

Technical Review

No. 2 · 1990

Gas Monitoring



Brüel & Kjær 

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by Jørgen Christensen

Optical Filters and their Use with the Type 1302 & Type 1306 Photoacoustic Gas Monitors

by Jørgen Christensen, M.Sc.

Abstract

The Brüel & Kjær Multi-gas Monitor Type 1302 and Toxic-gas Monitor Type 1306 both utilize interchangeable optical filters to select a band of infrared light at an appropriate wavelength for monitoring some particular gas. This article describes the range of optical filters available: their construction, specification and their selection and use with Type 1302 and/or Type 1306 for a particular monitoring task.

Sommaire

Le Moniteur multigaz Type 1302 et le Moniteur de gaz toxiques Type 1306 Brüel & Kjær utilisent des filtres optiques interchangeables permettant de sélectionner des bandes de lumière infrarouge à des longueurs d'ondes appropriées pour la surveillance de gaz particuliers. Cet article décrit la gamme des filtres optiques disponibles, leurs construction et spécifications, ainsi que leurs sélection et utilisation avec les 1302 et/ou 1306.

Zusammenfassung

Sowohl der Multigas-Monitor 1302 als auch der Gasmonitor 1306 von Brüel & Kjær arbeiten mit austauschbaren optischen Filtern, um das IR-Licht der Wellenlänge herauszufiltern, das für die Überwachung der jeweiligen Gase und Dämpfe geeignet ist. Dieser Artikel beschreibt die zur Verfügung stehenden optischen Filter, ihren Aufbau, ihre Spezifikationen, Selektivität und Anwendung mit den beiden Gasmonitoren.

1. Introduction

The photoacoustic transducer system used in the Brüel & Kjær Multi-gas Monitor Type 1302 and Toxic-gas Monitor Type 1306 was described in the Technical Review, No. 1-1990.

To summarise: in photoacoustic spectroscopy (PAS) the gas to be measured is irradiated by intermittent light of pre-selected wavelength. The gas molecules absorb some of the light energy and convert it into an acoustic signal which is detected by a microphone. The light source used in the Brüel & Kjær gas monitors is a heated black body emitting broad-band infrared light. The pre-selected wavelength is produced by passing this broad-band light through a particular narrow band optical interference filter.

A large range of optical filters are available for use with Brüel & Kjær gas monitors. To date, 23 different optical filters have been developed. A single optical filter can be installed in the Toxic-gas Monitor Type 1306, whereas the Multi-gas Monitor Type 1302 can be equipped with up to 6 optical filters from this range of 23 optical filters.

All the optical filters are characterized by an approximately square-shaped pass-band and very high attenuation outside the pass-band. This favours high *insensitivity* to interference from water vapour and carbon

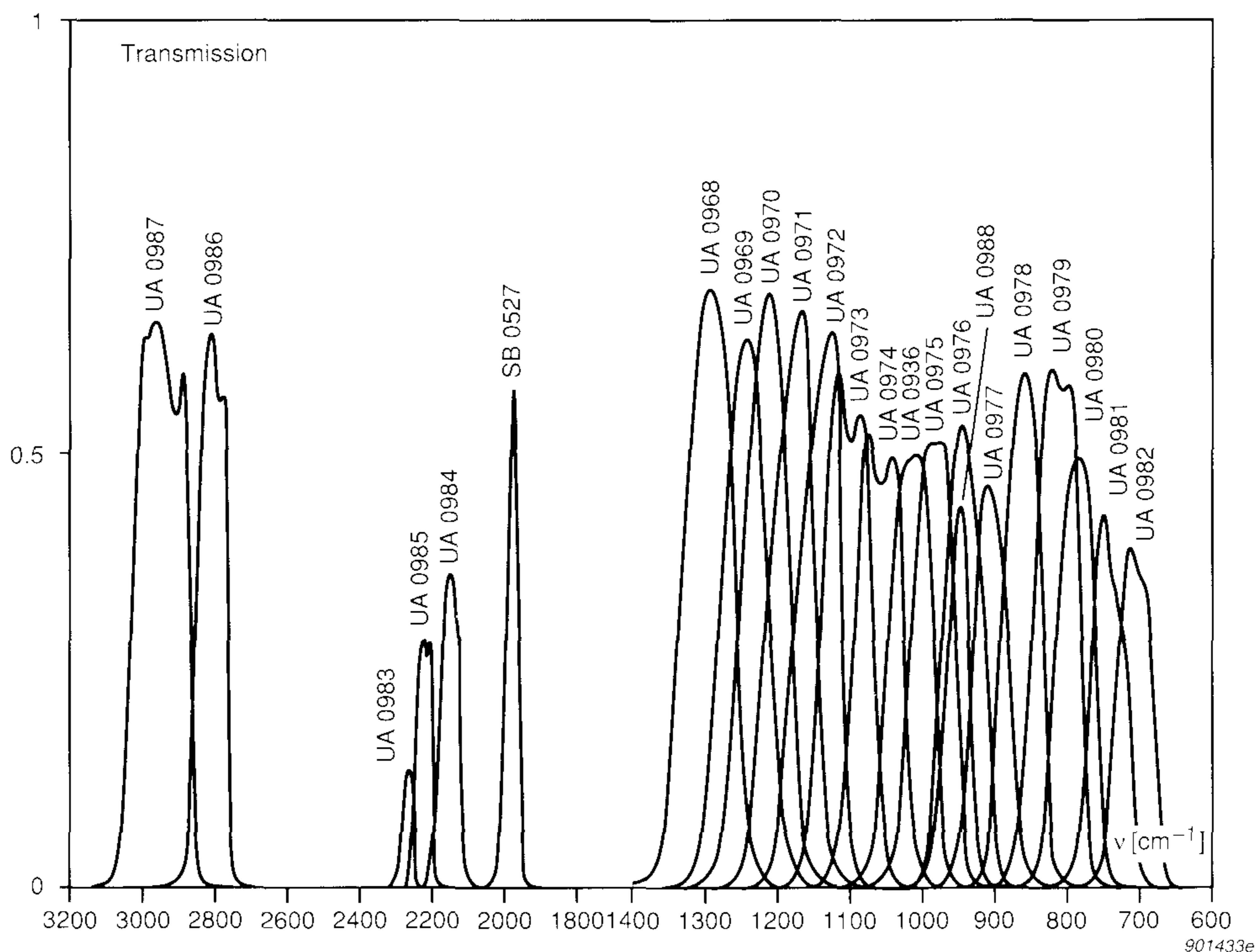


Fig. 1. Transmission characteristics of the Brüel & Kjær range of optical filters

dioxide as well as other gases present in the atmosphere. Fig. 1 shows typical transmission curves for all of the 22 optical filters available for use with Type 1302 and Type 1306, plus the transmission curve for the water-vapour filter SB 0527, which is always installed in the Type 1302. (Note that the frequency is given in units of cm^{-1} , which denotes the number of wavelengths per cm. Spectroscopists use the term “wavenumber” instead of frequency. We will use the greek letter ν to denote frequency and/or wavenumber).

This article will deal with: 1) construction of a typical optical filter; 2) optical filter specifications, and 3) the selection of optical filters for specific measuring tasks.

2. Construction of the Optical Filters

Optical filter number UA 0936 has been chosen as a typical filter in the Brüel & Kjær range. Fig. 2 illustrates how the optical filter is constructed. Each filter has three filter elements: 1) a narrow band pass (NBP) interference element, 2) a calcium fluoride (CaF_2) shortwave pass (SWP) element and 3) a wide band pass (WBP) interference element. These elements are separated from one another by thin spacers. Fig. 3 shows the transmission characteristics of each of the three elements. The transmission of the CaF_2 element is determined by both the inherent optical properties of the material itself as well as its thickness. The transmission characteristics of the interference elements will be explained in the following text.

Interference filters are multilayer thin film devices, and there are two basic kinds: (1) bandpass filters and (2) edge filters. The basic “building block” of bandpass interference filters is the Fabry Perot interferometer (or Fabry Perot cavity), which is shown schematically in Fig. 4. It consists of two parallel, partially transmitting mirrors, and its operating principle

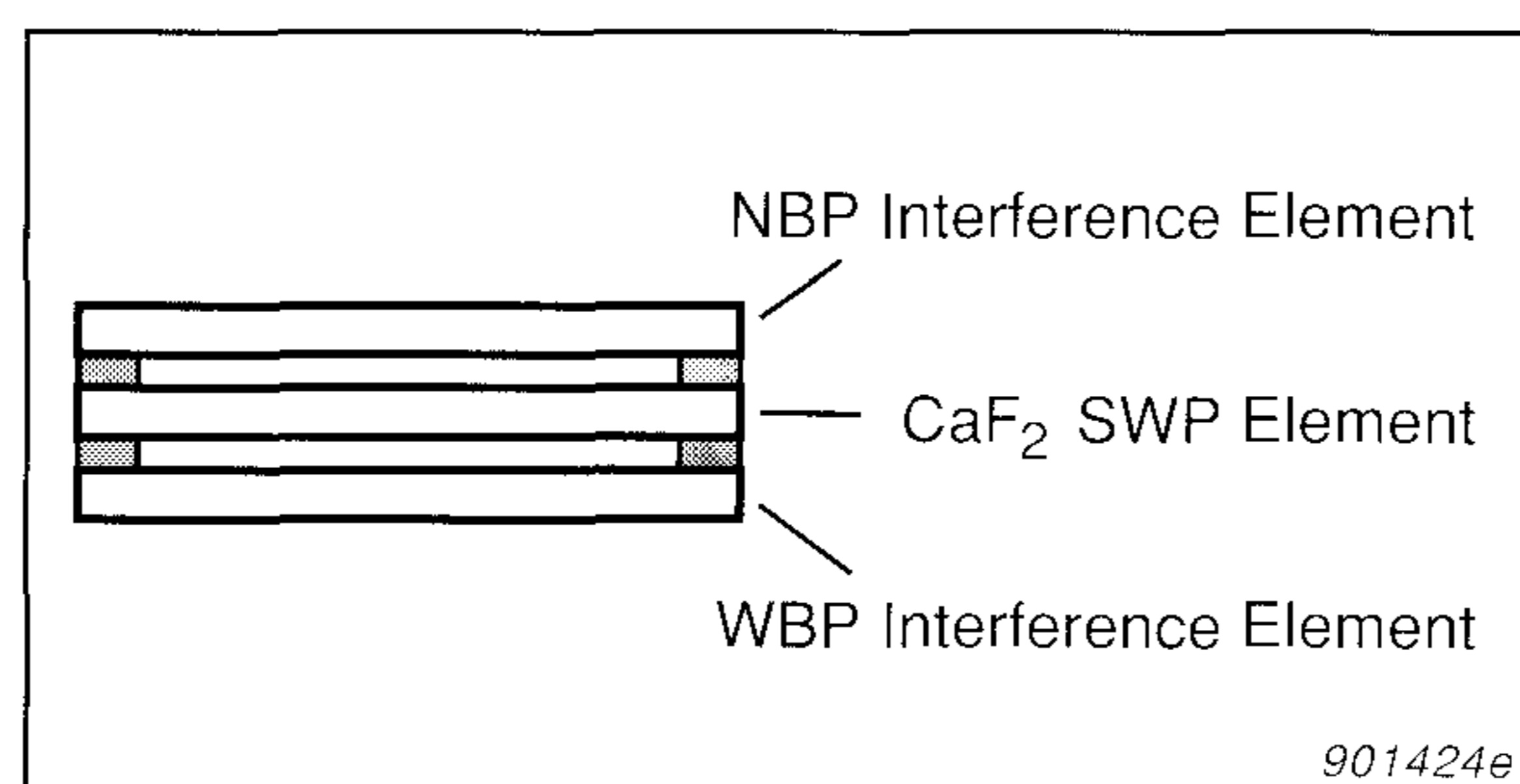


Fig. 2. Schematic construction of the optical filter UA 0936

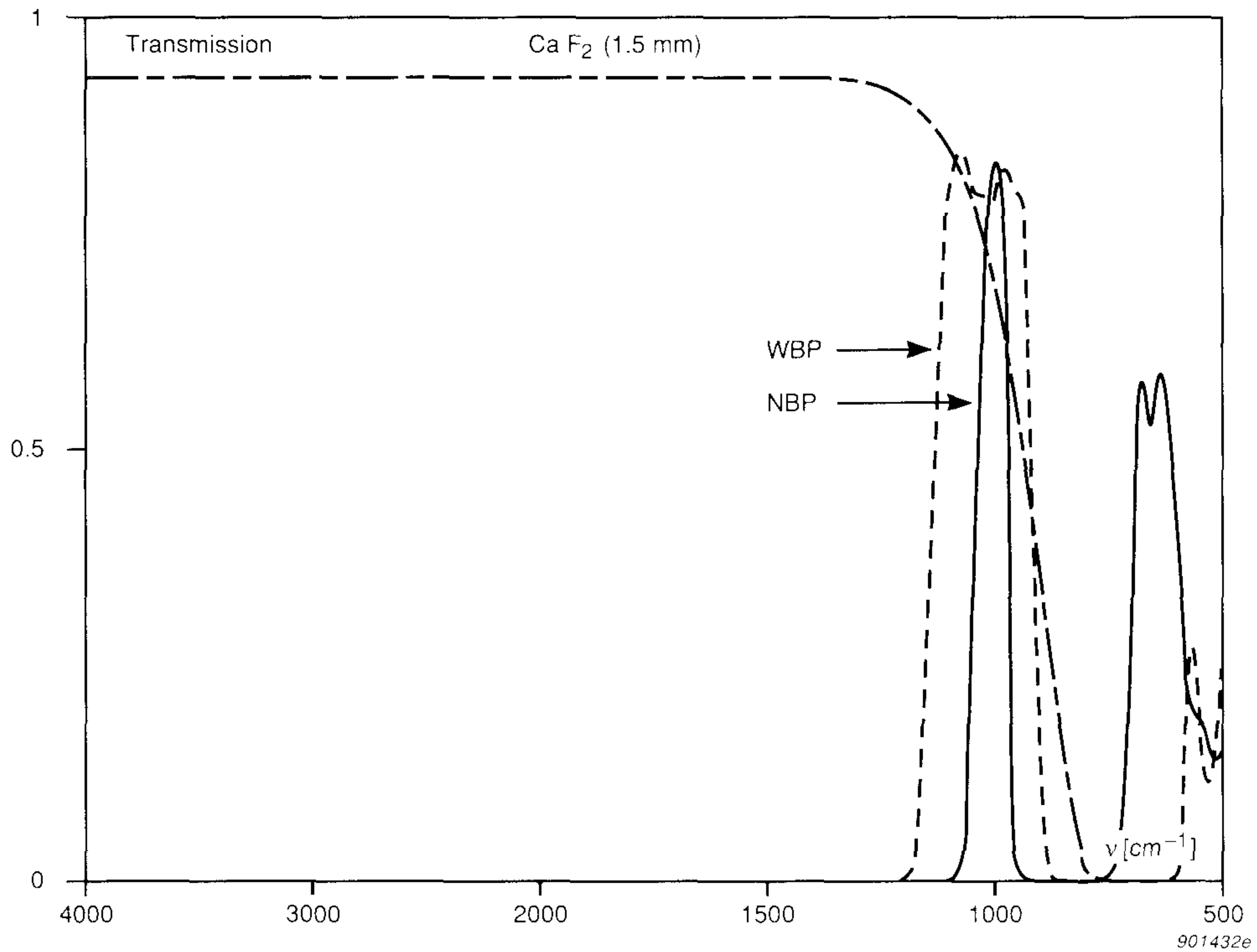


Fig. 3. Transmission characteristics of each of the three elements of UA 0936

relies on the interference of multiple reflected beams. Incident light undergoes multiple reflections between the two mirrors, and the intensity of the transmitted light beam which results, depends upon the relationship between the phases of each of the transmitted wavefronts. When there is

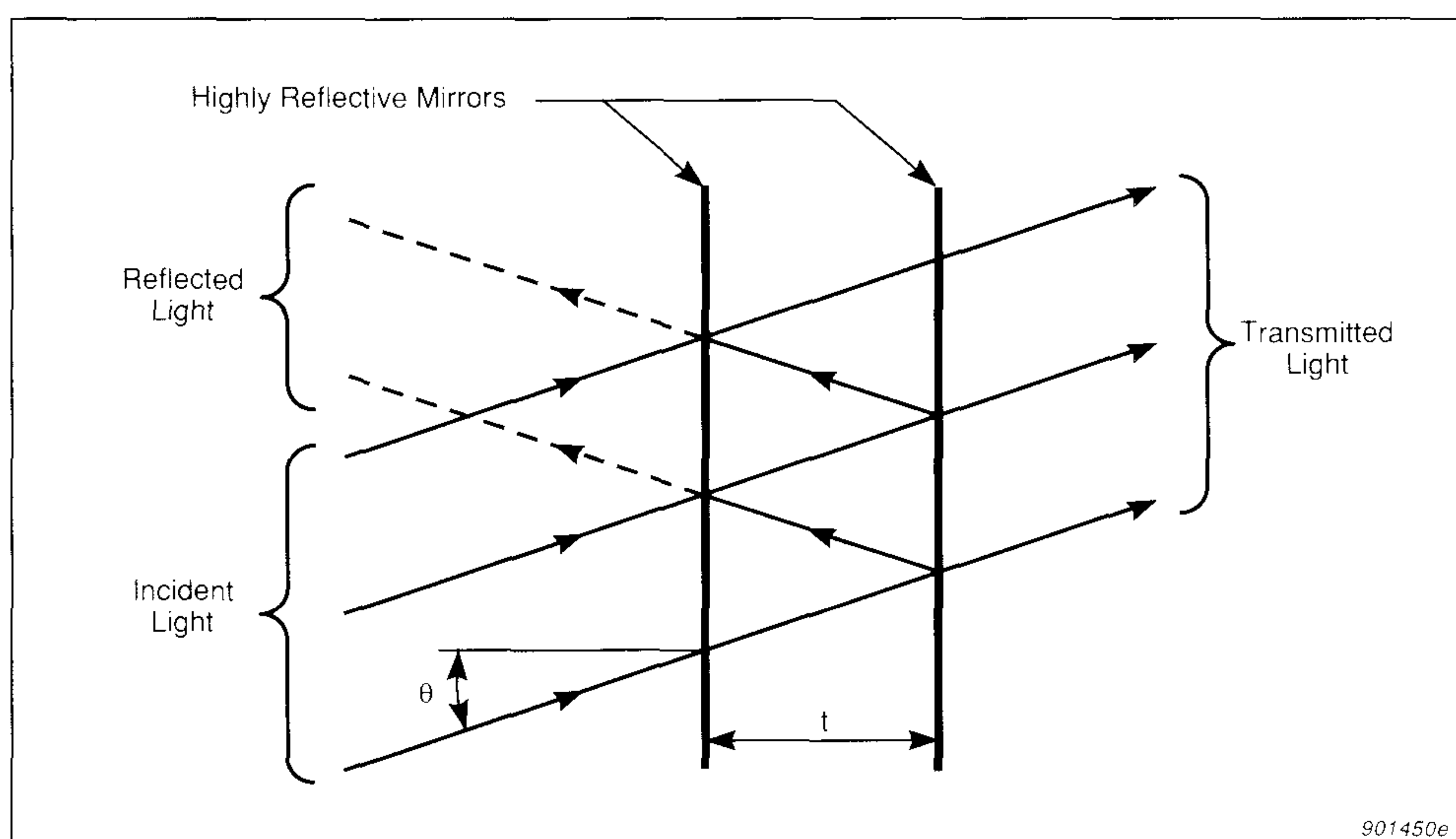


Fig. 4. A Fabry Perot interferometer

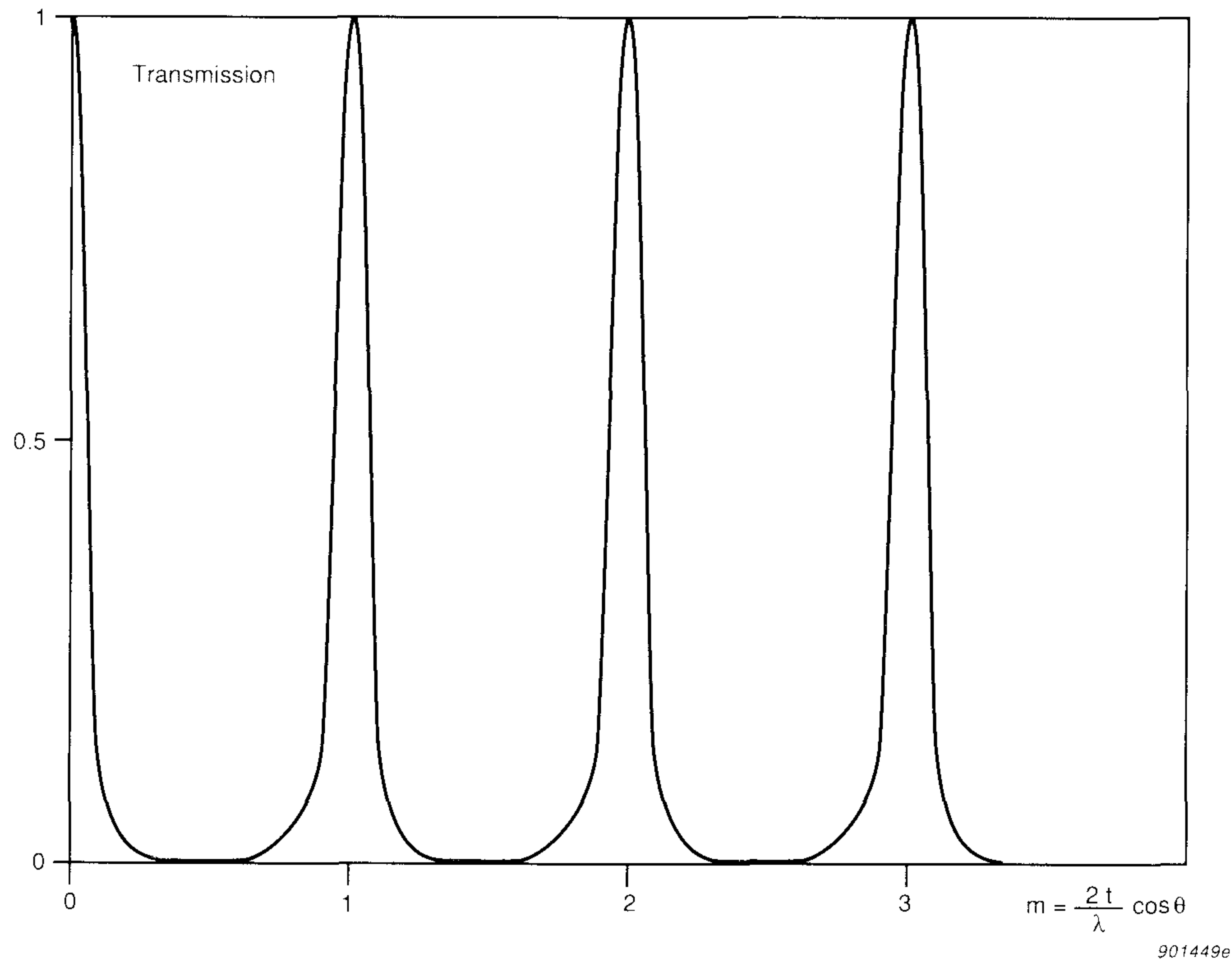


Fig. 5. The transmission of a Fabry Perot interferometer

no phase difference between the transmitted wavefronts, constructive interference occurs and the maximum amount of light will be transmitted. This will be the case if the optical pathlength between the two mirrors equals an integral number of half wavelengths of the transmitted light. At other wavelengths light will interfere destructively and reduce the intensity of the transmitted light towards zero (Fig. 5). The width of the transmission peaks depends on the reflectivity of the mirrors. The higher the reflectivity, the narrower the peak.

The Brüel & Kjær range of optical filters uses “all-dielectric” interference filters. Thin layers of different dielectric material are deposited under vacuum onto a substrate. In the case of the UA 0936 filter, the substrate is germanium. Each mirror of the Fabry Perot cavity consists of a stack of quarterwave dielectric layers, using materials with high and low refractive index alternately. The two reflector stacks (mirrors) are separated by a spacer, which is a thin layer of dielectric material with an optical thickness equal to half a wavelength (Fig. 6). Two or more such one-cavity filters can be deposited one on top of the other, separated by an appropriate coupling layer to form a multiple cavity filter. The advantage of multiple cavity filters are steeper band slopes, and a “square” passband.



Fig. 6. Cross section of a typical "all-dielectric" single-cavity filter. *L* and *H* denote low and high refractive index respectively

The Brüel & Kjær range of optical filters (UA0968 to UA0988 and UA0936) are all 3-cavity designs.

Additional edge filter coatings are used to suppress the unwanted transmission bands. Edge filters basically consist of a quarterwave stack (a mirror), but with some modifications to give the desired transmission function, either a longwave pass or a shortwave pass.

All of the UA 09xx filters are basically constructed in the same way as UA 0936, but the material chosen for the shortwave pass (SWP) blocking element, as well as the substrate material chosen for the interference elements depends on the actual centre wavelength of the filter being constructed. The number of elements used are different in some cases .

3. Design and Specification of the Optical Filters

a. The choice of centre frequencies and bandwidths

The Types 1302 and 1306 are primarily intended for measuring gases present in atmospheric air. This fact, of course, influenced the decision about how many optical filters were necessary, and what the centre frequency and bandwidth of these filters should be, in order to cover a suitable range of applications. Fig. 7 shows the absorption spectrum of normal atmospheric air. It is evident that atmospheric water vapour and carbon dioxide will strongly impede the measurement of other gases in certain frequency ranges. This left three usable ranges: 1) 700 cm^{-1} to 1300 cm^{-1} 2) 2000 cm^{-1} to 2300 cm^{-1} and 3) 2400 cm^{-1} to 3500 cm^{-1} .

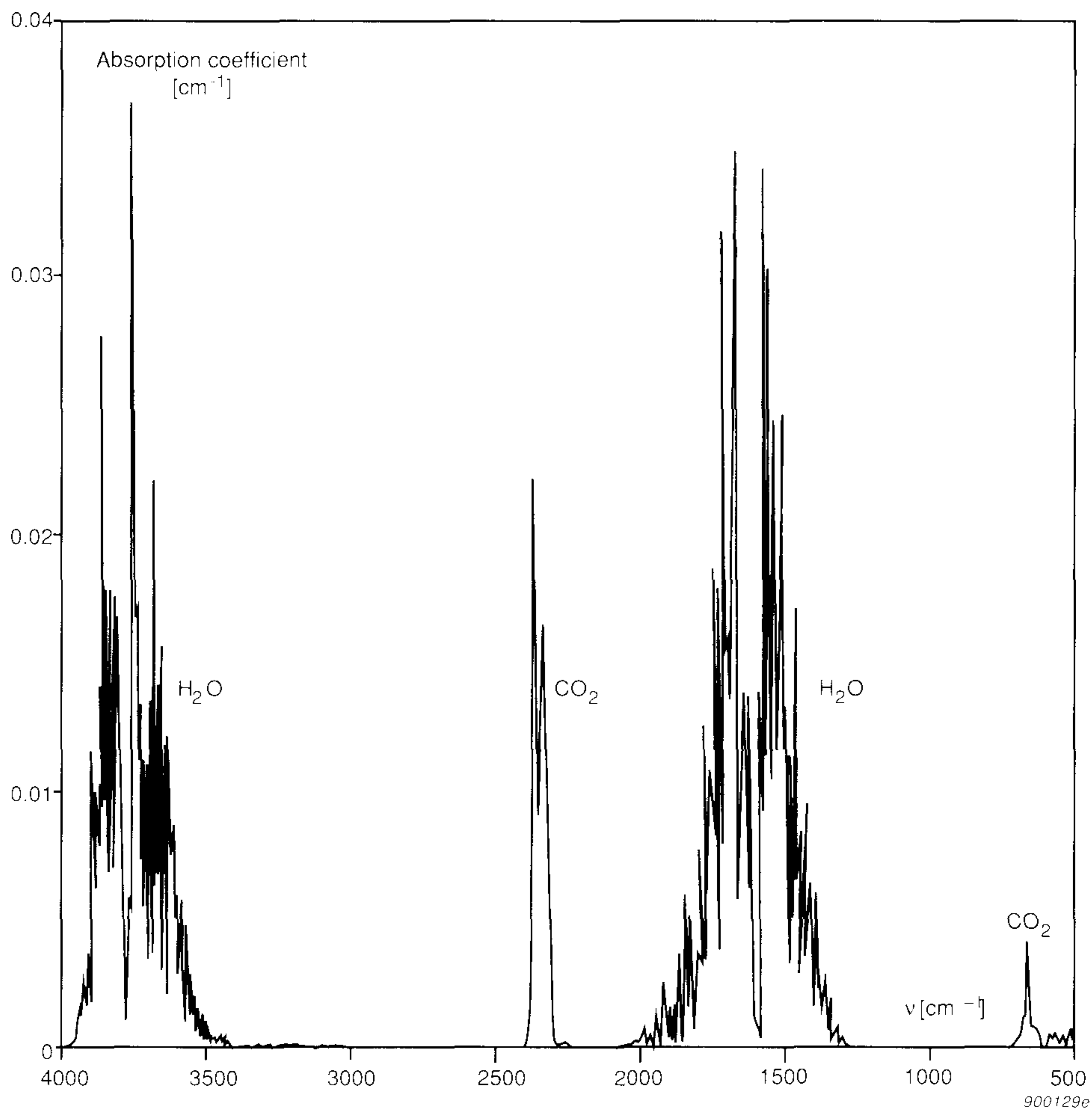


Fig. 7. The infra-red absorption spectrum of atmospheric air containing 20 000 ppmv water vapour and 340 ppmv carbon dioxide (res.: 10 cm^{-1})

A large number of gases have one or more strong absorption band somewhere in the 700 cm^{-1} to 1300 cm^{-1} range, which is part of the so-called “fingerprint”-region. The reason why this part of the spectrum is given this name is because the structure of the absorption spectrum of some gas molecules depends on the molecule as a whole — not only some of its functional groups. It was therefore a particularly important region in which to choose optical filters. Perhaps the most obvious way to choose a filter for measuring a particular gas would be to choose one whose centre frequency and bandwidth matched its strongest absorption band. This is, however, not a very flexible approach as it would require the development of a large number of different optical filters. Instead, a more systematic approach was chosen and 16 general purpose optical filters were designed to cover the “fingerprint”-region (UA 0936 and UA 0968 to UA 0988). This approach made it possible to design the optical filters, at the early stages of

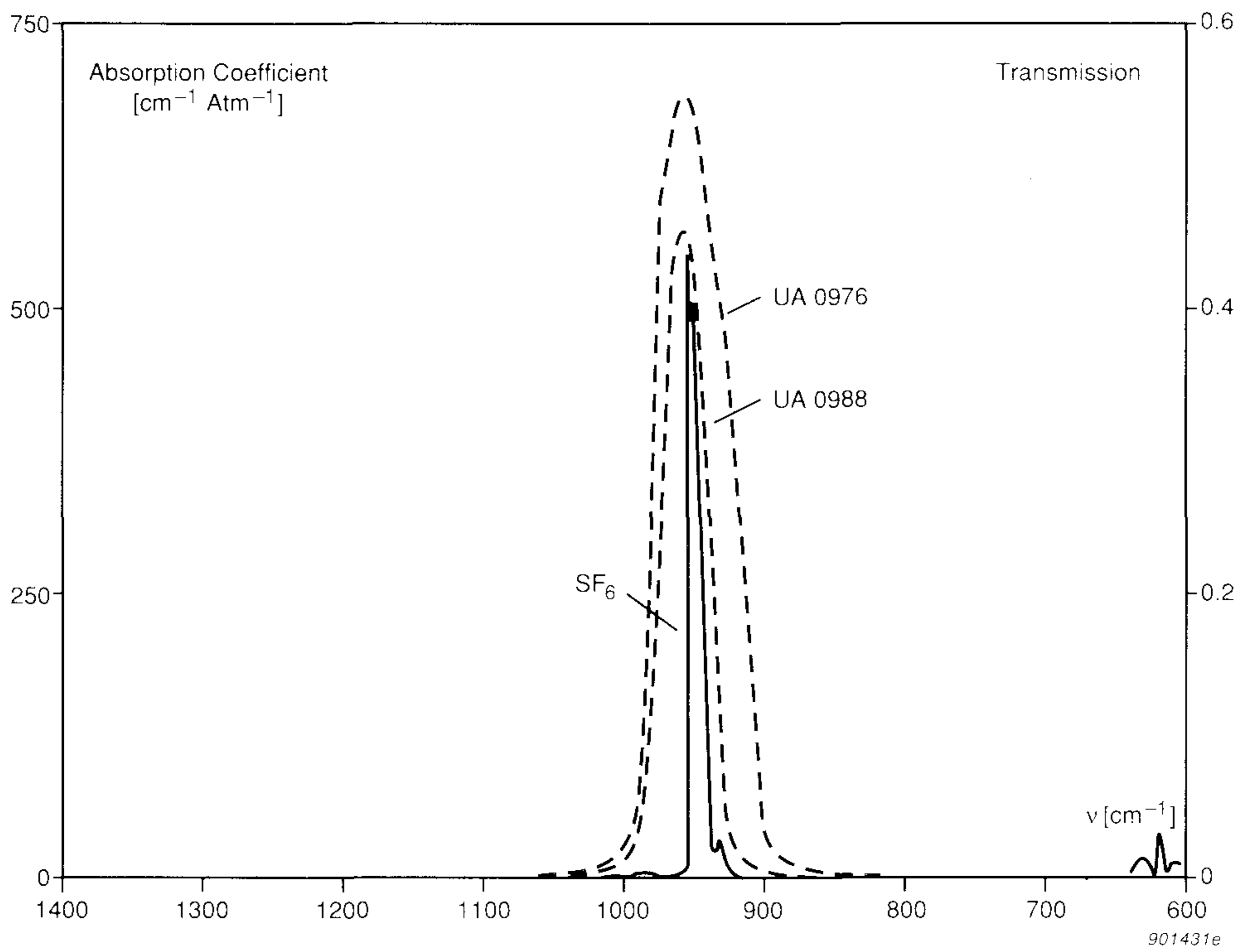


Fig.8. The absorption spectrum of SF_6 (res.: 2 cm^{-1}), and the transmission of filters UA 0976 and UA 0988

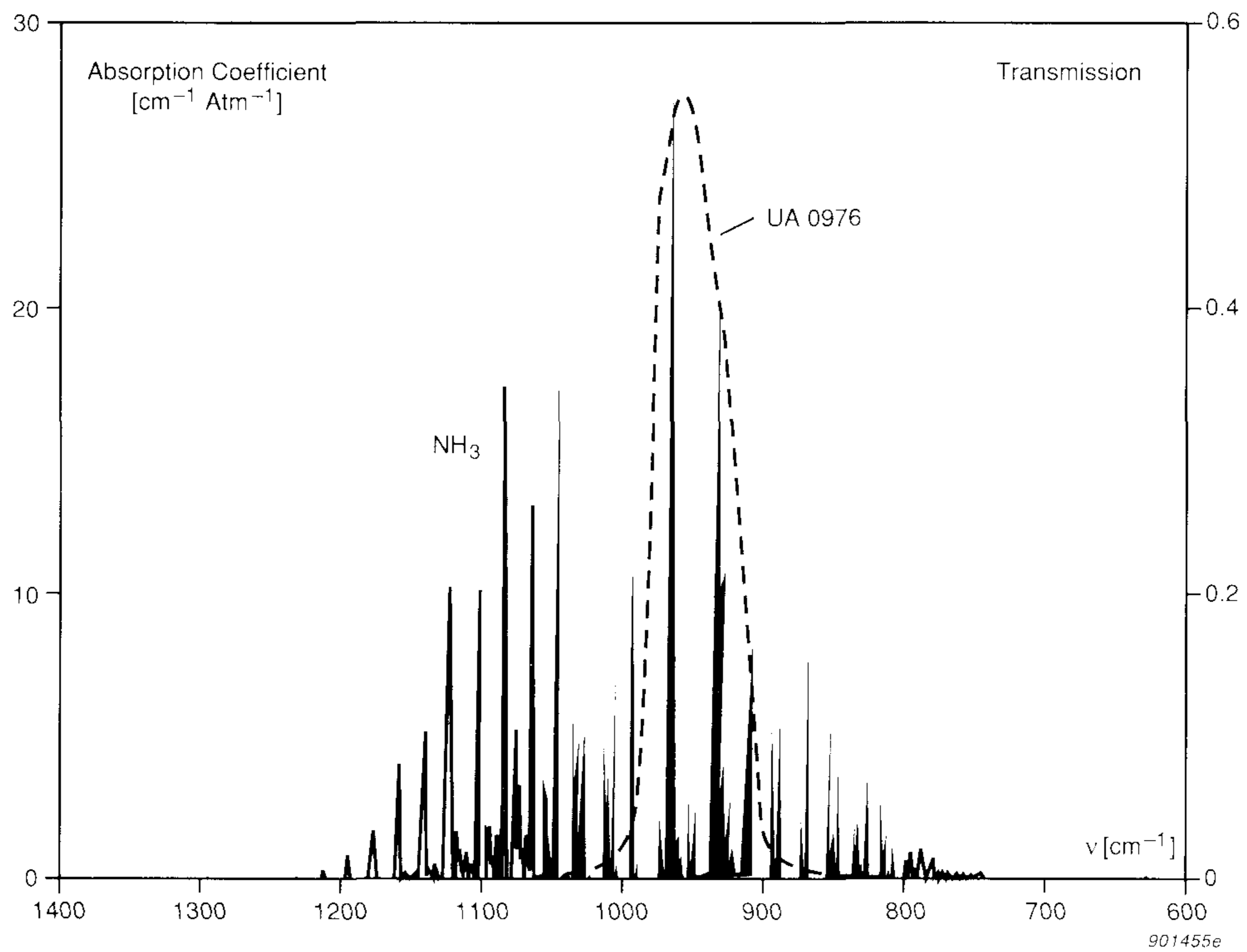


Fig. 9. The absorption spectrum of NH_3 (res.: 1 cm^{-1}), and the transmission of filter UA 0976

development, without prior knowledge about which gases the Type 1302 and 1306 should be able to measure. This was obviously an advantage. However, a general purpose optical filter cannot, of course, always be expected to be 100 percent optimal in all cases. This on the other hand is a disadvantage.

The bandwidth of the general purpose optical filters should, on the one hand, be as small as possible, in order to minimise possible interference from other gases present (including water vapour and carbon dioxide) as well as to minimise the zero-gas signal. On the other hand, the bandwidth should be wide enough to fully cover the absorption band of the gas to be measured so that the largest possible gas signal can be obtained, i.e. to maximize the sensitivity. Gas absorption spectra are so diverse that it is difficult to optimise the latter requirement. This can be exemplified by the spectra of SF_6 and NH_3 , shown in Fig. 8 and Fig. 9 respectively. The SF_6 spectrum is, for our purposes, very convenient as it has only one strong, narrow absorption band — approximately 10 cm^{-1} wide. The NH_3 spectrum, on the other hand, is very inconvenient as it consists of a lot of very narrow peaks spread over most of the 700 cm^{-1} to 1300 cm^{-1} range. Thus, if NH_3 is present, it will interfere with the measurement of practically any

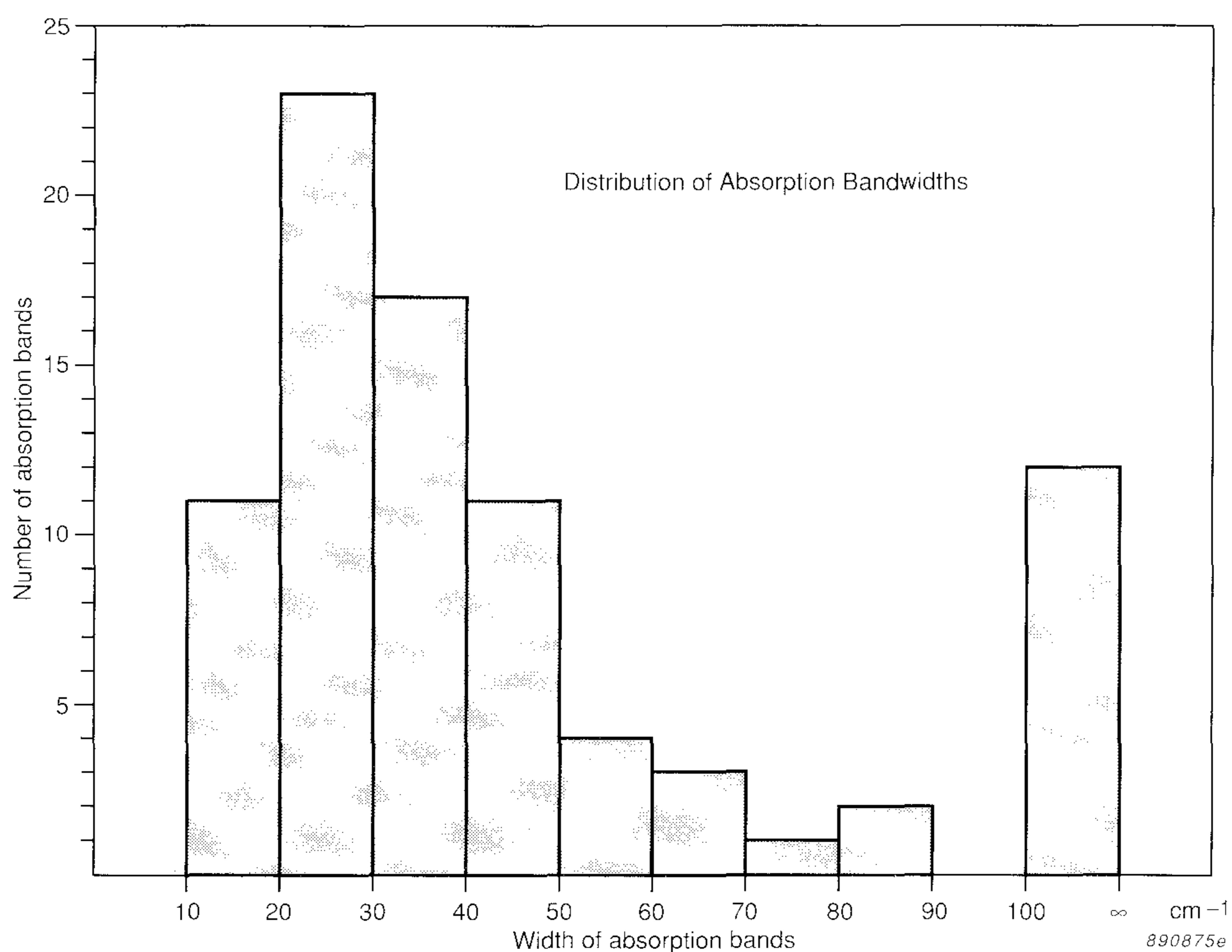


Fig. 10. Statistical distribution of widths of absorption bands for a number of gases

Optical Filter	Application	λ_o [μm]	ν_o [cm^{-1}]	$\Delta\nu$		T_f	L_ν [Wm^{-2} sr^{-1}cm]
				[cm^{-1}]	[%]		
UA 0968	General Purpose	7.7	1291	71	5.5	0.65	5.3
UA 0969		8.0	1254	69	5.5	0.65	5.1
UA 0970		8.2	1217	67	5.5	0.65	5.0
UA 0971		8.5	1179	71	6	0.65	4.9
UA 0972		8.8	1139	68	6	0.6	4.7
UA 0973		9.1	1101	66	6	0.6	4.5
UA 0974		9.4	1061	69	6.5	0.5	4.3
UA 0936		9.8	1020	66	6.5	0.5	4.2
UA 0975		10.2	981	64	6.5	0.5	4.0
UA 0976		10.6	941	66	7	0.5	3.8
UA 0977		11.1	900	63	7	0.5	3.6
UA 0978		11.6	862	60	7	0.6	3.4
UA 0979		12.2	822	62	7.5	0.6	3.2
UA 0980		12.8	783	59	7.5	0.5	3.0
UA 0981		13.4	746	56	7.5	0.4	2.8
UA 0982	14.1	711	53	7.5	0.4	2.6	
UA 0983	CO_2	4.4	2270	30	1.3	0.15	6.5
UA 0984	CO	4.7	2150	65	3	0.35	6.6
UA 0985	N_2O	4.5	2215	44	2	0.35	6.5
UA 0986	H_2CO	3.6	2800	84	3	0.6	5.8
UA 0987	CH_x	3.4	2950	177	6	0.6	5.5
UA 0988	SF_6	10.6	946	33	3.5	0.45	3.8
SB 0527	H_2O	5.0	1985	40	2	0.6	6.6

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Table 1. Centre wavelength λ_o , centre frequency ν_o , bandwidth $\Delta\nu$ and peak transmission T_f of the range of optical filters; spectral radiance L_ν of a 1050 K black body infrared source

other gas measured in this range, even if extremely narrow band optical filters are used. Furthermore, as the gas signal is proportional to the area of those of its spectral lines which are within the optical filter's passband, then in order to maximise the filters sensitivity to NH_3 the band width would have to be very wide. This is obviously a disadvantage as it intro-

duces interference problems, but if we chose a smaller bandwidth in order to reduce interference, then the sensitivity would be lower.

An investigation of the bandwidths of 40 different gases (which included 80 absorption bands) showed that the majority were greater than 10 cm^{-1} and less than 50 cm^{-1} wide, and a few, among these NH_3 , were very broad (Fig. 10). The investigation also showed that statistically, bandwidths are independent of their centre frequency. Thus, as a suitable compromise between selectivity and sensitivity, the frequency range from 690 cm^{-1} to 1310 cm^{-1} was divided into 16 intervals, each of them slightly less than 40 cm^{-1} wide, and it was then decided to assign one optical filter to each of these intervals; this resulted in 16 optical filters altogether. The bandwidths of the optical filters had to be made somewhat larger than the approx. 40 cm^{-1} width of the intervals they should cover, because of the unavoidable production tolerances of the centre frequency (typically $\pm 1\%$) and bandwidth (typically $\pm 15\%$). This resulted in nominal bandwidths ranging from 53 cm^{-1} , or 7.5% relative (to its centre frequency) at the low frequency end, to 70 cm^{-1} or 5.5% relative (to its centre frequency), at the high frequency end. Some important characteristics of the optical filters are given in Table 1.

So far we have only considered the general purpose optical filters in the 700 cm^{-1} to 1300 cm^{-1} interval. In addition to these, 7 more optical filters have been developed, each of them optimised for measuring a certain specific gas (see Table 1). Each of these filters will be discussed in more detail.

Carbon dioxide (UA 0983): This optical filter is dedicated to the measurement of carbon dioxide in an indoor environment, at concentrations ranging from approx. 340 ppmv (normal concentration in outdoor air) up to 5000 ppmv in badly ventilated, crowded rooms. CO_2 has two strong absorption bands (see Fig. 11). The strength of these bands combined with the high concentration levels of CO_2 gives rise to some potential problems. Firstly, the gas signal might not be linear over the whole CO_2 concentration range and thus the measurement will be less accurate, even if we compensate for its non-linearity. Secondly, the carbon dioxide content in the room surrounding the 1302/06 (or, more precisely in the air between the IR-source and the PAS cell) will attenuate that part of the light from the infra-red light source, which is coincident with the CO_2 spectral lines. In this way the signal could be affected in an unpredictable way. These potential problems were avoided by choosing a filter with a centre frequency equal to 2270 cm^{-1} , coincident with the skirts of the 2349 cm^{-1} CO_2 absorption band. This enabled us to avoid using the strong absorption part of the spectrum (see Fig. 12). The solution required an extremely well defined

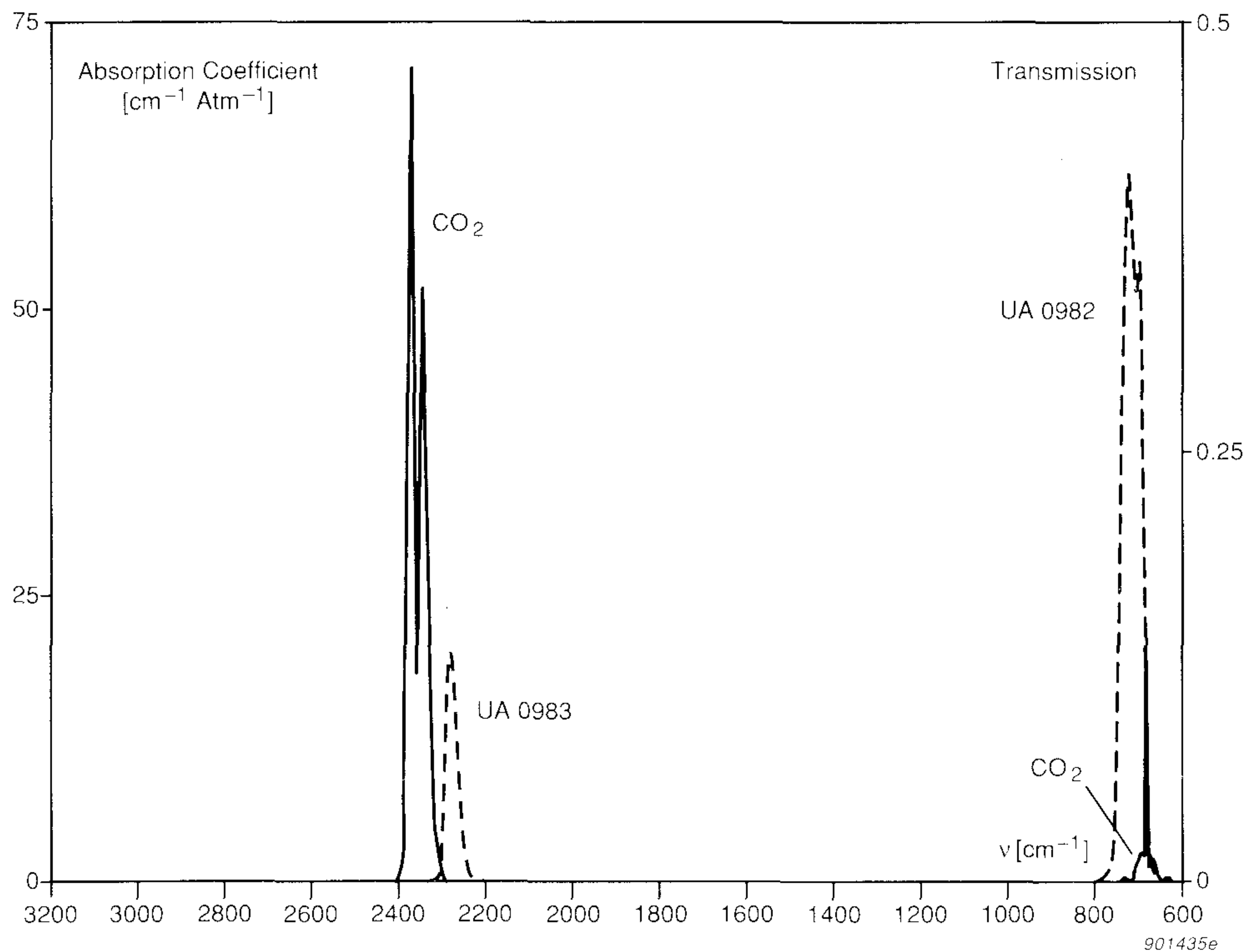


Fig. 11. The absorption spectrum of CO_2 (res.: 5 cm^{-1}), and the transmission of filters UA 0983 and UA 0982

high-frequency cut-off for the UA 0983 filter. This was obtained by using a special blocking material with low transmission above approx. 2300 cm^{-1} in combination with the interference elements (Fig. 13). It was not possible to produce the effect using the NBP-interference element alone as its dependence on angle of incidence and temperature, as well as production tolerances, did not allow it. (See Section 3 b).

The reason why the 2349 cm^{-1} band was chosen in preference to the weaker 670 cm^{-1} band is, that very few gases (one of them is N_2O) are likely to interfere with a measurement at the centre frequency (2270 cm^{-1}) of the UA 0983 filter. However, in cases where there are no interference problems, the UA 0982 filter (with a centre frequency of 710 cm^{-1}) could be an alternative choice for measuring CO_2 .

Besides its two strong absorption bands, CO_2 has weaker absorption bands in the 3500 cm^{-1} to 3800 cm^{-1} region, but unfortunately the use of these bands is prohibited due to strong water vapour interference.

Finally, it might be worthwhile mentioning, that part of the signal measured with the CO_2 filter is due to absorption by the $^{13}C^{16}O_2$ isotope of carbon dioxide, which represents approx. 1% of the carbon dioxide in its

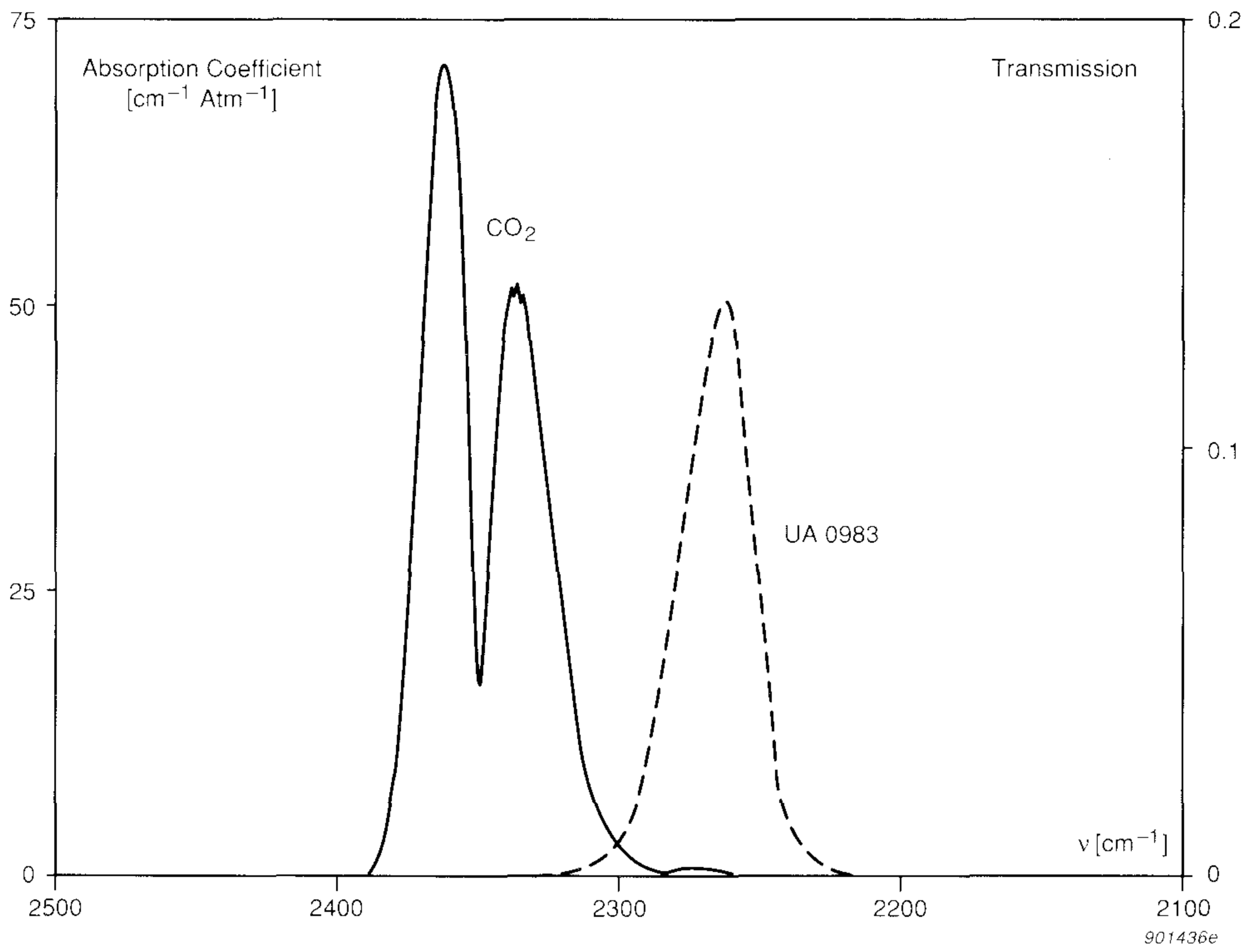


Fig. 12. A close look at the strongest CO₂ absorption band and the transmission of filter UA 0983

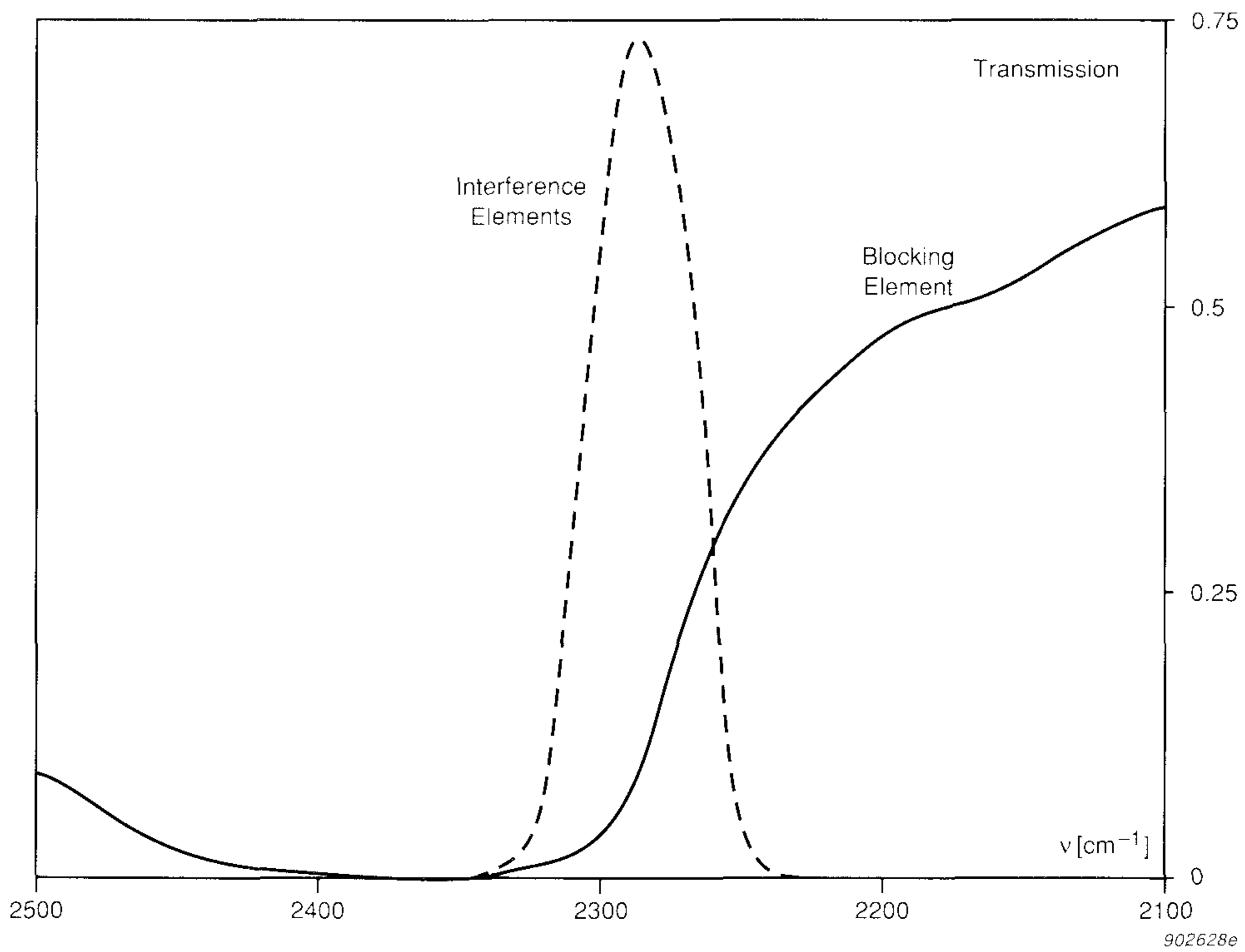


Fig. 13. The transmission of the interference elements and the blocking element of the UA 0983 filter

natural isotopic composition. This isotope absorbs in the region (small shoulder) to the right of CO_2 strongest absorption band (Fig. 12).

Carbon monoxide (UA 0984): CO only has one absorption band at 2143 cm^{-1} (Fig. 14). The band is quite broad, $100\text{--}150\text{ cm}^{-1}$, but the bandwidth of the UA 0984 has been chosen to be somewhat smaller (64 cm^{-1}) to minimise interference from water vapour as well as carbon dioxide. Carbon dioxide interference has been further reduced by using the same blocking material as used in the production of the carbon dioxide filter UA 0983.

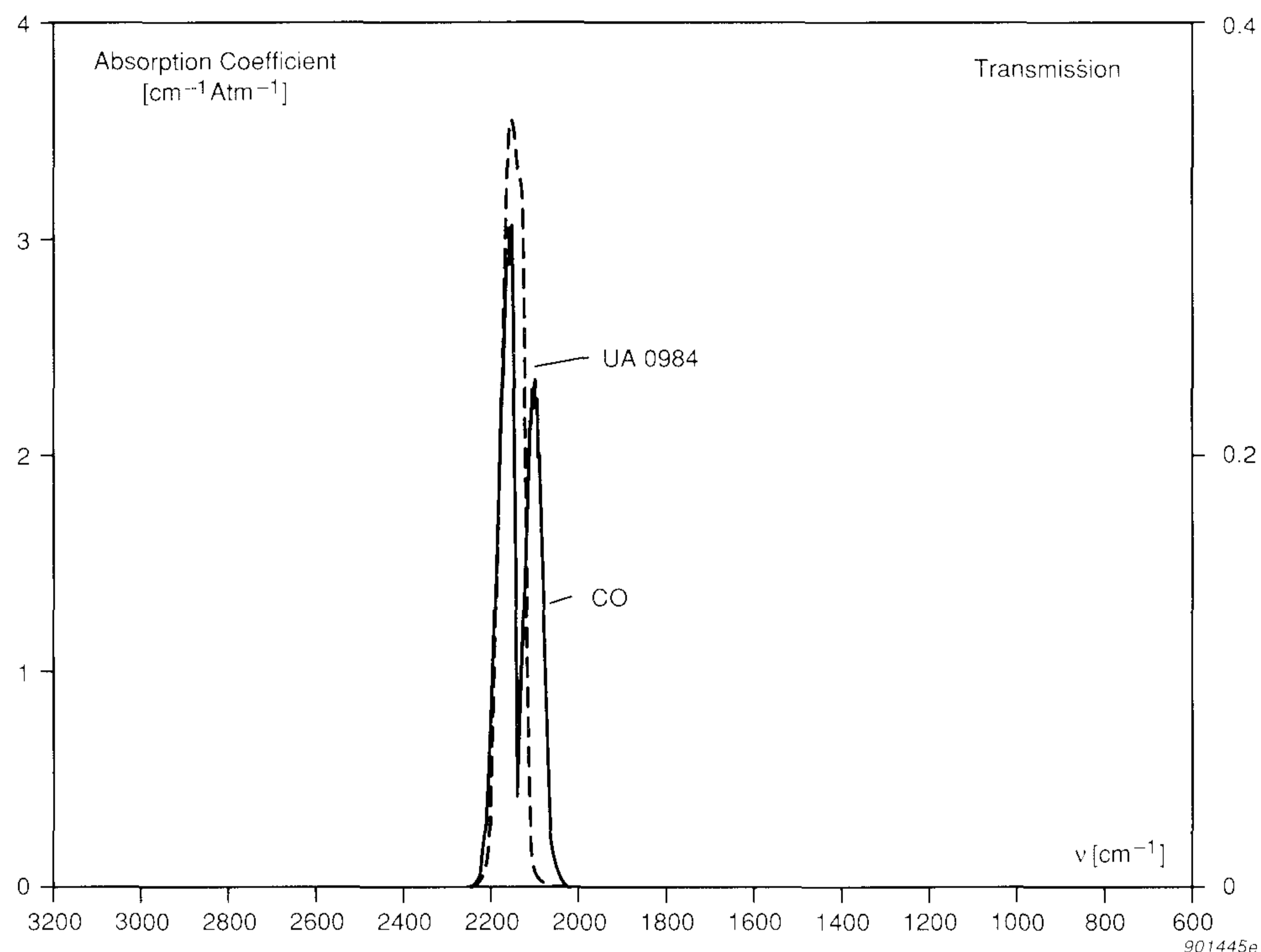


Fig. 14. The absorption spectrum of CO (res.: 5 cm^{-1}), and the transmission of filter UA 0984

Dinitrogen Oxide (UA 0985): The strongest absorption band of N_2O at 2224 cm^{-1} (Fig. 15) has been chosen for the measurement of N_2O in spite of the fact that it is very close to the strong carbon dioxide absorption band, which is the most serious interferent gas, and also close to the carbon monoxide band. Interference from these gases has been minimized by: 1) making the UA 0985 filter bandwidth very narrow; 2) by using a NBP interference element with a particularly small centre-frequency tolerance;

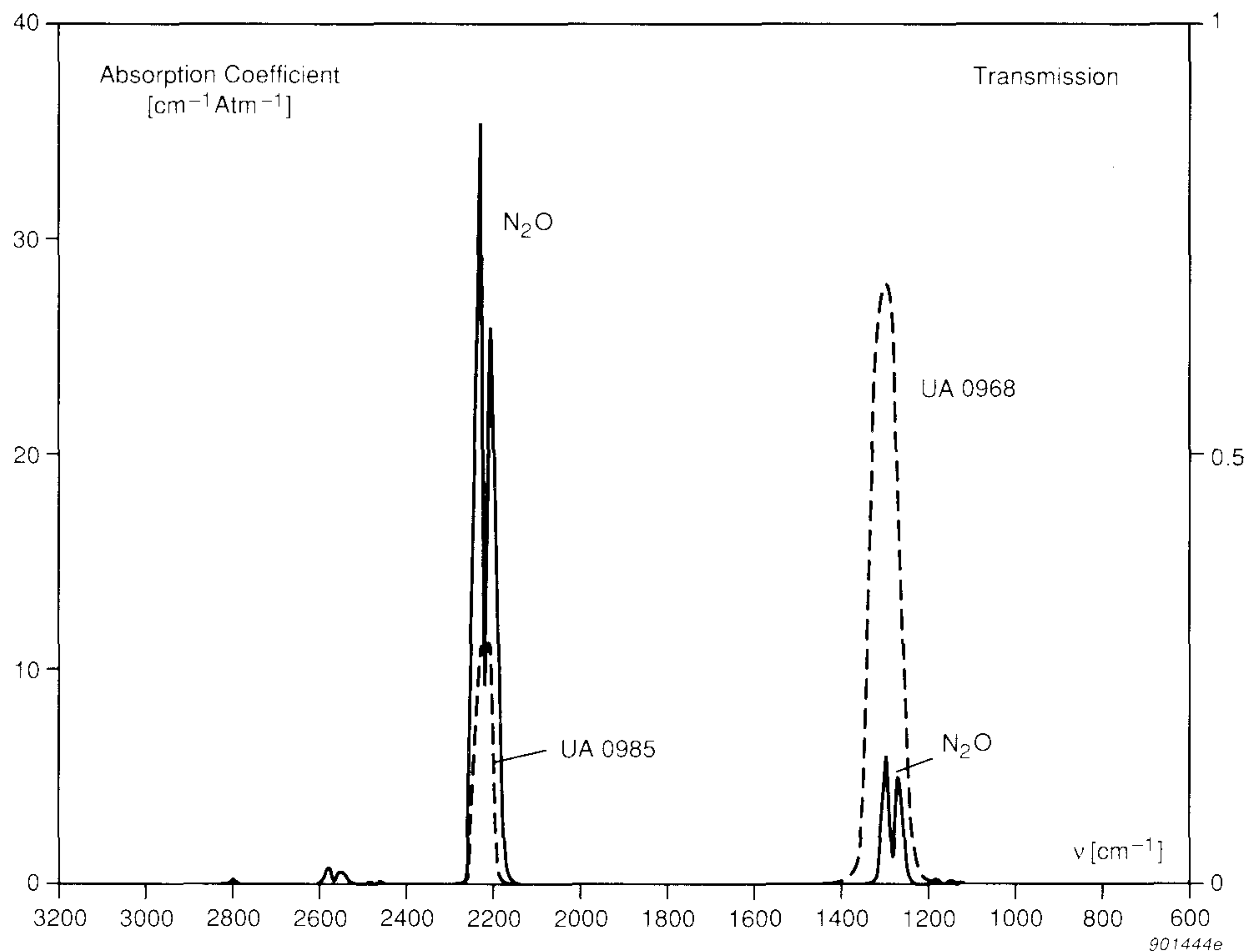


Fig. 15. The absorption spectrum of N_2O (res.: 5 cm^{-1}) and the transmission of filters UA 0985 and UA 0968

and 3) by using the same blocking material as used in the production of the carbon dioxide filter UA 0983.

Alternatively, if the UA 0968 filter is used, N_2O measurements can be made using the weaker N_2O absorption band, at 1290 cm^{-1} . However, water vapour interference will then be a limiting factor.

As a third possibility, the band at 2560 cm^{-1} could have been used, as it then would be easy to avoid interference from both water vapour and carbon dioxide, but this possibility was rejected because some organic vapours, including ethanol, would then interfere much more strongly. This would be a disadvantage because a typical application involving measurement of N_2O would be in a hospital environment, where ethanol vapours are very likely to be present as it is frequently used as a disinfectant.

Formaldehyde (UA 0986): The formaldehyde spectrum is shown in Fig. 16. A centre frequency of 2800 cm^{-1} has been chosen for the UA 0986 filter and the bandwidth is typically 84 cm^{-1} , which is considerably smaller than the width of the absorption band. This bandwidth was chosen in order to minimise interference from hydrocarbons and to reduce the zero-gas signal. There is only very little interference from water vapour and carbon dioxide.

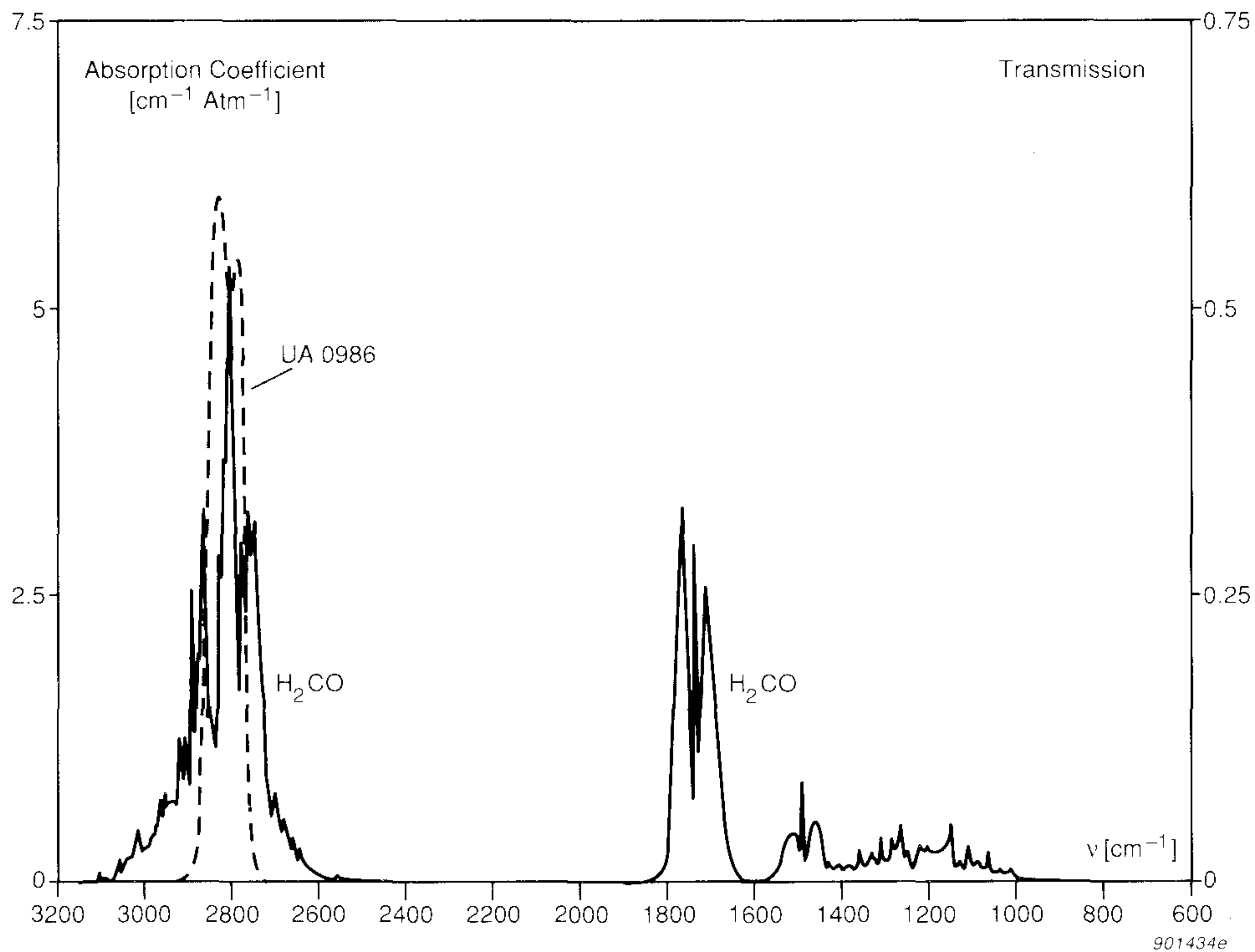


Fig. 16. The absorption spectrum of H_2CO (formaldehyde) (res.: 5 cm^{-1}), and the transmission of filter UA 0986

Hydrocarbons (UA 0987): In general, hydrocarbons (CH_x) have absorption bands in the vicinity of 3000 cm^{-1} which are due to the $C-H$ stretching vibration. This UA 0987 filter is intended for the measurement of hydrocarbons as a group, rather than for a single specific hydrocarbon gas. The sensitivity using this filter can be very different for different hydrocarbons. Ethane has been chosen as an example of a gas belonging to the hydrocarbon group. Fig. 17 shows the spectrum of ethane. The UA 0987 filter has to have a relatively large bandwidth (approx. 180 cm^{-1}) due to the spread of the different hydrocarbon gases absorption bands. It is important to consider water vapour interference when using the UA 0987 filter.

Sulphur Hexafluoride (UA 0988): SF_6 has only one usable absorption band at approx. 950 cm^{-1} (Fig. 8). The UA 0976 filter could be a possible choice for measuring SF_6 . However, its bandwidth is larger than the width of the SF_6 band and, as the measurement of SF_6 represents a particularly important application for the Type 1302, a dedicated optical filter UA 0988 with a narrower bandwidth was designed for measuring SF_6 . SF_6 is very commonly used as a tracer gas in ventilation efficiency and air change measurements.

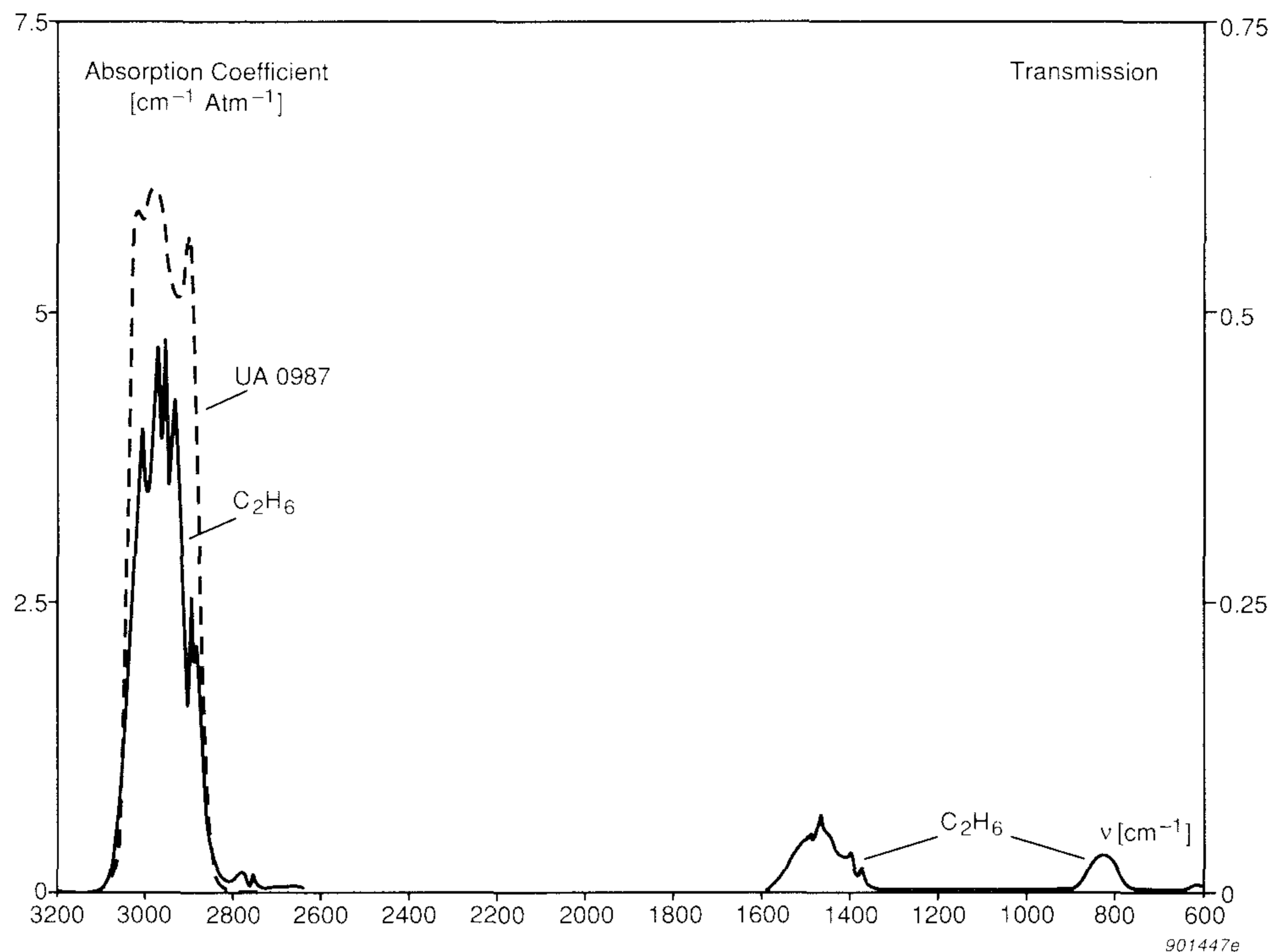


Fig. 17. The absorption spectrum of C_2H_6 (ethane) (res.: 5 cm^{-1}), and the transmission of filter UA 0987

Water Vapour (SB 0527): This optical filter is always installed in the Type 1302, as opposed to all the other filters which are only installed if they have been chosen to measure a particular gas. This filter measures the concentration of water vapour in the analysis cell and thus makes it possible for the 1302 to compensate for water vapour's influence on the gas to be measured. (The Type 1306 utilizes a different method for measuring and compensating for the water vapour, as we shall see later). The water vapour spectrum is shown in Fig. 18. It consists of narrow, widely separated spectral lines, which is a disadvantage with respect to sensitivity. However, as the typical water concentration in atmospheric air is in the 5000 ppmv to 20000 ppmv range, sensitivity is not a problem. A more serious problem, however, is the attenuation of the IR-light by the water vapour in the air inside the Type 1302 (similar to the effect of carbon dioxide in the air as mentioned earlier). To minimise this effect, it was necessary to change the centre frequency of the SB 0527 filter to a weaker absorption region of the spectrum (1985 cm^{-1}). At this frequency the water vapour signal is relatively low, and therefore, more sensitive to interference from other gases which have absorption bands near the centre frequency of the SB 0527 filter. Fortunately, only very few gases are likely to interfere at this fre-

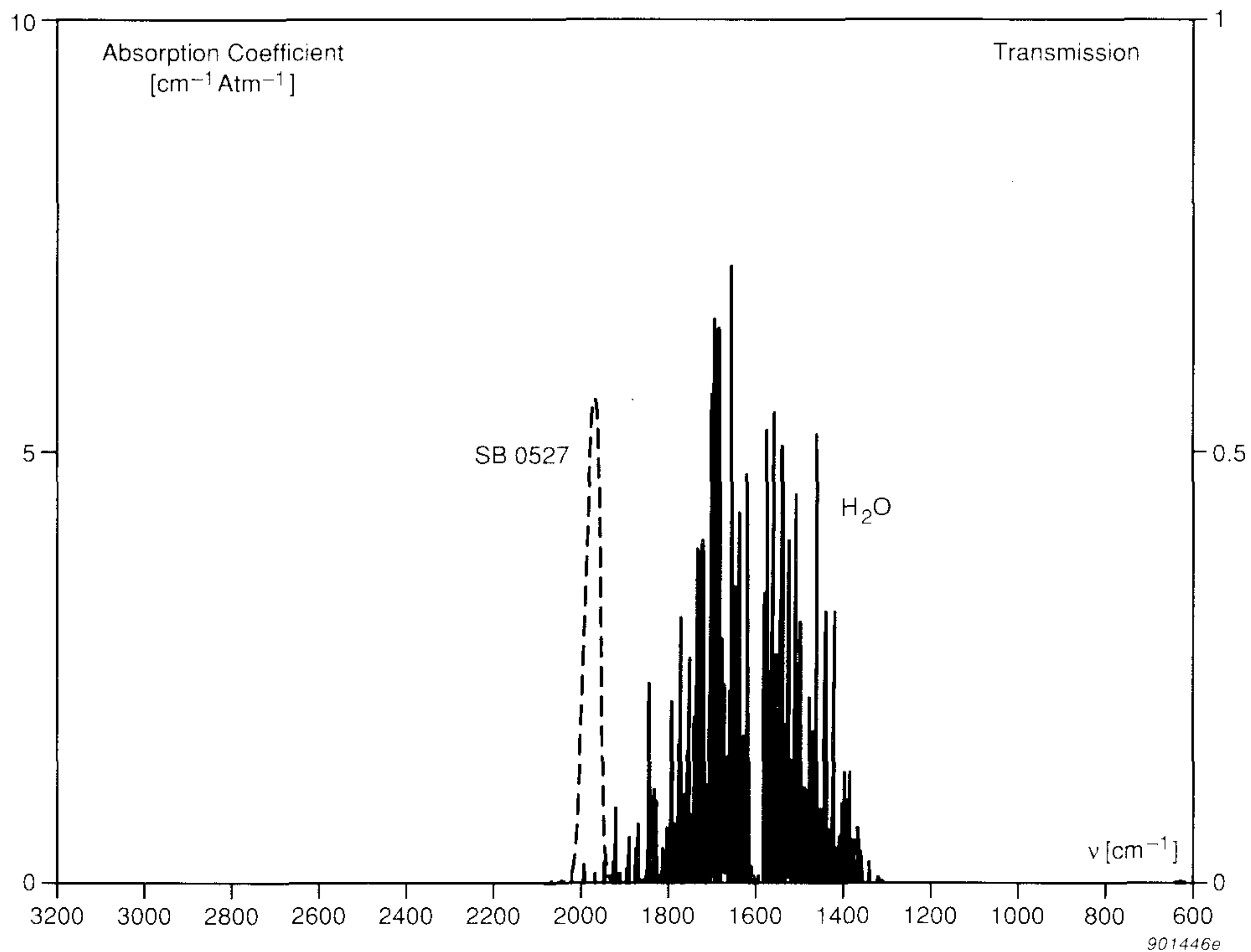


Fig. 18. The absorption spectrum of H_2O , (res.: 1 cm^{-1}), and the transmission of filter SB 0527

quency, unless they occur in very high concentrations. One interferent gas is benzene, but even at a concentration of 20 ppmv, which is several times greater than typical threshold values, its influence on the water measurement is negligible.

b. The angle of incidence effect

The centre frequency of an optical interference filter depends on the angle of incidence of the light. This is an important consideration when designing the optical filters because, in the Brüel & Kjær PAS system the incident light is a cone with a half cone angle equal to 33 degrees, thus the angle of incidence ranges from normal incidence to a 33 degree angle of incidence. If the centre frequency at normal incidence is ν_o , then the centre frequency corresponding to some angle of incidence θ will be:

$$\nu = \frac{\nu_o}{\sqrt{1 - \left(\frac{\sin \theta}{n_e}\right)^2}} \quad (1)$$

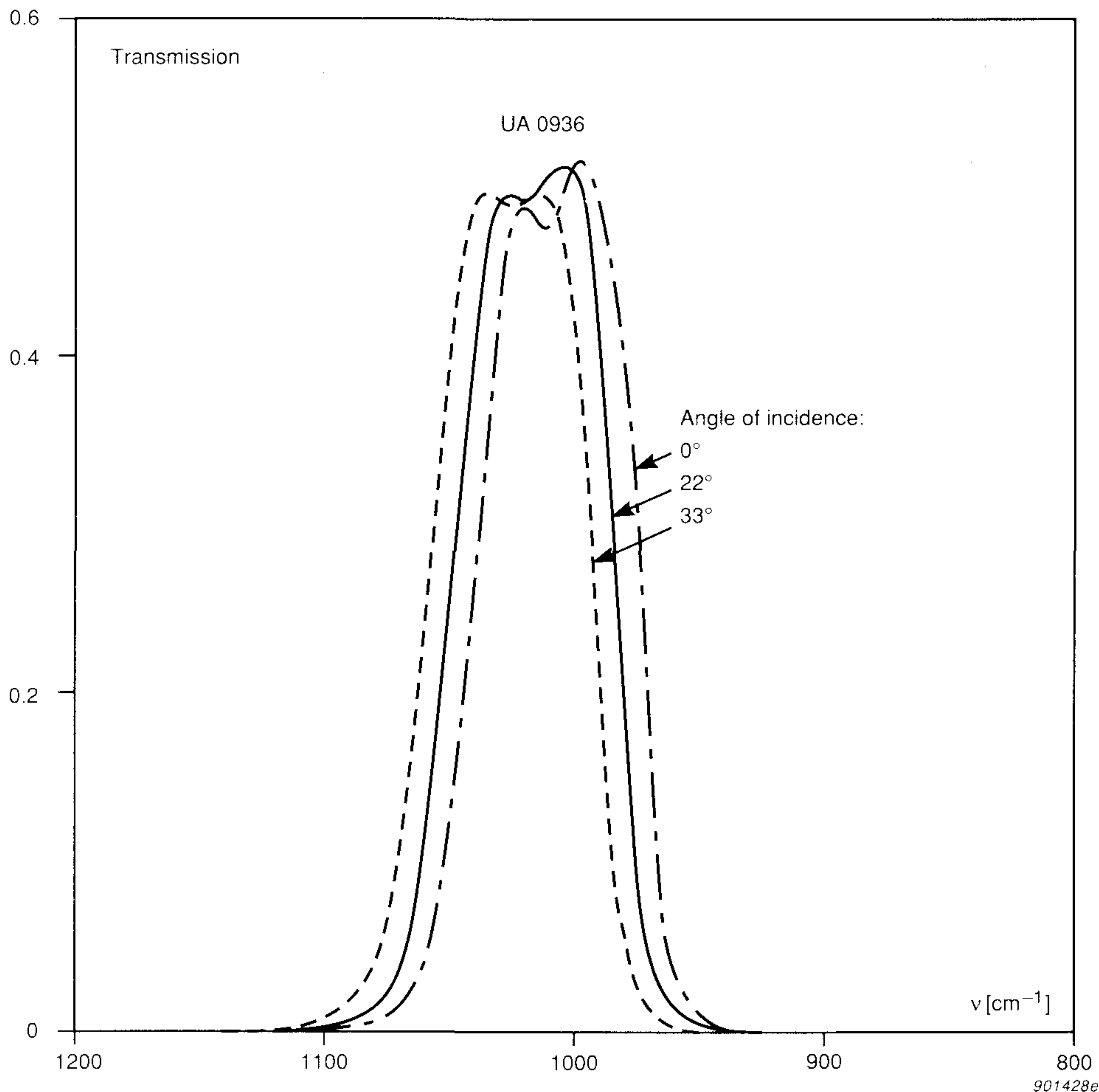


Fig. 19. The influence of the angle of incidence on the transmission of filter UA 0936

where n_e is the effective refractive index of the halfwave spacer layer. The wavelength shift $\Delta\nu = \nu - \nu_o$ can be expressed as:

$$\Delta\nu \approx \frac{1}{2} \left(\frac{\sin\theta}{n_e} \right)^2 \nu_o \quad (2)$$

The effective refractive index n_e depends on the coating materials used. In Brüel & Kjær optical filters, the choice of coating materials ensures minimum dependence on the angle of incidence, i.e. n_e is large.

Fig. 19 shows, as an example, the passband transmission corresponding to three different angles of incidence (0° , 22° and 33° respectively), measured with a Perkin Elmer model 1710 Infrared Fourier Transform Spectrometer. The relative frequency shift when the angle of incidence changes from 0° (normal incidence) to 22° is approx. 0.7%. The cone of

light not only influences the centre frequency, but also the bandwidth and transmission. However, it can be shown, that if the relative bandwidth of the optical filter is approx. 2% or more, then the influence will be small. This is the case with all of the Brüel & Kjær range of optical filters. It can then be shown, that the transmission function, if measured with the model 1710 spectrometer at 22° angle of incidence, is similar to the transmission function obtained if it had been measured using a cone of light with 33° half cone angle.

The centre frequencies, bandwidths and transmission values given in Table 1 correspond to an angle of incidence of 22° .

The centre frequency of an optical filter designed to minimize the angle-of-incidence sensitivity will generally be slightly more dependent on temperature. However, this dependence is small enough not to be a problem with the Brüel & Kjær optical filters. It is typically in the range 100–150

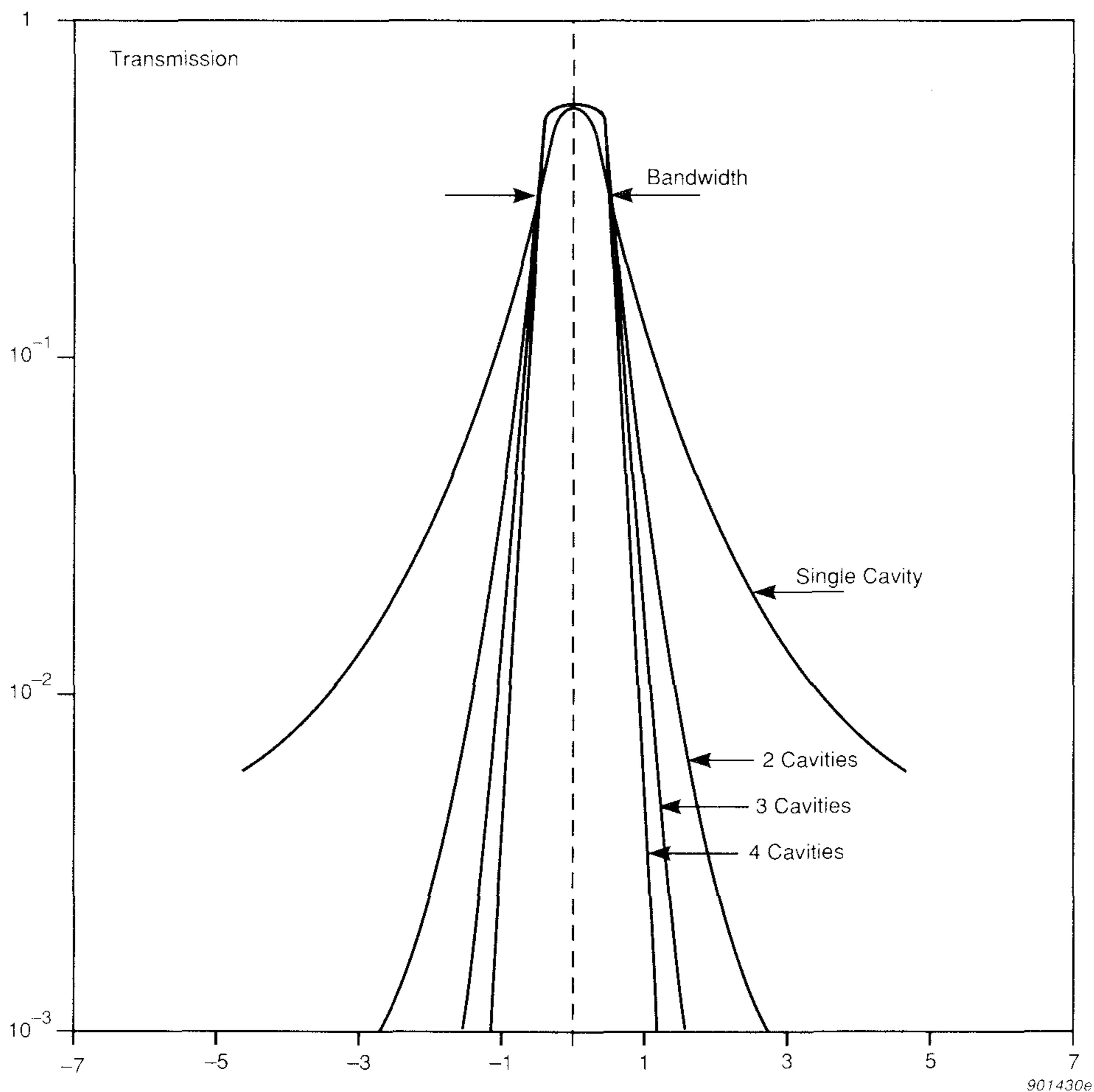


Fig. 20. Typical passband shapes of optical filters with 1, 2, 3 and 4 cavities respectively. The normalized bandwidth is equal to 1

ppm/°C. The centre frequency shifts towards a lower frequency with increasing temperature.

c. The passband shape

The selectivity of an optical filter depends, of course, on the bandwidth of the filter, but equally important, depends on the slope of the filter skirts. The slope of the filter skirts depends on the number of cavities in the filter. Typical bandpass shapes of interference filters with one-, two-, three- and four cavities respectively are illustrated in Fig. 20 on a logarithmic scale. The more cavities the filter contains, the better it will approximate the ideal square shape, and the more it will suppress interference from gases with absorption bands outside the filter's transmission band. To illustrate this, assume some unwanted absorption line at a distance of one bandwidth from the optical filter's centre frequency. From Fig. 20, the

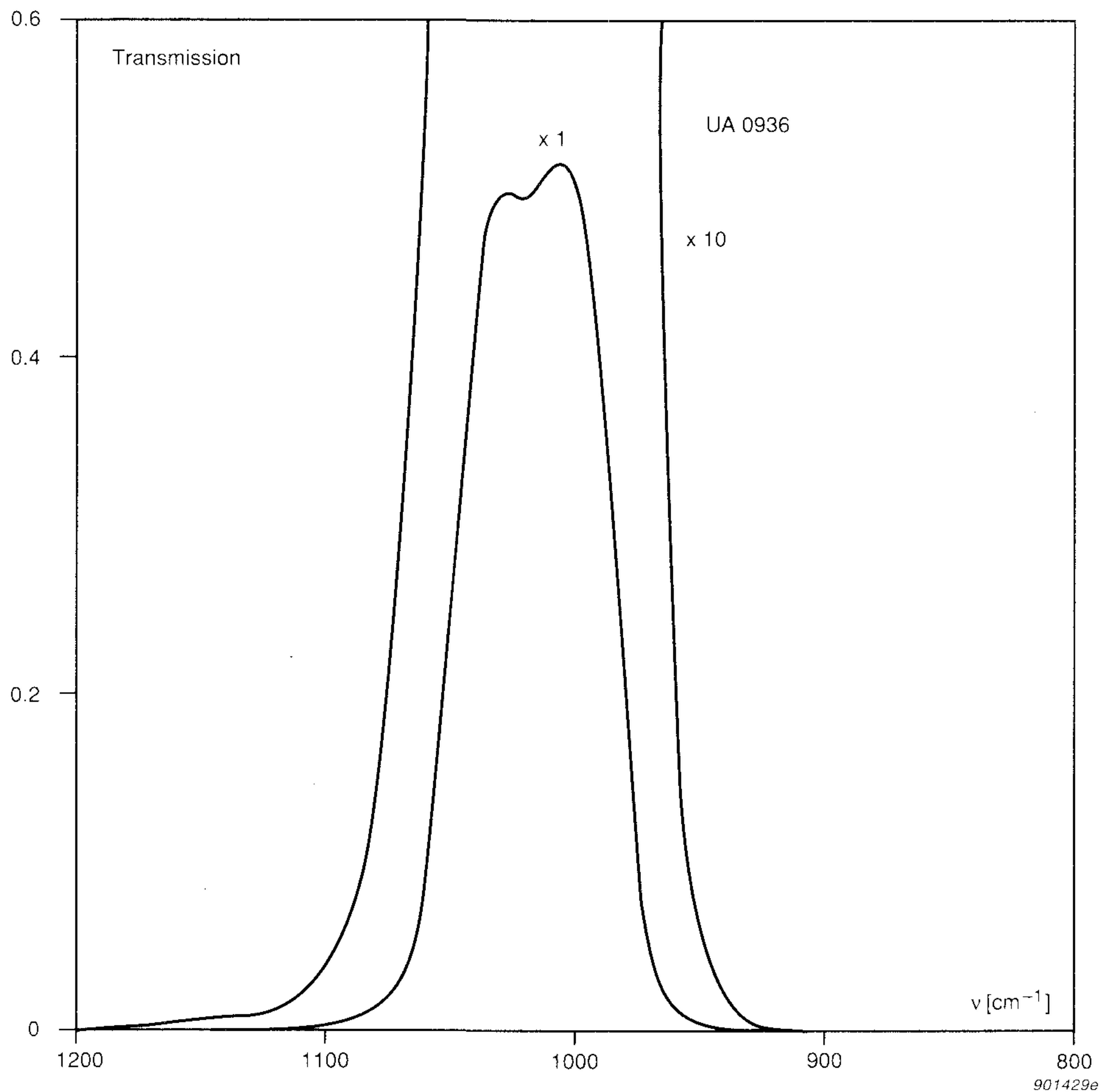


Fig. 21. Passband shape of filter UA 0936 ($\times 1$ and $\times 10$ transmission scale)

amount of suppression when using a 3-cavity filter will be 4 times better than the suppression when a 2-cavity filter is used, and 10 times better than if a single-cavity filter is used.

All Brüel & Kjær optical filters are 3-cavity filters and therefore provide high interference suppression. The bandpass transmission of the UA 0936 filter in Fig. 21 is illustrated both on a $\times 1$ linear transmission scale as well as a $\times 10$ expanded scale to elucidate the steepness of the filter skirts.

d. Transmission outside passband

Transmission occurring outside the optical filter's passband should ideally approach zero with increasing distance from its centre frequency. However, in practice there is always some, albeit very little transmission. This is called filter leakage. It was decided to design the optical filters so that the transmission outside passband would be less than 10^{-3} , or 0.1%. But in those frequency ranges, where water vapour and/or carbon dioxide absorb strongly, a much lower transmission is required to make the filter leakage contribution to interference negligible. In the two strong water absorption ranges: 1400 cm^{-1} to 2000 cm^{-1} and 3000 cm^{-1} to 4000 cm^{-1} for example,

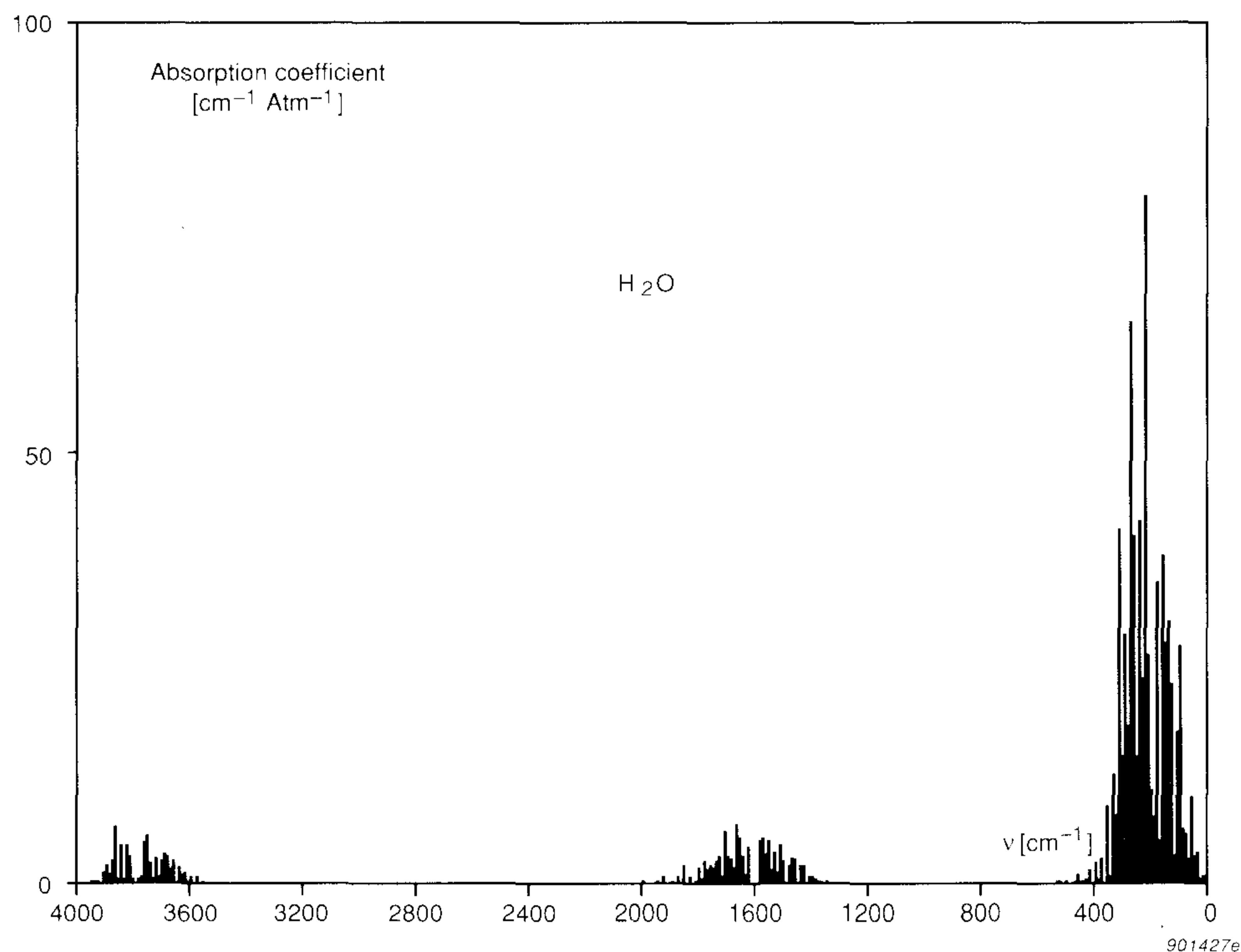


Fig. 22. Absorption spectrum of H_2O including the extremely strong rotational lines in the approx. 20 cm^{-1} to 400 cm^{-1} frequency range (res.: 1 cm^{-1})

the maximum allowed transmission is $1.5 \cdot 10^{-6}$ or 0.00015% for most of the optical filters. This explains why the optical filters are composed of several elements. The UA 0936 filter, for example, is composed of two interference elements plus a calcium fluoride element (see Fig. 2 and Fig. 3).

The fact, that the filter leakage contribution due to interference from water vapour and carbon dioxide has been made negligible, does not imply that there is no interference at all, especially from water vapour. Water vapour has an enormous number of spectral lines distributed over the entire infrared frequency range (more than 20 000 known lines in the range 400 cm^{-1} to 4000 cm^{-1}), and although most of them are weak, they are still strong enough to give an interference contribution with all of the optical filters. The same is true for the water continuum absorption (see Ref. [1]) which in a certain frequency range will be the dominant contributor to interference. Spectral interference is proportional to the concentration of water vapour, whereas the continuum interference is approximately proportional to the square of the concentration. Both these interference relationships are well defined and it is therefore easy to compensate for their contributions. Filter leakage interference is, however, not well defined because the amount of leak transmission depends on production tolerances during the filter coating process. Further, if the leak transmission coincides with the strong part of the water vapour spectrum, the signal due to the leak is 1) non-linearly related to the water concentration, and 2) sensitive to the water concentration in the air inside the 1302 due to water attenuation effect on the light from the IR-source. It would therefore be virtually impossible to compensate for, and this is why the filter leakage contribution has been made negligible.

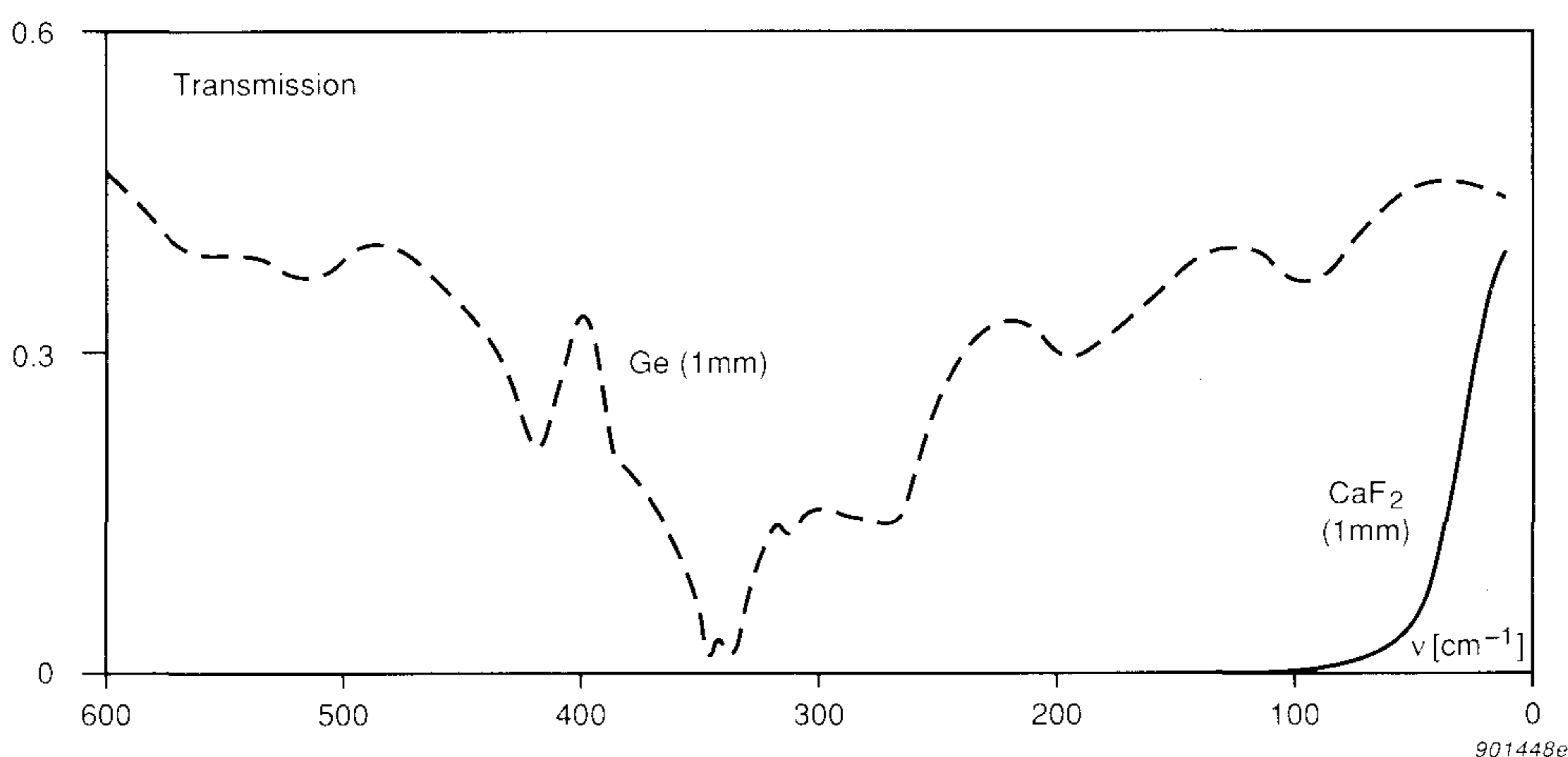


Fig. 23. Transmission of Ge and CaF_2 in the far IR-region

Detection Limits in parts per million at 25°C and 1 atmosphere pressure																							
Substance (gas/vapour)		Optical Filter UA-numbers																					
		Centre Wavelength (in micrometers): Centre Wave Number (in cm ⁻¹)																					
Name	Chemical Formula	*0987 3,4 2950	*0986 3,6 2800	*0983 4,4 2270	*0985 4,5 2215	*0984 4,7 2150	0968 7,7 1291	0969 8,0 1254	0970 8,2 1217	0971 8,5 1179	0972 8,8 1139	0973 9,1 1101	0974 9,4 1061	0936 9,8 1020	0975 10,2 981	*0988 10,6 946	0976 10,6 941	0977 11,1 900	0978 11,6 861	0979 12,2 822	0980 12,8 783	0981 13,4 746	0982 14,1 710
Dimethyl sulphate (DMS)	C ₂ H ₆ O ₄ S													0.03									
Dinitrogen oxide	N ₂ O				0.025																		
1,4-Dioxane	C ₄ H ₈ O ₂										0.03								0.08				
Dipropylnitrosamine	C ₆ H ₁₄ N ₂ O	0.025												0.05					0.35				
Dipropylene glycol methyl ether	C ₇ H ₁₆ O ₃											0.1											
Enflurane	C ₃ H ₂ ClF ₅ O									0.006	0.005	0.006											
Epichlorohydrin	C ₃ H ₅ ClO																			1.0			
Ethane	C ₂ H ₆	0.03																		1.73		4.1	
Ethanethiol	C ₂ H ₆ S	0.8																					
-																							
-																							
Freon 114	C ₂ Cl ₂ F ₄								0.01		0.01									0.02			
Freon 12B2	CF ₂ Br ₂					1.5						0.08									0.13		
Furfural	C ₅ H ₄ O ₂		0.20													0.5						0.2	
Furfuryl Alcohol	C ₅ H ₆ O ₂													0.8									
Halothane	C ₂ HBrClF ₃									0.02	0.02										0.08		
n-Heptane	C ₇ H ₁₆	0.006																					2.0
2-Heptanone	C ₇ H ₁₄ O	0.01									0.25						1.0						1.0
-																							
-																							

*These filters have very narrow bandwidths (see Fig. 1 overleaf) : For a colour guide to the optical filters- see text "Information about this Chart" overleaf.

901454e

Table 2. Section of the wall chart "Gas Detection Limits" (BG 0552). Please note that the detection limits on this chart are subject to change when the list is updated

We also need to consider water vapour's absorption in the far IR-region because water vapour's pure rotational spectral lines in the range from approx. 20 cm⁻¹ to 400 cm⁻¹ (25 μm to 500 μm) are extremely strong (see Fig. 22). Although the spectral output from the IR-source in this region is low, there will be considerable interference unless precautions are taken.

As a typical example, take filter UA 0936 where germanium is used as the substrate material for the interference elements. This material does not attenuate the IR-light much in the far IR-region. Fig. 23 shows the transmission of germanium in the range from 600 cm⁻¹ to 10 cm⁻¹. (Of course, the interference coating could improve the attenuation, but only to a limited extent). The window to the PAS cell is based on a germanium substrate and therefore does not help much. The third element in the

UA 0936 filter is a calcium fluoride disc. Transmission of calcium fluoride in the far IR-region is very low — down to a frequency of approx. 100 cm⁻¹, but it starts to increase at frequencies below 100 cm⁻¹ (see Fig. 23). In part of the range the low transmission is due to a very high reflectivity (termed "rest strahlen reflection"). The frequency range in which this low transmission occurs corresponds to the frequency of vibration of the ions in the crystal lattice when they interact directly with the light. Barium fluoride, which is used in some of the optical filters, has transmission properties similar to that of calcium fluoride in the far IR-region. Sapphire and quartz, which are used as substrate material for the interference elements in some of the optical filters, are not quite as well attenuating as calcium fluoride, but are still much better than germanium.

4. The Selection of Optical Filters

When selecting an optical filter for some specific purpose, several factors have to be considered. These factors include filter sensitivity, and possible interference from atmospheric water vapour and carbon dioxide as well as from other gases possibly present. Some of these factors were referred to in Technical Review No. 1–1990, but in this issue we will discuss these factors more specifically in relation to individual optical filters.

a. Sensitivity and detection limit

The sensitivity of the Types 1302 and 1306 depends, of course, on which gas it is to measure, and which optical filter is selected to measure the gas. The sensitivity is characterised by the sensitivity factor α , defined as the gas signal per unit gas concentration:

$$\text{Sensitivity factor, } \alpha = \frac{S}{c}, \quad (3)$$

where c is the gas concentration and S is the gas signal it causes.

The detection limit is defined as that gas concentration, which causes a gas signal which is equal to twice the RMS noise signal (S_{noise}) when a zero-gas (non-absorbing gas) is in the cell. The RMS noise signal is typically $0.10 - 0.15 \mu V$ at the output of the microphone preamplifier, i.e. the detection limit signal is approx. $0.25 \mu V$. The noise is mainly caused by the microphone preamplifiers, and is therefore independent of which optical filter is used. The detection limit c_{dl} is:

$$\text{Detection limit, } c_{dl} = \frac{2 \cdot c S_{\text{noise}}}{S} = \frac{c S_{dl}}{S}, \quad (4)$$

where S_{noise} and S_{dl} are the RMS noise signal and detection limit signal respectively.

The detection limit is inversely proportional to the sensitivity factor. From (3) and (4):

$$c_{dl} = \frac{S_{dl}}{\alpha} \quad (5)$$

The detection limit of a gas obviously represents the smallest concentration of that gas which can be measured with a particular optical filter when no interferent gases are present. In many cases this will also be true when measuring a gas in ambient air. However, with some of the optical filters, the interference from water vapour and carbon dioxide will be the limiting factor.

The detection limit and sensitivity factor can be most accurately determined by preparing a known concentration c of the gas and measuring the signal S it causes in excess of the zero-gas signal. The RMS noise signal S_{noise} can be determined as the RMS fluctuation of the signal when repeatedly measuring the zero-gas signal, that is the signal measured when high purity, dry nitrogen is in the analysis cell. The detection limit and sensitivity factor are then found by (4) and (3) respectively.

The concentration c should be high compared to the detection limit, preferably a factor of 100 or more, to obtain an accurate measurement. Because of the very high linearity range of the Types 1302/06, no purpose is served in using a low concentration, i.e. a concentration close to the detection limit.

When preparing a known gas concentration, it is generally recommended to use as the base gas a high purity, dry nitrogen similar to that used as the zero-gas, but there are some exceptions to this rule. The measurement of carbon monoxide using filter UA 0984; carbon dioxide using filter UA 0983; and dinitrogen oxide using filter UA 0985 requires the presence of some water vapour to ensure the generation of a photoacoustic signal. Ref. [1] explains why this is necessary. In these exceptional cases, the signal S used in equations (3) and (4) should, for example, when using carbon monoxide, be the difference between the signal measured with carbon monoxide in the presence of some water vapour and the signal measured using the zero-gas with addition of the same amount of water vapour. One way to do this in practice is to use some kind of tube which is permeable to water vapour, but not to carbon monoxide, so that the carbon monoxide mixture as well as the zero-gas can be humidified to the humidity level of the ambient air.

Alternatively, the detection limit and sensitivity factor can be calculated with reasonable accuracy by using the following equations (6) and (7), which are based on equation (24) from Ref. [1], taking the detection limit signal S_{dl} as equal to $0.25 \mu V$:

$$c_{dl} = \frac{44}{T_f \Delta\nu L_\nu k} \quad [\text{ppmv}] \quad (6)$$

$$\alpha = 5.7 \cdot 10^{-3} \cdot T_f \Delta\nu L_\nu k \quad [\mu\text{V/ppmv}] \quad (7)$$

where the optical filter's transmission T_f , its bandwidth $\Delta\nu$ and the black body spectral radiance L_ν at the optical filter's center frequency are given in Table 1 for each of the optical filters, in units compatible with eqs. (6) and (7). The term k is the absorption coefficient of the gas, averaged over the optical filter's bandwidth, and is in units of $\text{cm}^{-1} \text{Atm}^{-1}$. It can be calculated from an infrared spectrum of the gas of known concentration and pathlength. Such spectra can be found in literature, but unfortunately not all of them are quantitative. Brüel & Kjær have, therefore, in co-operation with the H.C. Ørsted Institute in Copenhagen, measured very accurate spectra of some 50 different gases. The spectra were digitized in order to calculate detection limits with the aid of a computer.

A detection limit chart, which is available from Brüel & Kjær, provides some guidelines for the selection of optical filters. A section of this chart is shown in Table 2 (see centre pages). The chart lists some of the gases and vapours which can be detected by the 1302/06, and shows the lowest possible detection limit which can be obtained when the indicated optical filter is used to measure the gas. The detection limits on this chart have been determined, in some cases, by actual measurements and, in other cases, by calculation from gases' absorption spectra.

The optical filters listed in Table 2 have been selected to ensure optimum measurement of a particular gas measured in ambient air. In most cases the selected optical filter's centre frequency coincides with the gas's strongest absorption band, thus providing the lowest detection limit. However, in cases where detection limits are likely to be compromised by the presence of atmospheric water vapour and carbon dioxide, alternative optical filters have been selected wherever possible.

Note in Table 2 for example, the detection limit of enflurane is given as 0.006 ppmv using filter UA 0971, 0.005 ppmv using filter UA 0972 and 0.006 ppmv using filter UA 0973. No detection limits are given for enflurane with any of the other optical filters, but that does not imply that enflurane only absorbs at frequencies corresponding to the three optical filters mentioned, it just indicates that it has its strongest absorption bands there. Actually enflurane absorbs to a greater or lesser extent across the whole frequency range covered by the range of filters. Using this example one can begin to understand that, when two (or more) optical filters need to be selected to measure two (or more) gases, the detection limit chart does not contain sufficient information to ensure that there is minimum

interference between the two gases during measurements. It is also necessary to look at the detailed spectra of the gases to be measured.

b. Water vapour interference

If water vapour interference is not compensated for, then, when water vapour is present in normal concentrations in atmospheric air, the signal it produces in the analysis cell ranges from a few times the detection limit signal, S_{dl} (with filter UA 0988) up to more than a thousand times (with filter UA 0968). Fig. 24 shows on a logarithmic scale, the water vapour absorption spectrum as well as the water continuum absorption for water at a concentration of 20000 ppmv, which corresponds to a dewpoint of 18°C.

Each of the optical filters can be characterised by its detection limit absorption, k_{dl} , which is defined as that absorption coefficient, averaged over the optical filters bandwidth, which produces a gas signal equal to the detection limit signal S_{dl} . The detection limit absorption is given by:

$$\text{Detection limit absorption, } k_{dl} = \frac{4.4 \cdot 10^{-5}}{T_f \Delta\nu L_\nu} \quad [\text{cm}^{-1}] \quad (8)$$

where T_f , $\Delta\nu$ and L_ν are given in Table 1. k_{dl} is shown in Fig. 24, where each filter is represented by a line, its length indicates the filters bandwidth and its centre frequency can be read on the horizontal axis by finding the midpoint of the line. The vertical position of the line gives k_{dl} for the optical filter.

To illustrate, let us take an example and look at the optical filter UA 0976 (which is one of the general purpose filters) and filter UA 0988 (the SF_6 filter). Their centre frequencies are nearly equal, but their bandwidths are different: 7% and 3.5% relative (to their centre frequencies), respectively. It can be seen from Fig. 24 that k_{dl} with filter UA 0988 is approx. twice as high as it is with filter UA 0976. This does not imply, that the UA 0976 is a better optical filter than UA 0988, but simply reflects the fact, that the ratio of their bandwidths equals 2. If the purpose is to measure SF_6 , which has a narrow absorption band which is within the pass-band for both of the optical filters, then the average absorption coefficient of SF_6 at any concentration will be twice as large with UA 0988 as with UA 0976, i.e. the SF_6 detection limit will be the same with both filters. However, if the purpose is to measure NH_3 , then the UA 0976 will give a lower detection limit, simply because it covers a greater part of the NH_3

spectrum, so for this purpose UA 0976 will be the best choice of the two (except when other gases are present which could interfere with the measurement).

Although Fig. 24 gives a good overview of water vapour's influence it is somewhat inconvenient to quantify the information presented in it. This

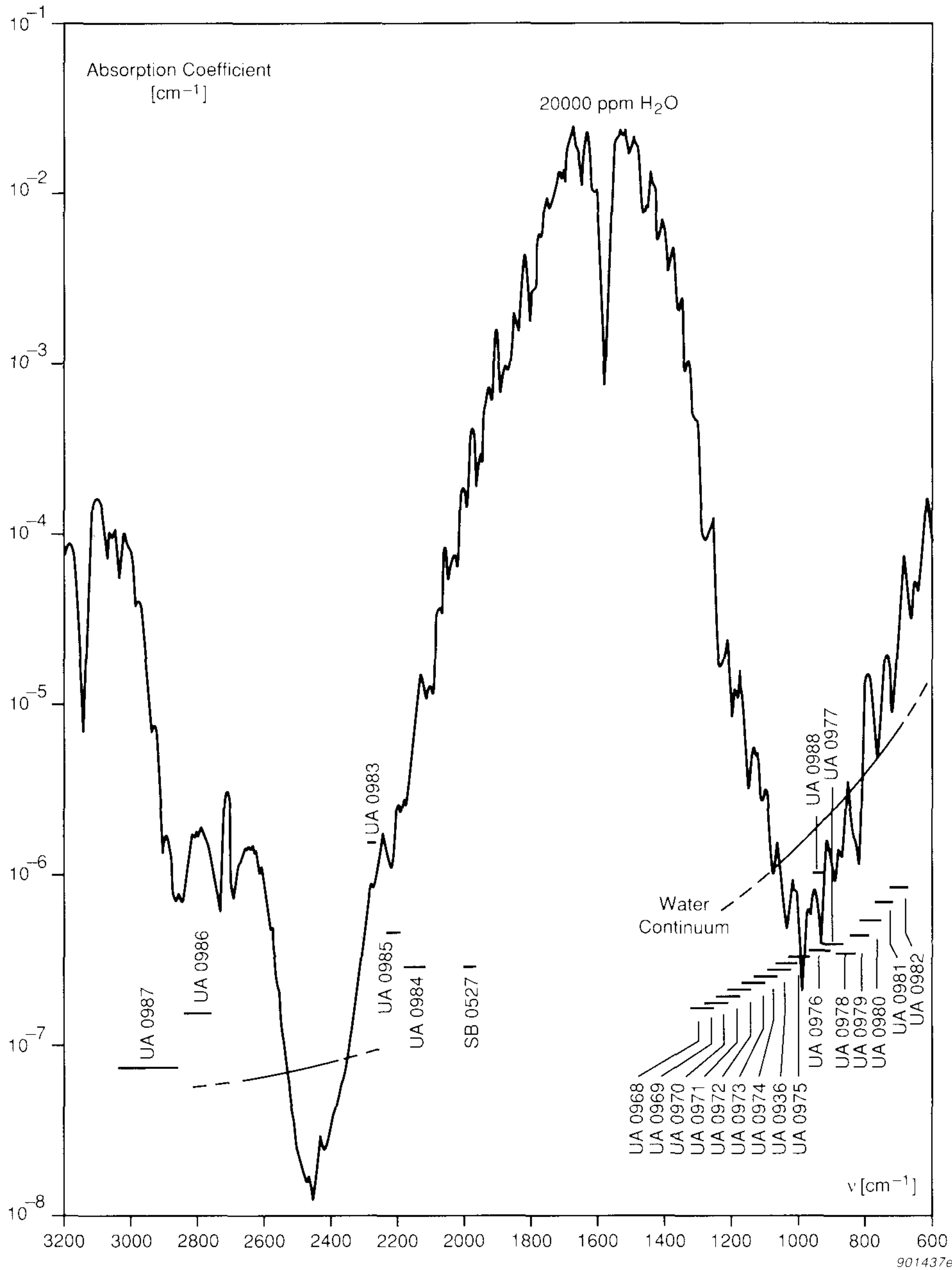


Fig. 24. The absorption spectrum (res.: 20 cm^{-1}) and the continuum absorption of 20000 ppmv water vapour; and the optical filters' detection limit absorption, k_{dl}

data is, however, quantified in Table 3 for each optical filter: it indicates the size of signal produced when water vapour is present at a concentration of 20000 ppmv. The water vapour interference data presented in Table 3 was obtained by measurement. This means that the contribution from water-vapour's absorption spectrum as well as from its continuum absorption are included. When properly calibrated, the Types 1302 and 1306 both measure the water concentration and automatically compensate for its influence on the measurement with a particular optical filter. Using this method, water-vapour's influence can be fully cancelled for many of the optical filters. This is possible, for example, when the UA 0936 filter is used, because the uncompensated water vapour signal (see Table 3), is as low as $2\ \mu V$ or 8 times the detection limit signal. How-

Optical Filter	H ₂ O 20000 ppm	CO ₂ 750 ppm		CO 1 ppm	SO ₂ 1 ppm	NO 1 ppm	NO ₂ 1 ppm	O ₃ 1 ppm	CH ₄ 1 ppm	N ₂ O 1 ppm	NH ₃ 1 ppm
		1302	1306								
Signal [μV]											
UA 0968	500	—	-40	—	3	—	—	—	1,6	6	—
UA 0969	100	—	-10	—	0,2	—	—	—	1	3	—
UA 0970	50	—	-4	—	0,5	—	—	—	0,3	0,5	—
UA 0971	20	—	-2	—	1	—	—	—	—	0,2	0,2
UA 0972	10	—	-1	—	1	—	—	0,2	—	0,2	1
UA 0973	5	—	—	—	0,5	—	—	0,5	—	—	1,5
UA 0974	3	—	—	—	—	—	—	4	—	—	1,5
UA 0936	2	—	—	—	—	—	—	3	—	—	1,5
UA 0975	2	—	—	—	—	—	—	0,5	—	—	1,5
UA 0976	3	—	—	—	—	—	—	—	—	—	3
UA 0977	3	—	—	—	—	—	—	—	—	—	1,5
UA 0978	4	—	—	—	—	—	—	—	—	—	0,6
UA 0979	6	0,6	—	—	—	—	—	—	—	—	0,5
UA 0980	7	1	—	—	—	—	—	—	—	—	0,2
UA 0981	7	15	15	—	—	—	—	—	—	—	—
UA 0982	10	120	120	—	—	—	—	—	—	—	—
UA 0983	2	60	60	—	—	—	—	—	—	1	—
UA 0984	10	0,4	—	1,2	—	—	—	0,5	—	3	—
UA 0985	2	3	3	0,5	—	—	—	—	—	10	—
UA 0986	5	—	-0,5	—	—	—	—	—	—	—	—
UA 0987	100	0,5	-8	—	—	—	1,5	—	4	—	—
UA 0988	1	—	—	—	—	—	—	—	—	—	1,5
SB 0527	300	1	—	—	—	—	—	—	—	—	—

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Table 3. Interference signals caused by H₂O, CO₂ and some trace gases in the given concentrations. By multiplying the given signal by 4 it is possible to determine how much larger the interference signal is relative to the detection limit signal

ever, with the UA 0968 filter, where water's contribution is as high as $500\ \mu V$ or 2000 times the detection limit signal, full compensation is not possible. As a rough guide, water compensation can reduce water's contribution to approx. 2% of its uncompensated value. This means, for example with the UA 0968 filter, that when water's contribution is compensated for, its contribution will be reduced from 2000 times the detection limit signal to 40 times the detection limit signal (2% of 2000). When this filter is used one can appreciate that it is water interference, not the detection limit, which is the limiting performance factor when measuring some gas in ambient air.

c. Carbon dioxide interference

The absorption spectrum shown in Fig. 25 is for carbon dioxide at a concentration of 750 ppmv. The detection limit absorption, k_{dl} , for each of the optical filters is also shown. Table 3 lists the signals caused by 750 ppmv carbon dioxide. Note, that there are two CO_2 columns in Table 3: one for Type 1302 and one for Type 1306. We will first consider the Type 1302. The interference caused by this concentration of carbon dioxide is small or even negligible with most of the optical filters, but high for two of them: filters UA 0982 and UA 0981. The same is true for the UA 0983 filter, which actually is the CO_2 filter. By measuring the CO_2 concentration with filter UA 0983 and using the cross compensation feature of Type 1302 (see Section 4f) interference from carbon dioxide can be totally cancelled except for filters UA 0982 and UA 0981, where it can only be partially cancelled.

Let us next consider interference from carbon dioxide when using the Type 1306, which is listed in the second CO_2 column in Table 3. Notice that in some cases negative figures are listed which means that when carbon dioxide is present a negative signal is measured. How can this fact be explained? The figures given in the Type 1306 CO_2 column in Table 3 assume that Type 1306 is using its water vapour compensation feature. This feature requires water vapour's concentration to be measured, and this measurement is, to some extent, influenced by the presence of carbon dioxide, whereas, in the 1302, it is virtually unaffected by the presence of carbon dioxide. As a result, in the 1306 an overcompensation will take place due to carbon dioxide, causing the compensated gas signal to become negative. The more sensitive the optical filter is to water vapour, the greater the error which will be introduced by the presence of carbon dioxide.

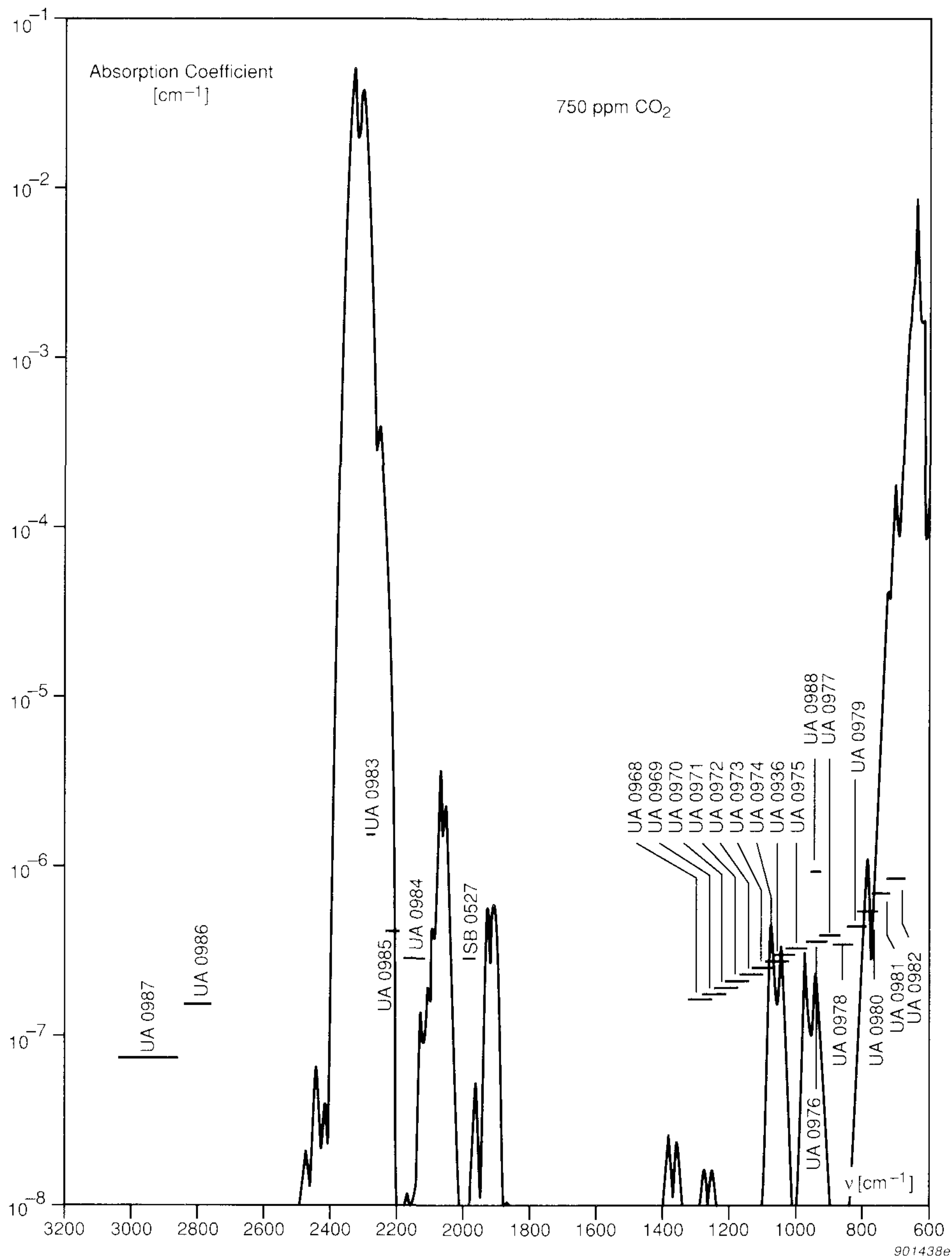


Fig. 25. The absorption spectrum of 750 ppmv CO₂ (res.: 10 cm⁻¹) and the optical filters' detection limit absorption, k_{dl}

In Type 1302 water concentration is measured by using a special optical filter SB 0527, whereas in Type 1306 a different method is used. The Type 1306 uses a flashing incandescent lamp as a light source, instead of the usual black body infrared source. No interference filter is used to shape the light. The spectral output from the lamp, which is determined by the combined effect of: 1) the black body curve corresponding to the filament temperature; 2) the shortwave pass filtering due to the lamp's quartz en-

velope; and 3) the longwave pass filtering due to the anti-reflex coated germanium optical window into the PAS cell, coincides quite well with the 3000 cm^{-1} to 4000 cm^{-1} water absorption band. Unfortunately, however, some of the spectral output coincides with the frequency of the strongest CO_2 band. The water vapour measurement in Type 1306 is simpler than that of the 1302 because no mechanical filter shift is needed. The performance of Type 1302 is therefore superior to that of Type 1306 when water-sensitive optical filters are used to measure gases in places where carbon dioxide concentrations are not stable.

d. Interference from some trace gases

In urban environments atmospheric air is frequently polluted by small amounts of a variety of gases due to industry, traffic, etc. These gases include the following: CO , SO_2 , NO , NO_2 , O_3 , CH_4 , N_2O and NH_3 . These gases have to be considered either as potentially interferent gases, or as gases to be measured. Two of the gases: CH_4 and N_2O are also found in non-polluted areas in small but (at least on a global scale) relatively stable concentrations: 1.5 ppmv (CH_4) and 0.3 ppmv (N_2O).

Figs. 26 to 33 show the absorption of each of these gases (at a concentration of 1 ppmv) as well as the detection limit absorption, k_{dl} , for each of the optical filters. Table 3 lists the signals caused by the gases at a concentration of 1 ppmv. This concentration is arbitrarily chosen, and should not be taken to indicate the typical concentration in which they are found —

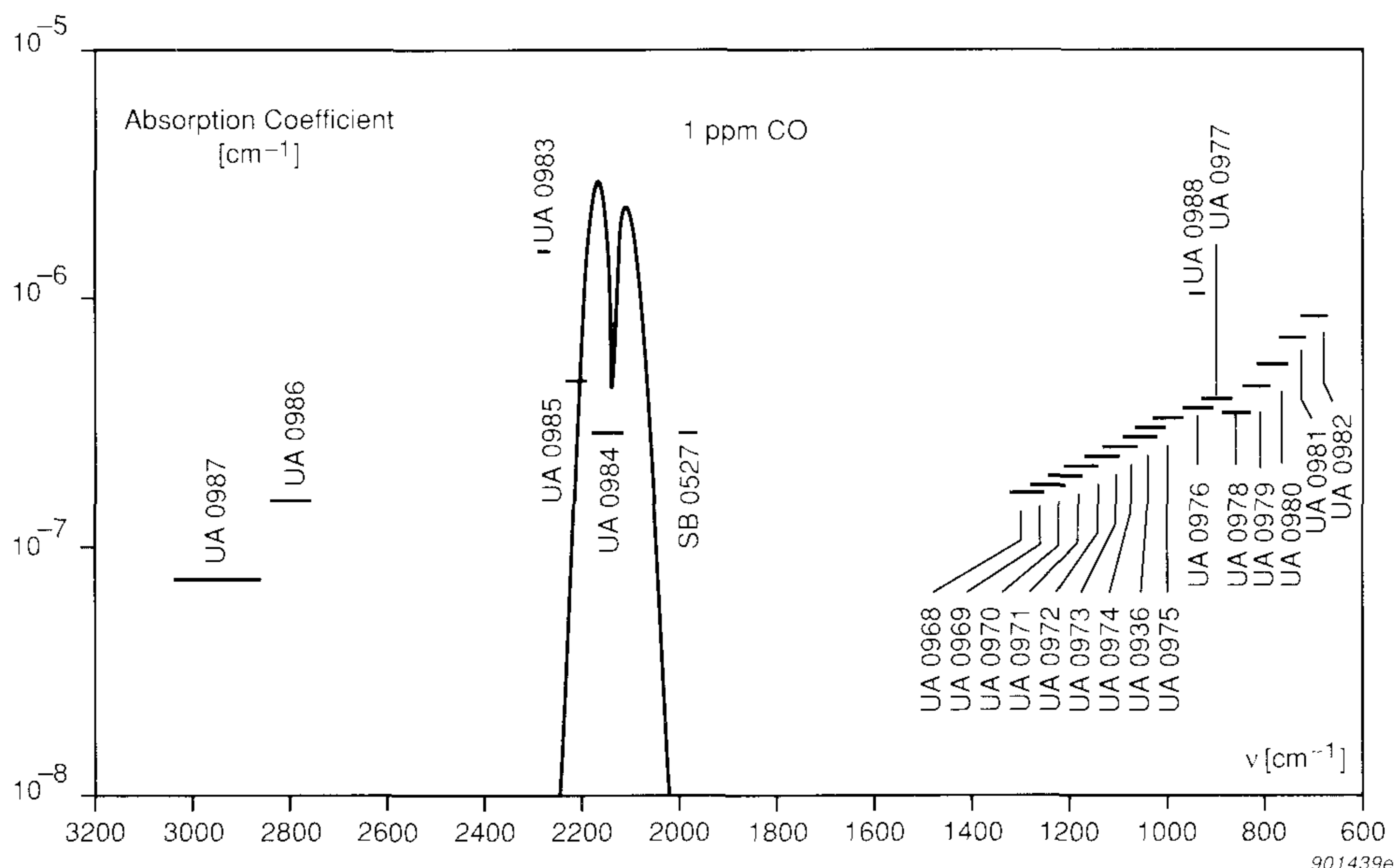


Fig. 26. The absorption spectrum of 1 ppmv CO (res.: 10 cm^{-1}), and the optical filters' detection limit absorption, k_{dl}

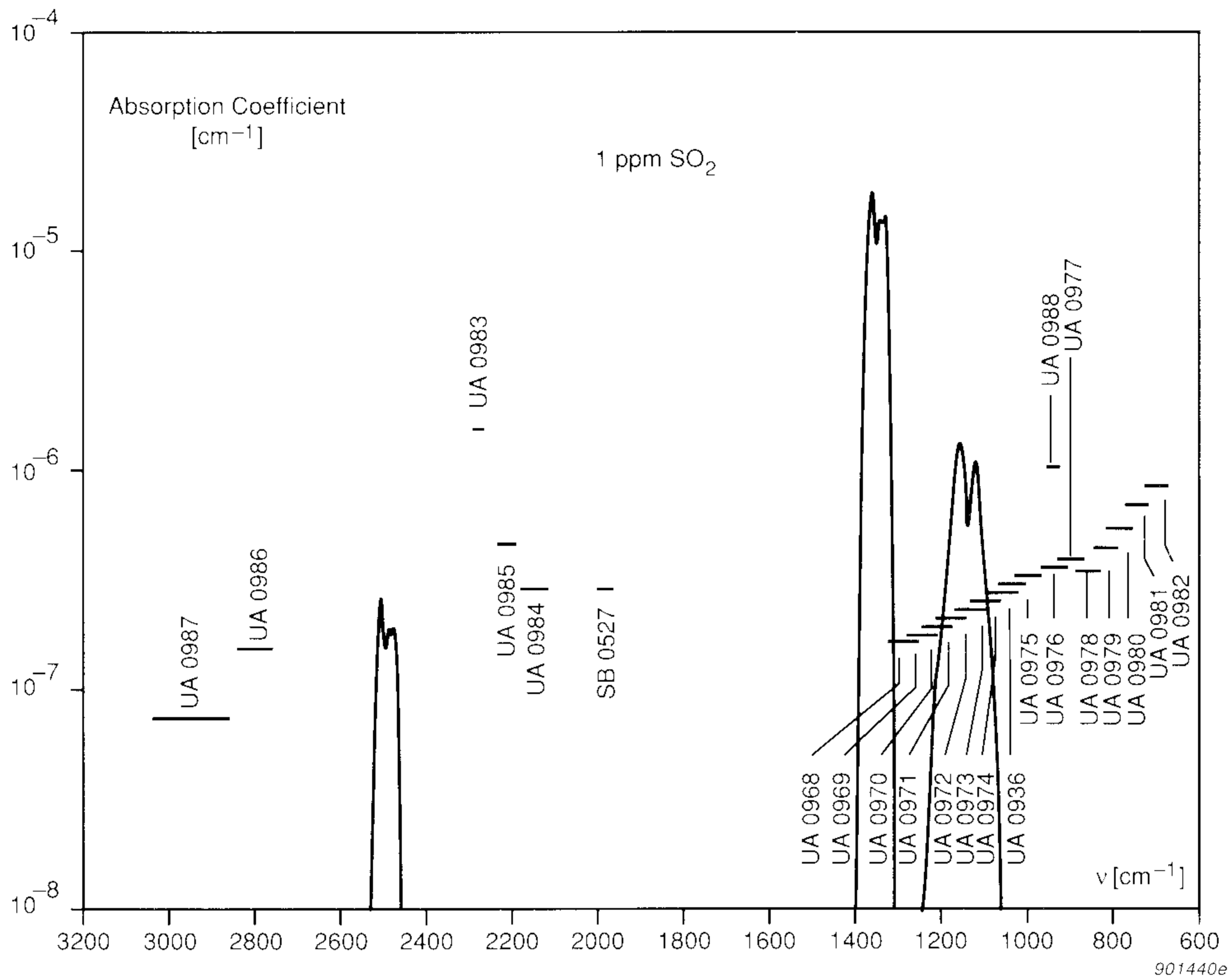


Fig. 27. The absorption spectrum of 1 ppmv SO₂ (res.: 10 cm⁻¹), and the optical filters' detection limit absorption, k_{dl}

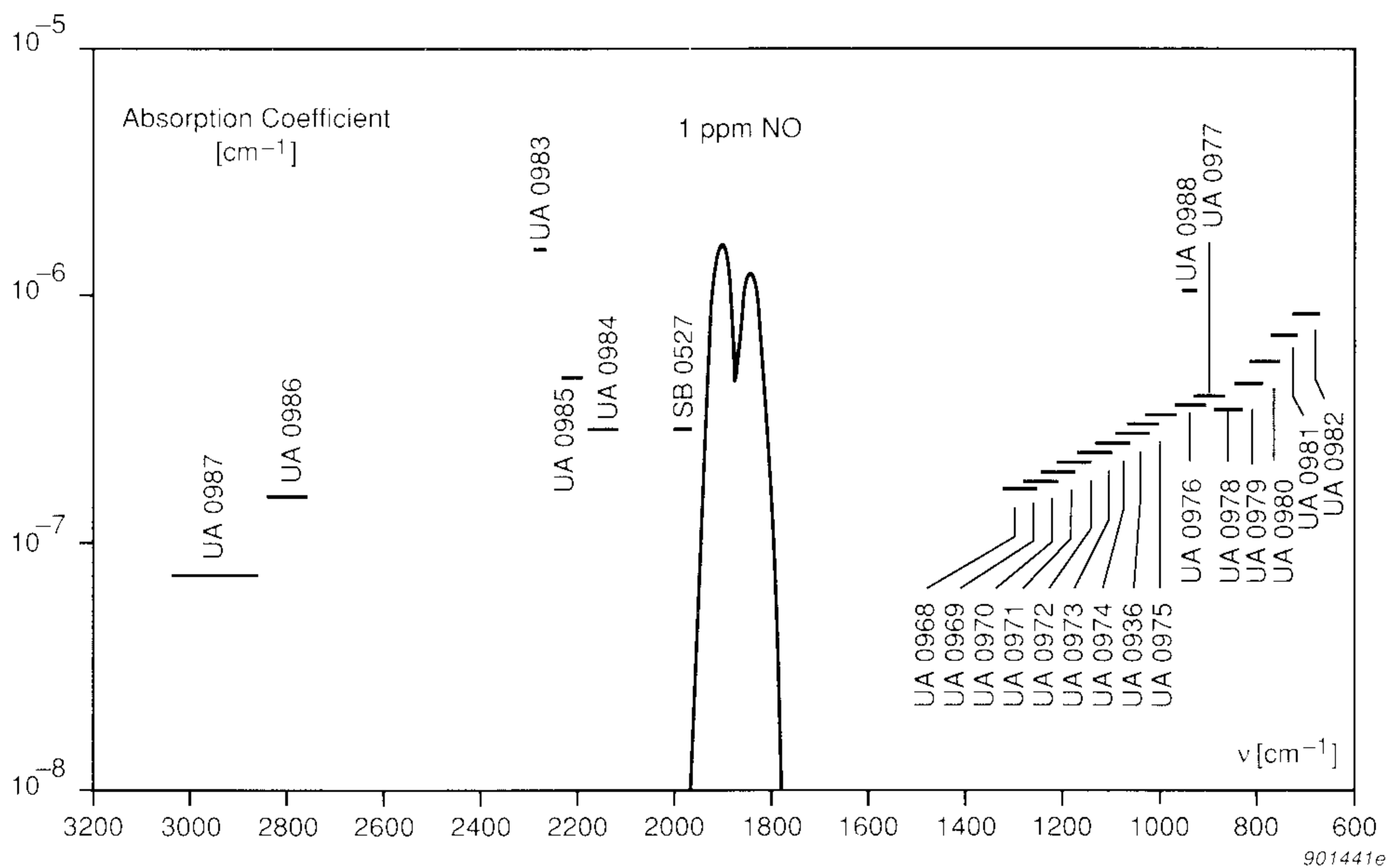


Fig. 28. The absorption spectrum of 1 ppmv NO (res.: 10 cm⁻¹), and the optical filters' detection limit absorption, k_{dl}

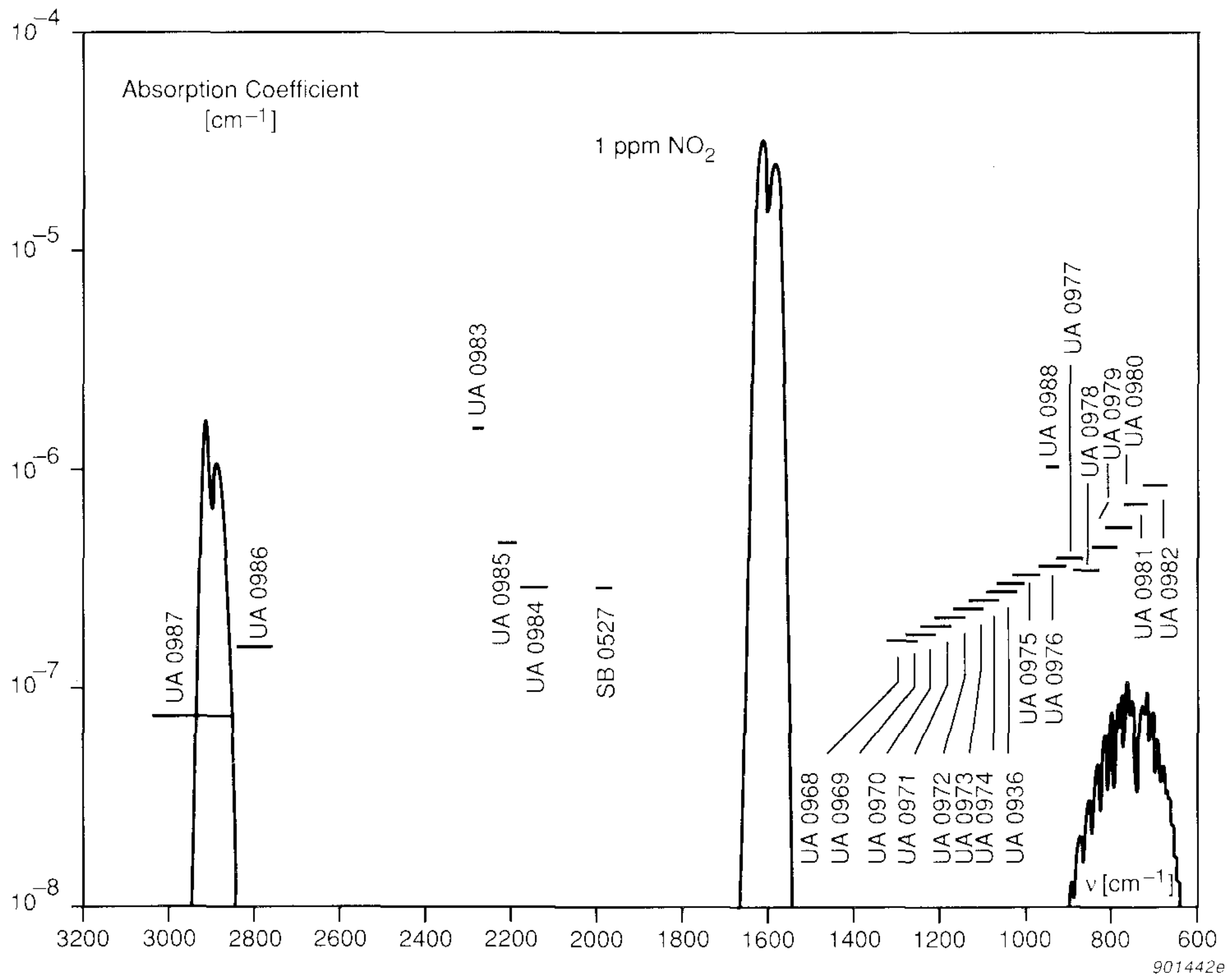


Fig. 29. The absorption spectrum of 1 ppmv NO₂ (res.: 10 cm⁻¹), and the optical filters' detection limit absorption, k_{dl}

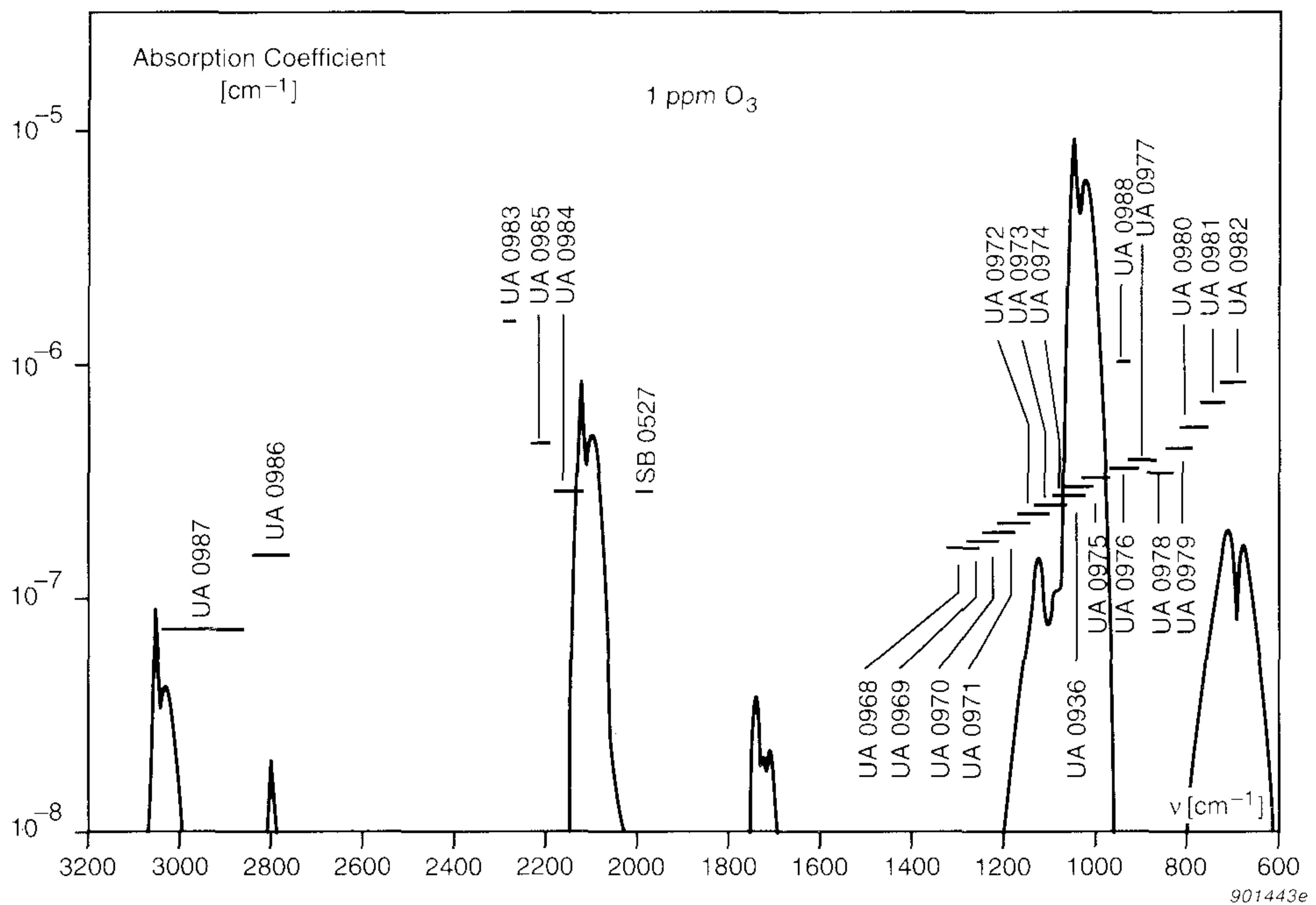


Fig. 30. The absorption spectrum of 1 ppmv O₃ (res.: 10 cm⁻¹), and the optical filters' detection limit absorption, k_{dl}

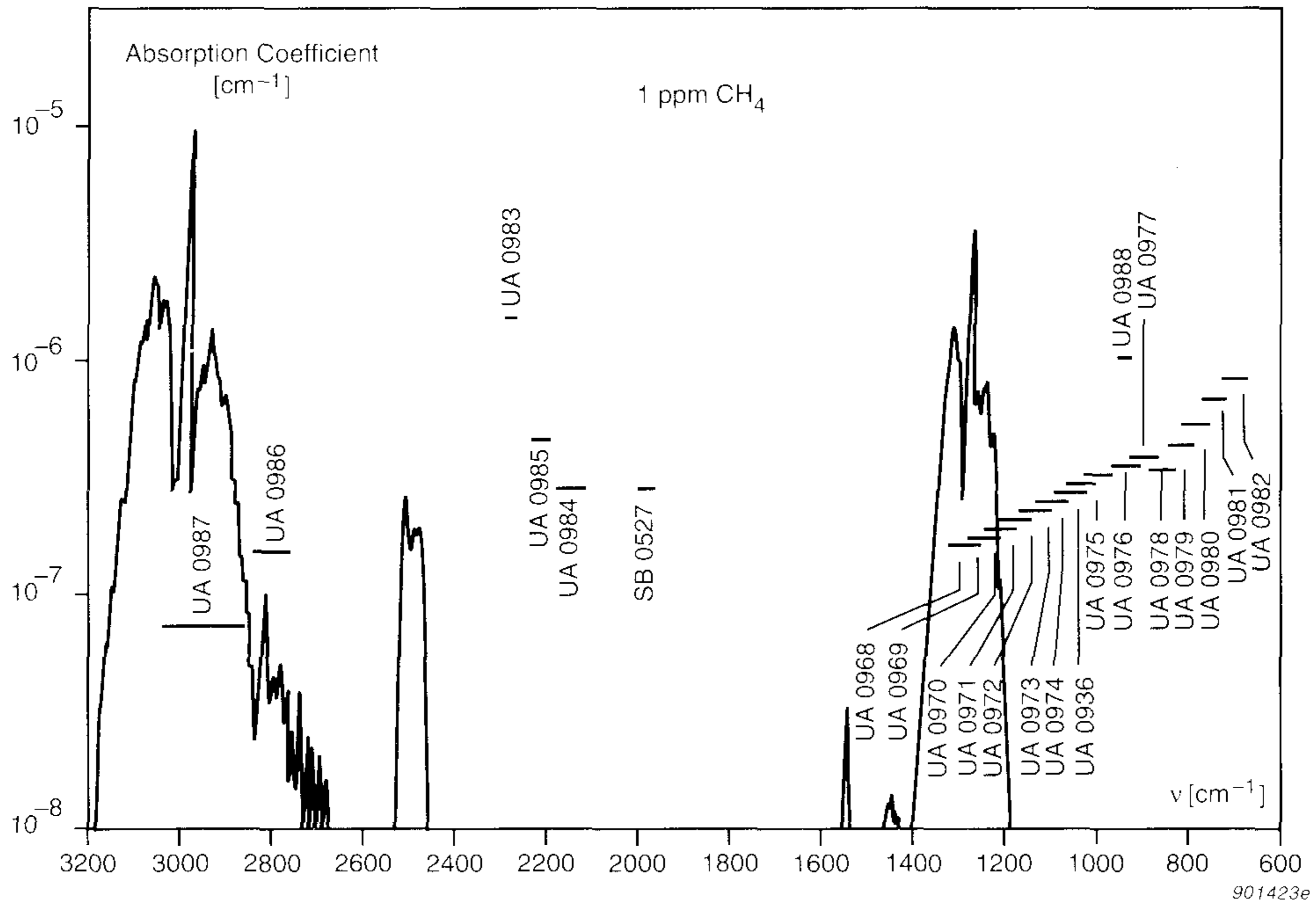


Fig. 31. The absorption spectrum of 1 ppmv CH₄ (res.: 10 cm⁻¹), and the optical filters' detection limit absorption, k_{dl}

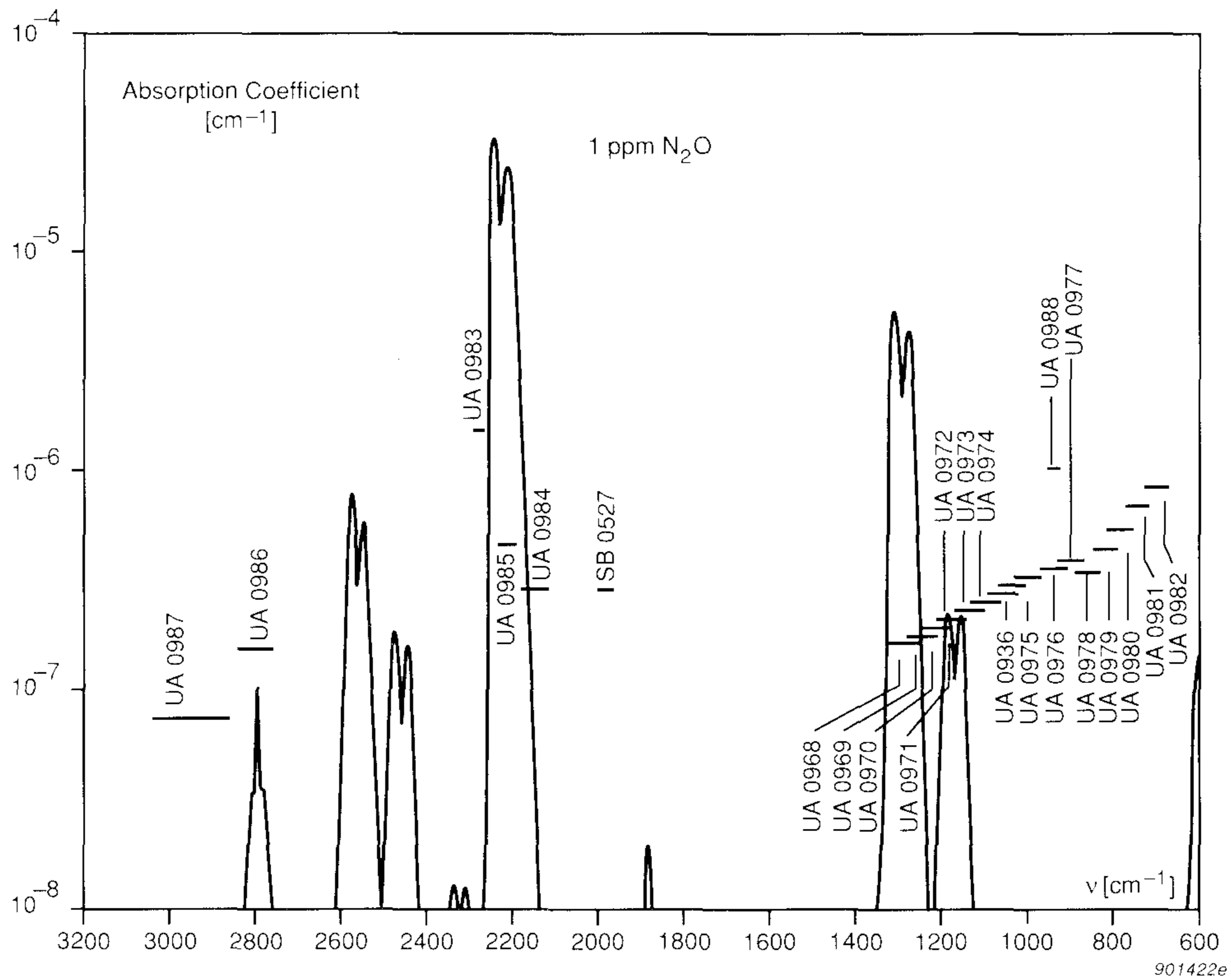


Fig. 32. The absorption spectrum of 1 ppmv N₂O (res.: 10 cm⁻¹), and the optical filters' detection limit absorption, k_{dl}

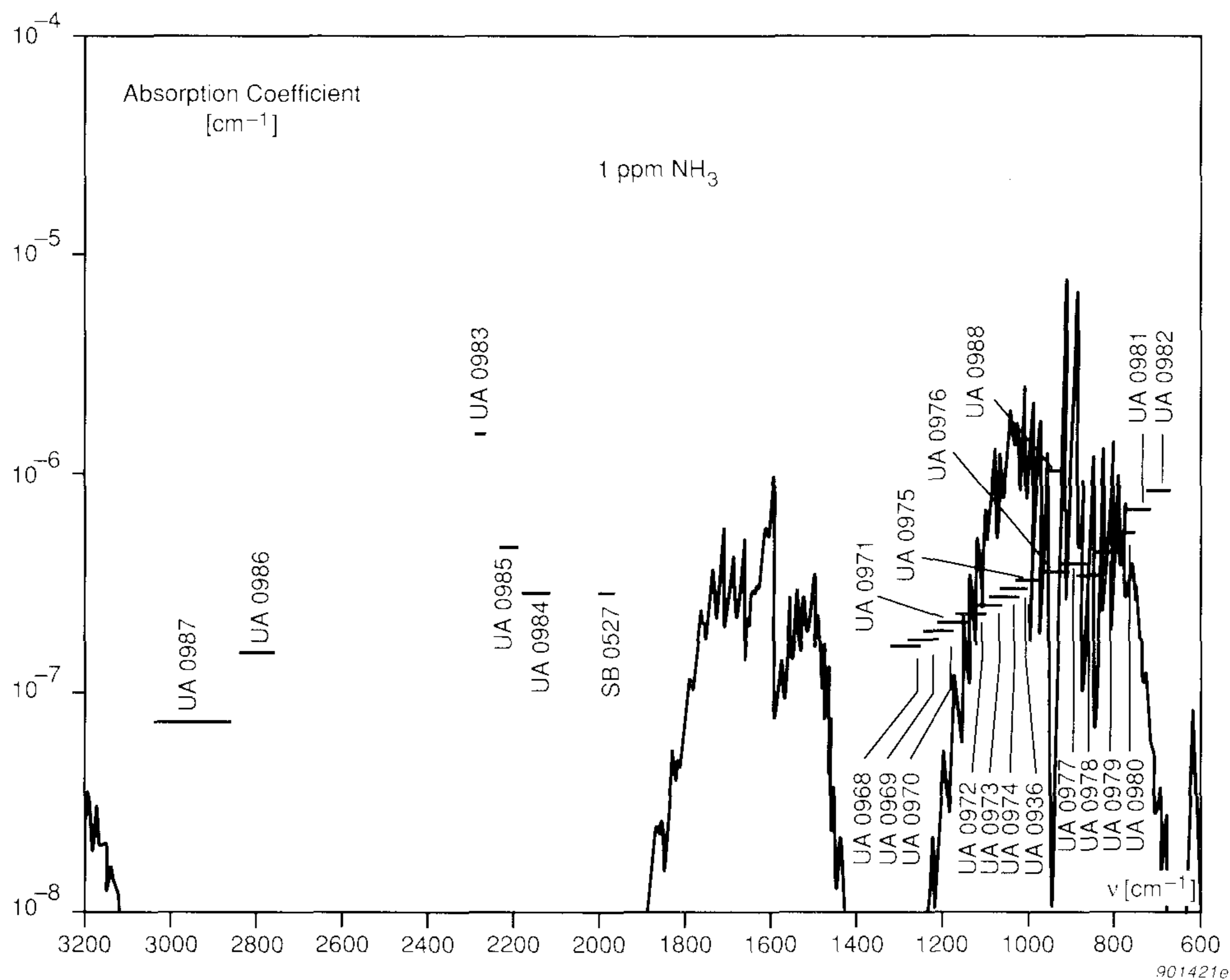


Fig. 33. The absorption spectrum of 1 ppmv NH_3 (res.: 10 cm^{-1}), and the optical filters' detection limit absorption, k_{dl}

hopefully typical concentrations are much smaller. As indicated in Table 3, the interference from these gases can, in many cases be neglected. In those cases where it cannot be neglected, interference can possibly be compensated for by using the cross compensation feature of the 1302 (see Section 4f). This involves measuring the interferent gas with an appropriate optical filter.

The interference from O_3 (ozone) requires an additional comment. The ozone data in Table 3 is based on calculations, but because ozone is a very reactive gas, which easily decomposes on contact with material surfaces, it may not be able to get into the analysis cell without undergoing a chemical change, however, no experimental investigation has been made.

e. Optical filters for multi-gas monitoring

In this section we will discuss how to select optical filters to monitor two or more gases with the Type 1302. To start with we shall consider selecting filters to measure only 2 gases.

In hospital operating rooms gases used for anaesthetizing patients include dinitrogen oxide as well as some volatile anaesthetic agent, for example, enflurane. Small amounts of the gas in the anaesthetic circuit

could possibly be accidentally released into the operating room environment, and expose nurses and physicians to these gases. In order to make the working environment more safe, a Type 1302 could be used to monitor the concentrations of dinitrogen oxide and enflurane in the operating room.

Before selecting optical filters for a particular multi-gas monitoring task, it is important to know the typical concentration in which each of the gases occur or, more precisely expressed, that we decide at which concentrations we want to obtain the optimum measurement. Let us assume, in our example, that the typical concentration level of N_2O is 25 ppmv; and of enflurane is 1 ppmv. We will refer to the typical concentration of a gas as the “reference concentration” of this gas. Hence, the reference concentration of N_2O and enflurane is 25 ppmv and 1 ppmv respectively.

The second step in the selection process is to look at the detection limit chart (illustrated in Table 2). For measuring dinitrogen oxide, the best choice is filter UA 0985 (with a detection limit of 0.025 ppmv). For measuring enflurane, three different optical filters UA 0971, UA 0972 and UA 0973, all having nearly equal detection limits around 0.005 ppmv, can be chosen. Notice that the detection limit of dinitrogen oxide and enflurane are fortunately lower than their reference concentrations.

The third step in the selection process is to find out, by reference to Table 3, how sensitive each of the named filters is to interference from atmospheric carbon dioxide and water vapour. Filter UA 0985 is only slightly sensitive to water vapour interference and therefore this can be easily compensated for by the Type 1302. The filter is sensitive to carbon dioxide interference: a 750 ppmv change in carbon dioxide concentration will cause the Type 1302 to indicate the presence of N_2O which is typically 12 times the detection limit, or $12 \times 0.025 \text{ ppmv} = 0.3 \text{ ppmv}$. This is, however, much lower than the reference concentration of N_2O , and this source of error could possibly be considered acceptable. However, if it is not considered to be an acceptable error, it could be compensated for by installing a CO_2 filter (UA 0983) in the Type 1302, and using the cross compensation feature (see section 4f). Remember that the background N_2O concentration level is 0.3 ppmv.

Looking at the possible filters for measuring enflurane one can see that there is no interference from carbon dioxide with any of the filters (see Table 3); and filter UA 0973 will be the best choice of the three regarding water vapour interference.

The fourth step involves studying the absorption spectra of N_2O and enflurane to check for possible mutual interference. Fig. 34 shows the

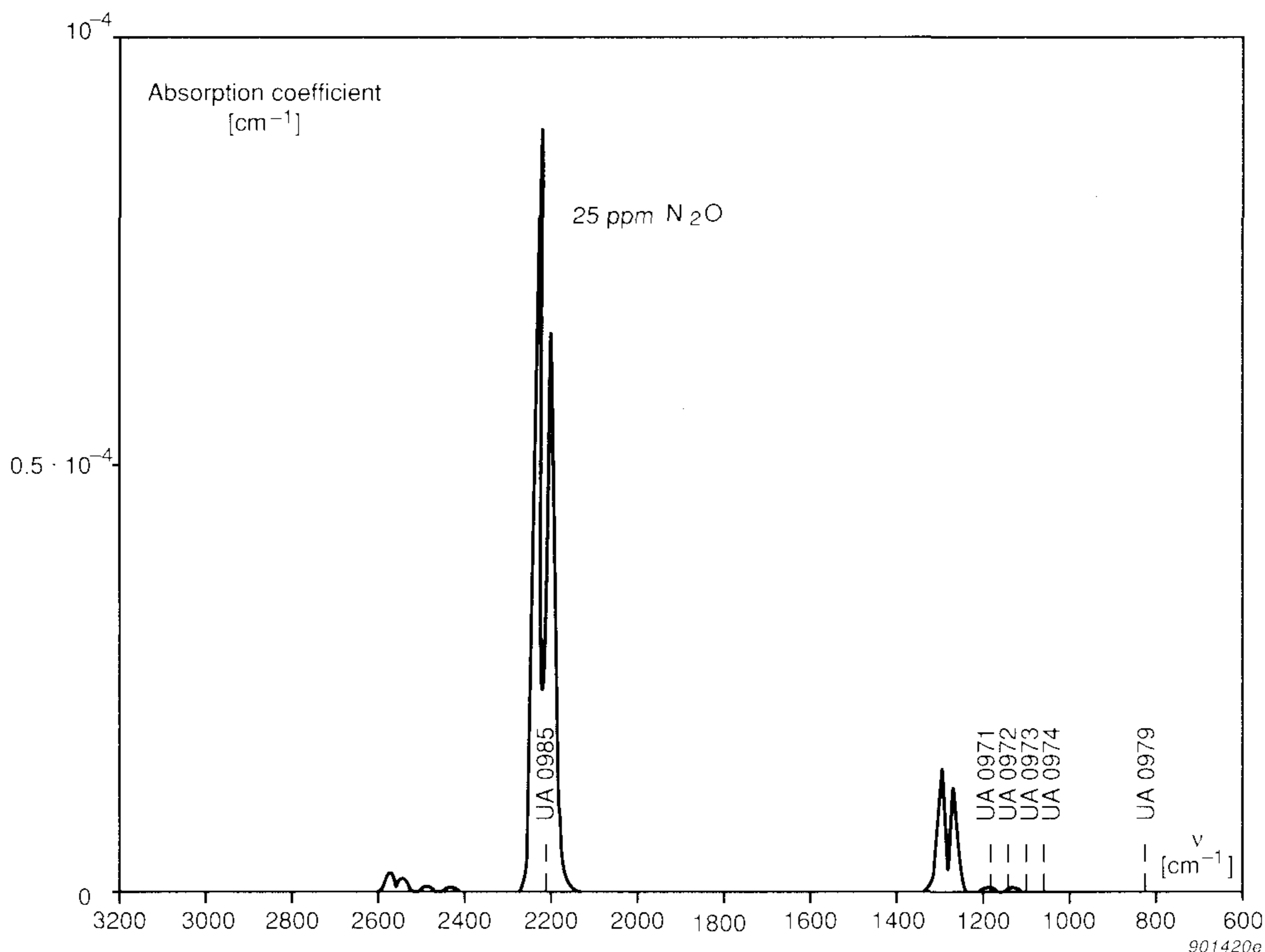


Fig. 34. Absorption of 25 ppmv N_2O (res.: 5 cm^{-1}), with indication of some of the optical filters' centre frequencies

N_2O absorption spectrum at a concentration of 25 ppmv together with an indication of the centre frequencies of the relevant optical filters. Obviously, filter UA 0973 is the best of the three filters for measuring enflurane as there is least interference from N_2O . (Note, that Table 3 also provides this information about N_2O .) Fig. 35 shows the enflurane absorption spectrum at a concentration of 1 ppmv, together with an indication of the centre frequencies of the relevant optical filters. It indicates that there is no significant influence from enflurane on the N_2O measurement.

To summarise: the best choice for measuring N_2O will be the UA 0985 filter and the UA 0973 filter for measuring enflurane. The absence of mutual interference when these two filters are used eliminates the need to utilize the Type 1302 cross compensation feature. In general, however, we will rarely be that lucky.

We will now introduce another gas into our hospital operating room environment, namely halothane. Halothane is often used as the volatile anaesthetic agent instead of enflurane, and consequently, we also need to be able to monitor its concentration with the Type 1302. Let us assume a 1 ppmv reference concentration for halothane.

Using the detection limit chart (Table 2), one can see that three different optical filters can be chosen for measuring halothane: UA 0971 and

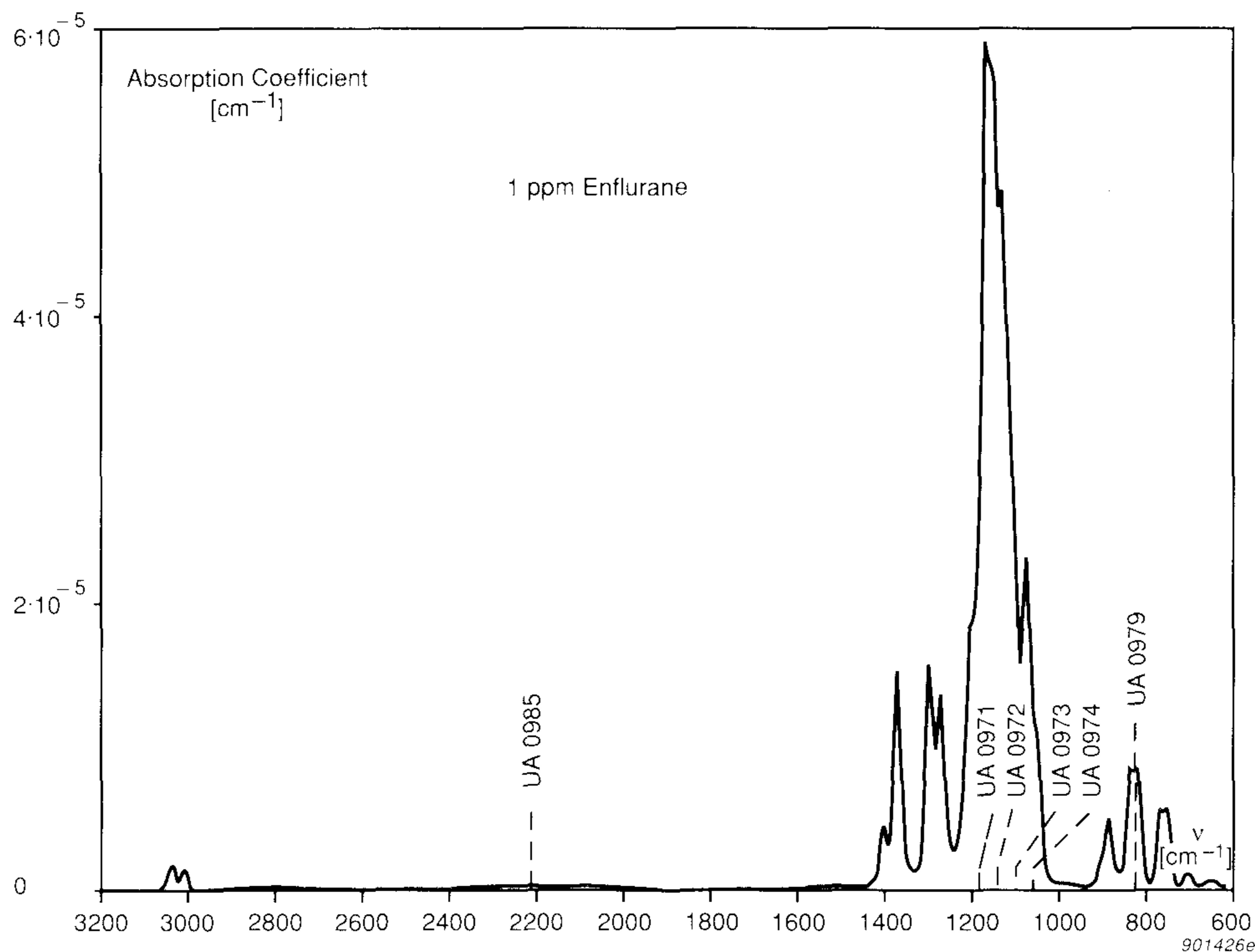


Fig. 35. Absorption of 1 ppmv enflurane (res.: 5 cm⁻¹), with indication of some of the optical filters' centre frequencies

UA 0972, which both have a detection limit of 0.02 ppmv; and UA 0979, which has a detection limit of 0.08 ppmv. Using the absorption spectra of enflurane and halothane (shown in Figs. 35 and 36 respectively), it is evident that there is very strong mutual interference between these two gases with almost any reasonable choice of filter. In this case, therefore, it would appear obvious that Type 1302's cross compensation feature should be utilized. However, before discussing this feature we will mention an alternative means of dealing with the problem of mutual interference.

If only one volatile agent, that is either enflurane or halothane, is used during a particular operation, then there will be no mutual interference to consider. If, for example, filter UA 0973 is used to measure enflurane, and filter UA 0972 to measure halothane, then by knowing which volatile agent is actually being used (ask the physician, he should know), say enflurane, then only those measurements made with the UA 0973 filter are relevant and need to be read. Measurements made with the UA 0972 filter can be neglected. However, it is not necessary to install two different optical filters to measure them, because both gases can be measured using the UA 0972 filter as long as the filter has been span calibrated to measure both gases. The calibration factors calculated during each span calibration can be stored separately in the Type 1302's filter-bank memory. When the

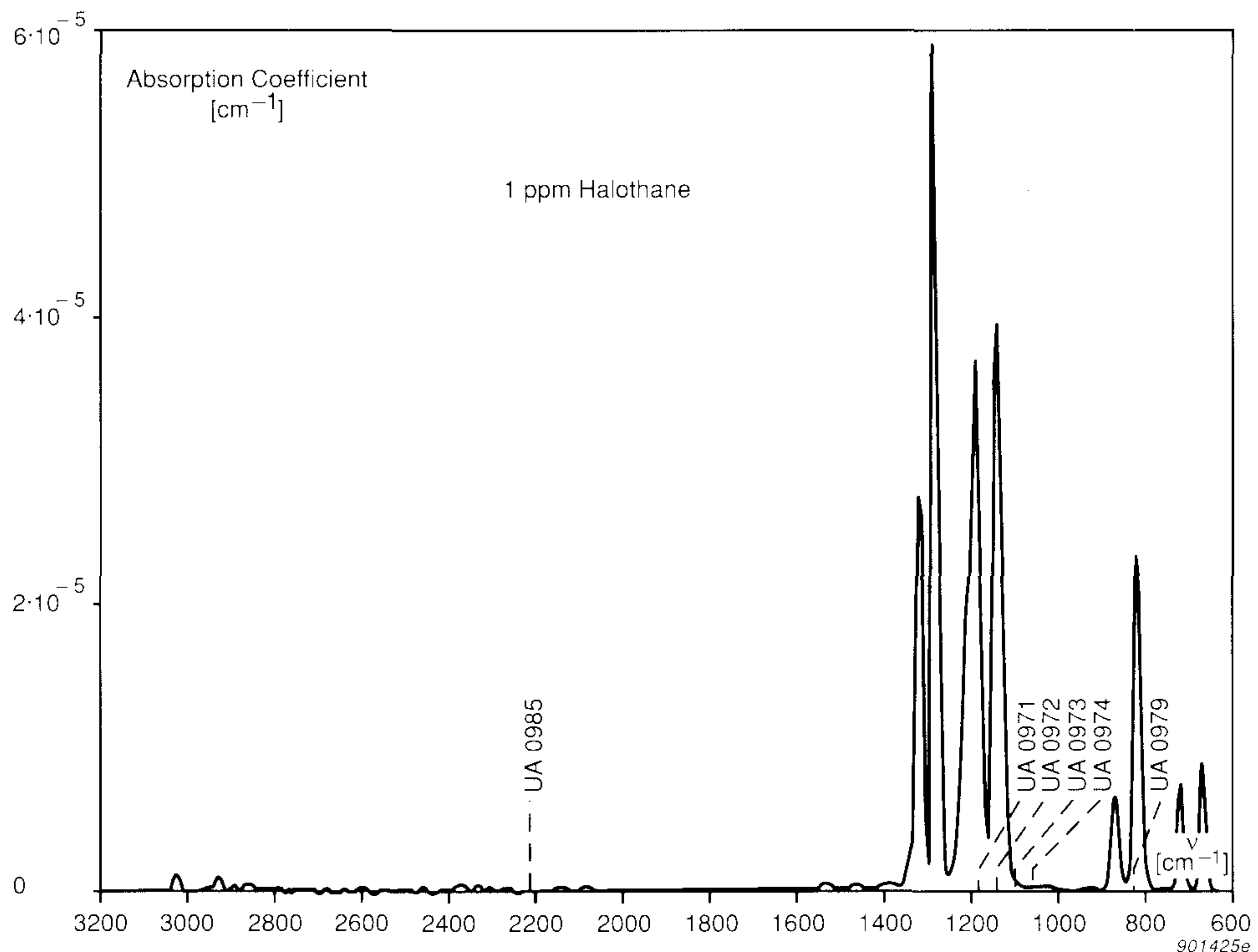


Fig. 36. Absorption of 1 ppmv halothane (res.: 5 cm^{-1}), with indication of some of the optical filters' centre frequencies

physician changes the volatile agent, you simply select the new gas you wish to measure and the Type 1302 will use the correct calibration factors to measure the gas.

f. Cross compensation and its influence on detection limit and accuracy

We will now discuss the cross compensation feature of the 1302. Assume we have selected two optical filters for measuring two gases. The signals measured with each of the two optical filters can be expressed as a linear function of the concentrations of the two gases:

$$\alpha_{11} c_1 + \alpha_{12} c_2 = S_1 \quad \text{and} \quad \alpha_{21} c_1 + \alpha_{22} c_2 = S_2 \quad (9)$$

where c_1 and c_2 are concentration of the two gases, S_1 and S_2 are the signals measured with the two optical filters and α_{11} , α_{12} , α_{21} and α_{22} are the sensitivity factors, which depend on the gases and the optical filters. (The first index refers to the optical filter, the second to the gas.) The concentrations of the gases can be expressed as follows:

$$c_1 = \frac{\alpha_{22} S_1 - \alpha_{12} S_2}{D} \quad \text{and} \quad c_2 = -\frac{\alpha_{21} S_1 - \alpha_{11} S_2}{D} \quad (10)$$

where D is the determinant of the sensitivity matrix of equation (9):

$$D = \alpha_{11} \alpha_{22} - \alpha_{12} \alpha_{21} \quad (11)$$

In the general case, when n optical filters are used ($n \leq 5$) for measuring n gases, the equations become:

$$[\alpha_{ij}] [c_j] = [S_i] \quad (12)$$

where $[\alpha_{ij}]$ is the n by n sensitivity matrix, and $[c_j]$ and $[S_i]$ are the n by one concentration matrix and signal matrix respectively. The solution of equation (12) is straightforward, using the theory of linear algebra.

When using the cross compensation feature, the Type 1302 automatically solves equation (12), but only if it has first been calibrated for cross-compensation. During the cross-interference calibration procedure, a known concentration of each of the n gases is supplied to the 1302, one by one, and measurements are made with all the installed filters. This procedure enables the 1302 to calculate the sensitivity matrix for this particular choice of optical filters and gases.

Measurements of all kinds are subject to inevitable sources of error such as random noise, temperature drift, etc. Any error in the measurement of signals S_i will cause errors in the concentrations c_j depending on the structure of the sensitivity matrix. In the ideal case, where there is no cross-interference at all, by proper arrangement of the n equations only the diagonal elements will be non-zero. In this case, the relative error in c_j is equal to the relative error of the corresponding signal S_j , whereas it is unaffected by the errors of all other signals S_i , where $i \neq j$. In a more typical case, some or even all, of the off-diagonal terms of the sensitivity matrix will be non-zero, and in this case the error in c_j will actually be affected by some or all the S_i 's.

In an extreme case, where the determinant of the sensitivity matrix is equal to zero, the solution of equation (12) would be indeterminate. This will, for instance, happen if any two of the n spectra are proportional as "seen by" the n optical filters, i.e. their sensitivity factors are proportional. It is intuitively evident, that in the vicinity of this extreme case, some error in the signals S_i may cause much larger errors of the concentrations c_j .

In the following text some expressions will be derived which can be used to quantitatively characterize the errors introduced when using the cross compensation feature. This should make optical filter selection easier. Two kinds of signal errors will be considered: 1) random noise, which will affect the detection limit, and 2) gain errors, which will affect the accuracy. We will only discuss the case with $n = 2$. (If $n > 2$, we will have to examine all 2 by 2 sub-matrices of the n by n sensitivity matrix).

If no gases are present which absorb infra-red light, then the residual signals S_1 and S_2 will only be due to random noise. If the cross compensation feature is not used, then from equation (5), the detection limits c_{dl} for the two gases become:

$$c_{dl} (\text{gas 1}) = \frac{S_{dl}}{\alpha_{11}} \quad \text{and} \quad c_{dl} (\text{gas 2}) = \frac{S_{dl}}{\alpha_{22}} \quad (13)$$

where S_{dl} is the detection limit signal.

When using cross compensation, and taking into account the random phase relationship between the noise signals S_1 and S_2 , the detection limits for the 2 gases can be determined from equations (10).

$$c_{dl} (\text{gas 1}) = \frac{S_{dl} \sqrt{\alpha_{22}^2 + \alpha_{12}^2}}{D} \quad \text{and} \quad c_{dl} (\text{gas 2}) = \frac{S_{dl} \sqrt{\alpha_{11}^2 + \alpha_{21}^2}}{D} \quad (14)$$

It is easy to verify, that in the ideal case with no cross interference, corresponding to $\alpha_{12} = \alpha_{21} = 0$, equation (14) reduces to equation (13). If however, α_{12} , α_{21} or both are different from zero, then the detection limits **with** cross compensation, expressed in equation (14), will be larger than (or equal to) the detection limits with no cross compensation, expressed in equation (13).

Let us now consider the influence of some gain error, which causes a corresponding relative error in the signals S_1 and S_2 . By partial differentiation of equation (10), we obtain:

$$\partial c_1 = \frac{\alpha_{22}}{D} \partial S_1 - \frac{\alpha_{12}}{D} \partial S_2 \quad \text{and} \quad \partial c_2 = -\frac{\alpha_{21}}{D} \partial S_1 + \frac{\alpha_{11}}{D} \partial S_2 \quad (15)$$

By using equations (15) and (9), and replacing the ∂ 's with Δ 's, the following equations are obtained after some rearrangement:

$$\frac{\Delta c_1}{c_1} = \frac{\Delta S_1}{S_1} + \Gamma_1 \left[\frac{\Delta S_1}{S_1} - \frac{\Delta S_2}{S_2} \right] \quad \text{and} \quad \frac{\Delta c_2}{c_2} = \frac{\Delta S_2}{S_2} + \Gamma_2 \left[\frac{\Delta S_2}{S_2} - \frac{\Delta S_1}{S_1} \right] \quad (16)$$

where:

$$\Gamma_1 = \frac{\alpha_{12} \left(\alpha_{21} + \alpha_{22} \frac{c_2}{c_1} \right)}{D} \quad \text{and} \quad \Gamma_2 = \frac{\alpha_{21} \left(\alpha_{12} + \alpha_{11} \frac{c_1}{c_2} \right)}{D} \quad (17)$$

The quantities Γ_1 and Γ_2 account for the additional errors introduced in the measurement of concentration by using the cross compensation feature (see equations 16). The first term represents the error if cross compensation had not been used.

Using equation (17), it is easy to verify that in the case of no cross interference, which corresponds to $\alpha_{12} = \alpha_{21} = 0$, then Γ_1 and Γ_2 are both zero.

If the relative errors of S_1 and S_2 are equal, they cancel each other (eqs. 16) i.e. no additional error is introduced by cross compensation.

According to our analysis above, when selecting optical filters where the cross-compensation feature of the Type 1302 is to be used, the following criteria are necessary:

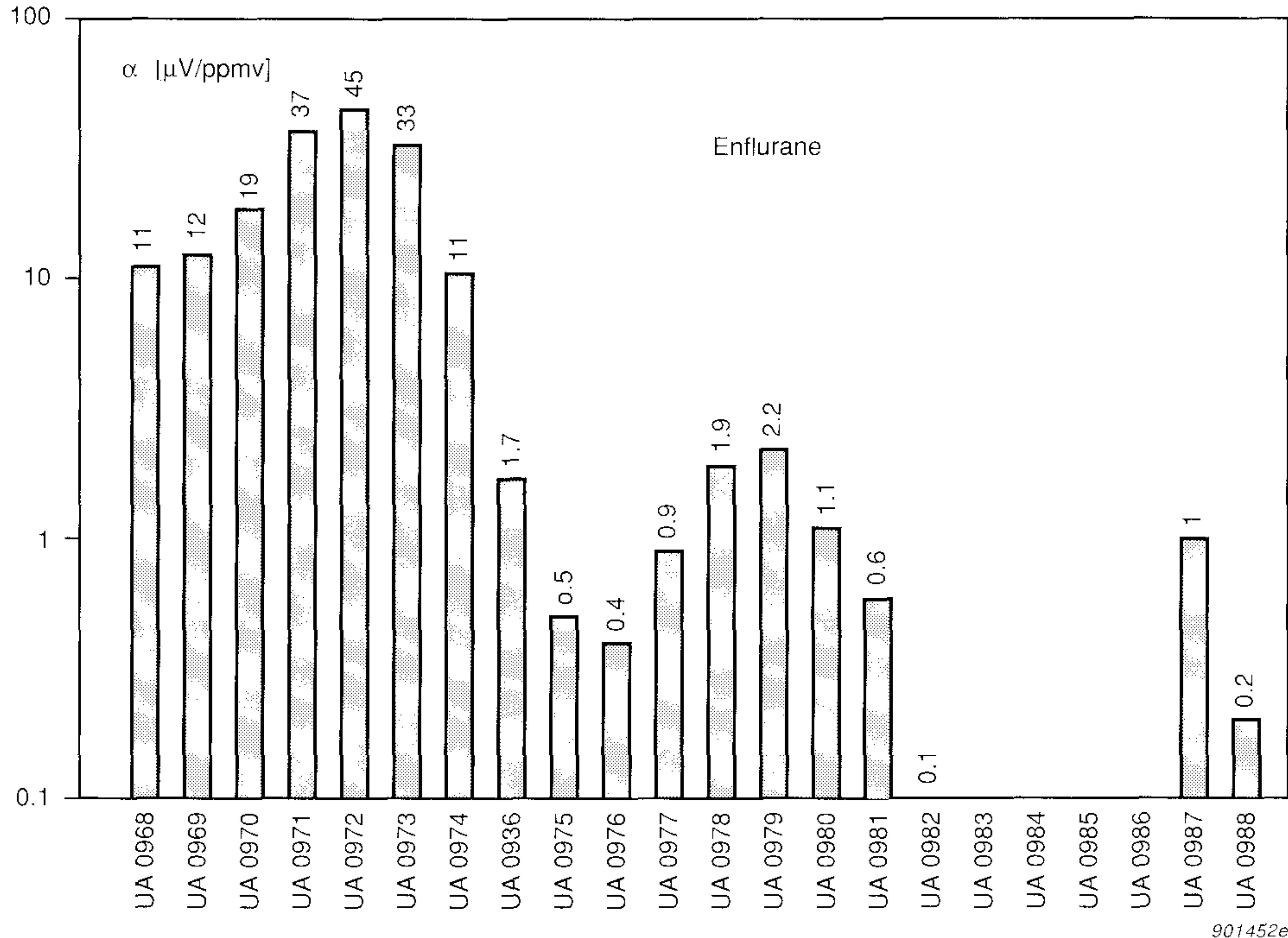


Fig. 37. The enflurane sensitivity factors, α

- 1) Γ_1 and Γ_2 should be small at the gases' reference concentrations.
- 2) The detection limits **with** cross compensation (see equations 14) should be small.

Let us now consider the same example used earlier (measurement of halothane and enflurane) but assume now that the 1302 has to accurately measure both halothane and enflurane if they are present in the operating room at the same time. Figs. 37, 38, & 39 show sensitivity factors for the gases enflurane, halothane and dinitrogen oxide for each of the 22 available optical filters. As one can see from Figs. 37 and 38, a number of possible optical-filter combinations exist for measuring halothane and enflurane.

Table 4 lists the six possible optical filter combinations using the following four filters: UA 0971, UA 0972, UA 0973 and UA 0974 plus the combination UA 0979 & UA 0973. Possible combinations including either UA 0968, UA 0969 or UA 0970 have been discarded due to higher interference from water vapour and dinitrogen oxide. Table 4 further lists for each of the seven combinations: 1) the elements of the sensitivity matrix 2) the detection limits of halothane and enflurane, both with and without cross compensation, and 3) Γ_1 and Γ_2 at the gases' reference concentrations.

Combination 2 (UA 0971 + UA 0973) shows the lowest detection limits **with** cross compensation among the seven: 0.040 ppmv and 0.013 ppmv

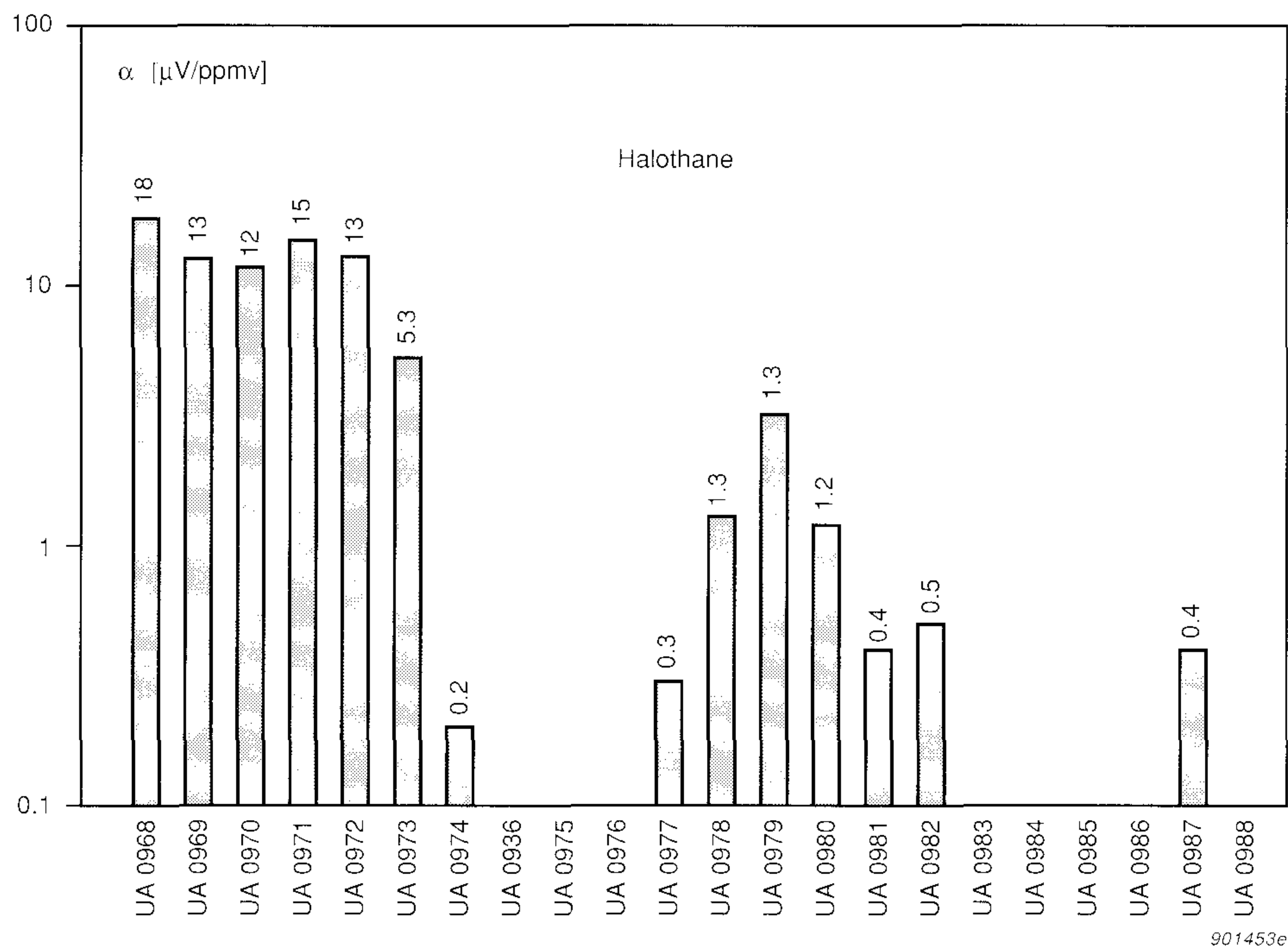


Fig. 38. The halothane sensitivity factors, α

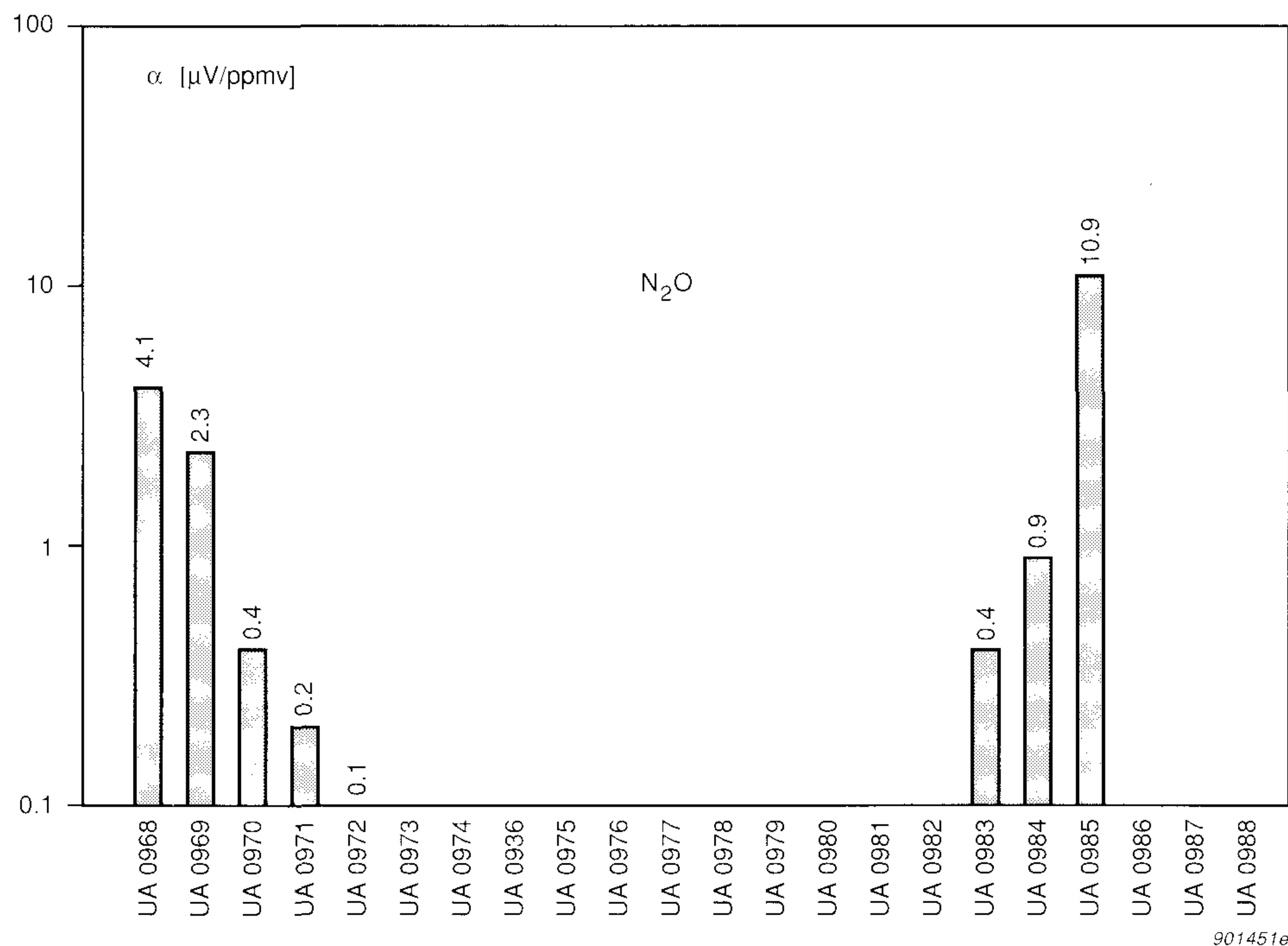


Fig. 39. The dinitrogen oxide sensitivity factors, α

with halothane and enflurane respectively. Γ_1 and Γ_2 are equal to 4.5 and 0.8 respectively, i.e. some possible error of either of the measured signals of say 0.01, or 1%, causes cross compensation induced errors of the halothane and enflurane measurements of 4.5% and 0.8% respectively when the gases are measured at their reference concentration level.

Combination 3 (UA 0971 and UA 0974) shows lower Γ values, but compared to combination 2, the detection limits (with cross compensation) are higher.

Combination 4 (UA 0972 + UA 0973) and combination 5 (UA 0972 + UA 0974) could be useful choices because of the comparatively smaller influence from water vapour and dinitrogen oxide. Actually, the combination 4 (UA 0972 + UA 0973), with addition of the UA 0985 for measuring dinitrogen oxide, was subjected to a test, which involved a cross compensation calibration including all of the gases: halothane, enflurane and dinitrogen oxide, and further involved a subsequent measurement using a gas mixture with all of the three gases in known concentrations. The test showed, that in spite of the high Γ_1 value ($\Gamma_1 = 9$), all of the gases were measured accurately, hence, this particular choice will probably be fully adequate for practical purposes.

Combination 7 (UA 0979 & UA 0973) shows a rather high halothane detection limit with no cross compensation because one of the weaker ab-

			Sensitivity Matrix [$\mu\text{V/ppmv}$]		Detection Limit [ppmv]		Γ Values at the Gases' Ref. Conc.
					Without Cross Comp.	With Cross Comp.	
Com- bina- tion	Optical Filter 1	Gas 1	α_{11}	α_{12}	$\frac{S_{dl}}{\alpha_{11}}$	$\frac{S_{dl} \sqrt{\alpha_{22}^2 + \alpha_{12}^2}}{D}$	Γ_1
	Optical Filter 2	Gas 2	α_{21}	α_{22}	$\frac{S_{dl}}{\alpha_{22}}$	$\frac{S_{dl} \sqrt{\alpha_{11}^2 + \alpha_{21}^2}}{D}$	Γ_2
1	UA 0971	HAL	15	37	0,017	0,071	10
	UA 0972	ENF	13	46	0,005	0,024	3
2	UA 0971	HAL	15	37	0,017	0,040	4,5
	UA 0973	ENF	5	33	0,008	0,013	0,8
3	UA 0971	HAL	15	37	0,017	0,061	2,5
	UA 0974	ENF	0,2	11	0,023	0,024	0,1
4	UA 0972	HAL	13	46	0,019	0,071	9
	UA 0973	ENF	5	33	0,008	0,017	1,5
5	UA 0972	HAL	13	46	0,019	0,088	4
	UA 0974	ENF	0,2	11	0,023	0,024	0,9
6	UA 0973	HAL	5	33	0,050	0,180	8
	UA 0974	ENF	0,2	11	0,023	0,026	0,2
7	UA 0979	HAL	3	2	0,083	0,093	0,9
	UA 0973	ENF	5	33	0,008	0,016	0,3

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Table 4. Examples of the influence from cross compensation on detection limits and accuracy

sorption bands of halothane has been utilized. However, due to the fairly low influence from enflurane, the errors due to cross compensation are small, i.e. there is only a slight increase of detection limit, and Γ values are small.

Finally, it should be stressed, that the example we have chosen to illustrate the cross compensation and its influence on detection limit and accuracy is a particularly complex one. That is why it has been chosen. If we instead had considered the measurement of dinitrogen oxide and enflurane with UA 0985 and UA 0973 respectively, we would have found that the cross compensation contributions to noise and accuracy were negligible.

5. Conclusion

The range of optical filters for use with the photoacoustic gas monitors Types 1302 & 1306 are based on thin-film interference elements, and they are designed to minimize the interference from atmospheric water vapour and carbon dioxide.

When selecting one optical filter for monitoring a single gas, the following should be considered:

- The detection limit or, alternatively, the sensitivity factor;
- Interference from atmospheric water vapour and carbon dioxide;
- Interference from other gases likely to be present in the monitoring environment, including some common trace gases.

If the purpose is to monitor several (up to five) gases, which all can be present at the same time, then 1302 has to be used, so that its cross compensation feature can be utilized. When selecting the optical filters for the monitoring task, one should consider the additional errors regarding detection limit and accuracy, which the cross compensation introduces, in order to minimise these errors.

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Erratum

In the first photoacoustic article published in Technical Review No. 1, 1990, Eqn. (23) should have read:

$$p_{\text{RMS}} = 1,13 \cdot 10^{-3} T_f L_\nu c k \Delta\nu, \quad \text{or:}$$

$$1,13 \cdot 10^{-3} T_f c \int F(\nu - \nu_o) L_\nu k(\nu) d\nu \quad (23)$$

For the record ...

With the advent of fast oxygen analyzers, it is possible to directly measure the oxygen uptake of an anesthetized patient. Changes in the patient's oxygen uptake – expressed as the difference between inspired and expired oxygen concentrations – provide a very fast indication of changes in the patient's condition. This method is a lot faster than the frequently-used SaO₂ method.

To permit continuous monitoring of the patient's O₂ uptake, it is possible to equip the O₂ measuring device with an audible indicator. The pitch of the audio signal is dependent on the difference between inspired and expired oxygen concentrations. Furthermore, the tone should be modulated with a signal that has a frequency that is dependent on the patient's heart rate. This frequency can be deduced by using, for example, ECG or pulse plethysmography.

Simultaneous measurement of end-tidal CO₂ makes it possible to use this parameter to control the pitch of the audio signal as an alternative to O₂ differences or SaO₂.

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