B(w=10) \\ A(v=2) + B(w=8) \end{cases}$$

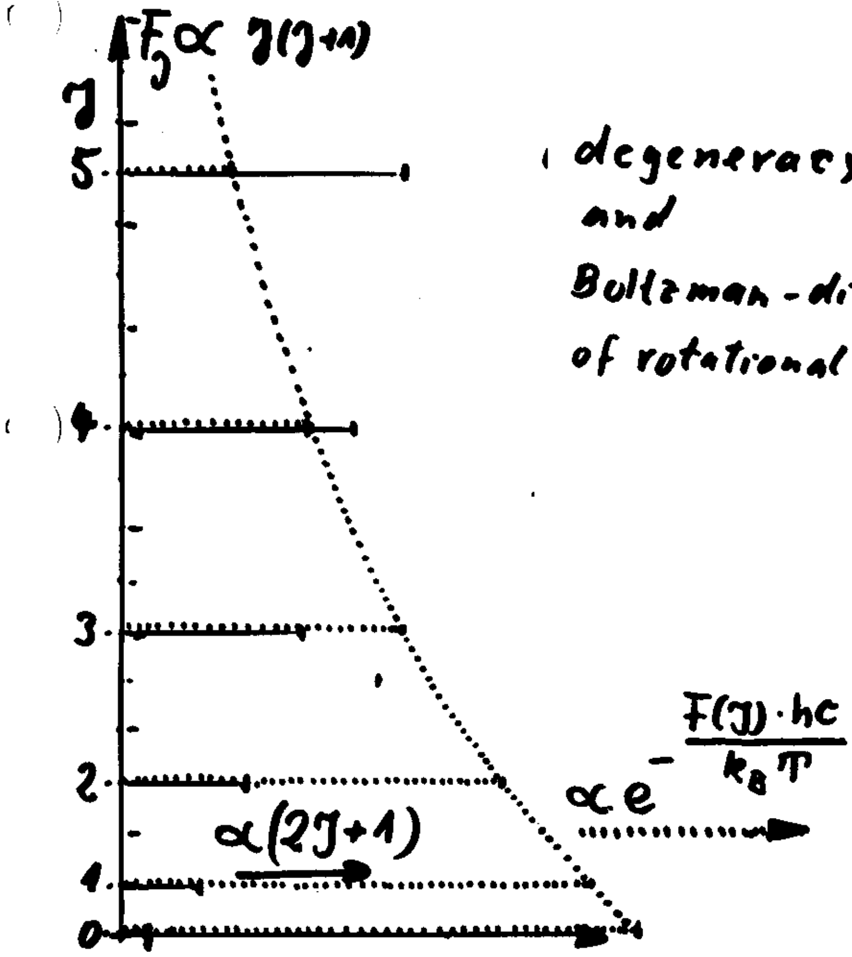


A (v=1) + B(w=9)

F17

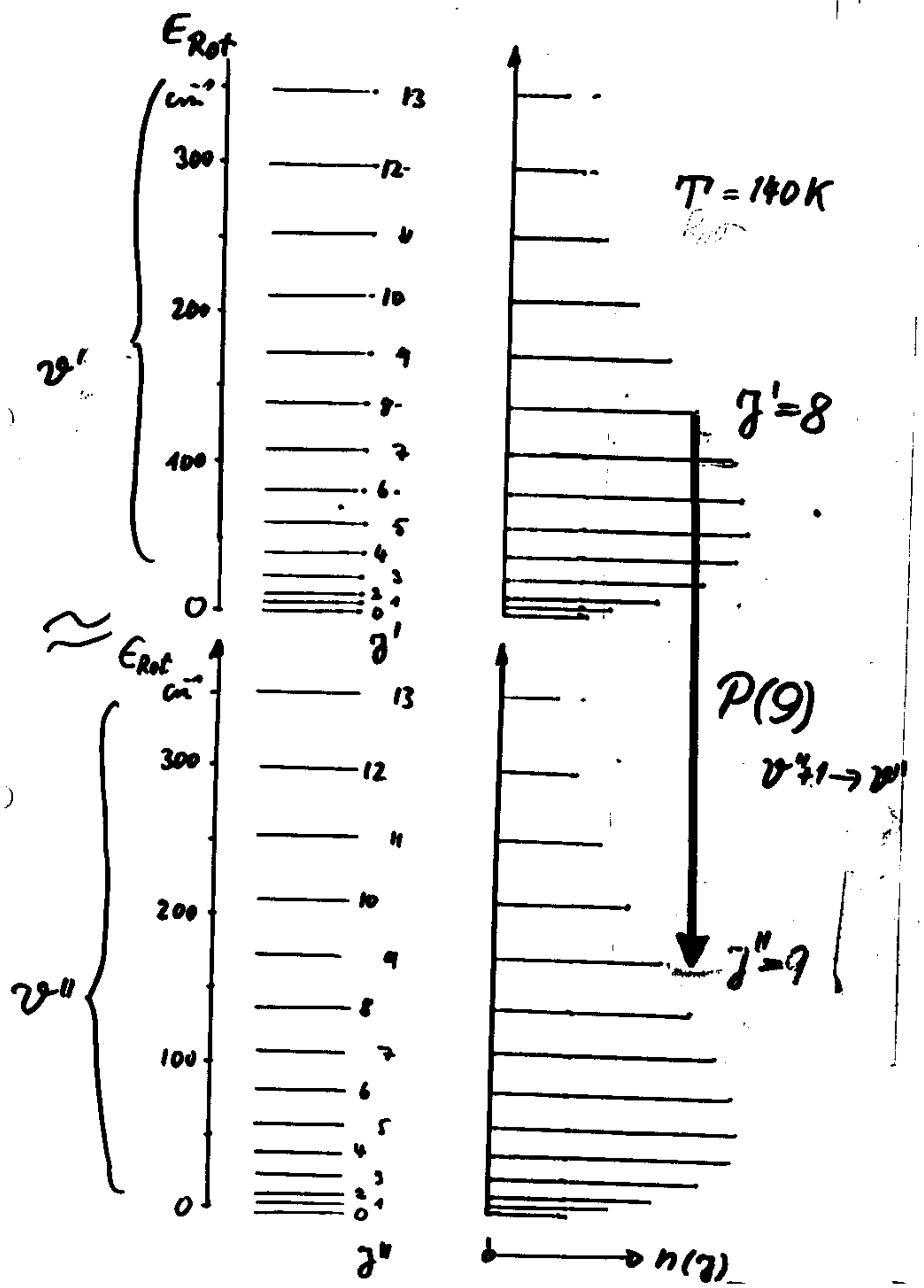
Boltzmannverteilg. der Vibrationsniveaus

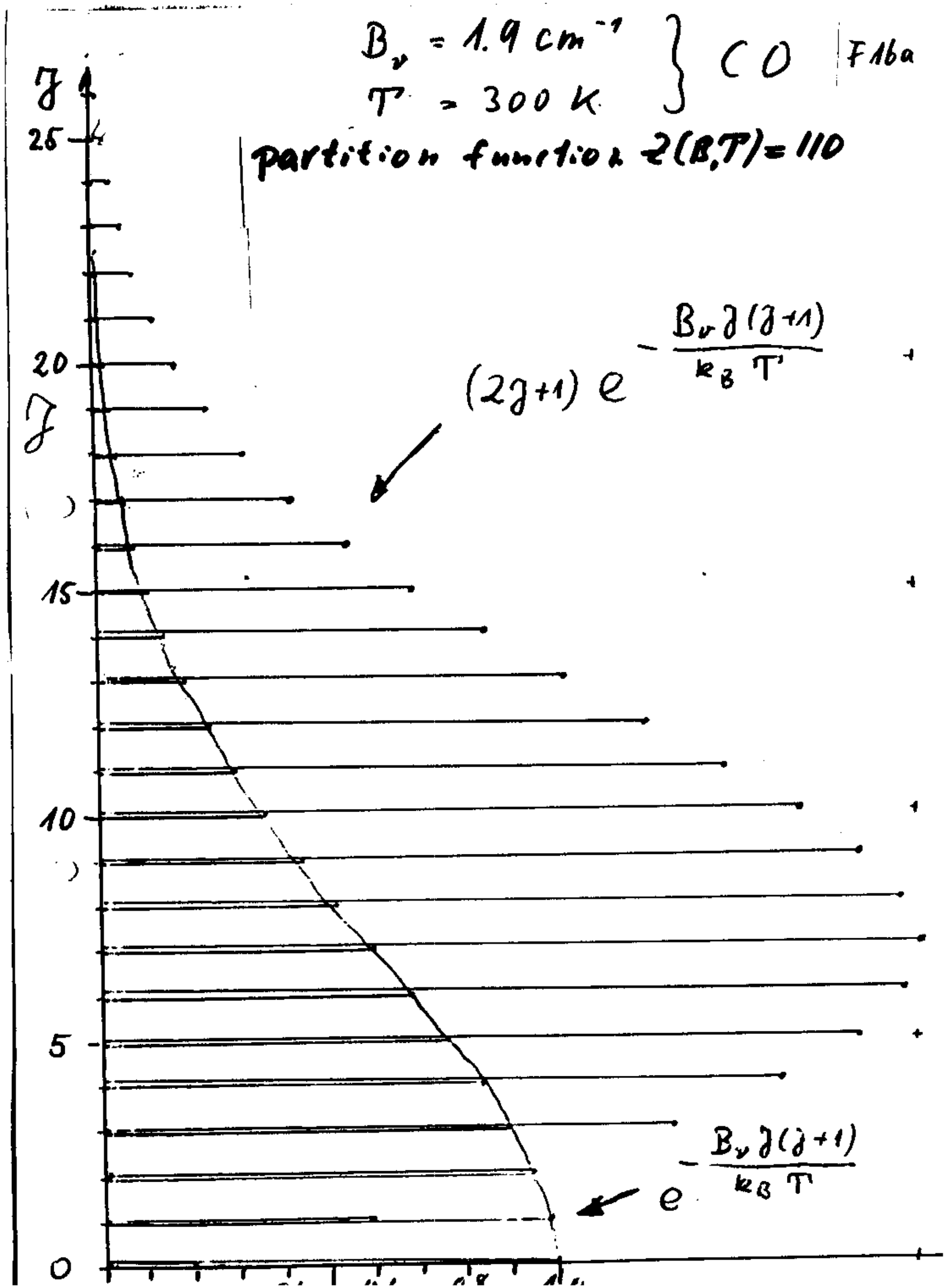




degeneracy and Boltzman-distrib. of rotational states

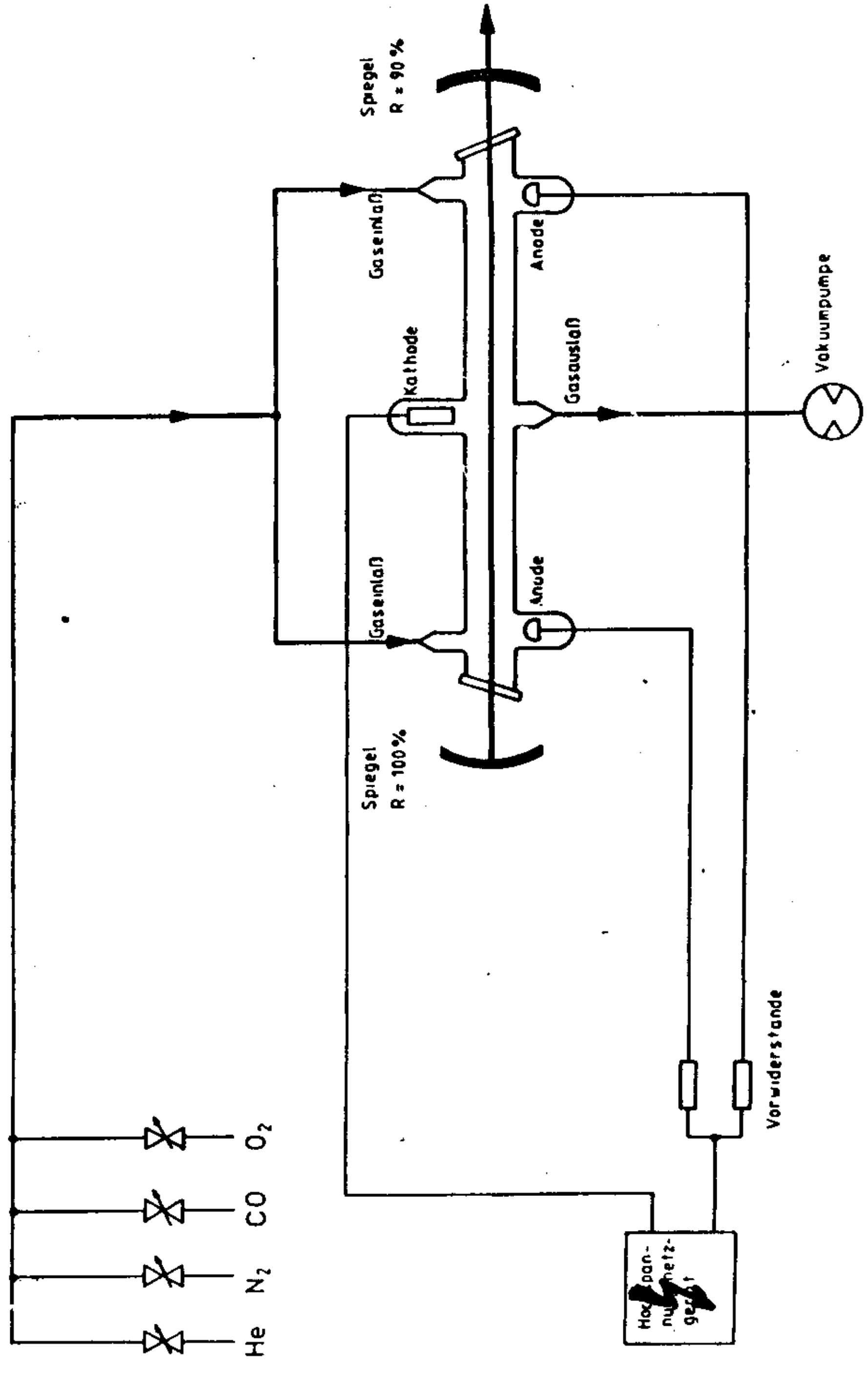
T16



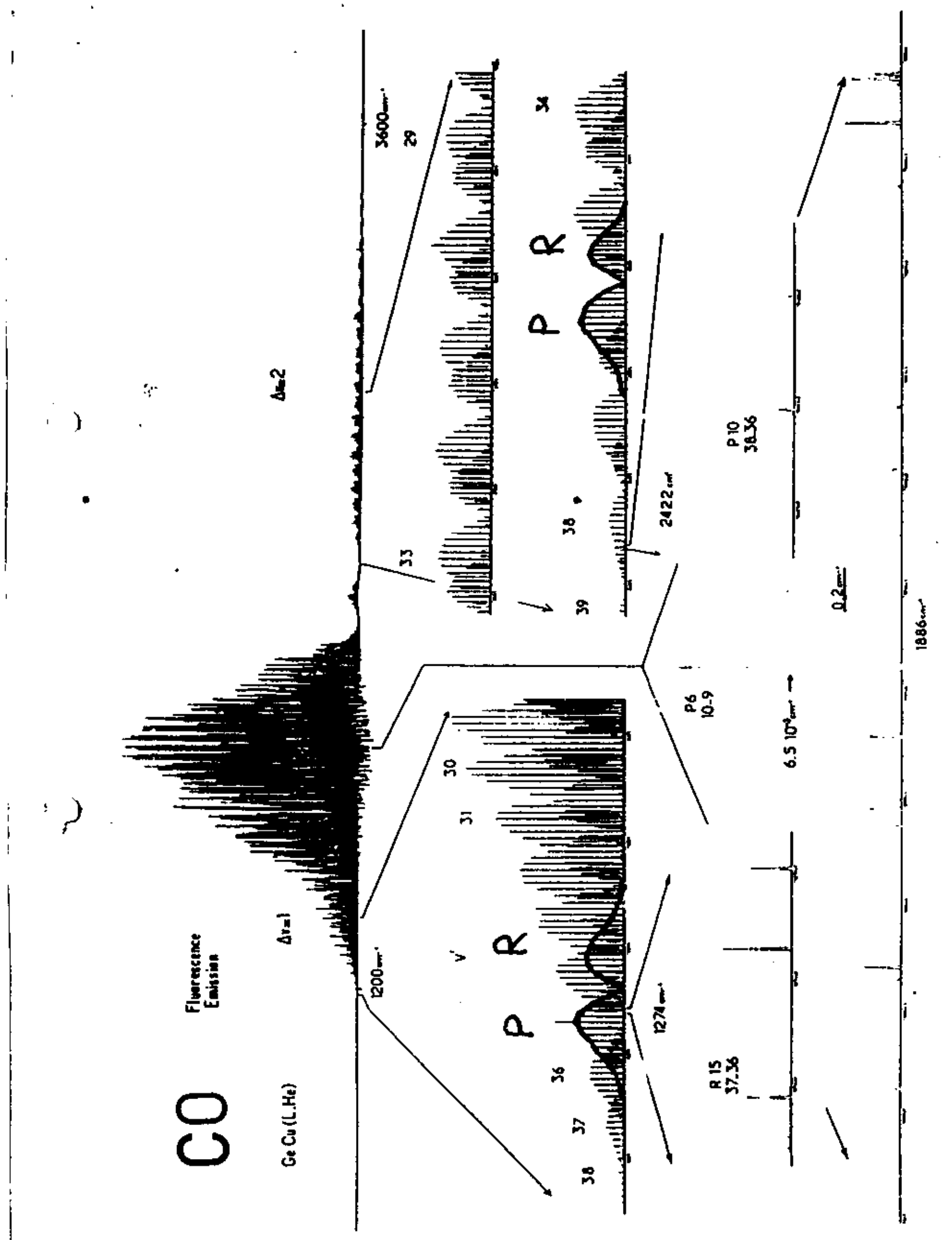


B_ν = 1.9 cm^-1
T = 300 K
CO
F1ba
partition function Z(B,T) = 110
J
25
20
15
10
5
0
(2J+1) e^{-B_ν J(J+1)/k_B T}
e^{-B_ν J(J+1)/k_B T}

CO LASER



Spiegel
R = 90 %
Gaseinlaß
Anode
Kathode
Gasauslaß
Vakuumpumpe
Gaseinlaß
Anode
Spiegel
R = 100 %
Vorwiderstande
O2
CO
N2
He



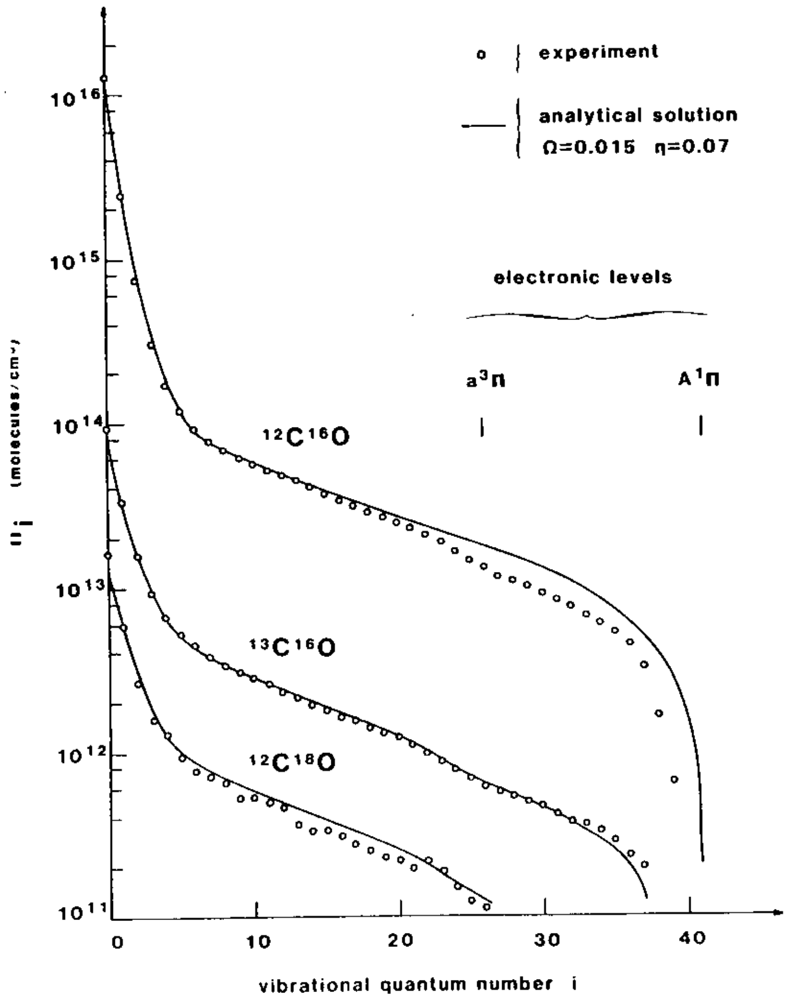
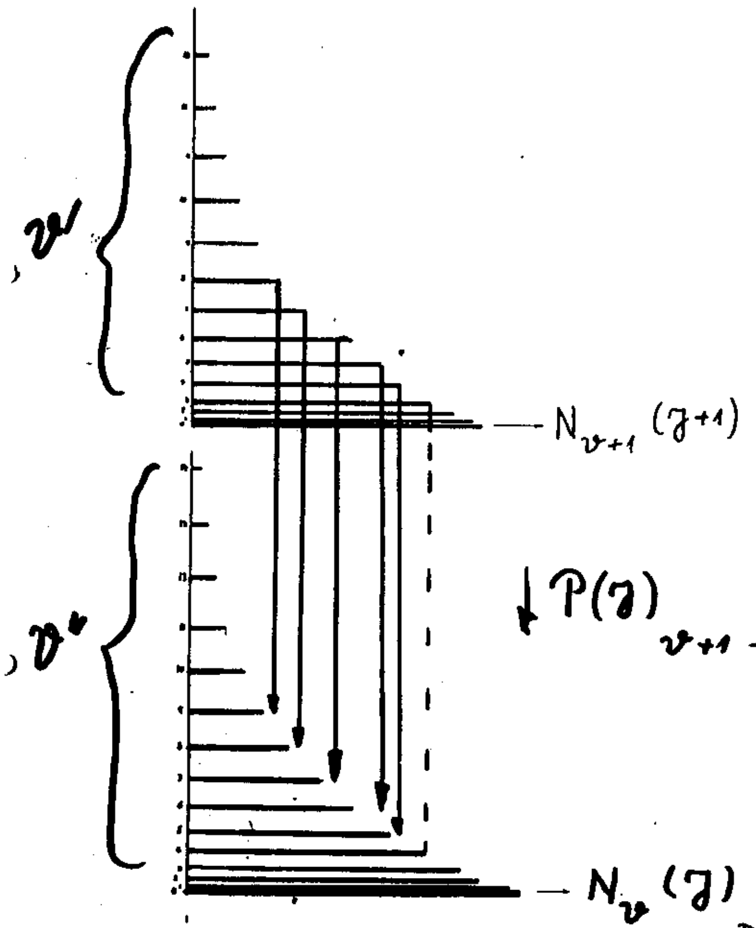


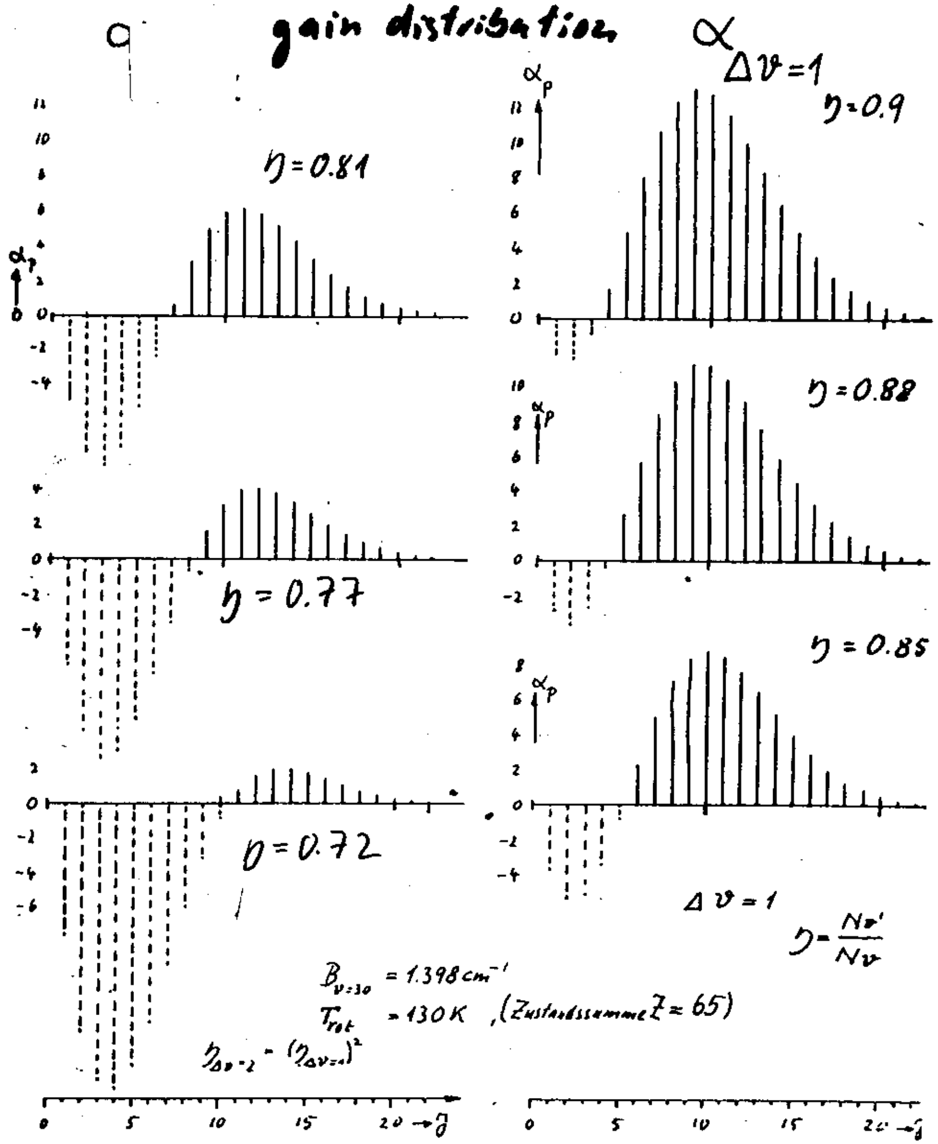
Fig.5 R.Farrenq, C.R.

Partial Inversion in CO

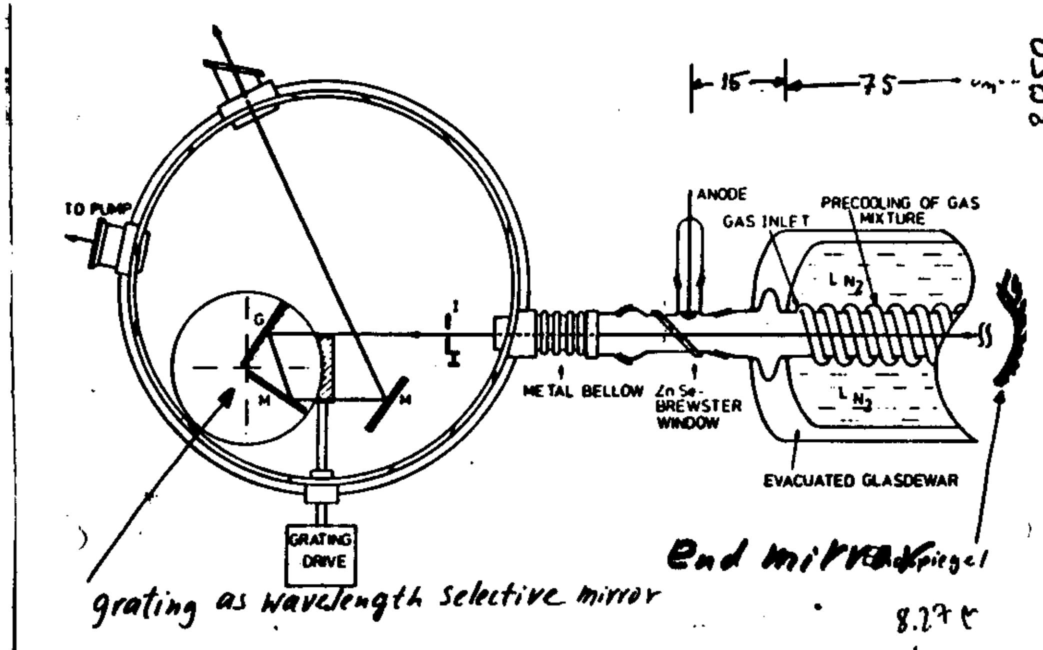


$$\alpha_P(v,J) = \Gamma(\sigma)\,(2J''+1)\,\frac{N(v'')}{Z(B_v,T)}\,e^{-\frac{B_v J''(J''+1)}{k_B T/hc}} \times$$

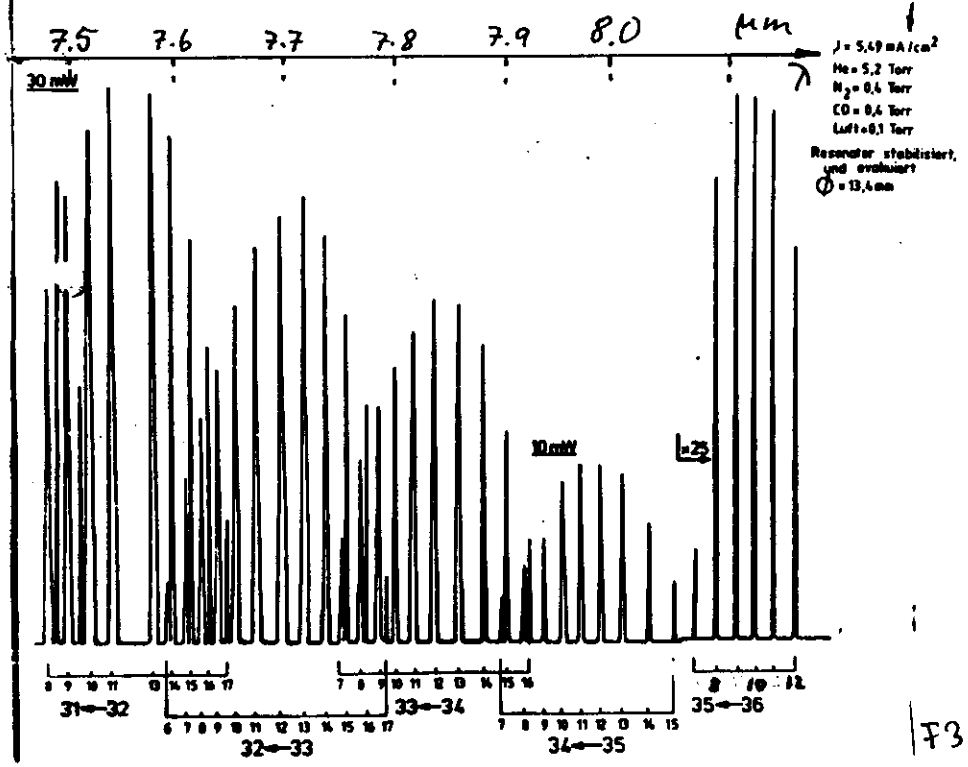
$$\times \left\{1 - \frac{N(v')}{\ldots}\, e^{\frac{2 B_v J''}{k_B T/hc}}\right\} \quad \text{, gain factor}$$



Variation of $\frac{N(v')}{N(v'')} = \eta$



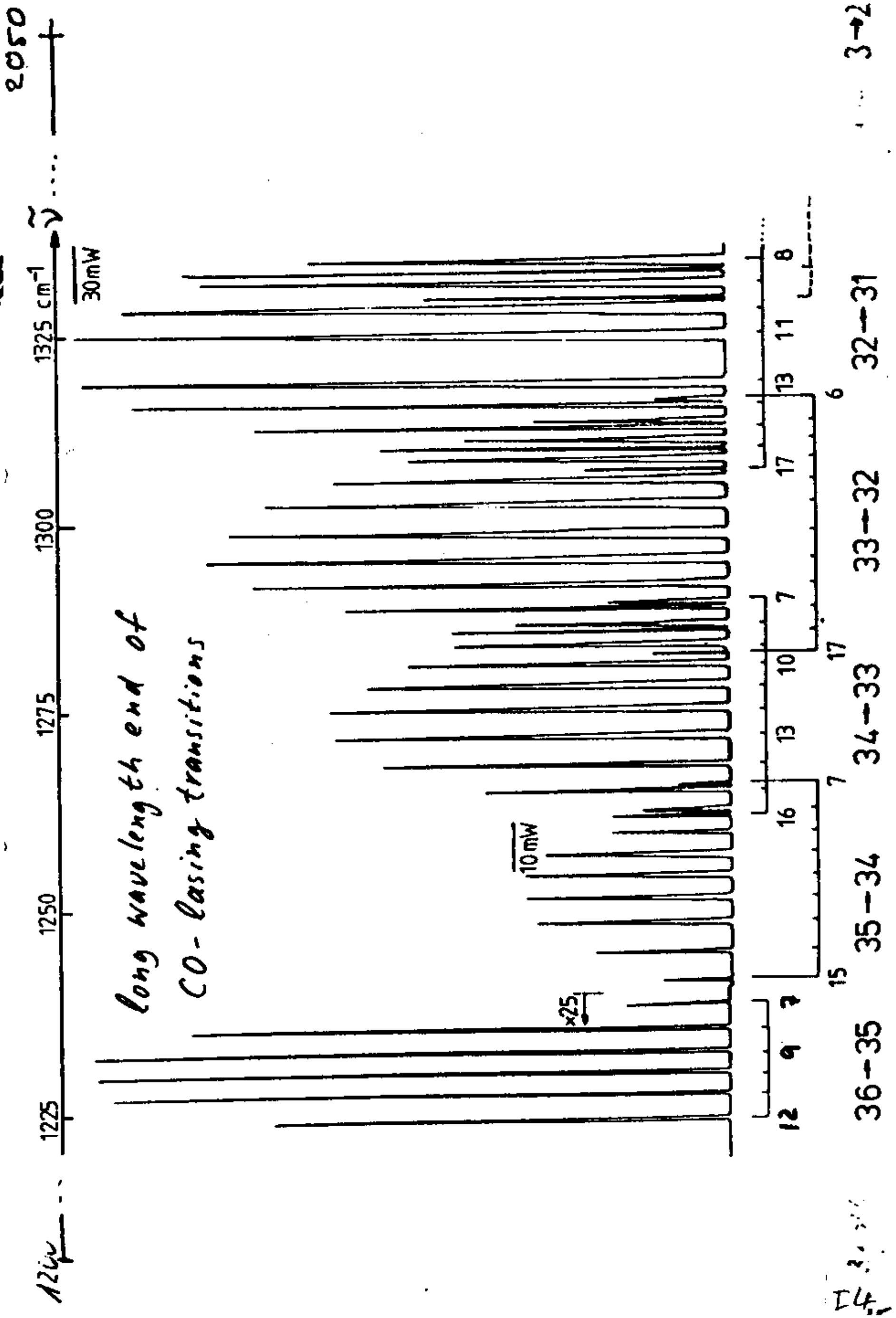
TO PUMP
G
M
M
GRATING DRIVE
ANODE
GAS INLET
PRECOOLING OF GAS MIXTURE
LN_2
LN_2
METAL BELLOW
ZnSe-BREWSTER WINDOW
EVACUATED GLASDEWAR
15
75
2050
End mirror
Endspiegel
grating as wavelength selective mirror



7.5
7.6
7.7
7.8
7.9
8.0
μm
λ
8.27
30 mW
10 mW
x25
J = 5,49 mA/cm²
He = 5,2 Torr
N₂ = 0,4 Torr
CO = 0,4 Torr
Luft = 0,1 Torr
Resonator stabilisiert, und evakuiert
Ø = 13,4 mm
31←32
32←33
33←34
34←35
35←36

F3

16



1325 cm⁻¹
1300
1275
1250
1225
30mW
10mW
x25
32–31
33–32
34–33
35–34
36–35
long wavelength end of CO-lasing transitions

I4

1.2 Colour Centre Laser

1.2.1 Physics of F-Centres

Lattice defects in alkalihalides, e.g. KCl

trapped electrons, spatial distribution in ground- and excited state

relaxation of lattice → differene in absorption and emission wavelength.

simple F-centre: extremely small transition moment
<u>not</u> lasing!

more complicated F_A(II)-centre
good lasing conditions!

Behaves like a good laser dye in IR!

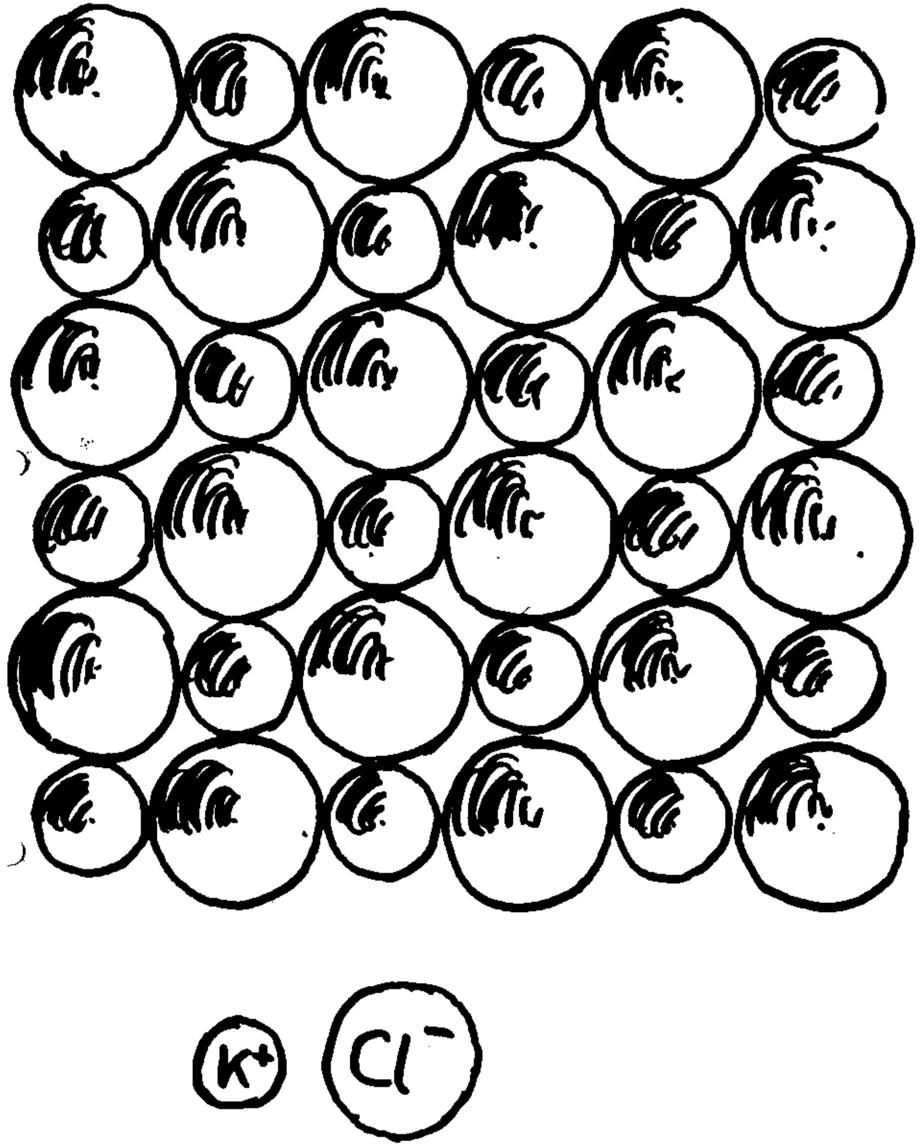
4-level pumping scheme

1.2.2 Experimental setup for CC Laser

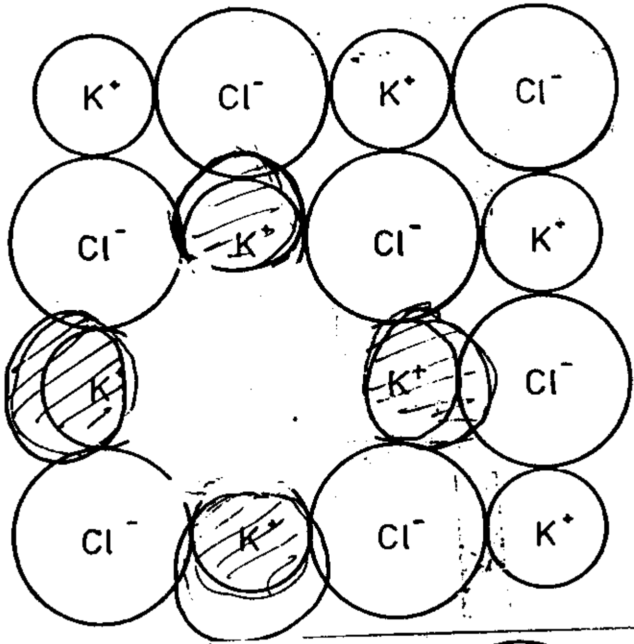
cooling to liquid nitrogen (quantum efficiency)

coarse tuning element: grating

fine tuning element: intracavity etalon
(resolving power of "active spectrometer")



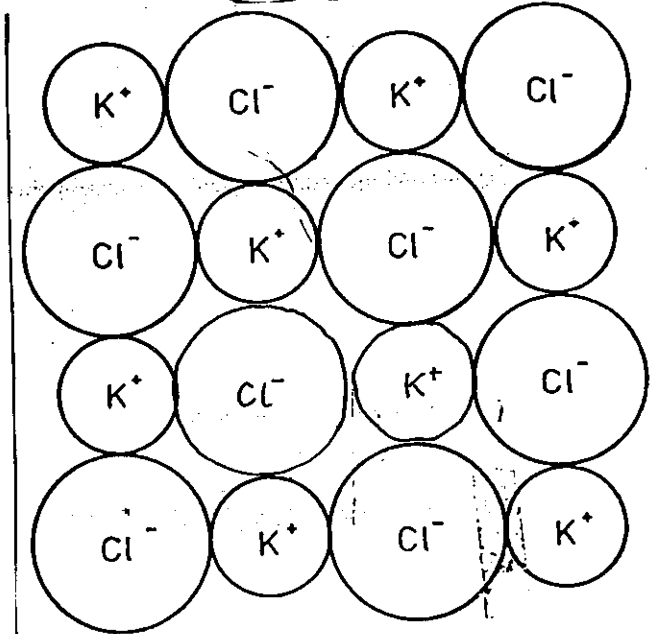
KCl, undistorted structure



K⁺
r=1,33 Å

Cl⁻
r=1,81 Å

Li⁺
r=0,68 Å



K⁺
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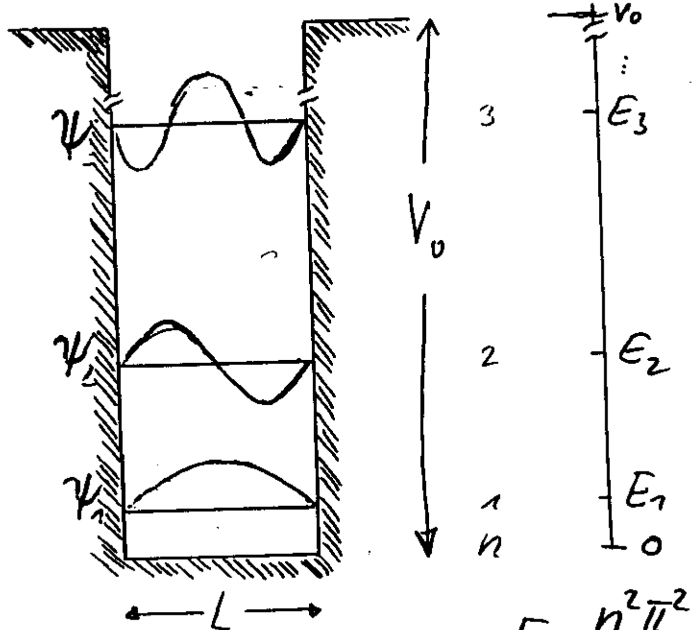
r=0,68 Å



$$E_n = \frac{n^2 \pi^2}{L^2}$$

$$\psi_n = \begin{cases} \cos\left(\frac{n\pi x}{L}\right), & \text{für ungerade } n \\ \sin\left(\frac{n\pi x}{L}\right), & \text{gerade } n \end{cases}$$

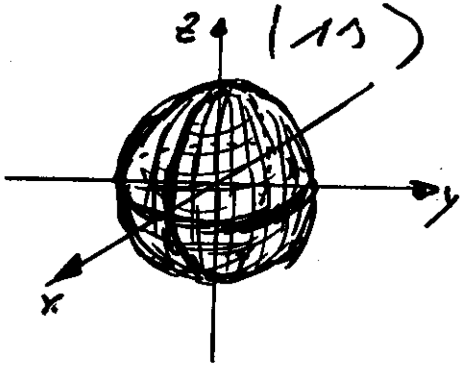
$n = 1, 2, 3, \ldots$

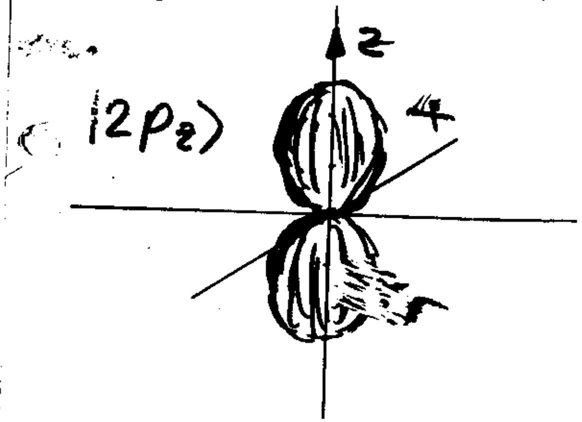
für $V_0 = \infty$

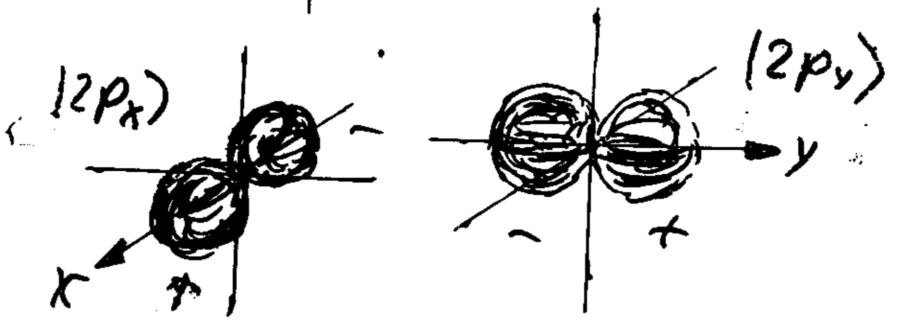
Teilchen im Kastenpotential

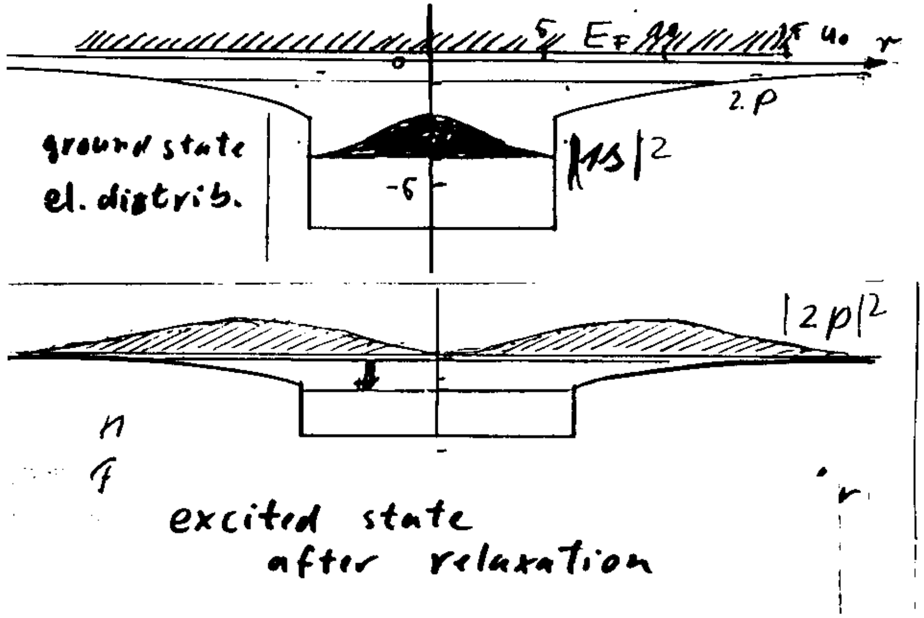
Energiestufen $\propto \frac{1}{L^2}$

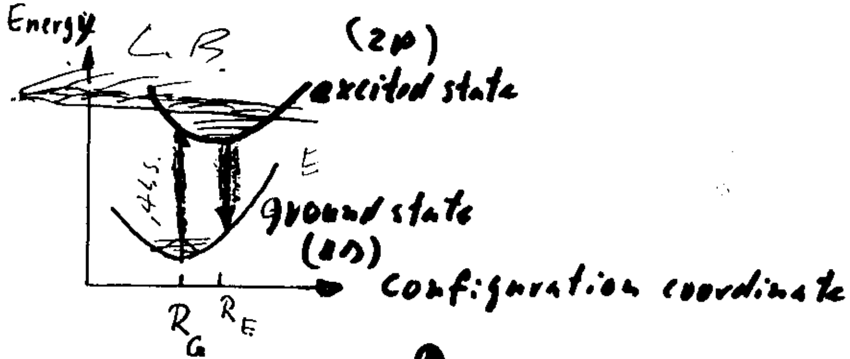
reelle Eigenfunktionen

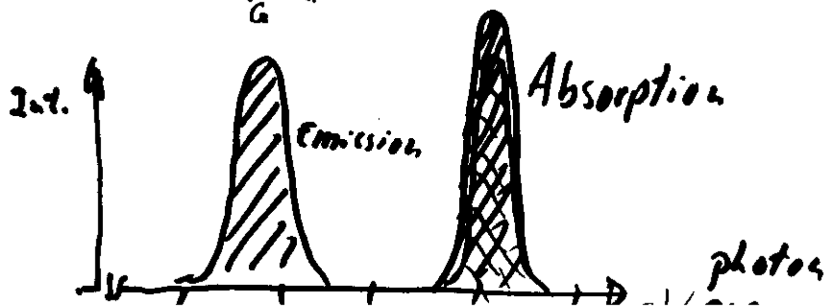


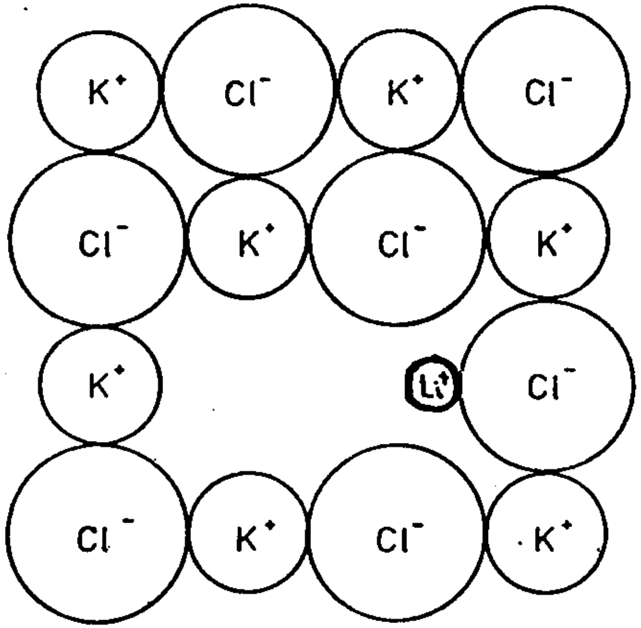








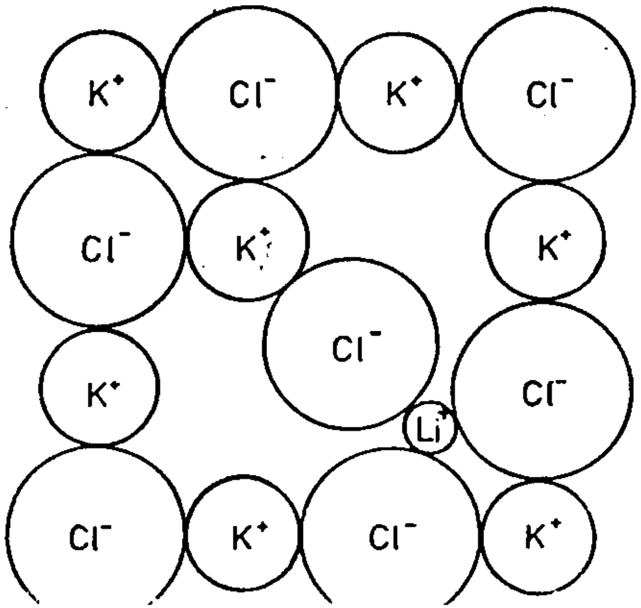


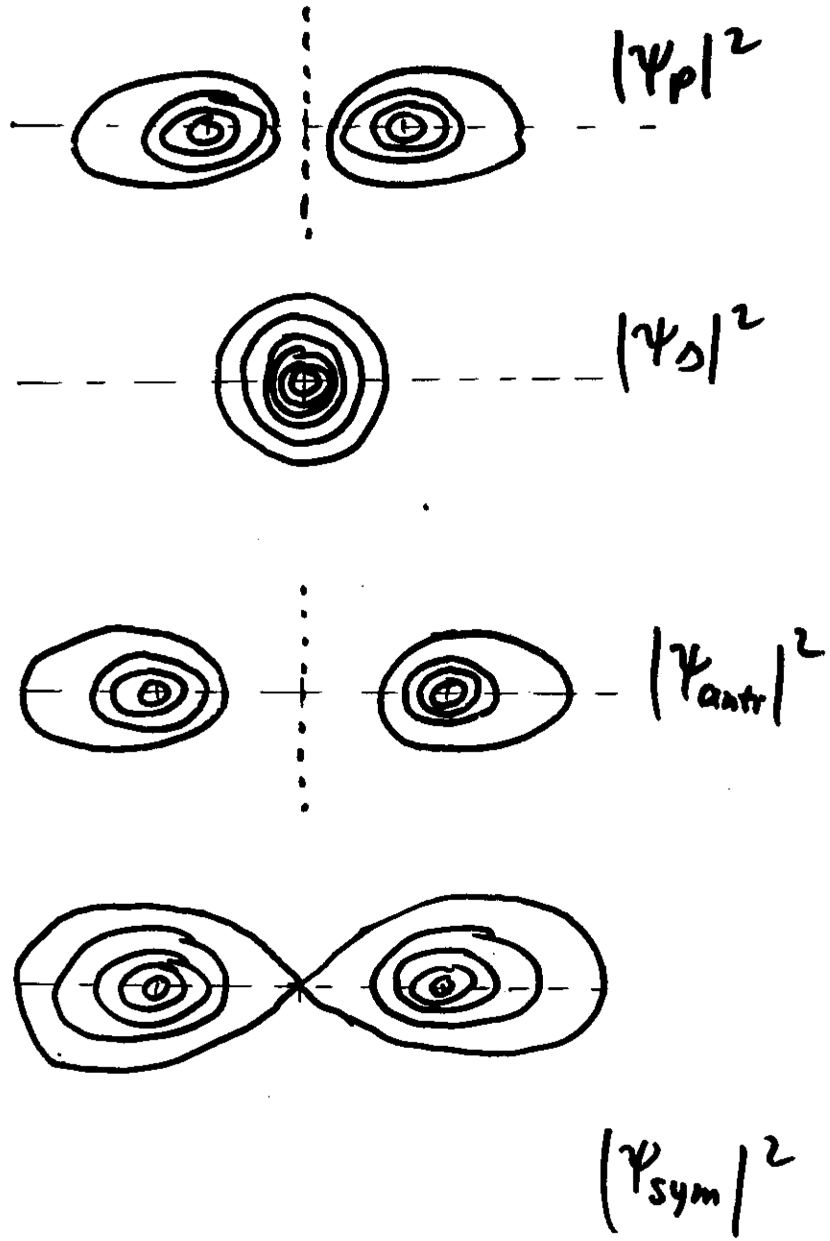


K^+
r=1,33 Å

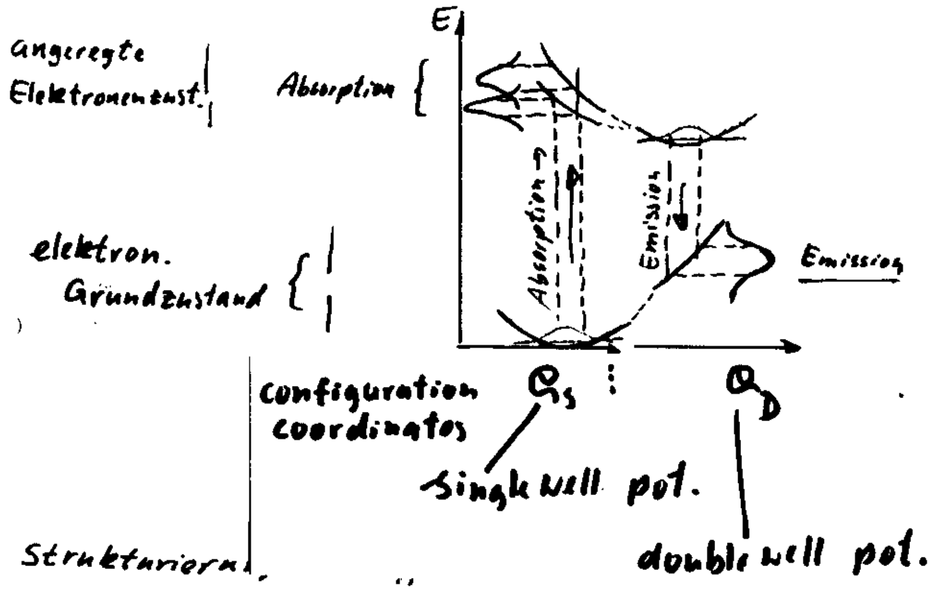
Cl^-
r=1,81 Å

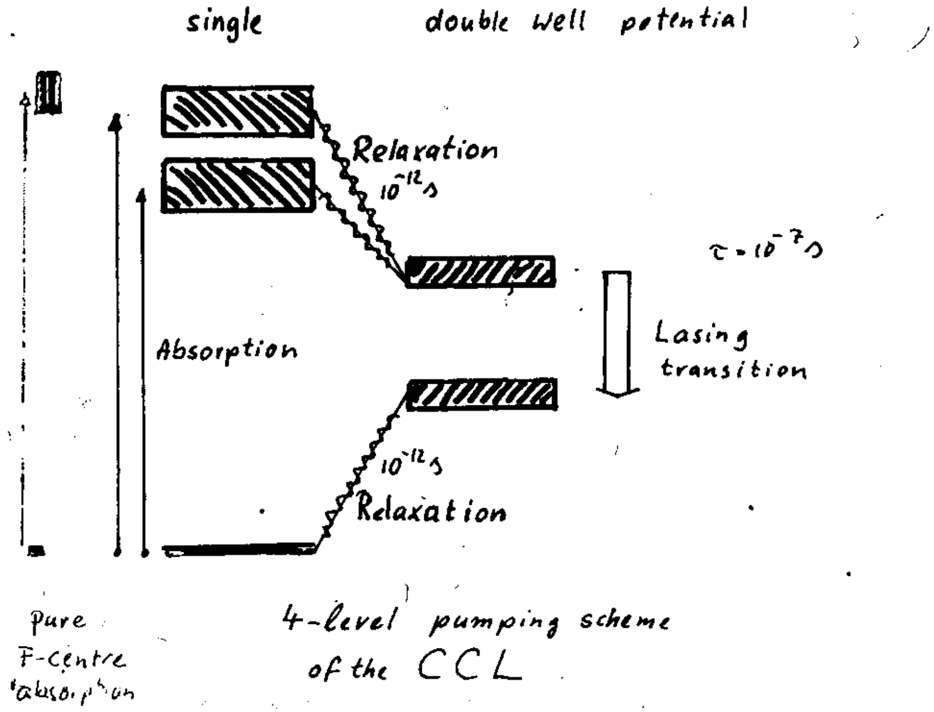
Li^+
r=0,68 Å



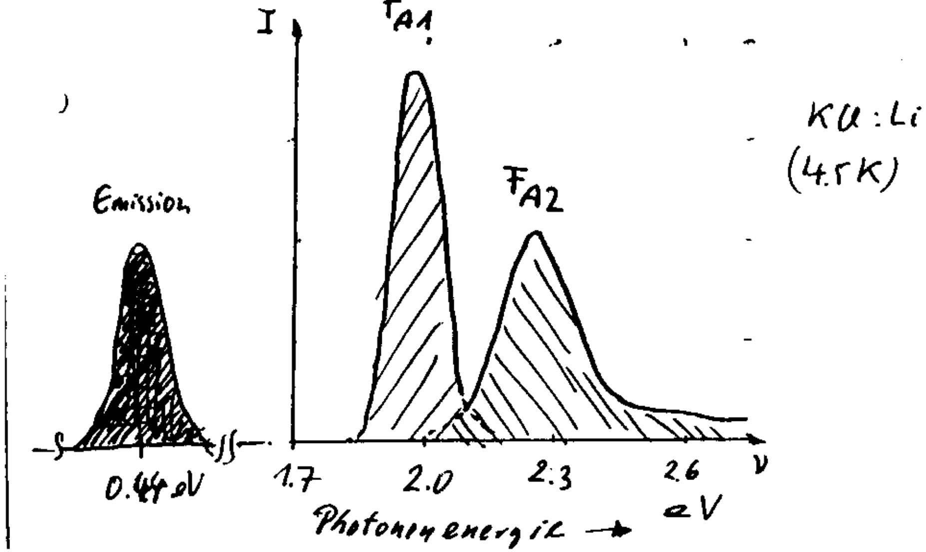


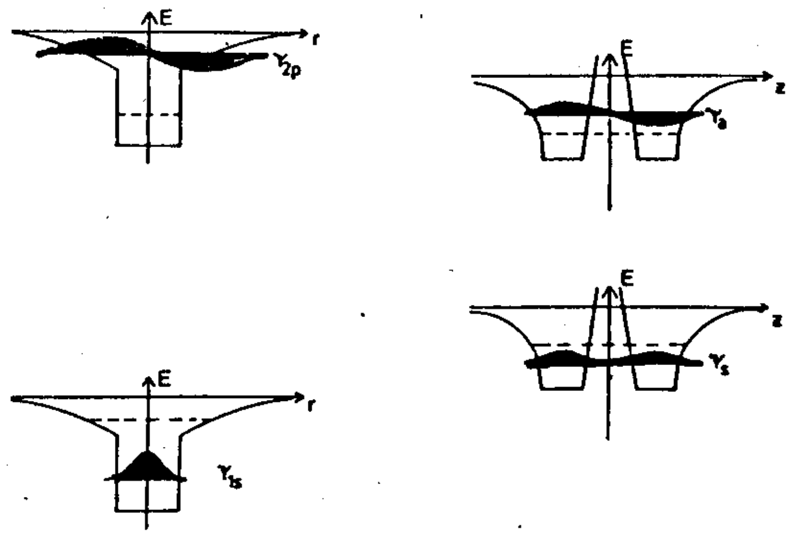
Konfigurationsschema für F_A(II)-Zentren

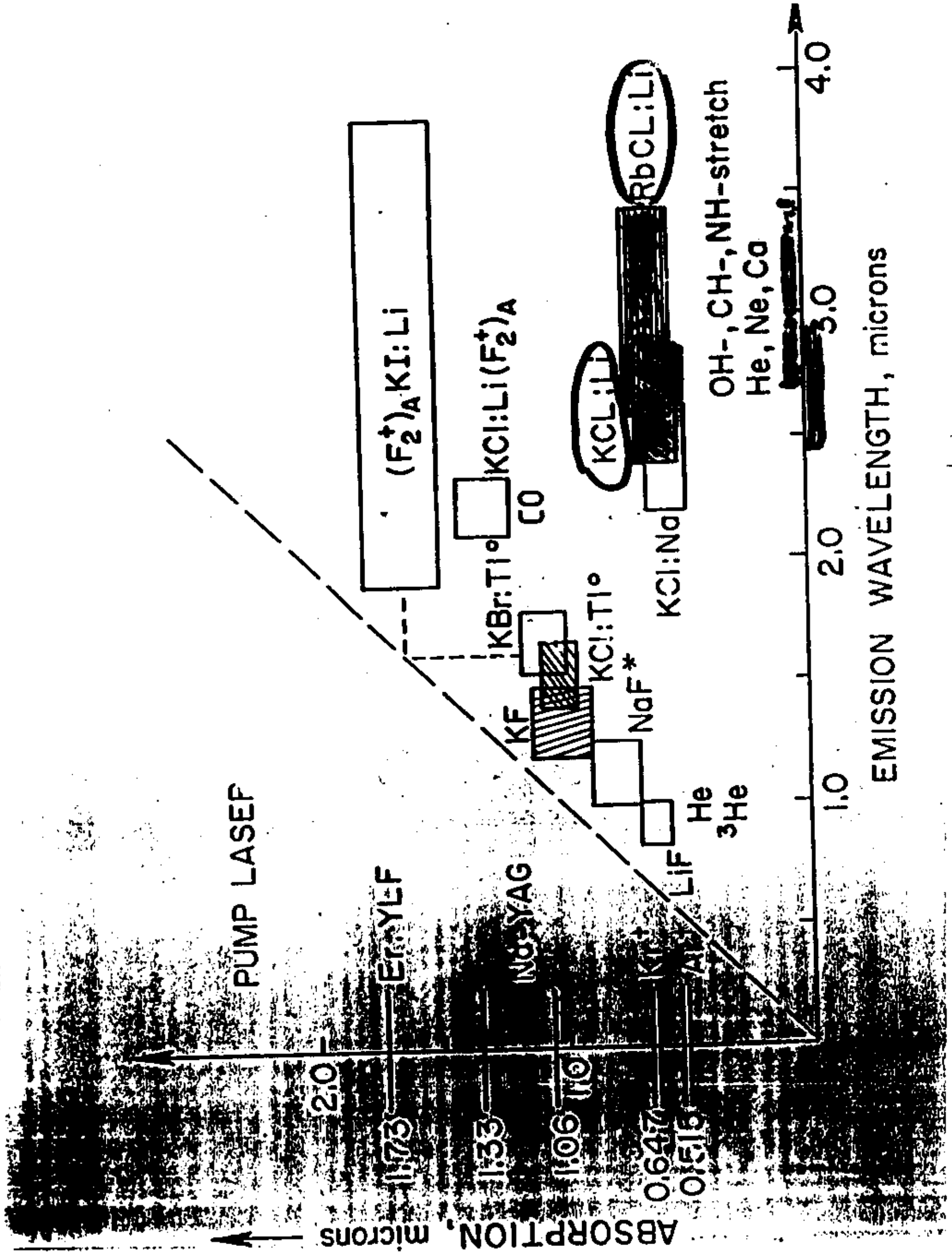


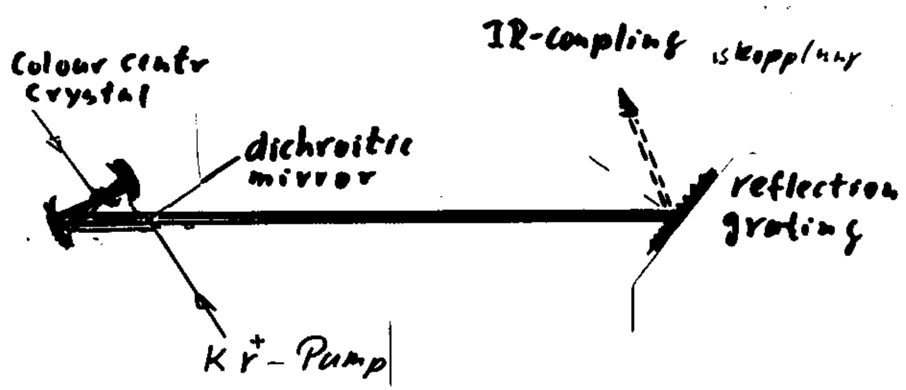


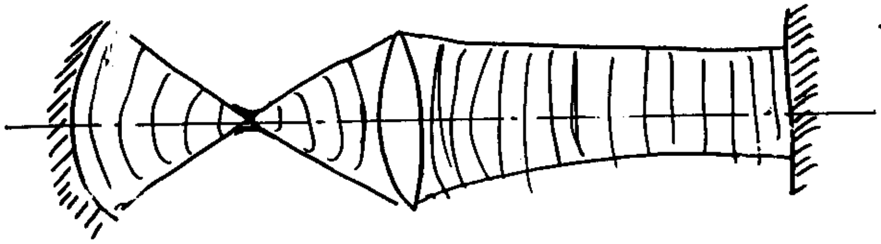
4-level pumping scheme
of the CCL



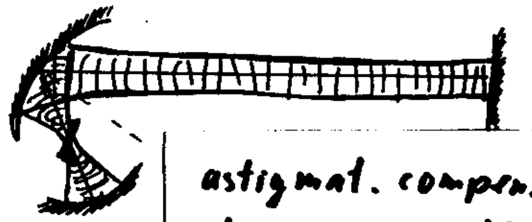






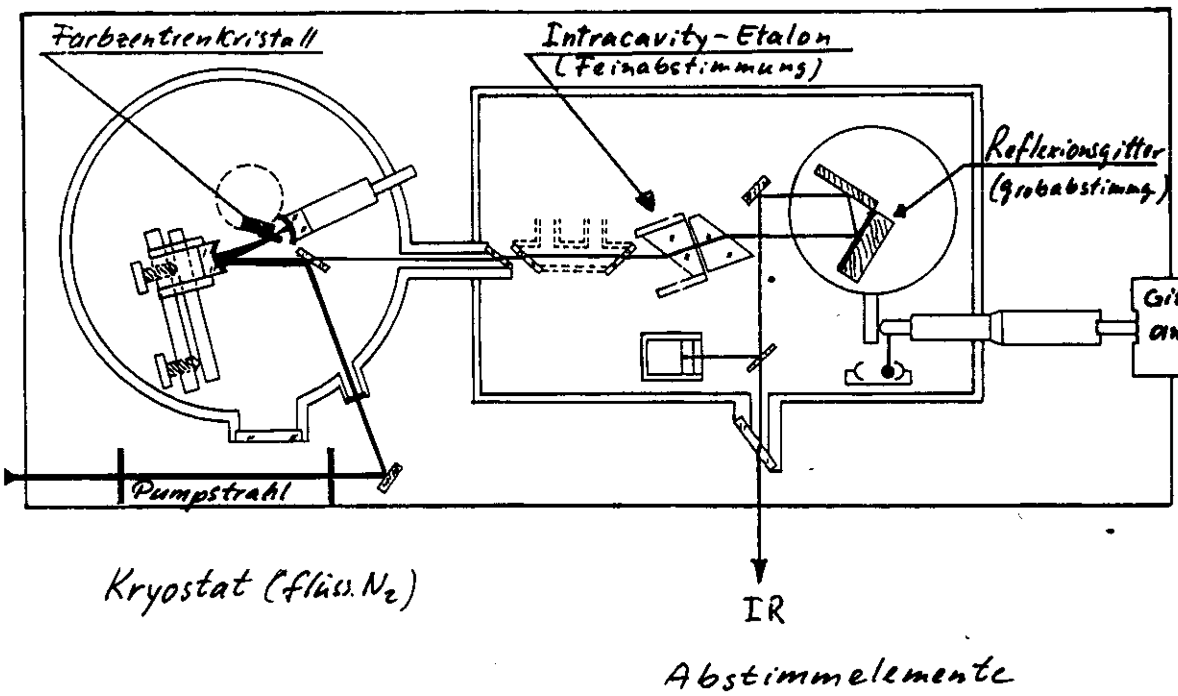


principle structure of resonator

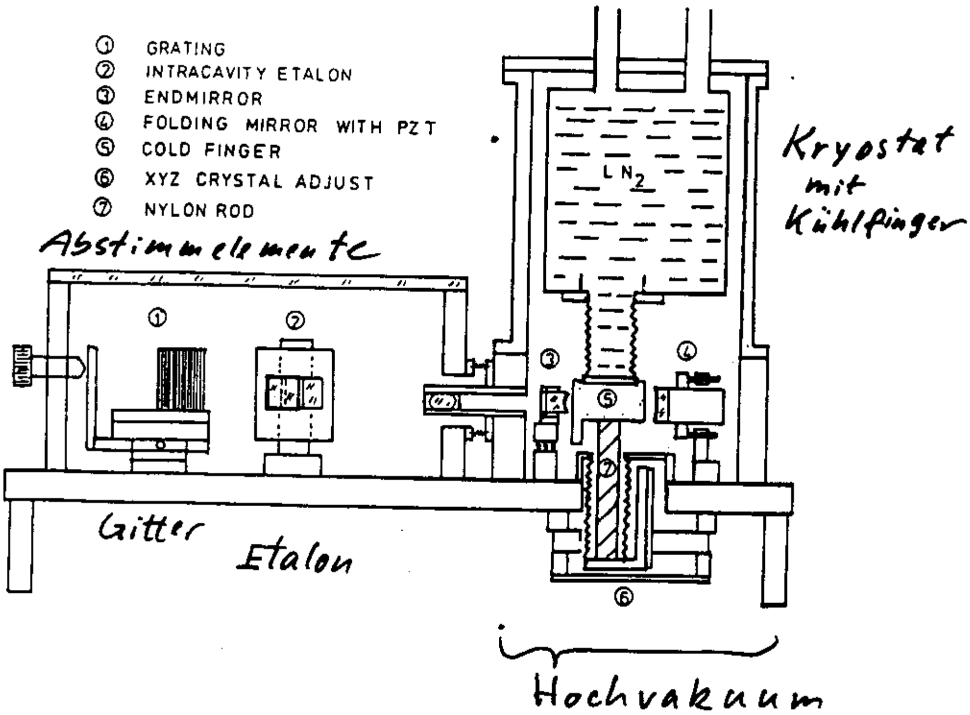


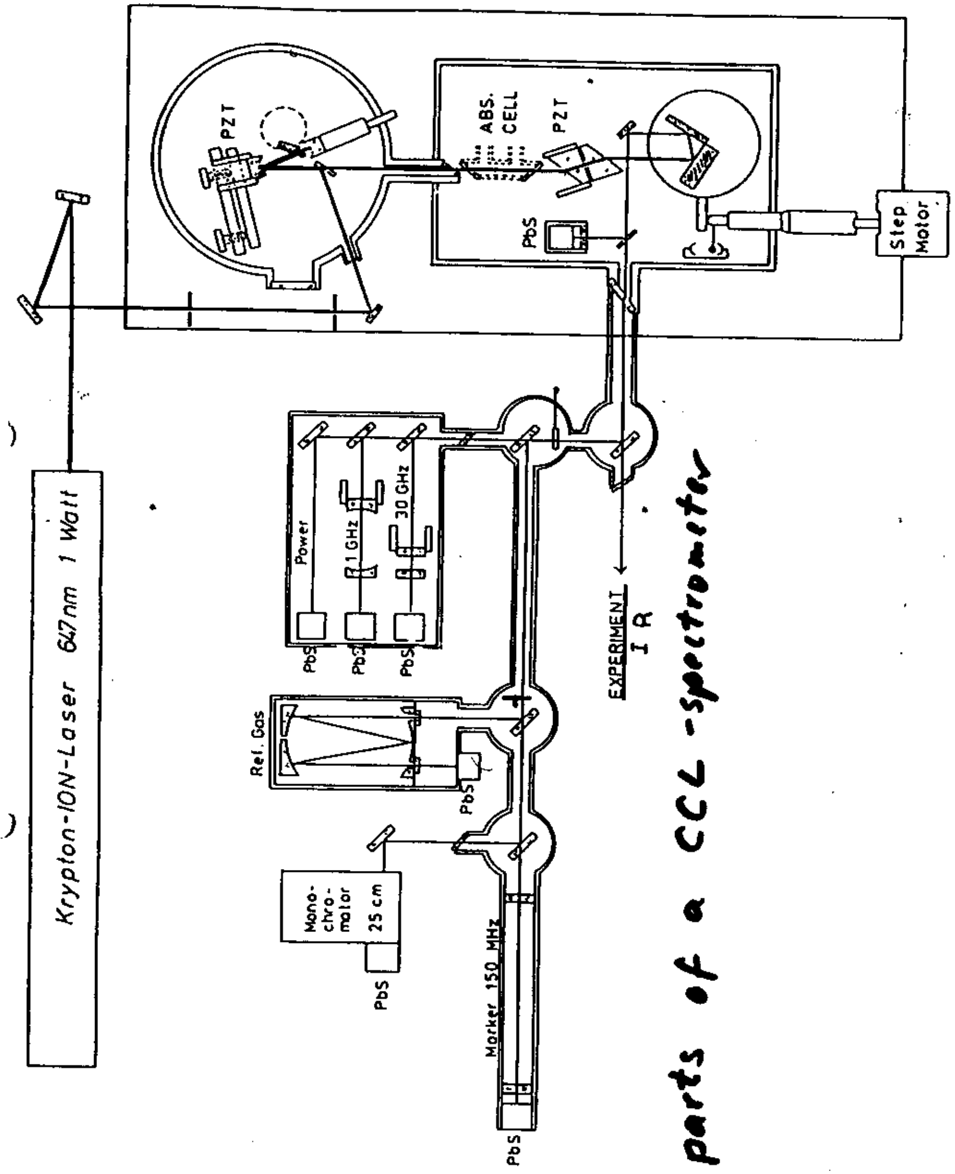
astigmat. compensated type after Kogelnik

construction of colour centre laser



Anordnung der Elemente des Farbzenten-Lasors





parts of a CCL-spectrometer

2. Techniques for Sensitive Spectroscopy of Open-Shell Molecules

2.1 Effect-modulation of paramagnetic Species

Zeeman-effect, transition rules $\Delta M_J = \pm 1$

Zero-field modulation with continuously tunable IR-lasers (CCL).

2.2 Laser Magnetic Resonance (LMR)

First developed by K.M. Evenson for FIR-transitions
also applicable for vib-rot-transitions.

Zeeman-tuning and modulation (near-coincidence)

tuning range and J-value

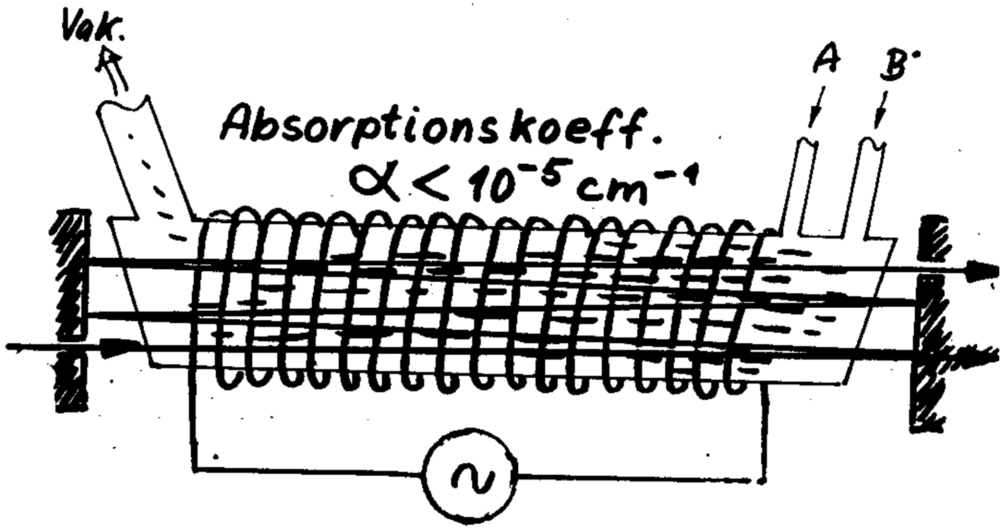
Intracavity-setup for high sensitivity

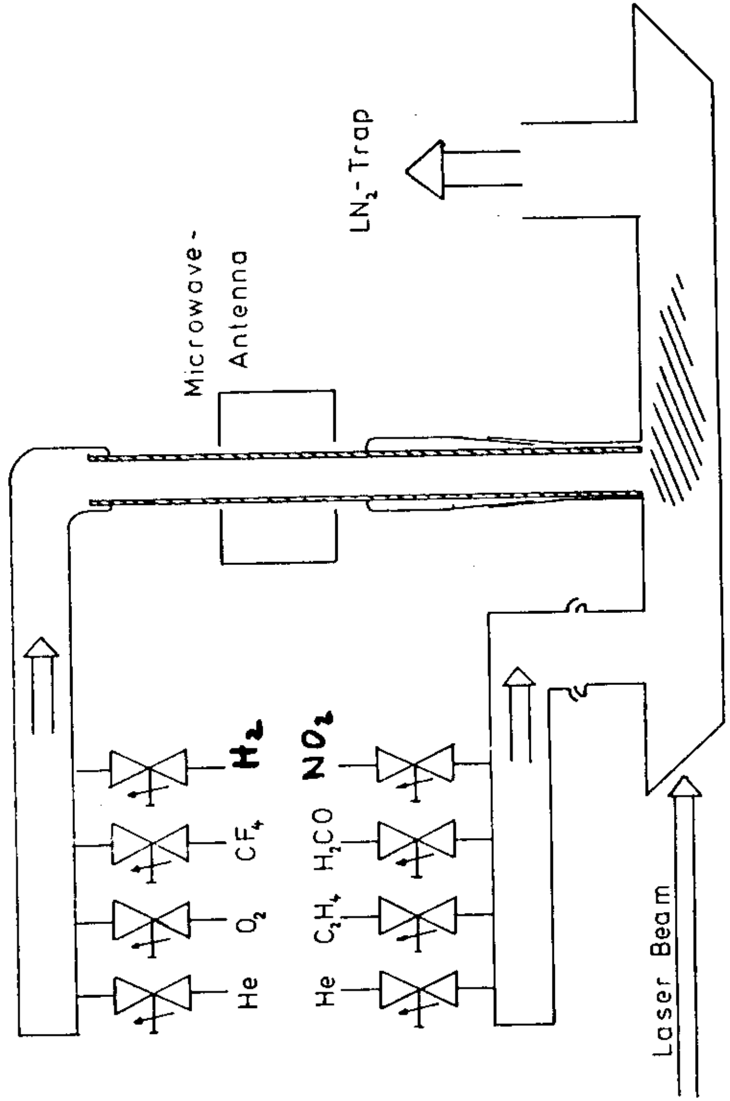
2.3 Polarisation Techniques

Laser noise as sensitivity limiting factor

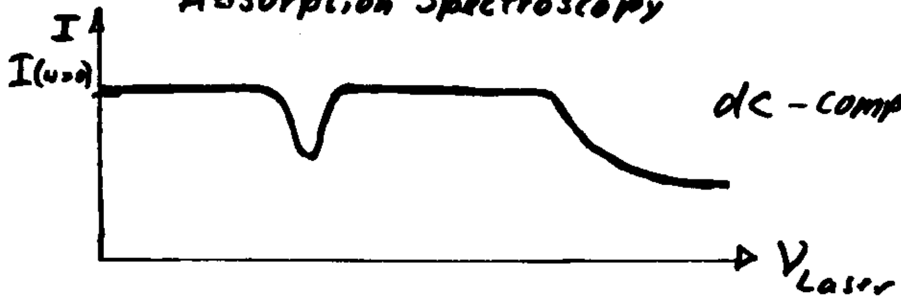
Polarisation effects with paramagnetic absorbers

Faraday- and Voigt-effect


Vak.
Absorptionskoeff.
$\alpha < 10^{-5}\,cm^{-1}$
A
B


LN$_2$-Trap
Microwave-Antenna
H_2
CF_4
O_2
He
NO_2
H_2CO
C_2H_4
He
Laser Beam

Absorption Spectroscopy

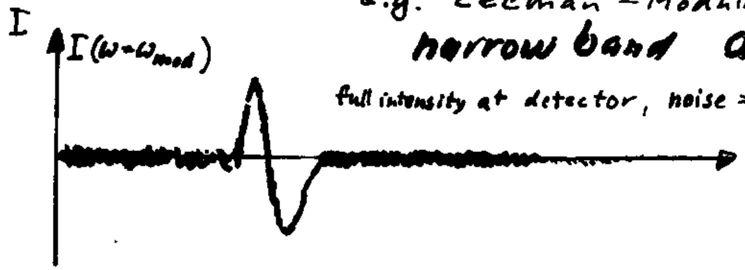


Effect-Modulation Detection

e.g. Zeeman - Modulation

narrow band ac-compon.

full intensity at detector, noise = Laser noise

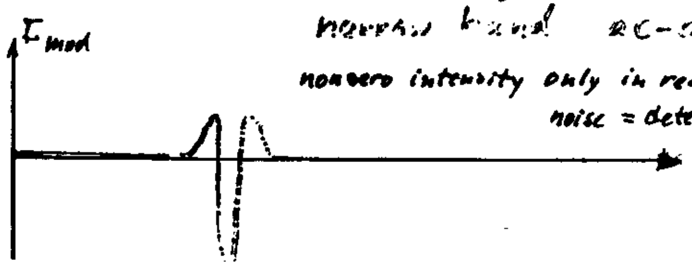


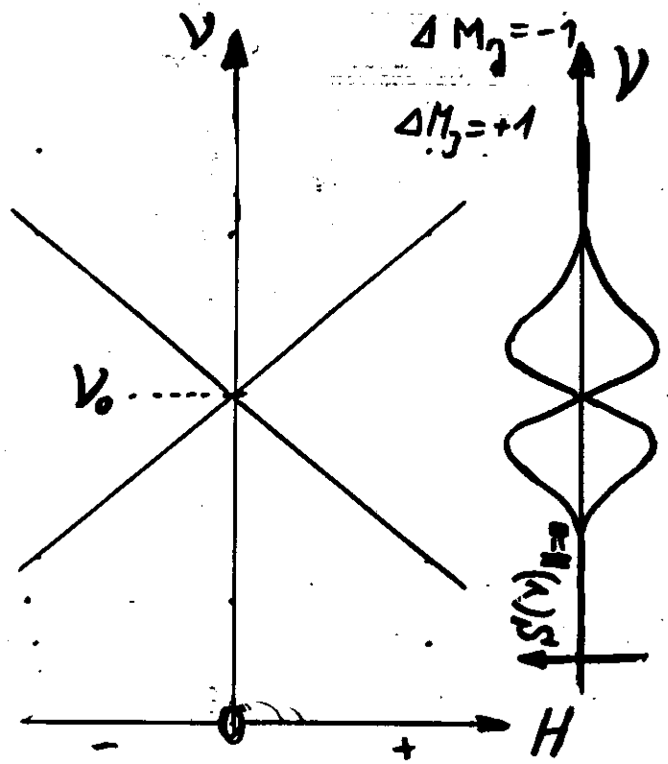
e.g. Faraday - Rotation

narrow band ac-compon.

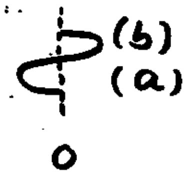
nonzero intensity only in resonance

noise = detector noise

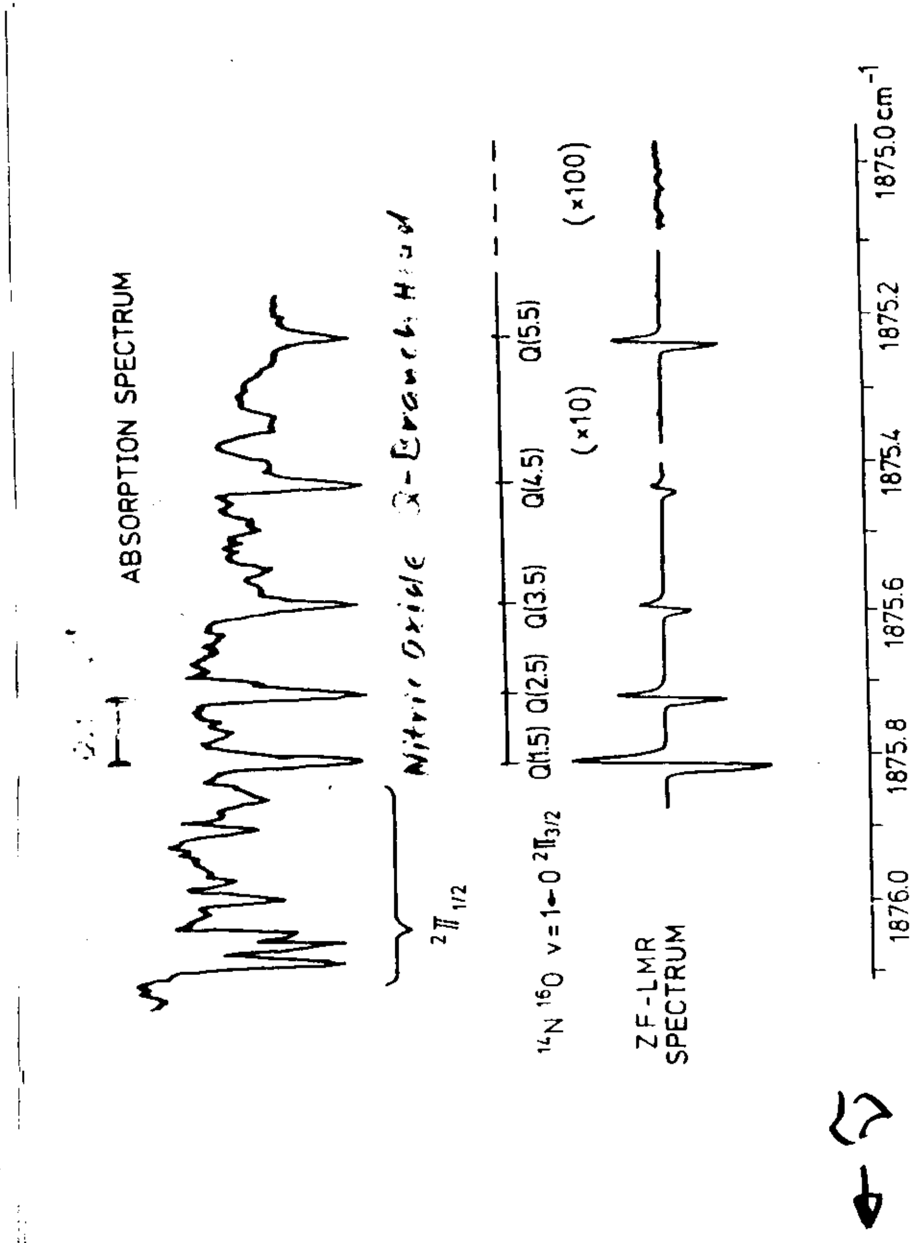


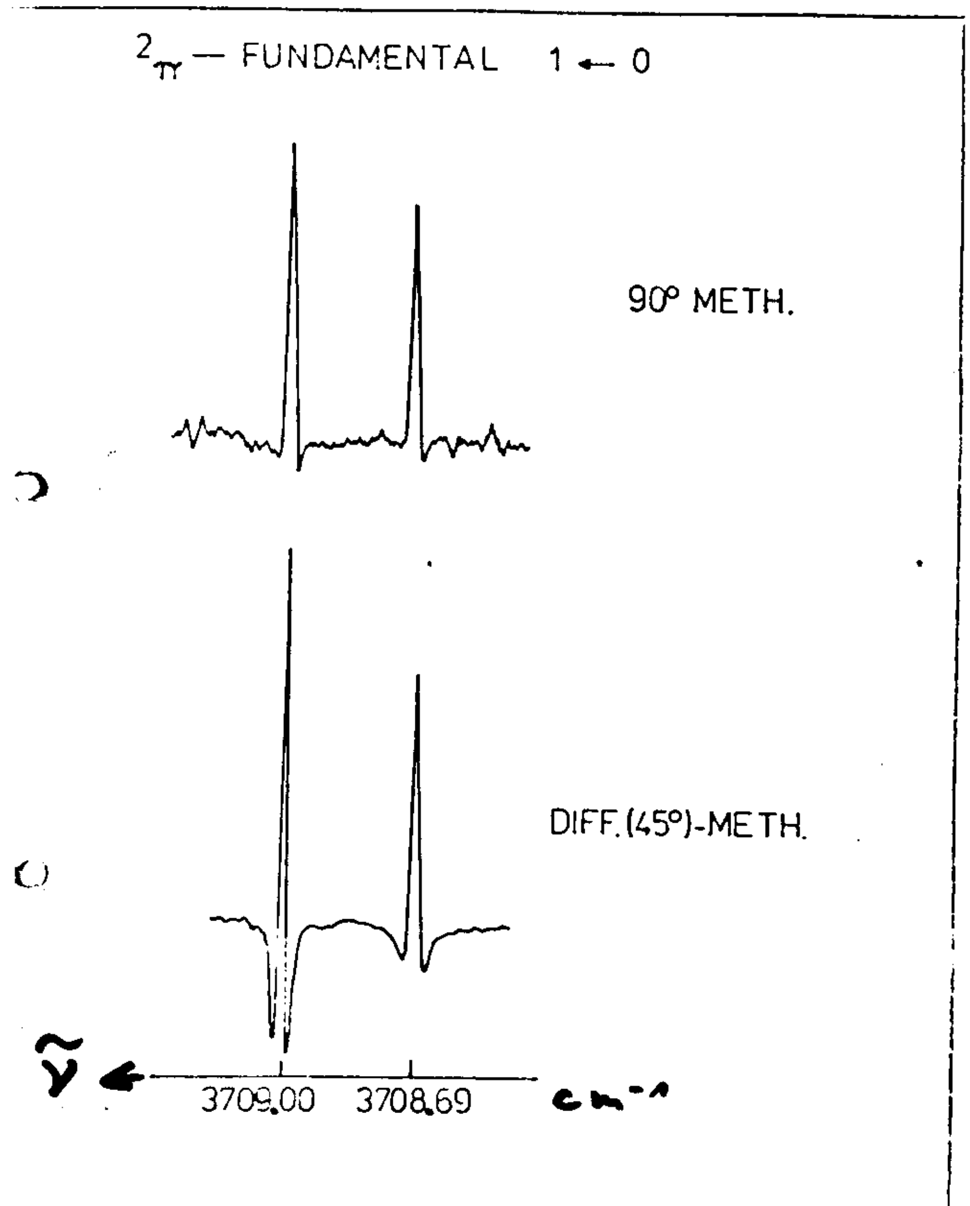


Mod. Phase

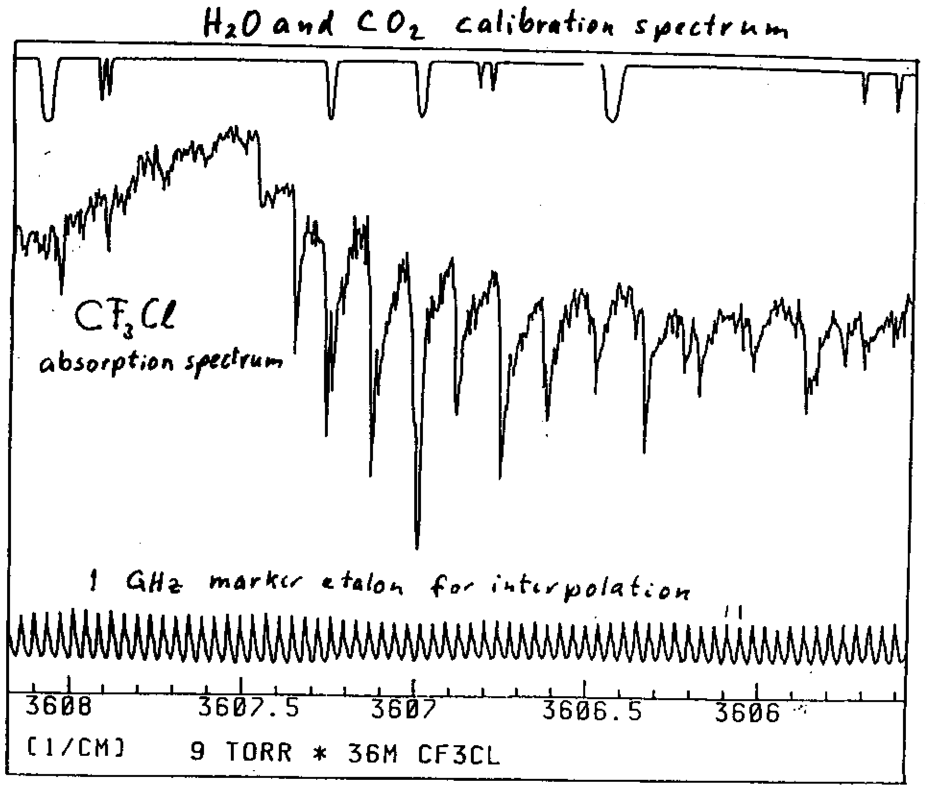


$$S(H,\nu) = \frac{\partial}{\partial H}\left\{G(H=0,\nu)\right\} \qquad \Delta M_J = \pm 1$$

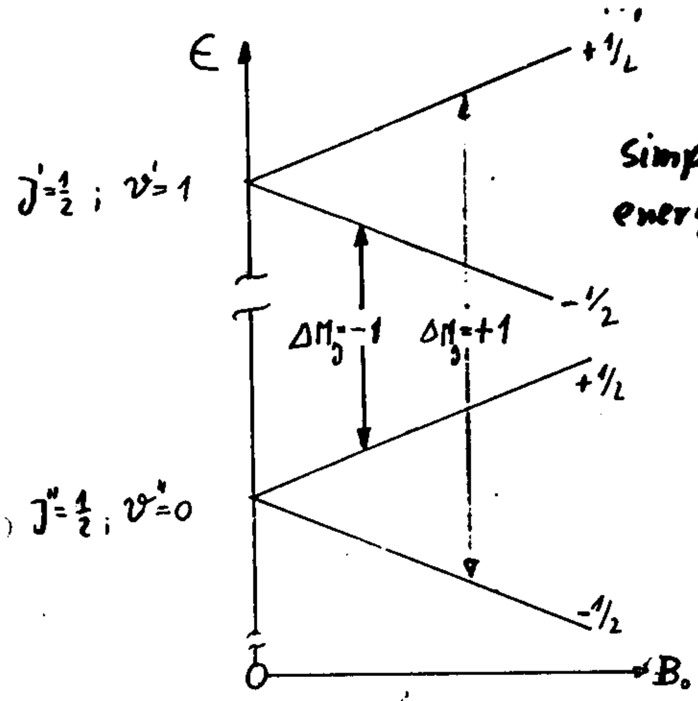




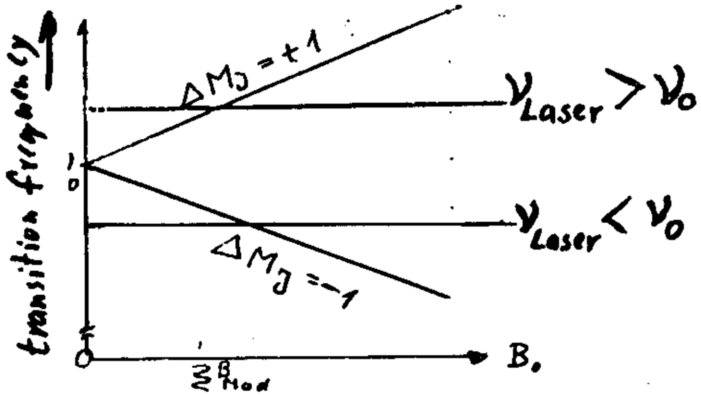
λ- DOUBLING IN OH R(3.5) F1 TRANSITION



colour centre laser spectroscopy



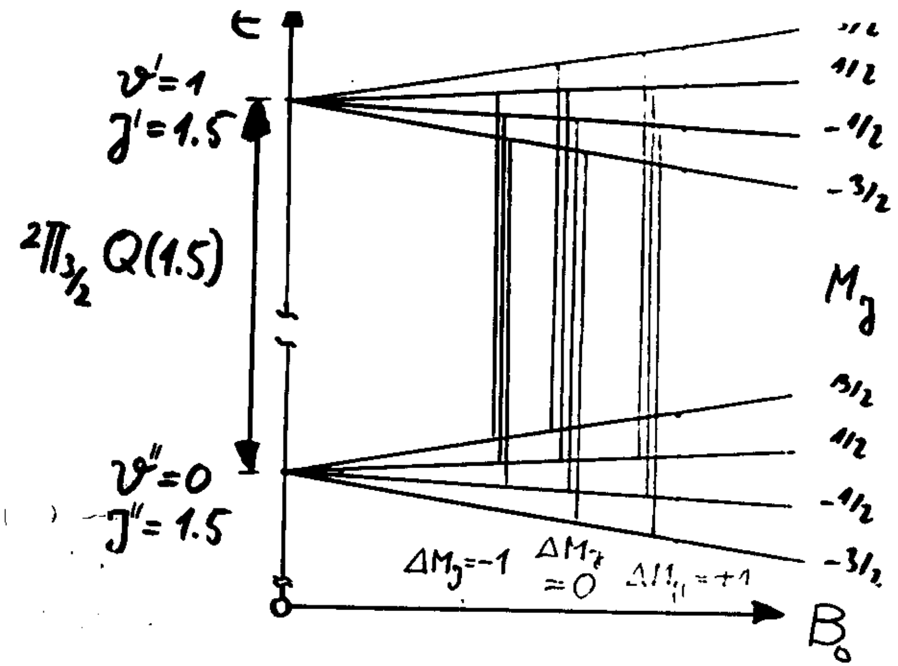
simplified energy diagram

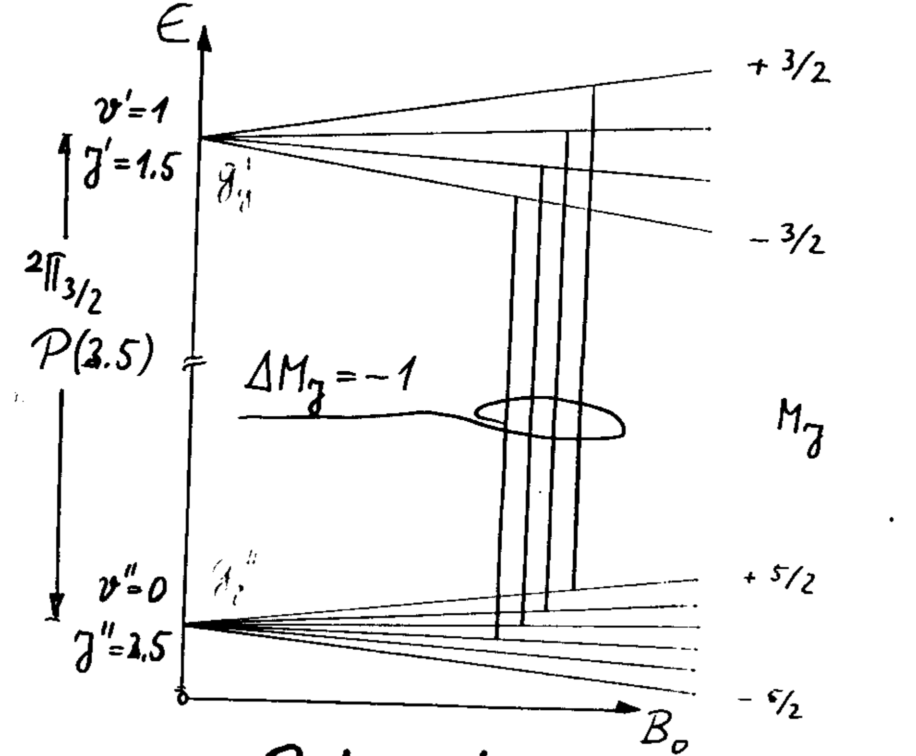


principle of LMR operation
ν_{Laser} = const,
Zeeman-tuning and Zeeman-modulation

F3

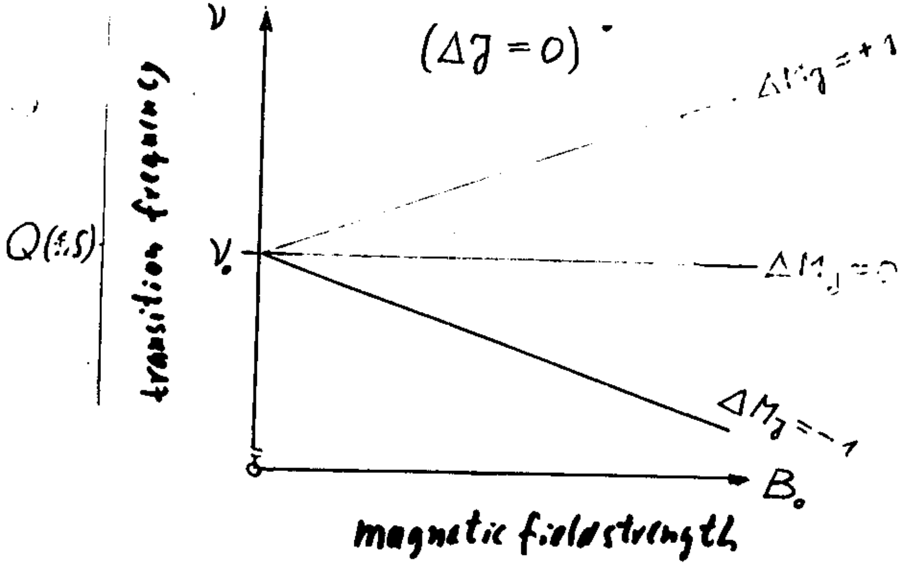
7





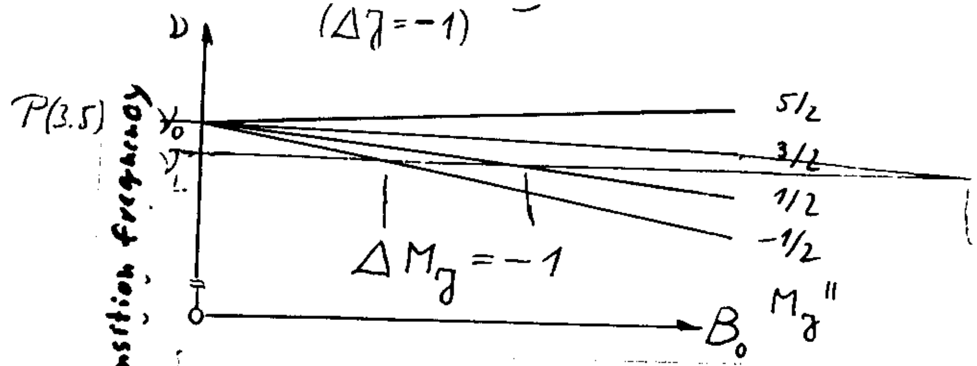
Q-branch

($\Delta J = 0$)

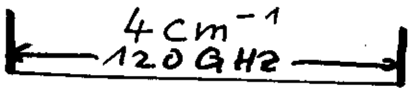


P-branch

($\Delta J = -1$)



$\frac{\partial \nu}{\ldots} = \mu\,(g' M' - g'' M'')$



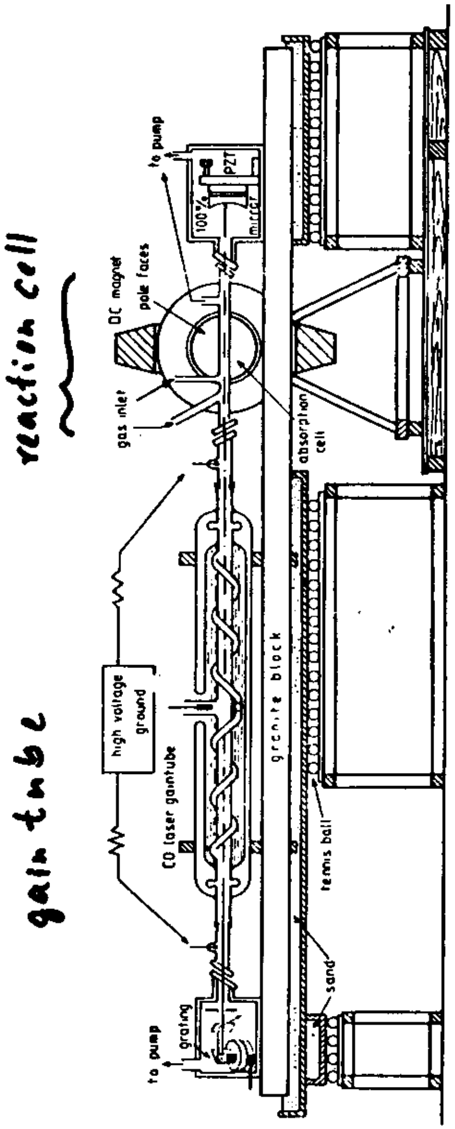
distance of neighbouring CO-Laserlines

tuning ranges for Hund's case (a) molecules at 1 Tesla field strength

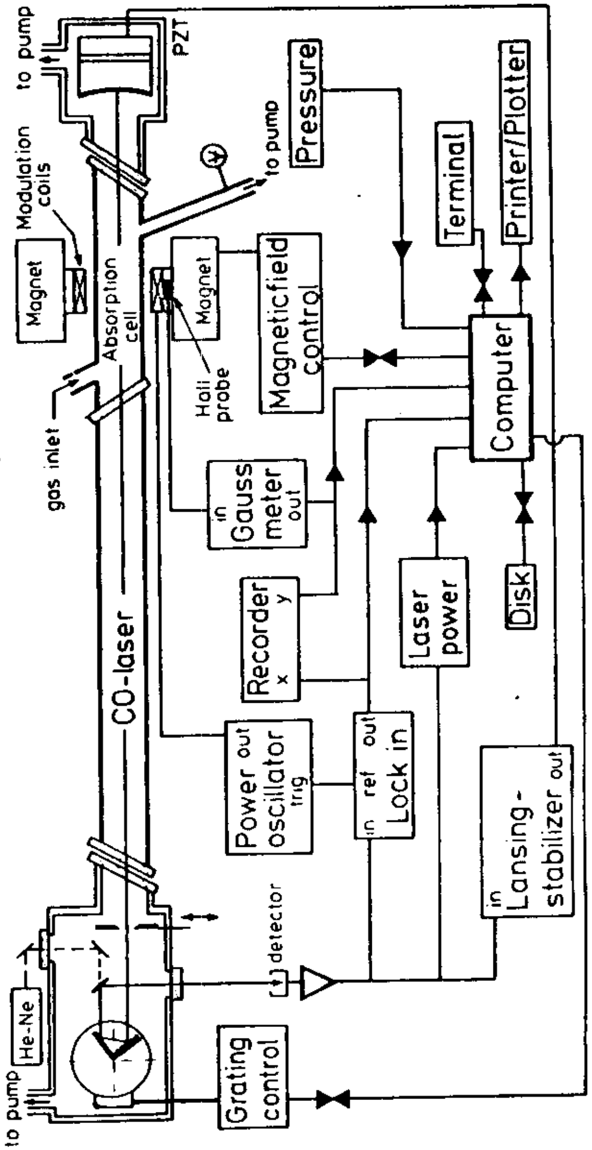
$J = \frac{3}{2}$	$J = \frac{5}{2}$	$J = \frac{7}{2}$
$\pm 0.37\,cm^{-1}$ ~10 GHz	$\pm 0.16\,cm^{-1}$	$\pm 0.09\,cm^{-1}$

CO-Laserlines

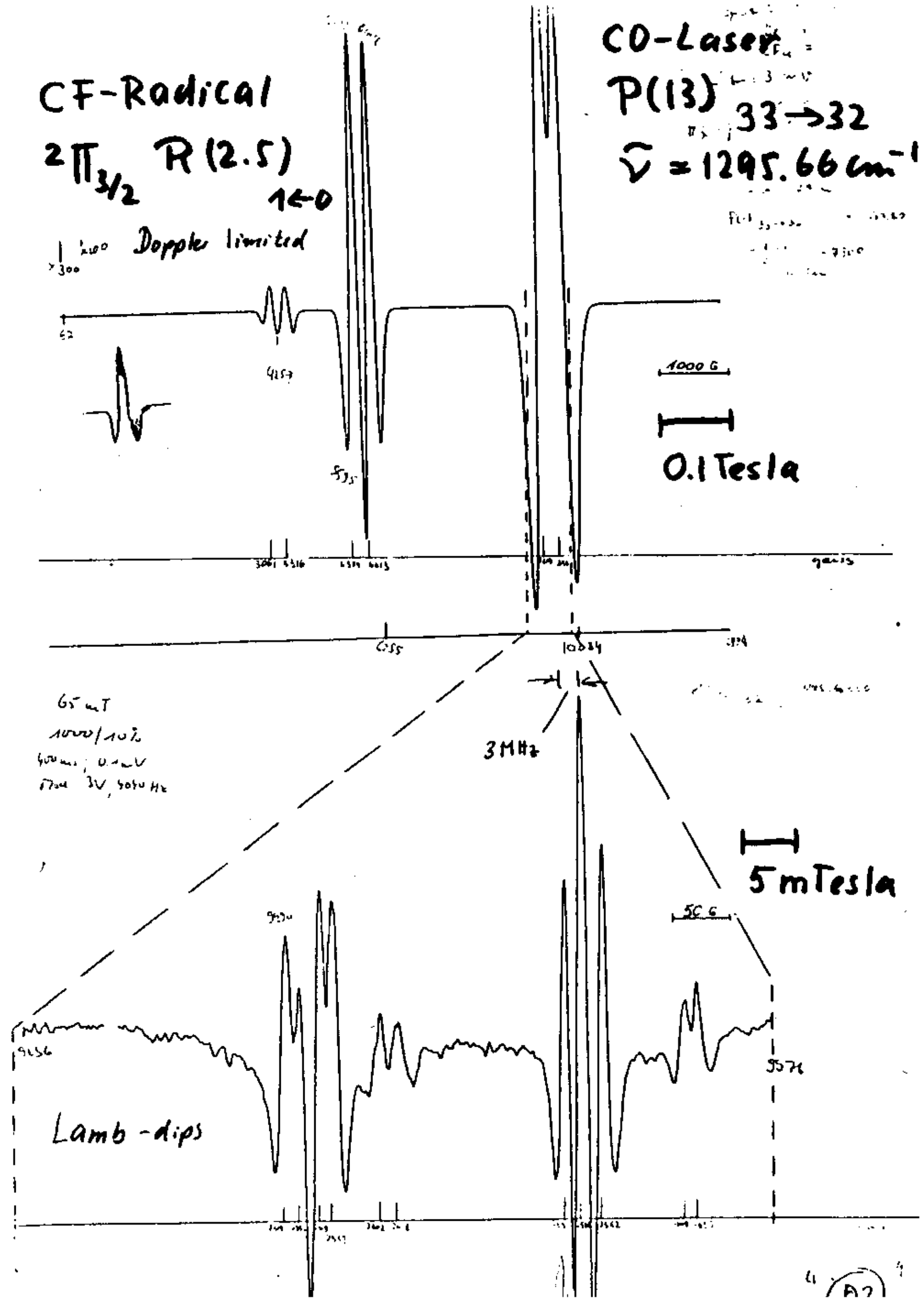
CO-Laser: 1200 – 2070 cm^{-1}, 450 Linien

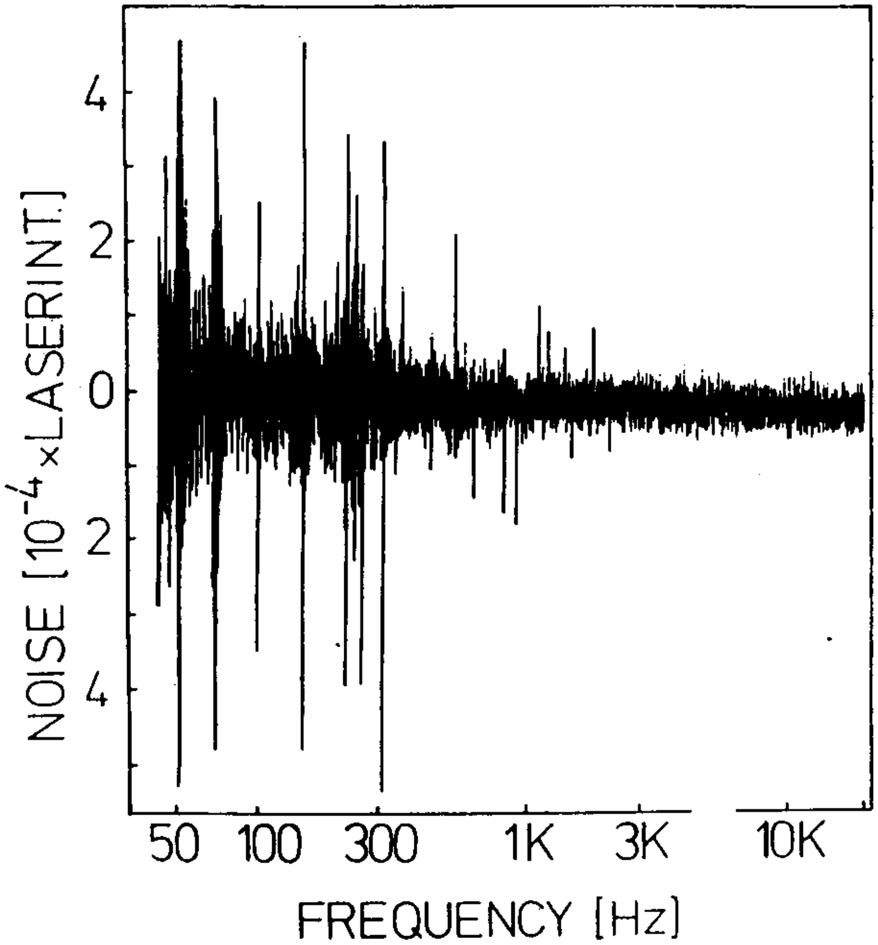


LMR - setup, intracavity arrangement



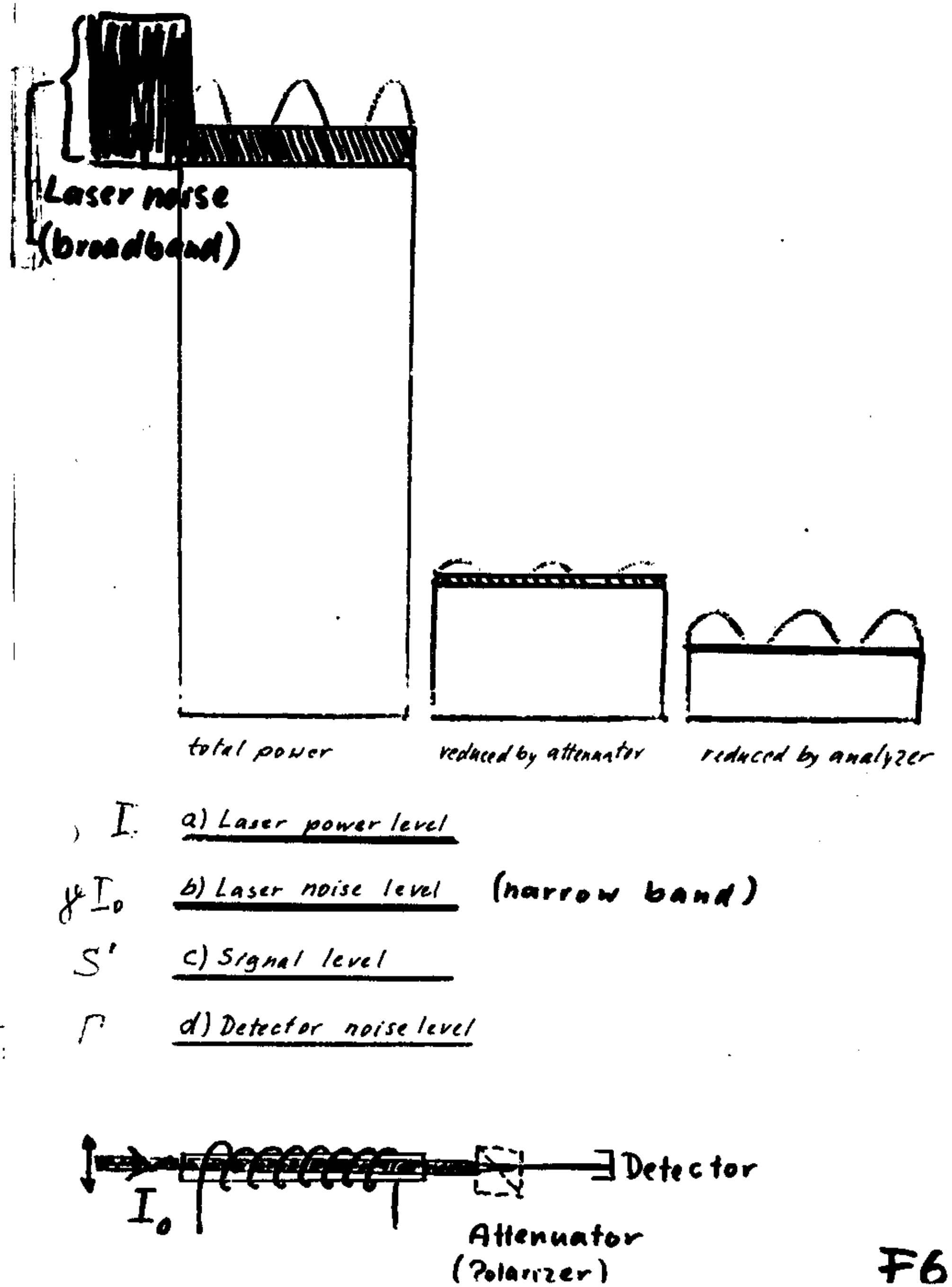
block diagram of LMR-setup.





NOISE [10^-4 × LASERINT.]
4
2
0
2
4
50
100
300
1K
3K
10K
FREQUENCY [Hz]

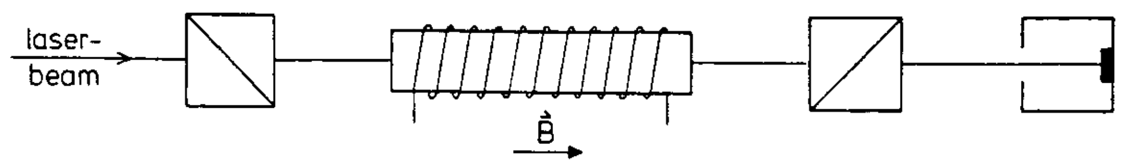
F5



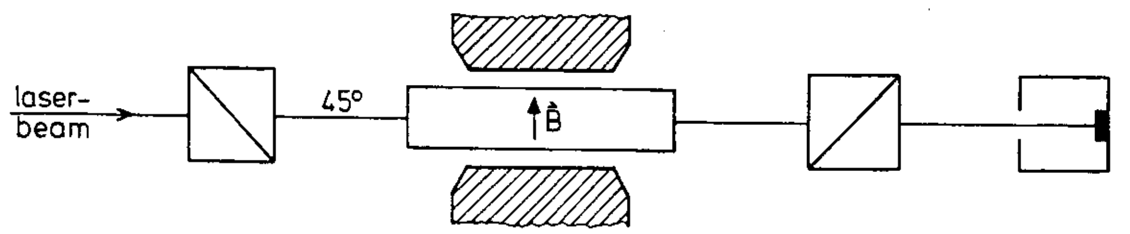
Laser noise (broadband)
total power
reduced by attenuator
reduced by analyzer
I a) Laser power level
γI₀ b) Laser noise level (narrow band)
S' c) Signal level
Γ d) Detector noise level
I₀
Detector
Attenuator (Polarizer)

F6

H. Hinz, ... Pfeiffer, W. Bohle, W. Urban   Mol. Phys. ..., 1131 (198.)

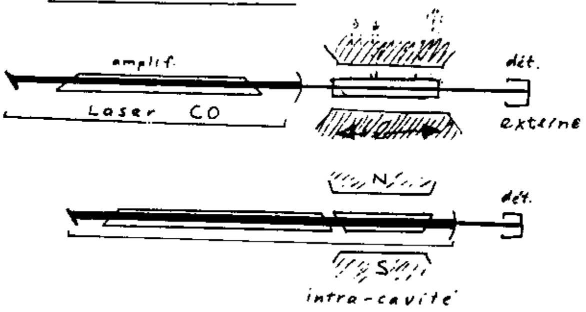


FARADAY-CONFIGURATION



VOIGT-CONFIGURATION

LMR "classique"   IV!



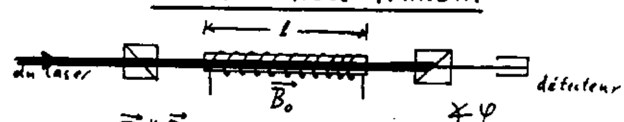
Intensité au détecteur :

$$I = I_o \{1 - 2 k_o \ell \varkappa\}$$

Intensité du laser; longueur du chemin d'absorption; coeff. d'absorbance

(1) $\begin{cases} \varkappa_L = \varkappa_x \\ \varkappa_I = \varkappa_y \end{cases}$

LMR Effect FARADAY   VII



$\vec{P} \parallel \vec{B}_o$

$$\vec{E} = \tfrac{1}{2} E_o e^{i(\omega t - kz)} \left\{ \binom{1}{i} + \binom{1}{-i} \right\}$$

$\Delta m = \pm 1$; $k_\pm = k_o (n_\pm - i\varkappa_\pm)$

après pass. 'ℓ'

$$\vec{E} = \tfrac{1}{2} E_o e^{i\omega t} \left\{ \binom{1}{i} e^{-ik_+\ell} + \binom{1}{-i} e^{-ik_-\ell} \right\}$$

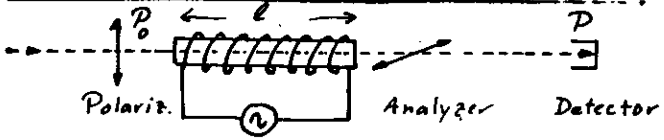
Intens. au dét. après pass. analys. $\measuredangle \varphi$ vers. $\perp$:

$\varphi \ll 1$

$$I = I_o \{ \varphi^2 - \varphi^2 k_o \ell (\varkappa_+ + \varkappa_-) + \varphi k_o \ell (n_+ - n_-) \}$$

Laser-Grundleistung und Rauschleistung   signal de dispersion   Signalleistung

Magnetic Rotation (MR) Technique



$$P = \frac{P_0}{2}\{(1-\cos 2\varphi) + R_\Delta l \sin 2\varphi\}$$ Power incident on detector

φ : ∡ deviation from crossed polarizer position

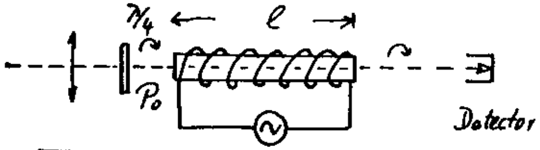
R_Δ : angle of polarization rotation per unit length of specimen

for small angles φ :

$$P_{MR}(\varphi) = P_0\left\{\varphi^2 + \frac{2\omega}{c}\,\underline{\delta\omega_{eff}(B)}\,\frac{dn}{d\omega}\,\varphi l\right\}$$

n = refractive index

Zeeman Modulation (ZM) Technique



$$P_{ZM} = P_0\left\{1 - \frac{2\omega}{c}\,\underline{\delta\omega_{eff}(B)}\,\frac{d\varkappa}{d\omega}\,l\right\}$$

ϰ = absorption coefficient

$\varphi^2 \ll 1$: noise (MR) ≪ noise (ZM)

$\varphi < 1$: signal (MR) < signal (ZM)

Modulation Sensitivity

one transition : $(v'', J'', M'') \rightarrow (v', J', M')$

$$\delta\omega(B) = \mu B\,(M' g^{v'}_{J'} - M'' g^{v''}_{J''})$$

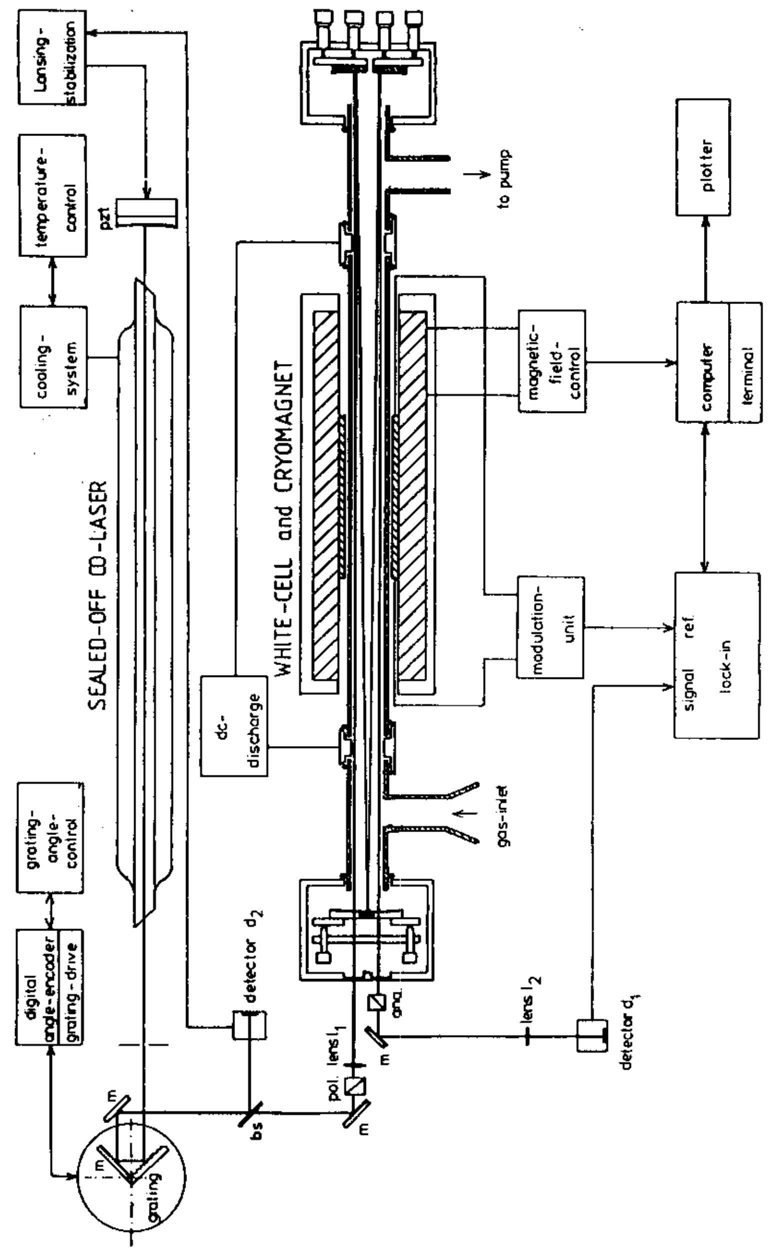
at zero external field : $(v'', J'') \rightarrow (v', J')$

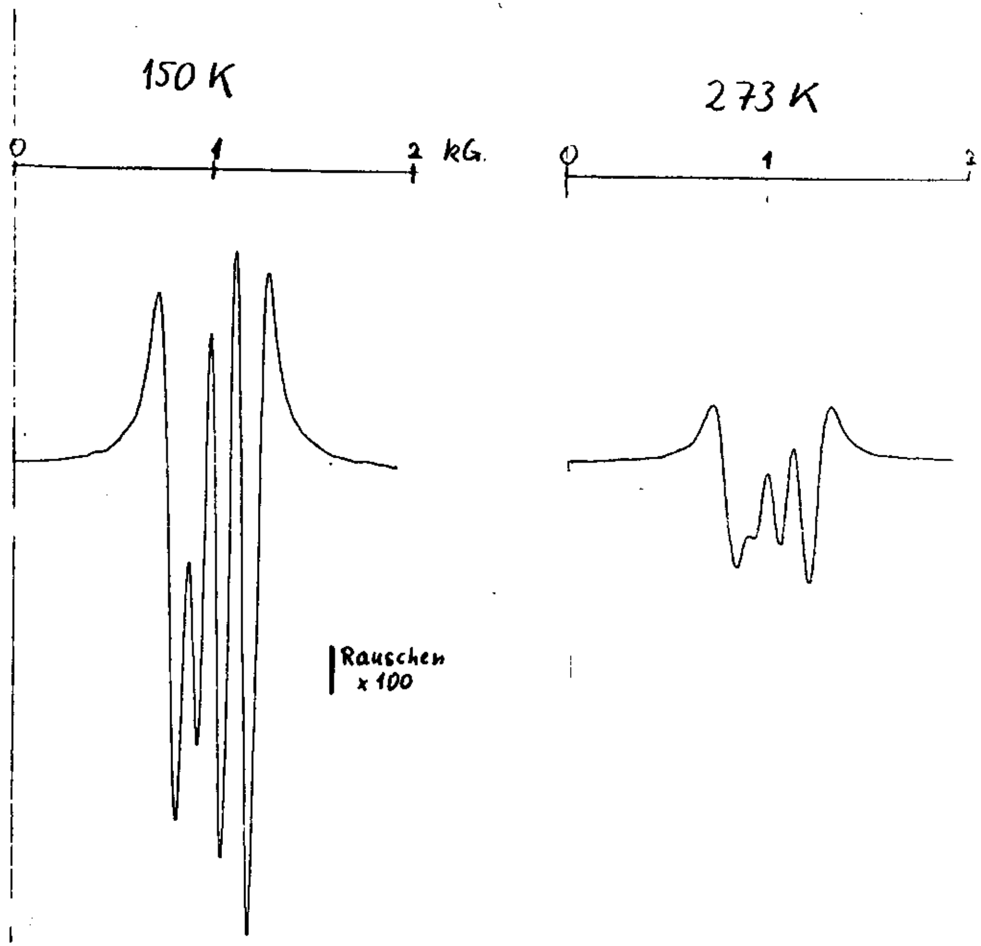
$$\delta\omega_{eff}(B) = \sum_{M' M''} \delta\omega(B) = \mu B\, g_{eff}$$

3. Examples of Faraday-Modulation Spectroscopy

Recent development : open-shell molecular ions

LMR in discharge systems





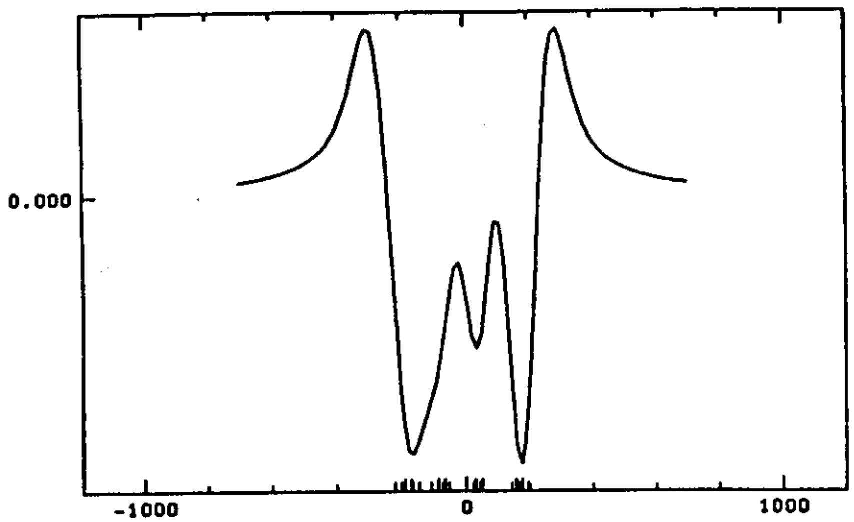
$D^{35}Cl^+$ $X\ ^2\Pi_{3/2}$ Q (1.5) $v = 1 \leftarrow 0$

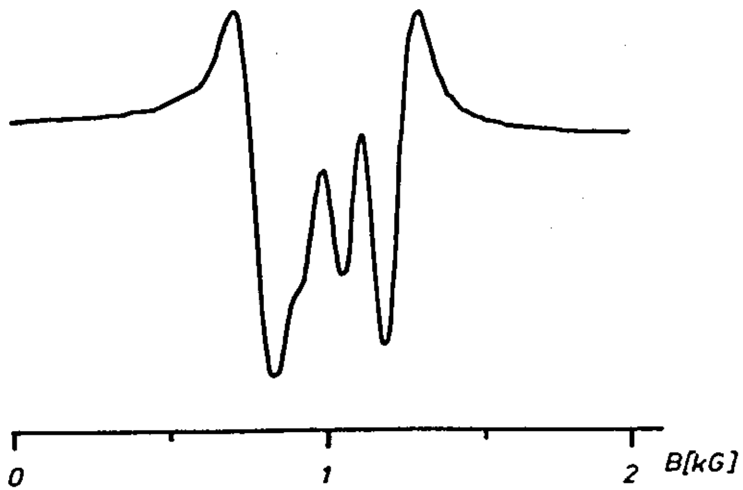
(single pass)

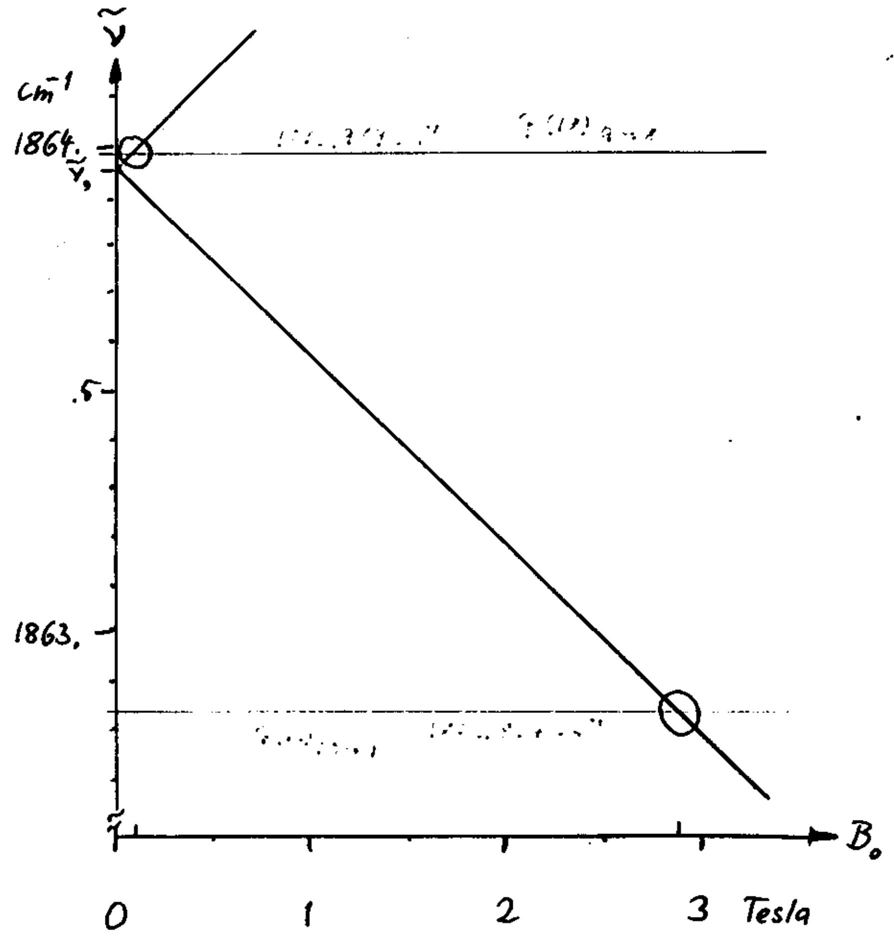
CO P(18)

.1817 cm^{-1}

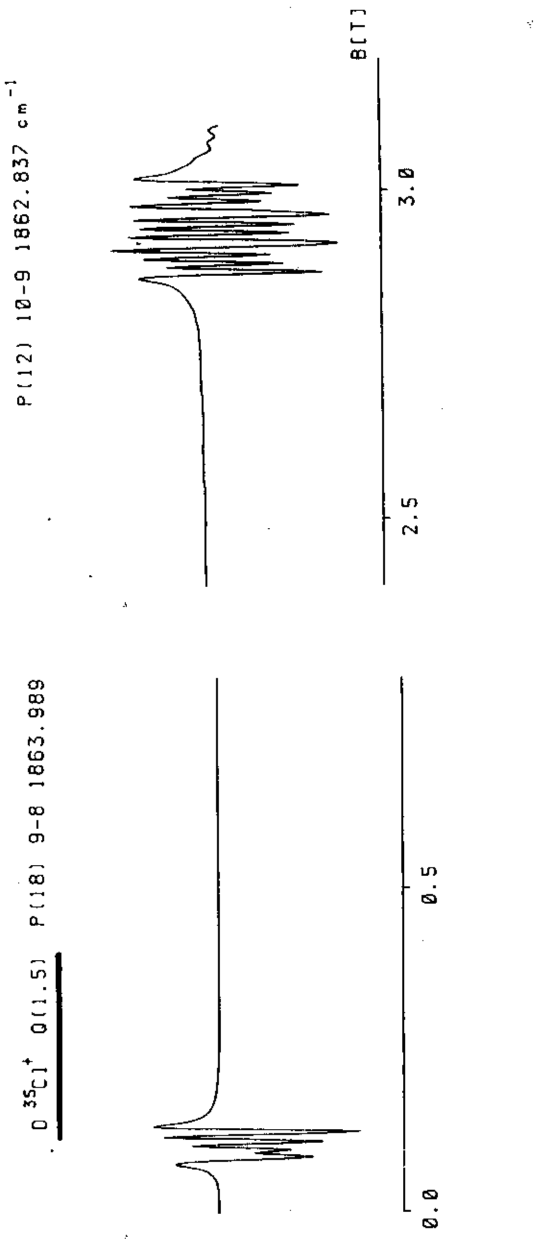
$D^{35}Cl^+$ Q(1.5) ZR P(18) 9 - 8
1863.98968 cm^{-1}

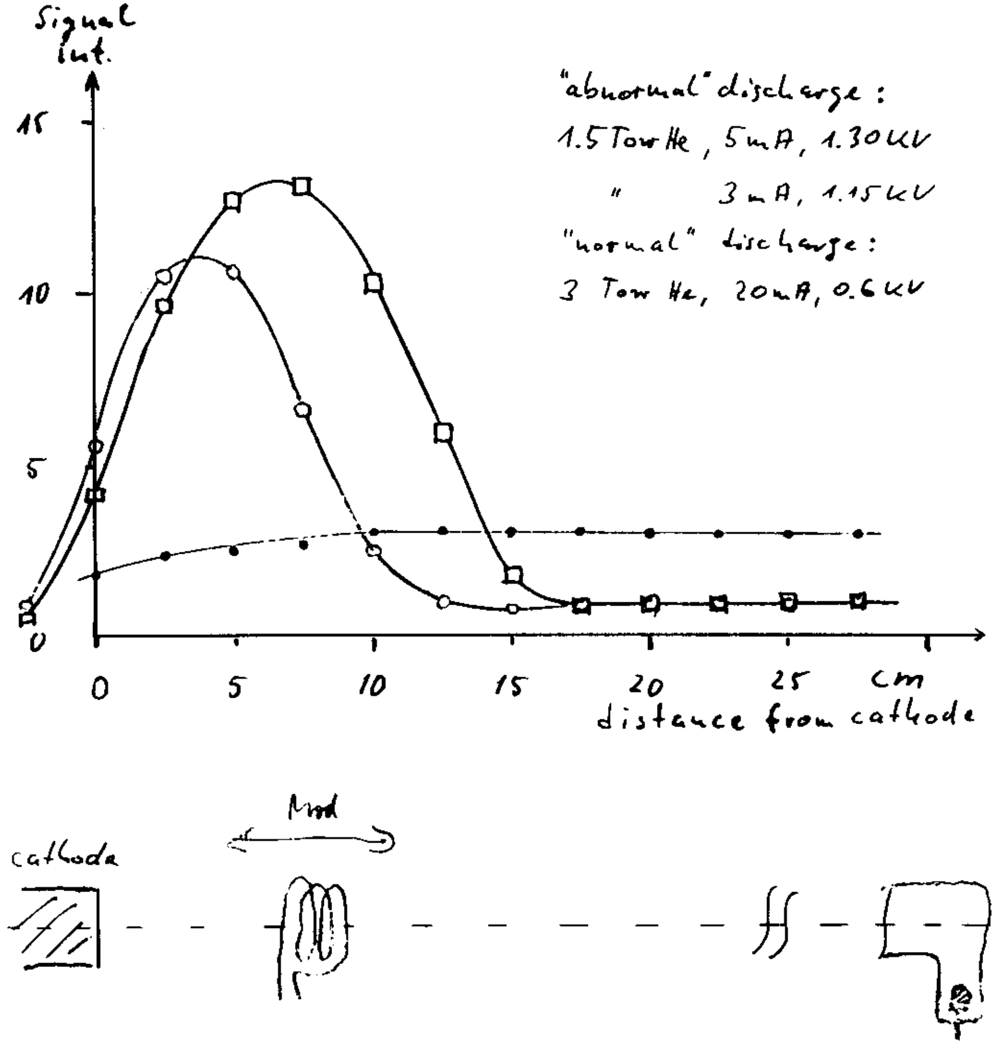


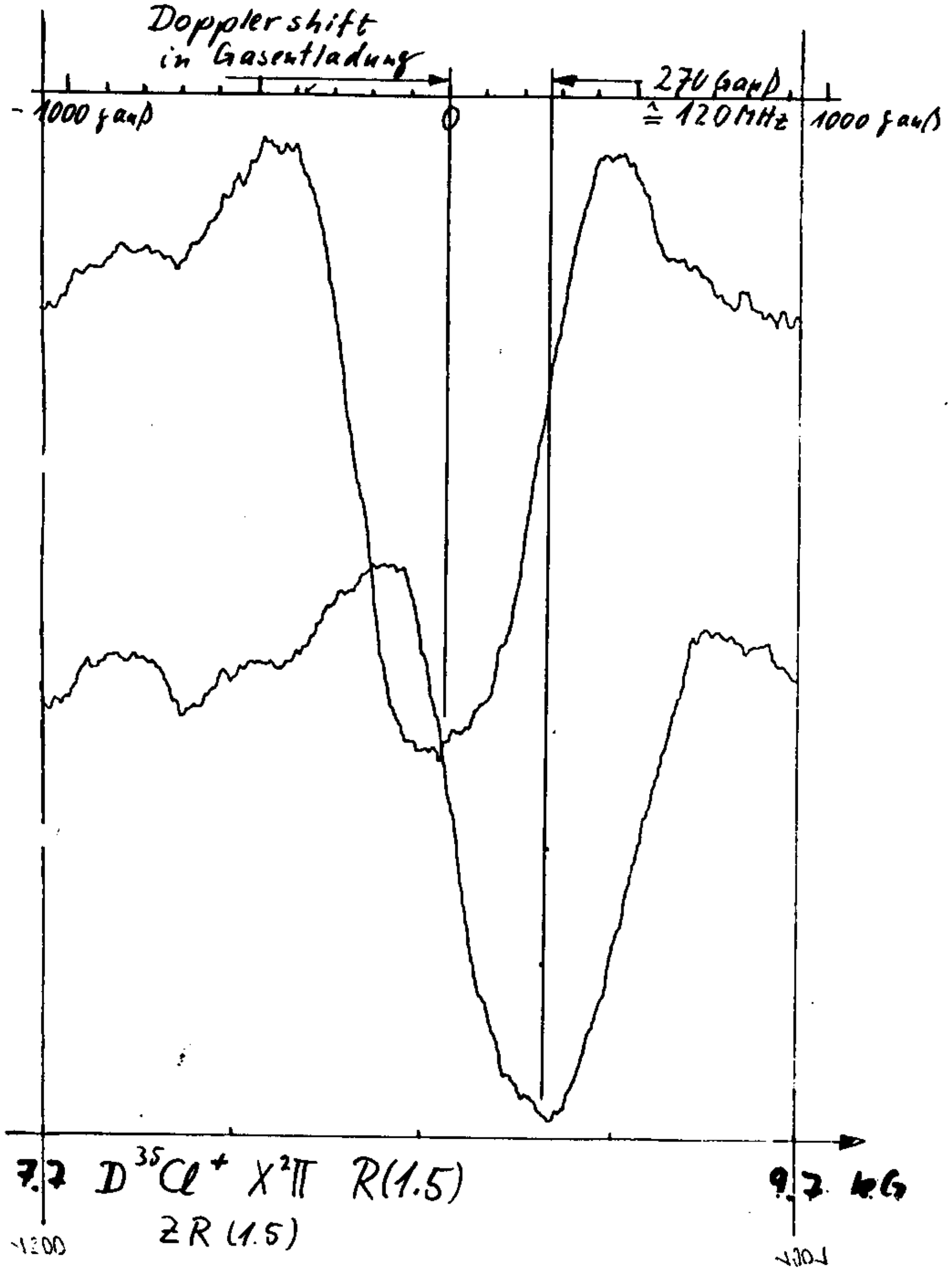


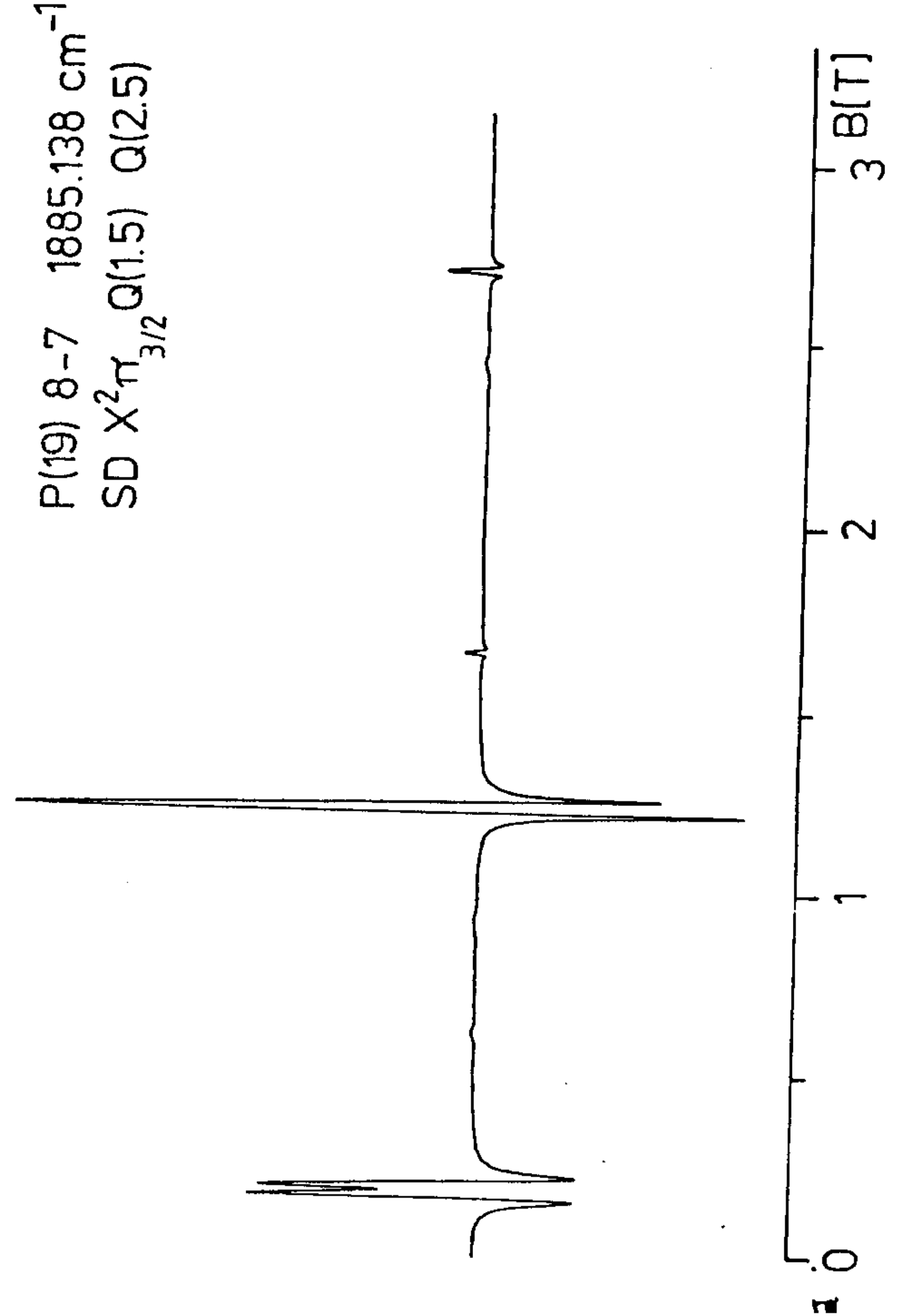


LMR - Observation of DCl^+
$X\ ^2\Pi_{3/2}$ Q(1.5) $v = 1 \leftarrow 0$


P(12) 10-9 1862.837 cm^{-1}
B[T]
3.0
2.5
D ^{35}Cl^{+} Q(1.5) P(18) 9-8 1863.989
0.5
0.0


Signal Int.
15
10
5
0
"abnormal" discharge:
1.5 Torr He, 5 mA, 1.30 kV
" 3 mA, 1.15 kV
"normal" discharge:
3 Torr He, 20 mA, 0.6 kV
0
5
10
15
20
25
cm
distance from cathode
Mod
cathode


Dopplershift in Gasentladung
-1000 Gauß
0
270 Gauß ≙ 120 MHz
1000 Gauß
7.7 D 35Cl+ X2Π R(1.5)
9.7 kG
2R(1.5)


P(19) 8-7 1885.138 cm-1
SD X2Π3/2 Q(1.5) Q(2.5)
B[T]
0
1
2
3

Publications on IR-Laser Spectroscopy

Continuously tunable lasers, (mainly CCL)

(1) Appl. Phys. 17, 325-330 (1978) W. Urban, W. Herrmann

(2) Appl. Phys. B26, 173-177 (1981) J. Pfeiffer, D. Kirsten, P. Kalkert, W. Urban

(3) Appl. Phys. B36, 179-185 (1984) H. Adams, D. Reinert, P. Kalkert, W. Urban

J. Opt. Soc. Am. (1985) in press
Special issue on tunable lasers
H. Adams, R. Brüggemann, D. Kirsten, H. Solka, W. Urban

Laser magnetic resonance (conventional type, CO-laser)

(4) Appl. Phys. B 31, 139-144 (1983) W. Rohrbeck, A. Hinz, P. Nelle, M.A. Gondal, W. Urban

(5) J. Molec. Spectrosc. 100, 290-302 (1983) M.A. Gondal, W. Rohrbeck, W. Urban, R. Blanchard, J.M. Brown

Laser magnetic resonance (Faraday-LMR)

(6) Molec. Phys. 45, 1131-1139 (1982) A. Hinz, J. Pfeiffer, W. Bohle, W. Urban

(7) Appl. Phys. B 36, 1-4 (1985) A. Hinz, D. Zeitz, W. Bohle, W. Urban

(8) Molec. Phys. 53, 1017-1021 (1984) A. Hinz, W. Bohle, D. Zeitz, J. Werner, W. Seebass, W. Urban

(9) Molec. Phys. 54, (1985) in press D. Zeitz, W. Bohle, J. Werner, A. Hinz, W. Urban

CO-Laser

Appl. Phys. B 26, 73-76 (1981) T.K. Lin, W. Rohrbeck, W. Urban