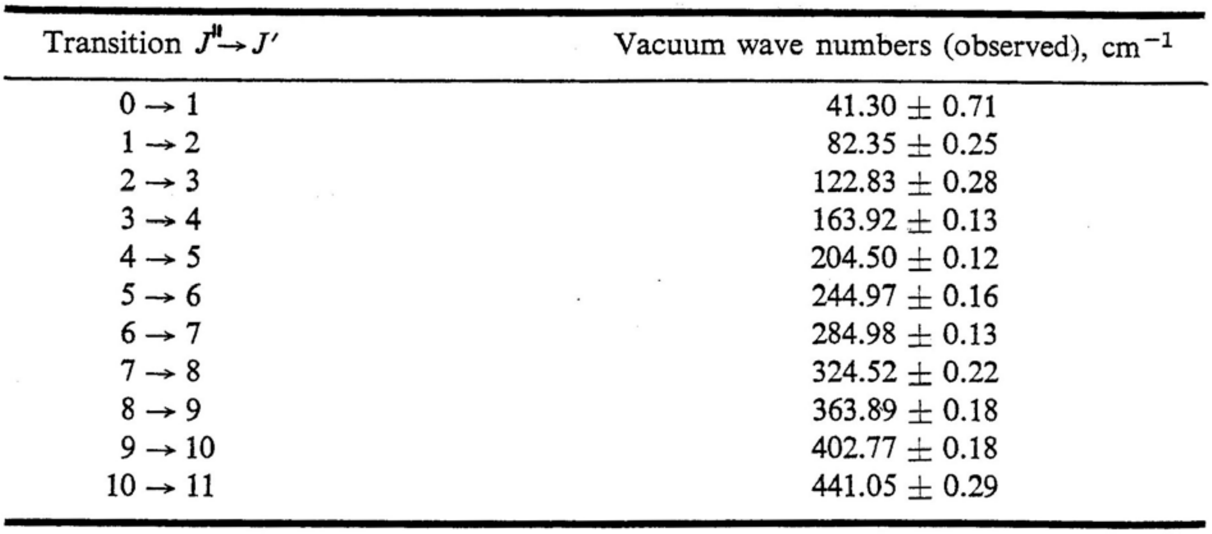
2.5.2. Calibration of FT-FIR spectrometers

Rotational spectra of gases

. A number of gases can be used, such as HCl, HBr, DBr, HI, CO, HF, HCN, N_2O, NH_3, and H_2O. Wavelength calibrations from 30 to 1000 μ using HCN, CO, N_2O and H_2O vapour have been cited by Rao et. al.[9]

Observed transitions for rotational spectrum of HF

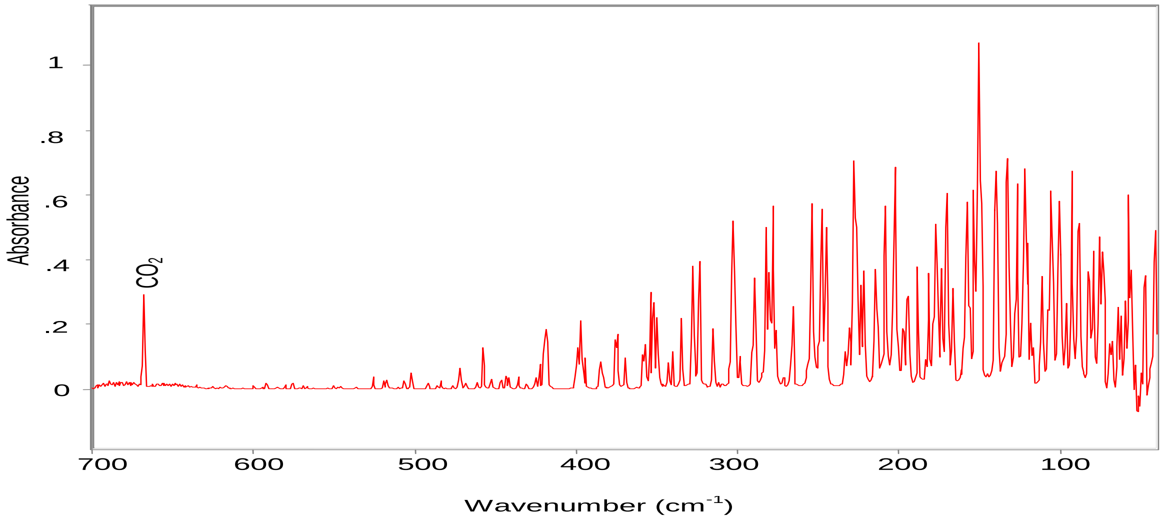


Transition $J'' \rightarrow J'$	Vacuum wave numbers (observed), cm^{-1}
$0 \rightarrow 1$	41.30 ± 0.71
$1 \rightarrow 2$	82.35 ± 0.25
$2 \rightarrow 3$	122.83 ± 0.28
$3 \rightarrow 4$	163.92 ± 0.13
$4 \rightarrow 5$	204.50 ± 0.12
$5 \rightarrow 6$	244.97 ± 0.16
$6 \rightarrow 7$	284.98 ± 0.13
$7 \rightarrow 8$	324.52 ± 0.22
$8 \rightarrow 9$	363.89 ± 0.18
$9 \rightarrow 10$	402.77 ± 0.18
$10 \rightarrow 11$	441.05 ± 0.29

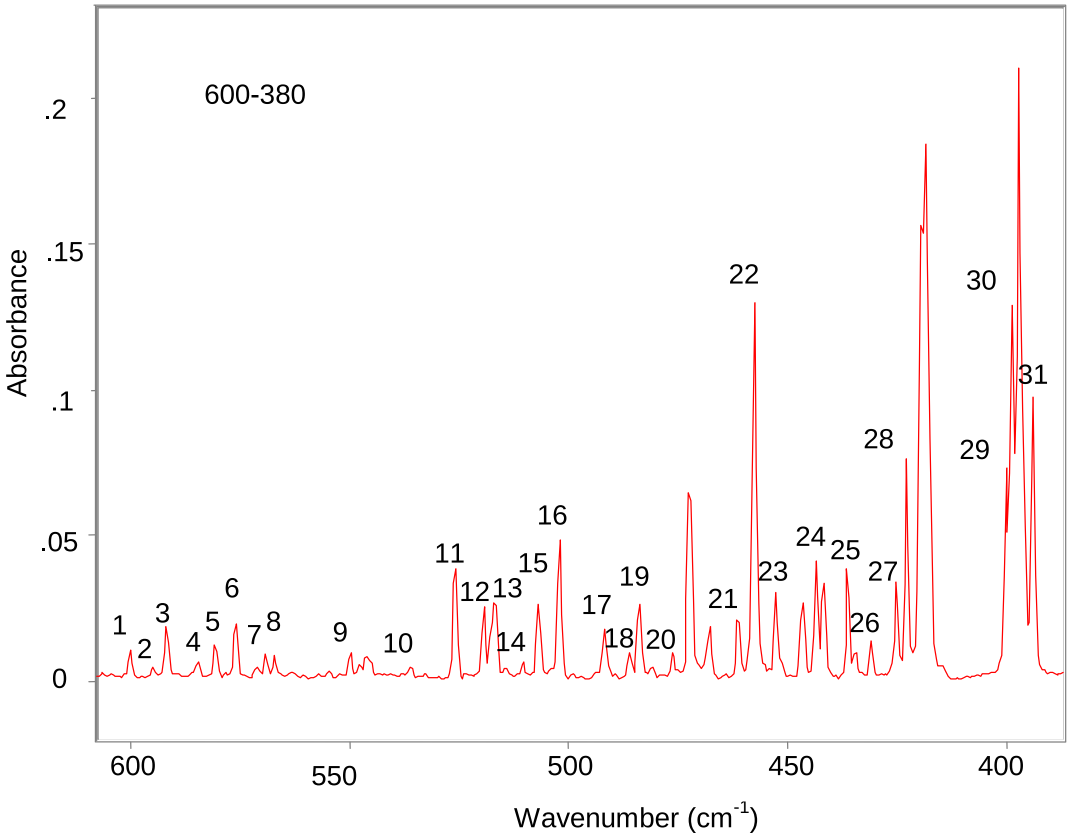
Rothschild[10] has measured the pure spectrum of HF vapour from 22 to 250 µ. table 3- above shows the transitions for the rotation spectrum of HF.

[9] K.N. Rao, R.V. de Vore and S.K. Pyler, *J. Res. Natl. Bur. Std.* **67A,** 351 (1963).

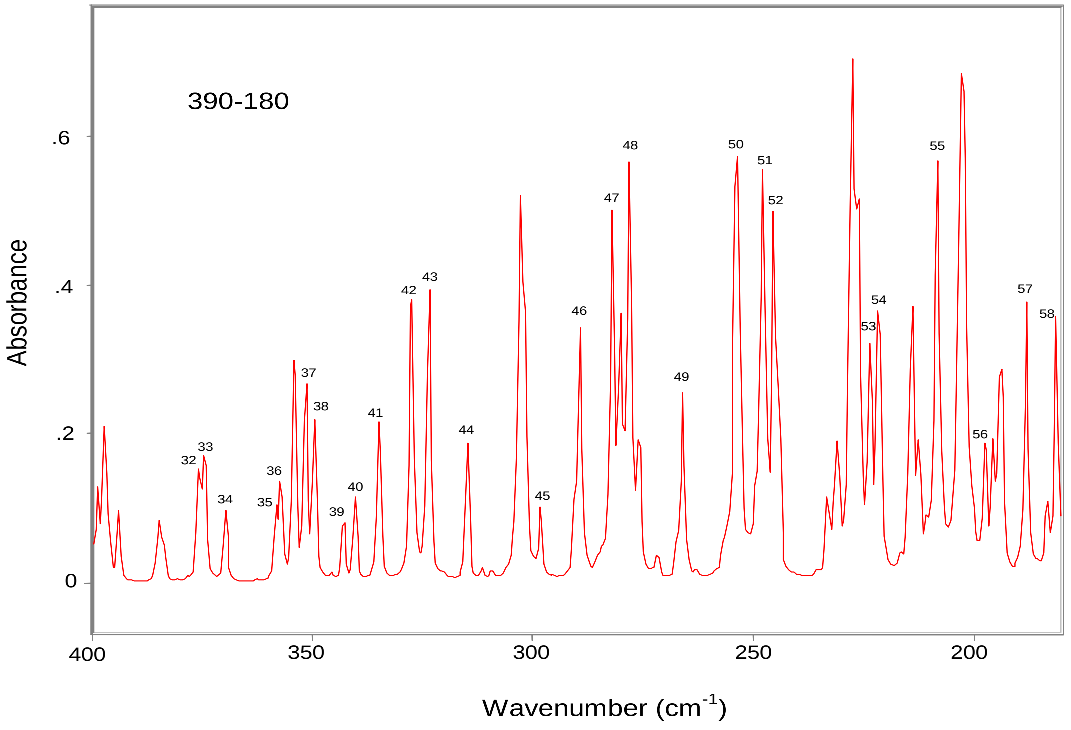
[10] W.G. Rothschild, *J. Opt. Soc. Am.*, **54**, 20 (1964).



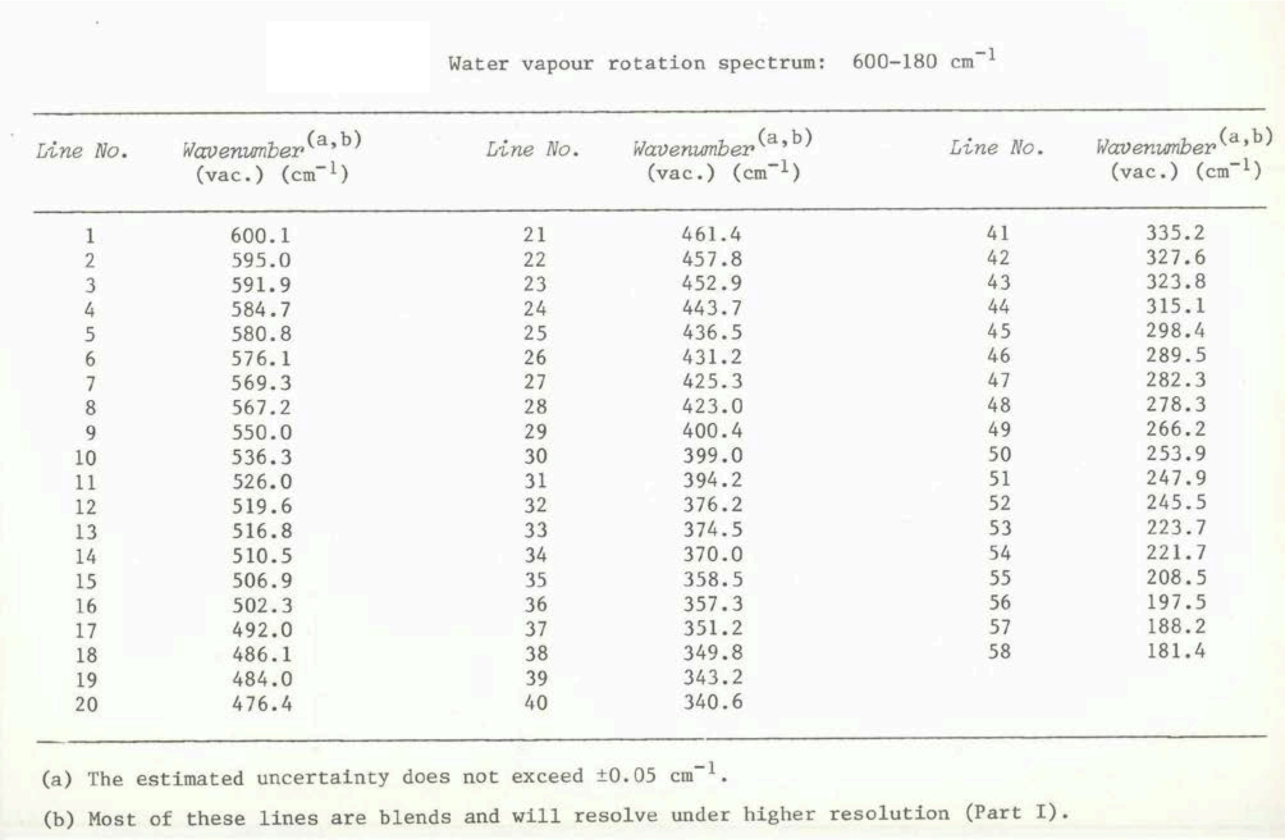
Rotational spectra of water in 700-40 cm^{-1} region
Resolution: 1 cm^{-1}



Enlarged part of rotational spectrum for water.
Resolution: 1 cm^{-1}, region: 600-380 cm^{-1}



Enlarged part of rotational spectrum for water.
Resolution: 1 cm^{-1}, region: 390-180 cm^{-1}

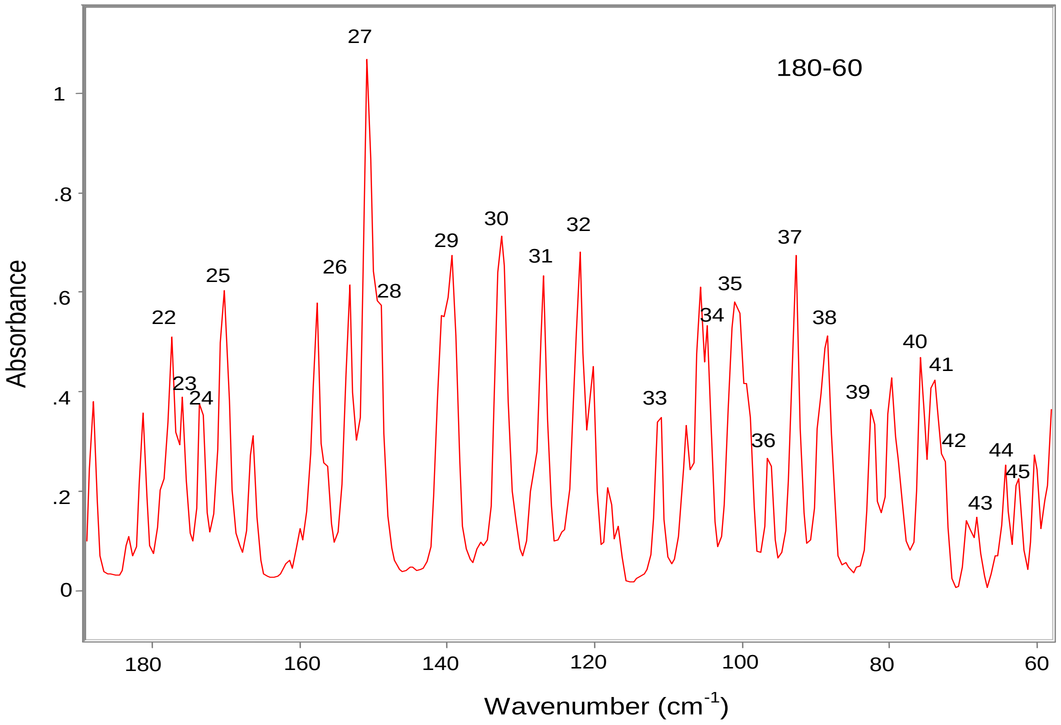


Water vapour rotation spectrum: 600-180 cm^{-1}

Line No.	Wavenumber$^{(a,b)}$ (vac.) (cm^{-1})	Line No.	Wavenumber$^{(a,b)}$ (vac.) (cm^{-1})	Line No.	Wavenumber$^{(a,b)}$ (vac.) (cm^{-1})
1	600.1	21	461.4	41	335.2
2	595.0	22	457.8	42	327.6
3	591.9	23	452.9	43	323.8
4	584.7	24	443.7	44	315.1
5	580.8	25	436.5	45	298.4
6	576.1	26	431.2	46	289.5
7	569.3	27	425.3	47	282.3
8	567.2	28	423.0	48	278.3
9	550.0	29	400.4	49	266.2
10	536.3	30	399.0	50	253.9
11	526.0	31	394.2	51	247.9
12	519.6	32	376.2	52	245.5
13	516.8	33	374.5	53	223.7
14	510.5	34	370.0	54	221.7
15	506.9	35	358.5	55	208.5
16	502.3	36	357.3	56	197.5
17	492.0	37	351.2	57	188.2
18	486.1	38	349.8	58	181.4
19	484.0	39	343.2		
20	476.4	40	340.6		

(a) The estimated uncertainty does not exceed ±0.05 cm^{-1}.

(b) Most of these lines are blends and will resolve under higher resolution (Part I).



Enlarged part of rotational spectrum for water. Resolution: 1 cm^{-1}, region: 180-60 cm^{-1}

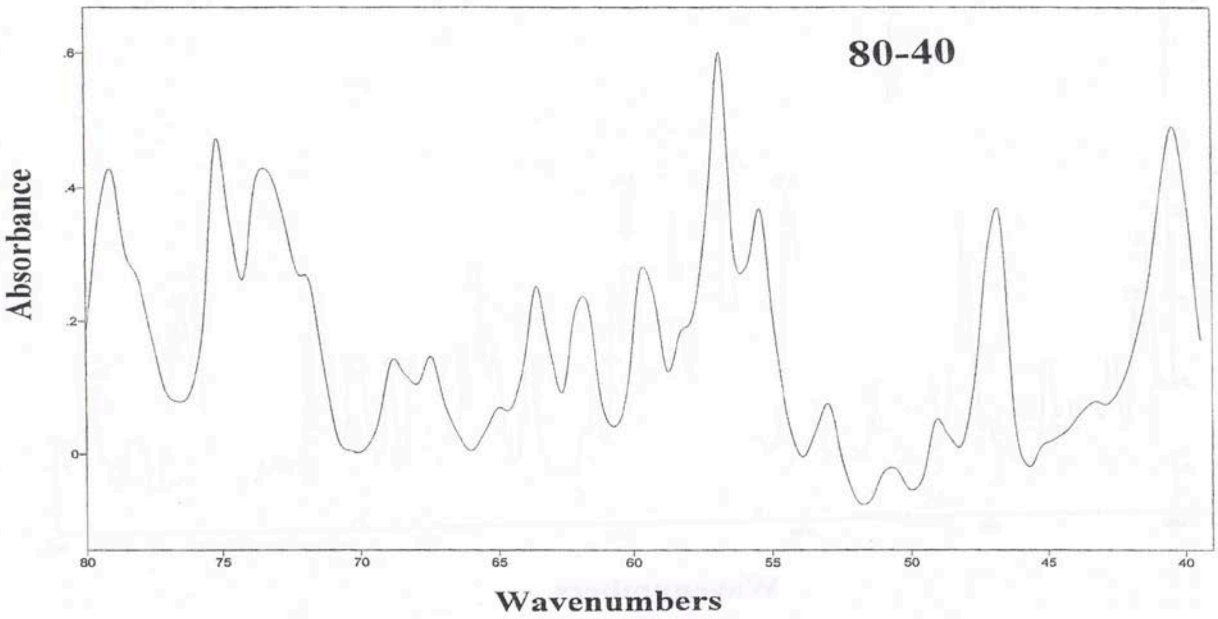
Water vapour rotational spectrum: 180-60 cm^{-1}

Line No.	*Wavenumber*$^{(a,b)}$ (vac.) (cm^{-1})	*Line No.*	*Wavenumber*$^{(a,b)}$ (vac.) (cm^{-1})	*Line No.*	*Wavenumber*$^{(a.b)}$ (vac.) (cm^{-1})
		23	176.05	35	100.51
		24	173.46	36	96.15
		25	170.36†	37	92.53†
		26	153.45	38	88.08†
		27	150.54	39	82.16†
		28	149.06	40	75.52
		29	139.02†	41	74.11
		30	132.66†	42	72.19
		31	127.00†	43	68.06
		32	121.90	44	64.02
		33	111.12†	45	62.30
22	177.54	34	104.52		

† Suitable for use under lower resolution *(Chart 35* covers part only).

(a) Many of these lines are blends and will resolve under higher resolution (Part I).

(b) The estimated uncertainty does not exceed ±0.05 cm^{-1}.



Enlarged part of rotational spectrum for water.
Resolution: 1 cm^{-1}, region: 180-60 cm^{-1}

Water vapour rotational spectrum: 180-40 cm^{-1}

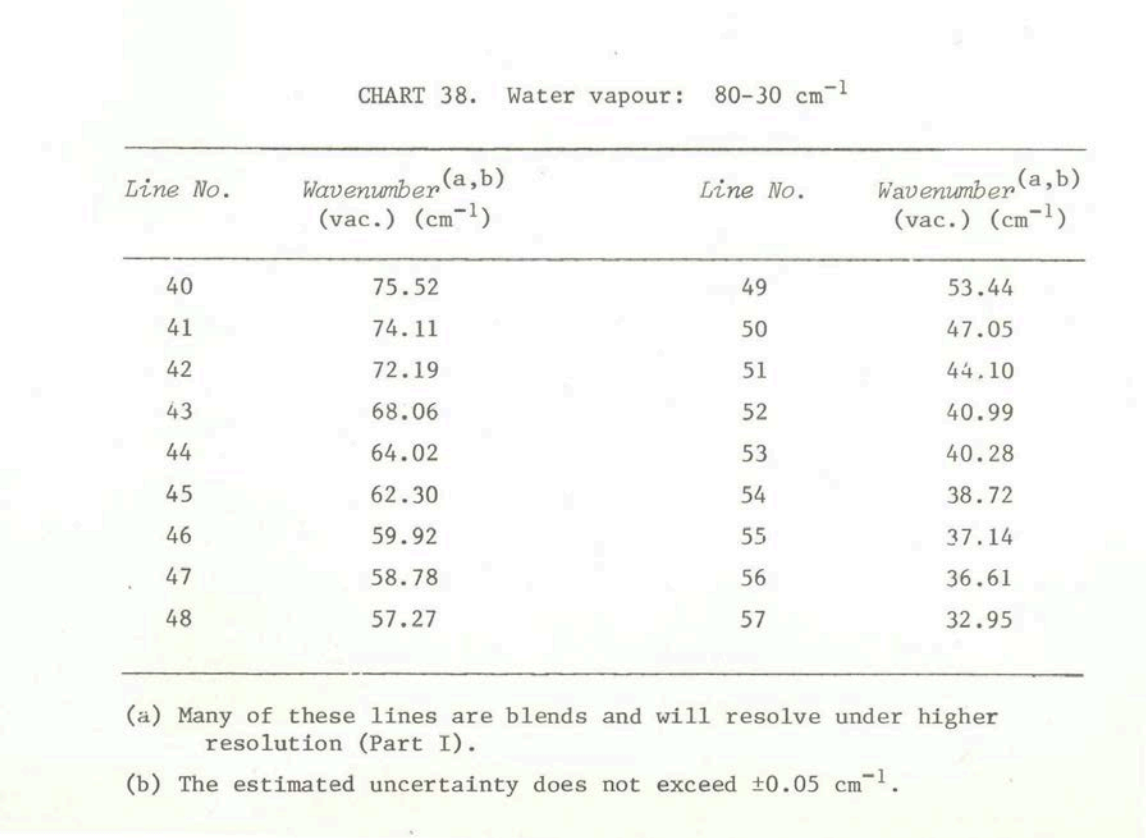


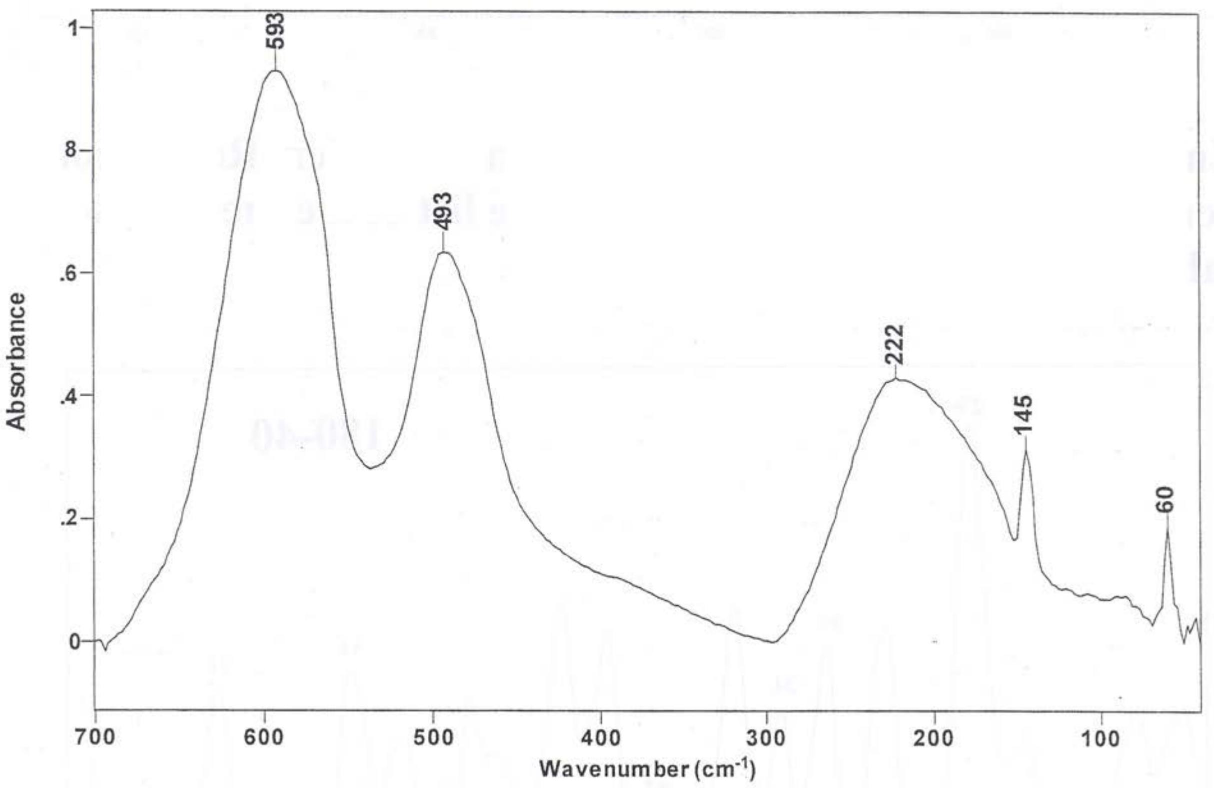
CHART 38. Water vapour: 80-30 cm^{-1}

Line No.	*Wavenumber*[(a,b)] (vac.) (cm^{-1})	*Line No.*	*Wavenumber*[(a,b)] (vac.) (cm^{-1})
40	75.52	49	53.44
41	74.11	50	47.05
42	72.19	51	44.10
43	68.06	52	40.99
44	64.02	53	40.28
45	62.30	54	38.72
46	59.92	55	37.14
47	58.78	56	36.61
48	57.27	57	32.95

(a) Many of these lines are blends and will resolve under higher resolution (Part I).

(b) The estimated uncertainty does not exceed ±0.05 cm^{-1}.

Mercuric oxide (yellow):

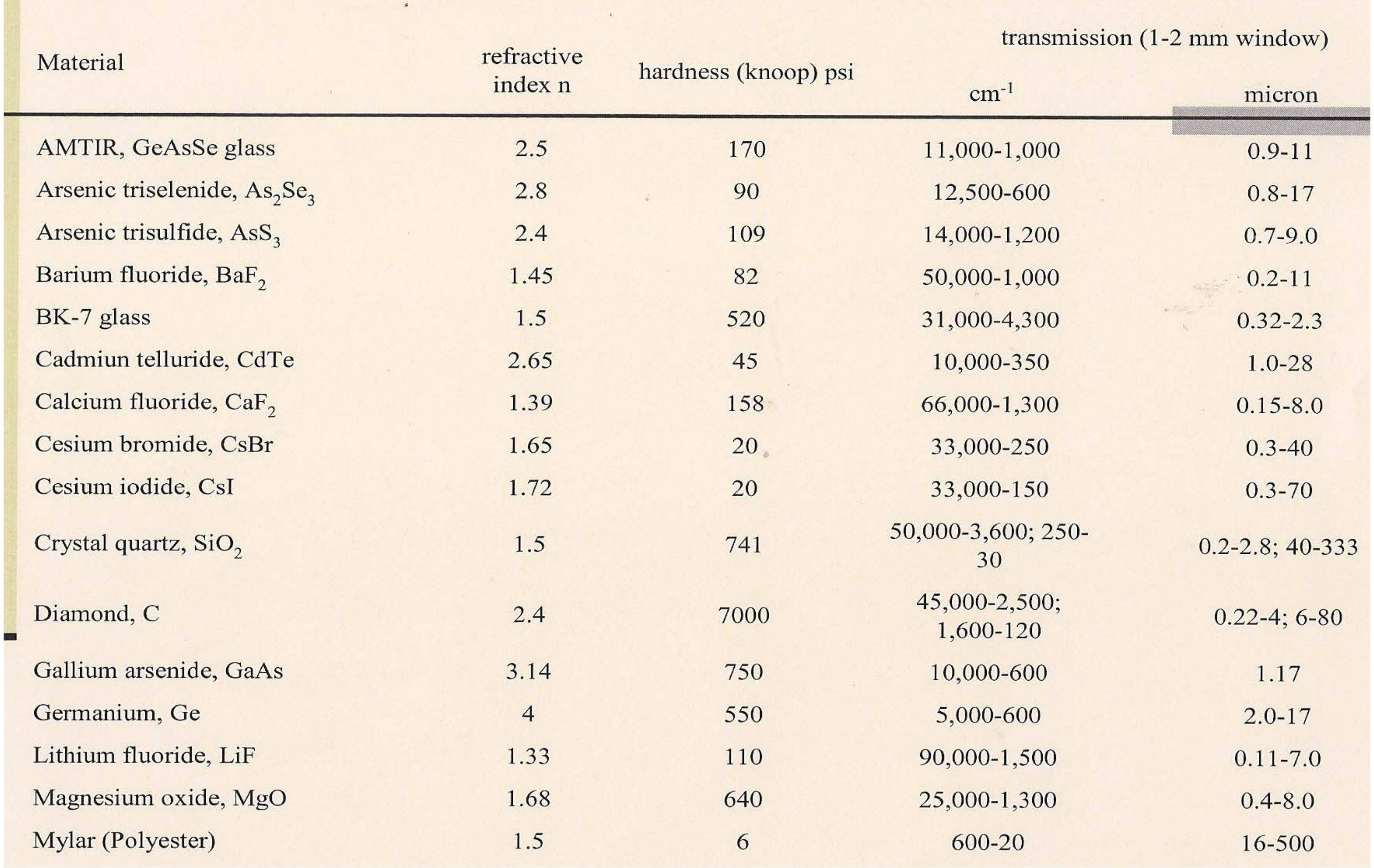


2.6. Sampling techniques for mid-IR spectroscopy

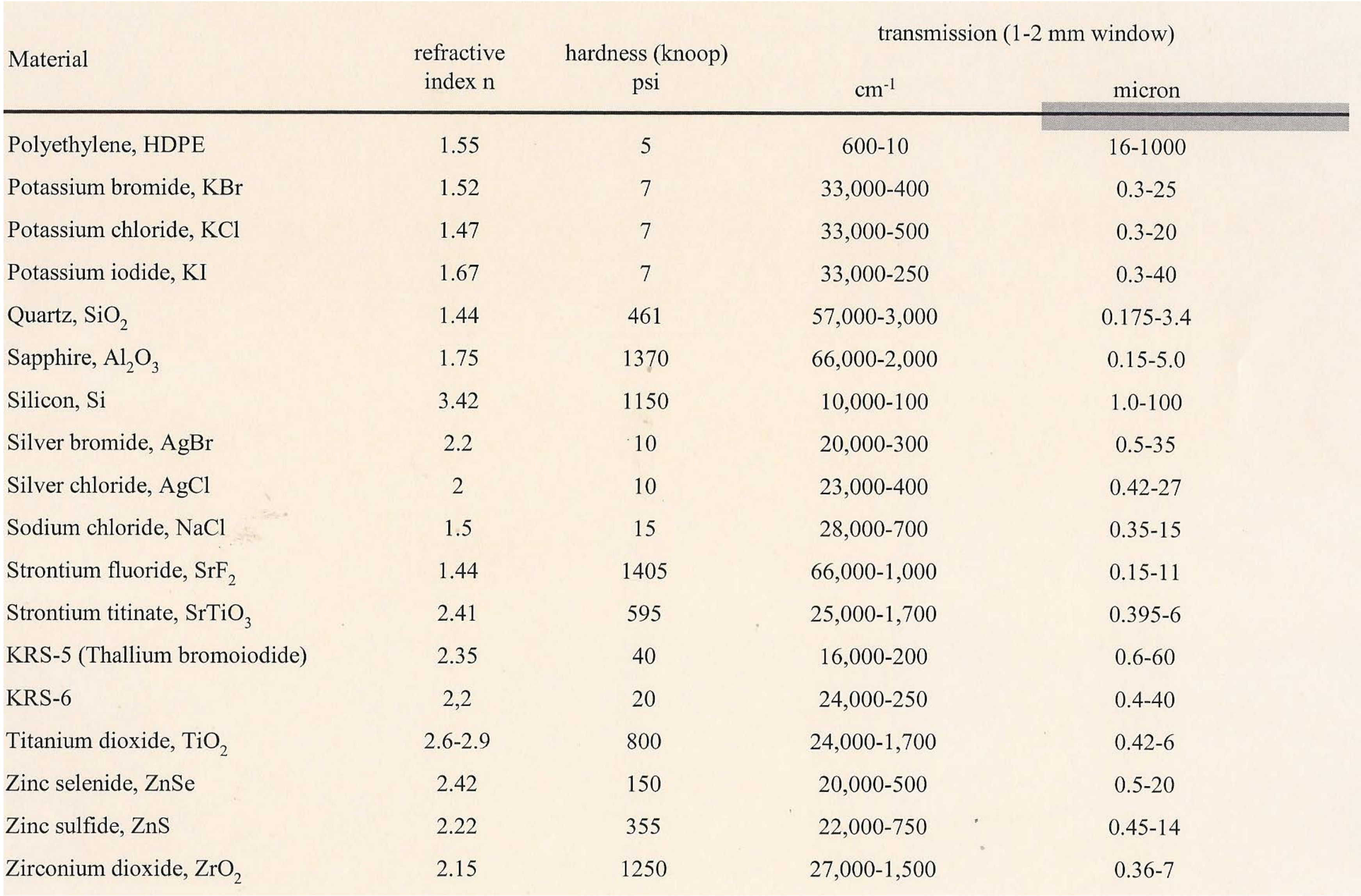
Window materials

- Transparent in broad spectral range (Si);
- No absorption bands (CsI);
- Not soluble in organic solvents (many);
- Not soluble in water (BaF_2);
- Mechanically hard (diamond);
- Low refractive index (CaF_2);
- High melting or softening temperature (sapphire);
- Easy to polish (CsI);
- Cheap (glass);
- Chemically inert (glass CaF_2).

Properties of optical materials (cell windows) used in IR, NIR and UV-VIS spectroscopy



Material	refractive index n	hardness (knoop) psi	transmission (1-2 mm window)	
			cm^{-1}	micron
AMTIR, GeAsSe glass	2.5	170	11,000-1,000	0.9-11
Arsenic triselenide, As_2Se_3	2.8	90	12,500-600	0.8-17
Arsenic trisulfide, AsS_3	2.4	109	14,000-1,200	0.7-9.0
Barium fluoride, BaF_2	1.45	82	50,000-1,000	0.2-11
BK-7 glass	1.5	520	31,000-4,300	0.32-2.3
Cadmiun telluride, CdTe	2.65	45	10,000-350	1.0-28
Calcium fluoride, CaF_2	1.39	158	66,000-1,300	0.15-8.0
Cesium bromide, CsBr	1.65	20	33,000-250	0.3-40
Cesium iodide, CsI	1.72	20	33,000-150	0.3-70
Crystal quartz, SiO_2	1.5	741	50,000-3,600; 250-30	0.2-2.8; 40-333
Diamond, C	2.4	7000	45,000-2,500; 1,600-120	0.22-4; 6-80
Gallium arsenide, GaAs	3.14	750	10,000-600	1.17
Germanium, Ge	4	550	5,000-600	2.0-17
Lithium fluoride, LiF	1.33	110	90,000-1,500	0.11-7.0
Magnesium oxide, MgO	1.68	640	25,000-1,300	0.4-8.0
Mylar (Polyester)	1.5	6	600-20	16-500

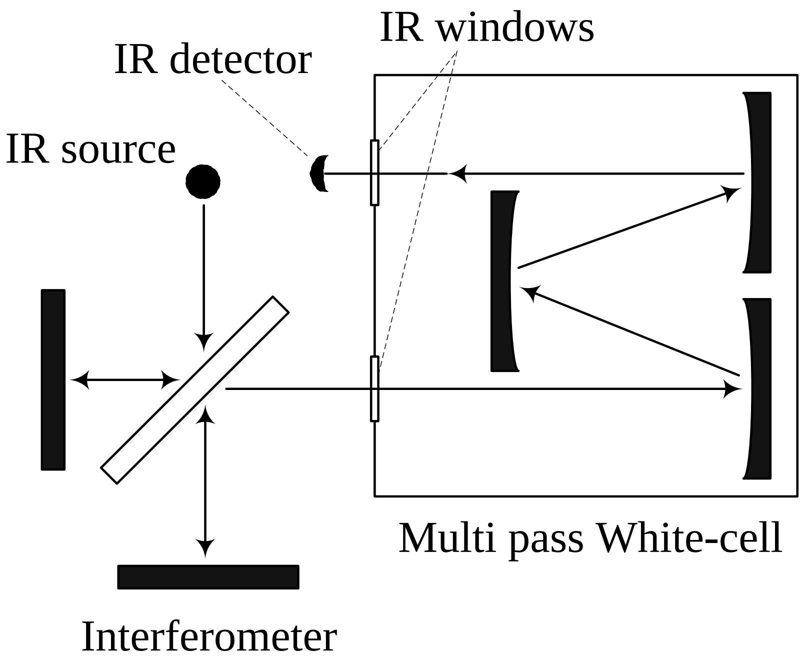


Material	refractive index n	hardness (knoop) psi	transmission (1-2 mm window)	
			cm^{-1}	micron
Polyethylene, HDPE	1.55	5	600-10	16-1000
Potassium bromide, KBr	1.52	7	33,000-400	0.3-25
Potassium chloride, KCl	1.47	7	33,000-500	0.3-20
Potassium iodide, KI	1.67	7	33,000-250	0.3-40
Quartz, SiO_2	1.44	461	57,000-3,000	0.175-3.4
Sapphire, Al_2O_3	1.75	1370	66,000-2,000	0.15-5.0
Silicon, Si	3.42	1150	10,000-100	1.0-100
Silver bromide, AgBr	2.2	10	20,000-300	0.5-35
Silver chloride, AgCl	2	10	23,000-400	0.42-27
Sodium chloride, NaCl	1.5	15	28,000-700	0.35-15
Strontium fluoride, SrF_2	1.44	1405	66,000-1,000	0.15-11
Strontium titinate, $SrTiO_3$	2.41	595	25,000-1,700	0.395-6
KRS-5 (Thallium bromoiodide)	2.35	40	16,000-200	0.6-60
KRS-6	2,2	20	24,000-250	0.4-40
Titanium dioxide, TiO_2	2.6-2.9	800	24,000-1,700	0.42-6
Zinc selenide, ZnSe	2.42	150	20,000-500	0.5-20
Zinc sulfide, ZnS	2.22	355	22,000-750	0.45-14
Zirconium dioxide, ZrO_2	2.15	1250	27,000-1,500	0.36-7

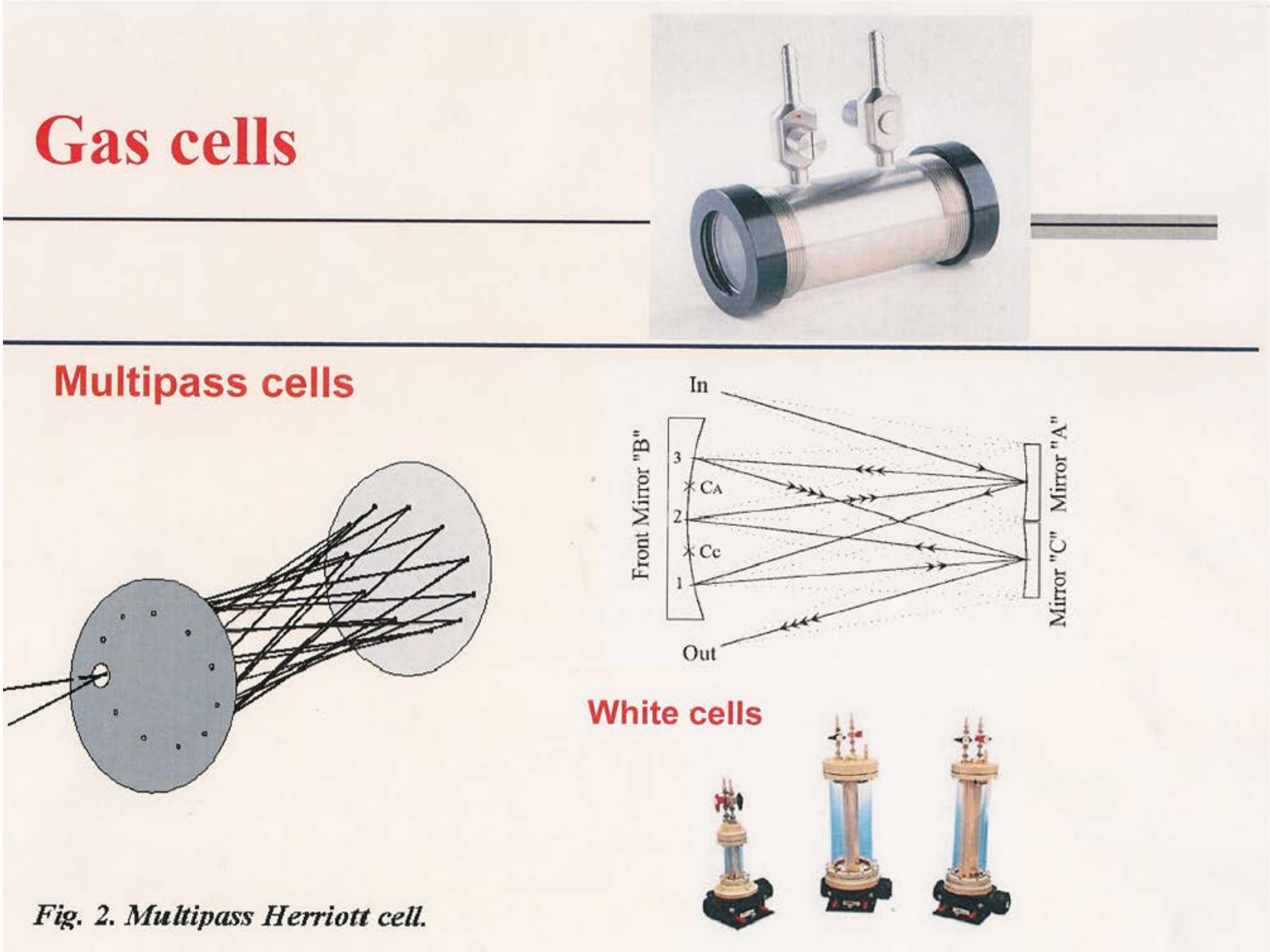
(a) Gas Cells

Some types of gas cells

10 cm path length laboratory gas cell



Principle of a long path White-type gas cell.
(Path length: from 1 –to 500 m)



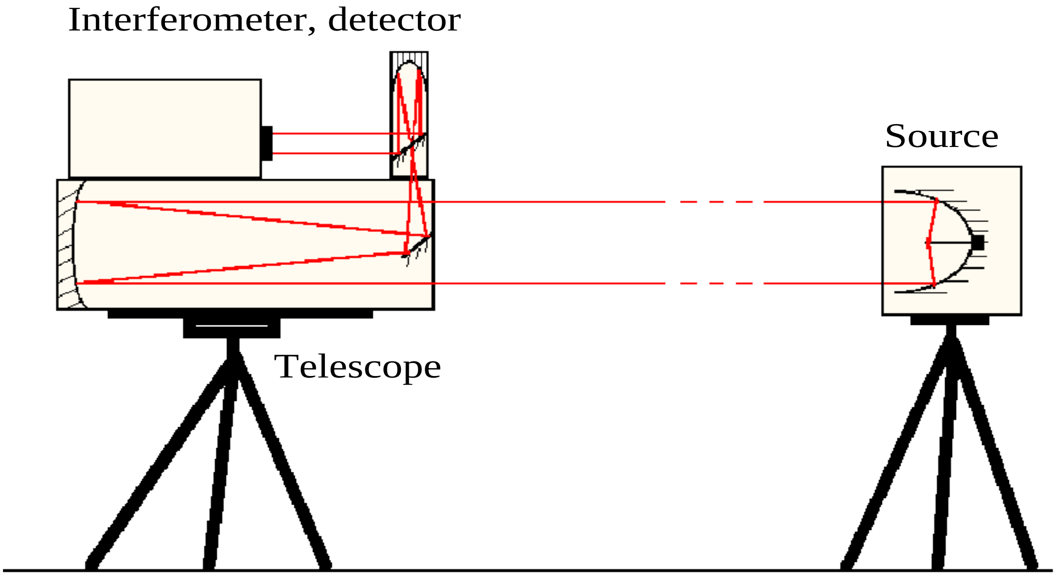
Gas cells

Multipass cells

Fig. 2. Multipass Herriott cell.

White cells

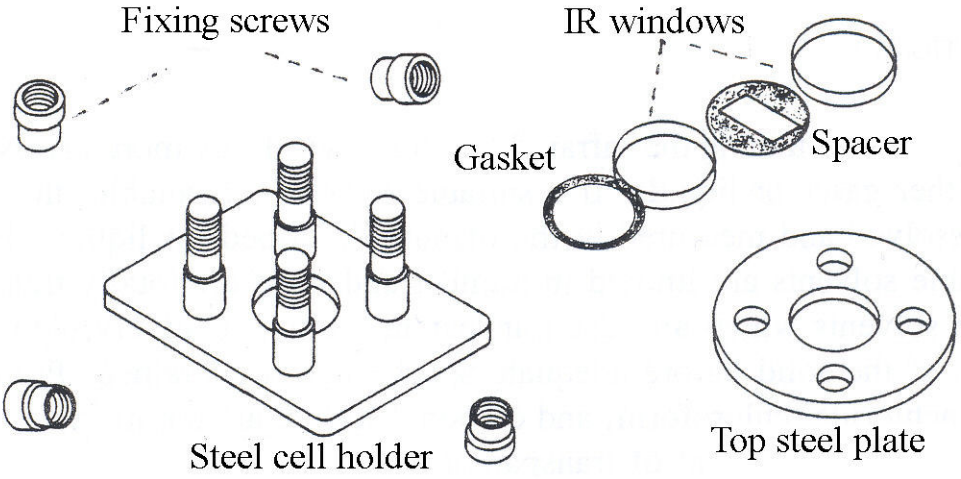
Open path (OP) FTIR detection of atmospheric pollutants



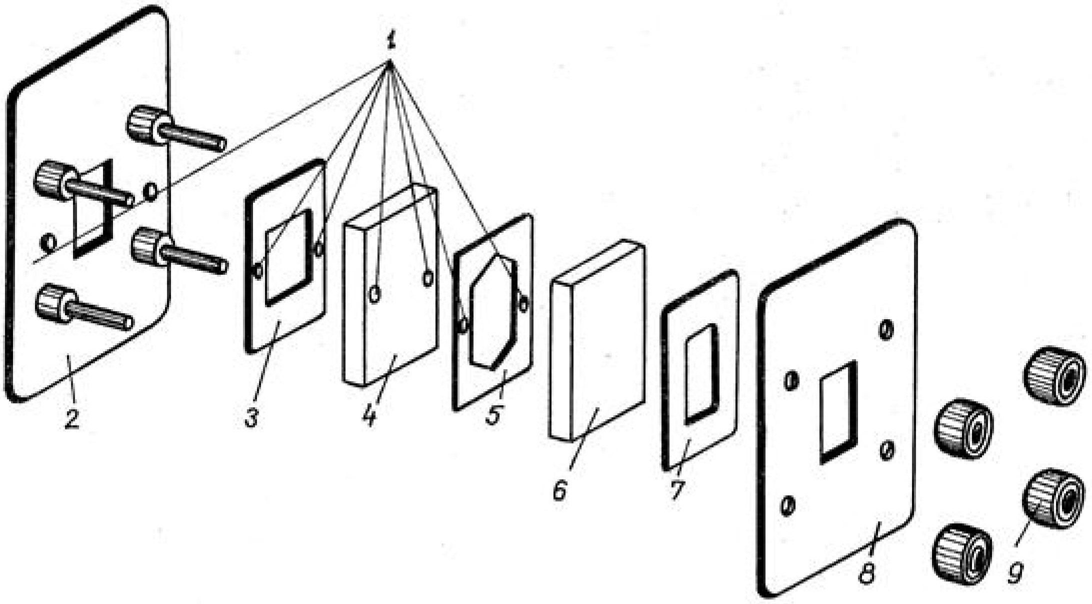
Active open path configuration

(b) Liquid cells

Type of liquid cells



Demountable-type infrared cell for liquids



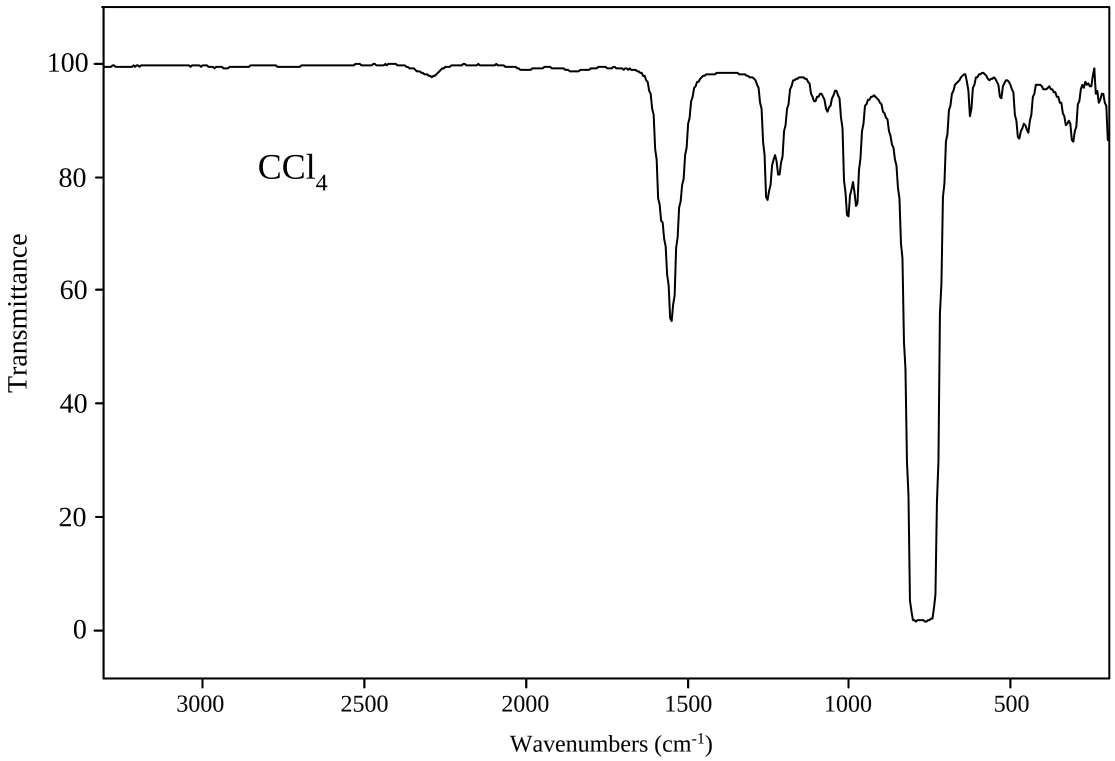
Fixed thickness or sealed cell for liquids
1 – Holes for cell filling; 2-2 'x3' steel cell holder; 3 – gasket with holes;
4 – IR window with holes; 5 – spacer; 6 – top IR window;
7 – top gasket; 8 – top steel plate; 9 – fixing screws

(c) Solutions

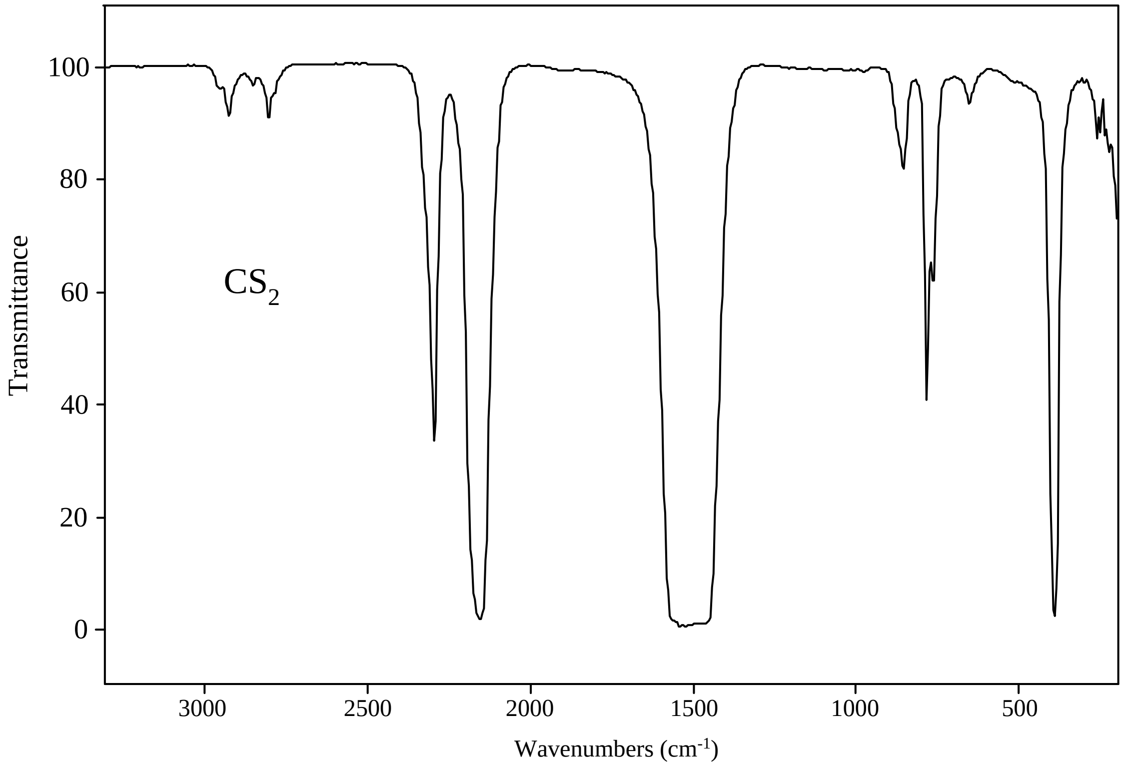
Properties of common solvents

Curve No.	Material	M.P.	B.P.	Allowable Exposure ppm in Air	Remarks
1	Acetone	-95.3	56.2	1000	Fire hazard
2	Acetone-d_6				
3	Acetonitrile	-45.7	81.6	20	
4	Benzene	5.5	80.1	10	Vapor toxic Use in hood
5	Benzene-d_6				
6	Bromoform	8.3	149.5	0.5	Vapor toxic Use in hood
7	t-Butanol	25.5	82.2	100	
8	Carbon disulphide	-112	45	20	Vapor toxic Use in hood
9	Carbon tetrachloride	-23.0	76.7	10	Vapor toxic Use in hood
10	Chloroform	-63.5	61.2	50	
11	Chloroform-d_1	-64.1	61.3	-	
12	Cyclohexane	6.5	81	300	
13	Dibromomethane	-52	97	-	Vapor toxic Use in hood
14	Dichloromethane	-97	40	500	
15	N,N-Dimethylformamide	-61	153	10	Affects NaCl
16	1,4-Dioxane	11.8	101	100	
17	Ethyl acetate	-83-6	77-1	400	
18	Ethyl ether	-116.2	34.6	400	Fire hazard
19	n-Heptane	-91	98.4	500	
20	Methanol	-93.9	65.0	200	Affects NaCl
21	Perchloroethylene	-22	121	100	
22	Tetrahydrofuran	-65	64	200	
23	2,2,4-Trimethylpentane (isooctane)	-107	99.2	-	

Useful combination of CCl_4 and CS_2

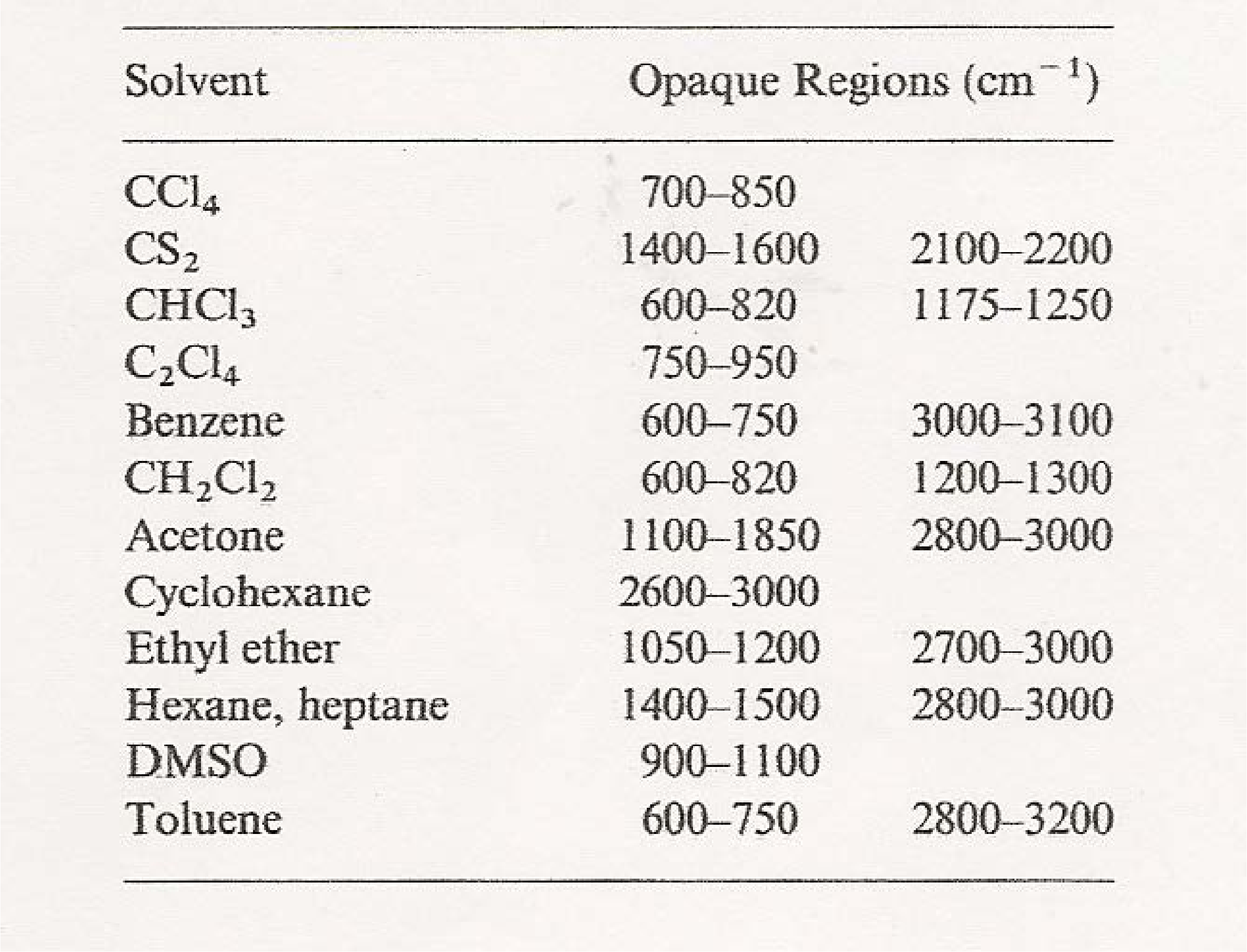


FTIR spectrum of CCl_4: 0.1 mm in CsI liquid cell



FTIR spectrum of CS_2: 0.1 mm in CsI liquid cell

Opaque regions in common IR solvents

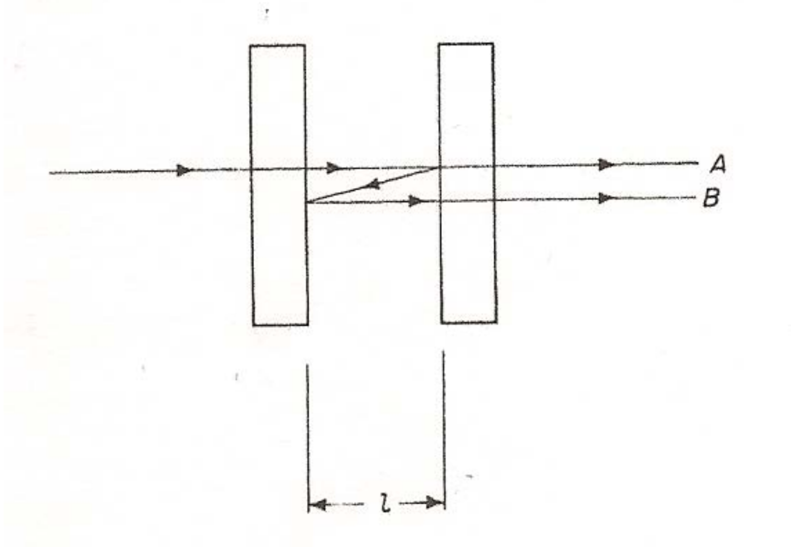


Solvent	Opaque Regions (cm^{-1})	
CCl_4	700–850	
CS_2	1400–1600	2100–2200
$CHCl_3$	600–820	1175–1250
C_2Cl_4	750–950	
Benzene	600–750	3000–3100
CH_2Cl_2	600–820	1200–1300
Acetone	1100–1850	2800–3000
Cyclohexane	2600–3000	
Ethyl ether	1050–1200	2700–3000
Hexane, heptane	1400–1500	2800–3000
DMSO	900–1100	
Toluene	600–750	2800–3200

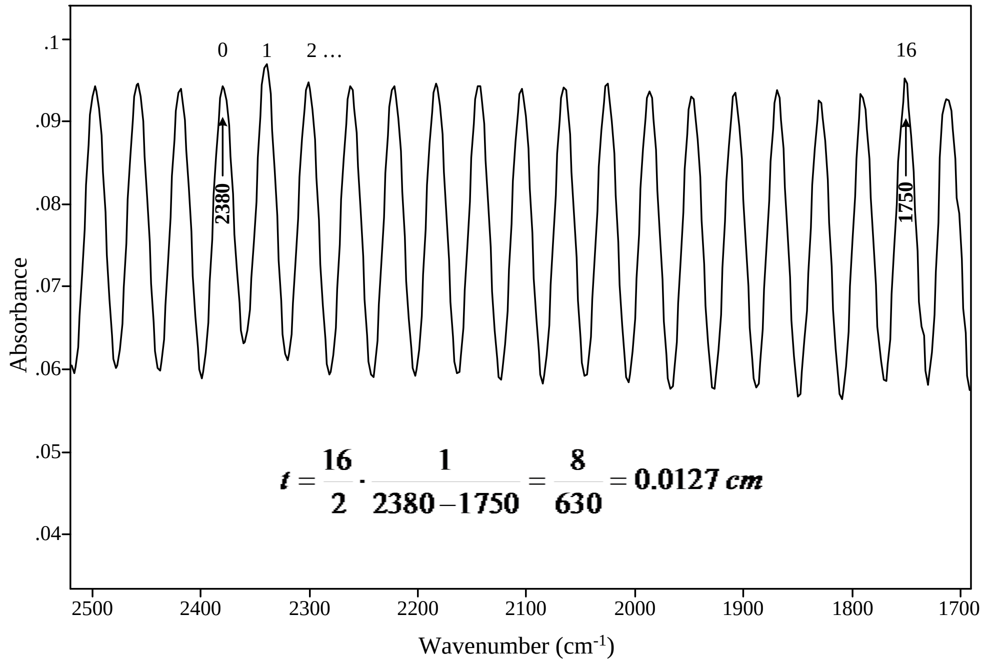
(d) Cast Films

An alternate technique most useful for soluble polymers is to prepare a film of the solid by evaporating of the material directly on an IR transmitting window, or on a material from which the dried film can be peeled. Water solutions can be readily evaporated on ZnS or AgCl plates for example.

Calculation of cell or solid film thickness:



Passage of radiation through the cell. Pass through (beam A), double reflection at the inner surface (beam B)



Example of cell thickness calculation.

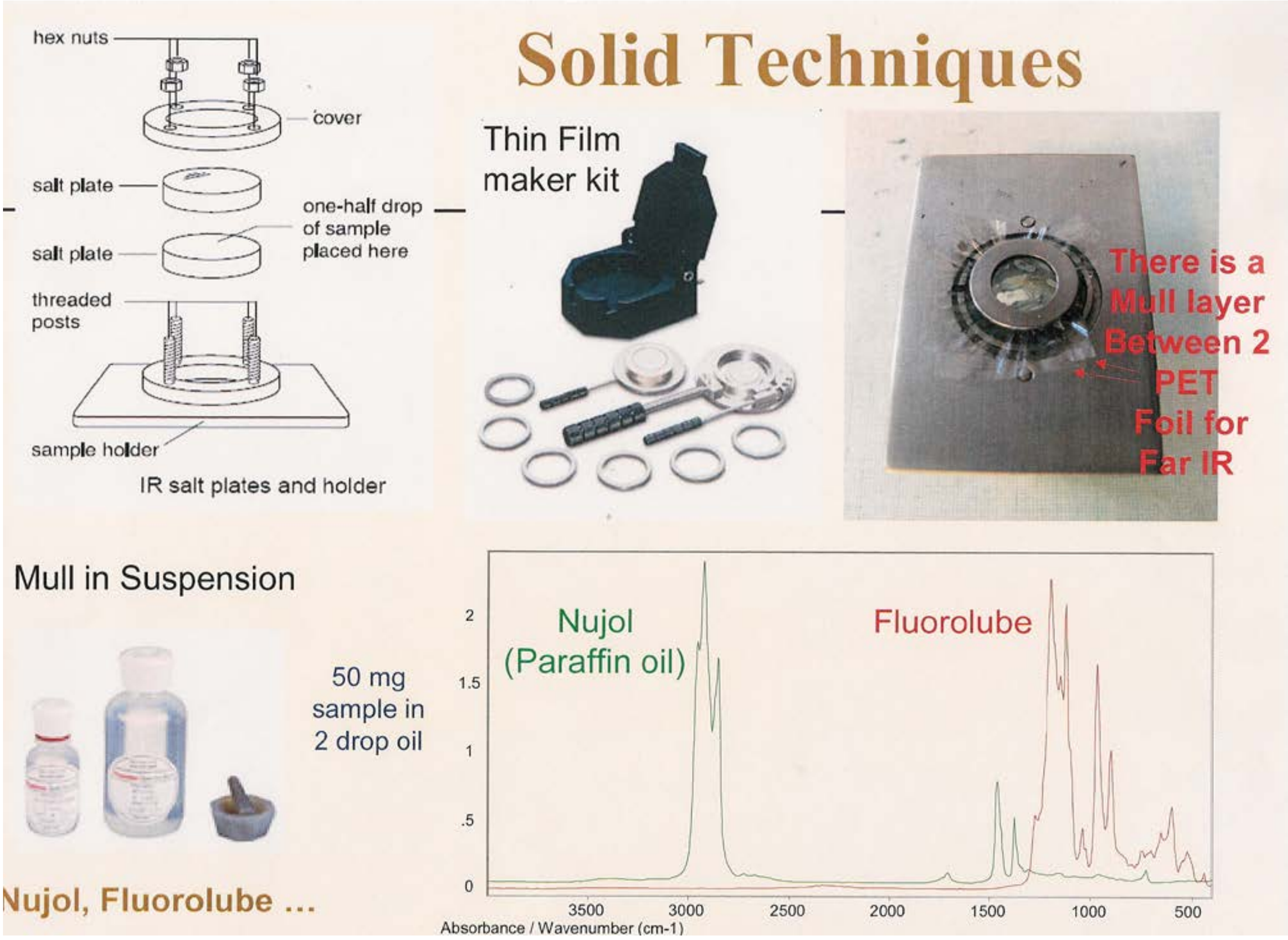
For an empty cell,

$$t(cm) = \frac{n}{2} \cdot \frac{1}{\nu_1 - \nu_2} \quad \text{or} \quad t(cm) = \frac{n}{2} \cdot \frac{\lambda_1\ \lambda_2}{\lambda_1 - \lambda_2} \text{ x } 10^{-4}$$

t = thickness
λ_1 and λ_2 = wavelength of two maxima in micrometers
ν_1 and ν_2 = wavenumber of two maxima in cm^{-1}
n = number of maxima counted (choose n between 10 and 20) (count λ_1 or ν_1 as zero)

(e) **Mulls and pellets**

.



Solid Techniques

Thin Film maker kit

There is a Mull layer Between 2 PET Foil for Far IR

Mull in Suspension

50 mg sample in 2 drop oil

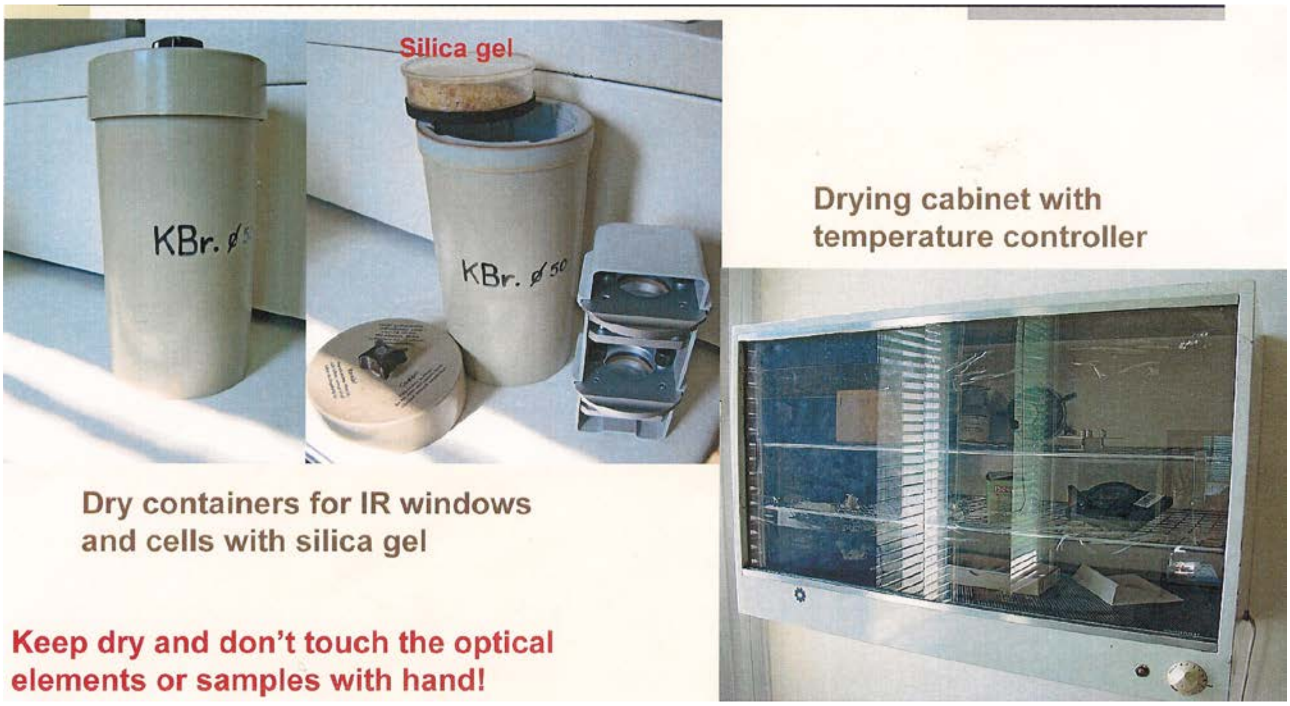
Nujol, Fluorolube …

KBr Disc

Demountable-type infrared cell for mulls

Die for pressing 13 mm pellets from NaCl, KCl, KBr, KI, CsBr, CSI, TlBr, polyethylene, etc.

Most of IR optical materials are hygroscopic



Drying cabinet with temperature controller

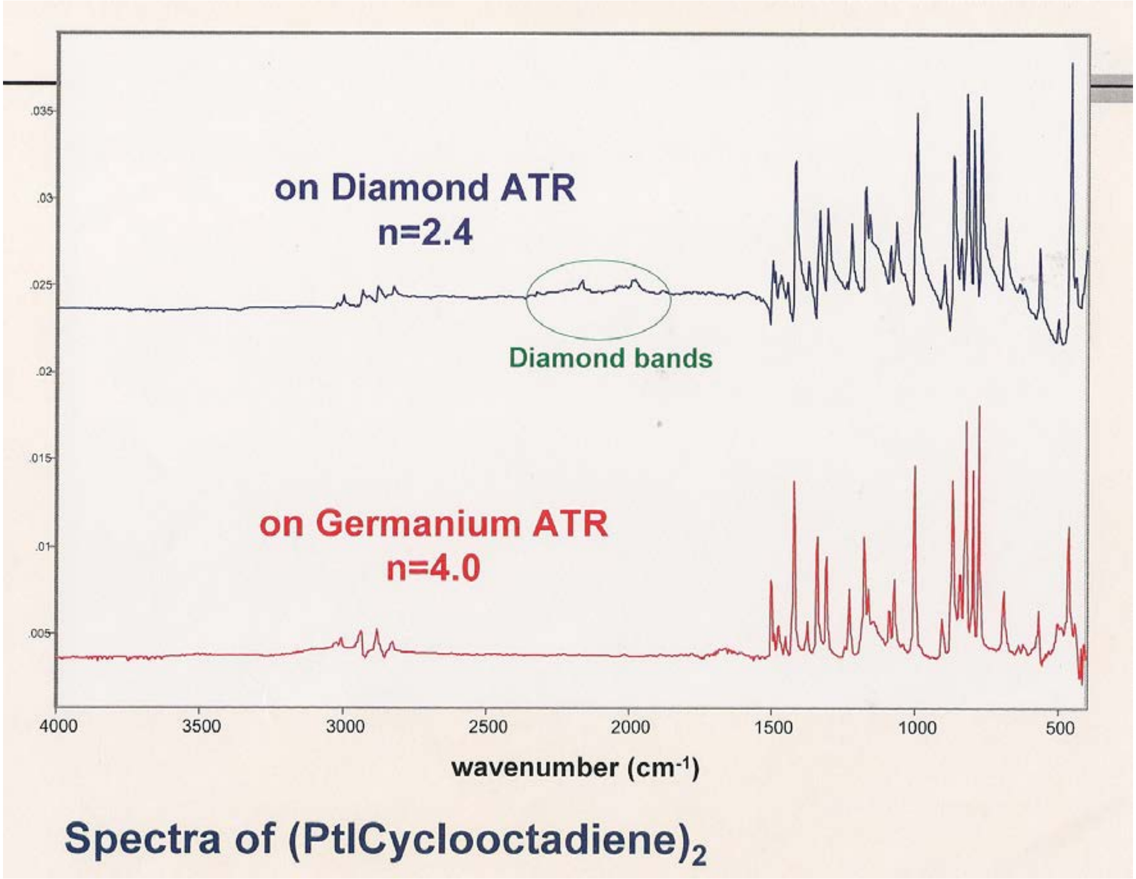
Dry containers for IR windows and cells with silica gel

Keep dry and don’t touch the optical elements or samples with hand!

The Christiansen effect

Sloping baseline. This is usually due to a poorly dispersed sample. Some substances are too hard (polymers) or too crystalline (e.g. Anthraquinone) to disperse properly. The latter can also cause bands to appear like a first derivative spectrum. This is due to refractive index changes and is known as the *Christiansen Effect*

Effects of high refractive index of the sample



2.7. Basic sampling methods for far-infrared spectroscopy

a.) Window materials for cells

Material	Practical frequency limit, cm^{-1}	Remarks
KBr	250	
TlBr	400	
CsBr	200	
CsI	145	
KRS-5	225	High refractive index – high reflection losses
Polyethylene	10	Very versatile at ambient temperatures
Polypropylene	[a]	Can be used to 150°C
4-Methylpentene-1	[a]	Can be used to 200°C
Teflon	[a]	Can be used to 200°C
Polystyrene	40	
Kel-F[b]		
Fluorothene[c]	< 100	For fluorine compounds
Germanium		High refractive index
Silicon[1,2]	[a]	High refractive index, shows conduction bands of impurities at -196 °C
Diamond	5	Can be used ambient and nonambient temperatures
Quartz (crystal)	< 150	
Mica	< 50	
TPX polymer	10	Transparent, hard, polymer

[a] Has far-infrared absorption;

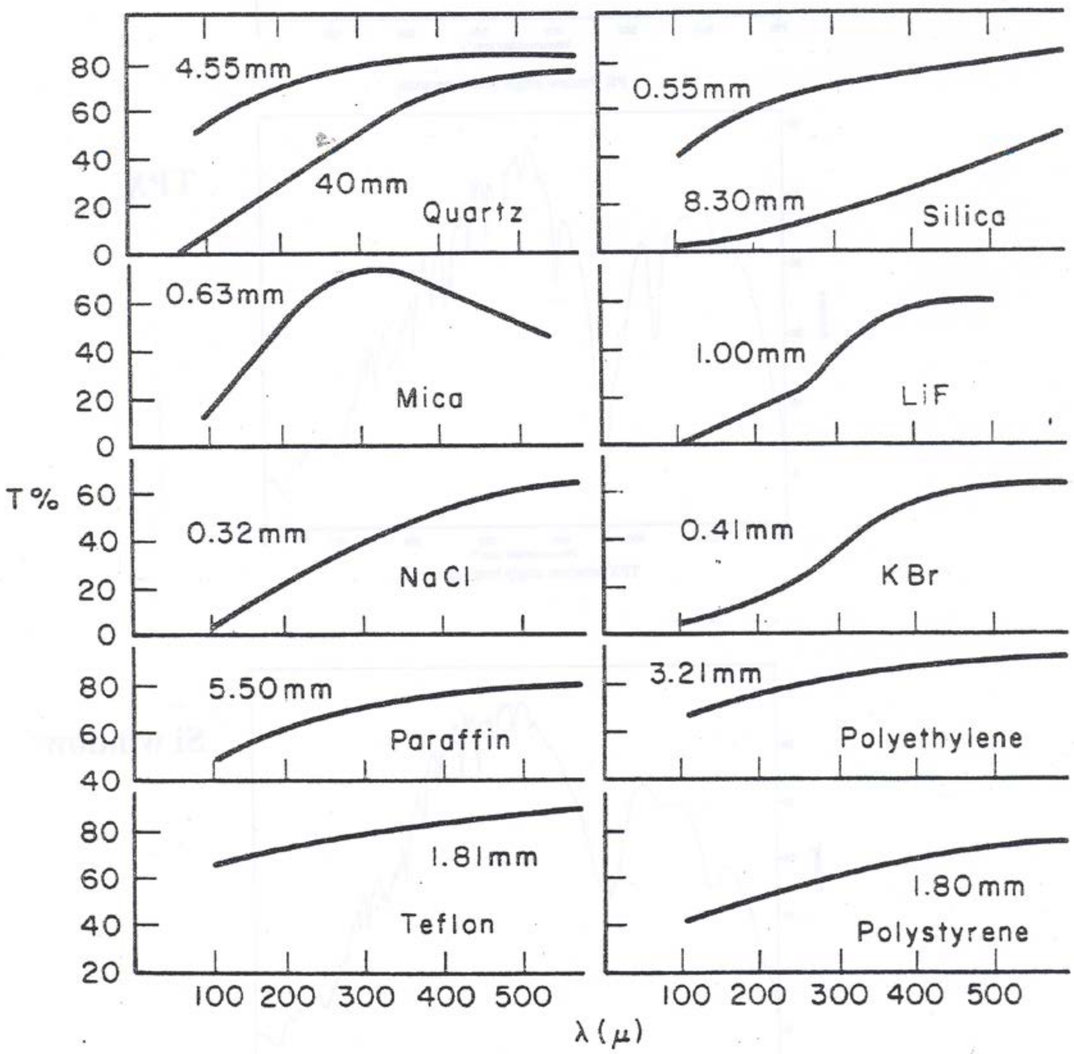
[b] Chlorotrifluoroethylene-vinylidene fluoride copolymer;

[c] Formed by putting fluorine compounds in polyethylene-fluorthene formed on surface.

TPX = methylpentene resin

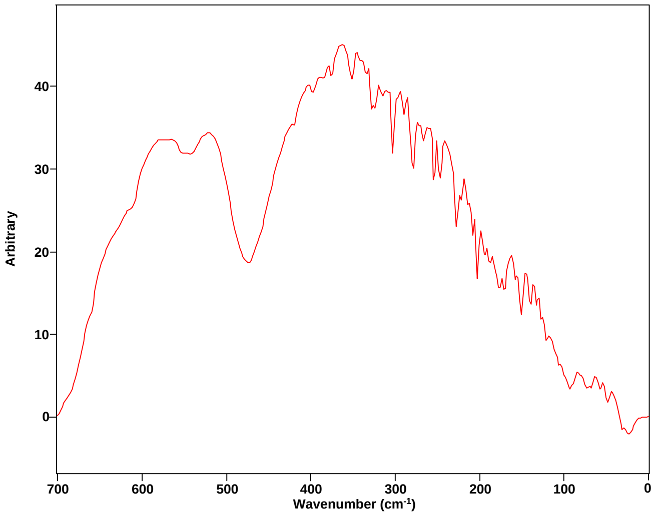
Silicon, Germanium, and Diamond Windows

The semiconducting materials such as silicon and germanium show promise as far-infrared windows. However, they have high refractive indices, and, therefore, show high reflective losses. Diamond appears to be the most versatile far-infrared window available. It is hard, chemically resistant, transparent, and can be used at temperatures of 300°C or higher. Unfortunately it is expensive.

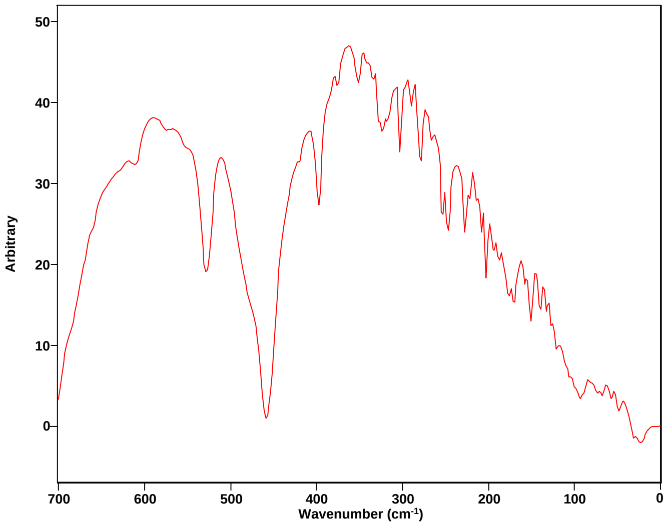


Transmission of various windows materials in the far-infrared region

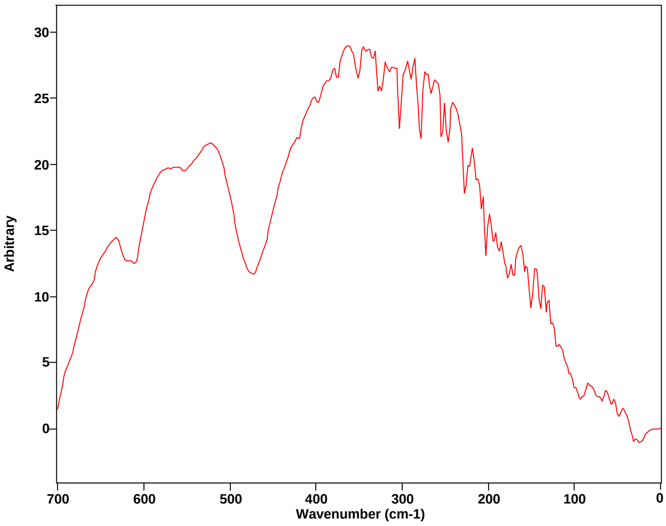
Comparison of single beam FIR spectra of different window materials



PE window single beam spectrum



TPX window single beam spectrum



Si window single beam spectrum

b.) Sampling techniques

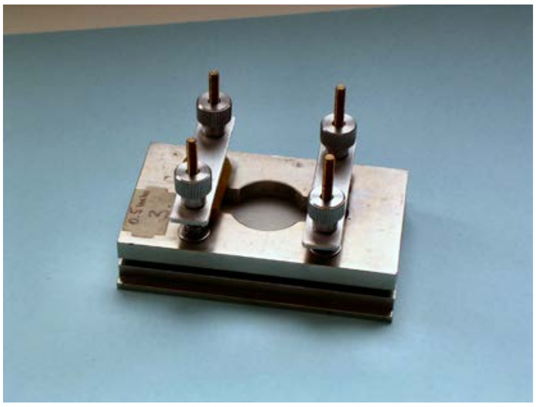
In the far-infrared region one is usually concerned with spectra of solids, solutions, and liquids. Table 3.2 lists the possible techniques available for sampling of those materials. The choice of method depends on the particular compound whose spectra is to be determined.

Table 3.2 Sampling techniques in the far-infrared

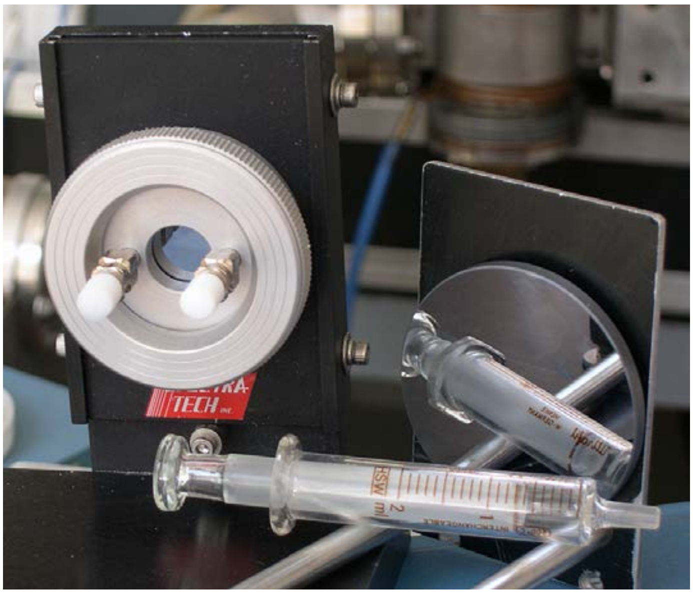
Solids	**Remarks**
Nujol mull	Use polyethylene windows
KBr pellet	
CsBr pellet	
CsI pellet	
Polyethylene pellet	
Between diamond windows	No matrix necessary
Molten spectra	Quartz, CsI, or Teflon windows
Solid on polyethylene sheet	Rub solid into polyethylene
Liquids	
Liquid film	Use polyethylene windows
Solution	
Dissolve in appropriate solvent	Use polyethylene windows

Far infrared liquid cells

Commercial full polyethylene-body cell with different (0.5-2.5 mm) thickness



Home made demountable liquid cell for different (PE, Si, TPX) window materials



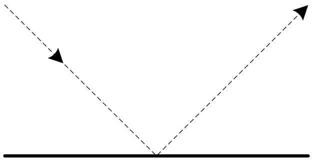
Commercial Si windowed cell used for aqueous solutions

2.8. Special (new) accessories

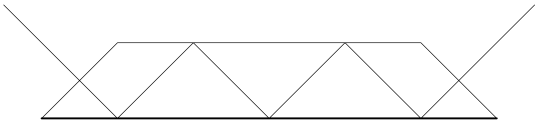
Although absorption methods are by far the most common way to collect infrared vibrational data, there are other methods to collect the same spectral information from light reflected from surface. This method is particularly useful if the sample is opaque in the spectral region of interest.

Reflection methods

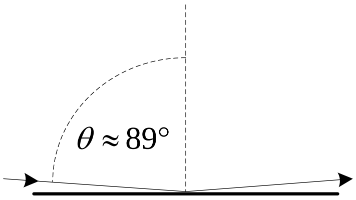
General ways of light reflections:



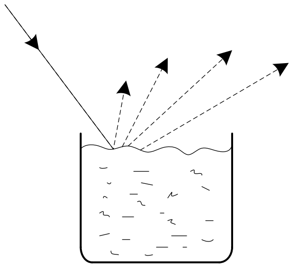
Specular (SR)



Internal (ATR)



Specular reflection (SR)

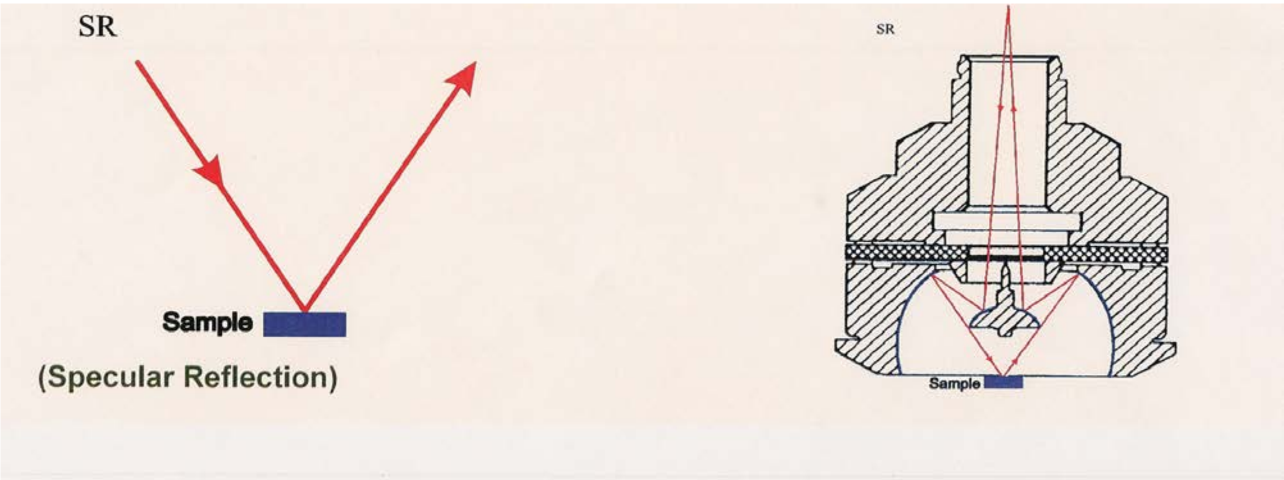


Diffuse reflection (DR)

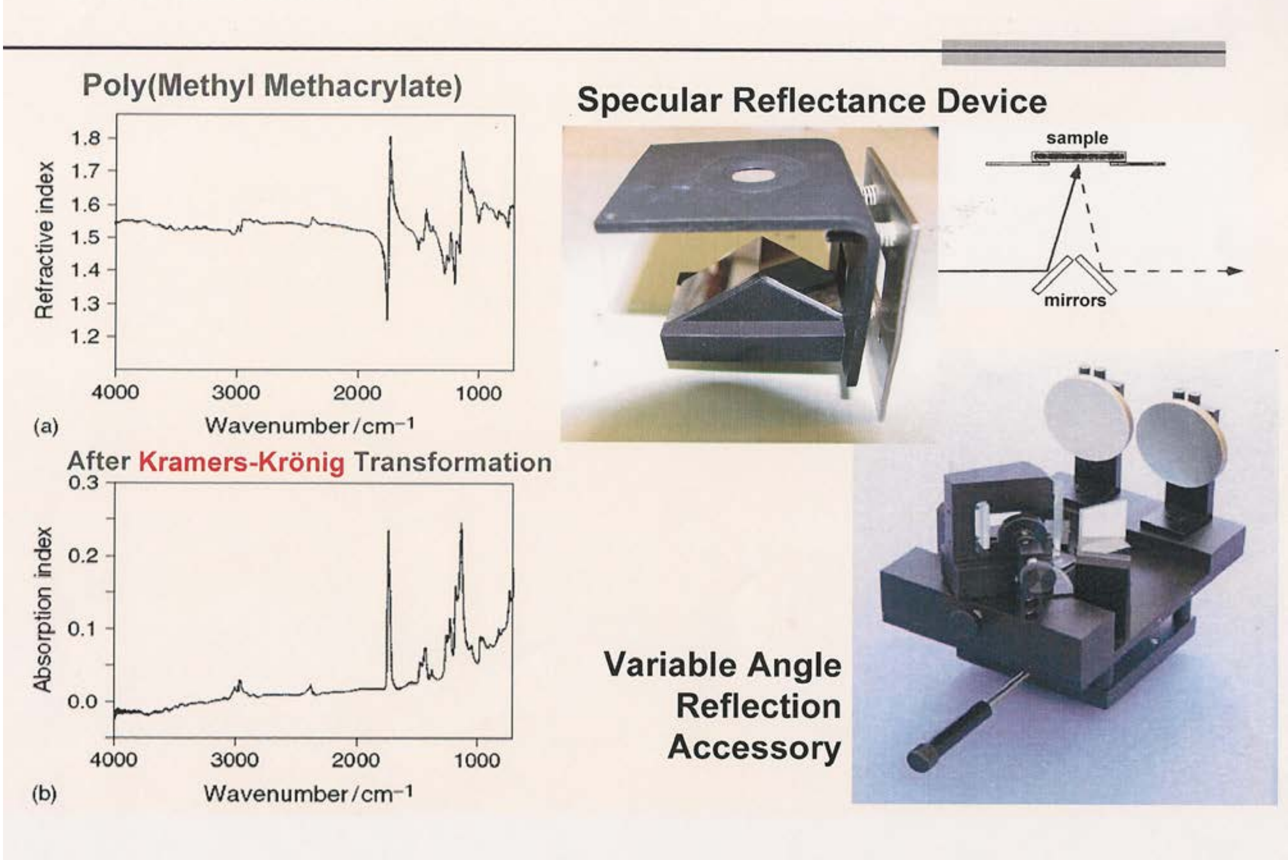
Specular reflection (SR)

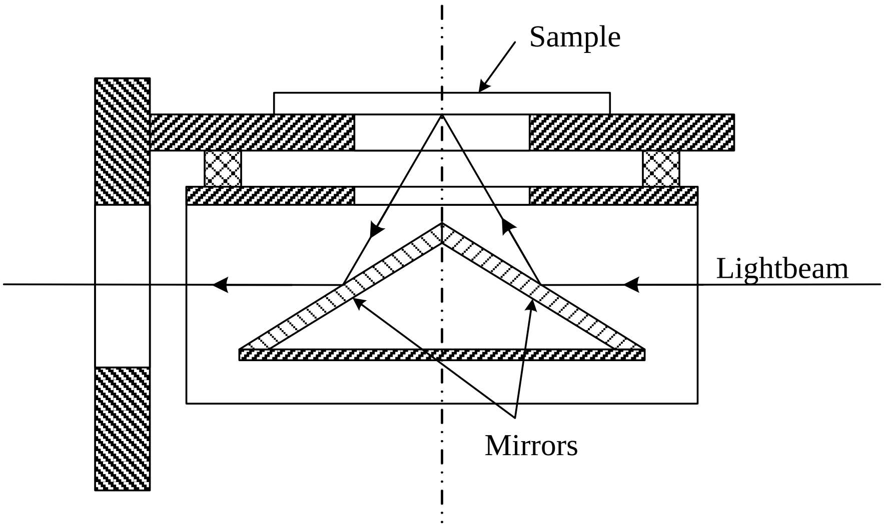
Specular reflection is not frequently used in IR spectroscopy, due to the strong distortion of the band shapes. Correction of the experimental spectra can be performed by the Kramer-Kronig transformation.

“MACRO” “MICRO”



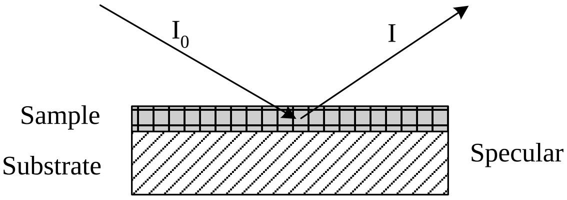
SR devices and spectra

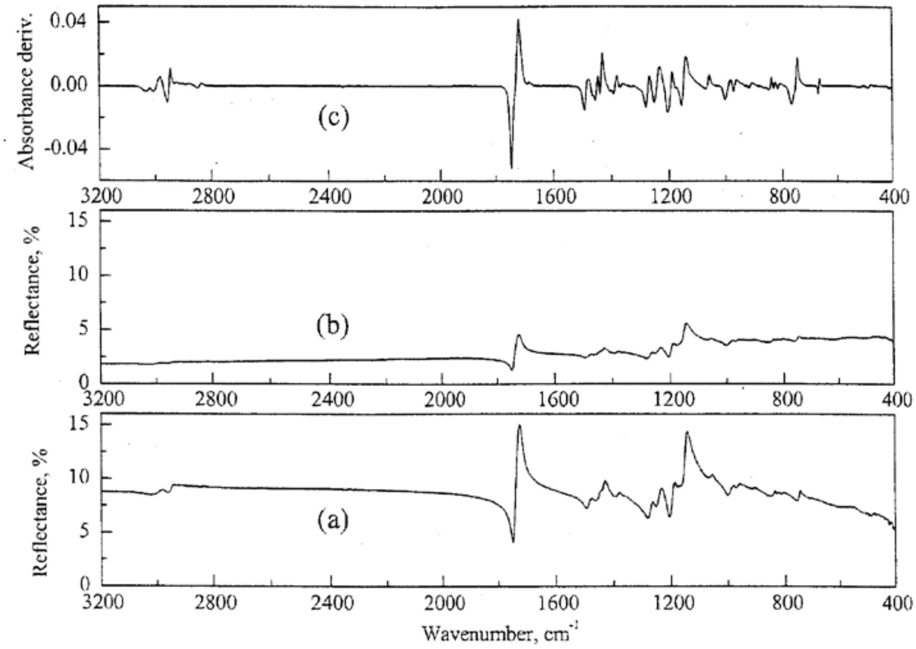




Simple specular reflection accessory

Principle:



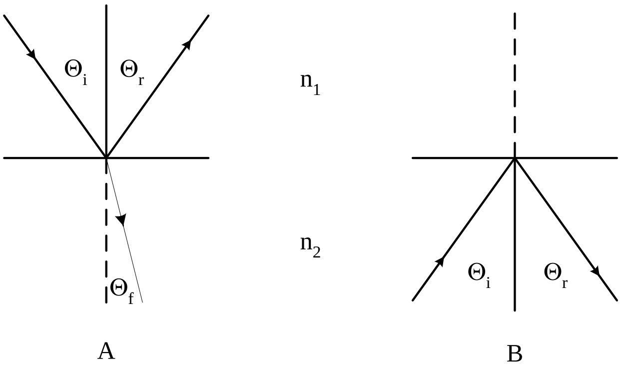


Specular-reflectance spectra of a Plexiglas slab compared to derivative absorbance spectrum; (a) Reflection from shiny surface, (b) Reflection from roughened surface, (c) First derivative of the absorbance spectrum of PMMA

Internal reflection (Attenuated Total Reflection , ATR)

.
When a beam of light travelling in a more dense medium strikes the interface, as shown in below a number of phenomena may occur depending on the angle of incidence Θ_i, and the ratio of refractive indices, n_1/n_2.

$$\sin \Theta_i > n_1/n_2$$

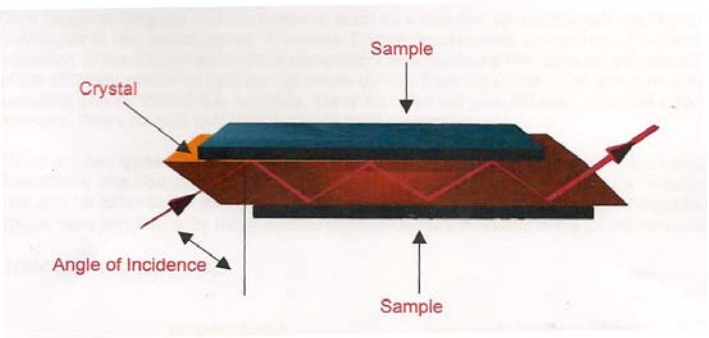


(A) Reflection and refraction. (B) Total internal reflection. Θ_i, angle of incidence; Θ_r, angle of reflection, Θ_f, angle of refraction. Medium 2 is optically denser than medium 1: $n_2 > n_1$.

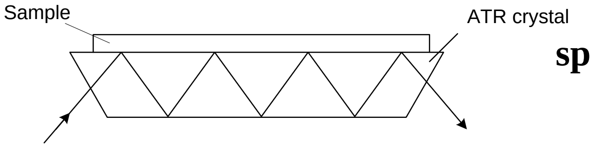
If Θ_t is undefined and total reflection occurs within the dense medium. If then

$$\sin \Theta_i = n_1/n_2$$

then Θ_i is known as the critical angle, and the refracted beam disappears into the surface. If medium 2 is a crystal material with high refractive index, such as ZnSe or KRS-5, and medium 1 is a typical organic liquid, it is easily seen that internal reflection takes place at moderate angles of incidence.



A typical type of ATR experimental set up.



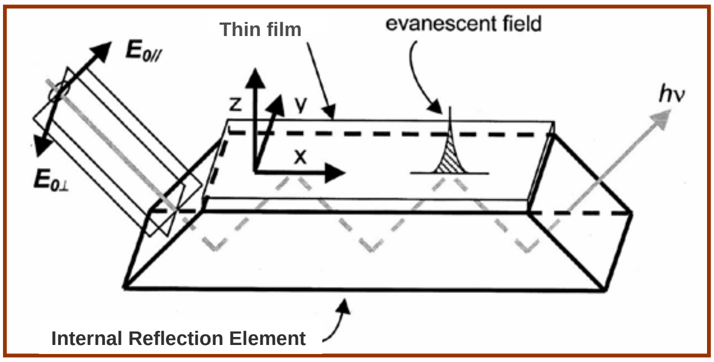
Horizontal arrangements for ATR spectroscopy: multiple internal reflections in trapezoidal crystal

Attenuated total reflection (ATR) spectroscopy uses this principle to allow infrared spectral data to be collected from samples where transmission spectroscopy does not work. In ATR, the IR beam is totally reflected within a transparent crystal (typically ZnSe or KRS-5)

An important method called internal reflection spectroscopy (IRS) or attenuated total reflection (ATR) for obtaining the infrared spectra of solids or films has been described by Fahrenfort.[10] Harrick has also discussed the theory in considerable detail.[11-13]

[10] Fahrenfort, *Spectrochim. Acta*, **17**, 698 (1961)
[11] N.J. Harrick, *Ann. N.Y. Acad. Sci*., **101**, 928, (1963).
[12] N.J. Harrick, *J. Opt. Soc. Amer*., **55**, 851, (1965).
[13] N.J. Harrick, „Internal Reflection Spectroscopy.“ Wiley (Interscience), New York, 1967.

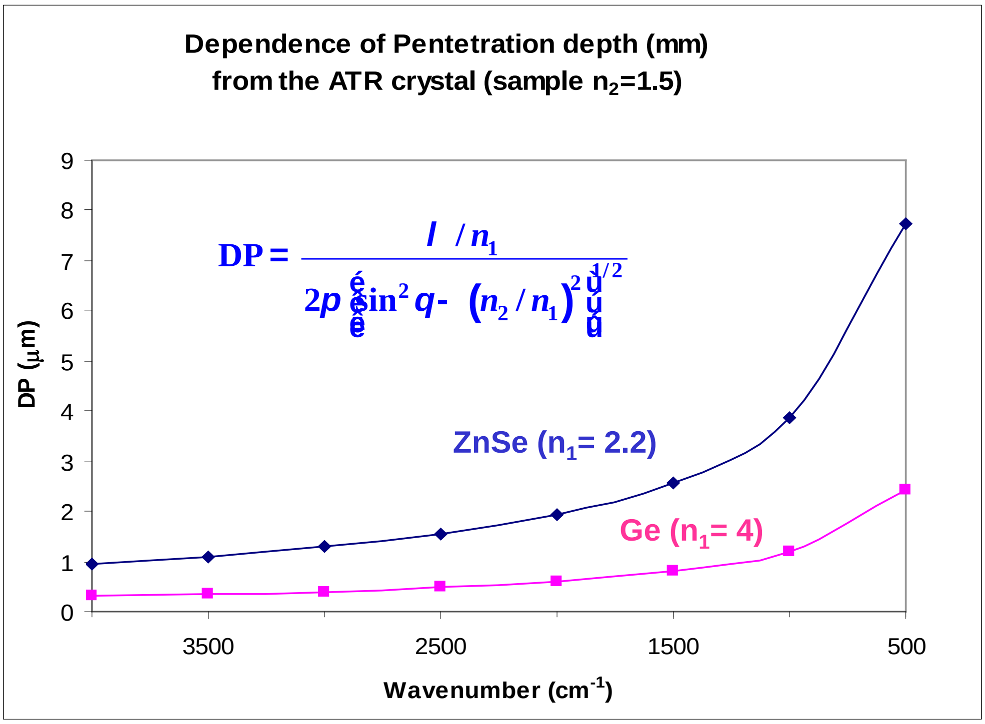
A typical type of ATR experimental set up:

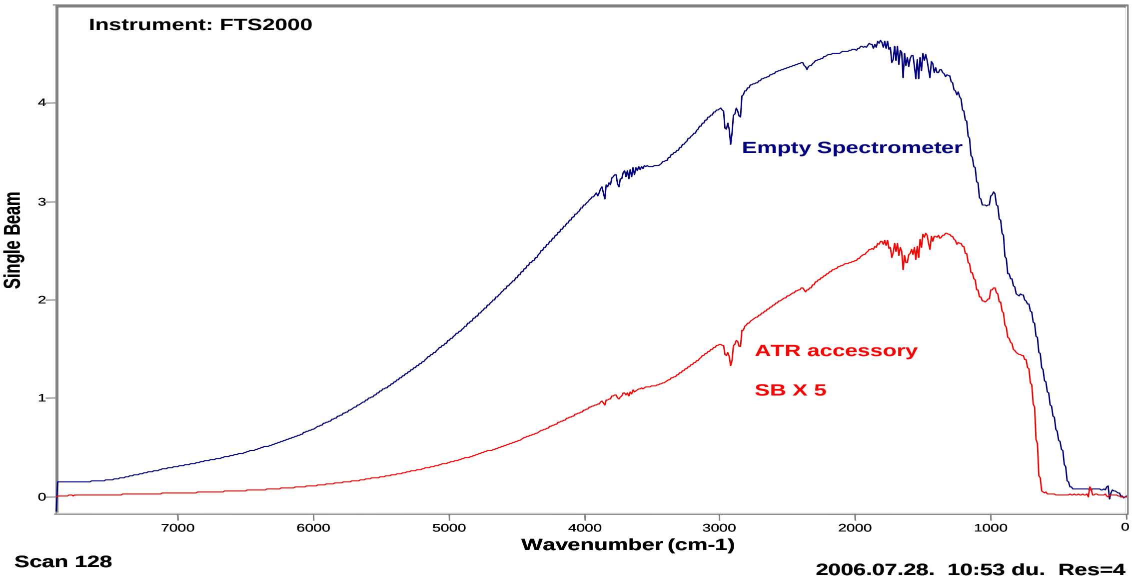


ATR penetration depth:

$$d_p \sim f(1/n_{ATR}) \qquad\qquad d_p = \frac{1}{2\pi\nu n_1\sqrt{\sin^2\theta - n_{2,1}^2}}$$

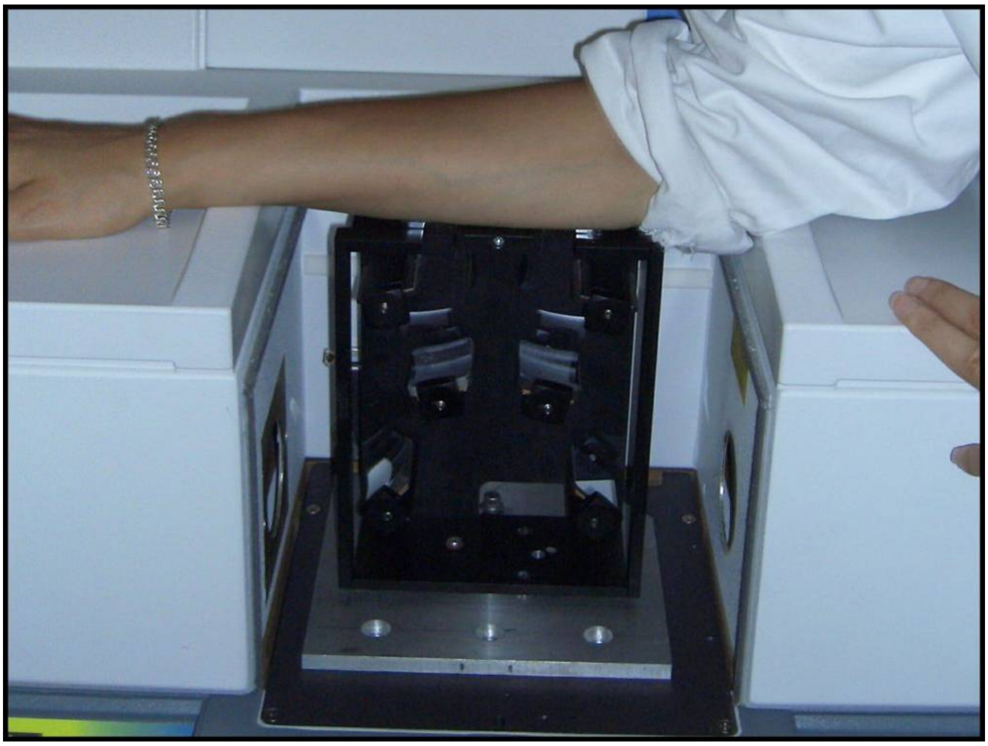
Penetration depth

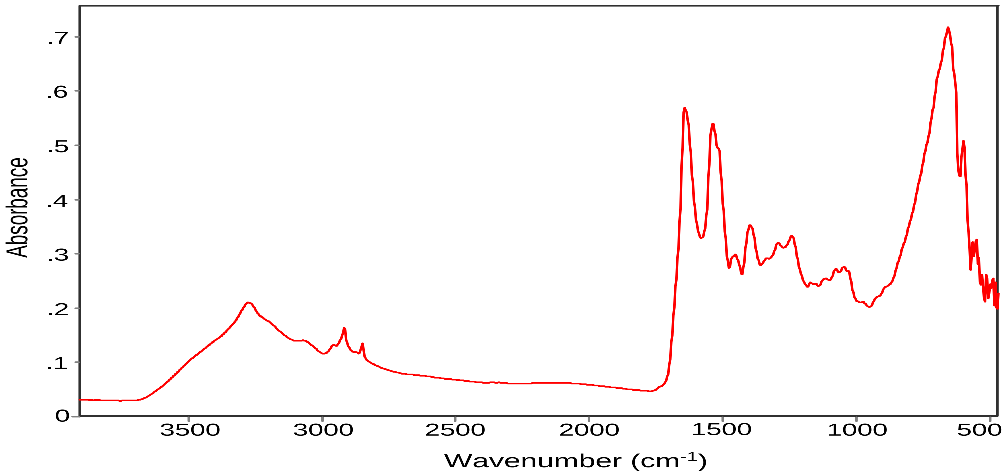




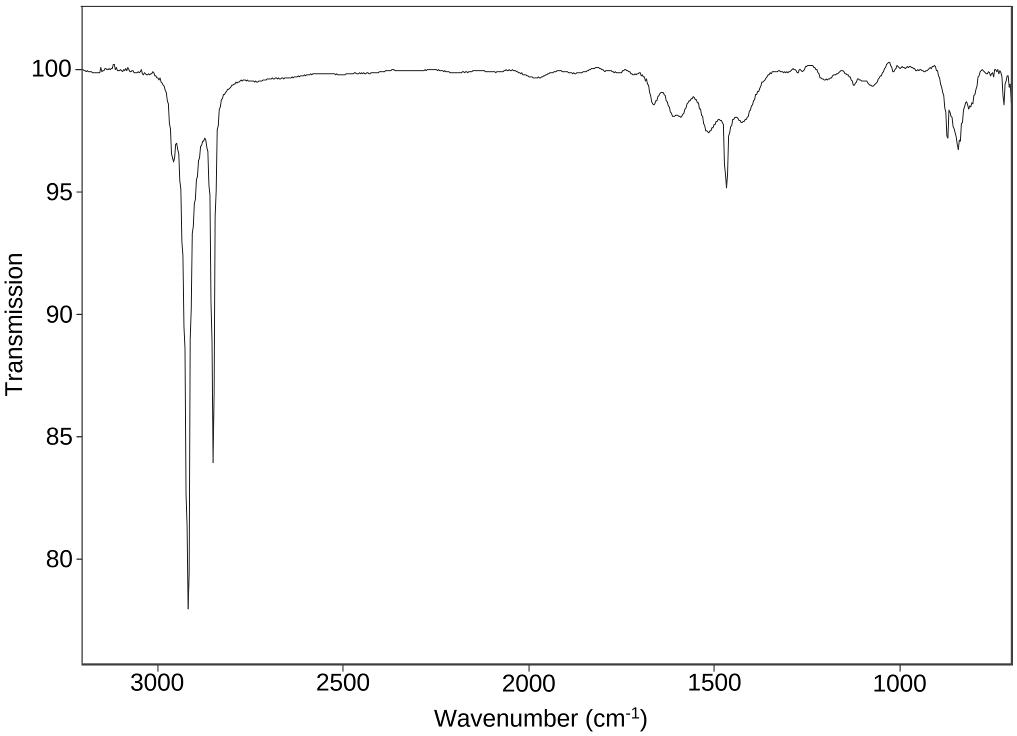
Comparison of energy throughput between the empty beam and a horizontal (Golden-Gate) ATR accessory. (Approximate ratio: 10:1)

Skin analyser:





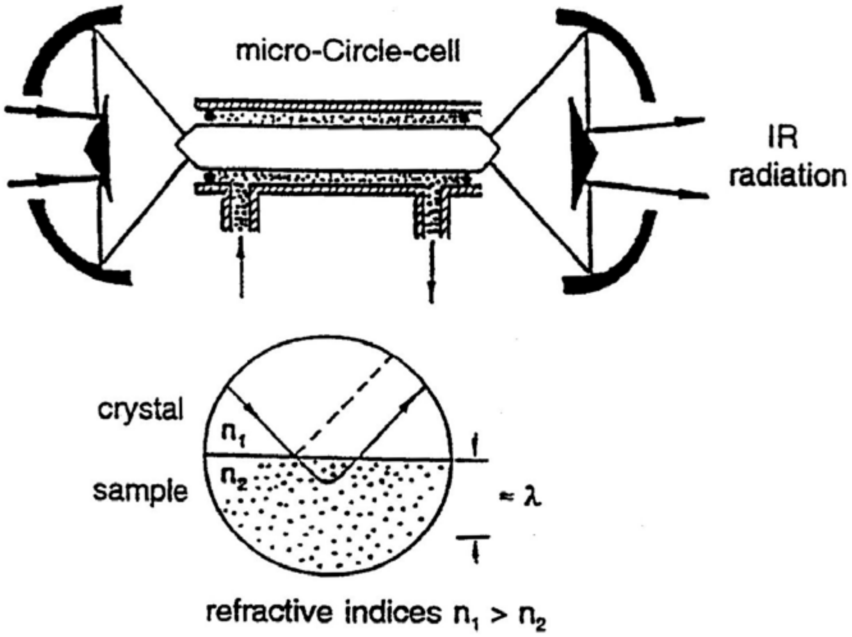
FTIR ATR spectrum of human skin measured with the horizontal ATR (ZnSe) accessory.



FTIR ATR spectrum of LB monolayer measured on a Ge ATR element (1,5-diphosphato-pentane)

Micro ATR accessories

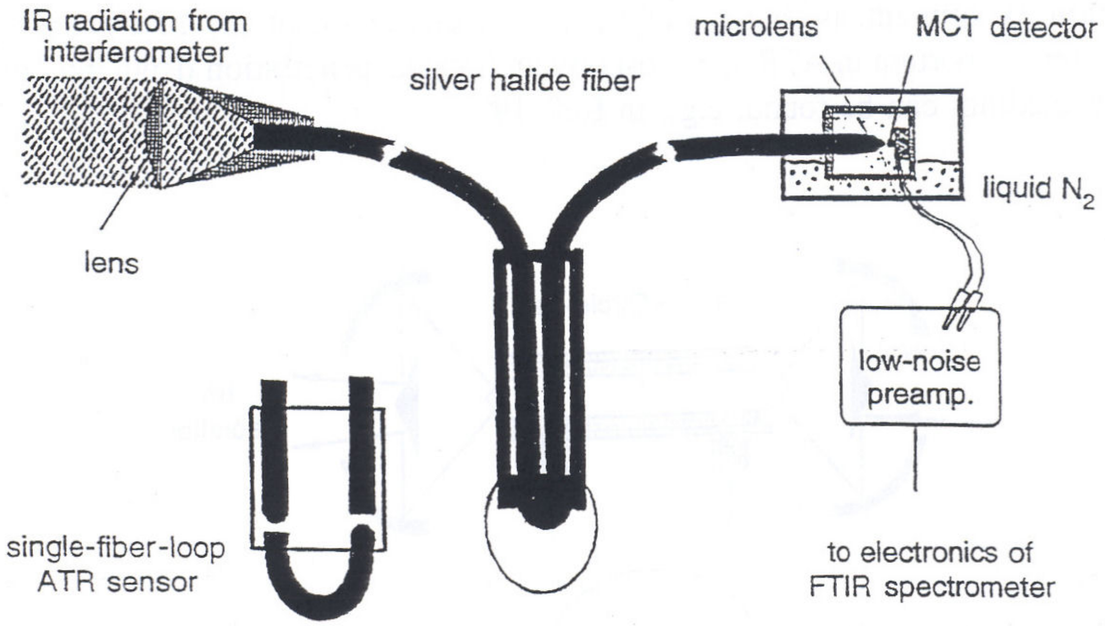
Micro circle cell



Micro-Circle cell accessory with schematics of the electromagnetic wave leakage into the sample medium

19. H.M. Heise, L. Küpper, R. Marbach, LEOS Newsletter 13, 12-15, 1999.
20. L. Butvina, In: J. Sanghera, I. Aggarwal, eds. Infrared Fiber Optics, Boca Raton, Fl: CRC Press, 1998, pp. 209-249.
21. H.M. Heise, A. Bittner, L. Küpper, L.N. Butvina, J. Mol. Stict, 410-411, 521-525, 1997.
22. H.M. Heise, A. Bittner, In H.H. Mantsch, M. Jackson, eds. Infrared Spectroscopy: New tool in medicine. Proc. SPIE 3257, 2-12, 1998.
23. H.M. Heise, L. Küpper, L.N. Butvina, Sensors Actuators B 51, 84-91, 1998.

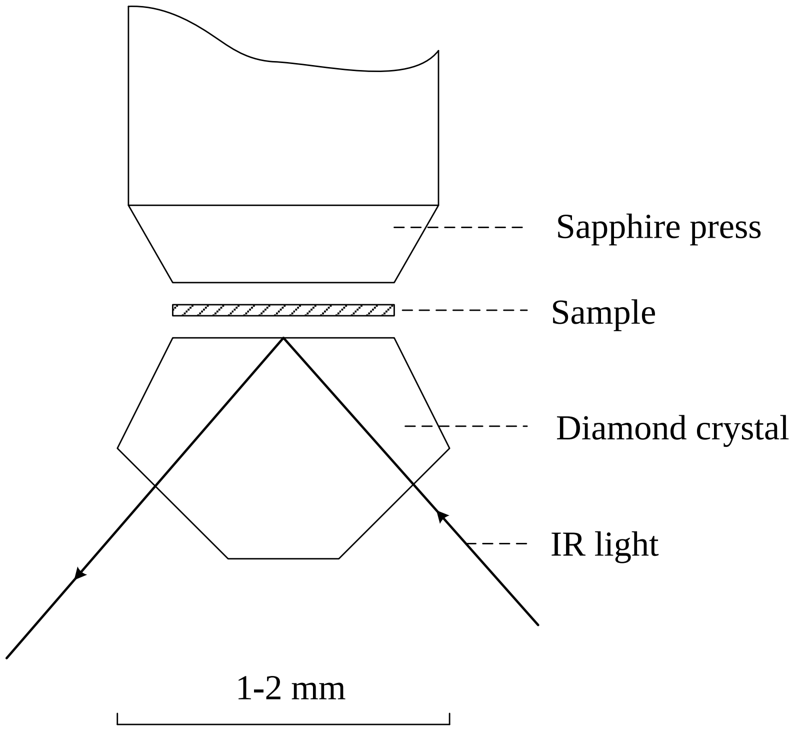
Fiber optics based ATR:

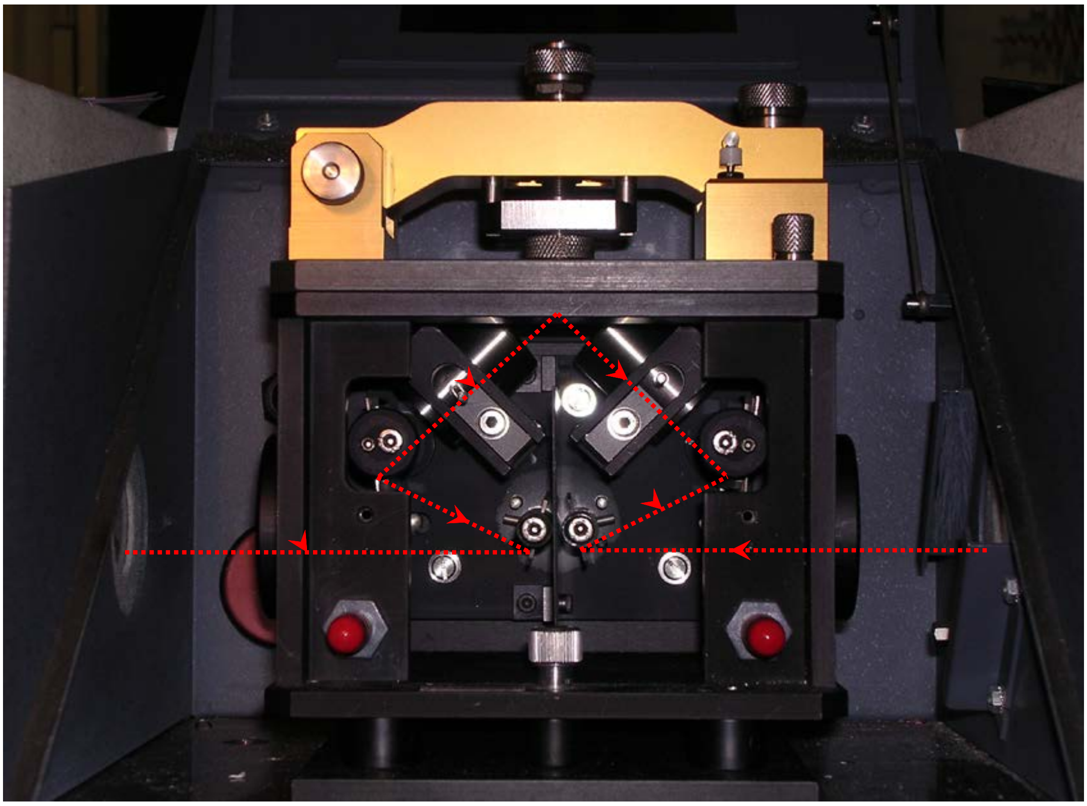


Simple inexpensive setup for evanescent wave spectroscopy using fiber optics.

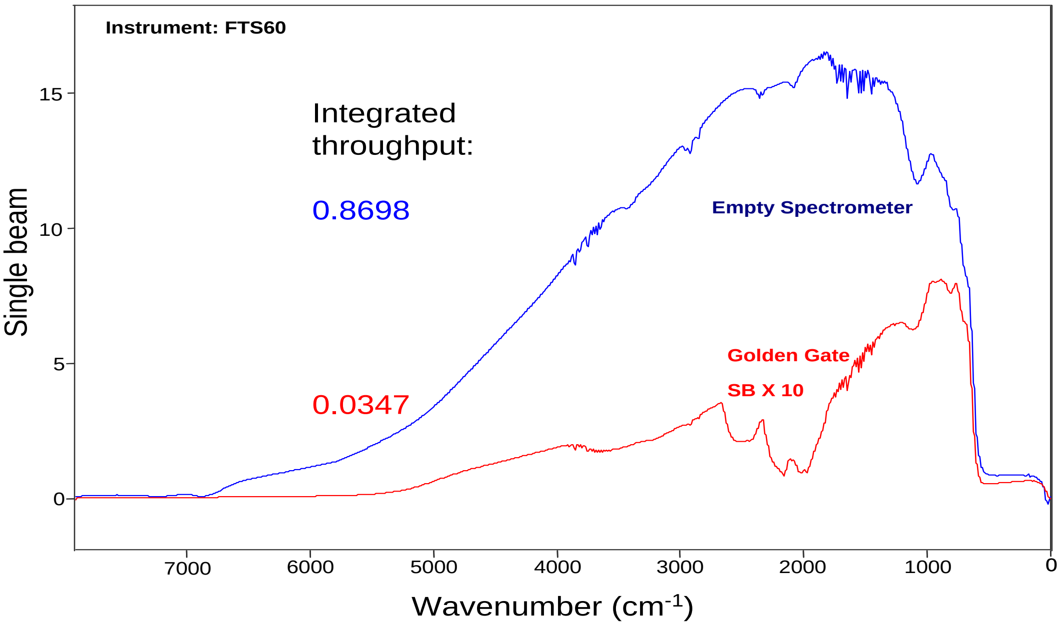
Golden Gate micro ATR:

Principle:

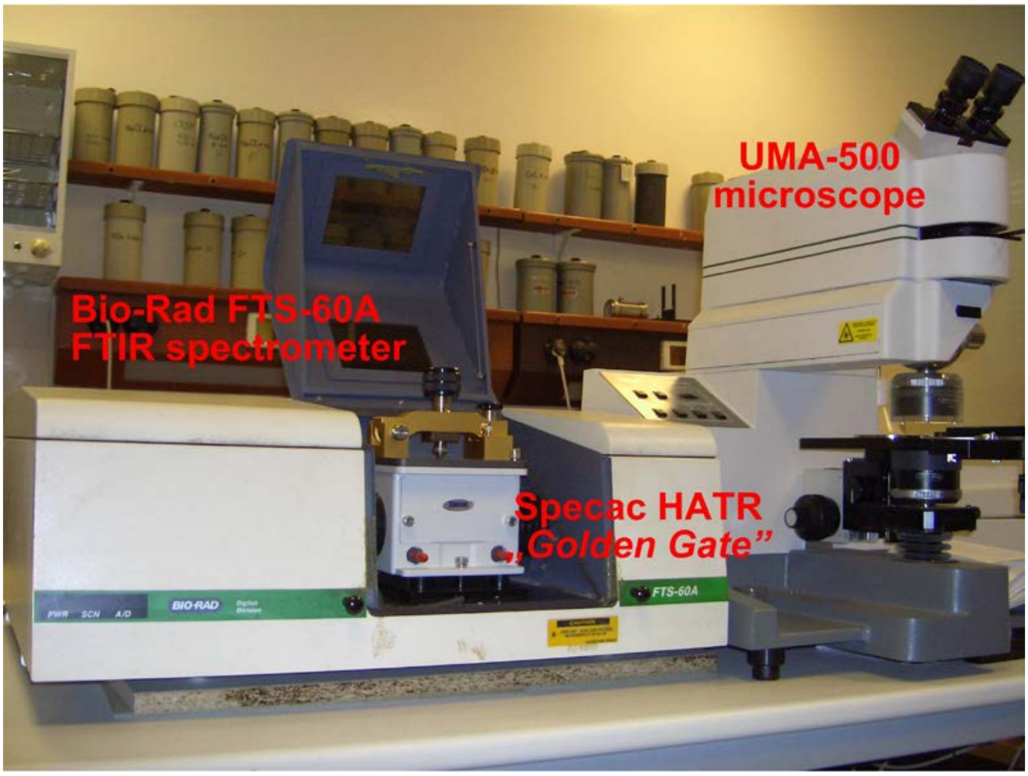




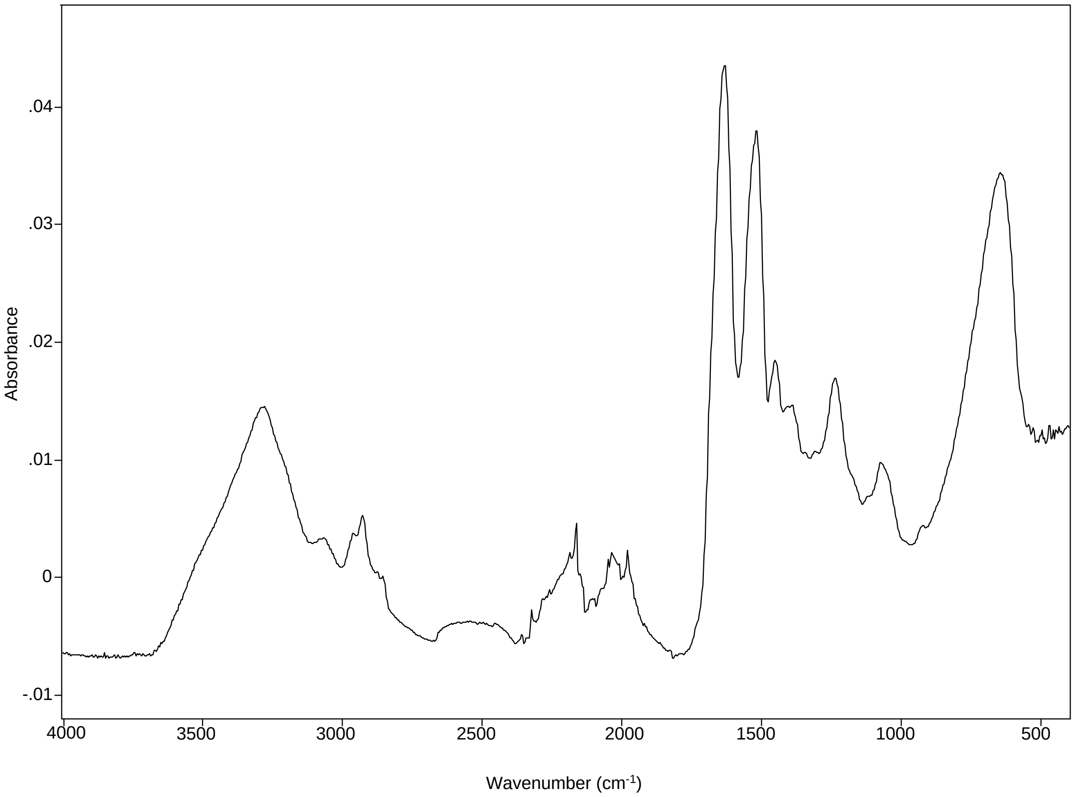
Golden Gate



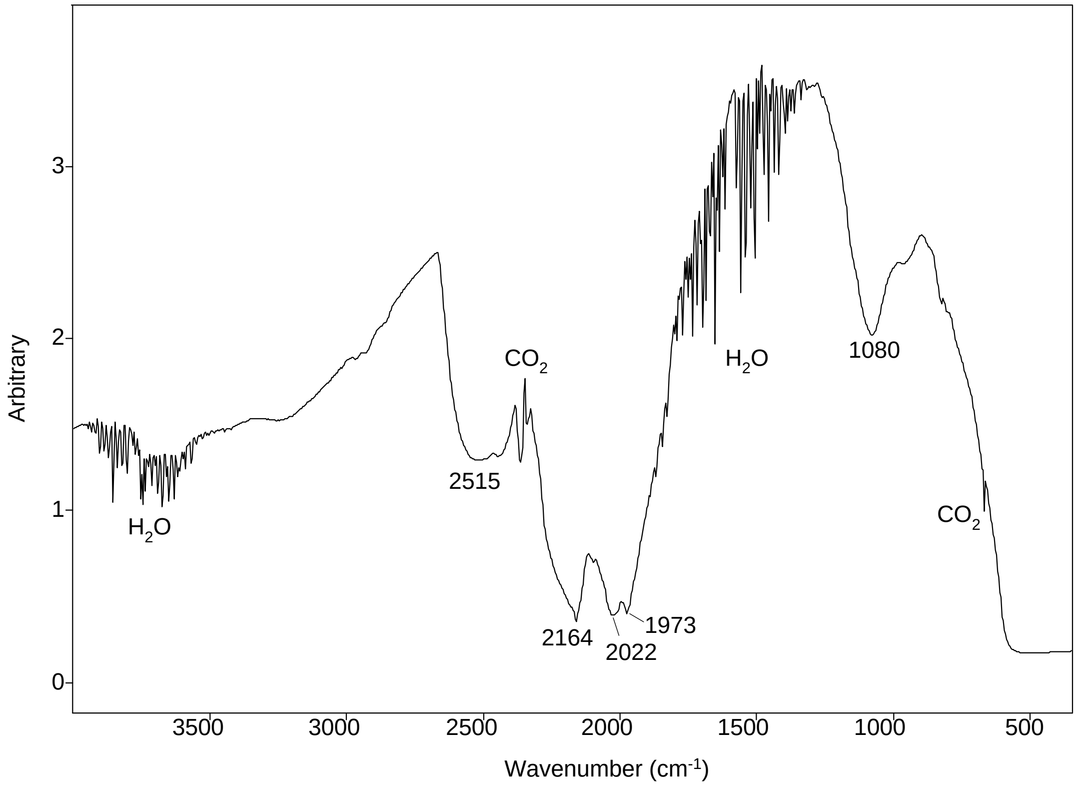
Comparison of energy throughput between the empty beam and the Golden-Gate ATR accessory. (Approximate ratio: 25:1)



Measurement system

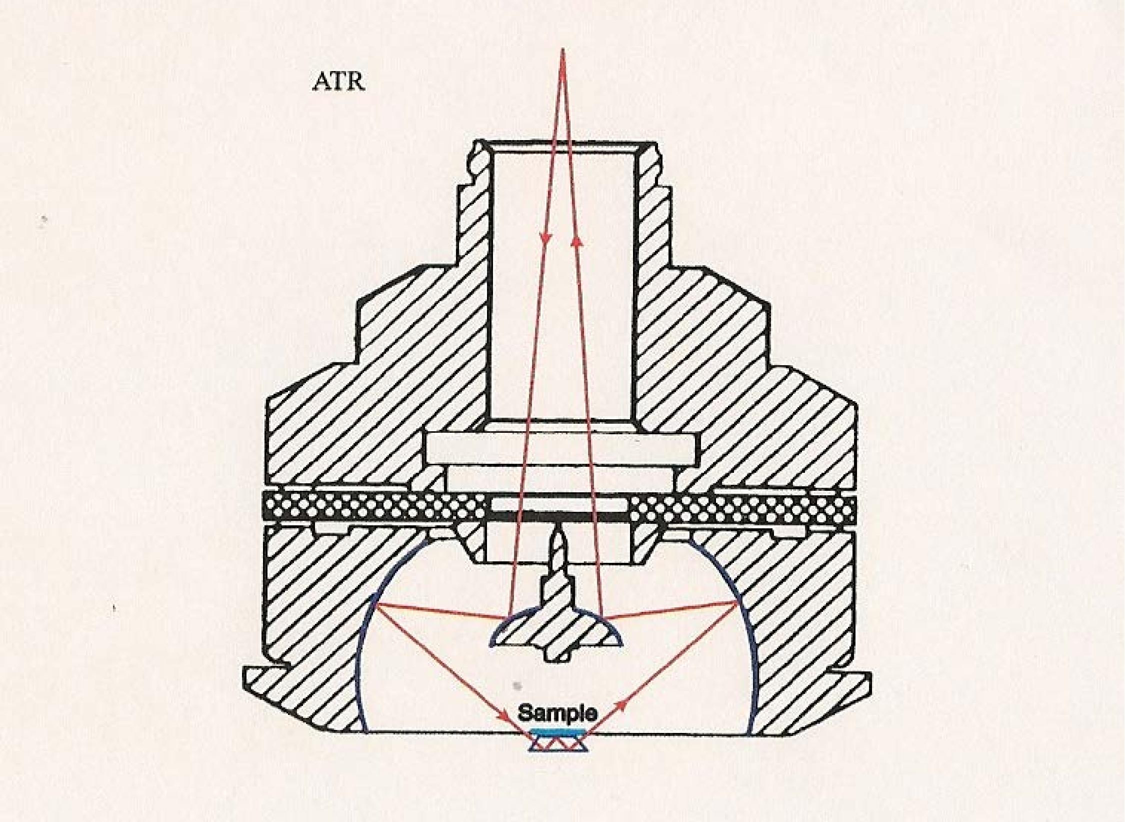


FTIR ATR spectrum of human hair measured with the Golden-Gate diamond ATR accessory.



Single beam spectrum of a micro diamond cell.

ATR accessory of IR microscope:



Reflection-absorption infrared spectroscopy (RAIRS)

A very sensitive method for study of thin layers on polished (mirror type) metal surfaces.

Basic applications:

- Study of chemisorbed molecules on metal single crystals at sub monolayer coverage;
- Langmuir-Blodget (LB) films on solid substrates;
- Corrosion layers on metals;
- Vapour deposition technologies;
- Paint surfaces;
- Thin polymer layers on solid flat surfaces;
- Etc.

Due to the tangential light illumination the IR beam interacts practically with all molecules on the surface. The illuminated area is about 2-4 cm^2. This is the basic reason of sensitivity.

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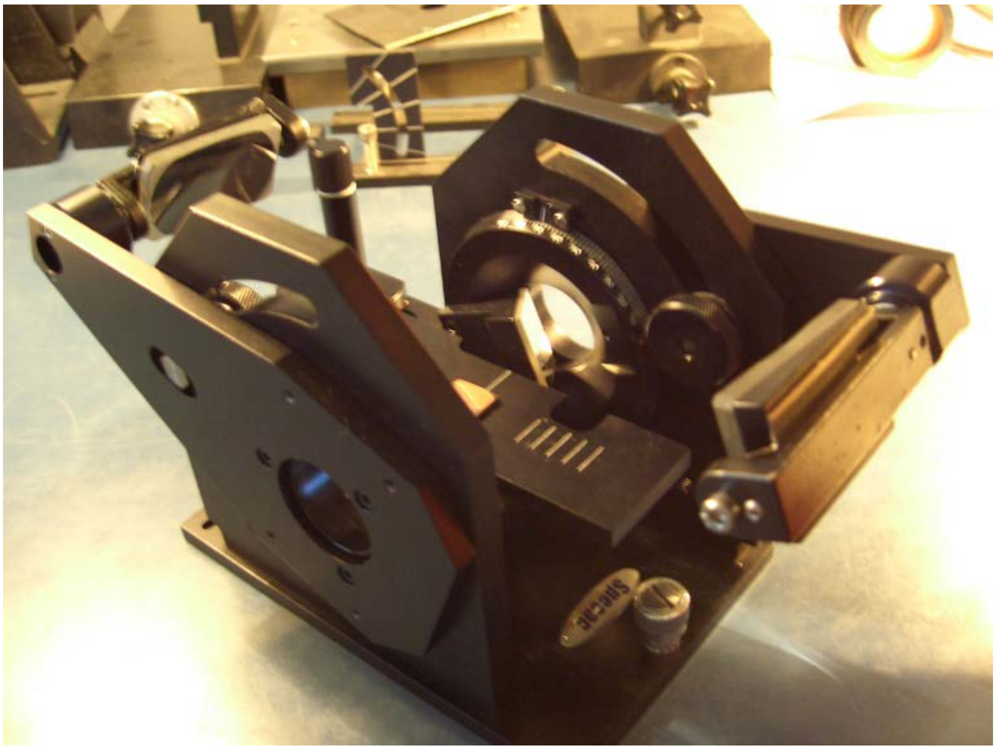
Langmuir-Blodgett films: nanolayers in corrosion protection

Langmuir-Blodgett technique is a method of forming molecular surface films in highly controllable way



Special optical accessory for RAIRS measurements

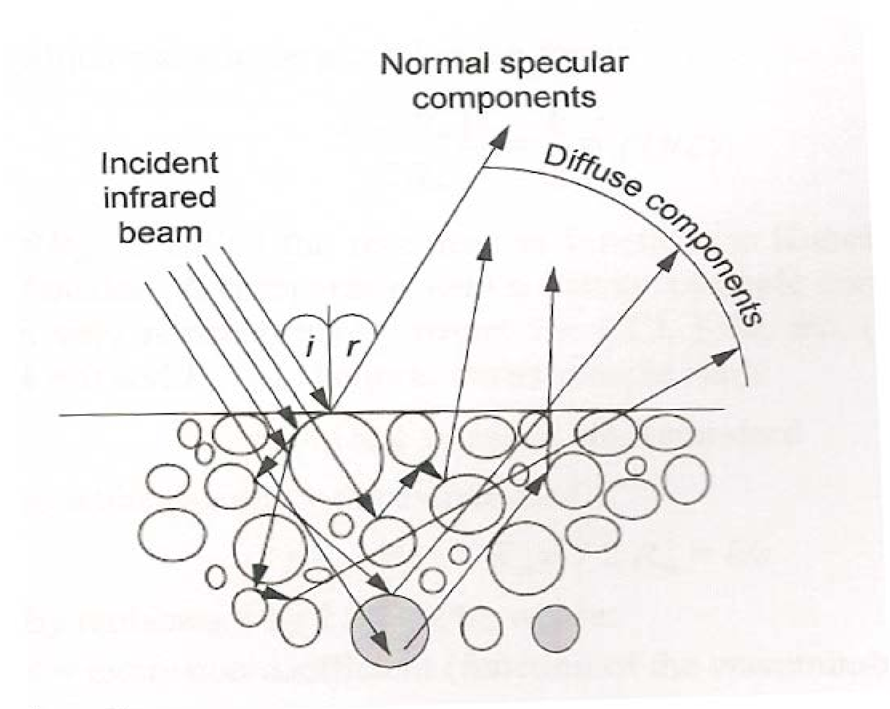
RAIRS spectra of 1, 3, 9 and 11 layers on copper substrate

Benzhydroxan acid

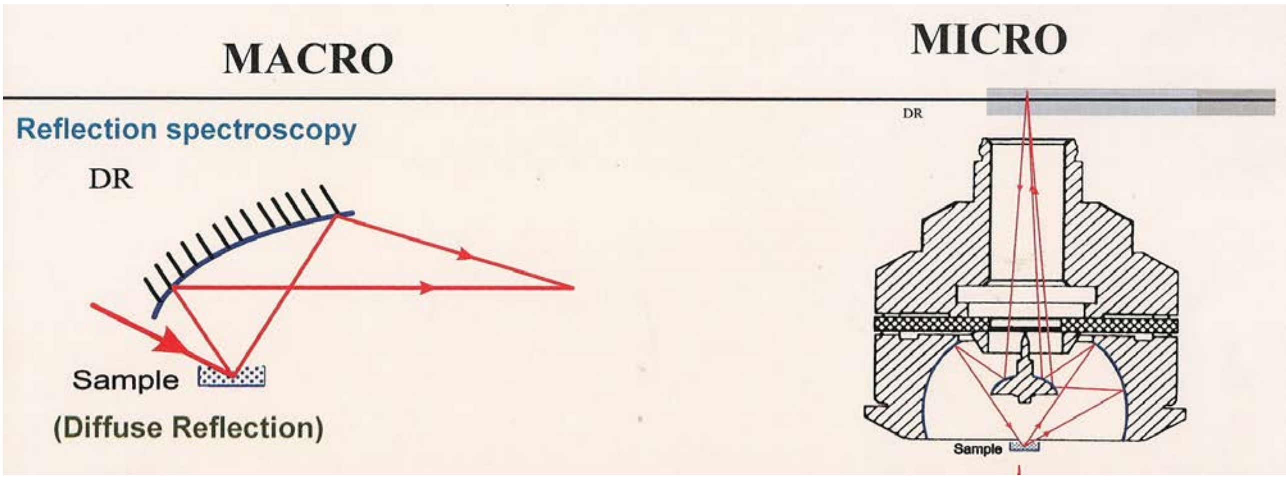
Intensity of CH_3 stretching vibrations vs. the number of monolayer

Diffuse reflectance infrared spectroscopy (DRIFT)

Diffuse reflectance is a technique where source radiation strikes a powdered sample and is diffusely reflected in different derictions. This weak diffuse radiation is collected and is measured by the spectrometer which is usually an FTIR instrument. Usually the finely powdered sample is diluted to a concentration of 5 to 10% in powdered KBr or KCl for mid-IR diffuse reflectance spectra. No dilution is required in the near-IR region, where the bands are weaker [4,5]



Mechanisms generating infrared spectrum of powders



Pure powdered KBr or KCl is used as a reference against which the sample spectrum is ratioed as shown below, where R_∞ is the reflectance of a thick scattering layer.

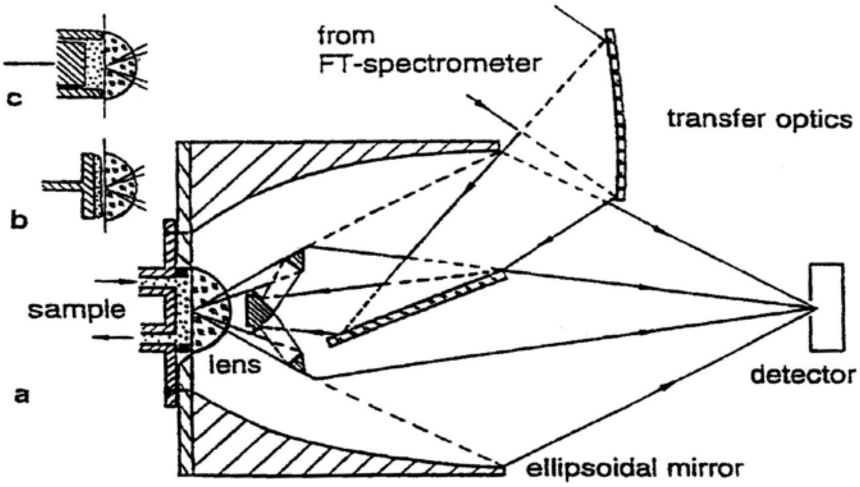
$$R_\infty = \frac{R_\infty(sample)}{R_\infty(reference)} \qquad \text{(Eq. 2.7)}$$

A function derived by Kubelka and Munk[5], $f(R_\infty)$, can be used in a computer program to change the reflectance spectrum into a spectrum resembling a linear absorbance spectrum.

$$f(R_\infty) = \frac{(1-R_\infty)}{2R_\infty} = \frac{k}{s} \qquad \text{(Eq. 2.8)}$$

Here k is molar extinction coefficient and s is a scattering coefficient which varies with particle size and packing..

[4] M.P. Fuller, R.P. Griffiths, *Anal. Chem.*, **50**, 1906, (1978).
[5] P. Kubelka, *J. Opt. Soc. Amer.*, **38**, 448 (1948).



Diffuse-reflectance accessory used for IR spectrometry of scattering samples: (a) liquid samples, (b) solid films, and (c) powders

J. Coates, *Appl.Spectrosc. Rev*. **33**, 367-425, 1998.
L.A. Cassis, J.Yates, W.C. Symons, R.A. Lodder, *J. Near Infrared Spectrosc.* **6**, A21-A25, 1998.

A. Bittner, H.M. Heise, In: J.A. de Haseth, ed. Fourier Transform Spectroscopy, 11th International Conference, New York: American Institute of Physics, AIP Conf. Proc. **430**, 278-281, 1998.

.R. Marbach, H.M. Heise, *Appl. Optics* **34**, 610-621, 1995.

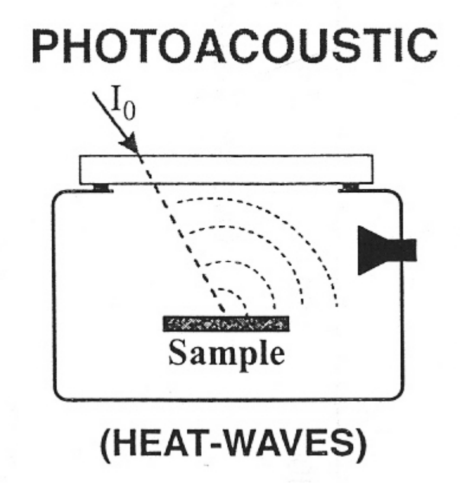
H.M. Heise, A. Bittner, R. Marbach, *Clin. Chem. Lab. Med.* **38**, 137-145, 2000.

PAS (Photoacoustic spectroscopy)

Photoacoustic spectroscopy (PAS) was invented by Alexander Graham Bell in 1880 during his research to develop the photophone, a device that communicated via light waves

Bell was successful in demonstrating PAS and the photophone but practical devices fir PAS and optical communications have taken approximately a hundred years to develop to the point of great utility.

Principle:



- Modulated incident light
- Heat generation in the sample
- Temperature fluctuation at the surface
- Pressure changes in the gas phase (He)
- Detector = microphone

The efficiency of the heat transfer is determined by the thermal diffusion coefficient $\boldsymbol{a_s}$ and the modulation frequency ω

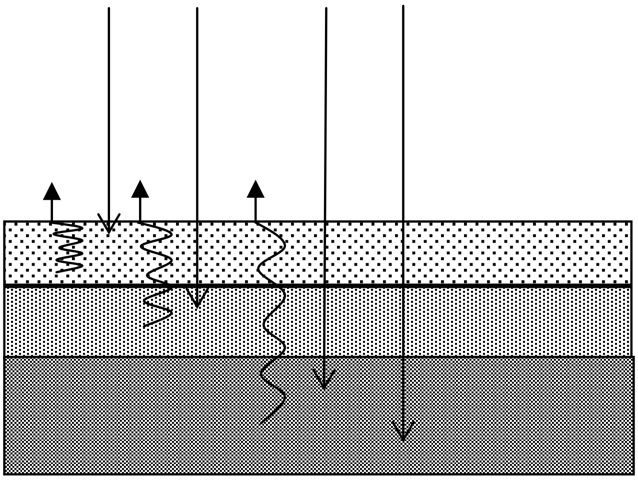
$$a_s = \left[\frac{\omega}{2\alpha}\right]^{1/2}$$

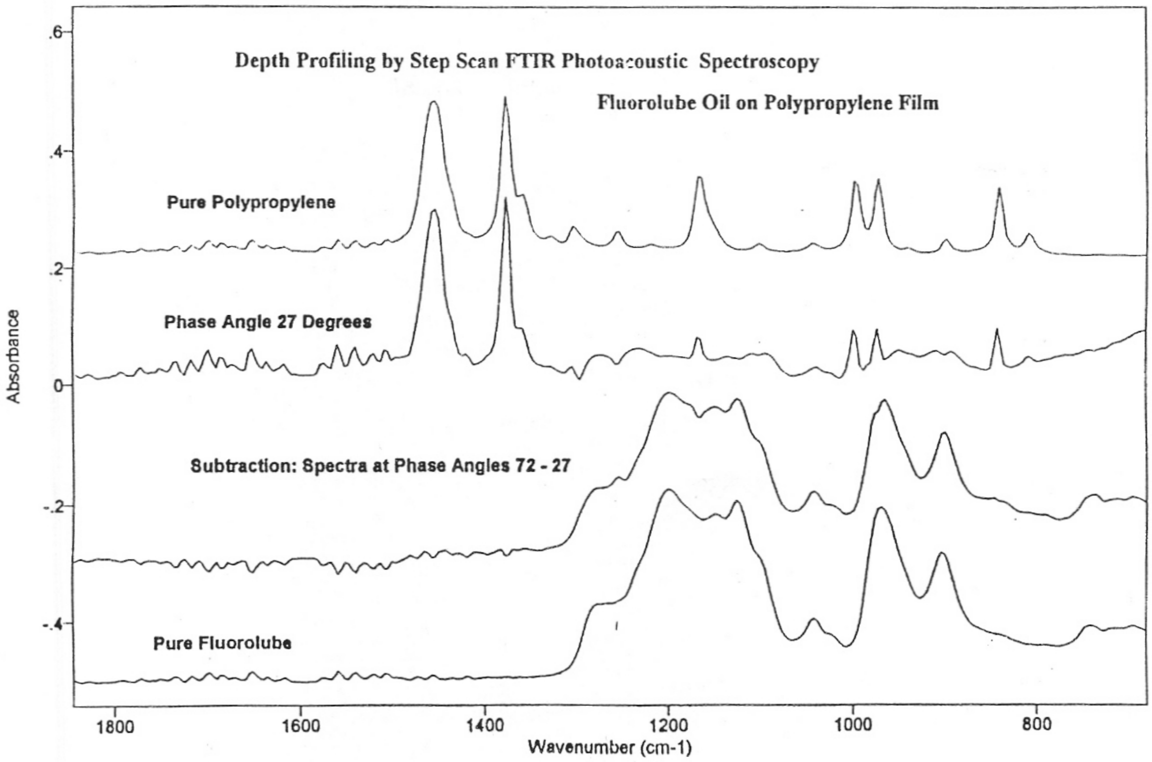
α – thermal diffusivity

The thermal diffusion length μ_{th}

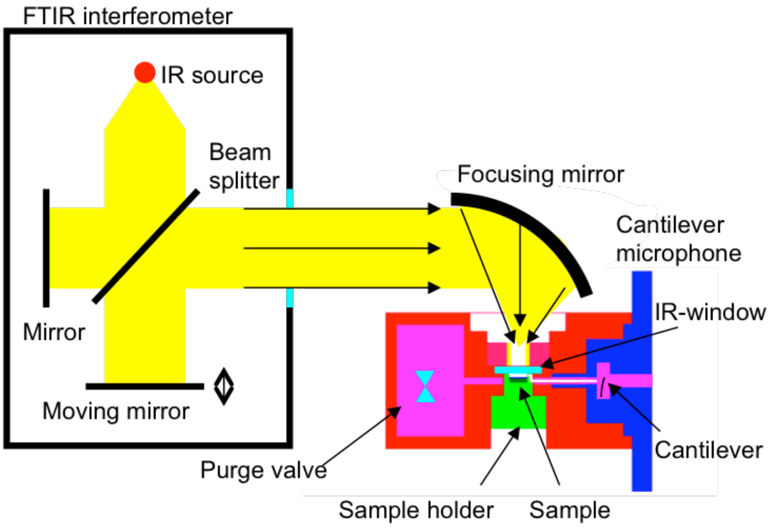
$$\mu_{th} = \frac{1}{a_s} = \left[\frac{2\alpha}{\omega}\right]^{1/2}$$

Photoacoustic penetration depth:





New experimental set up: Gasera (Turku, Finland)



Typical photoacoustic Fourier transform infrared (FTIR-PAS) setup for analysis of solid and liquid samples.

.The FTIR analysis of solid- and liquid-phase samples has a great variety of applications and advantages compared to other techniques. The most important and best-known advantages are:

- minimal sample preparation required,
- suitability for opaque materials,
- possibility for depth profiling,
- and non-destructive measurement, which means that the sample is not consumed.

The typical applications of solid- and liquid-phase photoacoustic FTIR are the study of

- carbons,
- coals,
- hydrocarbons,
- hydrocarbon fuels,
- corrosion,
- clays and minerals,
- wood and paper,
- polymer layers,
- food products,
- biology and biochemistry e.g. proteins, bacteria and fungi,
- medical applications such as human tissue,
- drug characterization and penetration,

- teeth, hair and bacteria,
- and non-destructive measurement of carbonyl compounds, textiles, and catalysts.

In fact the PA301 is over **100x faster** that other competing PA solutions in the market. Furthermore, ambient air can be used as the carrier gas to obtain a signal-to-noise ratio (SNR) that is still significantly better compared to other commercial photoacoustic detectors used with helium carrier gas.

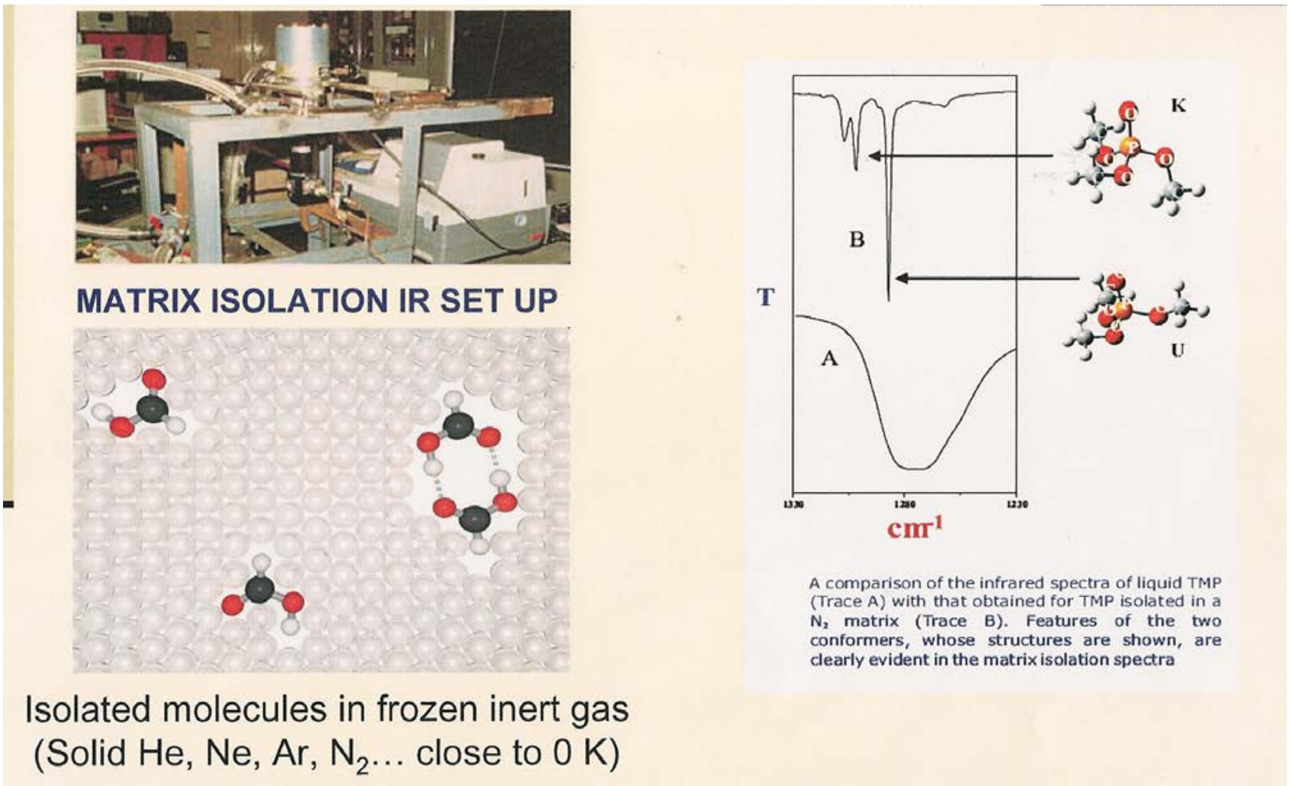
Variable temperature IR measurements

Application of low temperature :
*Conformers, isomers
*Isotopic species
*Instable species

*Phase transition

Application of high temperature gas cell:
*Increase vapour pressure
*Emission measurements
*Measurement of non volatile samples

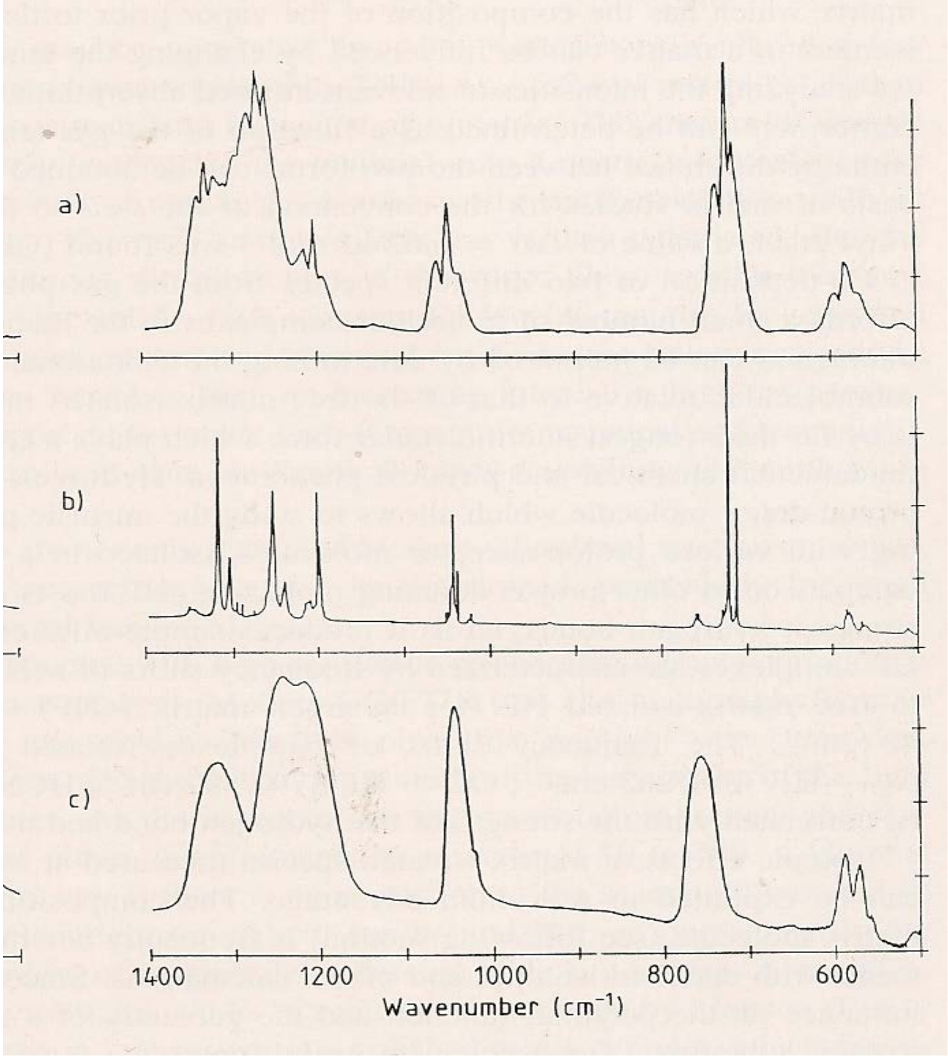
Matrix isolation spectroscopy


MATRIX ISOLATION IR SET UP

Isolated molecules in frozen inert gas (Solid He, Ne, Ar, N_2… close to 0 K)

A comparison of the infrared spectra of liquid TMP (Trace A) with that obtained for TMP isolated in a N_2 matrix (Trace B). Features of the two conformers, whose structures are shown, are clearly evident in the matrix isolation spectra

Applications:
*Conformers, isomers
*Isotopic species
*Instable species
*Phase transition
*Decreasing band shifts to 0.1-2 cm^{-1}
*Weak associations
*Instable species, radicals, ions etc.



Infrared spectra of $HClO_4$

a.) In gas phase

b.) Isolated in Ar matrix at 11 K, 0.7 mM molar ratio 1:500

c.) As a solid film at 50 K after slow evaporation of Ar from the matrix isolated sample