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OPTICAL GAS SENSORS USING CORRELATION SPECTROSCOPY

Report for
Shell Research
by

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Abstract

This report reviews the feasibility of detection of impurities, in particular water vapour, in natural gas, using real-time correlation spectroscopy. The general concept relies on using a gas sample, contained in a reference cell, as a matched optical filter, to preferentially detect similar absorption spectra of the same gas in the measurement cell. All variations of the method have the advantage of excellent selectivity, provided the gases to be detected have narrow line spectra, even when using broadband sources for illumination. They are also suitable for direct-path measurements or for remote detection over optical fibre leads.

The report focuses on two main areas. Firstly, the Stark modulation method has been used to detect water and ammonia vapour. Secondly, we present an alternative correlation spectroscopic arrangement, in which the route of the light path is modulated. This new arrangement has been tested with both water vapour and ammonia. We give a comparison of the characteristics of both methods and discuss their suitability for determining water vapour contamination in natural gas.

Our conclusions are that the switched-path method has some potential of being developed to meet the Shell application for trace measurement of water vapour in high-pressure natural gas.

Introduction

Many common gases of industrial and environmental importance exhibit their fundamental optical absorption in the infrared region. Weaker overtone bands extend into the near infra-red and visible region, thus coinciding with the low loss transmission window of silica fibre. Absorption in these regions is usually due to transitions between vibrational-rotational energy levels of the molecule. As the fine-line structure within an absorption band is highly specific to the gas species, recognition of these features allows highly selective gas detection. The band positions of a selection of common gases are shown in simple form in Figure 1. Because there may also be interest in detection over fiber leads, the absorption spectrum of silica optical fibre is also shown. (Infra-red fibres, typically manufactured from fluoride glasses, are also available with acceptable loss at wavelengths up to 5µm.) However, in this application, direct operation using bulk optics is likely to be more convenient and sensitive than using fiber-based systems.

Early optical gas sensing methods used broadband LED sources [3] and thus had poor selectivity. Other recent methods have used laser sources [4]. However, lasers are only available for a limited range of IR wavelengths, and they usually require very careful selection and stabilisation for sensor applications. In addition, the high coherence of lasers can lead to problems of interference between reflection from optical surfaces, which can result in considerable transmission changes.

Correlation spectroscopy [5,6,7,8] allows the use of a broadband source, yet still monitors the fine spectral features of the gas spectrum. It has the further advantage of employing all of the spectral information contained in the selected gas absorption band, rather than just examining a single line. thereby enhancing the cognitive nature of the technique.

The basic methods of real-time correlation spectrometry all involve modulation of the absorption spectra of the reference gas sample, relative to the gas to be measured. Modulation can be achieved directly by varying the absorption spectrum of the reference gas. In an earlier paper [8], workers at the University have reviewed progress with three modulation techniques, each using the correlation spectroscopy method. These included Stark, pressure and phase modulation. A common optical configuration was adopted for all of the schemes investigated in the study, as shown schematically in Figures 2(a) and 2(b). The apparatus comprised two gas cells, through which light from a broadband source was passed sequentially, prior to detection. In our fibre-remoted version, light was conveyed to the cells via multimode optical fibre, and a bandpass filter was included before the detector in order to attenuate light outside the absorption band of the relevant gas. The gas to be detected was directed into the measurement cell, whereas the reference cell was filled with a known concentration of the gas to be detected and then sealed.

Modulation of the absorption spectrum of either gas cell resulted in a change in the correlation between the spectrum of the measurement gas sample and the reference gas, thereby causing a variation in the overall transmission of the system, and hence in detected signal. The absorption spectrum of the gas contained in the reference cell was modulated, either directly or indirectly, in order to produce the desired signal. The synchronously-detected output signal then depended on the concentration of the correlating gas in the measurement cell. Modulation methods which act directly on the gas include Stark and pressure modulation, as depicted in Figure 2(a).

Stark modulation of gases occurs only with polar molecules and results from the splitting (or, at atmospheric pressure, the broadening) of individual absorption lines when a large electric field is applied. The pressure modulation technique is more generally applicable, as the gas can have broad absorption lines and there is no need for polar molecules. This method involves periodically pressurising the gas within the reference cell, causing a variation in both the strength and width of the absorption lines.

Another approach to achieve correlation spectroscopy is, instead of modulating the optical properties of the reference gas, to alternately switch the light path through the reference cell and via a bypass route. This is achieved by using a fixed beamsplitter and a chopper wheel, which alternately blocks one light path and opens the by-pass, and vice versa (see Fig. 6). A relative change in absorption between these two modes of transmission indicates the presence of the target gas in the measurement cell, the difference signal being proportional to concentration of gas in the measurement cell.

Gas Sensing using Stark Modulation Spectroscopy

We shall firstly describe the Stark method in more detail and report on our recent experimental feasibility tests.

In our earlier paper [8], Stark Modulation was used for the detection of ammonia gas. The Stark effect is potentially very attractive, as it is only necessary to apply an electric field to the gas cell in order to cause a synchronous modulation of the detected signal. The only disadvantages are the high field strength required to produce even a low amplitude modulation index in the detected signal and the fact that only certain gases are Stark-active. In order to be Stark-active (i.e. suffer line splitting, or broadening, under the influence of electric field) a gas must have a strong electrical dipole moment.

Traditional water vapour sensors have many applications in industry and meteorology. Despite having been commercially available for many years, there are few, if any, hygrometers which perform reliably over an extended temperature range, and most have poor performance for trace measurements.

The H_2O molecule is strongly polarised and therefore has the necessary dipole moment for Stark modulation. However, as water is not particularly volatile at room temperature, a heated Stark cell was necessary, firstly to maintain a sufficiently high vapour pressure in the cell to produce a strong absorption and secondly to prevent the possibility of condensation on the windows or electrical components, which would occur if the cell were to cool below the dew point.

The basic design of our prototype cell is shown in Fig 3. The 160 mm x 18 mm x 5 mm electrodes were held 6 mm apart using polymer spacers. The electrode/spacer structure was mounted in a horizontal glass tube, fitted with end windows. The optical pathlength of the reference cell was 180 mm. The horizontal tube (the reference gas cell) was connected to a lower-level water reservoir. Both gas cell and water reservoir could be heated electrically, with the reservoir being held at a lower temperature. The gas cell electrodes were connected to an electrical drive unit, via feed-through leads sealed into the glass walls, in order to provide a high field strength across the water vapour.

The electrical drive to the Stark cell was from a combined, AC + DC, high voltage unit, capable of applying a 2.0 kV p-p AC signal at 7.1 kHz and adding a 2.0 kV DC bias signal. Both of these drive signals can be produced by up-conversion from lower voltage supplies. The D.C. bias was necessary to ensure a Stark modulation component at the fundamental frequency of 7.1 kHz. (Stark modulation of the optical amplitude is approximately proportional to the square of the applied voltage and therefore an AC signal alone would result in a modulation at the 2nd harmonic of the applied frequency.) The Stark effect results in a modulation of the linewidth of the gas absorption in the reference cell, which changes the overlap integral between the gas absorption in the reference cell, and that in the measurement one [8].

In order to detect the small AC modulation signal at the detector, the lock-in amplifier arrangement shown in Figure 4 was used. In order to determine the modulation index of the received light, and hence reference the detection scheme, a DC signal was also derived from the output of the transimpedance receiver.

Figure 5(a) shows the detected signal when light from a tungsten halogen source was collimated through the Stark cell and detected via a narrow band interference filter corresponding to the water band 1.94 µm ± 10 nm. A GaInAs-photodiode with a responsivity of 0.3 A/W at 1900 nm was used as a detector. The DC voltage level, measured after preamplification with a transimpedance amplifier (R_f = 1 GOhm) was 1.8 V. The light power measured with the diode therefore was 6 nW. The integration time constant of the lock-in was 3 s. The two states represent conditions when the beam was allowed to reach the detector and when the beam was blocked off. Using a monochromator, it was confirmed that the modulation only occurred in the main water bands at 1.4 and 1.9 μm.

The modulation arises from the change in the (pressure-broadened) width of the absorption lines under the action of the electric field in the reference cell (i. e. the Stark cell). When the absorption lines are strong (partially saturated), the Stark modulation leads to a change in the average optical loss in the cell as the lines are broadened. The water vapour content of the laboratory air (estimated water partial pressure ~ 12 hPa (1 hPa = 1 mbar, and ~ 0.1 % at atmospheric pressure)) was monitored in a 300 mm long measurement cell, in line with the reference cell. In order to check the signal change due to the H_2O absorption in this path, it was alternatively filled with water vapour at a partial pressure of 24 hPa (mbar) and with dry nitrogen. Again, the measurements were taken with a lock-in time constant of 3 s. The resulting change in detected signal was very weak, but it was discernable and reproducible, and represents the first detection of water vapour by this method (see Fig 5(b)).

It should be noted that our gas sensing result using this novel arrangement is a preliminary one. However, unfortunately, it appears unlikely that this method will be applicable to the trace water vapour measurement, desired by Shell (down to 3 ppm in natural gas, but at 100 bar pressure), even though long-term averaging could be used to improve the signal/noise ratio. In addition, at higher pressures, the selectivity of the method is likely to be much worse due to pressure broadening effects.

Gas Sensing using Correlation Spectroscopy, Based on Modulating the Light Path

We shall now describe our new gas sensor arrangement, where a mechanical chopper wheel is used to switch light alternatively through and past a reference cell, before it enters the measurement cell (Fig. 6).

Fig. 6

For convenience, the system used two separate white light sources, although an additional beamsplitter and/or mirrors could be used with a single source. After collimation, one beam passes through the reference cell, and then joins the second collimated beam in a beam combiner. Before this combiner, both beams pass through the plane of the chopper wheel, where they are alternately blocked. The united beams pass on through the measurement cell, through the monochromator (or interference filter) to select the gas band, and then on to the detector. The light intensity of each source was independently adjustable by changing the supply voltage, enabling the detected intensities from each beam to be balanced. The optical pathlength of the reference cell was 180 mm, whereas the pathlength of the measurement cell was 300 mm.. The signal was detected with a GaInAs-photodiode with a responsivity of roughly 0.3 A/W between 1500 and 2000 nm. The detected signal was recorded with a phase-independent lock-in amplifier, synchronized to the chopping frequency. The mean detected optical power was found to be approximately 6.6 nW at 1505 nm, and 2.6 nW at 1920 nm, calculated from the detected signal and the data sheet value for the responsivity of the detector.

With the reference cell filled with the reference gas, and the monochromator set to the absorption band, the relative intensity in each channel was adjusted. This was set to the condition where, with no gas present in the measurement cell, the difference in detected signals was minimized. After this initial setup-procedure, to "zero" the system without gas, the measurement cell was alternately filled with sample gas and dry air to perform the measurements.

For our first measurements, a test gas mixture was generated by filling a flask about half full of a concentrated ammonia solution in water. The head space of the flask therefore contained a mixture of water vapour, ammonia gas, and a very small quantity of residual air, at atmospheric pressure and room temperature (i. e. at N.T.P.). We estimate that the partial pressure of water vapour in the head space was approximately 24 hPa (24 mbar, ~2.4 vol%) at this temperature, and the partial pressure of ammonia to be 976 hPa. Fig. 7 shows the near-IR absorption of such a gas mixture in a cell with a path length of 160 mm, recorded with a Perkin-Elmer FTIR spectrometer. The absorption band with its maximum at 1510 nm was caused by ammonia, whereas the water vapour band was centred on 1920 nm.

Fig. 7

The correlation signal was recorded at three different wavelengths, at 1505 nm, 1920 nm, and 1400 nm. The latter wavelength was used to verify the origin of the correlation signal, as the absorption of both H_2O and NH_3 is low at this wavelength (see Fig. 7). Fig. 8 shows the signals recorded at these three wavelengths, with the system of Fig. 6 with a relatively short integration time constant of 300 ms (The rise and fall time in Fig. 8 are longer, in practice, due to the cell filling times being longer than the measurement response time). The DC voltage level of the preamplified signal (transimpedance amplifier, R_f = 1 GOhm) was 2.0 V at 1505 nm, 800 mV at 1920 nm, and 2.1 V at 1400 nm. The signal change caused by the presence of ammonia vapour at 1505 nm was ~ +22 mV, the signal change due to the presence of water vapour at 1920 nm was 5.6 mV.

Fig. 8

By showing that there was virtually no correlation signal when measuring at 1400 nm, it was confirmed that the system output was only significant when there was a matched absorption of the reference and the sample gas. To further corroborate the origin of the correlation signal, another measurement at 1505 nm was performed while the reference cell was removed from the lightpath, and the measurement cell was alternately filled with sample gas (a gas mixture containing water vapour of a partial pressure of 24 hPa (24 mbar, 2.4 vol%), and ammonia of 976 hPa (976 mbar, 97.6 vol%), generated as described above) and dry inert gas. The correlation signal intensity measured in this experiment was about 5% of the correlation signal measured with the reference cell in the lightpath. This crosstalk is attributed to two likely causes.

Firstly, both the collimated beams are combined in a beam combiner. However, it is difficult to achieve an identical light path for the two combined beams. Therefore, one beam may be reflected or absorbed, by the walls and windows of the measurement cell, to a different extent than the other one. Any change in the concentration of the gas in the measurement cell, resulting in a change in absorption, may therefore have an effect of different magnitude on the detected signal component from each beam path.

Secondly, even after optimum adjustment of the intensity of the two light sources, the detected signal is not exactly zero. This is because, during the transition from one light path to the second, there are usually short periods when more than half the energy of each beam is fed into the beamsplitter, and also more than half of each beam is blocked out at the same time. This gives rise to periodic transients in detected signal during the changeover period. These periodical variations in light intensity would not normally give a correlation signal, when the system is nulled, but they may do if there is any nonlinearity in the detector of the lock-in system. However, it is expected that this second effect would make only a very small contribution to the cross talk signal when using a good lock-in amplifier with a low-level detected signal. Also, any nonlinear response of the lock-in, is expected to be preceeded by an "overload" message. Because of this, we believe the problem was probably due to the differences in the passages of the beams through the cell, rather than to our second possible explanation.

The noise of the signal at the output of the lock-in, with an integration time constant of 300 ms, was found to be about 1.5% of the total signal. For our water vapour measurement (at ~24 hPa partial pressure), we estimate a limit of detection of approximately 0.4 hPa (= 0.4 mbar, equivalent to 0.04 vol% = 400 ppm at N.T.P.). However, the limit of detection can be easily enhanced, either by increasing the measurement time constant, increasing the path length of the measurement cell, or by using a reference cell containing a higher partial pressure of water vapour. The latter can easily be achieved by heating the reference cell, particularly if it is pressurized to permit partial pressures above 1 bar. In addition, there are brighter light sources at 1.9 μm available. For example use of a fluorescent Tm-doped fiber source, in conjunction with a detector having a 2.0 μm cut-off, would give much better signal/noise. The method would, with development, appear to have some possibilities for detection at the ppm level. With a partial pressure of 1 bar in the reference cell, a detection limit of 5 ppm would be expected, even at N.T.P.

At the high pressure required by Shell (100 bar), with a typical concentration of 200 ppm water vapour, the partial pressure of water would be 20 hPa (20 mbar). The target limit of detection is 3 ppm at 100 bar (partial pressure 0.3 mbar). Therefore, in principle, even with our present limit of detection (400 ppm at N.T.P.), we would expect to be able to achieve a noise-limited sensitivity of 3 ppm water vapour at 100 bar. However, some deterioration of the sensitivity and selectivity of the method is likely to take place due to high-pressure-broadening of the absorption band of water. (Of course, we could use a pressurized reference cell, maintained at high temperature, to increase the concentration of water vapour in this cell).

Comparison of the Perfomance of the Described Gas Sensing Methods

In the following, we give a short summary of the advantages and disadvantages of the above methods.

Gas sensing using Stark modulation spectroscopy is potentially very attractive, as it is only necessary to apply an electric field to the gas cell in order to cause a synchronous modulation of the detected signal. No moving mechanical parts are required. The disadvantages are the high field strength required to produce even a low amplitude modulation index in the detected signal, and the fact that only certain gases (including water vapour) are Stark-active. However, in view of the particularly small signals we observed in our trials, it is expected that the application of the method will almost certainly be limited to the detection of water vapour at high concentrations (i. e. 1% to 100%). Any application for high pressure measurement would require the Stark cell to be at atmospheric (or lower) pressure, as otherwise the pressure broadening will suppress the effect of Stark-effect-induced broadening..

Gas sensing using correlation spectroscopy, based on modulating the light path is a more generally applicable method, as, in principle, all gases with an appropriate absorption band are detectable with this method. The modulation index with our switched-path arrangement is very high, since the optical modulation arises as a result of the *total* absorption of the gas in the reference cell. Thus, the modulation index is equivalent to a 100 % pressure modulation index in a pressure-modulated system. It presents no particular safety hazards, as no high voltage is involved. This method was primarily tried in order to obtain estimates of the ultimate sensitivity possible for the correlation spectroscopy method using broadband sources. However, it appears, that, with some development, it could be quite suitable to use this method for trace water vapour detection. The primary disadvantage of the sensor is that, as undertaken presently, it requires the use of moving parts (the chopper wheel). The performance should be better with pressurized gases as the effective modulation index will increase due to the greater integrated gas absorption. However, at higher pressures, the selectivity will, of course, be poorer due to the inevitable pressure broadening. Any practical system may need optical routing through a separate measurement cell, containing a known concentration, of gas to calibrate the system.

Conclusions

We have reported the first measurements of water vapour concentration using Stark modulation of a reference cell. A second method, based on alternately switched light paths, has been demonstrated for water and ammonia vapour.

Both these developments represent promising new ways for the selective detection of water vapour at higher concentrations. However, by using the switched light path method, it is expected, with development, to be possible to extend the limit of detection to the ppm range. It is potentially capable of development to measure trace water vapour absorption in natural gas, provided the sensitivity and selectivity requirements can be met in practice. In addition, most organic gases and vapours (e. g. methane), as well as many inorganic gases (ammonia, nitrous oxides,...), should be detectable with this method.

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Figure captions

Figure 1	Absorption bands of some common gases within the transmission window for silica fibre
Figure 2	Schematic diagram for the correlation spectroscopy scheme, (a) pressure and Stark modulation, and (b) angle modulation
Figure 3	Schematic of experimental Stark cell for applying electric field to a water vapour sample. (Upper cell is heated above temperature of lower cell to avoid condensation).
Figure 4	Functional block diagram of electronic system for driving a Stark cell and detecting the modulation signal from the transmitted light.
Figure 5(a)	Detected signal transmitted through the Stark Cell after phase-sensitive detection with the arrangement of Figure 4. The curve shows the signal change when the light beam is periodically blocked by a shutter. This modulation is only observable in the main H_2O absorption bands at 1.4 μm and 1.9 μm.
Figure 5(b)	Signal change due to H_2O absorption in the measurement cell. The cell was alternatively filled with air (containing 12 mbar H_2O-vapour) and dry nitrogen. After each cycle, the beam from the tungsten halogen source was blocked.
Figure 6	Correlation spectroscopic setup using two light sources and a chopper wheel.
Figure 7	Near-IR absorption of a gas mixture containing water and ammonia vapours in air, recorded with a Perkin-Elmer FTIR spectrometer. The band with a maximum at 1510 nm is caused by ammonia, and water vapour absorbs at 1920 nm.
Figure 8	Correlation signals, recorded at 1505 nm, 1920 nm, and 1400 nm.

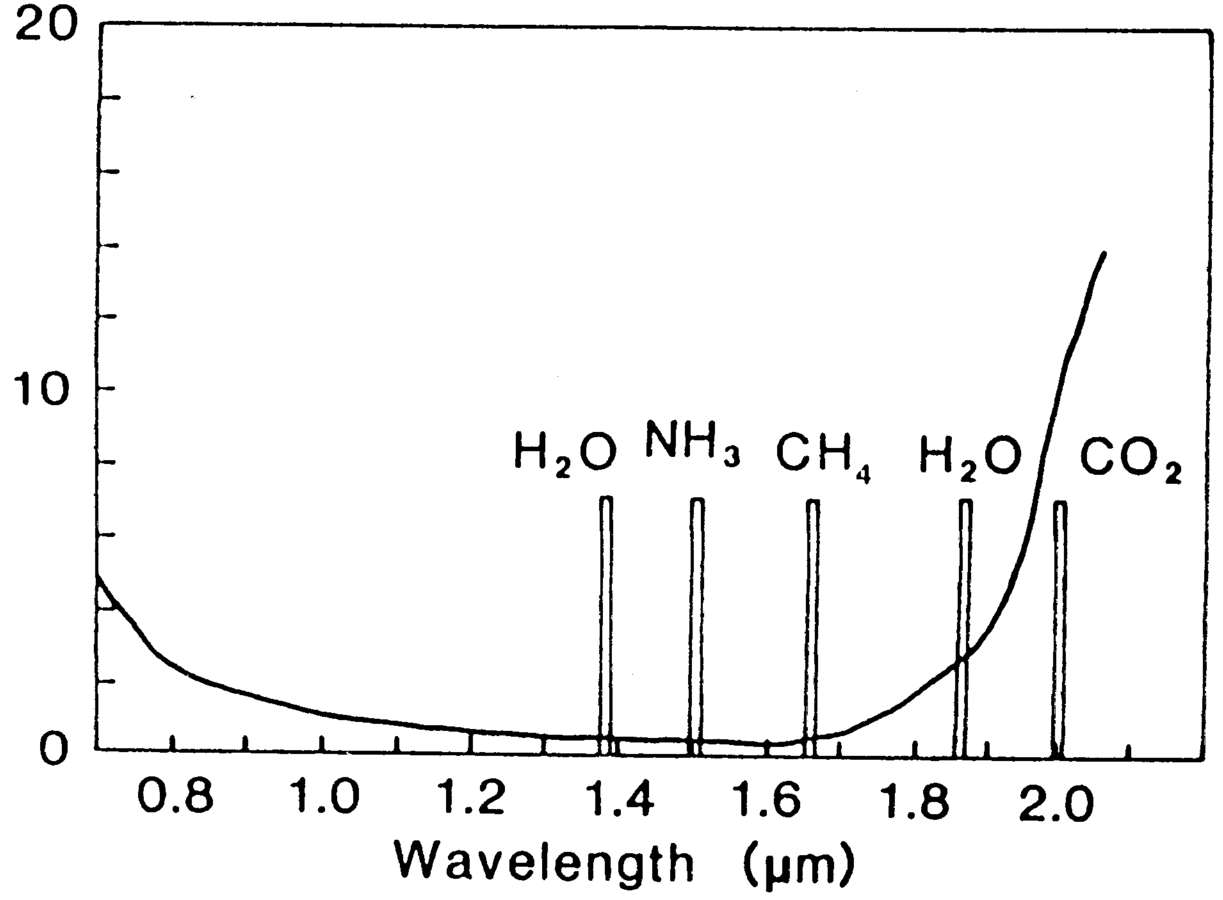

Figure 1 : Absorption bands of some common gases within the transmission window for silica fibre

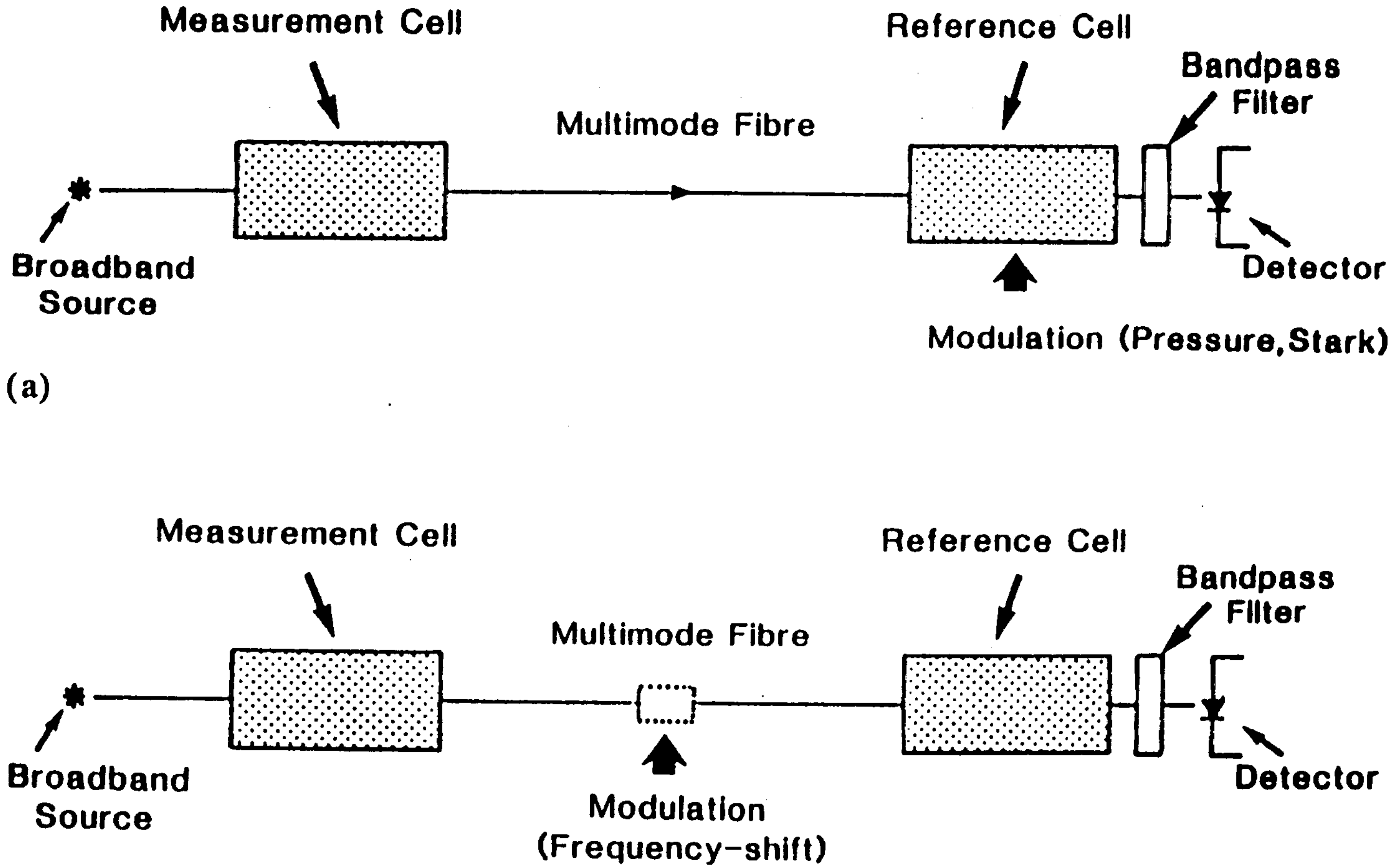

Figure 2 : Schematic diagram for the correlation spectroscopy scheme, (a) pressure and Stark modulation, and (b) angle modulation

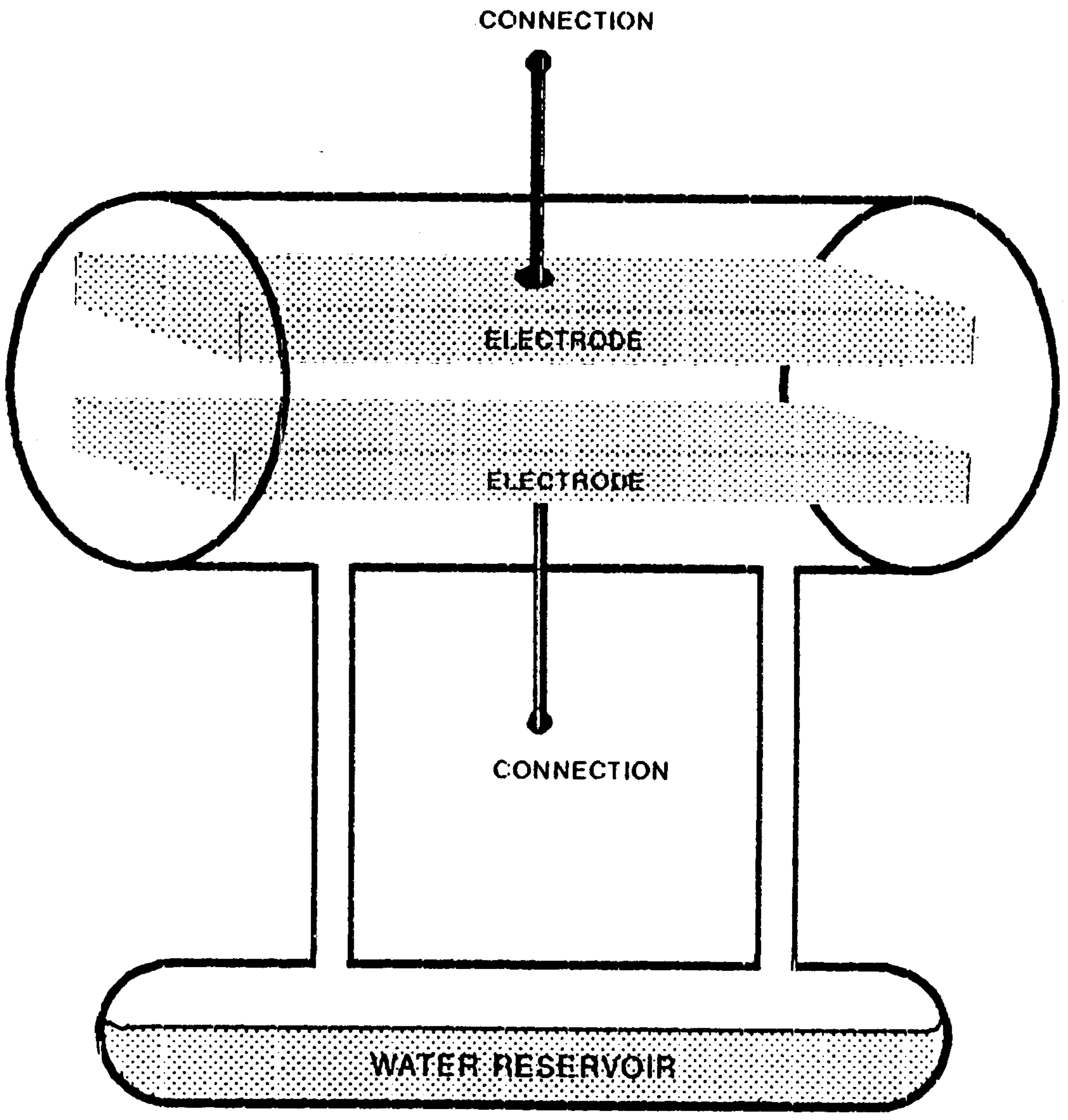

Figure 3 : Schematic of experimental Stark cell for applying electric field to a water vapour sample. (Upper cell is heated above temperature of lower cell to avoid condensation)

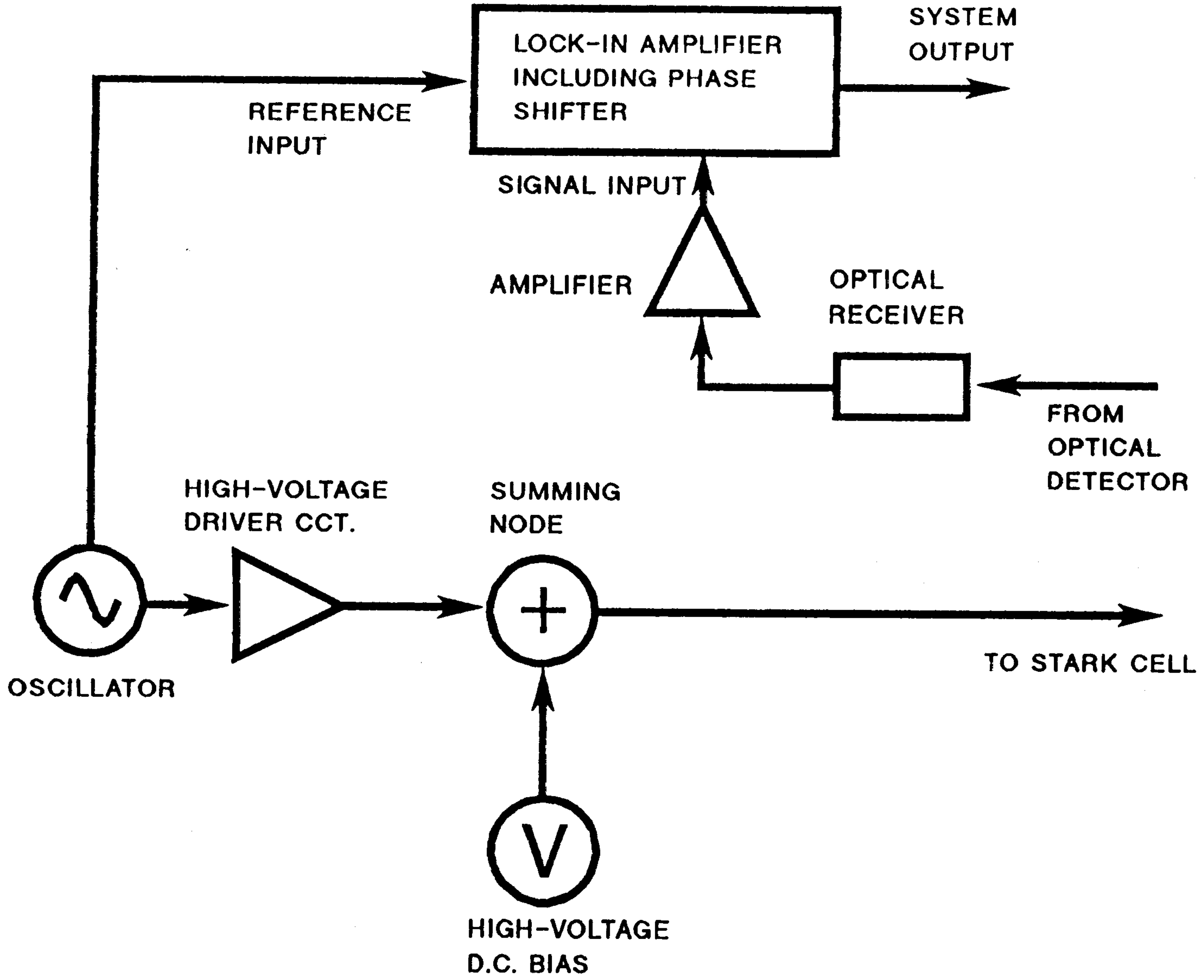

Figure 4 : Functional block diagram of electronic system for driving a Stark cell and detecting the modulation signal from the transmitted light.

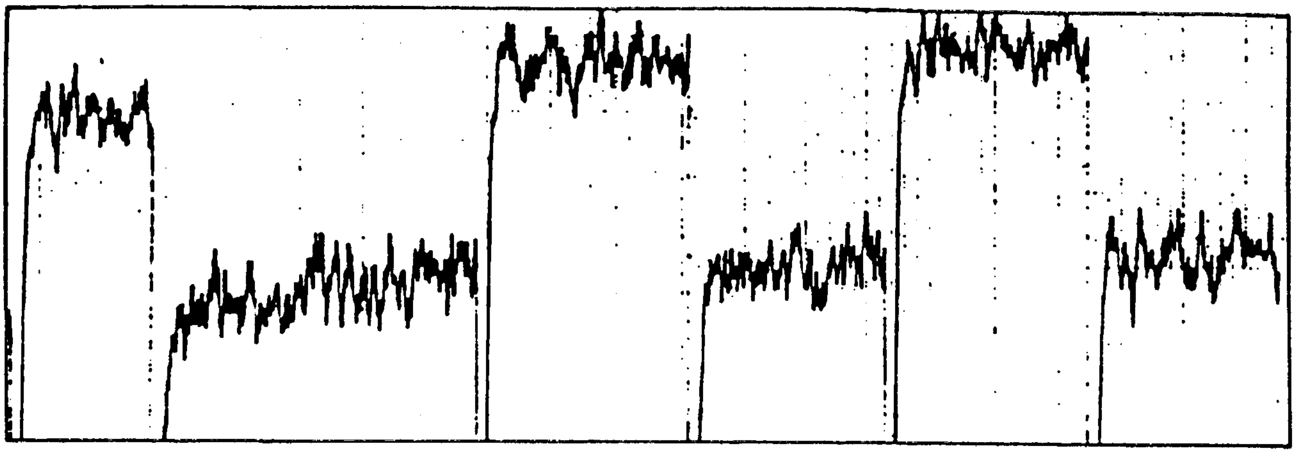

Figure 5(a) : Detected signal transmitted through the Stark Cell after phase-sensitive detection with the arrangement of Figure 4. The curve shows the signal change when the light beam is periodically blocked by a shutter. This modulation is only observable in the main H_2O absorption bands at 1.4 µm and 1.9 µm.

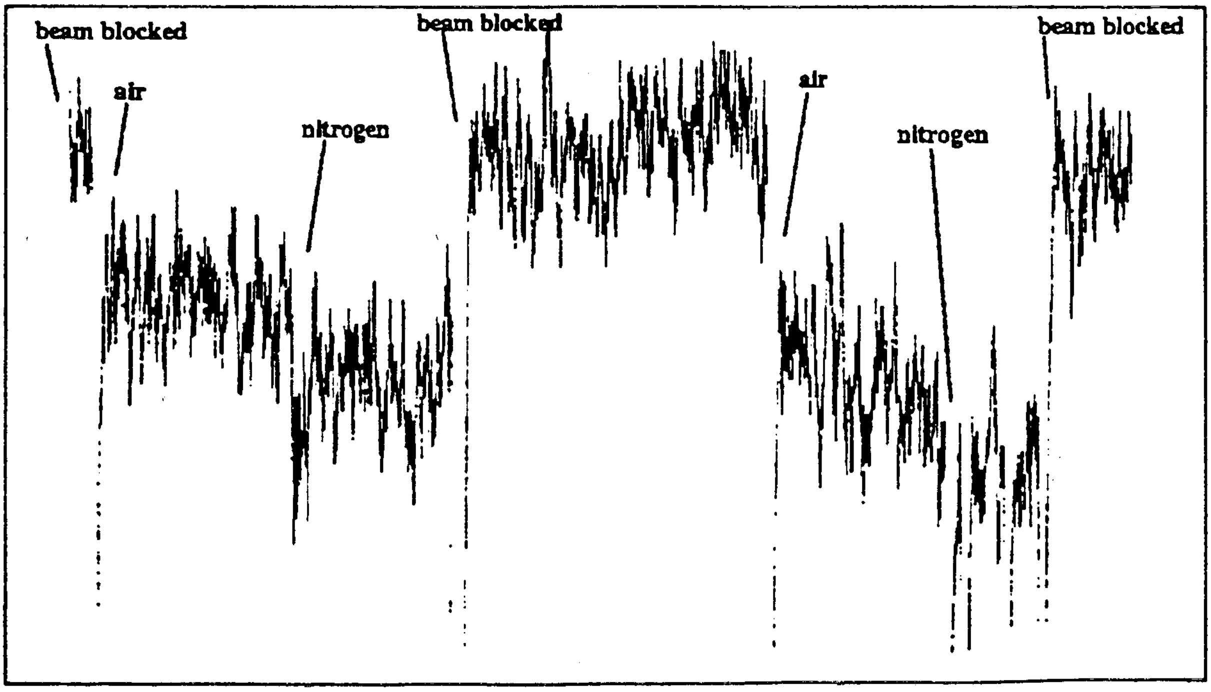

Figure 5(b) : Signal change due to H_2O absorption in the measurement cell. The cell was alternatively filled with air (containing 12 mbar H_2O-vapour) and dry nitrogen. After each cycle, the beam from the tungsten halogen source was blocked.

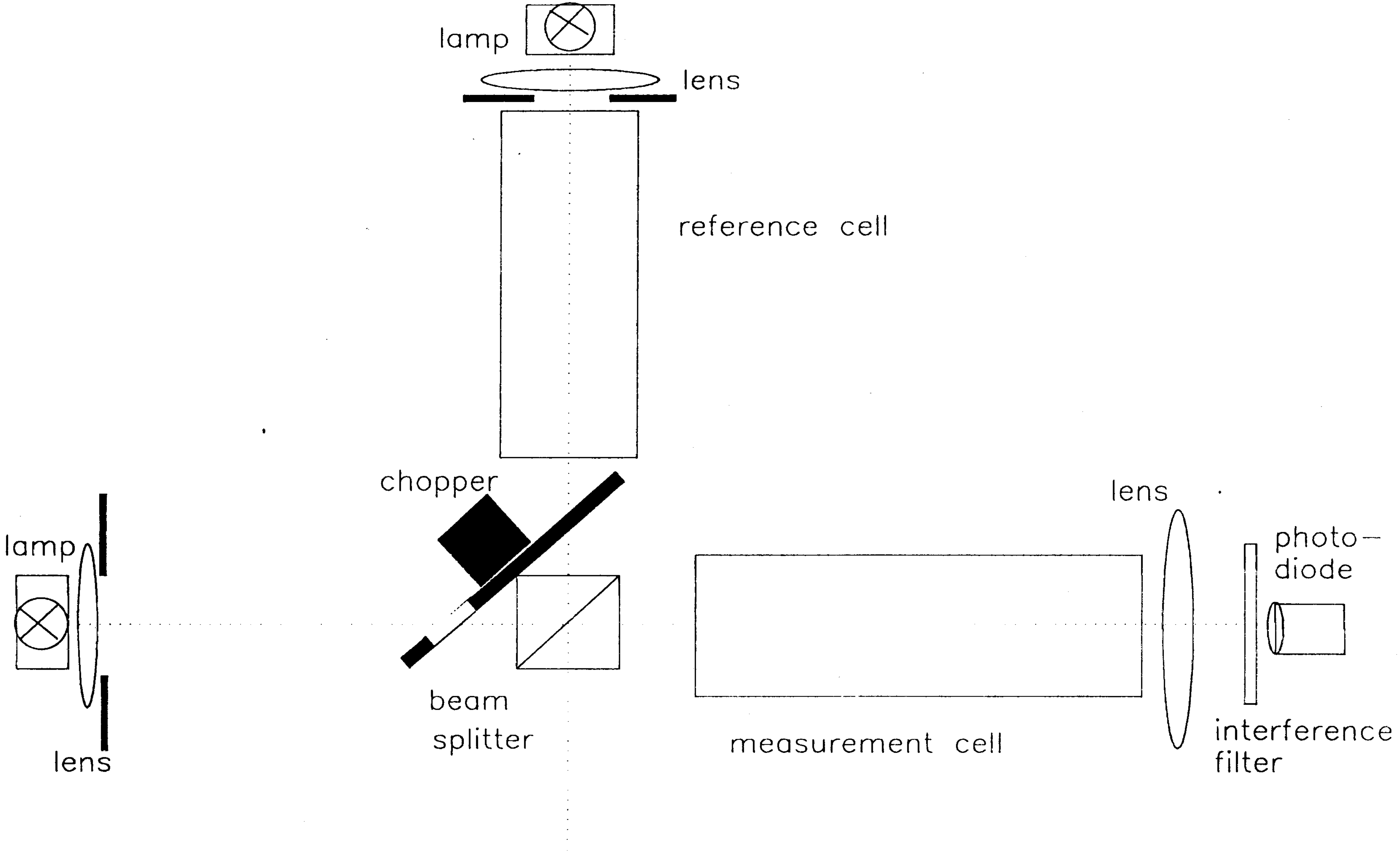
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Fig. 6

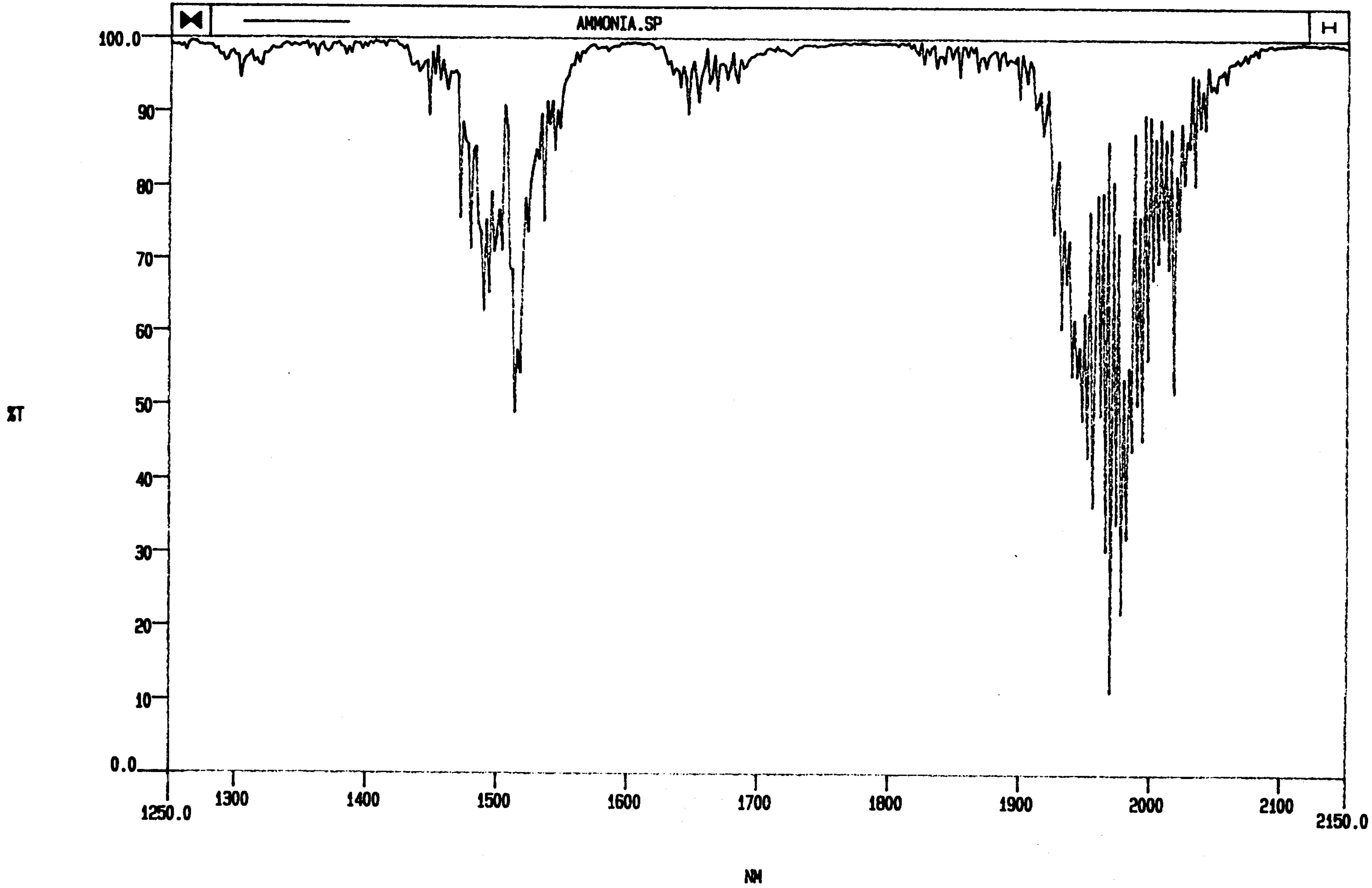
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Fig 7

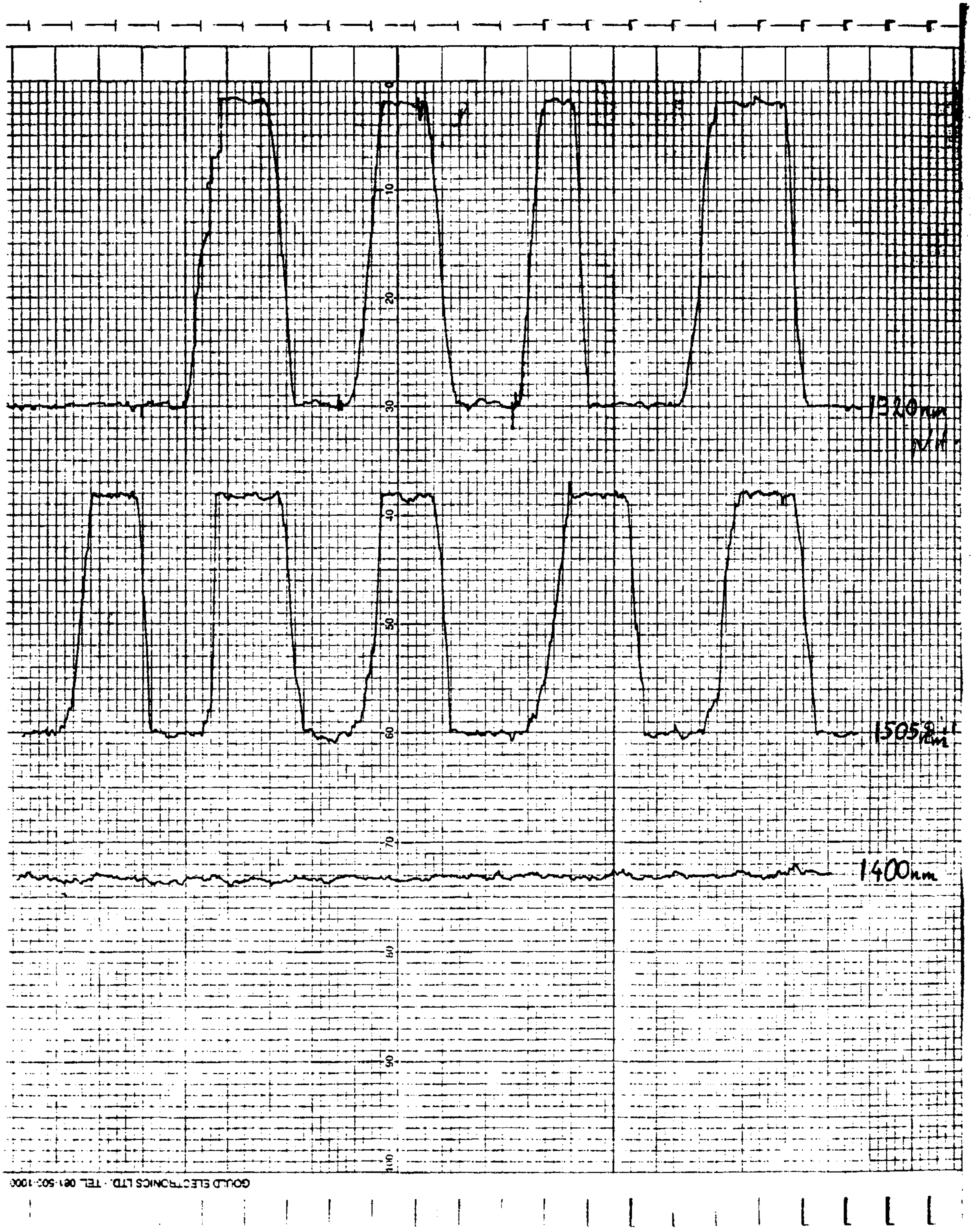
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Fig. 8