
The Departmental Graduate Center NAT offers this lecture:

Course “Practical IR and Raman spectroscopy”

by Prof. Dr. Janos Mink (Hungarian Academy of Science, Budapest)

Course Dates: October 11 – October 27 2023
Location: Lecture hall 21019, Time: 9:00 am-12:00pm
Lectures 3h per day (upon negotiation on the first day), practical demonstrations and exam (to test your gained knowledge).

Highlights:

- **Determine how local symmetry in your molecule influences the pattern in your spectrum**
- **Learn how IR and Raman spectrometers work and how you can use them efficiently**
- **Valuable contribution of Dr. N.P. Ivleva about “Vibrational Spectroscopy in Analytical Chemistry: Focus on Applicability of Raman Microspectroscopy”**
- **Interpret your spectrum for common (mostly organic) compounds**

Everybody (master student, doctorate student, postdocs) is cordially invited.

Dr. Markus Drees

Practical Infrared and Raman Spectroscopy

Content: **2**

Introduction 6

1. Vibrational and rotational transitions of molecules. 8

1.1. Molecular rotation of diatomic molecules. 9

1.2. Molecular rotation-vibration of diatomic molecules 16

1.3. Rotation of linear polyatomic molecules. 19

1.4. Rotation-vibration of linear molecules 21

1.5. Rotation-vibration of symmetric-top molecules 24

1.6. Rotation-vibration of spherical-top molecules 25

1.7. Rotation and rotation- vibration of asymmetric-top mol. 27

1.8. Vibrations of diatomic molecules 30

2. Basic experimental methods in vibrational spectroscopy 33

2.1. Mid and far infrared spectroscopy. 36

Interferometry 36

Michelson interferometer 38

Principles of interference 39

2.2. Basic components and specialities of FTIR spectrometers. 47

1 .Sources 47

2. Beamsplitter 49

3. Detectors 51

4. Role of the He-Ne laser 56

5. Dynamic alignment 57

6. Resolution 59

7. Spectrometer performance influencing the throughput 61

2.3. UV-Visible Fourier spectroscopy. 65

2.4. Far-infrared (FIR) spectroscopy 67
Basic components of FIR spectrometers 68
1. Sources 68
2. Beamsplitters 71
3. Detectors 74
Critical point of FIR spectrometry 75

2.5. Calibration of FTIR spectrometers. 74
2.5.1. Calibration of FT-MIR spectrometers 78
2.5.2. Calibration of FT-FIR spectrometers 82

2.6. Sampling techniques for mid-IR spectroscopy 87
Window materials 87
a) Gas cells 90
b) Liquid cells 92
c) Solutions 93
d) Cast films 95
e) Mulls and pellets 97

2.7. Basic sampling methods for far infrared. 100
a.) Window materials for cells1 100
b.) Sampling techniques 103

2.8. Special (new) accessories. 105
Specular reflection (SR) 105
Internal reflection (Attenuated Total Reflection, ATR) 109
Micro ATR accessories 113
Reflection-absorption infrared spectroscopy (RAIRS) 118
Diffuse reflectance infrared spectroscopy (DRIFT) 121
PAS (Photoacoustic spectroscopy) 123
Variable temperature IR measurements 126

Matrix isolation spectroscopy 127

3. Raman Spectroscopy 129
Developments 130
Background 131
The Raman Effect 131
Raman scattering of simple homonuclear diatomic Molecules 132
Fluorescence problems 136
Classical theory of Raman Effect, molecular polarisation 138
Polarization of Raman scattering 140
Measurements of depolarization ratios 141
Vibrational Raman spectra 145
Examples 147
Selection rules contrasting IR and Raman spectra 150
Examples for structural determination 154
Lasers for Raman spectroscopy 156
Detectors for Raman spectroscopy 162
3.1. Dispersive single detector systems 165
3.2. Multichannel dispersive spectrometers 169
3.3. Fourier transform Raman spectrometers 171
3.4. Basic sampling techniques. 176
3.5. Laboratory Raman spectroscopy 180
3.6. Calibration of Raman spectrometers 183
3.7. Fermi resonance 185

4. Symmetry of molecules and molecular vibrations 189
Symmetry 190
Point groups 193
Character tables 196
Examples for determination of point groups 198
4.1. Point group analysis of vibrations using Adams-Newton tables 205

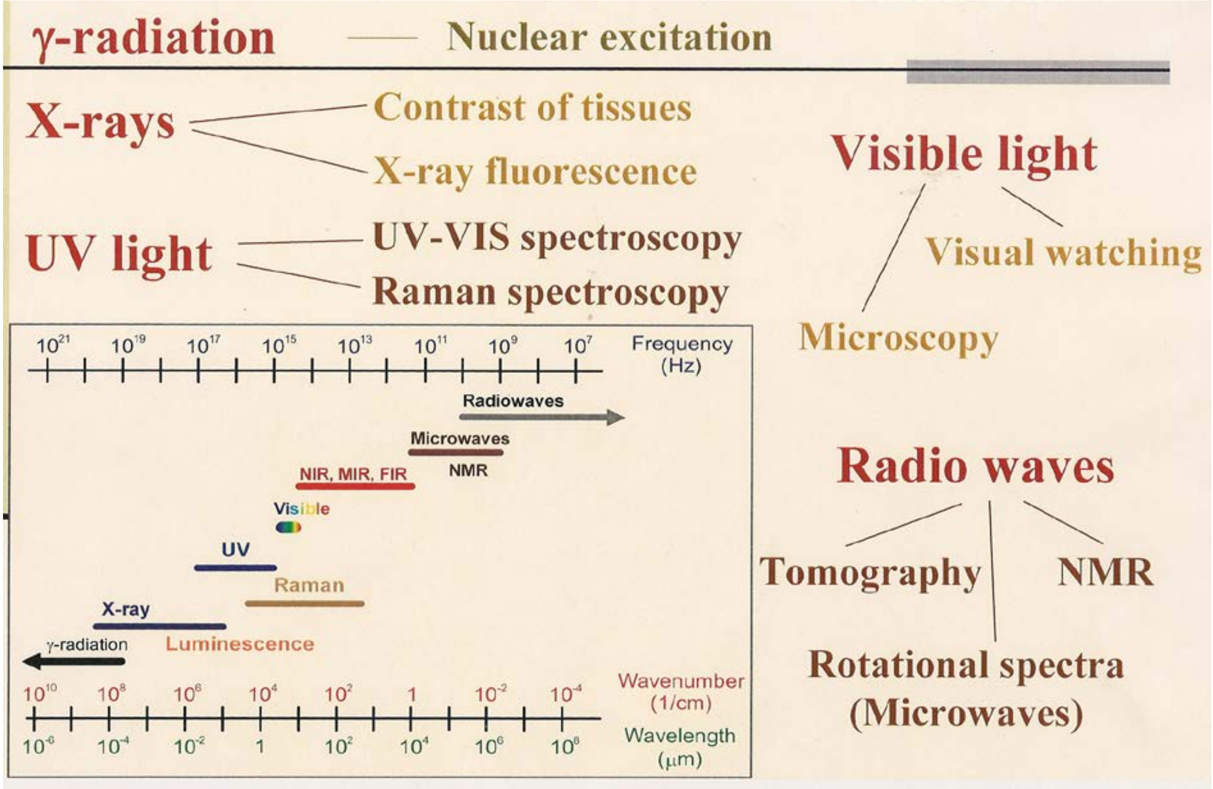
Examples for point group analysis 212
Short summary 214
Point group analysis generally used in literature 218

5. Interpretation and assignment of IR and Raman spectra 221

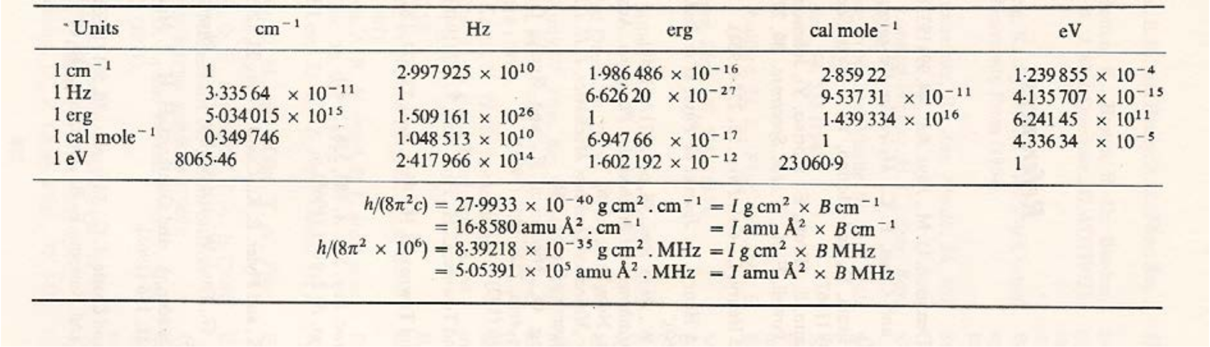
5.1. Basic ideas of theory of vibrations 221
5.1.1. Normal coordinates and normal frequencies 225
5.1.2. Internal Coordinates 228
5.1.3. Normal Coordinates 233
5.1.4. Calculation and characterisations of the kinetic energy matrix 236
5.2 Principles of the origin of group frequencies 244
5.3 Group frequencies of organic molecules 248
5.3.1 Hydrocarbons 248
Aliphatic hydrocarbons 248
Alkenes 262
5.3.2. Benzene and its derivatives. 272
5.3.3. Oxygen containing compounds. 286
Ethers 286
Alcohols, phenols 292
Carbonyl compounds 300
Aldehydes 304
Carboxylic acids, anhydrides, esters 309
Anhydrides 323
Esters 326
Ketones 332
5.3.4. Nitrogen containing compounds. 340
Amines 340
Amines, C=N and N=O compounds 345
Cyanides, isonitriles 347
Organic nitro compounds 353
5.3.5. Amino acids, ureas, carbamates. 355
Ureas 361

INTRODUCTION

Regions of electromagnetic radiation (light)


γ-radiation — Nuclear excitation
X-rays
Contrast of tissues
X-ray fluorescence
UV light
UV-VIS spectroscopy
Raman spectroscopy
Visible light
Visual watching
Microscopy
Radio waves
Tomography
NMR
Rotational spectra (Microwaves)
10^21 10^19 10^17 10^15 10^13 10^11 10^9 10^7
Frequency (Hz)
Radiowaves
Microwaves
NMR
NIR, MIR, FIR
Visible
UV
Raman
X-ray
γ-radiation
Luminescence
10^10 10^8 10^6 10^4 10^2 1 10^-2 10^-4
Wavenumber (1/cm)
10^-6 10^-4 10^-2 1 10^2 10^4 10^6 10^8
Wavelength (μm)

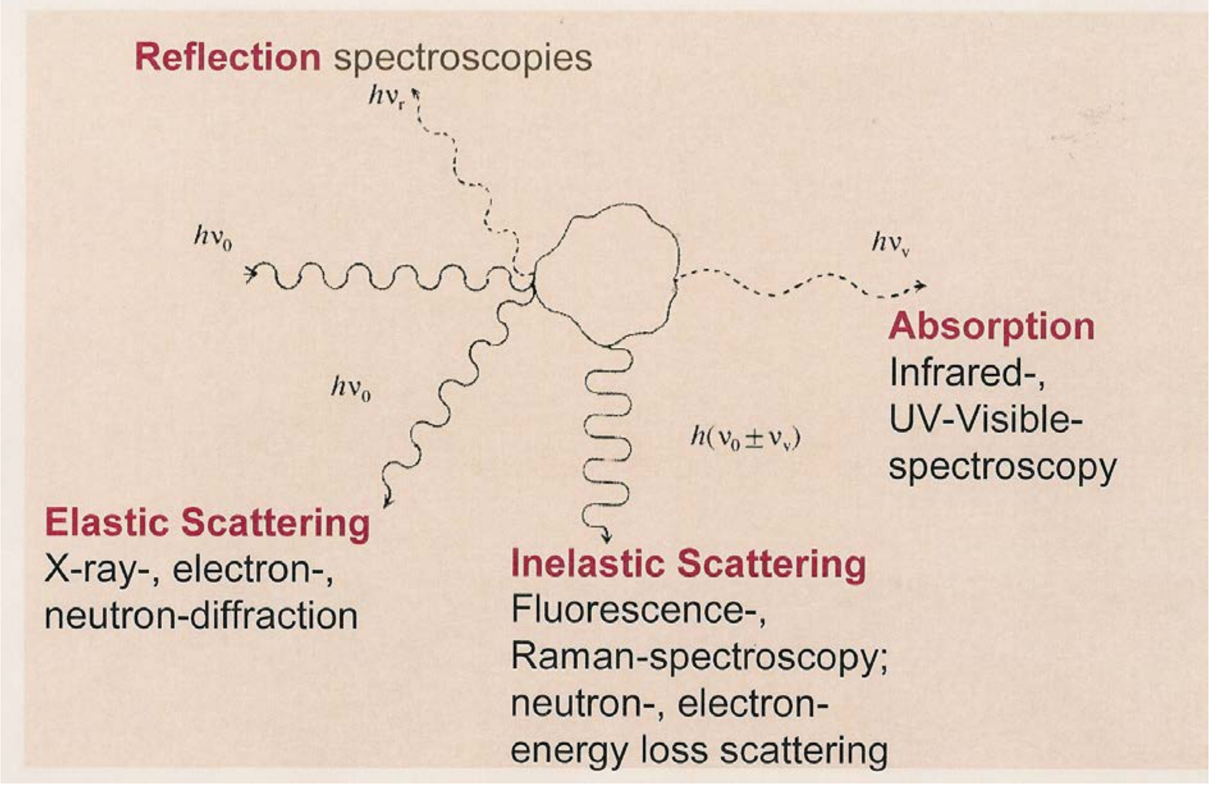
Conversion factors



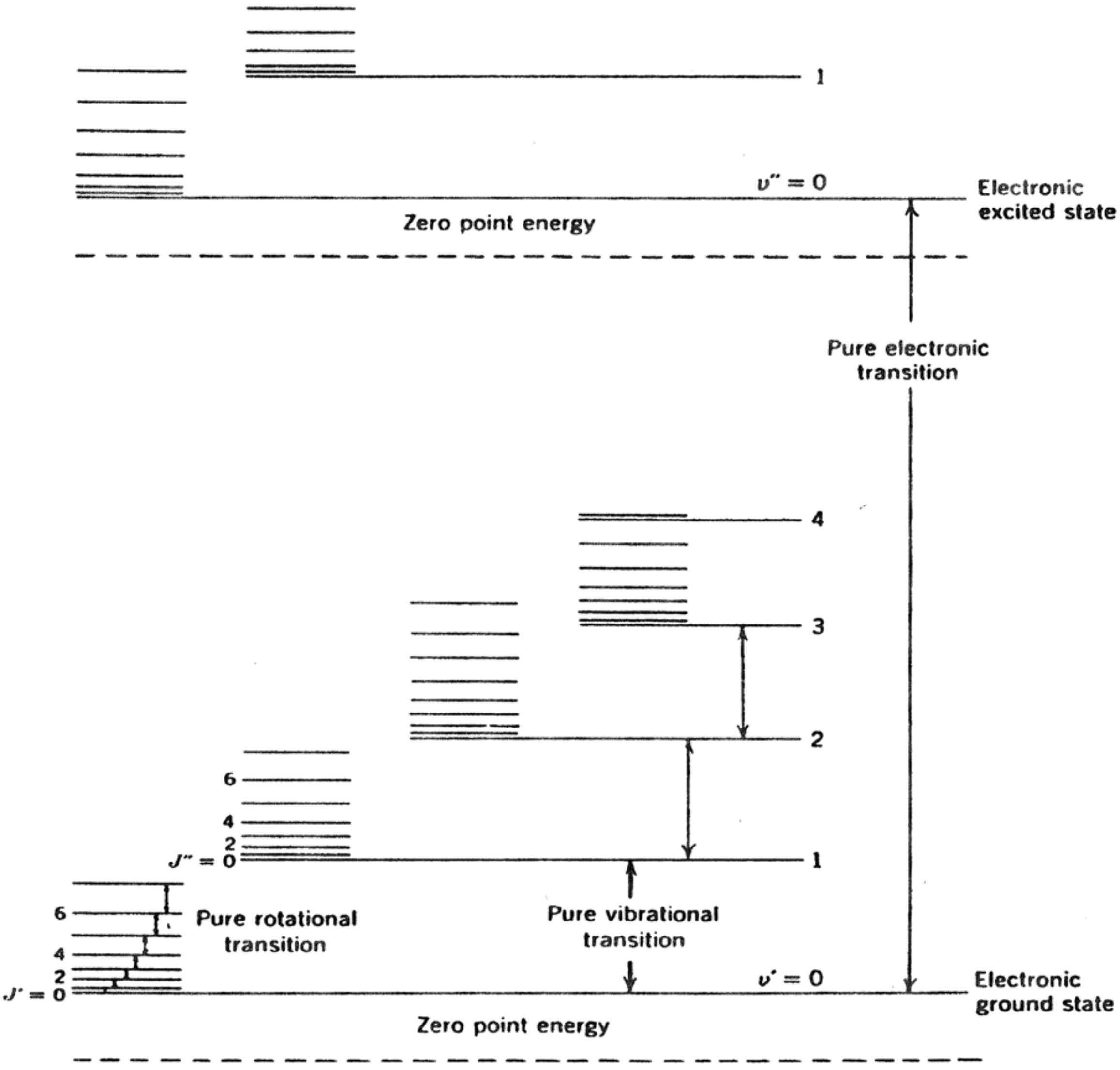
Units	cm^{-1}	Hz	erg	cal $mole^{-1}$	eV
1 cm^{-1}	1	$2{\cdot}997\,925 \times 10^{10}$	$1{\cdot}986\,486 \times 10^{-16}$	$2{\cdot}859\,22$	$1{\cdot}239\,855 \times 10^{-4}$
1 Hz	$3{\cdot}335\,64 \times 10^{-11}$	1	$6{\cdot}626\,20 \times 10^{-27}$	$9{\cdot}537\,31 \times 10^{-11}$	$4{\cdot}135\,707 \times 10^{-15}$
1 erg	$5{\cdot}034\,015 \times 10^{15}$	$1{\cdot}509\,161 \times 10^{26}$	1	$1{\cdot}439\,334 \times 10^{16}$	$6{\cdot}241\,45 \times 10^{11}$
1 cal $mole^{-1}$	$0{\cdot}349\,746$	$1{\cdot}048\,513 \times 10^{10}$	$6{\cdot}947\,66 \times 10^{-17}$	1	$4{\cdot}336\,34 \times 10^{-5}$
1 eV	$8065{\cdot}46$	$2{\cdot}417\,966 \times 10^{14}$	$1{\cdot}602\,192 \times 10^{-12}$	$23\,060{\cdot}9$	1

$$\begin{aligned} h/(8\pi^2 c) &= 27{\cdot}9933 \times 10^{-40}\ \mathrm{g\,cm^2\,.\,cm^{-1}} = I\ \mathrm{g\,cm^2} \times B\ \mathrm{cm^{-1}} \\ &= 16{\cdot}8580\ \mathrm{amu\,Å^2\,.\,cm^{-1}} = I\ \mathrm{amu\,Å^2} \times B\ \mathrm{cm^{-1}} \\ h/(8\pi^2 \times 10^6) &= 8{\cdot}39218 \times 10^{-35}\ \mathrm{g\,cm^2\,.\,MHz} = I\ \mathrm{g\,cm^2} \times B\ \mathrm{MHz} \\ &= 5{\cdot}05391 \times 10^5\ \mathrm{amu\,Å^2\,.\,MHz} = I\ \mathrm{amu\,Å^2} \times B\ \mathrm{MHz} \end{aligned}$$

Basic interactions between matter and electromagnetic radiation

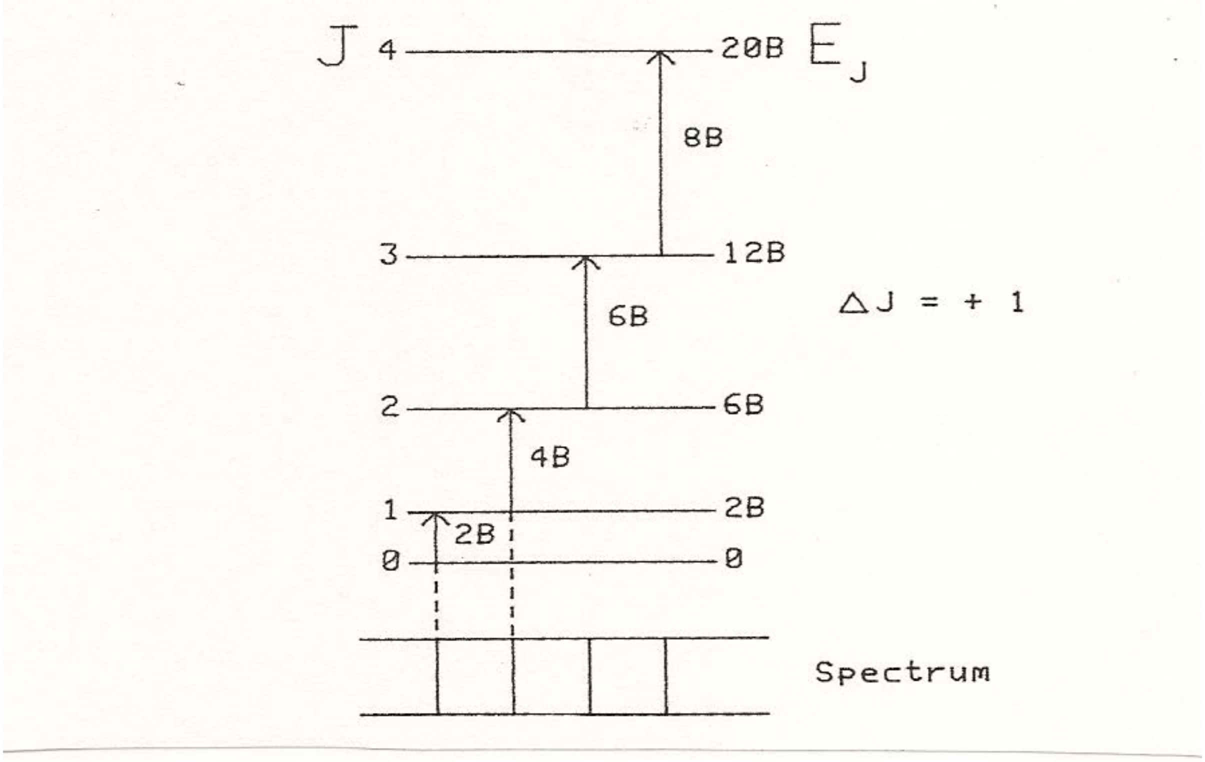

Reflection spectroscopies
$h\nu_r$
$h\nu_0$
$h\nu_v$
Absorption
Infrared-,
UV-Visible-
spectroscopy
$h\nu_0$
$h(\nu_0 \pm \nu_v)$
Elastic Scattering
X-ray-, electron-,
neutron-diffraction
Inelastic Scattering
Fluorescence-,
Raman-spectroscopy;
neutron-, electron-
energy loss scattering

1. Vibrational and rotational transitions of molecules


1
υ″ = 0
Electronic excited state
Zero point energy
Pure electronic transition
4
3
2
6
4
2
J″ = 0
1
6
4
2
J′ = 0
Pure rotational transition
Pure vibrational transition
υ′ = 0
Electronic ground state
Zero point energy

Energy level of a diatomic molecule (the actual spacings of electronic levels are much larger, and those of rotational levels are much smaller, than that shown in the figure).

1.1. Molecular rotation of diatomic molecules


J
4
3
2
1
0
20B
12B
6B
2B
0
E_J
8B
6B
4B
2B
ΔJ = + 1
Spectrum

Rotational transition for the rigid rotor

Permanent dipole moment: FIR absorption

QUANTUM THEORY

Selection rule: $\Delta J = +1$ **(absorption)**

$\Delta J = -1$ **(emission)**

Rotational energy: $E_{rot}/hc = BJ(J+1)\ (\mathrm{cm}^{-1})$

Where: $B = h/8\pi^2 cI$ *(rotational constant)*

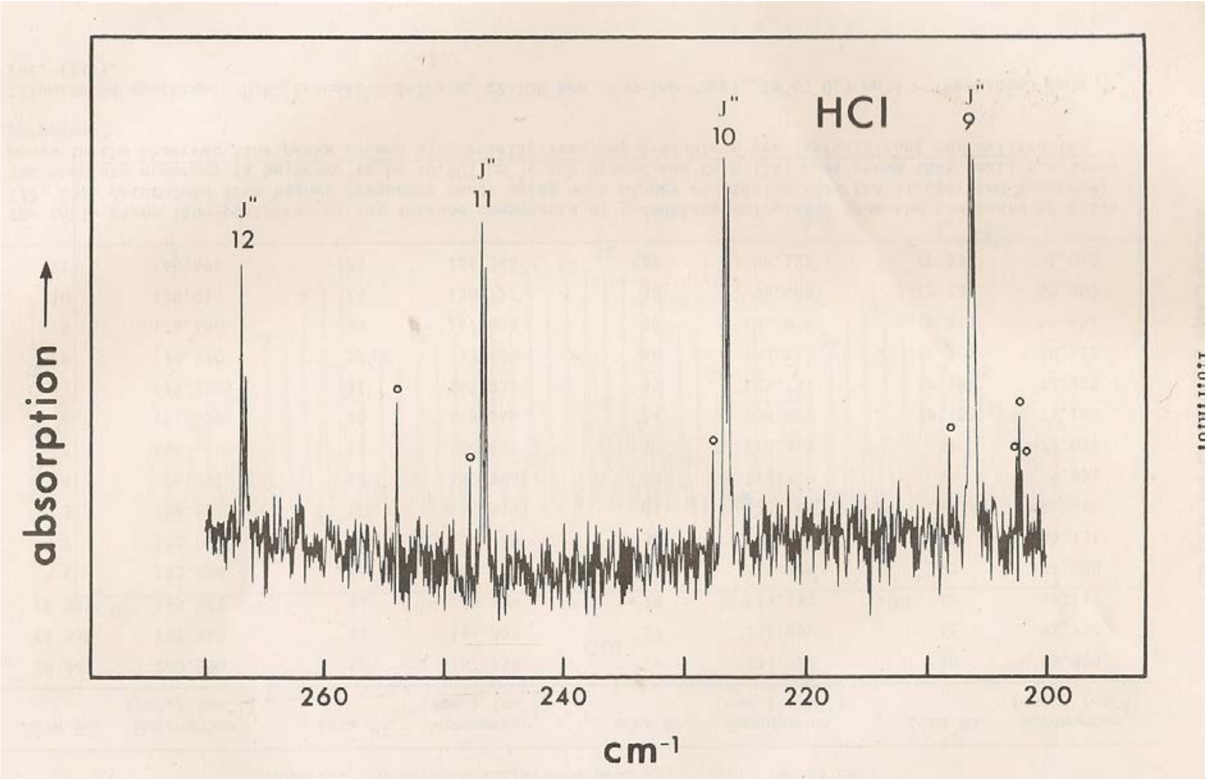
$B = 16.85804/I\ (\mathrm{cm}^{-1})$

Where: $I = \mu r^2 = (m_1 m_2/m_1+m_2)\, r^2$ ***(moment of inertia)***

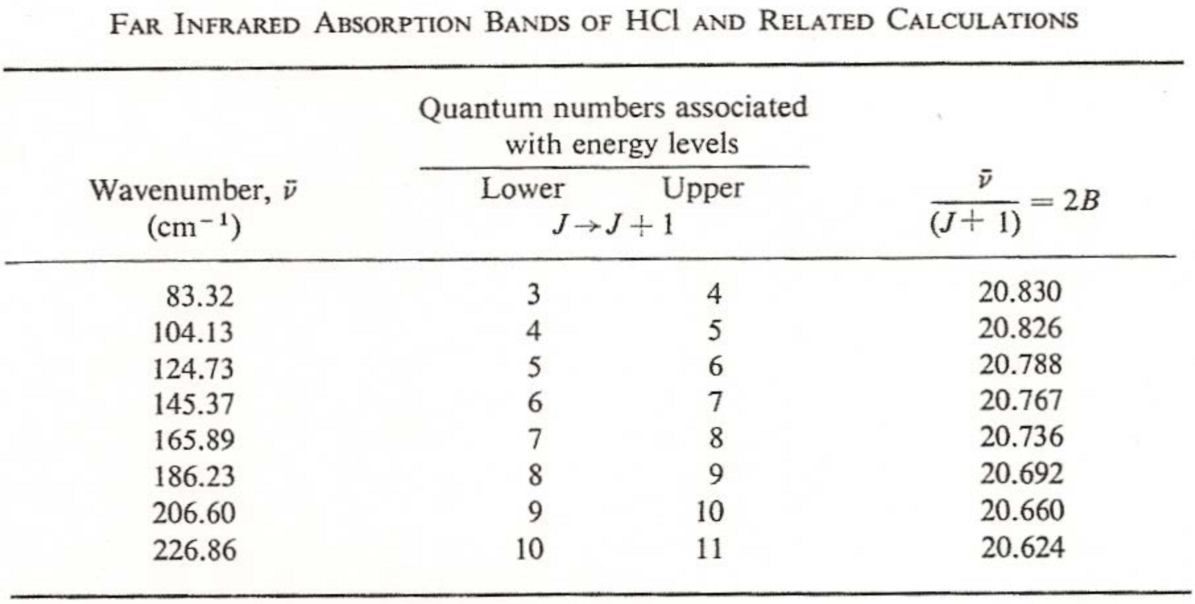
(μ-reduced mass, m_1 and m_2 - atomic weights and r- bond distance in Å)

Considering transition $\Delta J = +1$ e.g from *J* level to *J+1* level:

$$E(J+1) - E(J) = B(J+1)(J+2) - BJ(J+1) = 2B(J+1) = \nu$$



Pure rotational spectrum of HCl (Resolution 0.12cm^{-1}, 3 m path length and 12 Torr pressure)



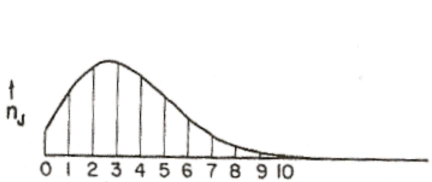
FAR INFRARED ABSORPTION BANDS OF HCl AND RELATED CALCULATIONS

Wavenumber, $\bar{\nu}$ (cm^{-1})	Quantum numbers associated with energy levels Lower	 Upper	$\frac{\bar{\nu}}{(J+1)} = 2B$
	$J \rightarrow$	$J+1$	
83.32	3	4	20.830
104.13	4	5	20.826
124.73	5	6	20.788
145.37	6	7	20.767
165.89	7	8	20.736
186.23	8	9	20.692
206.60	9	10	20.660
226.86	10	11	20.624

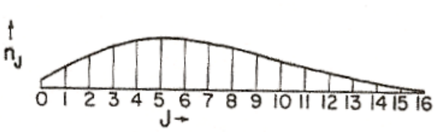
(For H^{35}Cl: B= 10.44023 and D= 0.00052 cm^{-1}, r_0=1.28387Å)

Rotational line intensities

$$J_{\max} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2}$$



HCl 300°K



HCl 1000°K

Rotational transition for the non-rigid rotors

QUANTUM THEORY

Selection rule: $\Delta J = +1$ (absorption)
$\Delta J = -1$ (emission)

Rotational energy: $E_{rot}/hc = BJ(J+1)-DJ^2(J+1)^2$ (cm^{-1})

Where: $B = h/8\pi^2 cI$ (rotational constant), cm^{-1}

D=centrifugal distortion constant, cm^{-1}

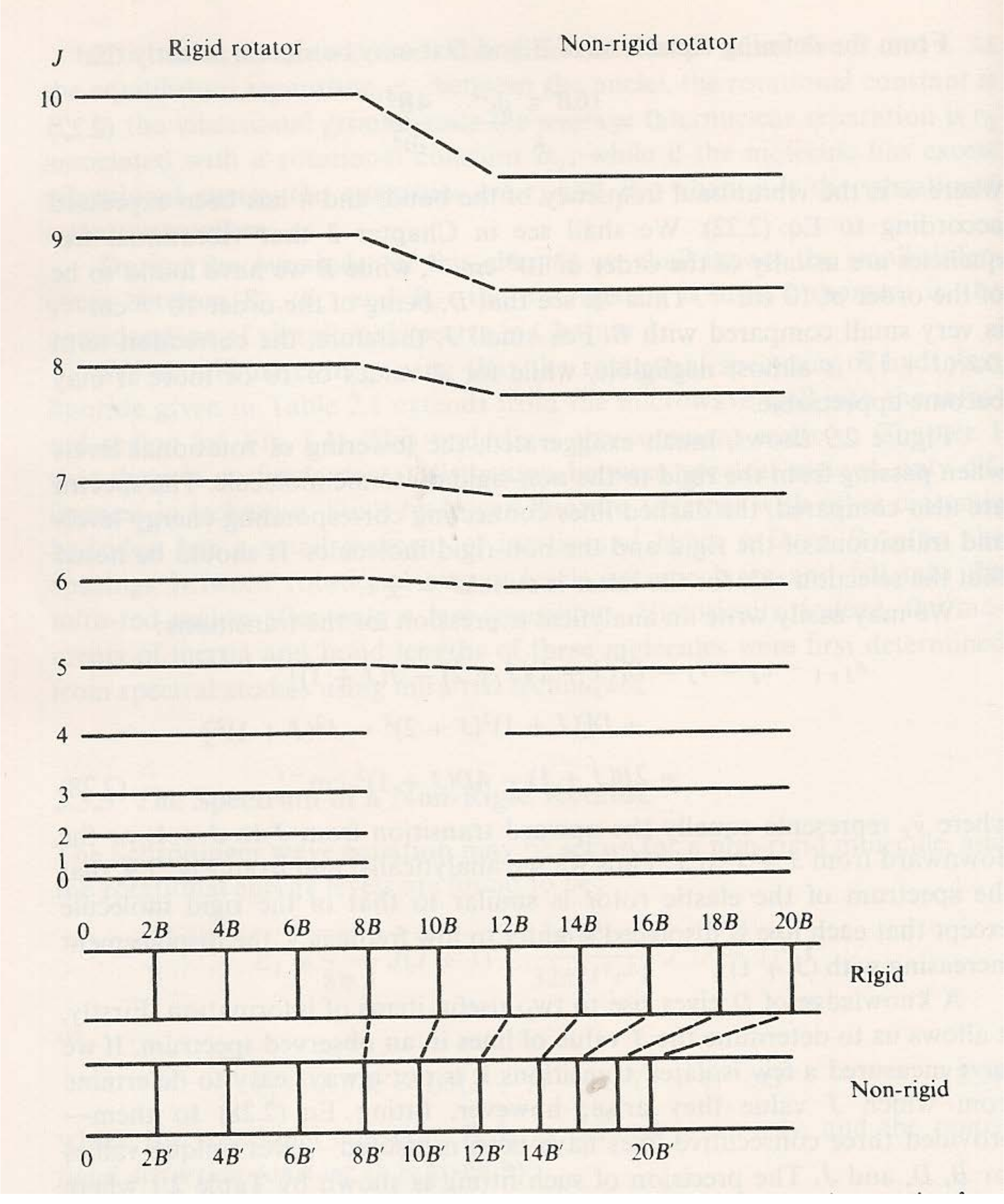
Considering transition $\Delta J = +1$ e.g from J level to $J+1$ level:

$v = E(J+1) - E(J) = 2B(J+1) - 4D(J+1)^3$ (cm^{-1})
From the defining equations of B and D it may be shown directly that

$D = 1/k(16B^3\pi^2\mu c^2) = 4B^3/\omega^2$

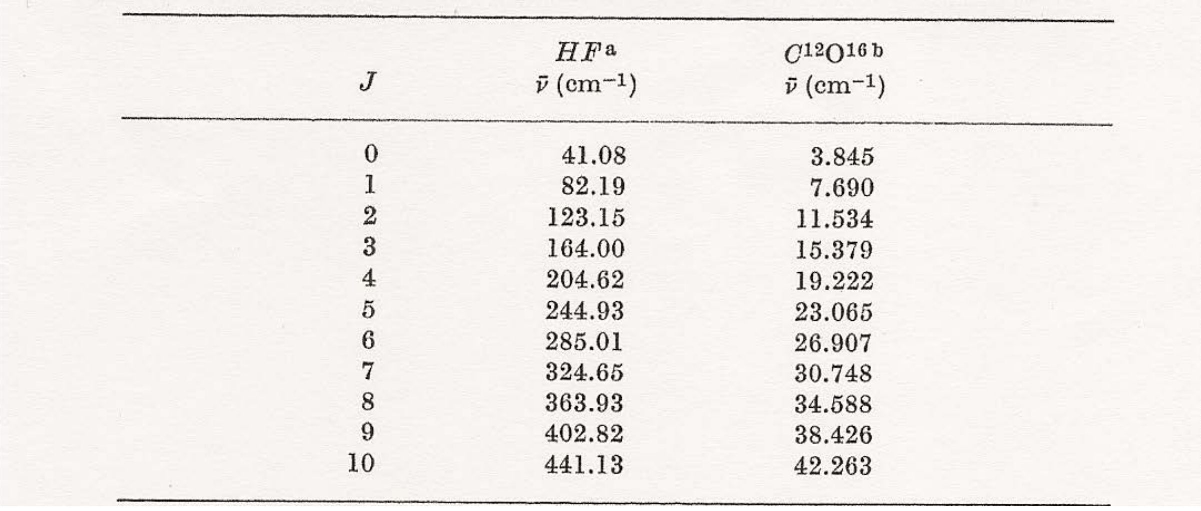
Where k is the force constant, μ is the reduced mass and ω is the harmonic stretching frequency.
Rotational spectrum of HF can be fitted by expression:

$v = 41.122(J+1) - 8.52\times10^{-3}(J+1)^3$ (cm^{-1})


J
Rigid rotator
Non-rigid rotator
10
9
8
7
6
5
4
3
2
1
0
0 2B 4B 6B 8B 10B 12B 14B 16B 18B 20B
Rigid
Non-rigid
0 2B′ 4B′ 6B′ 8B′ 10B′ 12B′ 14B′ 20B′

The change in rotational levels and rotational spectrum are shown when passing from rigid to non-rigid diatomic molecule. Levels on the right calculated using $D=10^{-3}B$

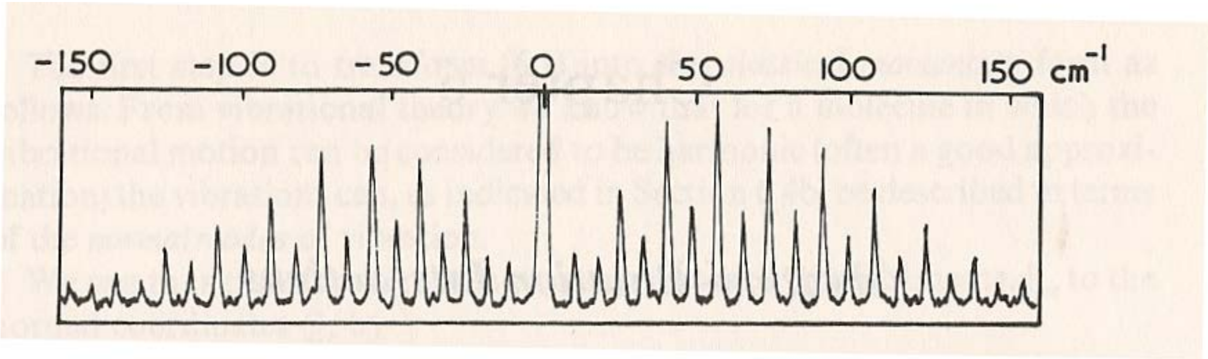
Pure rotational IR lines of HF and CO



J	HF^a $\tilde{\nu}$ (cm^{-1})	$C^{12}O^{16\,b}$ $\tilde{\nu}$ (cm^{-1})
0	41.08	3.845
1	82.19	7.690
2	123.15	11.534
3	164.00	15.379
4	204.62	19.222
5	244.93	23.065
6	285.01	26.907
7	324.65	30.748
8	363.93	34.588
9	402.82	38.426
10	441.13	42.263

(For HF: *B*= 20.555 and *D*= 2.13x10^{-3} cm^{-1}, r_0=0.929Å; for $^{12}C^{16}O$: *B*= 1.92250 and *D*= 6.1x10^{-6} cm^{-1}, r_0=1.1282Å)

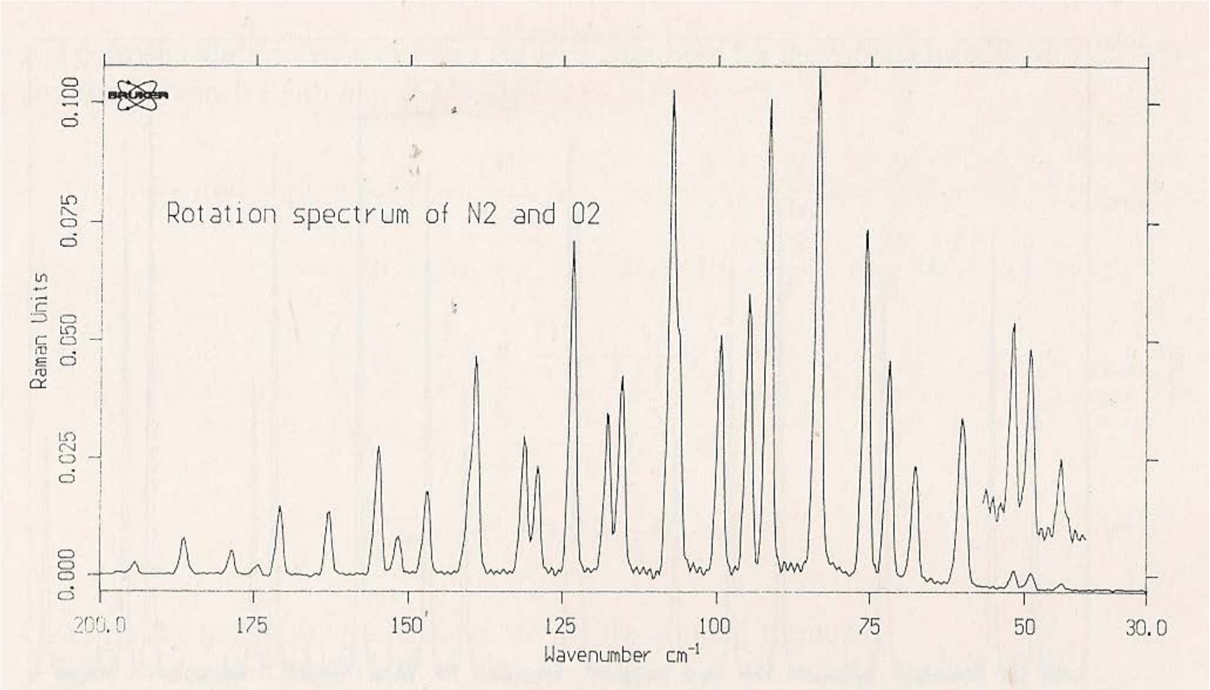
Rotational Raman spectra of diatomic molecules



Pure rotational Raman spectrum of N_2 using 6328 Å He-Ne laser line and photoelectric recording. The 2:1 intensity alteration is due to the spin statistics of the equivalent N atoms (I = 1).

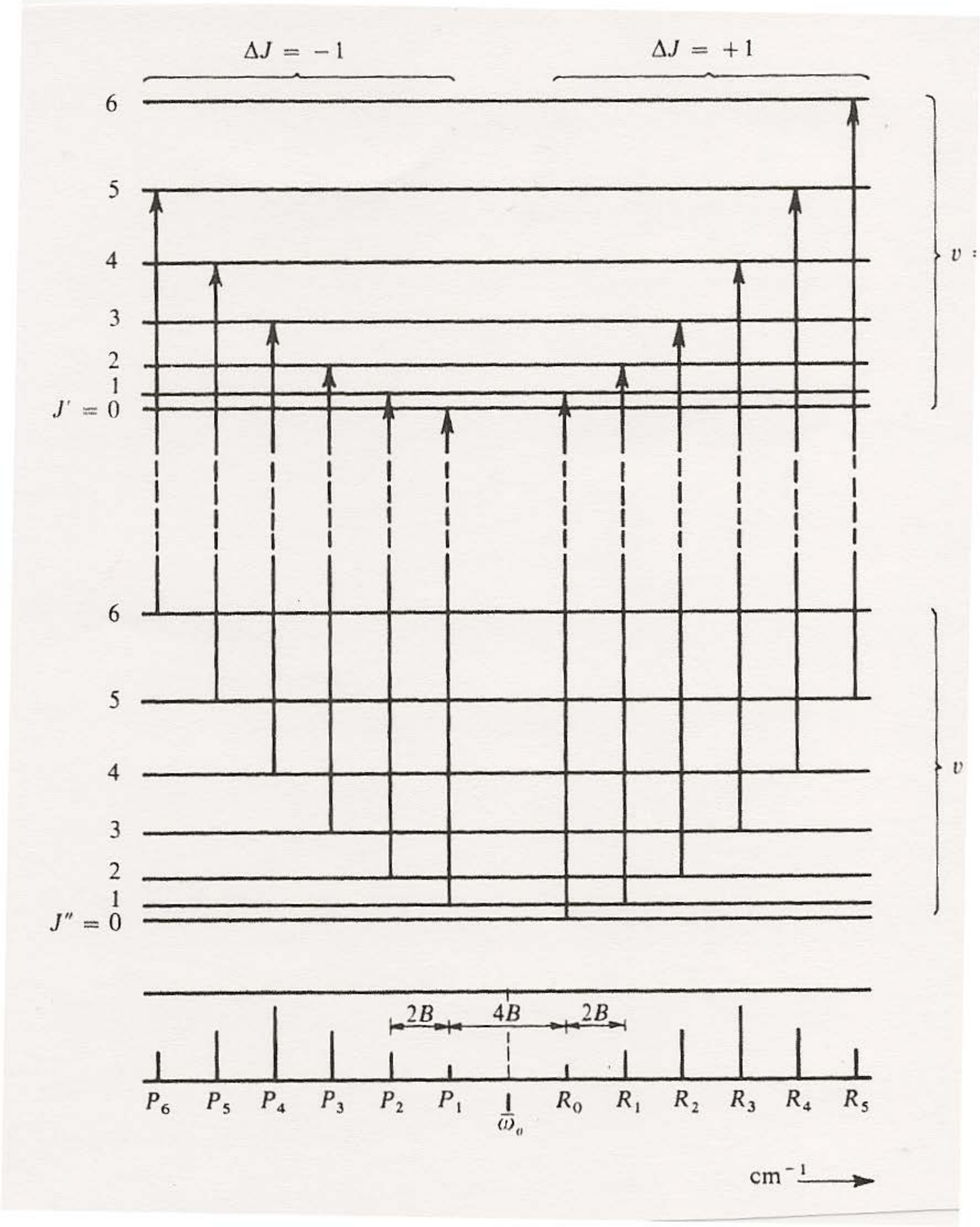
Sellection rule: *!J* = ± 2
Band positions: ν (cm^{-1}) = *4B (J + 3/2)*
Band separation: *4B* cm^{-1}

First line from Rayleigh line is *6B* cm^{-1}
When *J* is even, intensity is twice
N nuclei posses unit spin and therefore follow Bose-Einstein statistic (not Fermi-Dirac)



Pure rotational FT-Raman spectrum of air (N_2 + O_2)

1.2. Rotation-vibration of diatomic molecules


ΔJ = −1
ΔJ = +1
6
5
4
3
2
1
J′ = 0
v
6
5
4
3
2
1
J″ = 0
v
2B
4B
2B
P6
P5
P4
P3
P2
P1
ω0
R0
R1
R2
R3
R4
R5
cm⁻¹

Rotational energy levels and infrared- allowed transitions for the v=0 and 1 levels of a diatomic molecule.

QUANTUM THEORY

The total energy is $E_{r+v}/hc = \nu_0 (v+1/2) + BJ(J+1)$ (cm^{-1})

Substituting v=1 and J= J' for upper state and v=0 and J=J" for ground state yields

$E_{r+v}/hc = \nu_0 + B[J'(J'+1) - J''(J''+1)]$ (cm^{-1})

Inducing or changing of dipole moment: IR absorption

Selection rule: $\Delta J = -1$ (P branch)
$\Delta J = +1$ (R branch)
$\Delta J = 0$ (Q branch forbidden for diatomic molecules, since the only band is "parallel" mode)

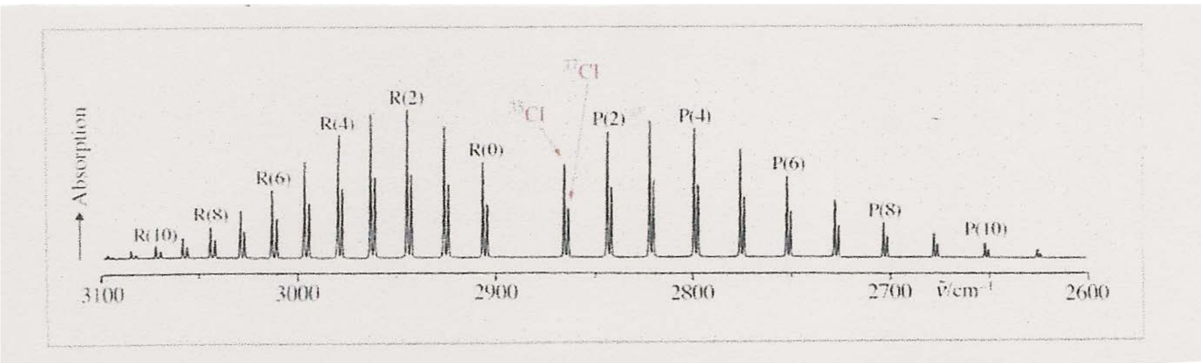
Rotational P branch: $P(cm^{-1}) = \nu_0 - (B_1 + B_0)J + (B_1 - B_0)J^2$
($\Delta J = -1$, $J = 1, 2, 3\ldots$)

Rotational R branch: $R(cm^{-1}) = \nu_0 + 2B_1 + (3B_1 - B_0)J + (B_1 - B_0)J^2$
($\Delta J = +1$, $J = 0, 1, 2, 3\ldots$)

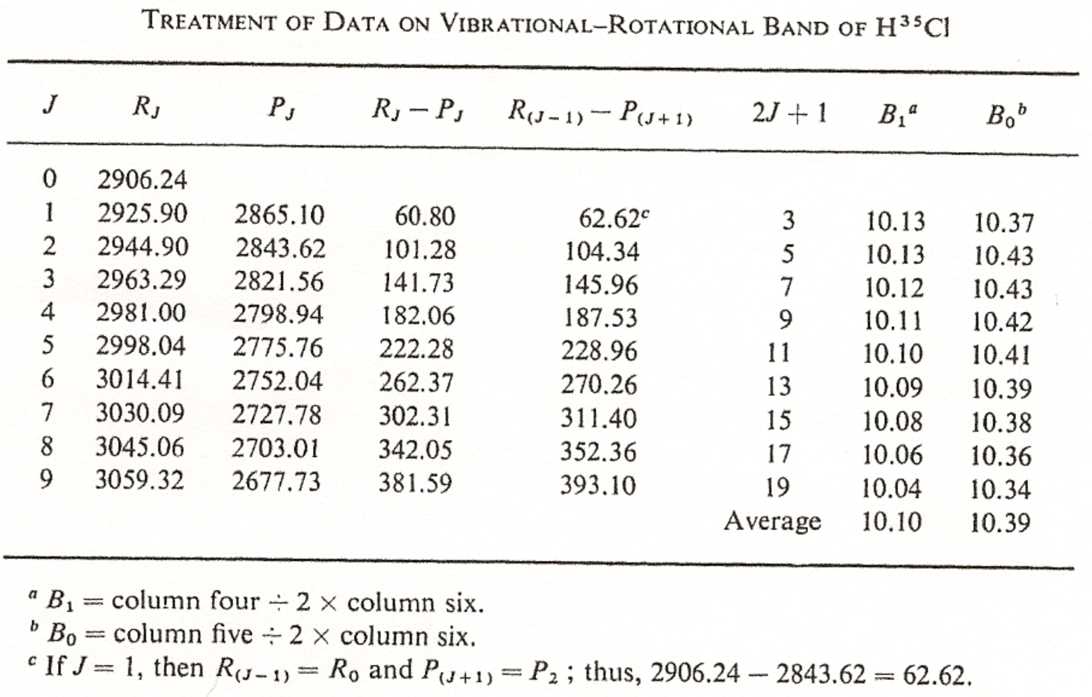
Where: ***B_0 rotational constant at (v=0) ground state***

B_1 rotational constant at v=1 excited state

ν_0 band origin



Rotational fine structure of the v= 1-0 infrared spectrum of HCl



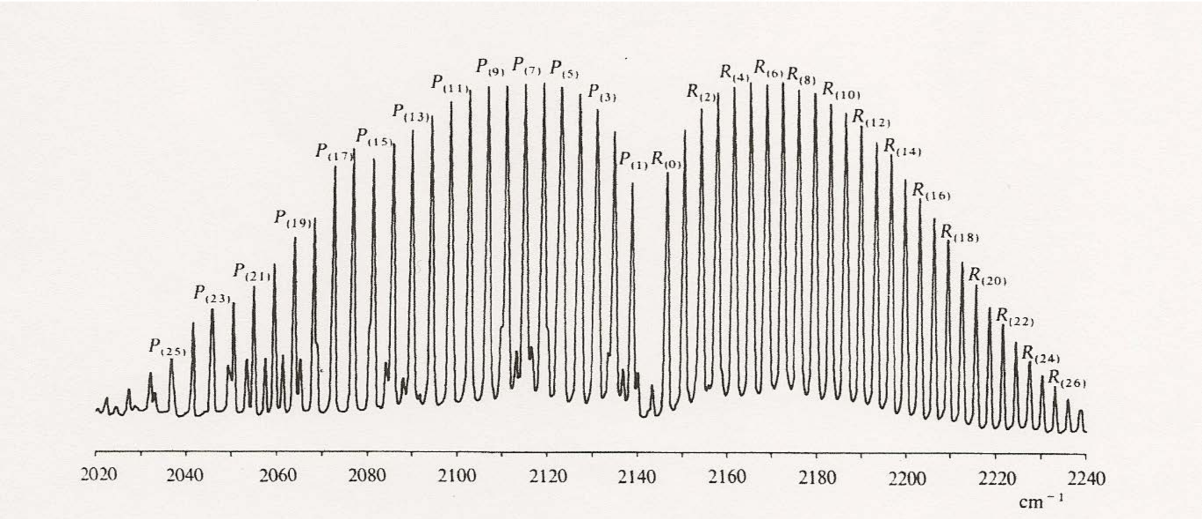
TREATMENT OF DATA ON VIBRATIONAL–ROTATIONAL BAND OF $H^{35}Cl$

J	R_J	P_J	$R_J - P_J$	$R_{(J-1)} - P_{(J+1)}$	$2J+1$	$B_1{}^a$	$B_0{}^b$
0	2906.24						
1	2925.90	2865.10	60.80	62.62^c	3	10.13	10.37
2	2944.90	2843.62	101.28	104.34	5	10.13	10.43
3	2963.29	2821.56	141.73	145.96	7	10.12	10.43
4	2981.00	2798.94	182.06	187.53	9	10.11	10.42
5	2998.04	2775.76	222.28	228.96	11	10.10	10.41
6	3014.41	2752.04	262.37	270.26	13	10.09	10.39
7	3030.09	2727.78	302.31	311.40	15	10.08	10.38
8	3045.06	2703.01	342.05	352.36	17	10.06	10.36
9	3059.32	2677.73	381.59	393.10	19	10.04	10.34
					Average	10.10	10.39

[a] B_1 = column four ÷ 2 × column six.

[b] B_0 = column five ÷ 2 × column six.

[c] If $J = 1$, then $R_{(J-1)} = R_0$ and $P_{(J+1)} = P_2$; thus, 2906.24 − 2843.62 = 62.62.



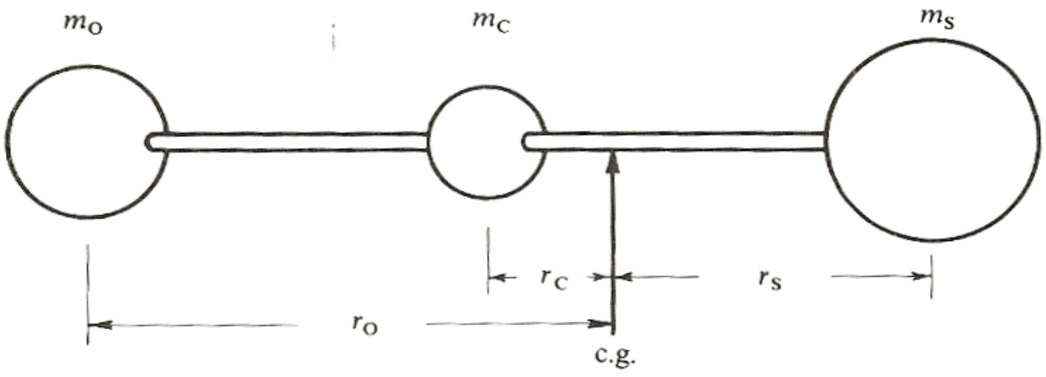
Fundamental band of CO. The lines are labeled according to their J” values.

1.3. ROTATION OF LINEAR POLYATOMIC MOLECULES

This type of molecules gives rise to particularly simple spectra in the far-IR or microwave region. Since $I_B = I_C$; $I_A=0$, as for diatomic molecules, the energy levels are given by formula identical with the above expression:

rotational energy: $E_{rot}/hc = BJ(J+1)-DJ^2(J+1)^2$ (cm^{-1})

and the spectrum will show the same *2B* separation modified by the distortion constant.
All the expressions are valid what were discussed for diatomic molecules.
But there is on important difference. The linear molecules have N-1 bond lengths.
Let us consider the rotation of OCS.



Molecule OCS, showing the distances of each atom from the centre of gravity.

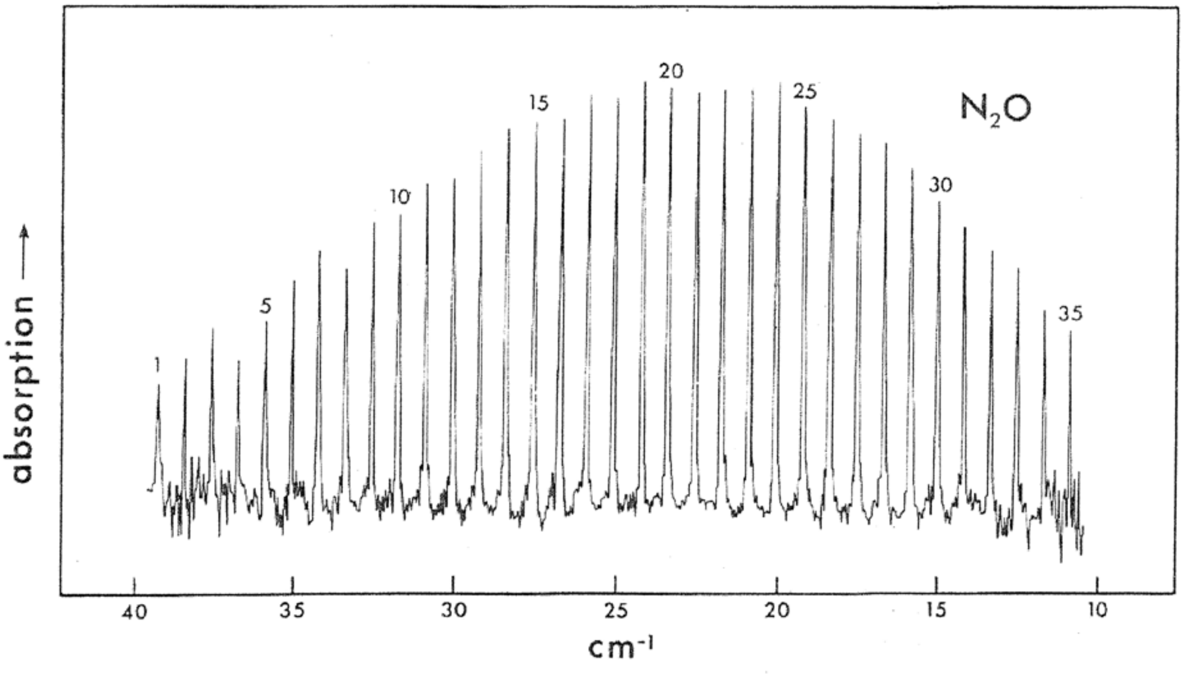
The moment of inertia is:

$$I= m_o r_o^2 + m_c r_c^2 + m_s r_s^2$$

We wish to determine the bond lengths r_{co} and r_{cs} and the final expression is:

$$I = m_o r_{co}^2 + m_s r_{cs}^2 - (m_o r_{co} - m_s r_{cs})^2/M$$

where m_i are the atomic weights and M is the total mass of the molecule.
From observation of one $^{16}OC^{34}S$ species it is impossible to determine two unknowns (r_{co} and r_{cs}) but the use of experimental data for $^{18}OC^{34}S$ the difficulty can be overcome.



Pure rotational spectrum of N_2O

Rotational constants of some linear molecules.

Molecule	B_0(cm^{-1})	$D_0 \times 10^{-6}$ (cm^{-1})
HCN	1.478222	2.910
DCN	1.207751	1.929
NNO	0.419011	0.1788

OCS	**0.202857**	**0.0437**
HCCD	**0.991527**	**0.0112**
HCCCN	**0.151740**	**0.0190**

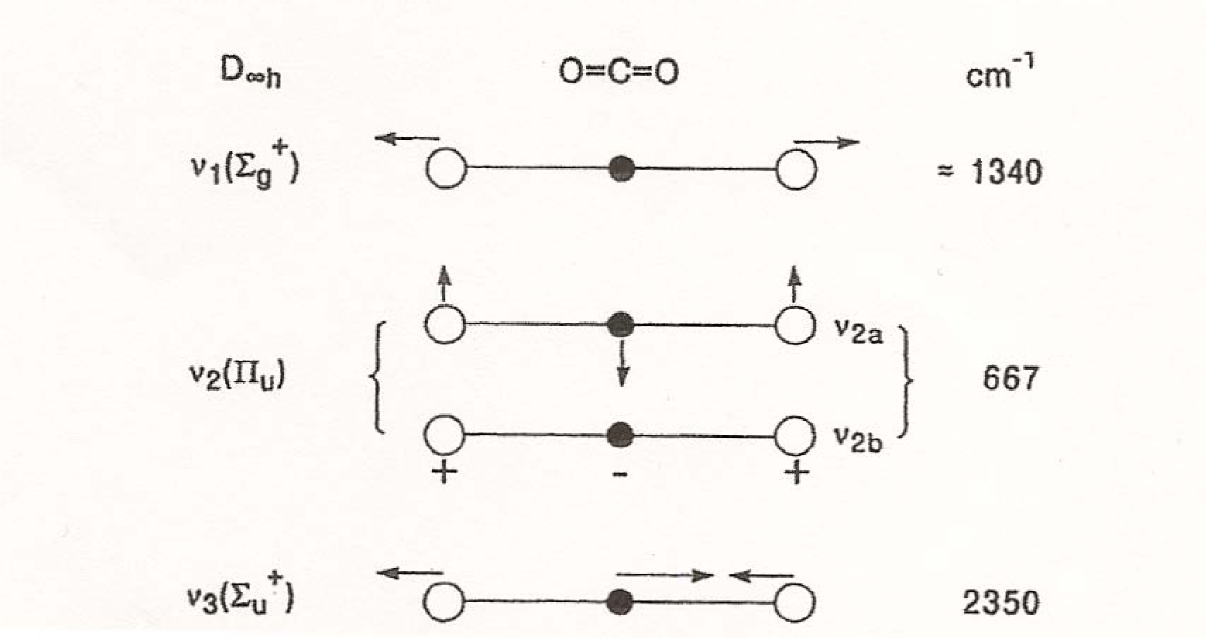
1.4. ROTATION-VIBRATION OF LINEAR MOLECULES

Expressions for *P* and *R* branches of parallel bands are similar to those of diatomic molecules (see above). For CO_2 v_3 is a parallel mode and v_2 is a perpendicular vibration since the induced dipole moment is perpendicular to the molecular axis. In this vibration $\Delta J = 0$ is allowed.

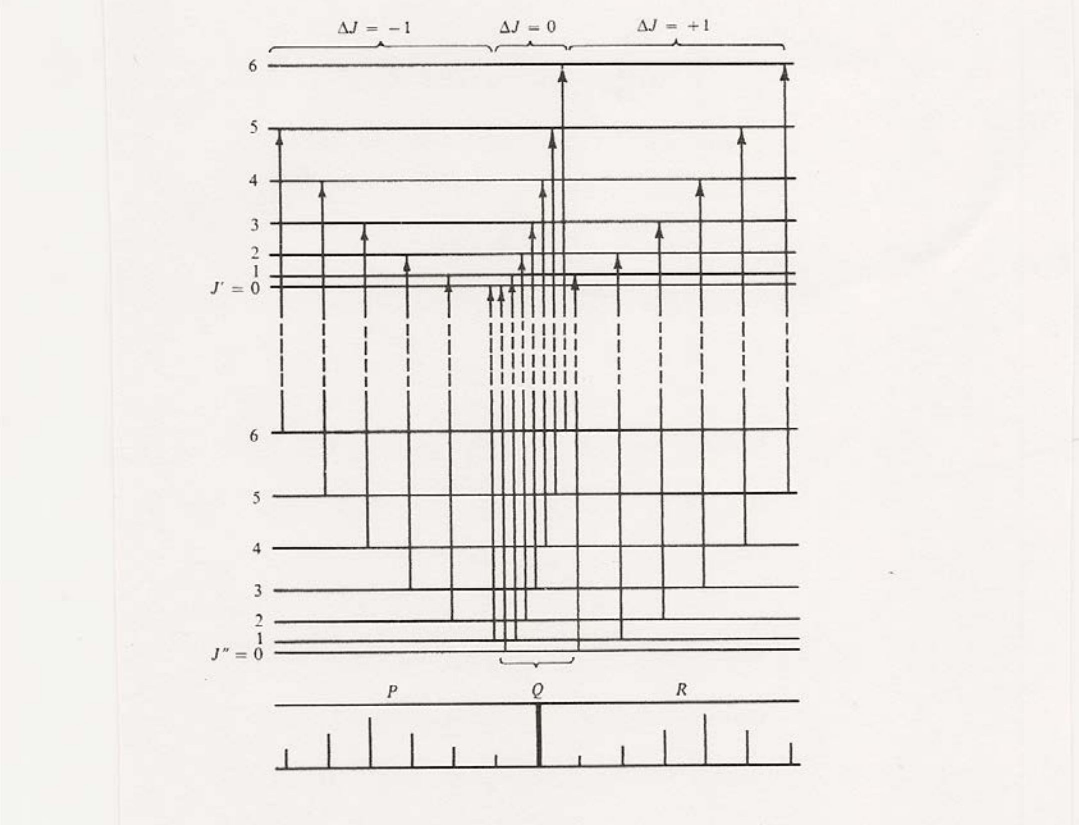
The fine structure of *Q* branch ($\Delta J = 0$) will be:

$$Q(cm^{-1}) = v_0 - (B_1 - B_0)J^2 + (B_1 - B_0)J$$

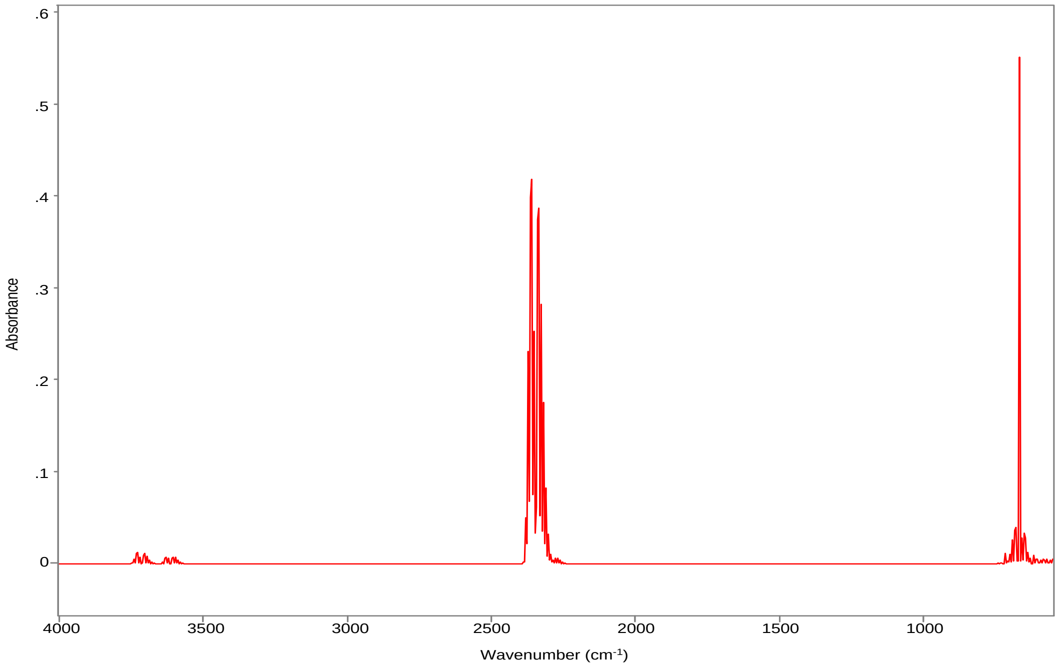
($B_1 = 0.3897$ *and* $B_0 = 0.3899\ cm^{-1}$ *for* CO_2*; but*
$B_e = 0.3906\ cm^{-1}$)


D∞h
O=C=O
cm⁻¹
ν₁(Σg⁺)
≈ 1340
ν₂(Πu)
ν2a
ν2b
667
+
-
+
ν₃(Σu⁺)
2350

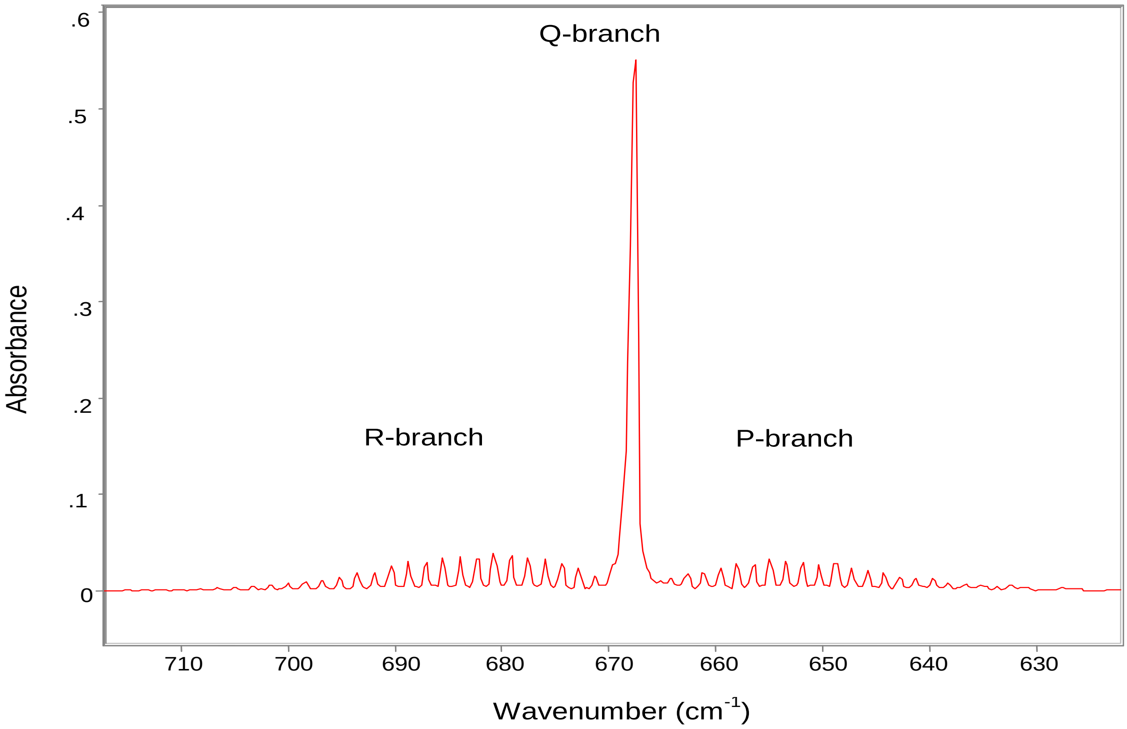
Normal vibrations of CO_2. (+ and – denote vibrations are going upward and downward, respectively, in the direction perpendicular to the plane of picture).


ΔJ = −1
ΔJ = 0
ΔJ = +1
6
5
4
3
2
1
J′ = 0
6
5
4
3
2
1
J″ = 0
P
Q
R

Rotational transitions for perpendicular bands, for transitions where $\Delta J = 0$ is also allowed



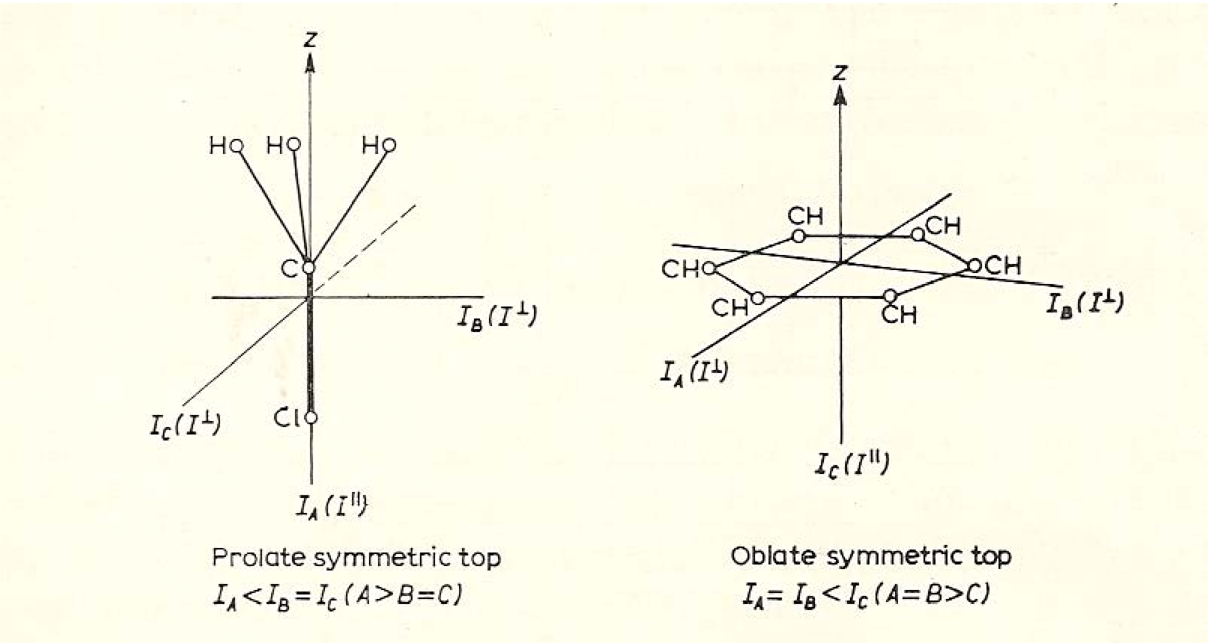
Rotational–vibrational infrared spectrum of CO_2 exhibiting parallel and perpendicular bands.



Perpendicular band (ν_2) structure of CO_2

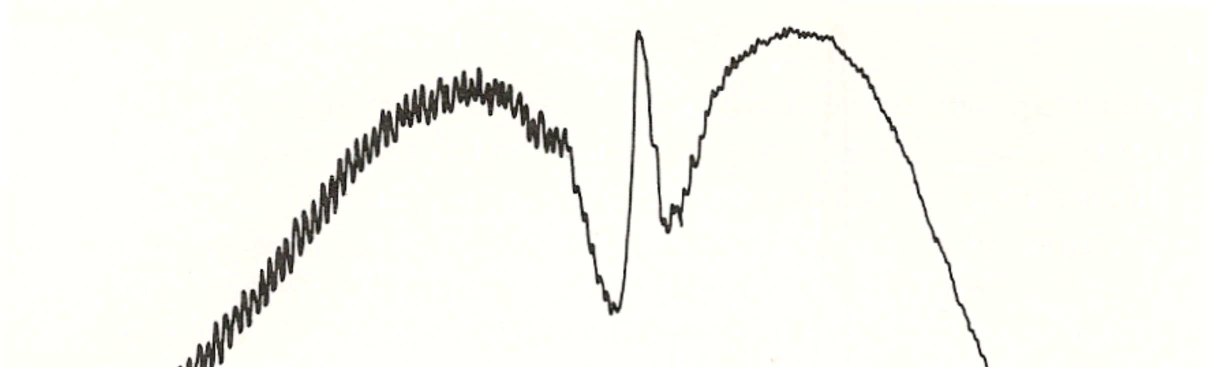
1.5. ROTATION-VIBRATION OF SYMMETRIC TOP MOLECULES

Methyl chloride and benzene, two representative molecules of these classes, are shown below:

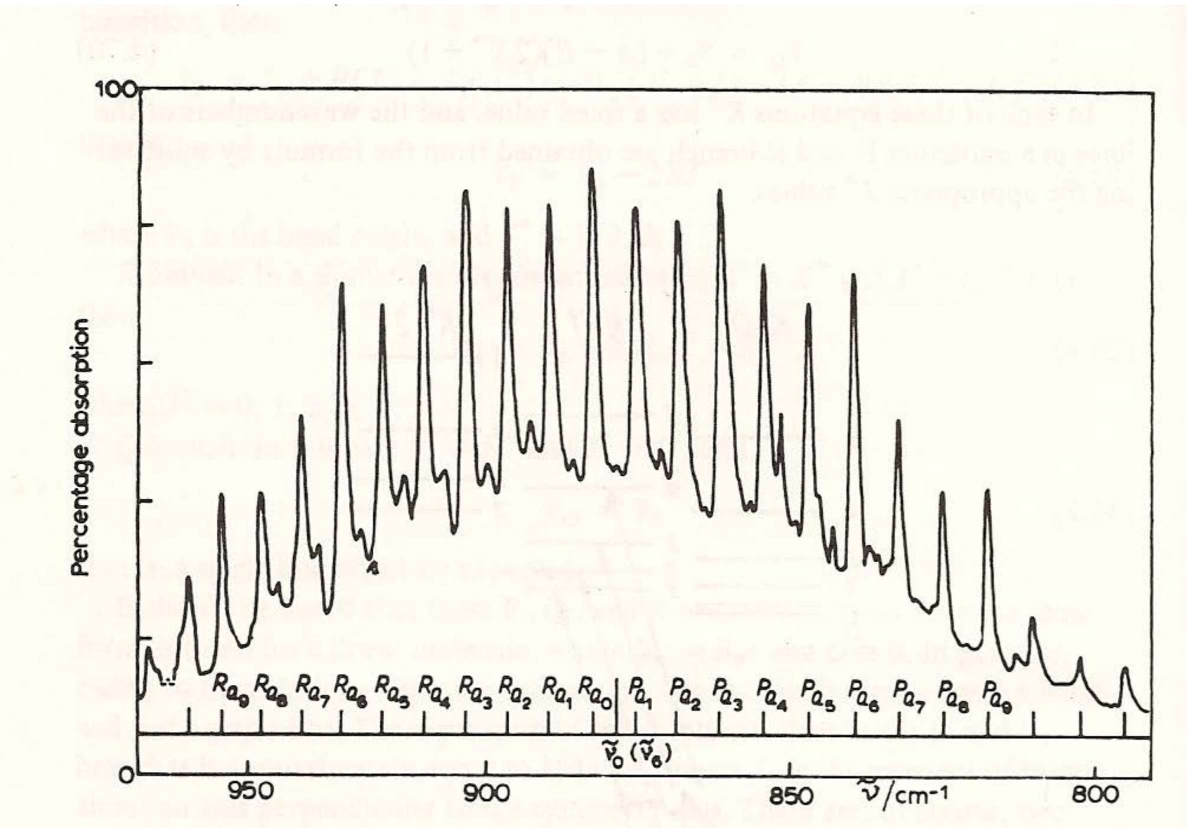

z
H
H
H
C
Cl
$I_B(I^\perp)$
$I_C(I^\perp)$
$I_A(I^\parallel)$
z
CH
CH
CH
CH
CH
CH
$I_B(I^\perp)$
$I_A(I^\perp)$
$I_C(I^\parallel)$

Prolate symmetric top
$I_A < I_B = I_C \; (A > B = C)$

Oblate symmetric top
$I_A = I_B < I_C \; (A = B > C)$



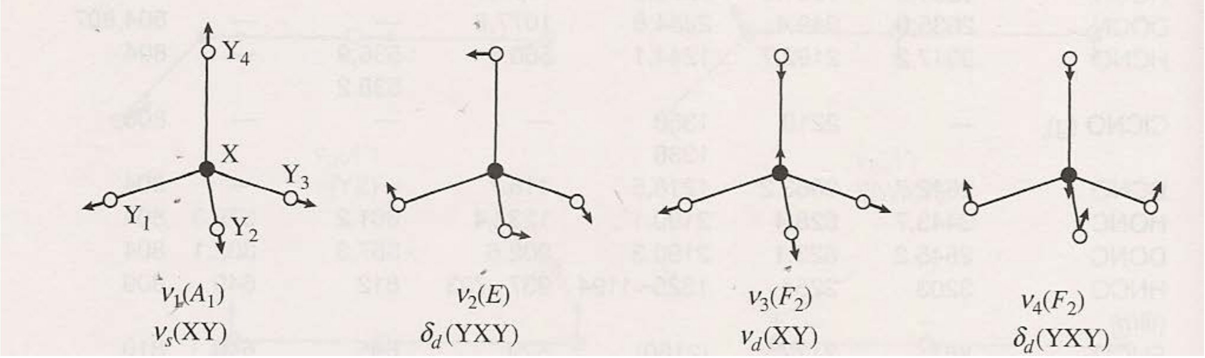
The parallel umbrella vibration of CH_3I, showing the typical PQR contour.



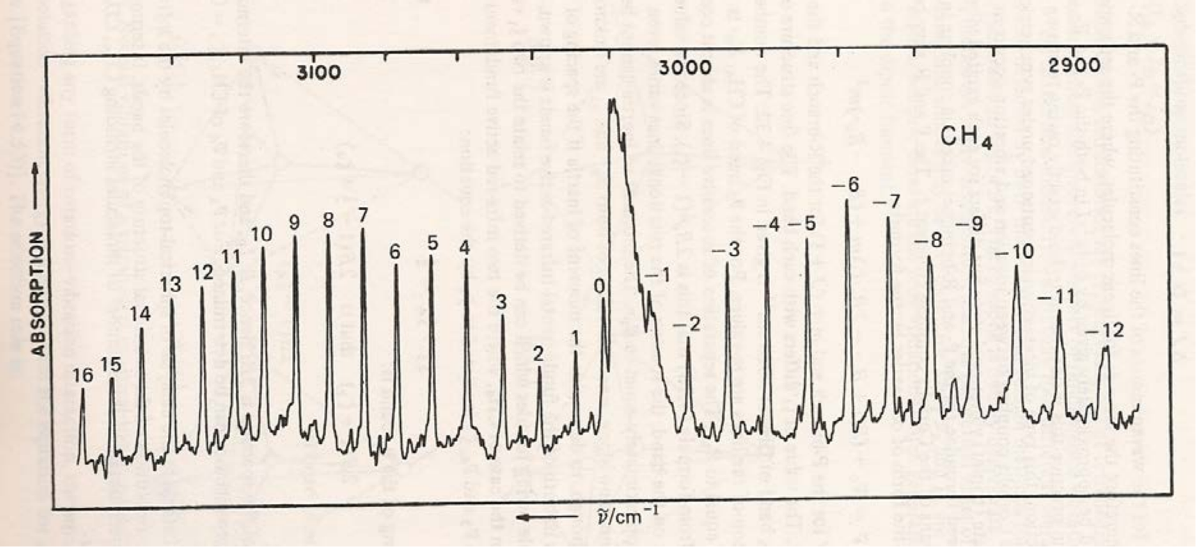
CH_3 rocking (perpendicular) band of CH_3I (240 Torr, 10cm cell)

1.6. ROTATION-VIBRATION OF SPHERICAL-TOP MOLECULES

Methane and carbon tetrachloride are typical examples of tetrahedral spherical-top molecules. For molecules of point group T_d only class F_2 fundamentals are IR active.

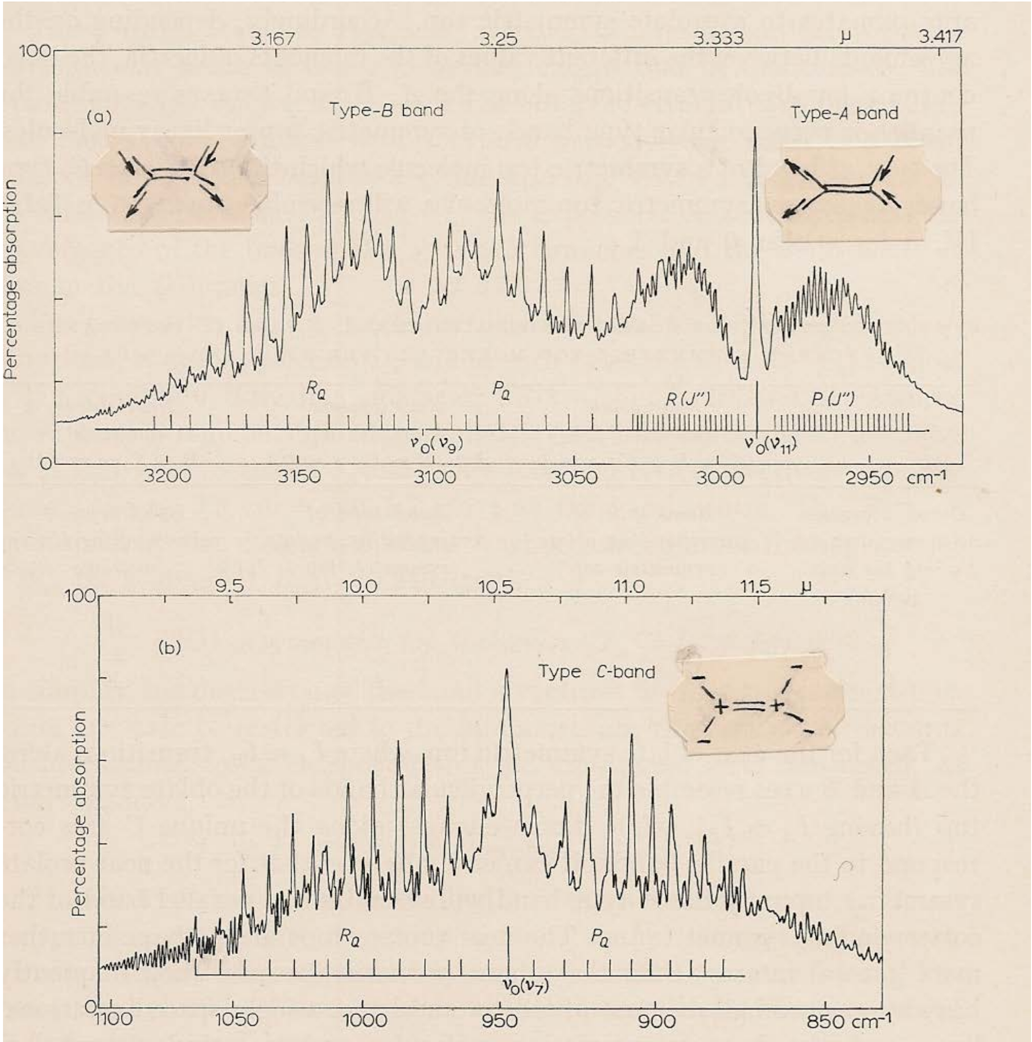

Y4
X
Y3
Y1
Y2
ν1(A1)
νs(XY)
ν2(E)
δd(YXY)
ν3(F2)
νd(XY)
ν4(F2)
δd(YXY)

Normal modes of vibrations of tetrahedral XY_4 molecule

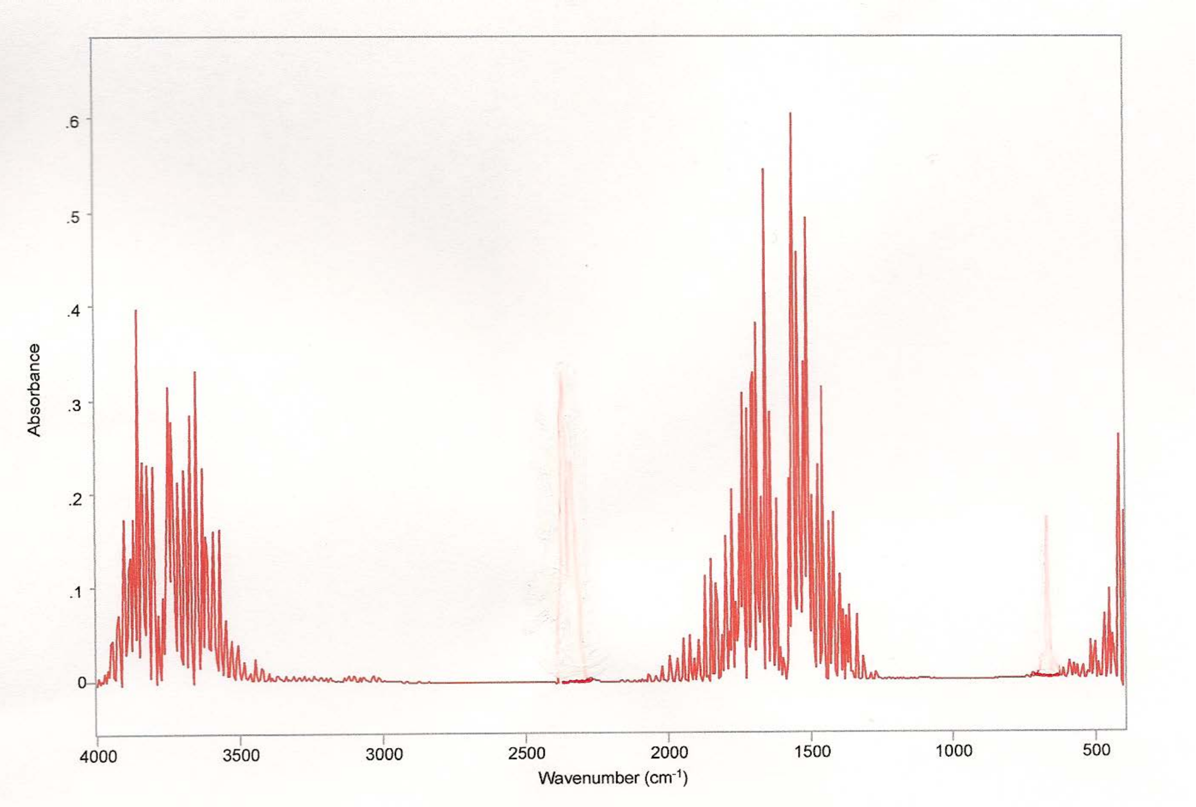


Rotational fine structure of v_3 fundamental of CH_4.

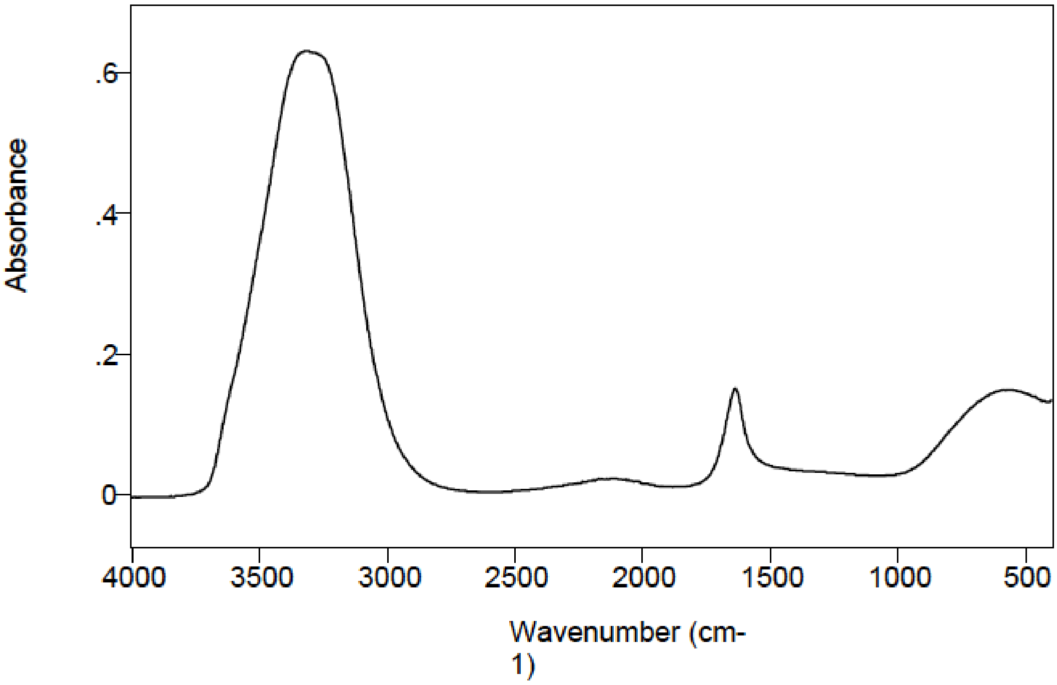
1.7. ROTATION-VIBRATION OF ASYMMETRIC-TOP MOLECULES



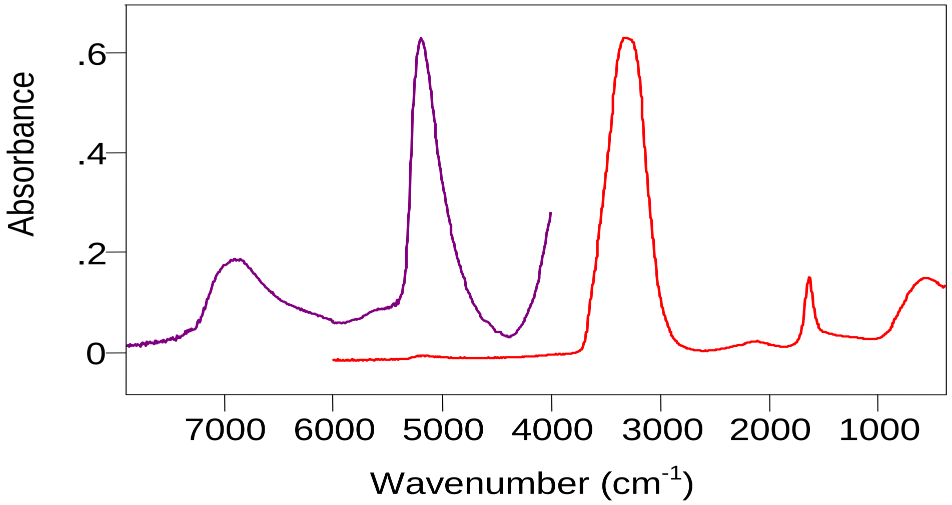
Observed type-A, type-B and type-C bands of ethylene



Rotational–vibrational spectrum of H_2O vapours together with part of pure rotational spectrum



Infrared spectra of liquid water (ATR corrected)



NIR (blue) and MIR (red) spectra of liquid water.
(NIR, 0.2mm CaF_2 cell, MIR spectrum is ATR corrected)

1.8.Vibrations of diatomic molecules.

m_1 m_2

Reduced mass: $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$

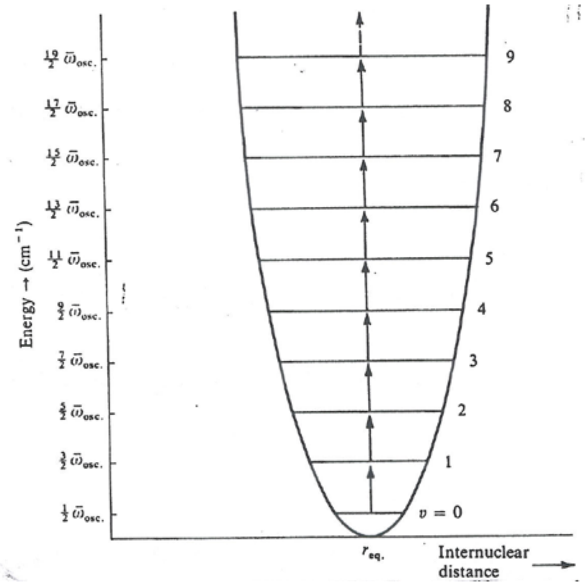
Harmonic oscillator.

Potential energy: $V = \frac{1}{2}Kq^2$

Schrödinger's wave equation:

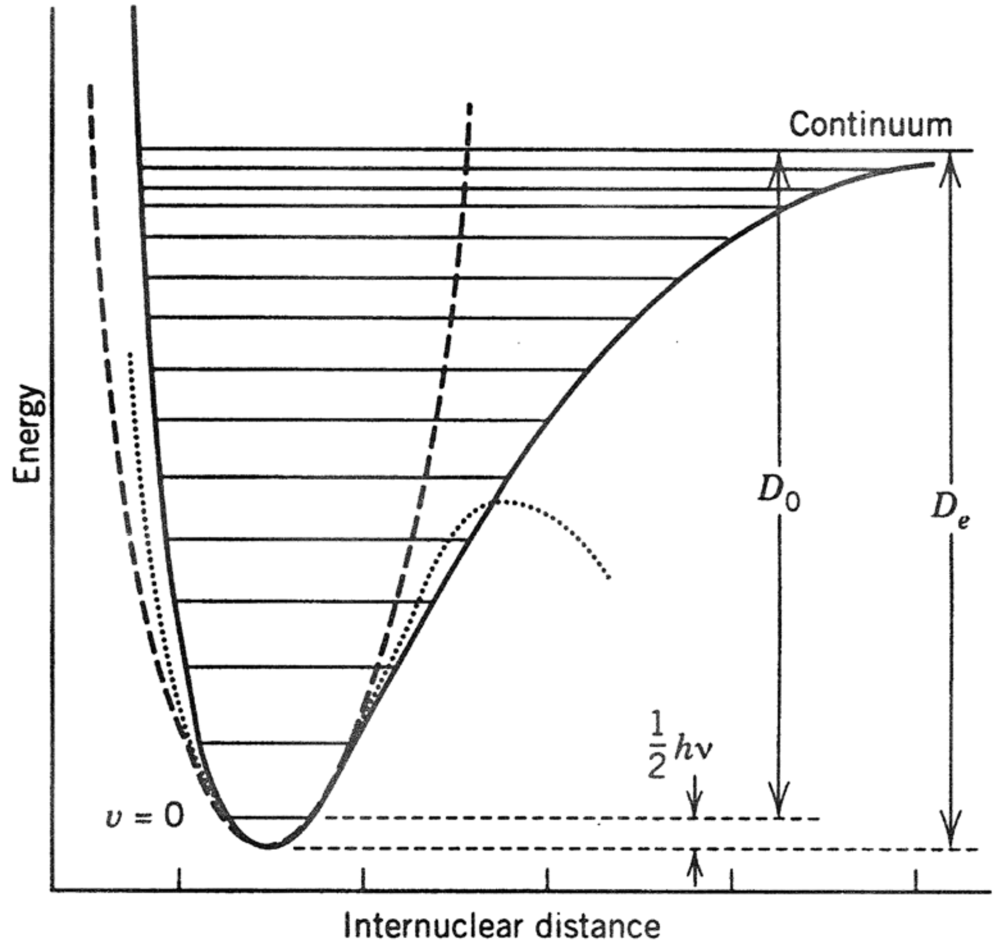
$$\frac{d^2\psi}{dq^2} + \frac{8\pi^2\mu}{h^2}\left(E - \frac{1}{2}Kq^2\right)\psi = 0$$

Solution gives the eigenvalues:


$\frac{19}{2}\bar{\omega}_{osc.}$
$\frac{17}{2}\bar{\omega}_{osc.}$
$\frac{15}{2}\bar{\omega}_{osc.}$
$\frac{13}{2}\bar{\omega}_{osc.}$
$\frac{11}{2}\bar{\omega}_{osc.}$
$\frac{9}{2}\bar{\omega}_{osc.}$
$\frac{7}{2}\bar{\omega}_{osc.}$
$\frac{5}{2}\bar{\omega}_{osc.}$
$\frac{3}{2}\bar{\omega}_{osc.}$
$\frac{1}{2}\bar{\omega}_{osc.}$
Energy → (cm^{-1})
9
8
7
6
5
4
3
2
1
$v = 0$
$r_{eq.}$
Internuclear distance →

1.)
2.)
3.)

Potential energy curve for a diatomic molecule.


Continuum
Energy
D_0
D_e
$\frac{1}{2}h\nu$
$v = 0$
Internuclear distance

Potential energy curves for a diatomic molecule: actual potential (solid line), parabolic potential (dashed line), and cubic potential (dotted line).

Experimental (anharmonic) fundamental frequencies and first overtones for diatomic molecules (cm^{-1})

Molecule	ν_{exp}	$2\nu_{exp}$	ω_e	$x_e\omega_e$
HH	4160	8082		
HD	3632	7064		
DD	2994	5852		
HF	3962	7738		
DF	2907	5722		
$H^{35}Cl$	2886	5664		
$D^{35}Cl$	2091	4127		
HBr	2558	5030		
HI	2233	4380		
$^{14}N^{16}O$	1876	3724		
$^{12}C^{16}O$	2143	4259		

1. Calculate the harmonic frequency (ω_e) and the correction for anharmonicity ($x_e\omega_e$).
2. Calculate the energy levels of diatomic molecules in cm^{-1} for vibrational quantum numbers 0, 1, 2, 3 and 4.

2. Basic experimental methods in vibrational spectroscopy

Infrared
Far infrared
Raman

Regions:	13000-4000 cm^{-1}	NIR
	4000-400 cm^{-1}	MIR
	400-10 cm^{-1}	FIR

Advantages

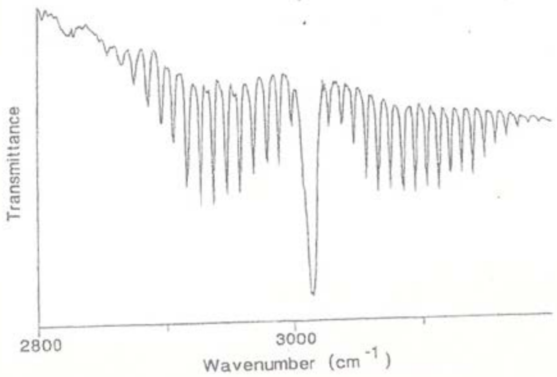
- All molecules (~10^9-10^{10}) have IR or Raman spectra
- Fingerprint of molecules
- Group frequencies
- Solid, liquid, gas phases
- Non destructive
- Cheapest and most effective method for structural codetermination
- The *only* experimental method for determination of bond strengths (force constants)
- Analytical applications
- Biological, medical etc.

Extent of Spectral information depends on the **quality** of the spectrum

Good quality spectrum	**Bad quality spectrum**
- Good S/N	- Bad S/N (noisy)
- Good band intensities	- Weak, noisy bands
- Flat baseline	- Slope baseline
- No H_2O and CO_2 vapour lines	- Atmospheric distortion
- No interference	- Interference pattern
- Proper resolution	- Improper resolution
- Good looking	- Bad looking
- Can be published	- Can not be published

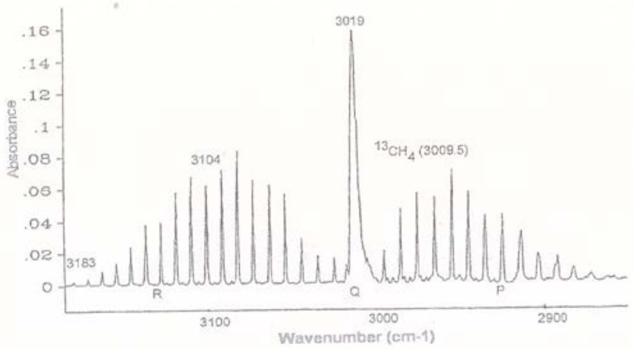
Basic factors determining the quality of measured spectra

1. Operator
2. Instrument (performance, scanning parameters, etc.)
3. Sample preparation
4. Spectral manipulations
5. Easy or difficult sample



High resolution

rotational vibrational spectrum of the ν_3 vibration of methane.



2.1. Mid and far- infrared spectroscopy

HISTORICAL DEVELOPMENT OF INFRARED AND RAMAN SPECTROSCOPY

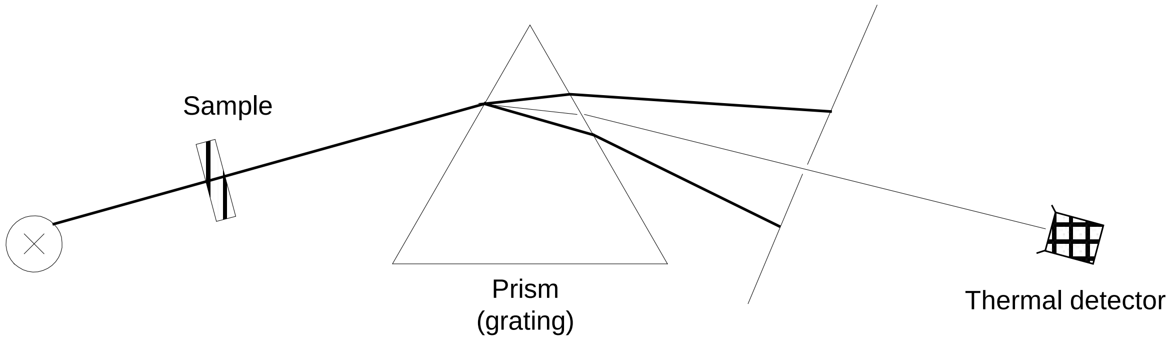
Initial period:	before	1945
Basic developments:		1945-1965
New Vibrational spectroscopy:		1965-

INTERFEROMETRY

Problems with dispersive systems.

a. No multiplex advantage

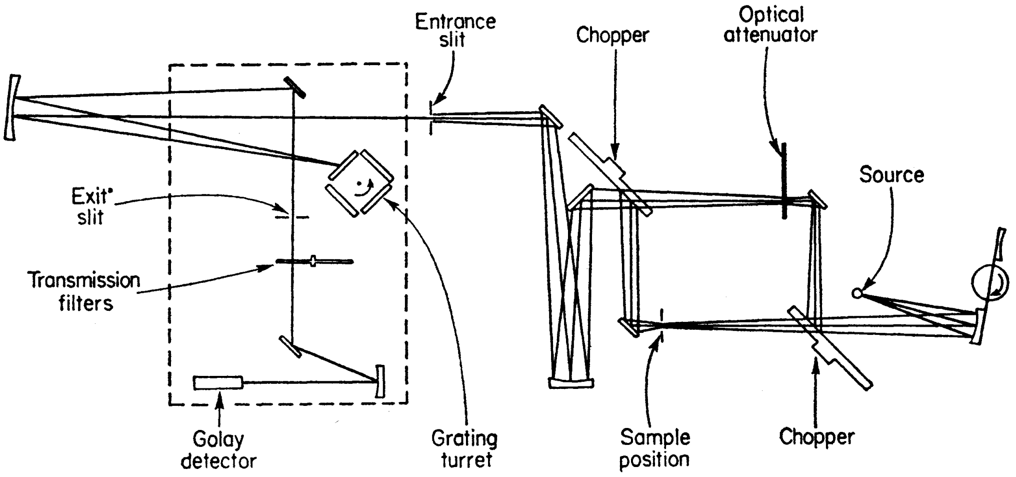
Dispersive system



N-resolution elements

Each element recorded at $\frac{T}{N}$ time (T scanning time)

b. Great amount of reflections and optics


Entrance slit
Chopper
Optical attenuator
Source
Exit* slit
Transmission filters
Golay detector
Grating turret
Sample position
Chopper

Optical diagram for the Beckman IR 11 far-infrared spectrometer

Problems:

Slow

Expensive

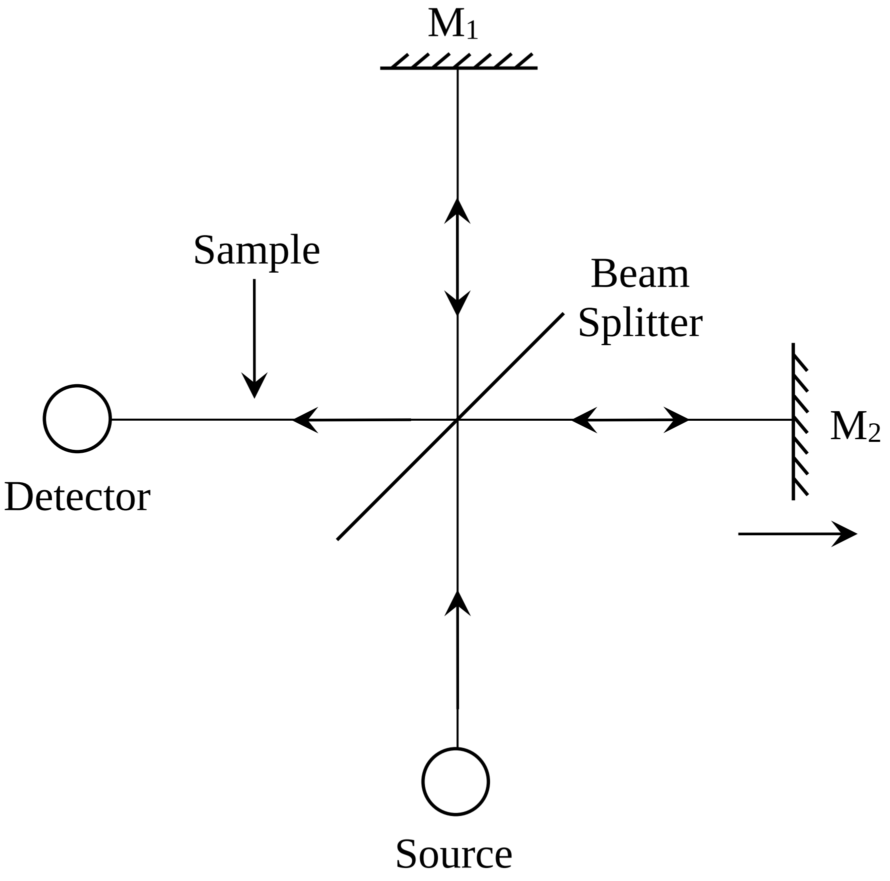
12 mirrors + 4 gratings

Detector illumination (spectral range 0-400 cm^{-1})

Resolution (cm^{-1})	Spectral elements	Fragments of energy at the detector
8	50	0.0200 (2%)
4	100	0.0100 (1%)
1	400	0.0025 (0.25%)
0.5	800*	0.0012 (0.12%)

*With very narrow slit

MICHELSON INTERFEROMETER


M1
Sample
Beam Splitter
M2
Detector
Source

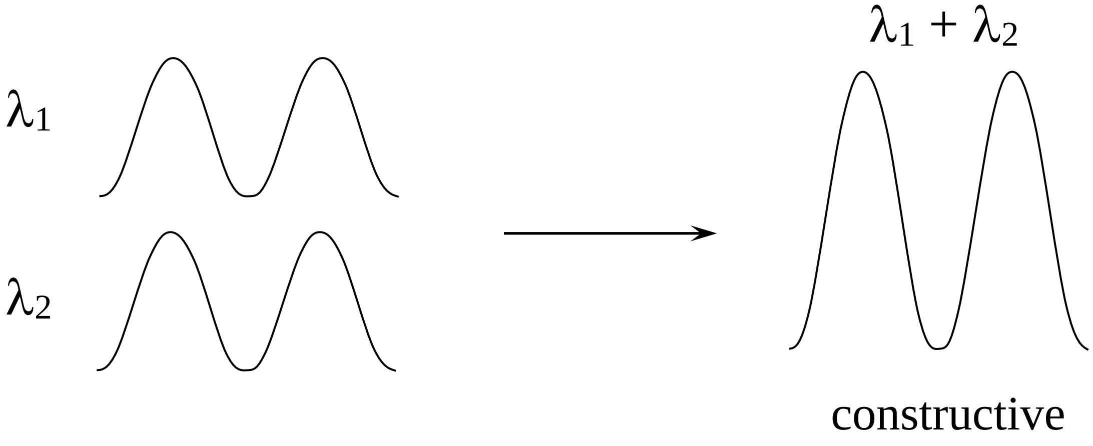
$$I(x) = S(1+\cos 2\pi \nu x)$$

S – the separated beam intensity
x – path difference
ν – wavenumber
I(x) – resultant intensity of the detector (interferogram)

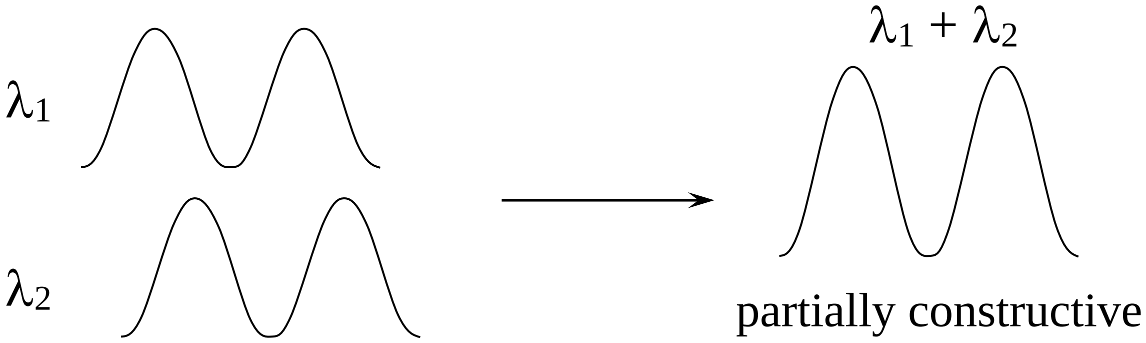
Advantages:
- simple
- no slits, choppers
- only 2-4 mirror
- 50% of source energy reaches the detector

PRINCIPLES OF INTERFERENCE

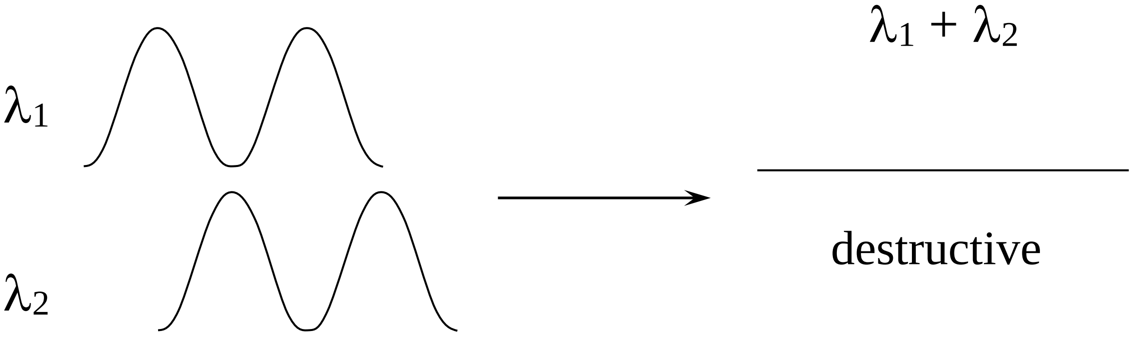
a.) Phase difference ($\varepsilon = 0$)


$\lambda_1 + \lambda_2$
λ_1
λ_2
constructive

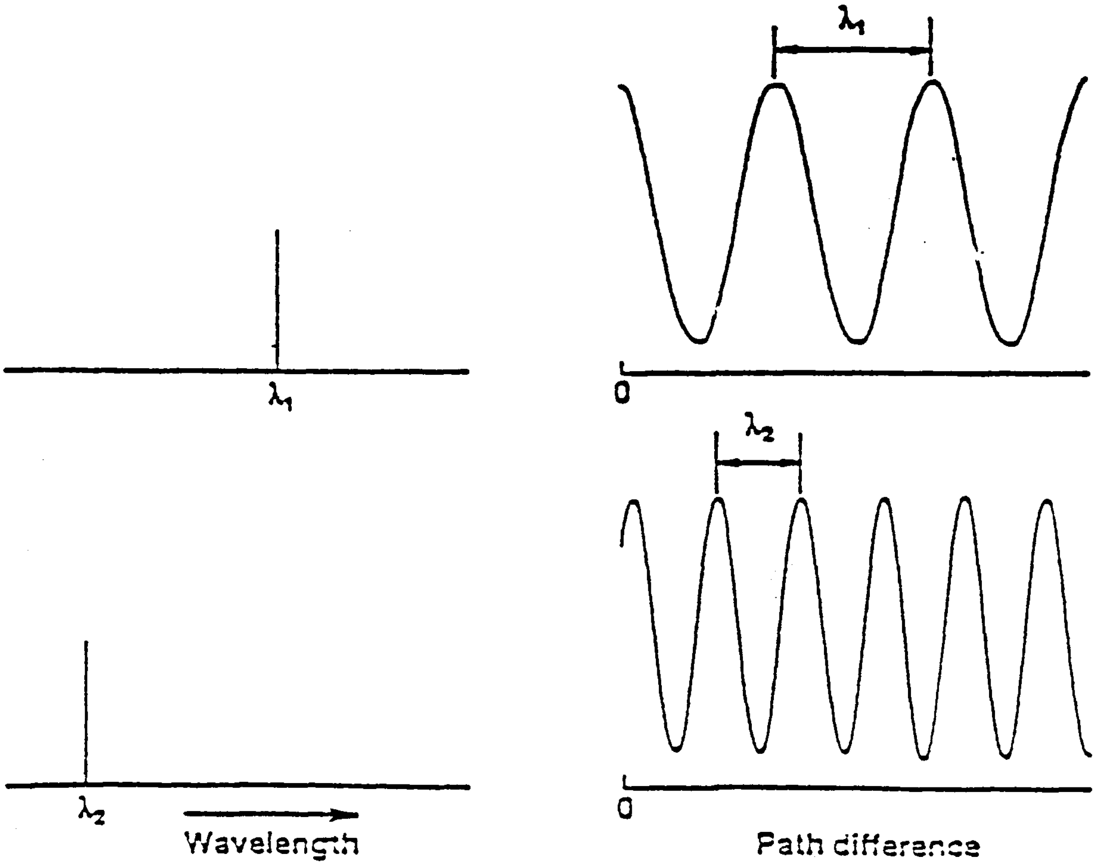
b.) $\varepsilon = \pi/2$


$\lambda_1 + \lambda_2$
λ_1
λ_2
partially constructive

c.) $\varepsilon = \pi$


$\lambda_1 + \lambda_2$
λ_1
λ_2
destructive

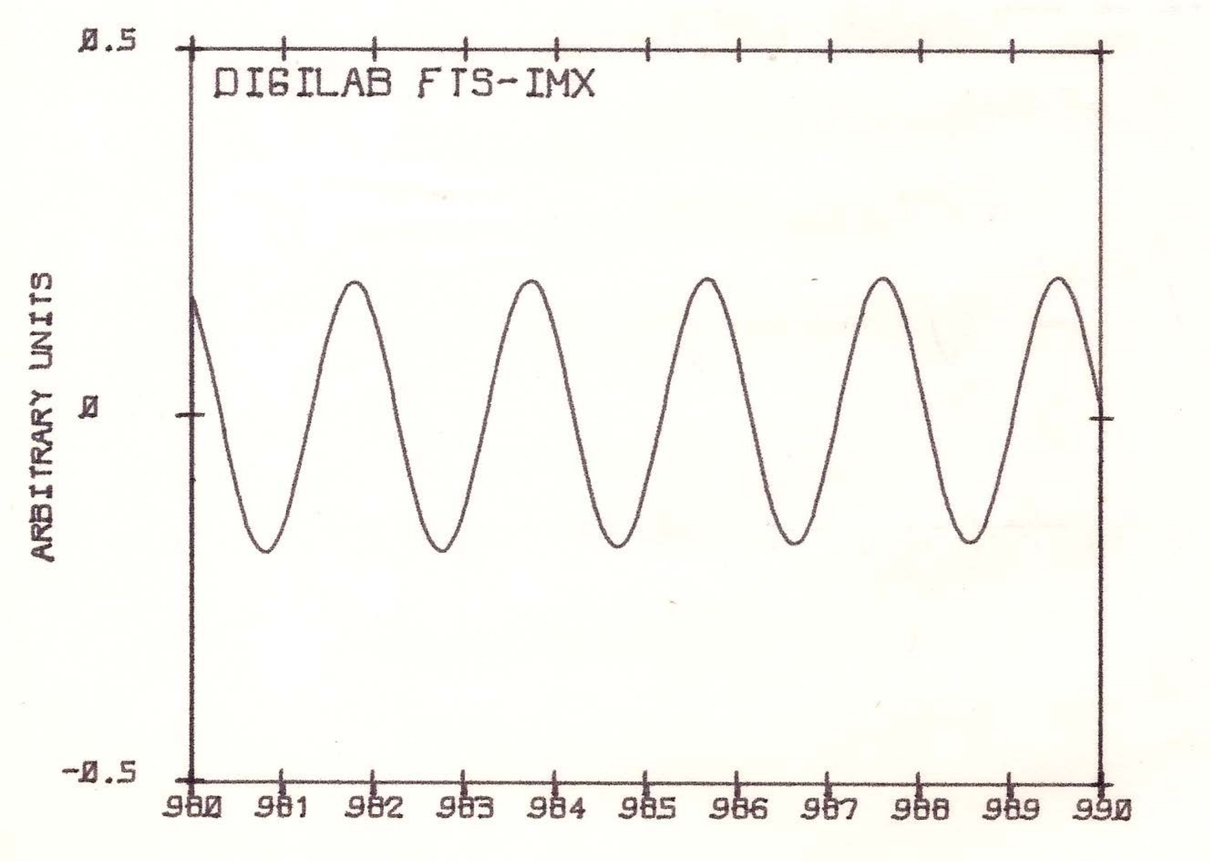
INTERFERENCE OF MONOCHROMATIC LIGHT



Single frequency source

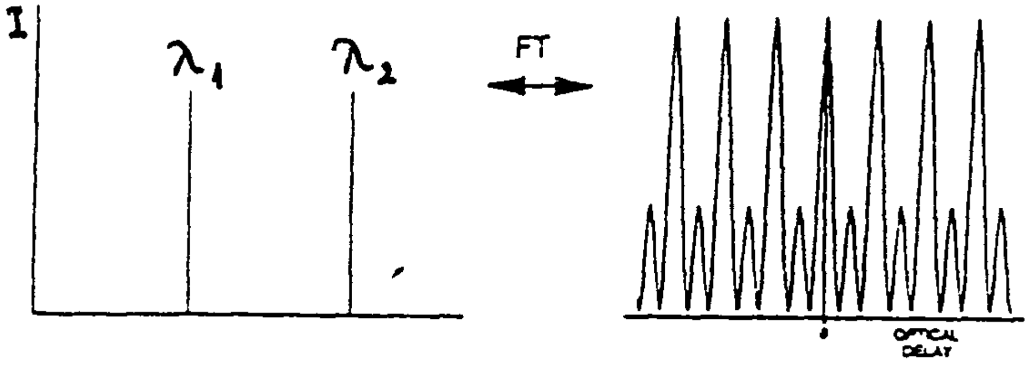
Interferogram

λ_1
λ_1
0
λ_2
λ_2
Wavelength
0
Path difference

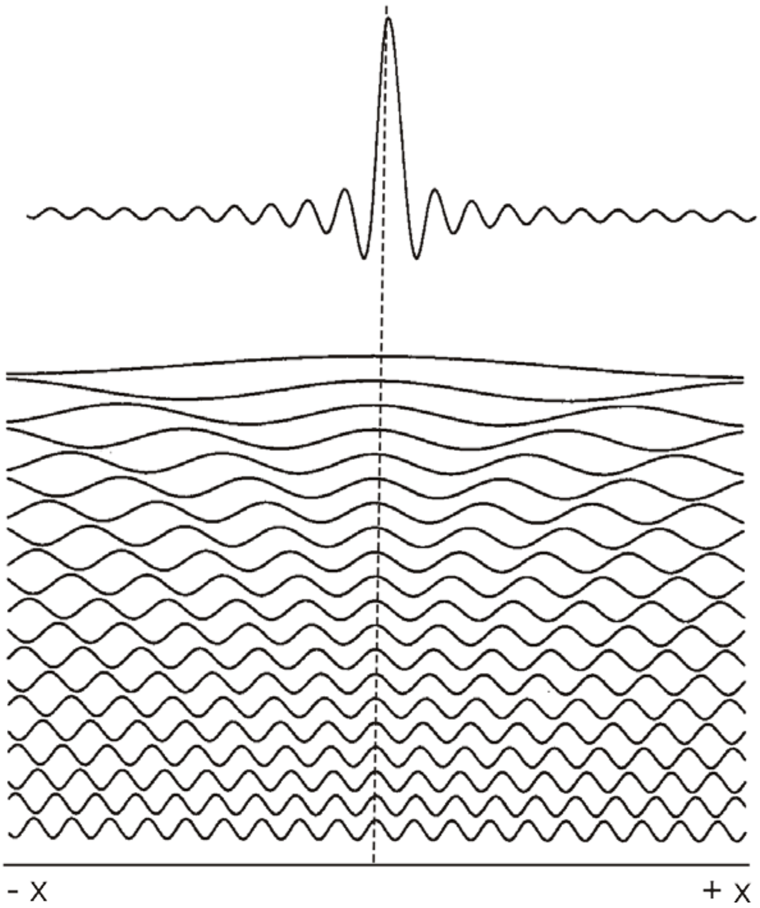


Recorded interferogram of R34 rotation-vibrational line (ν=984.38 cm^{-1}) from CO_2 laser

TWO MONOCHROMATIC LIGHTS


I
λ1
λ2
FT
0
OPTICAL DELAY

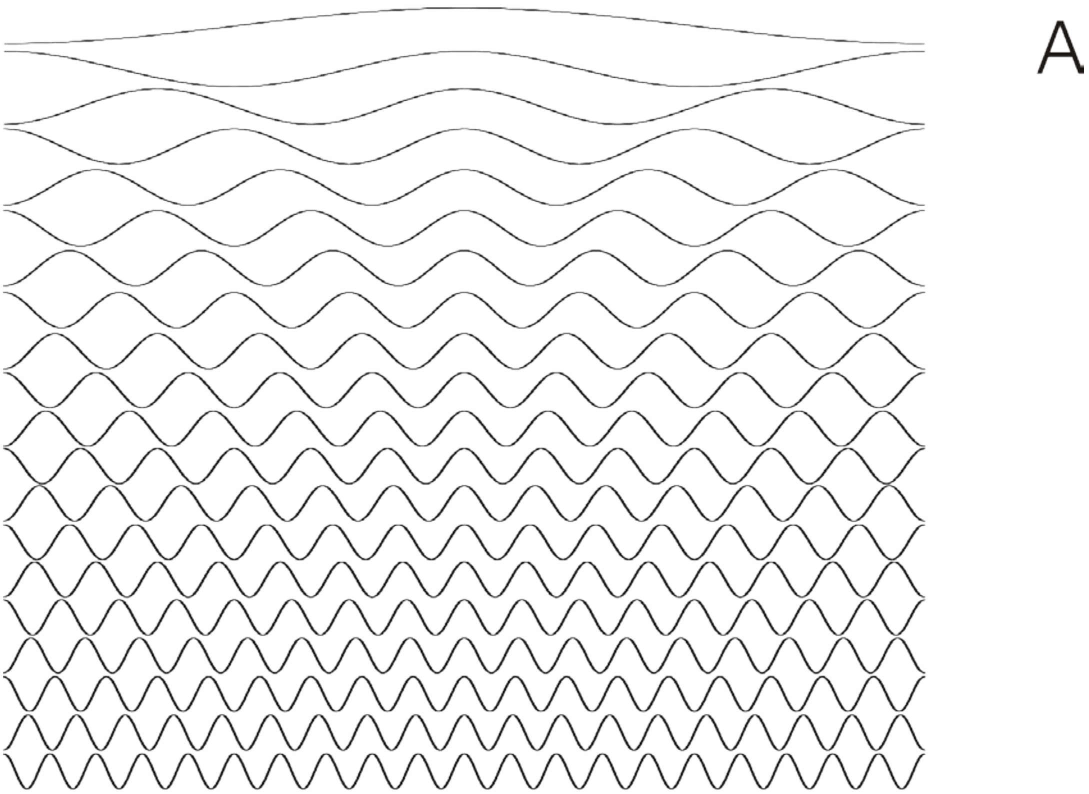
POLYCHROMATIC LIGHT



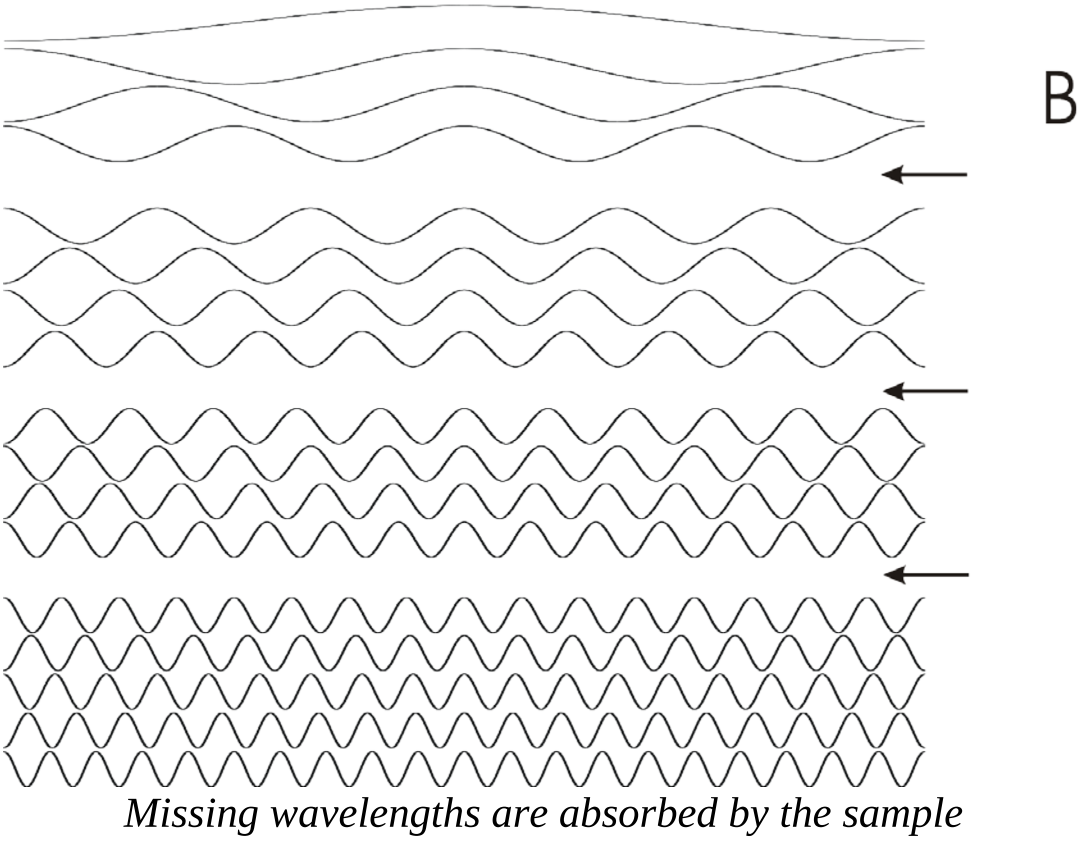
FOURIER TRANSFORMATION (FT)

$$S(\nu) = 4\sum_{i=1}^{h}[I(x_i) - \frac{1}{2}I(0)]\cos(2\pi\nu x_i)\Delta x$$

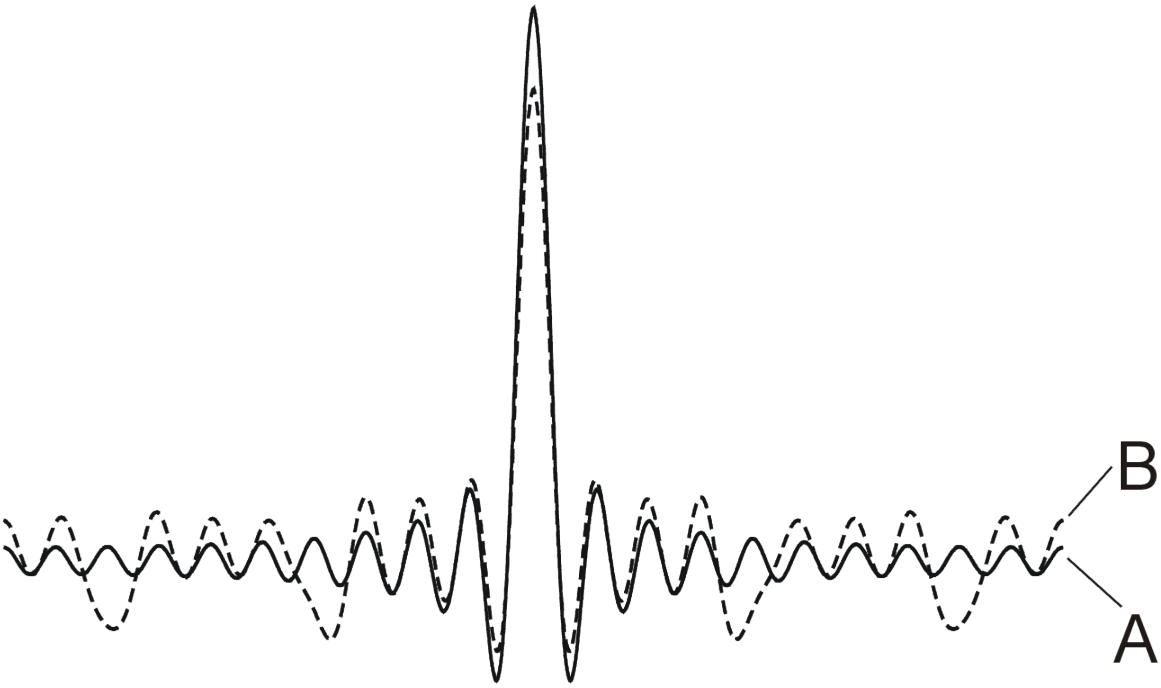
$S(\nu)$ – single beam spectrum
$I(x_i)$ – interferogram
$I(0)$ – intensity of center burst
ν – wavenumber
x_i – mirror displacement
Δx – sampling interval



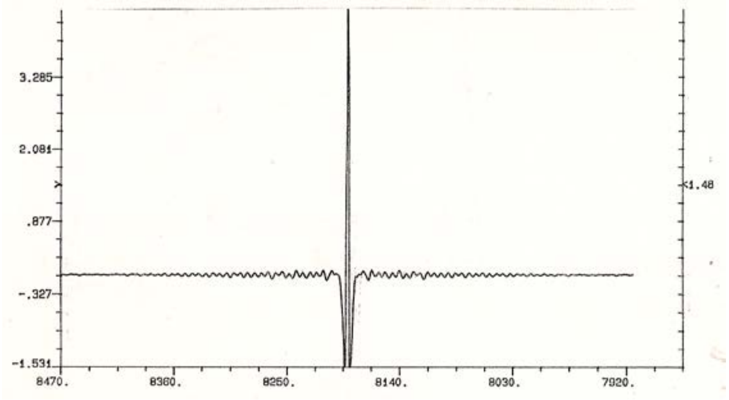
Polychromatic



Missing wavelengths are absorbed by the sample



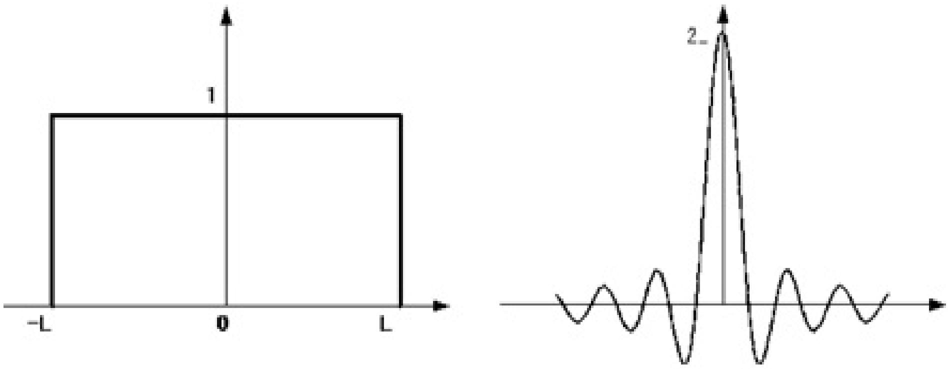
Apodization



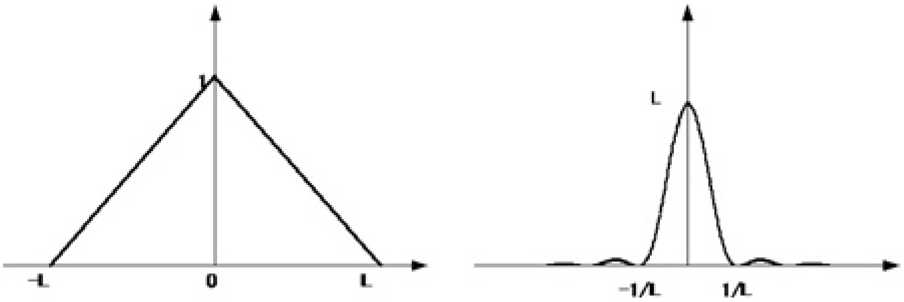
Measured interferogram

Apodization functions

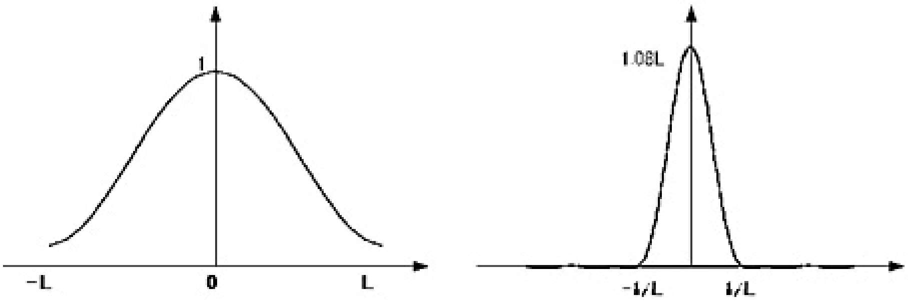
a.) Box-car:

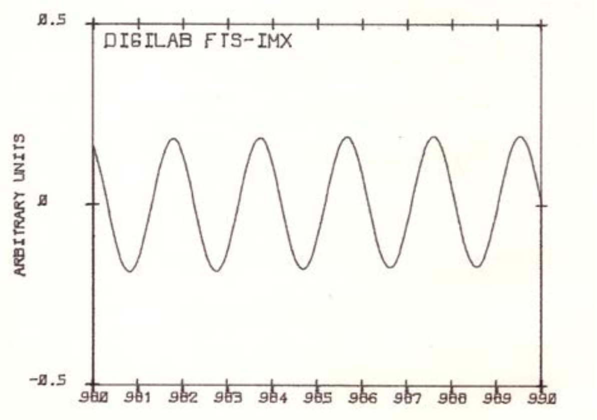


b.) Triangular:

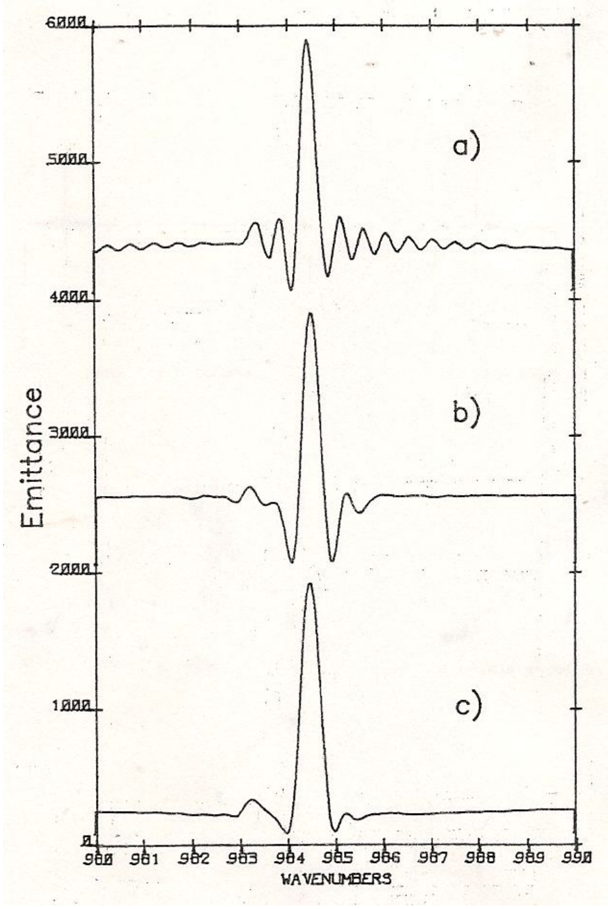


c.) Happ-Genzel:





Recorded interferogram of R34 rotation-vibrational line (ν=984.38 cm^{-1}) from CO$_2$ laser



Fourier-transformed band from the above interferogram of R34 line of CO_2 laser at 984.38 cm^{-1} with resolution of 0.5 cm^{-1}.withh different Apodization function

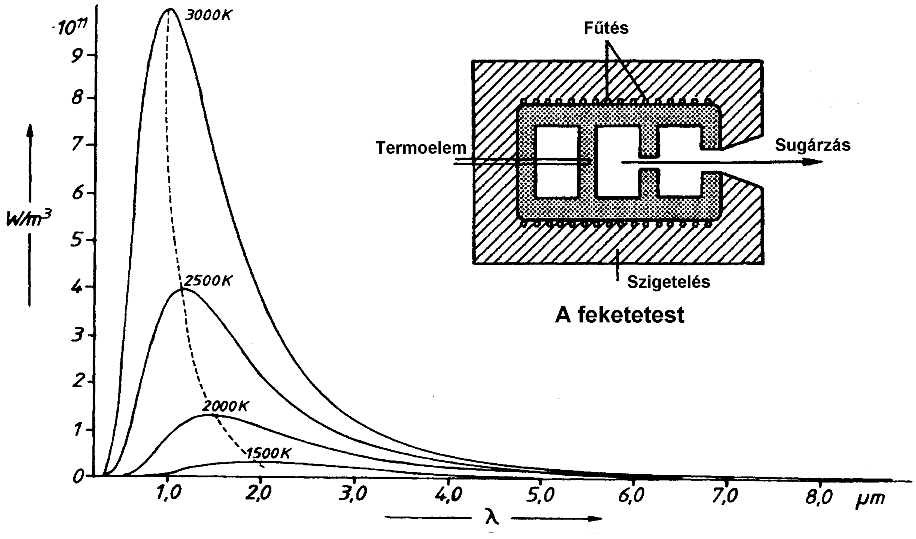
2.2. BASIC COMPONENTS AND SPECIALITIES OF FTIR SPECTROMETERS

Shape and Range of the Single Beam Spectra

1.) *Source* emission
2.) *Beamsplitter* characteristic
3.) *Detectors response*
4.) *Absorption of* atmosphere (H_2O, CO_2)

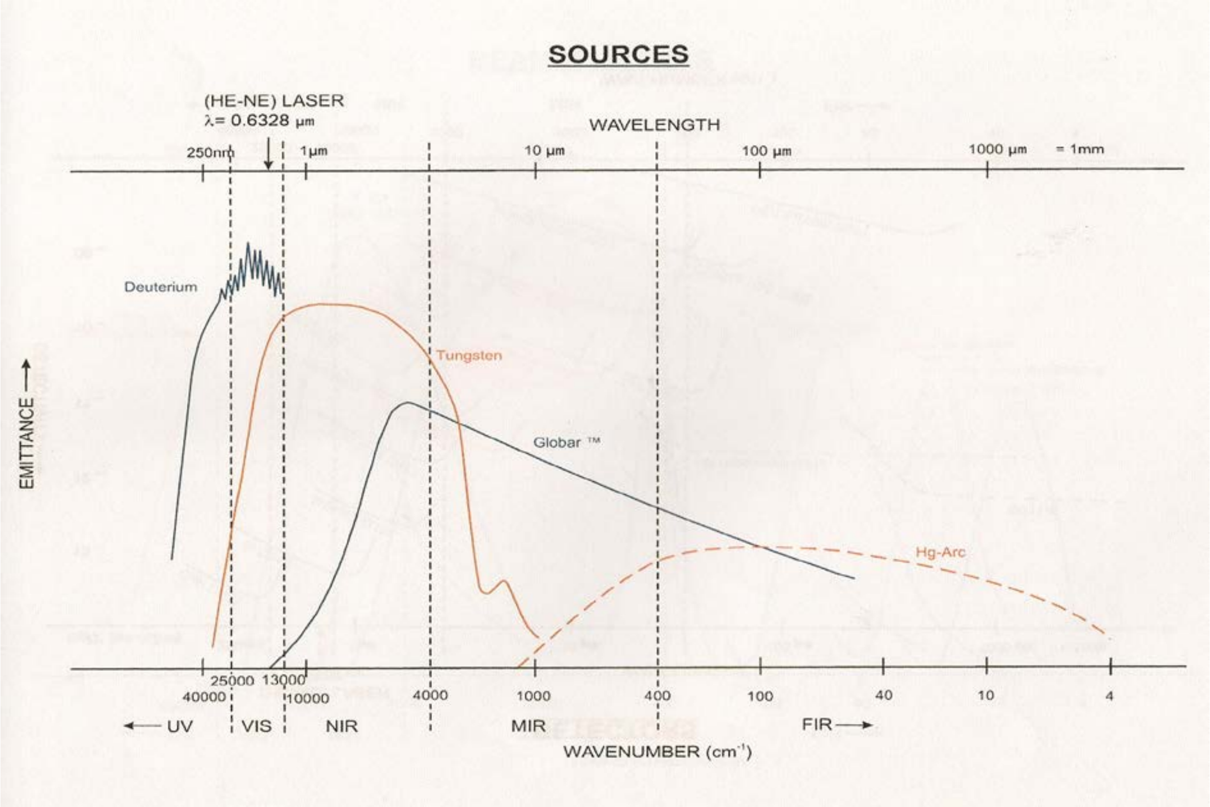
1. SOURCES

Broad band sources (blackbody)



A feketetest

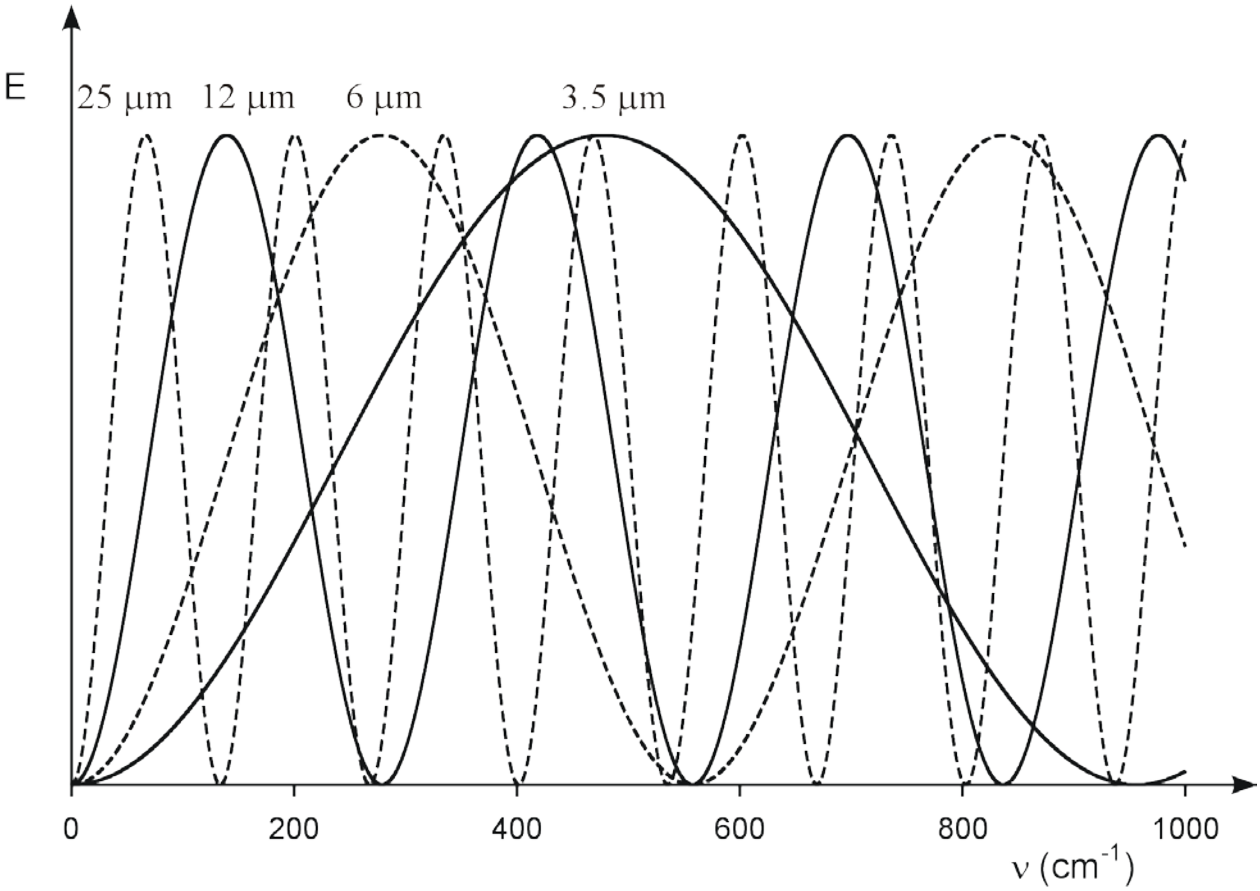
Spectral radiant emittance of a blackbody at various temperatures.



2. Beamsplitters

FIR (no supports)
Mylar (polyethylene tereftalate)

Thickness (μm)	Range (cm^{-1})
100	25-4
50	40-8
25	110-15
12	300-30
6	550-40
3.5	800-60
Metal mesh (300 l/inch)	800-8



MIR (with supports)

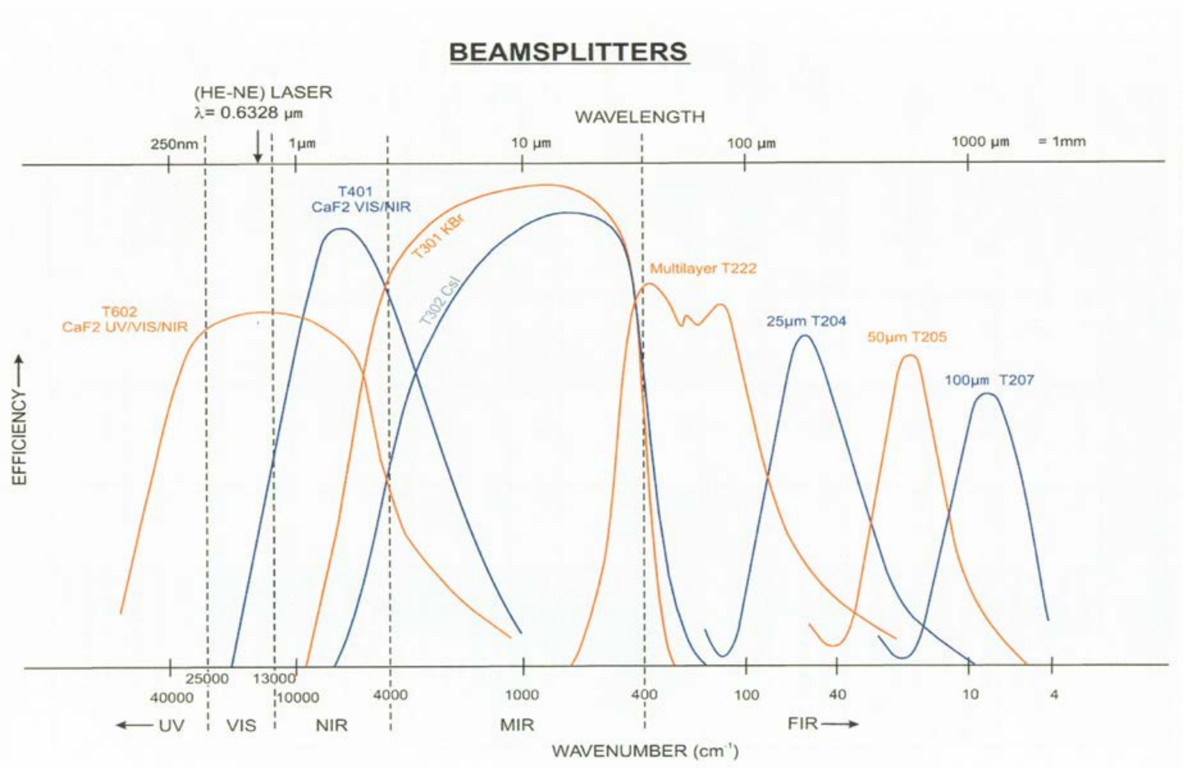
Beamsplitter	Thickness (μm)	Support	Range
Ge	1.5	CsI	6000-150
Ge	1.5	KBr	7000-350

NIR (with supports)

Beamsplitter	Thickness (μm)	Support	Range
Fe_2O_3	0.8	CaF_2	14000-900

VIS (with supports)

Beamsplitter	Thickness (μm)	Support	Range
TiO_2	0.4	Quartz	30000-4000

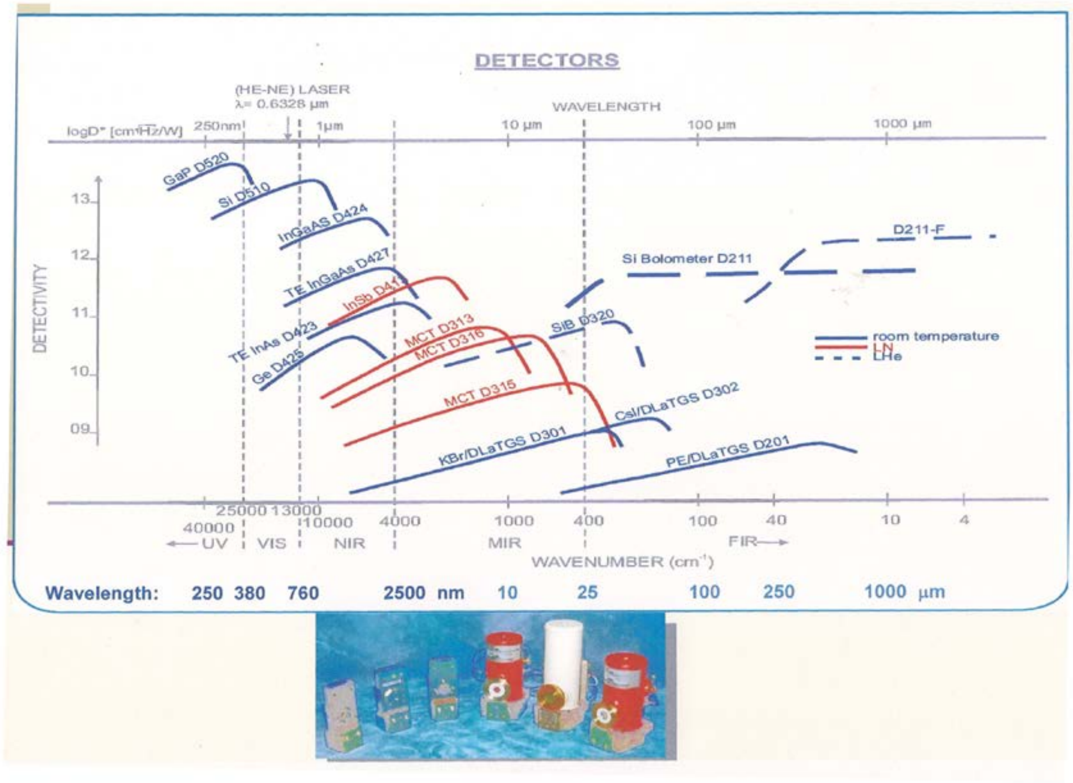


3. DETECTORS

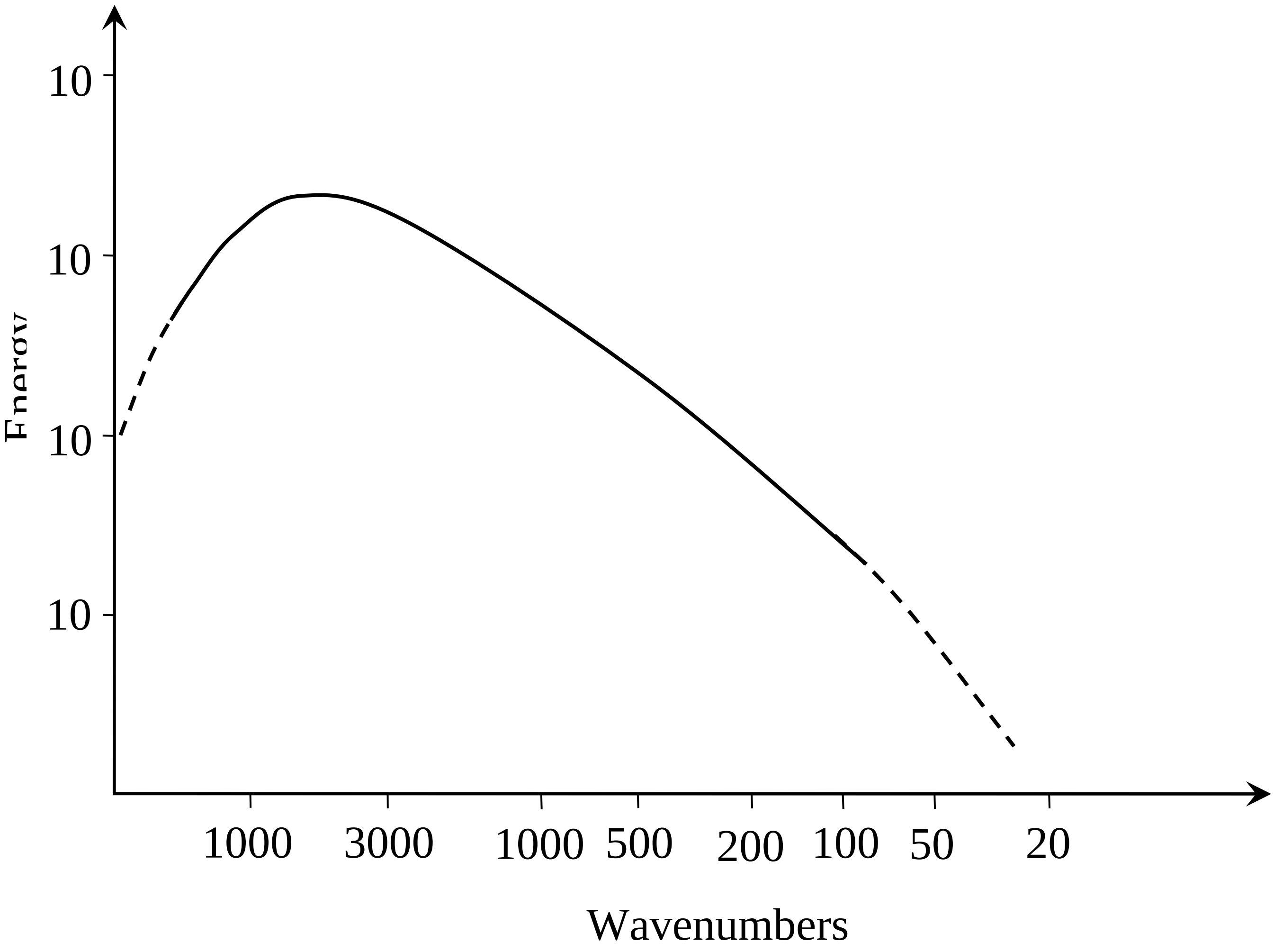
Types:

- TGS: triglicine sulphate
- DTGS: deuteron-triglicine sulphate (better)
- MCT: HgCdTe
- InSb

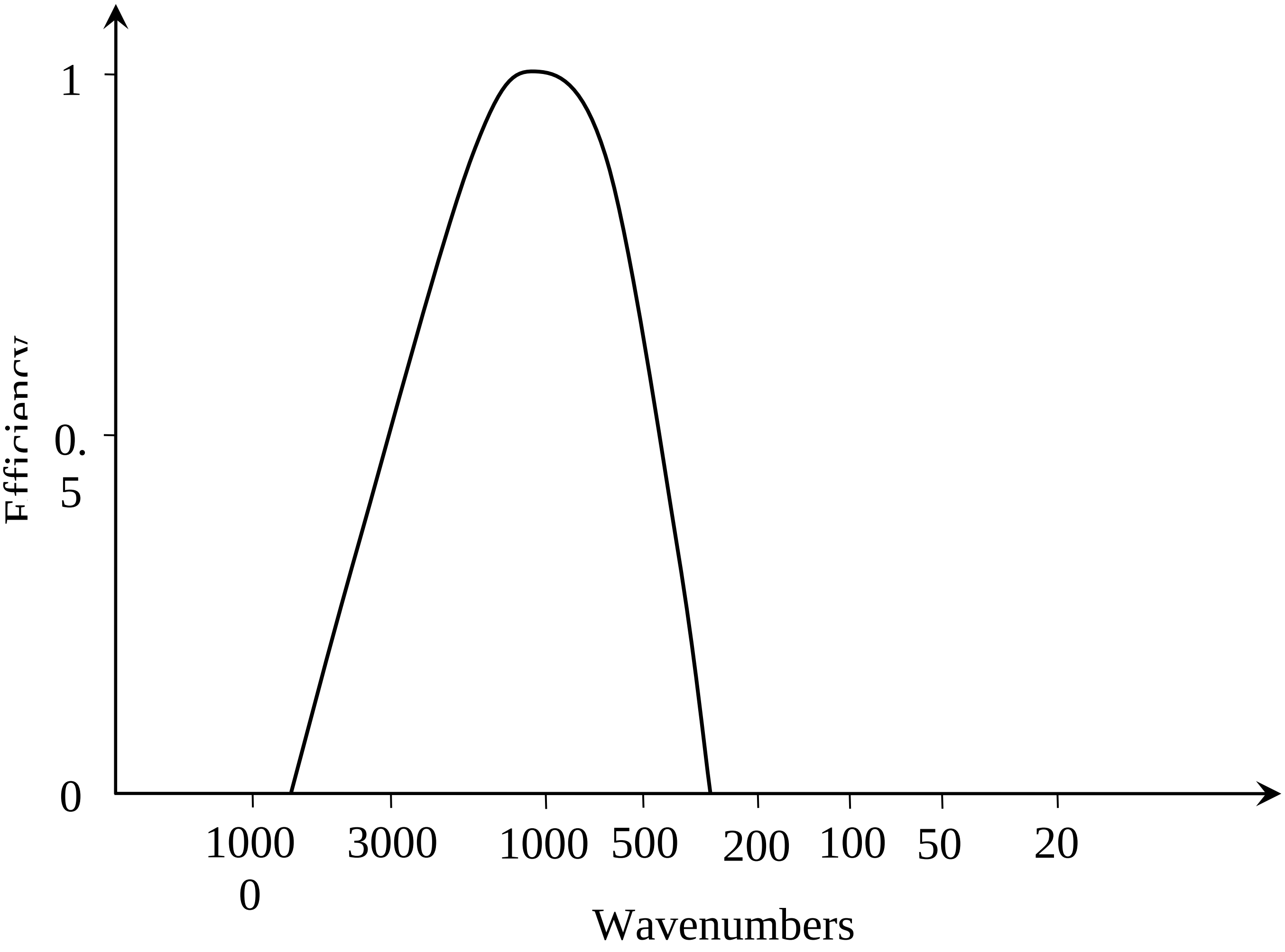
	Detector type	Range (cm^{-1})	Response time (sec)	Operating temperature
MIR	DTGS/CsI window	9000-150	10^{-3}	room temp.
	DTGS/KBr window	9000-350	10^{-3}	room temp.
	MCT (broad band)	7000-400	10^{-6}	liquid N_2
MIR	MCT (narrow band)	7000-750	10^{-6}	liquid N_2
NIR	InSb	10000-1700	10^{-6}	liquid N_2
	InAs	33000-12000	10^{-7}	liquid N_2
	PbSe	10000-2000	10^{-6}	room temp.
	PbS	12000-3100	10^{-4}	room temp.



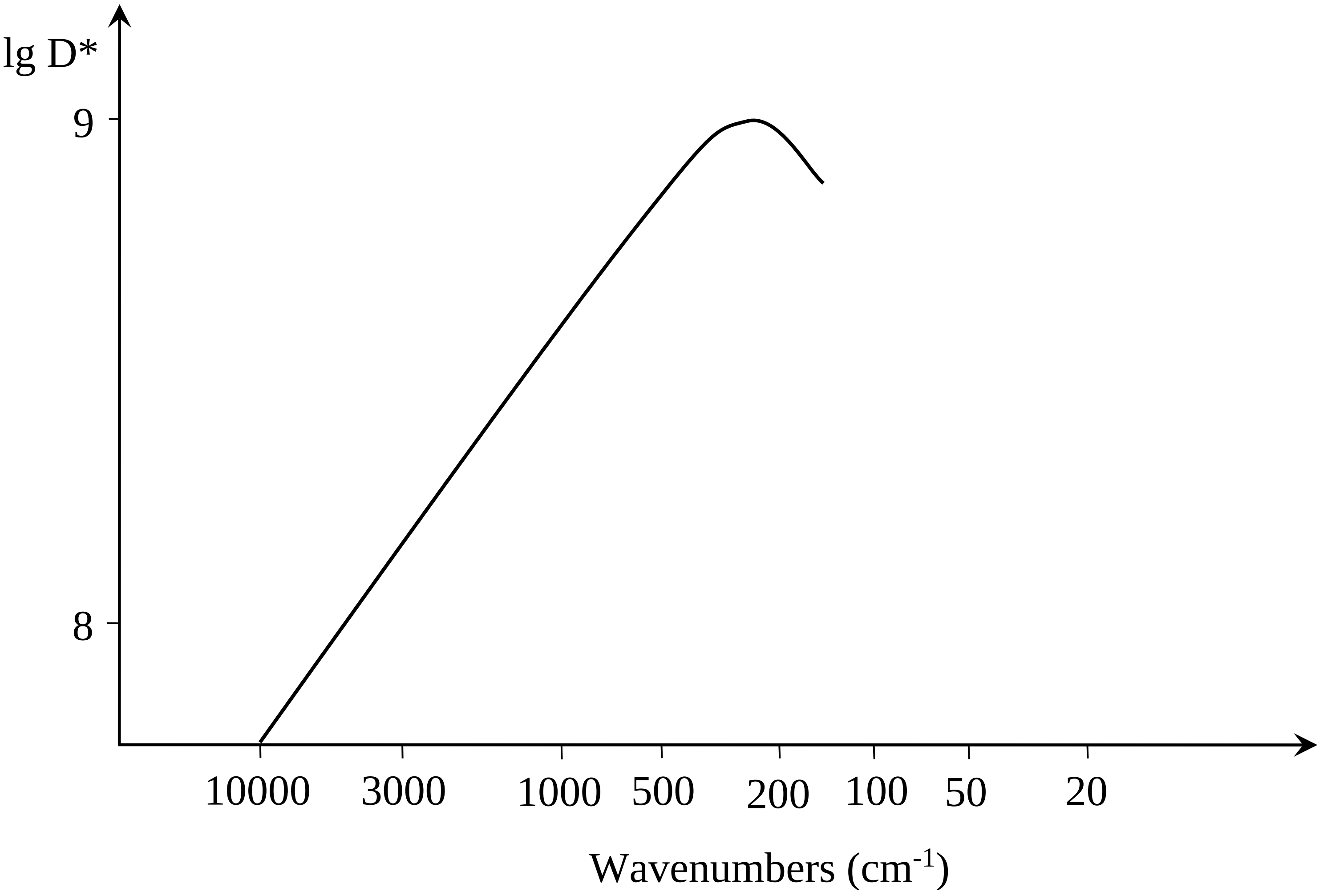
SOURCE

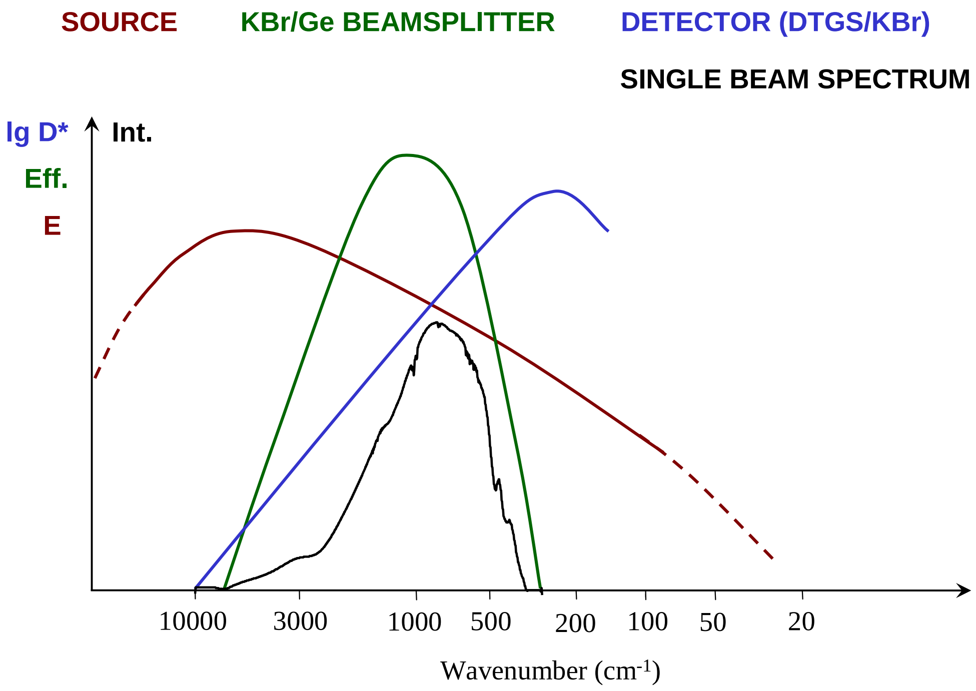

10
10
Energy
10
10
1000
3000
1000
500
200
100
50
20
Wavenumbers

KBr/Ge BEAMSPLITTER



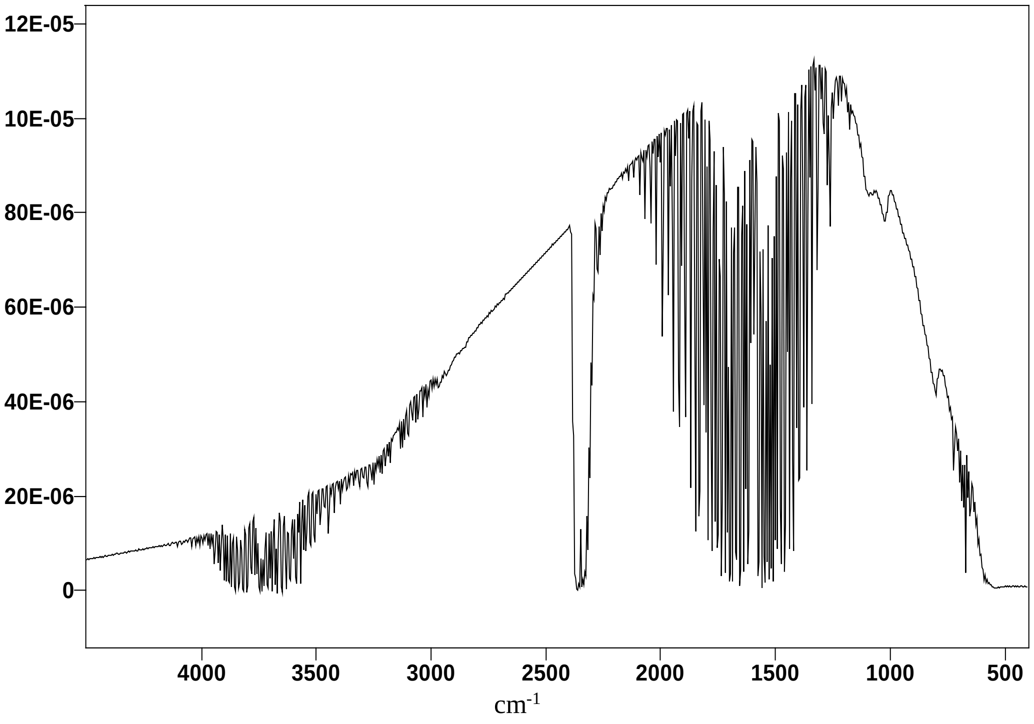
DETECTOR (DTGS/KBr)



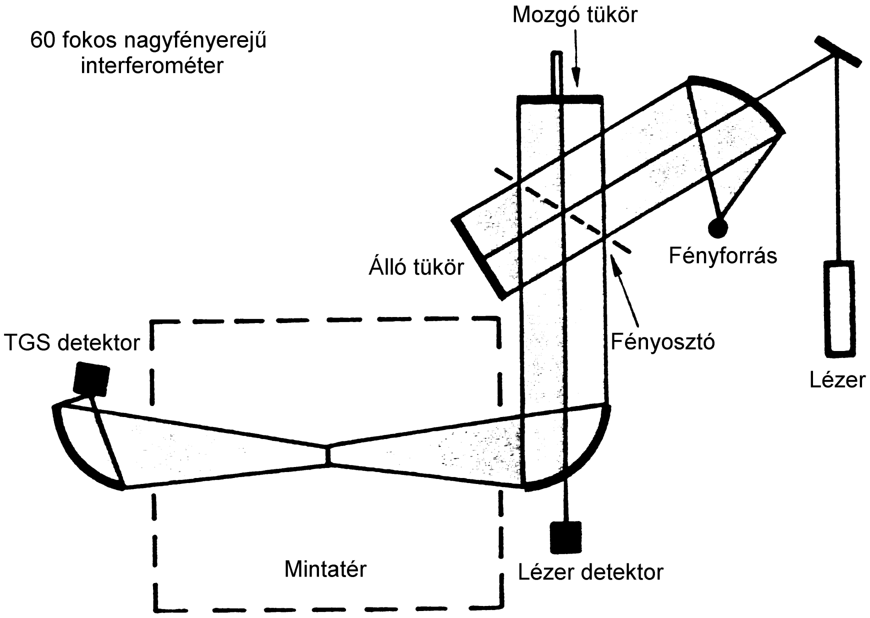


2nd NanoCat Weekend Workshop,
December 15-16, 2007, Munich

A + B + C

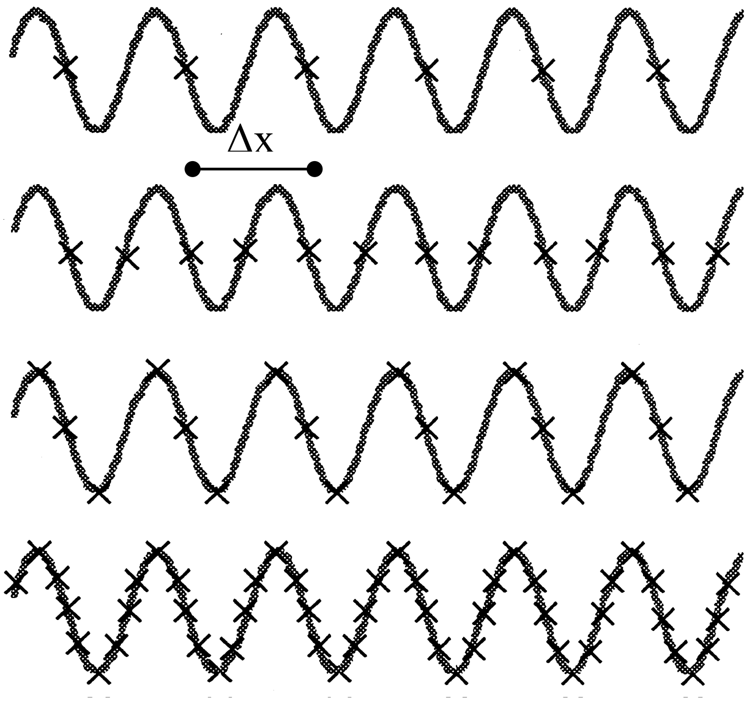


4. ROLE OF THE HE-NE LASER


60 fokos nagyfényerejű interferométer
Mozgó tükör
Álló tükör
Fényforrás
Fényosztó
Lézer
TGS detektor
Mintatér
Lézer detektor

A 60° Michelson interferometer

SAMPLING → He-Ne interference



Range:

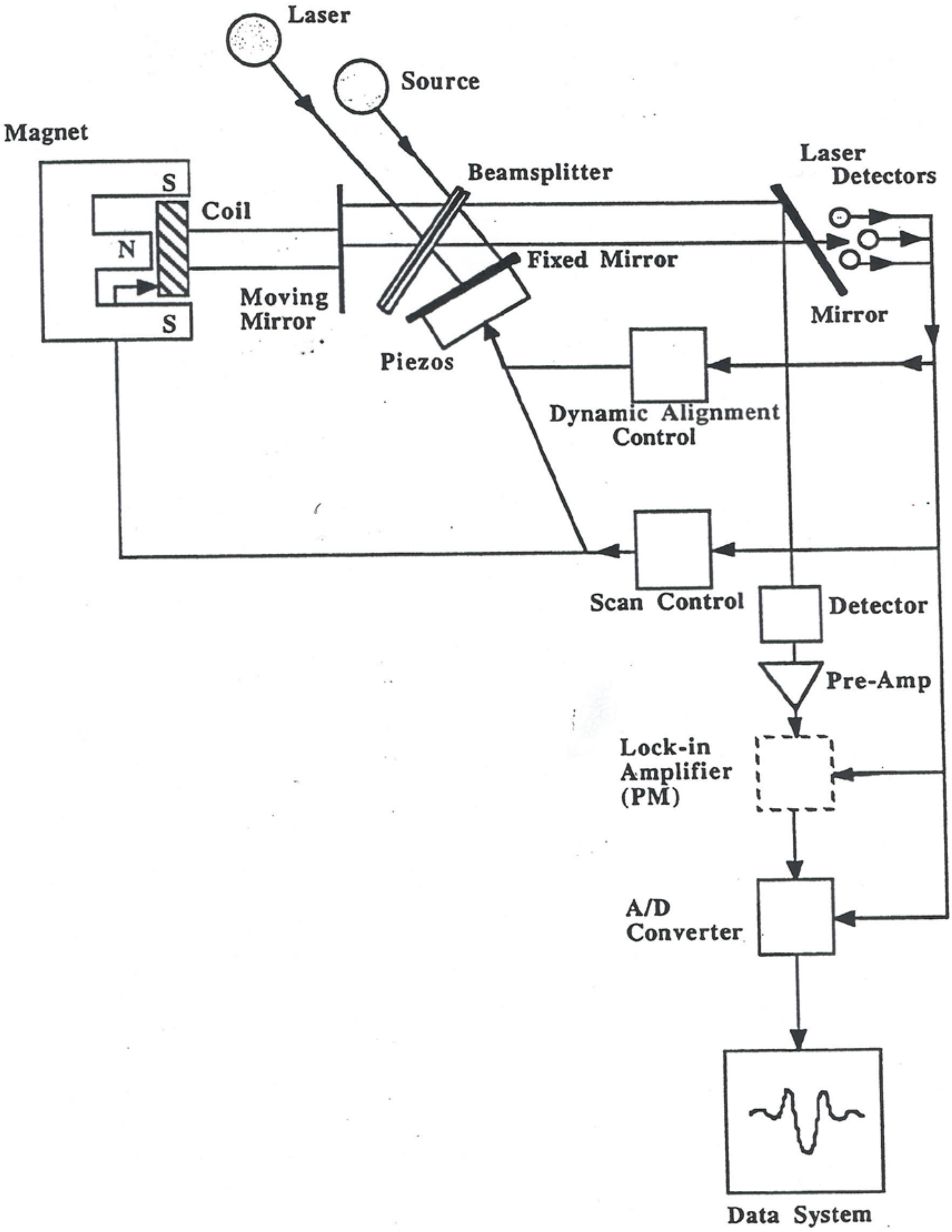
0-7900 cm^{-1}

0-15800 cm^{-1}

0-31600 cm^{-1}

0-63200cm^{-1}

5. DYNAMIC ALIGNMENT

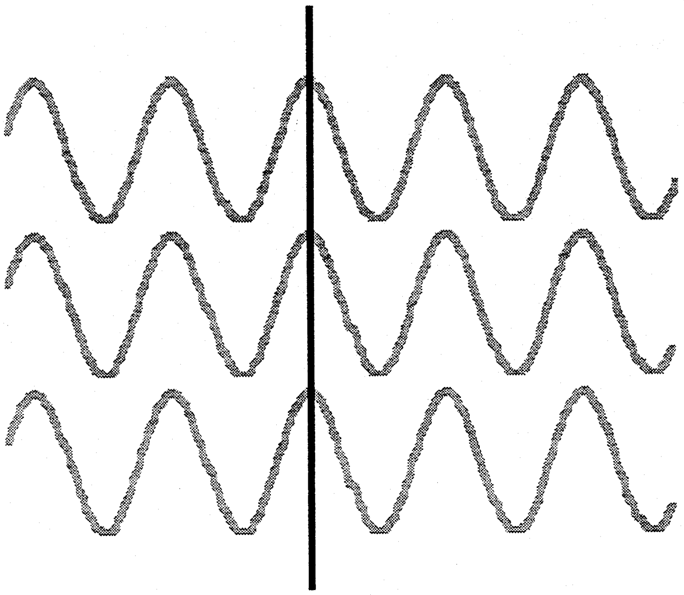

Laser
Source
Magnet
Beamsplitter
Laser
Detectors
S
Coil
N
Fixed Mirror
Moving
Mirror
S
Mirror
Piezos
Dynamic Alignment
Control
Scan Control
Detector
Pre-Amp
Lock-in
Amplifier
(PM)
A/D
Converter
Data System

A simplified diagram of the interferometer control and signal processing electronics. The piezoelectric actuators are used for dynamic alignment and as part of the scan control.

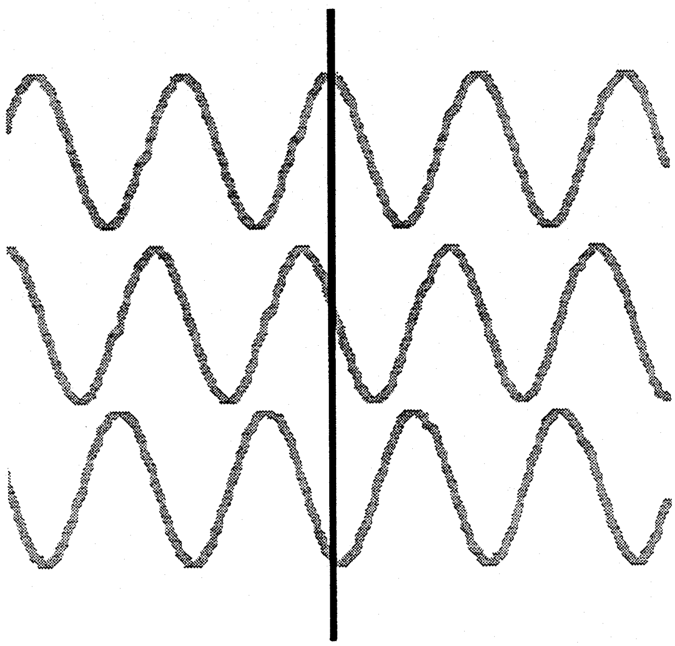
Principles of Dynamic Alignment

Signals of the three red detectors

a.) Properly aligned



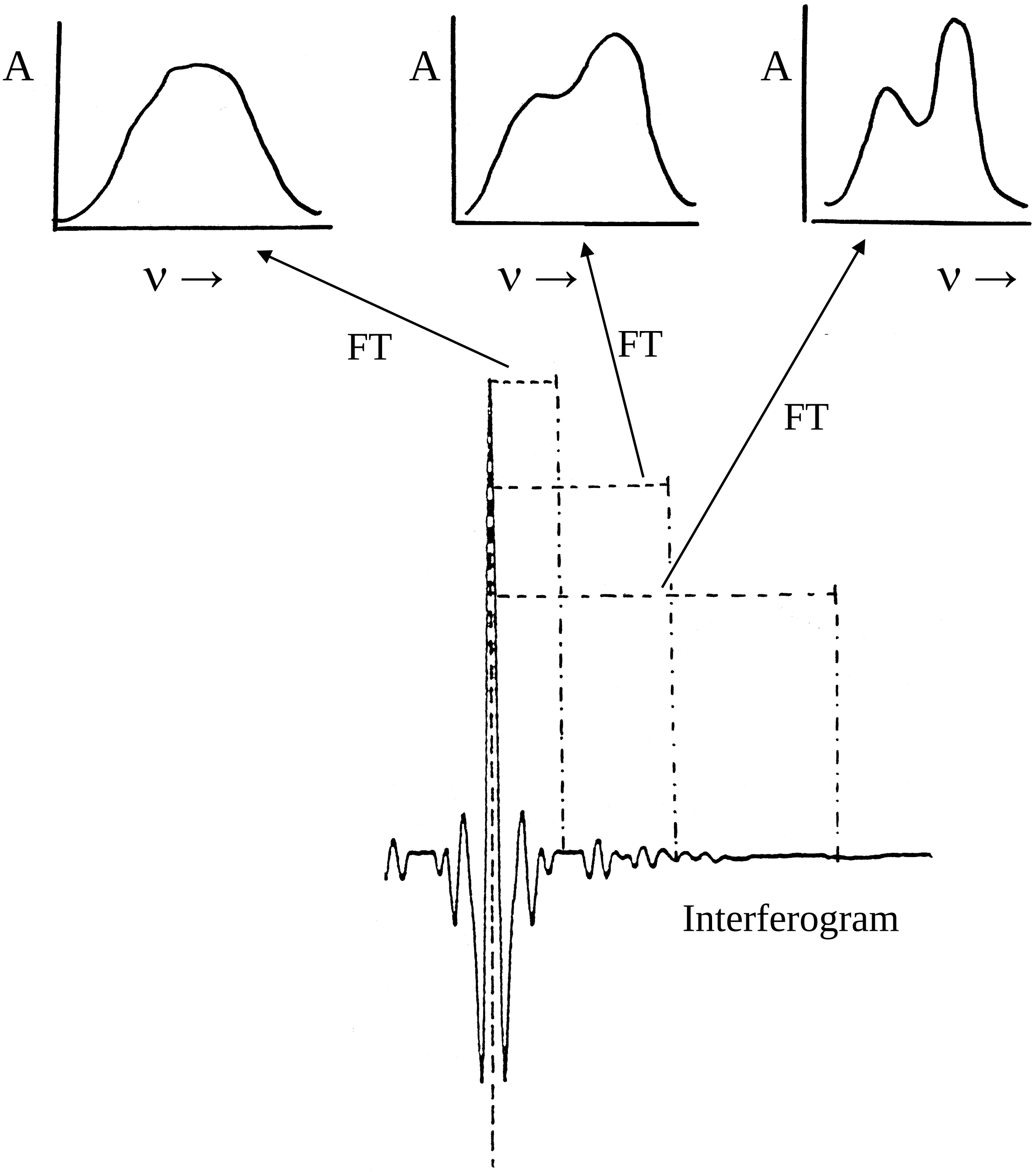
b.) Improper alignment



6. RESOLUTION

RES =
2Δx – path difference
Δx – retardation (cm)

Spectra of different resolutions


A
A
A
ν →
ν →
ν →
FT
FT
FT
Interferogram

Resolution

- Separate different wavelength in the spectrum
- High resolution: - exact location of narrow bands
  - reduces spectral overlap
- "Infinite" resolution: no deviation from L.-B.'s law in wide concentration range.

Theoretical

$$\mathrm{Res}(\Delta\nu) = \frac{1}{2\Delta x}$$

Practical

$$\mathrm{Res}(\Delta\nu) \approx \frac{1.3}{2\Delta x}$$

Δx – The maximum optical path difference in the interferometer.
In all spectral range is the same!

	Maximum Resolution (cm^{-1})
Routine spectrometer	1-2
Advanced	0.1
Special	0.01
Very special	0.001 and lower (not commercial)

For condensed phase Res = 4-8 cm^{-1} is fine.

7. Spectrometer performance influencing the throughput

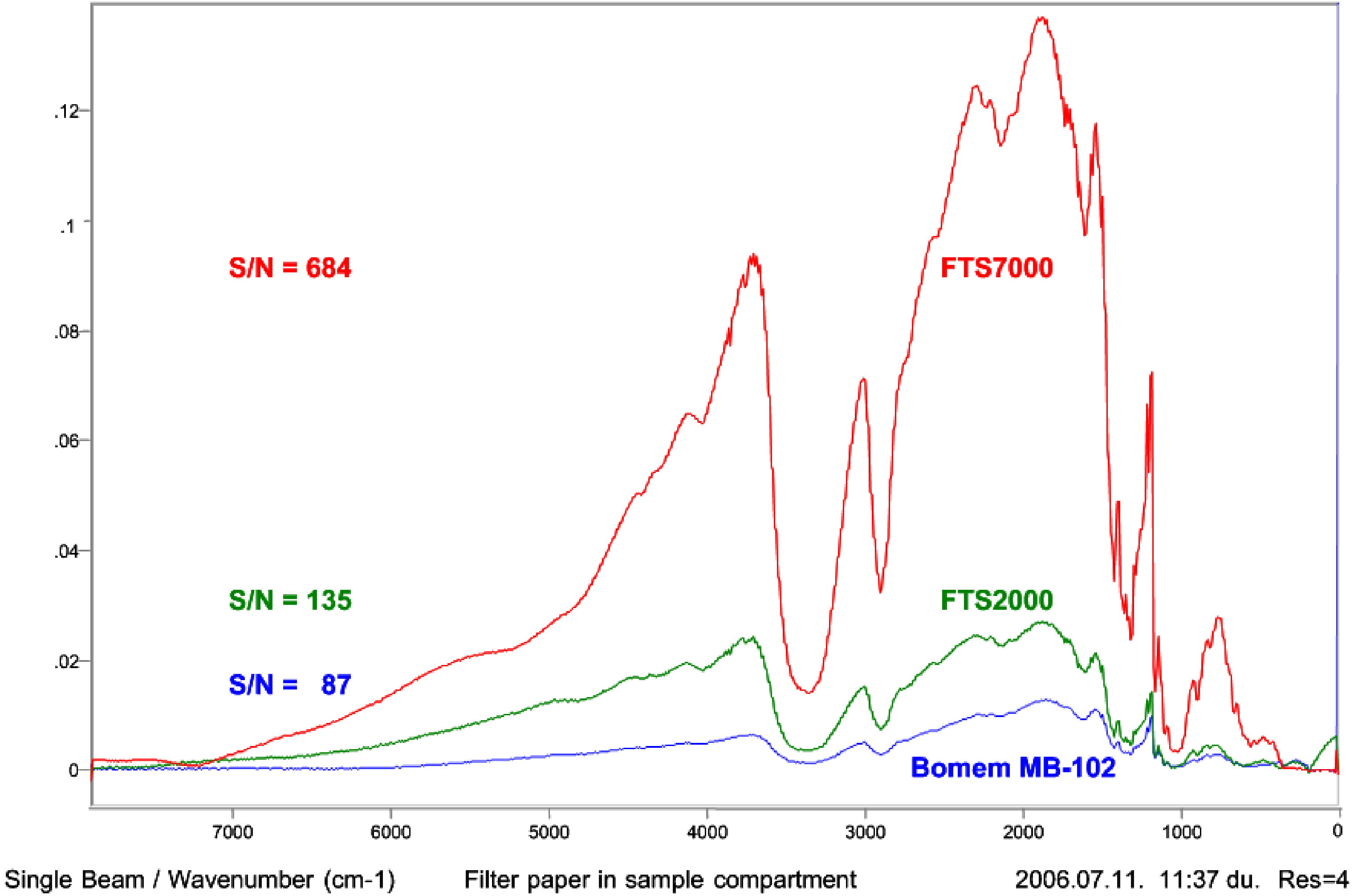
Parameters	**Interferometer "A"**	**Interferometer "B"**	**Ratio**[a]
Beam size (diameter)	1" (4.91 cm^2) (1)	2" (19.6 cm^2)	~ 4
Number and type of mirrors	14[b] (Al), R%= 0.652	3(Au), R%= 0.97	1.49
Source intensity	80 w (1)	180 w	2.25
Aspherical source mirror	1	~ 1.3	~ 1.3
Dynamic alignment	1	~ 3	~ 3
Sum of the relative values	5		12
Averaged values	1		2.4

Remarks:

[a] parameters of spectrometer "A" taken as unit

[b] The two interferometer mirrors are not counted

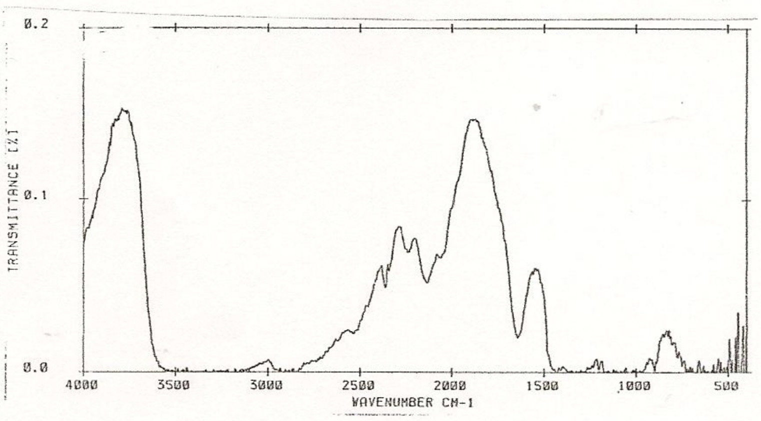
“Filter paper test”



Signal to Noise Ratio:

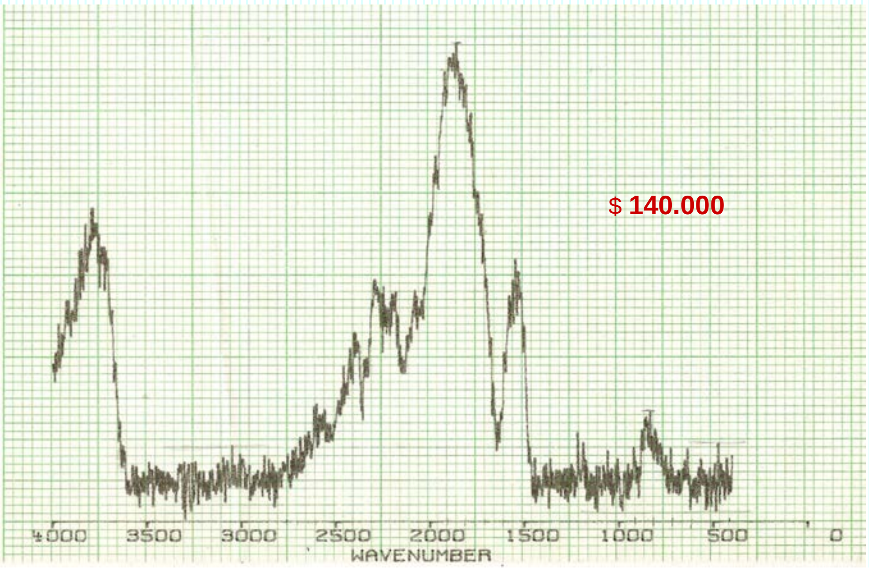
Max intensity at 1855-1880 cm^{-1}/ Noise at 3400 cm^{-1}

Research grade spectrometer

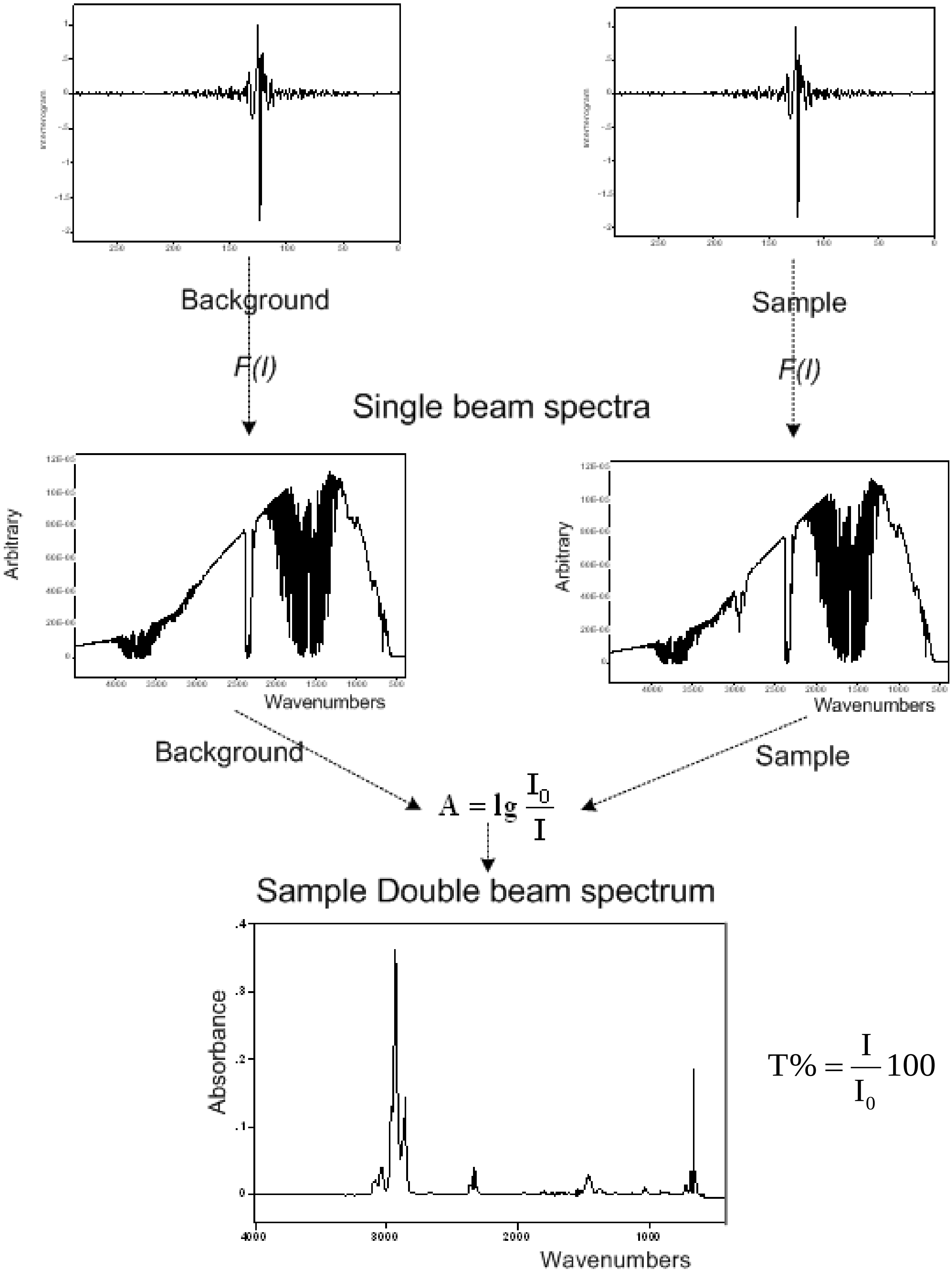


$

Research grade spectrometer



$ **140.000**

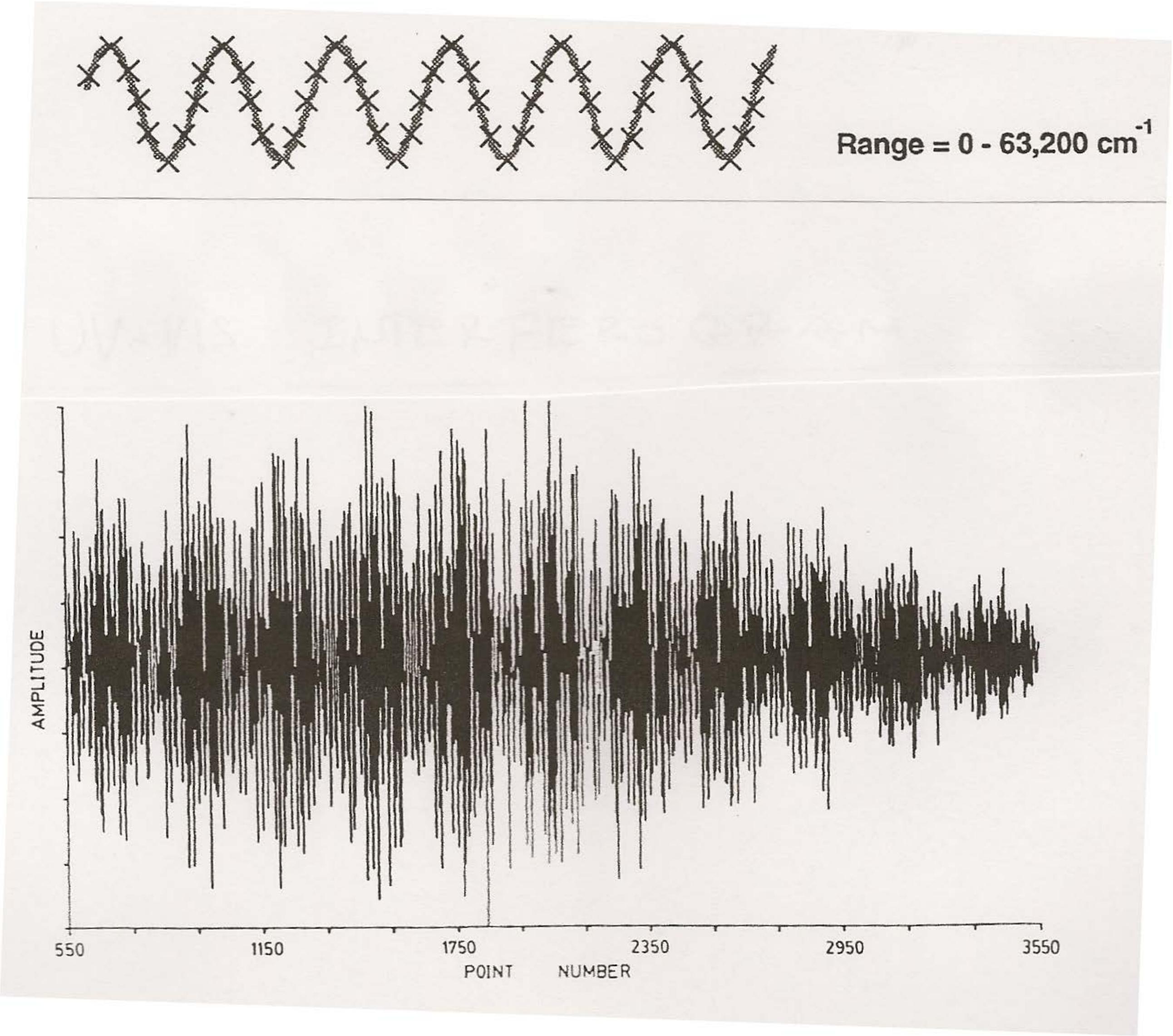


Interferogram
1
.5
0
-.5
-1
-1.5
-2
250
200
150
100
50
0
Background
Sample
F(I)
F(I)
Single beam spectra
Arbitrary
Wavenumbers
Arbitrary
Wavenumbers
Background
Sample
$A = \lg \frac{I_0}{I}$
Sample Double beam spectrum
Absorbance
.4
.3
.2
.1
0
4000
3000
2000
1000
Wavenumbers

$$T\% = \frac{I}{I_0} 100$$

How to produce double beam spectrum

2.3. UV-Visible Fourier spectroscopy.



Sampling intervals (upper trace) and typical UV/VIS interferogram (lower trace) recorded with a dynamically aligned interferometer (source: Xe lamp, TiO2/quartz beamsplitter and PM-detector)

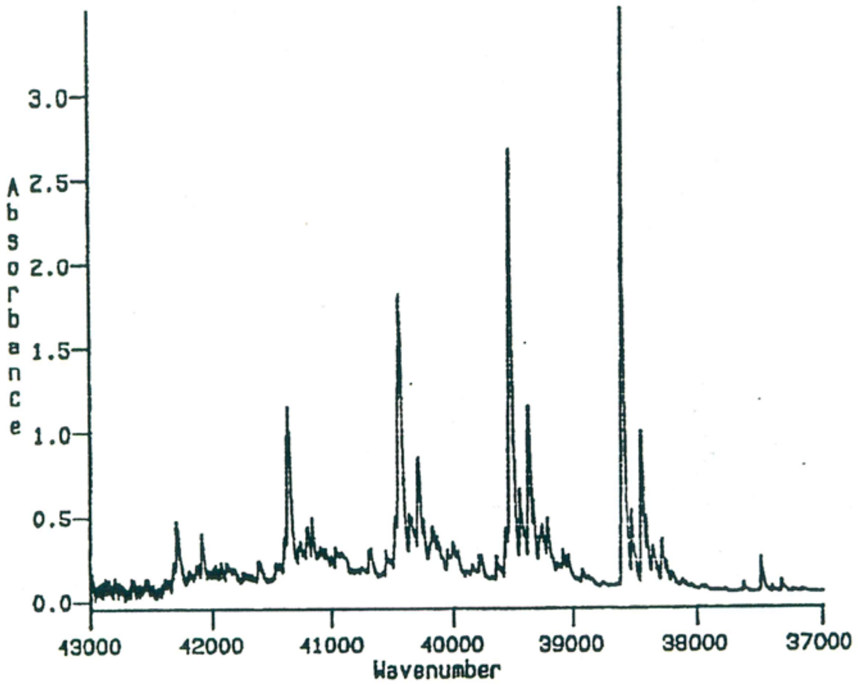
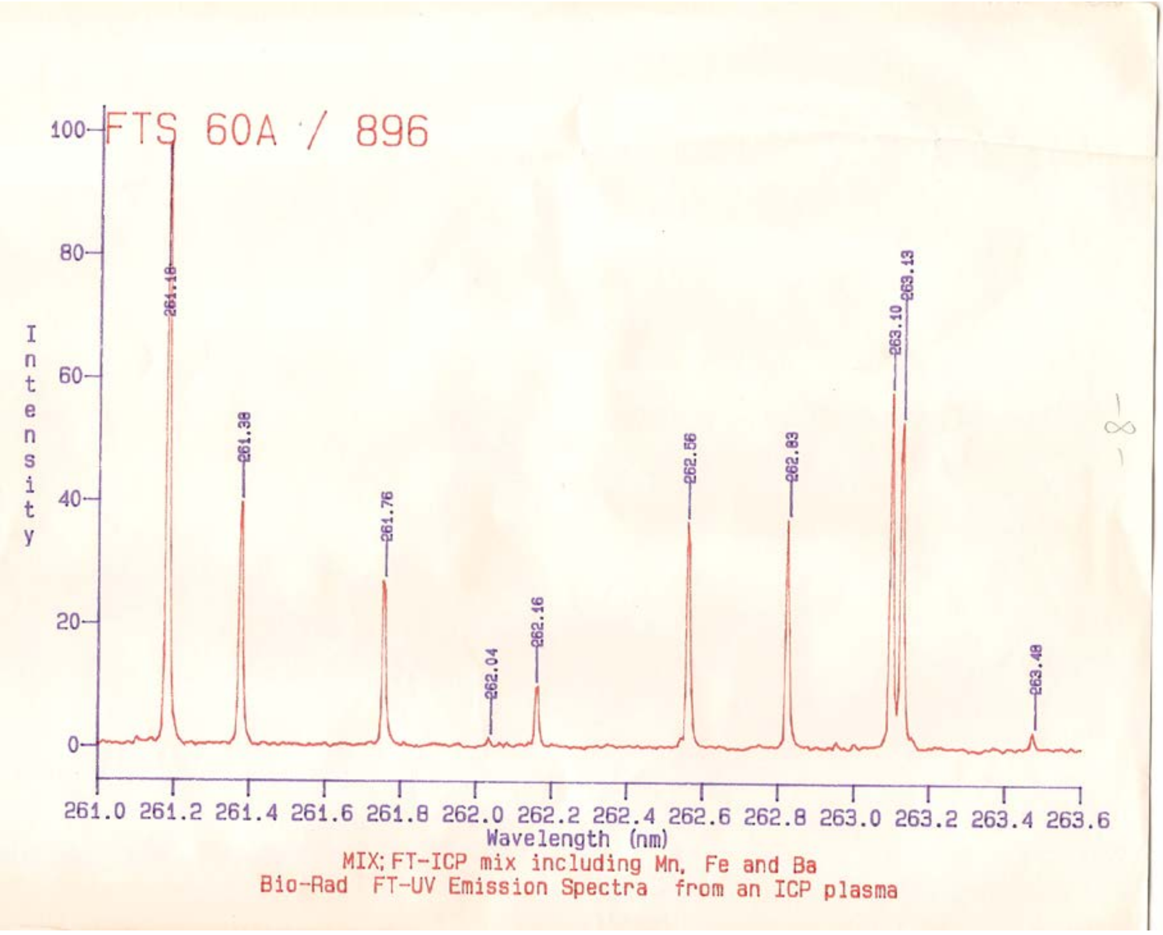


Figure 6-6. FT-UV spectrum of benzene vapor in 1 mm quartz cell.



ICP atomic emission spectrum containing Mn, Fe, and Ba elements recorded by FT-UV spectrometer

2.4. Far-infrared (FIR) spectroscopy.

Different from NIR and MIR:

- nature of the instrumentation (gratings, detectors, sources or beamsplitters, etc.)
- types of transitions

1962, Commission for spectroscopy (*J. Opt. Soc. Am.* **5**2, (1962) 476.)

MIR: 4000-200 cm^{-1} (Gratings)

FIR: below 200 cm^{-1}

1970, KBr supported Ge-beamsplitters ~350 cm^{-1} limit

CsI ~180 cm^{-1} limit

FT-technique: 4000-400 cm^{-1} MIR

$$\left.\begin{array}{l}400\text{-}10\ \text{cm}^{-1}\\ 25\text{-}1000\ \mu\text{m}\end{array}\right\}\ \text{FIR}$$

below MW

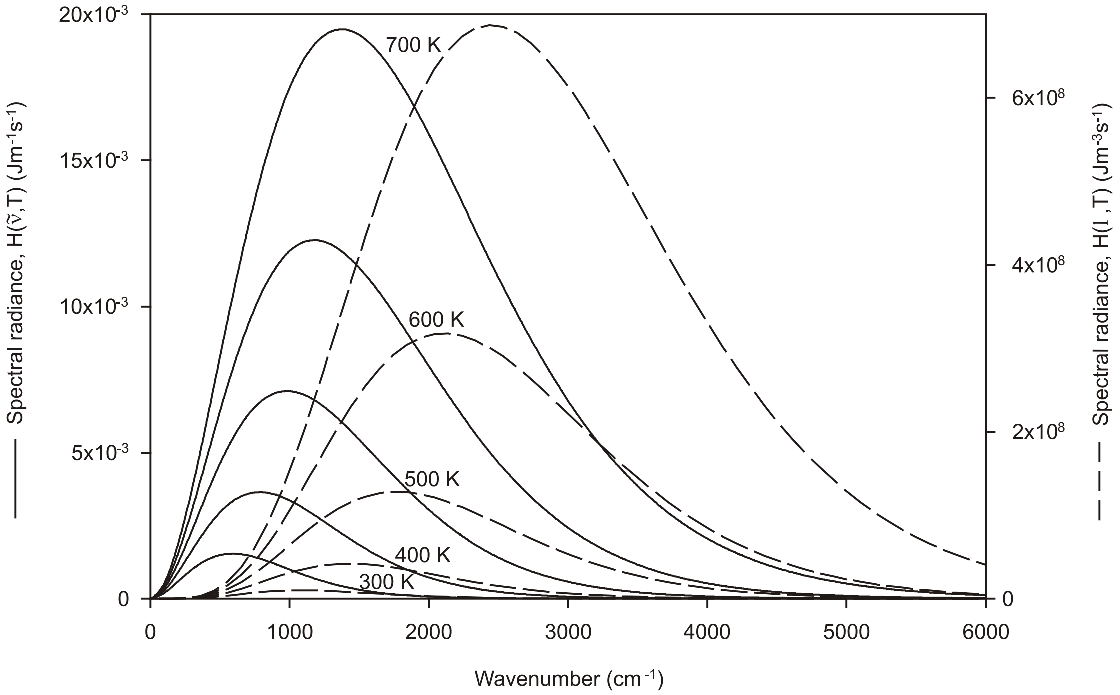
$$\boxed{\boldsymbol{\lambda = 1\ \text{mm} \qquad \nu = 10\ \text{cm}^{-1}}}$$

BASIC COMPONENTS OF FIR SPECTROMETERS

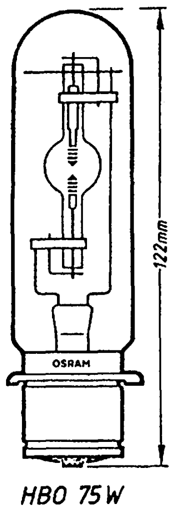
1. Sources:
Nernst
Globar
Hg-lamp

Radiation energy problems in FIR region:

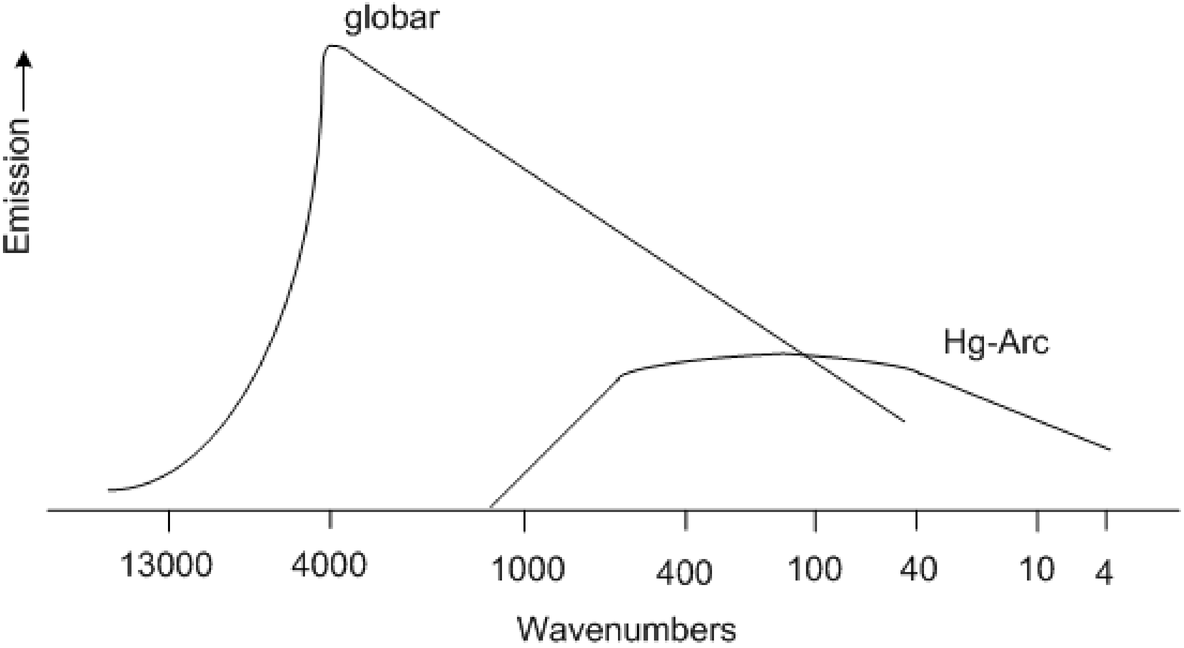
Blackbody (source) radiation



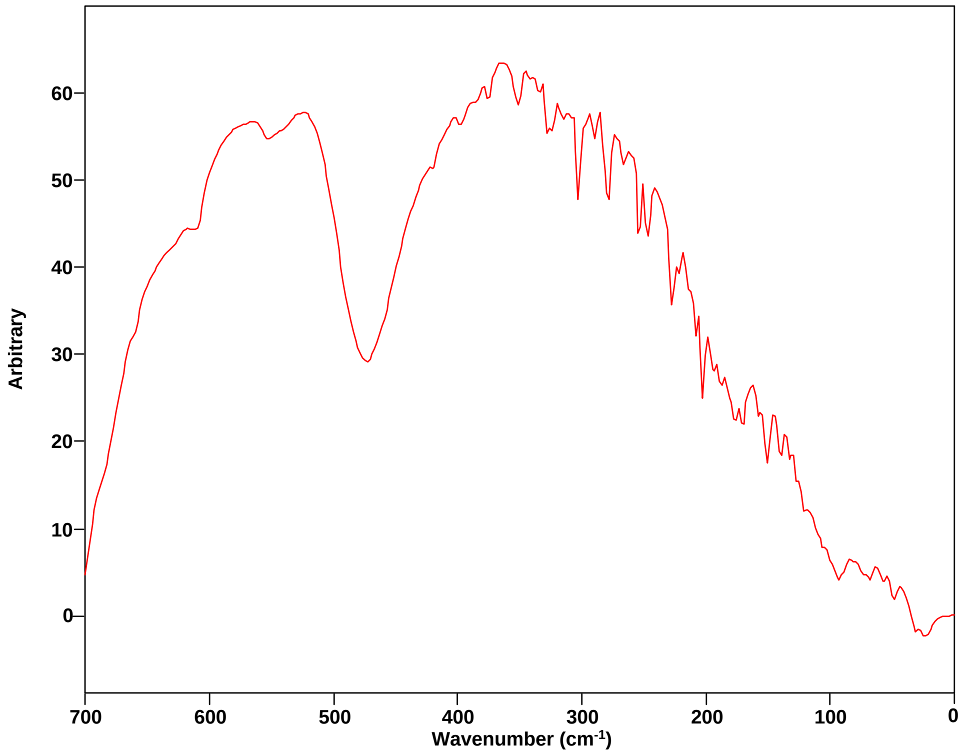
Special radiant emittance of a blackbody at various temperatures



High pressure mercury lamp used as FIR source

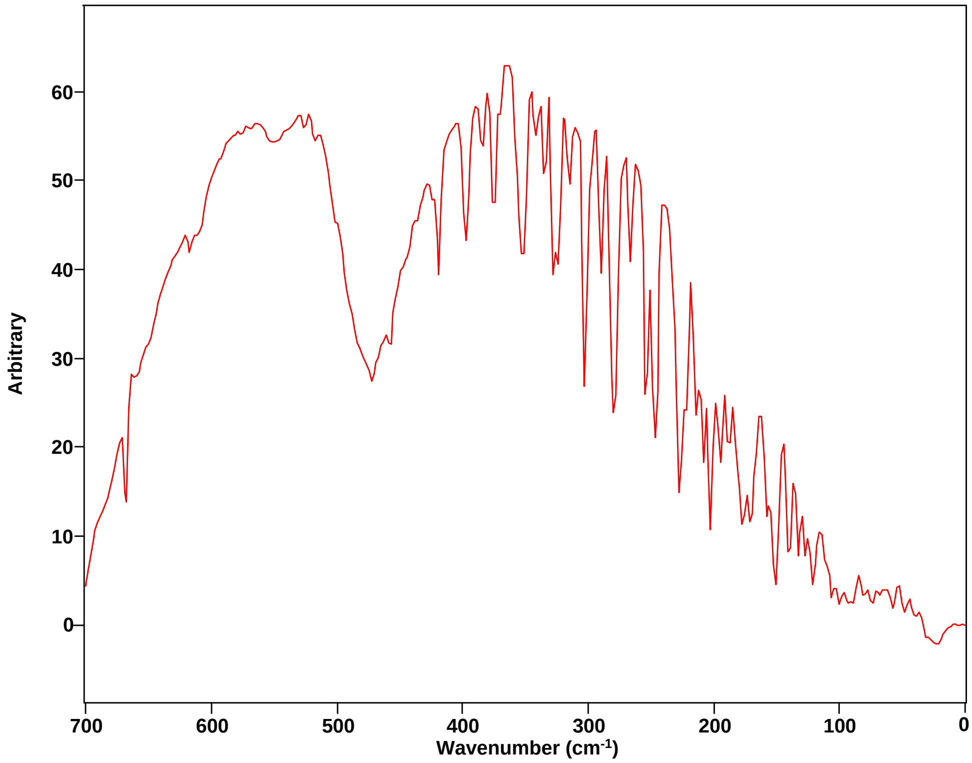

globar
Emission
Hg-Arc
13000
4000
1000
400
100
40
10
4
Wavenumbers

Purged:



Empty (closed) sample compartment single beam spectrum

Unpurged:



Empty (open) sample compartment single beam spectrum

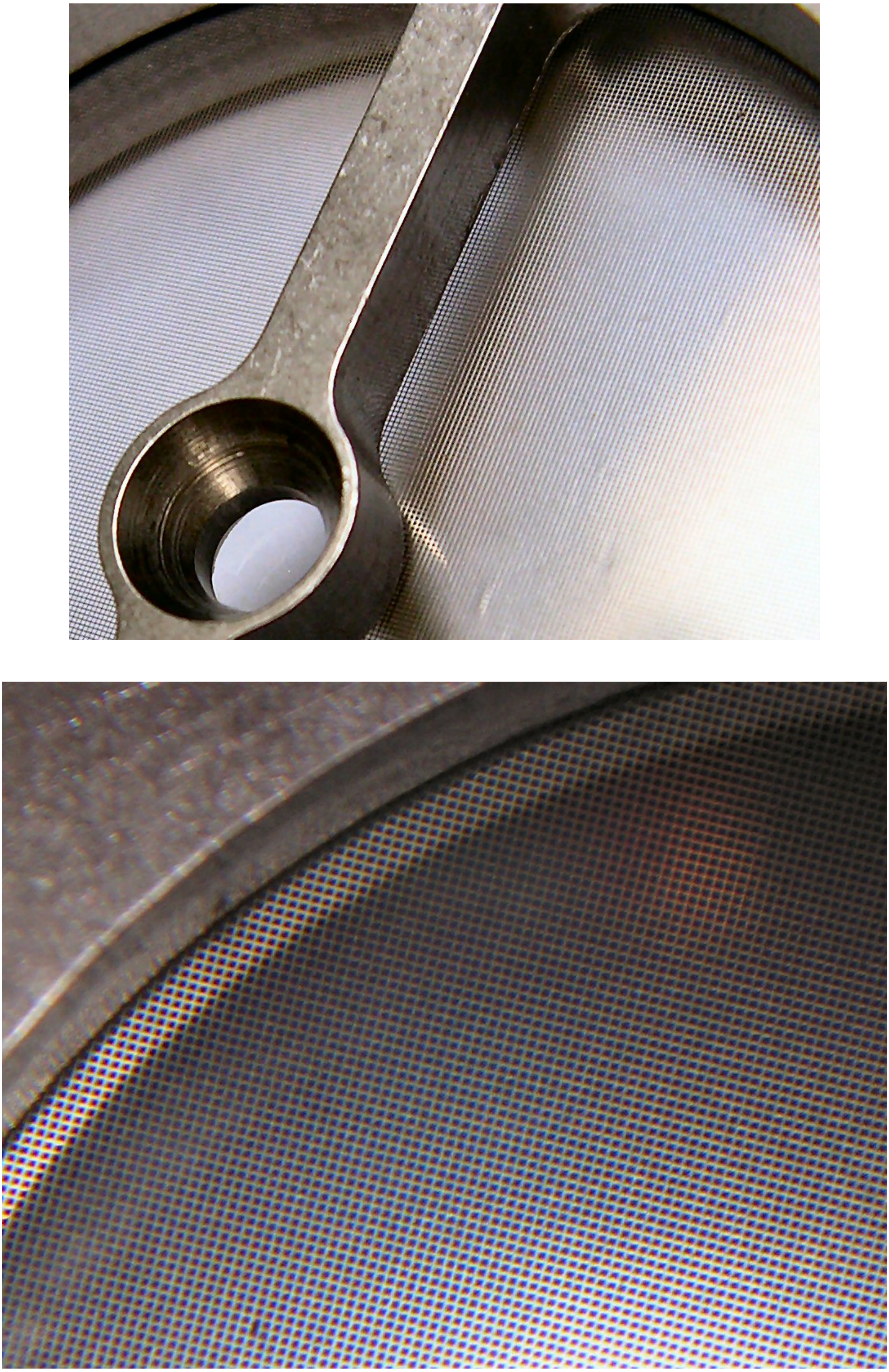
Source: Hg-lamp; Beamsplitter: Wire mesh; Resolution: 4 cm^{-1}

2. Beamsplitters

Already discussed (Mylar beamsplitters)

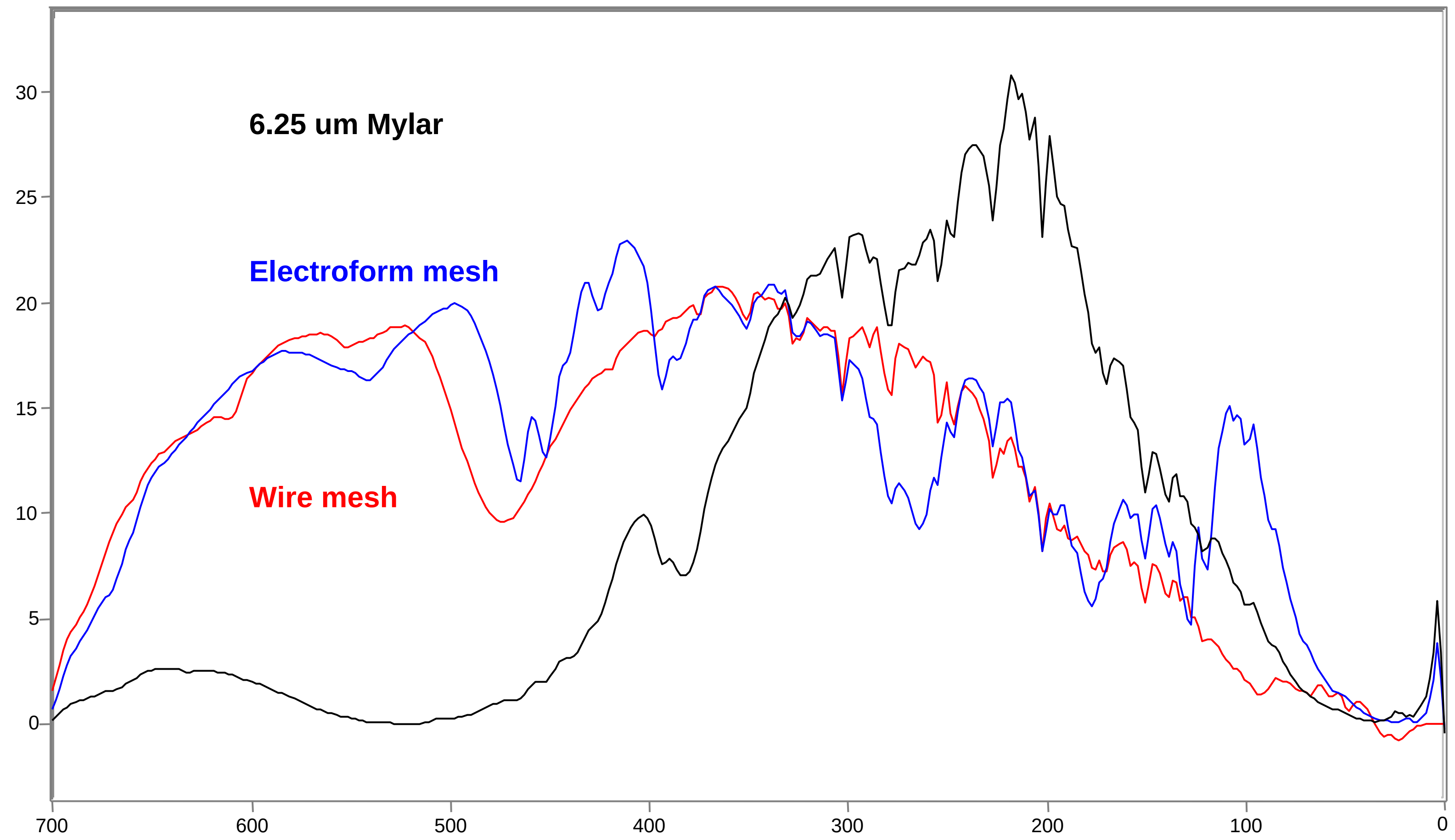
Special beamsplitters:

- Si-based (Nicolet)
- Metal mesh, 300 lines/inch
- Electroform mesh



Picture of metal mesh beamsplitter

FAR-IR BEAMSPLITTERS



Single Beam / Wavenumber (cm-1)

File # 3 = MYLAR

6.25 Mylar with PEI

2006.07.12. 9:50 du. Res=4

3. DETECTORS

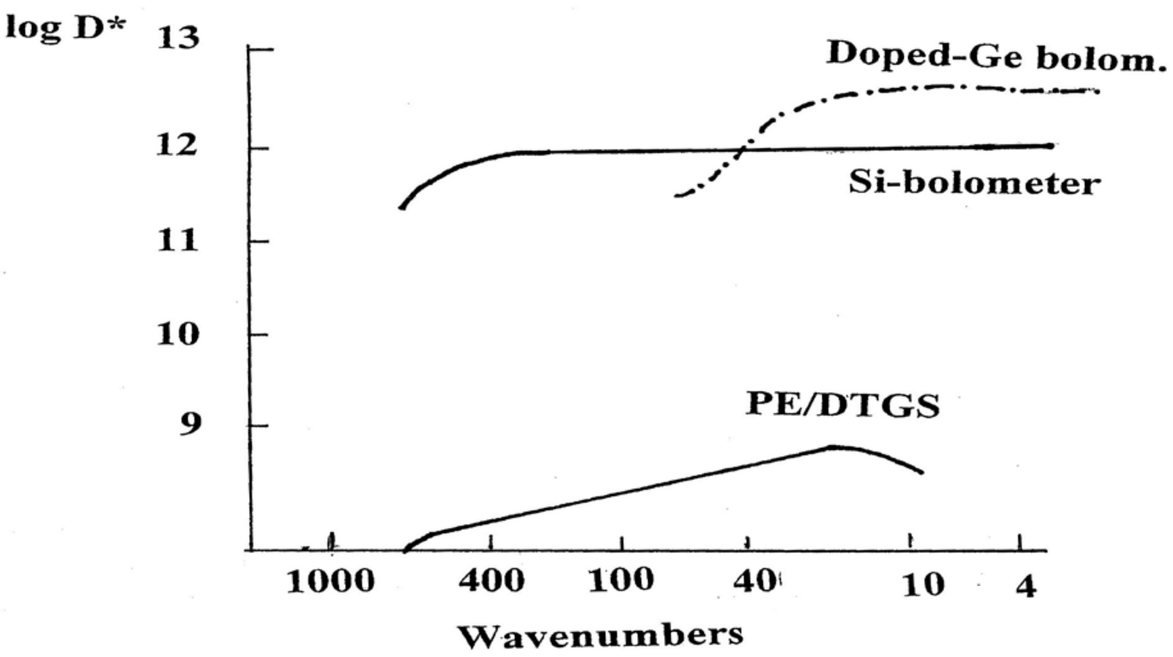
- Pneumatic (Golay)
  Universal, in FIR w. diamond window

- Pyreelectric, TGS, DTGS
  With polyethylene window

- Si-bolometer

- Doped- Ge-bolometer

Sensitivity (detectivity, D*) of FIR detectors:



$D^* = 1/\Phi_N\,(A \times \Delta f)^{1/2}$ $[W^{-1}\ cm\ s^{-1/2}] = [W^{-1}\ cm\ Hz^{1/2}]$ (Detectivity)

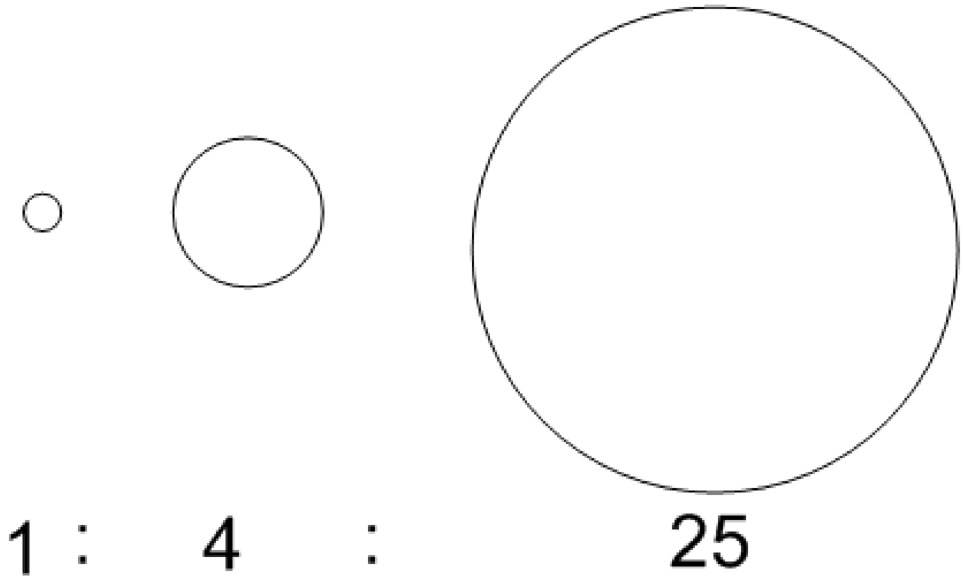
Φ_N - Noise equivalent power (NEP)

A - Sensitive area of the detector element

Δf - Bandwidth of the measurement

CRITICAL POINTS OF FIR SPECTROMETRY

- Weak source energy (Hg-lamp, synchrotron),
- Beam sizes (1, 2, 5 inches),
- Vibrations of Mylar beamsplitters,
- Rotational lines of water vapour,
- Strong absorption of liquid water,
- Strong absorption of polar solvents,
- Etc.



Beam sizes (1, 2, 5, inches)

2.5. Calibration of FTIR spectrometers

- Great importance in dispersive systems.
- FT-instrument: He-Ne laser, internal standard, λ = 632.8 nm, ν= 15802.8 cm^{-1}

Importance of calibration

- wavenumber agreement with other instruments,
- Agreement with Raman spectra,
- Detection of small frequency differences:
  weak dimerisation (associations)
  intermolecular lattice interaction,
  weak complexation
  small isotope shifts
  etc.

References:
[1] Pure and Applied Chemistry, Vol. 1,№4, 537-699 (1961)
[2] A. R. H. Cole: Tables of wavenumbers for the calibration of infrared spectrometers, Second edition, IUPAC, Pergamon Press (1977)

Summary of data for Charts 1–39
(All vapour phase spectra are measured at 10 cm path length)

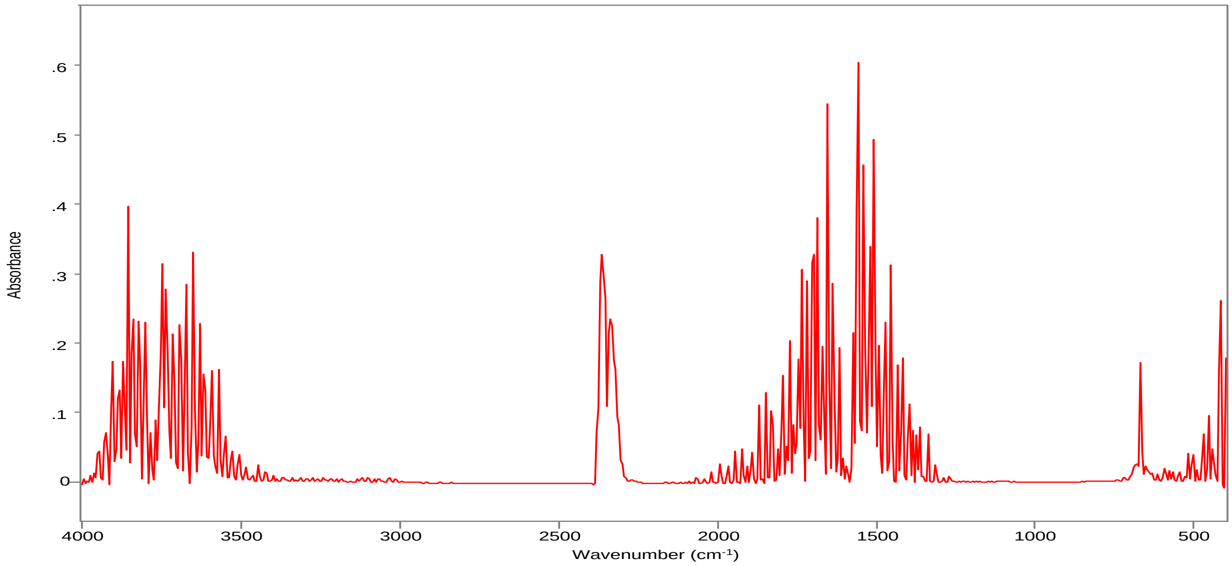
Substance	*Region* (cm^{-1})	*Pressure* (mm)
Water vapour	3943–3744	sat.
Carbon dioxide	3737–3683	200
”	3681–3591	400
”	3608–3569	200
Ammonia	3540–3491	300
”	3509–3394	75
Hydrogen cyanide	3399–3381	450
”	3378–3245	20
”	3231–3207	450
Methane	3183–3158	300
”	3149–2958	60
Hydrogen chloride	3045–2624	120
Hydrogen bromide	2710–2393	140
Carbon dioxide	2386–2298	20
”	2311–2292	50
”	2282–2236	250
Carbon monoxide	2233–2055	150
Deuterium chloride	2047–1894	250
Water vapour	1943–1374	sat.
Deuterium bromide	1909–1727	60
Ammonia	1613–1580	75
Methane	1368–1266	60
”	1260–1212	250
Ammonia	1213– 972	50
”	967– 962	15
”	960– 934	50
”	927– 924	15
”	921– 771	50
”	761– 745	75
Hydrogen cyanide	786– 635	30
Acetylene	720– 694	15
Carbon dioxide	702– 632	70
Nitrous oxide	630– 593	300
Deuterium cyanide	630– 591	60
Indene	3929– 693	*
Polystyrene	3082– 699	†

* Liquid films of thickness 200 μ and 30 μ.
† Solid films of thickness 70 μ and 7 μ.

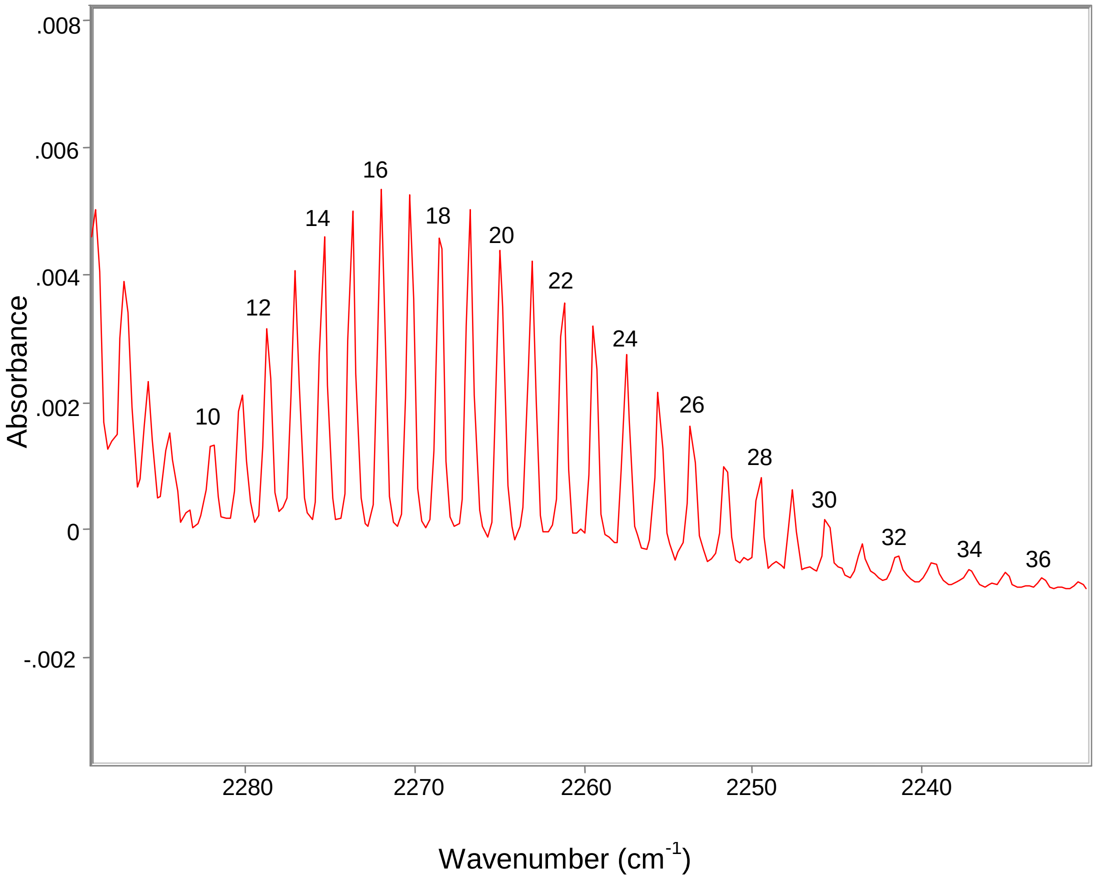
2.5.1. Calibration of FT-MIR spectrometers

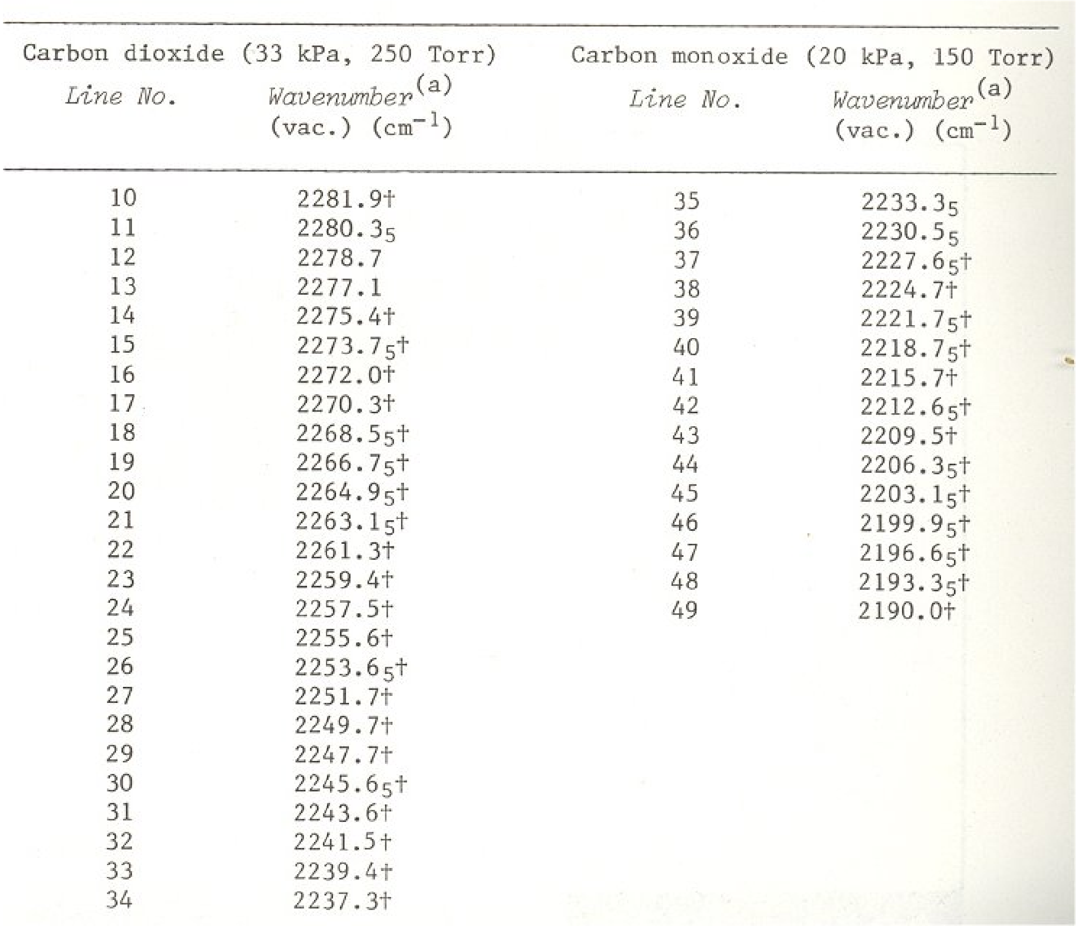
Spectral ranges of rotational-vibrational bands used for calibration

Gases		Range (cm^{-1})		
		From		To
CO_2	overtones	3750	-	3560
H_2O	OH stretching	3950	-	3500
$^{12}CO_2$	asym. stretch	2390	-	2290
$^{13}CO_2$	asym. stretch	2280	-	2230
H_2O	scissoring	1950	-	1300
CO_2	deformation	710	-	630
H_2O	pure rotation	600	-	10

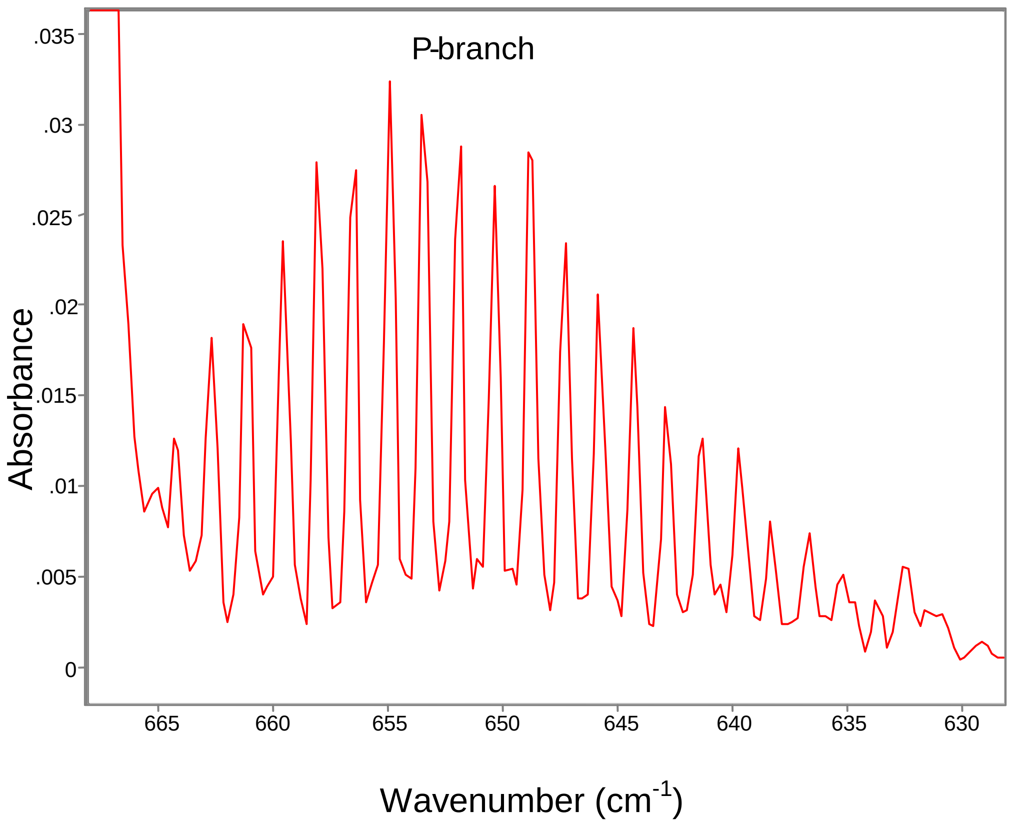


Empty sample compartment (open) absorbance spectrum (H_2O and CO_2)Carbon dioxide (rotational fine structure)





Carbon dioxide (33 kPa, 250 Torr)		Carbon monoxide (20 kPa, 150 Torr)	
Line No.	*Wavenumber*$^{(a)}$ (vac.) (cm^{-1})	*Line No.*	*Wavenumber*$^{(a)}$ (vac.) (cm^{-1})
10	2281.9†	35	2233.3_5
11	2280.3_5	36	2230.5_5
12	2278.7	37	2227.6_5†
13	2277.1	38	2224.7†
14	2275.4†	39	2221.7_5†
15	2273.7_5†	40	2218.7_5†
16	2272.0†	41	2215.7†
17	2270.3†	42	2212.6_5†
18	2268.5_5†	43	2209.5†
19	2266.7_5†	44	2206.3_5†
20	2264.9_5†	45	2203.1_5†
21	2263.1_5†	46	2199.9_5†
22	2261.3†	47	2196.6_5†
23	2259.4†	48	2193.3_5†
24	2257.5†	49	2190.0†
25	2255.6†		
26	2253.6_5†		
27	2251.7†		
28	2249.7†		
29	2247.7†		
30	2245.6_5†		
31	2243.6†		
32	2241.5†		
33	2239.4†		
34	2237.3†		

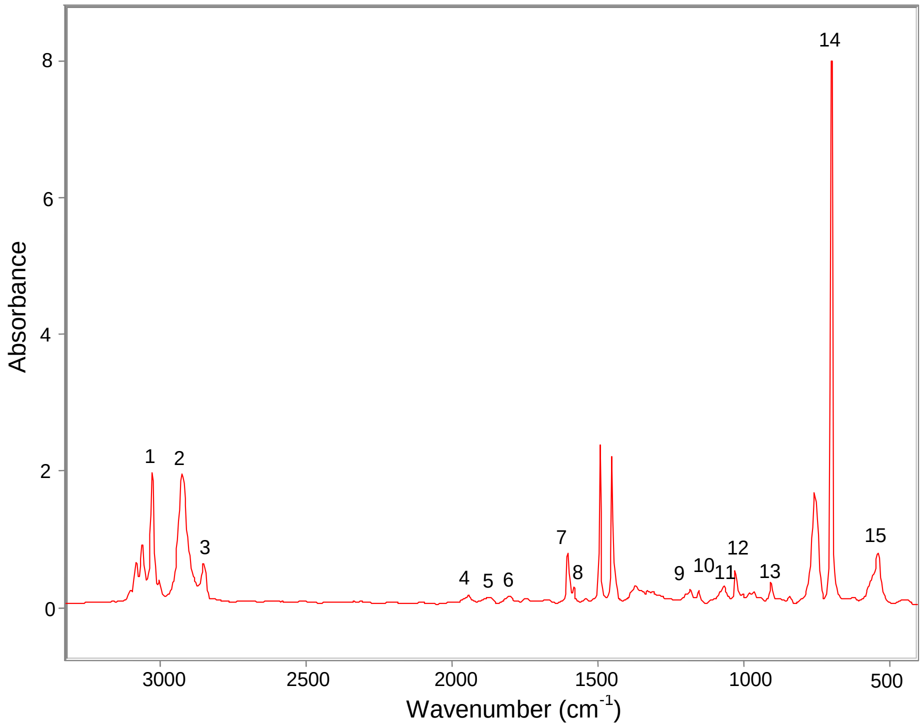


Polystyrene (solid film): 3350-400 cm^{-1}

Band No.	Wavenumber (cm^{-1})	Relative intensities
1	3027.1 ± 0.3	47
2	2924 ± 2	51
3	2850.7 ± 0.3	16
4	1944.0 ± 1	4
5	1871.0 ± 0.3	3
6	1801.6 ± 0.3	3
7	1601.4 ± 0.3	19
8	1583.1 ± 0.3	6
9	1181.4 ± 0.3	5
10	1154.3 ± 0.3	4
11	1069.1 ± 0.3	6
12	1028.0 ± 0.3	12
13	906.7 ± 0.3	8
14	698.9 ± 0.5	100
15	539.0 ± 0.5	20

Films from commercial sources of polystyrene frequently exhibit strong interference patterns; such films should be slightly bent or otherwise deformed before using for calibration purposes.

Ref.: IUPAC tables for the calibration of infrared spectrometers, Butterworths, Washington, D.C., 1961.

IR spectrum of polystyrene film: