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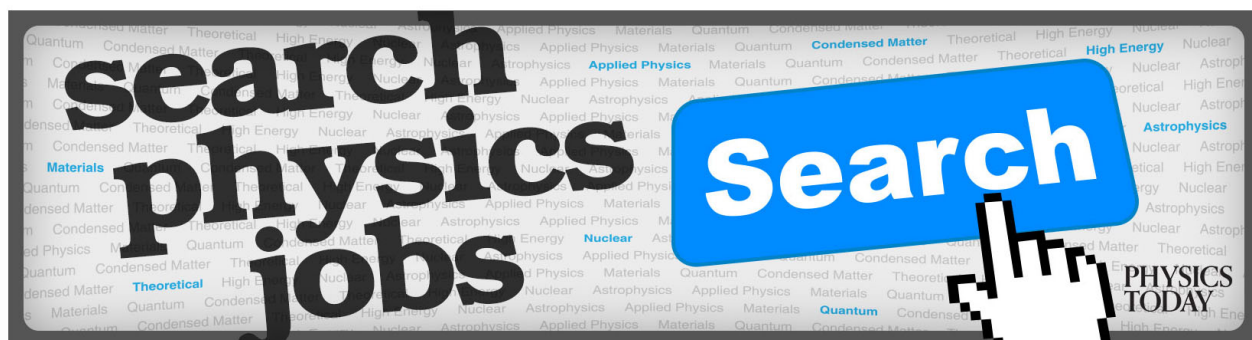
A microwave spectrometer with a frequency control system employing a frequency "scanning window" locked to the rotational absorption peak

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This article reports a microwave spectrometer with a novel technique of locking a frequency "scanning window" $[F_1, F_3]$ in the radiation source to a microwave rotational absorption peak. The center (F_2) of the scanning window is initially locked to the resonant frequency (F_r) of a tunable resonant cavity so that the center of the scanning window may be tuned by changing the resonant frequency of the cavity. Microwaves are then input to a nonresonant gas cell containing the analyte gas at low pressures and by means of Stark modulation the lower sideband (F_1, F_2) and upper sideband (F_2, F_3) of the scanning window are amplitude modulated at different phases. After demodulation of the two sidebands, an error signal is derived through addition of the two demodulated signals (being zero when the scanning window exactly overlaps with the absorption peak) and this is used to lock the resonant frequency (F_r) of the tunable cavity (and thus the center (F_2) of the scanning window) to the center (F_0) of the absorption peak of the analyte gas. For quantitative measurement, a signal is derived through subtraction of the two demodulated signals (being maximum when the center of the scanning window is approximately at the center of the absorption peak). This spectrometer system has been used to measure ethylene oxide gas (absorption line 23.123 GHz) at concentrations up to 100% and water vapor (absorption line 22.235 GHz) at concentrations from $-40\,°C$ dewpoint (127 ppm) to $50\,°C$ dewpoint (138,736 ppm). The detect limit of the spectrometer has been tested and found to be approximately 3×10^{-9} cm^{-1} (signal-to-noise ratio equal to 2). © *1995 American Institute of Physics.*

I. BACKGROUND

Microwave spectra of analyte gases at low pressures (of the order of 10^{-2} to 1 mbar) are characterized by very narrow bandwidth absorption lines which necessitates an accurate frequency control system for stabilizing or measuring the microwave source frequency in a microwave spectrometer. Various frequency control systems have been employed in the past. In the Hewlett Packard 8460A Analytical spectrometer,[1] the microwave radiation source, a backward wave oscillator (BWO), with a frequency range 8.0–40.0 GHz was stabilized by phase locking it to a harmonic of a 400–420 MHz reference oscillator. However, given that the radiation source frequency was phase locked to the reference oscillator, the process of scanning across an absorption peak for quantitative analysis of the analyte gas was time consuming. Also, the means of phase locking the source frequency to a reference oscillator (based on frequency synthesis) was overly complicated in design and costly. In the Cambridge Scientific spectrometer,[1,2] a frequency marker system with a free sweeping BWO was used. The fundamental frequency standard was a crystal controlled 1 MHz oscillator which was phase locked to 1 MHz, 10 MHz, 100 MHz, and 1 GHz local oscillators. These local oscillators acted as frequency references in a series of frequency marking stages and were compared with the source frequency, giving an appropriate marker (measurement) at each stage. For quantitative analysis of the analyte gas, in order to measure the line area the BWO was set to scan between two frequencies containing the absorption peak of the analyte gas and the source frequency was monitored by the frequency marker system. As

with the Hewlett Packard system, the process of measuring the line area was time consuming and the means of phase locking the crystal reference oscillator to various local oscillators was again complicated in design and costly.

Some designs employing a resonant cavity gas cell seek to lock the source frequency to the resonant frequency of the gas cell by coupling a Gunn oscillator to a high Q cavity through a coupling iris.[3–5] The Gunn oscillator itself operates as a low Q resonant circuit to excite the microwave radiation at a frequency near one of the absorption lines of the analyte gas. The resonant frequency of the high Q cavity gas cell is tuned until its resonant frequency equals that of the Gunn oscillator. The output frequency of the Gunn oscillator is then locked to the high Q resonant frequency and can be tuned by changing the resonant frequency of the cavity gas cell. In the design by Uehara *et al.*[4] used to monitor ammonia, the resonant frequency of the cavity gas cell was fixed slightly above the natural center of the absorption peak of the analyte gas and the Stark electrode was provided with a 100 kHz sinusoidal modulation voltage and a dc sweep voltage. By sweeping the dc voltage,[6,7] the center of the absorption peak was "shifted."[8] A derivative signal extracted from the 100 kHz Stark modulation[8] was initially recorded in order to search for the "shifted center" of the absorption peak on the voltage scale, i.e., the zero crossing point of the derivative signal. For quantitative analysis, the dc sweep voltage was held at a fixed voltage which gives a maximum value of the derivative signal. However, the shifted center of the absorption peak is actually the result of superimposition of several Stark components resulting from different energy levels associated with the M quantum number $M = 0, \pm 1, \pm 2, ...,$

±J, where J is the J quantum number.[8] Since the linewidth of each Stark component varies widely with many factors such as pressure, the composition of the gas mixture,[8,9] the shifted center is in principle not unique for a given Stark dc electric field. Since there was no feedback control loop to monitor the shifted center in this case, the quantitative measurement was liable to be affected by many factors dependent upon the shifted center. In the design by Thirup et al.,[5] instead of having a dc sweeping voltage, a pure sinusoidal Stark voltage of modulation frequency $f=4.5$ kHz was applied to the cavity gas cell. Output of the second harmonic of the modulation frequency (which has a zero value approximately at the center of the absorption peak) was used in a control loop to alter the dimensions of the cavity so that the resonant frequency of the cavity (thus the source frequency) was locked approximately to the center of the absorption peak of the analyte gas. For quantitative analysis of the analyte gas, the fourth harmonic, which reaches a maximum approximately at the center of the absorption peak, was amplified and detected. However, a slight variation in the linewidth may result in a huge change in the fourth harmonic as it is approximately proportional to $1/\delta F^3$, where δF is the half linewidth of the absorption peak. Since δF varies with pressure and the composition of the gas which may fluctuate during measurement, this factor may upset the stability of the measurement.

We have reported a cavity spectrometer earlier.[10] In that system, since there was no feedback control loop for controlling the resonant frequency of the cavity, it was necessary to scan regularly the resonant frequency of the cavity across the absorption peak by means of altering one of dimensions of the cavity in order to search for the center of the absorption peak. That was also a time consuming process.

II. THE SCANNING WINDOW METHOD

This article reports a novel frequency control system employed in an analytical microwave spectrometer which has different features from the systems mentioned above. In this microwave spectrometer system, referring to Figs. 1 and 2, a scanning window (F_1, F_3) in the microwave source frequency is preset at a width of approximately full linewidth of one of the absorption lines of the analyte gas, e.g., for ethylene oxide gas (absorption line 23.123 GHz) the scanning window is preset to approximately 4 MHz and for water vapor (absorption line 22.235 GHz) to approximately 1 MHz. This is achieved in each case by applying a sweeping signal (of frequency $f_1=38$ kHz) to the voltage controlled frequency terminal of a varactor-tuned Gunn diode oscillator (GDO), see Fig. 2(c). The center (F_2) of the scanning window [see Fig. 2(a)] is initially locked to the resonant frequency (F_r) of a tunable resonant cavity [see Fig. 2(b)] (which operates as a microwave band pass filter, BPF) through a feedback control loop (FCL) (see next section), so that the center of the scanning window may be tuned by changing the resonant frequency of the cavity. The BPF converts the scanning window into a resonant peak with the center at $F_2=F_r$. The microwaves are then input into a nonresonant gas cell where a Stark modulation of frequency of 3.9 kHz is applied (see Fig. 1). Having passed through the
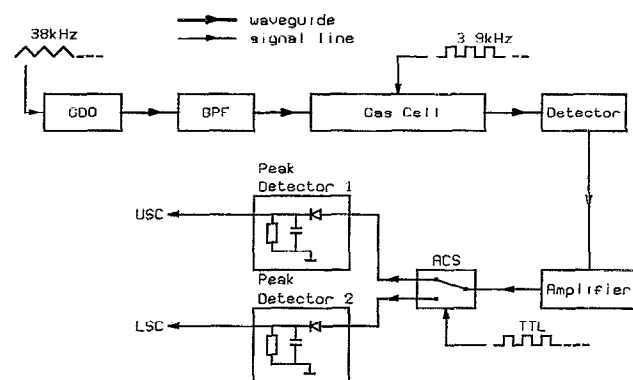

FIG. 1. Schematic diagram of the frequency locking system employing a "scanning window" (Keys: GDO—Gunn diode oscillator, BPF—band pass filter, ACS—analog changeover switch, USC—upper sideband carrier, LSC—lower sideband carrier).

Stark gas cell, the microwaves are detected by a power detector (Det). The resonant frequency (F_r) of the cavity divides the source frequency scanning window into two bands, lower sideband (F_1, F_2) and upper sideband (F_2, F_3). These are then input to the analyte gas and by means of Stark modulation they are amplitude modulated at different phases. There exists a position where as the scanning window overlaps with the absorption peak, the scanning window center is approximately at the center of the absorption peak of the analyte gas and at this position the two sidebands are amplitude modulated at exactly opposite phases. In order to extract separately the AM signal carried by the two sidebands, an analog changeover switch (ACS) and two peak detectors (PDs) are used to separate the AM sidebands, see Fig. 1. As the scanning signal is swept back and forth [see Fig. 2(c)], the frequency-domain scanning window is transformed into a time-domain signal, as shown in Fig. 2(d), and the detected signal consists of sequential peaks, each peak being a mirror image of its adjacent one. These peaks are separated by the ACS, as shown in Figs. 2(e) and 2(f). Each PD (which has
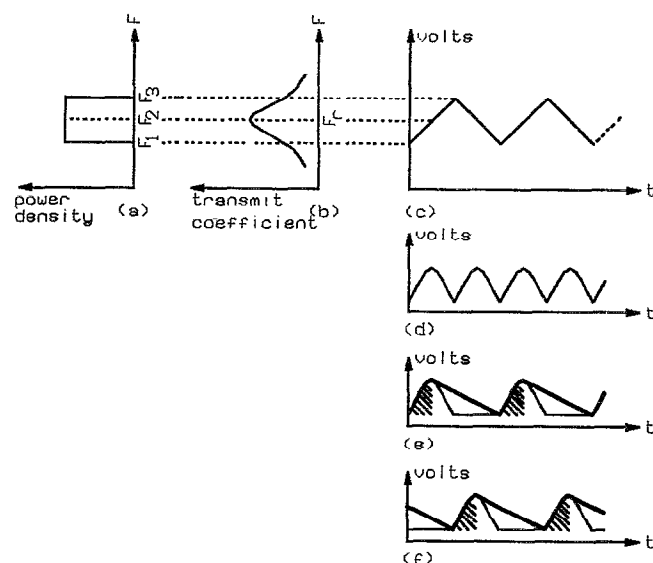

FIG. 2. Separation of the lower sideband carrier signal (LSC) and upper sideband carrier signal (USC).
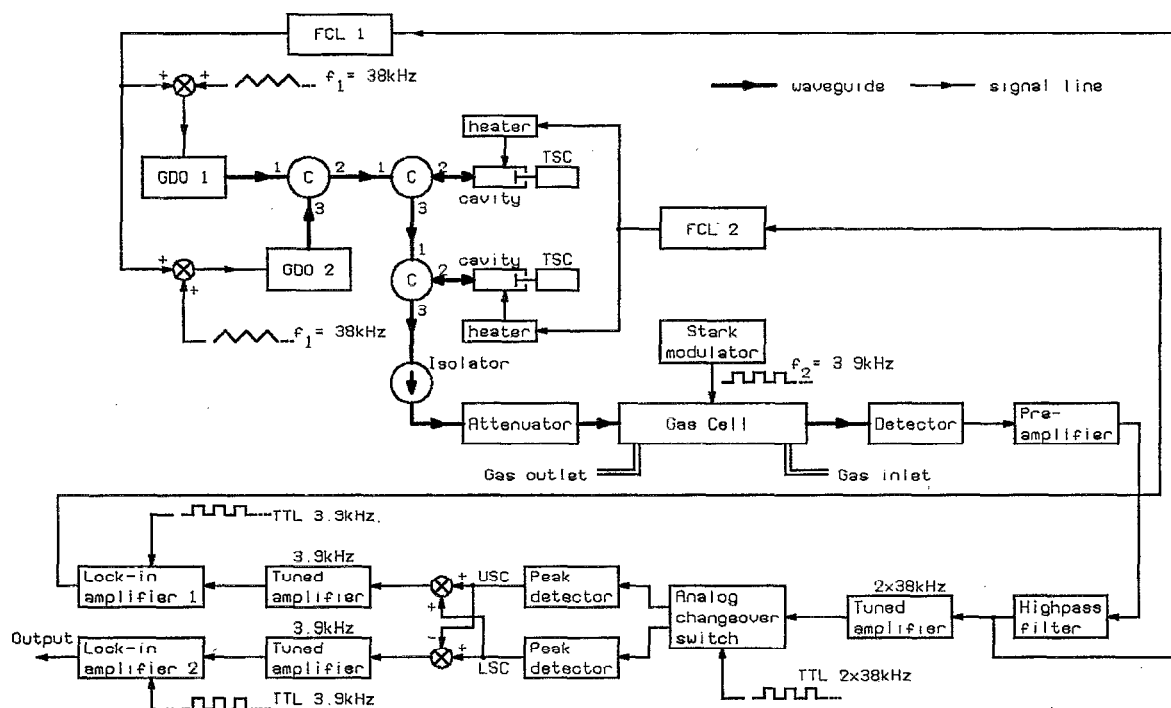
FIG. 3. Schematic diagram of the spectrometer system (Keys: GDO—Gunn diode oscillator, C—circulator, FCL—feedback control loop, USC—upper sideband carrier, LSC—lower sideband carrier).

the sort of output waveform as shown by bold lines in Figs. 2(e) and (f), allows part of the signal contained within the shadow areas to pass through so that peak detector 1 responds only to the lower sideband carrier signal (LSC), while peak detector 2 responds only to the upper sideband carrier signal (USC). An error signal is derived through addition of LSC and USC (being zero when the scanning window exactly overlaps with the absorption peak) and this is used in an FCL (see next section) to lock the resonant frequency (F_r) of the tunable cavity (BPF) [and thus the center (F_2) of the scanning window] to the center (F_0) of the absorption peak of the analyte gas. For quantitative measurement, a signal is derived through subtraction of LSC and USC (being maximum when the center of the scanning window is approximately at the center of the absorption peak). The numerical value of this signal is approximately proportional to the absolute value of the definite integral from F_1 to F_3 of the resultant Stark modulation signal.

This spectrometer system is particularly suited for quantitative measurement of the analyte gas since the salient information about the degree of microwave absorption inherent in the absorption peak (the half linewidth of which is contained within the scanning window of frequency range, F_1 to F_3) can be extracted simultaneously. This could not be achieved by the Hewlett Packard and Cambridge spectrometer systems where a very slow process had to be engaged to scan through the absorption peak. In the spectrometer reported here, the measurement takes place while the source frequency is swept back and forth in the frequency range of the absorption peak at a frequency of 38 kHz (rather than fixing the radiation frequency as was the case in the cavity spectrometer systems mentioned above) and is thus much less susceptible to the phase noise from the radiation source

since it has a power spectrum characteristic of $1/f$, where f is the scanning frequency.[11]

Also, for a relatively low magnitude of Stark voltage, the resultant modulation signal may, as a first approximation, be considered as the first order differential of the absorption peak. The numerical value of the output signal of the spectrometer system is then approximately proportional to the absolute value of the definite integral from F_1 to F_3 of the first order differential of the absorption peak, and is thus proportional to the height of the absorption peak, α_{max}, which in turn is proportional to the number of molecules per unit volume of the analyte gas.[2] α_{max} is also proportional to $1/\delta F$ and the output signal of spectrometer system reported here is thus much less susceptible to the variation in δF as is opposed to the design by Thirup et al.[5] where the output of the fourth harmonic of Stark modulation was proportional to $1/\delta F^3$.

III. SPECTROMETER SYSTEM

A schematic diagram of the spectrometer system which has been used to measure ethylene oxide and water vapor is shown in Fig. 3.

(1) *Microwave Route*: A GDO generates microwave radiation and its frequency is tuned by means of a voltage applied to the control terminal of a built-in varactor. However, the tuning range of a varactor-tuned GDO currently commercially available is limited to the order of tens of MHz in K band. In order to measure absorption peaks of water vapor at 22.235 GHz and ethylene oxide at 23.123 GHz, two GDOs (MA87828-3,4 MACOM USA) are used, preset at approximately 22.235 and 23.123 GHz, respectively. The electrical voltage (6 V) is applied to the GDOs through a change-over

switch such that one is powered on while other is off. The microwaves are fed into the system through a circulator (C) which routes microwaves from port 1 to 2 while GDO1 is on and routes microwaves from port 3 to 1 then to 2 while GDO2 is on. In the latter case, GDO1 is off and acts as a short circuit which reflects microwaves back to the circulator without loss. The microwaves are then transmitted into and reflected back from two cavities via two respective circulators. The resonant frequency of each cavity can be varied by altering the position of the tunable short circuits (TSCs) situated at one end of the cavity. Once tuned, i.e., at approximately 22.235 GHz for water vapor and 23.123 GHz for ethylene oxide, each cavity resonant frequency is locked mechanically. Fine tuning of the cavities is carried out by altering the temperature of the cavities thus the dimensions of the cavities and in turn the resonant frequencies. This is achieved by applying electrical power to heating wires wrapped around the cavities. The cavities will only absorb microwaves of frequencies near their resonant frequencies and thus produce peaks at their resonant frequencies. Having passed through the cavities, the microwaves are fed into the gas cell (made of a 50 cm WG 20 waveguide, incorporating a stainless steel electrode) via an isolator and an attenuator (Att) and detected by a crystal detector (Det).

(2) *Modulation Signal Treatment*: The manner in which we treat various modulation signals in this system is taken from our previous work.[12] The microwave source (GDO) is frequency modulated by means of the varactor such that the microwave frequency F is swept at a relatively high frequency $f_1 = 38$ kHz around a cavity resonant frequency F_r (which is contained within a half linewidth of the absorption peak of the analyte gas), such that the microwaves are amplitude modulated by the resonant peak of the cavity. Upon leaving the cavity, the microwaves are fed into the gas cell. At the same time, an additional modulation of relatively low frequency $f_2 = 3.9$ kHz (Stark modulation) is applied in the gas cell. This is achieved by applying a 0–150 V square wave voltage to the electrode situated in the middle of the gas cell. Subsequently, the microwaves are fed into the crystal detector, where the complex microwave signal is converted into an electrical signal comprising relatively low-frequency components (around $f_2 = 3.9$ kHz) and relatively high-frequency components [around $2 \times f_1 = 76$ kHz, see Fig. 2(d)]. It is the relatively high-frequency components, i.e., those resulting from the application of the sweeping modulation signal [see Figs. 2(c) and 2(d)] that are of interest, therefore, after a high pass filter and a preamplifier, a tuned amplifier of $2 \times f_1 = 76$ kHz is employed to extract them, i.e., those sequential peaks as shown in Fig. 2(d). Those peaks are separated by the analog changeover switch, resulting in two sets of sequential peaks of frequency around $f_1 = 38$ kHz [see Figs. 2(e) and 2(f)]. A Fourier analysis of those signals shows that those signals consist of the following components:[12] f_1, $f_1 \pm f_2$, $f_1 \pm 2f_2$, ..., and so on. Only frequency components $f_1 \pm f_2$ are of interest. The peak detectors are used not only to separate lower sideband and upper sideband of the frequency scanning window but also to operate as a simple demodulator[13] which translates the complex signal of components $f_1 \pm f_2$ downwards to frequency com-
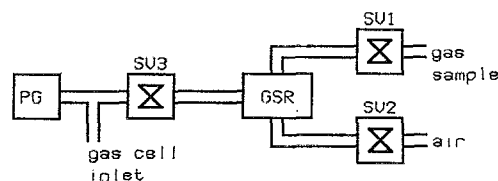

FIG. 4. Gas sampling system (Keys: SVs—solenoid valves, PG—Pirani gauge, GSR—gas sample reservoir).

ponents around f_2, the amplitude of which is proportional to the amplitude modulation of the absorption peak. Therefore, two respective tuned amplifiers of frequency $f_2 = 3.9$ kHz are used to extract the frequency component f_2 contained in the signals of (LSC+USC) and (LSC-USC), and demodulated by two respective lock-in amplifiers.

(3) *Feedback Control Loops (FCLs)*: In order to lock the center of the source frequency scanning window to the resonant frequency of the cavity and then also to the center of the absorption peak of the analyte gas, a double FCL system is employed. Referring to Figs. 2(a)–2(d), as the source frequency is swept across the resonant frequency of the cavity, the microwaves are amplitude modulated and sequential mirror peaks are produced as shown in Fig. 2(d). If the center of the source frequency scanning window is equal to the resonant frequency of the cavity, i.e., $F_2 = F_r$, then there will be no relative phase shift between the mirror peaks. However, if $F_2 > F_r$ or $F_2 < F_r$, then there will be relative phase shifts between the mirror peaks but in different directions. This phase error signal is detected and used in the FCL1 to lock F_2 to F_r. As mentioned in Sec. II, an error signal can be obtained through addition of the LSC and USC if F_2 deviates from the center of absorption peak. This signal is obtained from a lock-in amplifier (see Fig. 3), and is used in the FCL2 to lock F_2 to F_0 by adjusting the electric current applied to the heaters surrounding the cavities.

(4) *Gas Sampling System*: The spectrometer system described above was packed into an instrument case in conjunction with a gas sampling device consisting of three solenoid valves (SVs) and a gas sample reservoir (GSR), as shown in Fig. 4. The inlet pressure of the gas cell was monitored by a Pirani gauge (PG). The operation of the gas sampling device was as follows: (1) with SV1 closed and SV2 and SV3 opened, the GSR and the gas cell are flushed by air through the vacuum pump; in fact this stage of the sample cycle is done in a "pulsed" manner by periodically closing and opening SV2. (2) SV1 and SV2 are then closed and SV3 is opened until the GSR pressure is approximately below 1 mbar. (3) SV3 is closed and SV1 opened to admit sample to the GSR; SV1 is then closed isolating the sample. (4) SV3 is opened and measurement of the gas concentrations takes place at pressure of 0.3 mbar for ethylene oxide (absorption line at 23.123 GHz) and 0.08 mbar for water vapor (absorption line at 22.235 GHz).

IV. EXPERIMENTAL PROCEDURE AND RESULTS

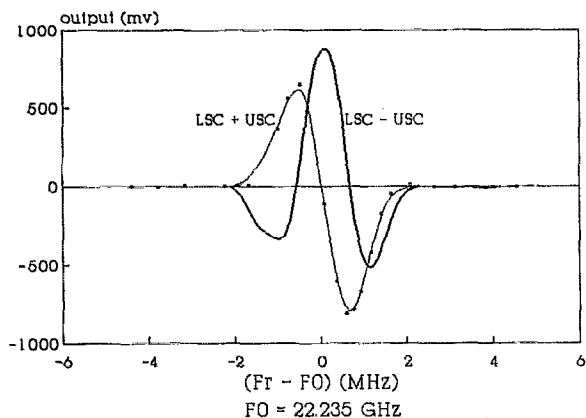Measurements were initially carried out on the spectrometer system described above to monitor the demodula-

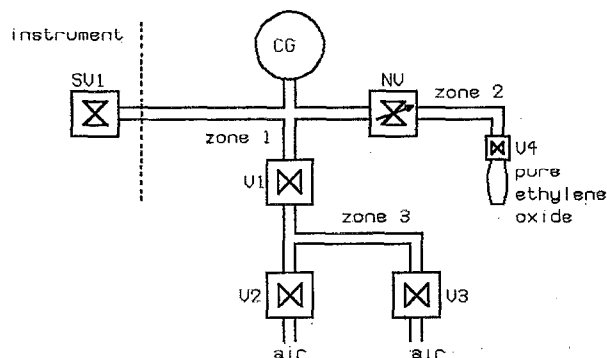FIG. 5. Demodulation signals of the Stark modulated (LSC+USC) and (LSC-USC).

FIG. 6. Ancillary equipment for calibration of the spectrometer with ethylene oxide (EO) (Keys: Vs—isolation valves, SV—solenoid valve, NV—needle valve, CG—capsule gauge).

tion signals of the Stark modulated (LSC+USC) and (LSC−USC), i.e., the outputs of the two lock-in amplifiers (see Fig. 3), while the FCL2 is open (disconnected). The microwave power incident to the gas cell was set approximately 1 mW and the time constants of the two lock-in amplifiers were set to 2.2 s. The gas cell was filled with ambient air containing approximately 7000 ppm water vapor to a pressure of approximately 0.08 mbar by means of a vacuum pump connected to the cell outlet and a needle valve connected to the cell inlet. The resonant frequency of one of the cavities, F_r, hence the center of the source frequency scanning window, F_2, was stepped across the water vapor absorption line at $F_0 = 22.235$ GHz by means of the tunable short circuit (TSC). The outputs of the two lock-in amplifiers were recorded as shown in Fig. 5 with respect to the resonant frequency of the cavity, F_r, hence the center of the source frequency scanning window, F_2. Figure 5 shows that the output of lock-in amplifier 1, i.e., the demodulation signal of the Stark modulated (LSC+USC), has positive values at $F_r = F_2 < F_0$, negative values at $F_0 < F_r = F_2$ and zero value at approximately $F_r = F_2 = F_0$ and the output of lock-in amplifier 2, i.e., the demodulation signal of the Stark modulated (LSC−USC), reaches a maximum at approximately $F_r = F_2 = F_0$. Thereafter, the FCL2 was closed (connected) and the output of lock-in amplifier 1 (the time constant of which was then set to 0.1 s) was used to lock F_r hence F_2 to F_0 while the output of lock-in amplifier 2 was used for quantitative measurements.

For calibration of the instrument with ethylene oxide, ancillary equipment, as shown in Fig. 6, was used. In order to avoid a gas dead zone between SV1 on the instrument side and the pure ethylene oxide gas cylinder, with SV1 and the needle valve (NV) opened and isolation valve V1 closed, zone 1 and zone 2 were evacuated until the pressure indicated by the pressure capsule gauge (CG) was below 1 mbar by means of the vacuum pump inside the instrument and then SV1 was closed. With V4 opened, pure ethylene oxide was leaked into zone 1 through the needle valve (NV) until the pressure indicated by CG reached a given value (partial pressure of ethylene oxide) and NV was fully closed. Zone 3 was filled with air at ambient pressure. With V2 and V3 closed and V1 opened, pure ethylene oxide in zone 1 was

mixed with air in zone 3. Given that the volume ratios of zone 1 and zone 3 and the partial pressure of ethylene oxide are known, one can work out the concentration of ethylene oxide in the mixture in terms of ppm (parts per million). Figure 7 gives the calibration curve of the output of lock-in amplifier 2 with respect to the ethylene oxide concentrations.

For calibration of the instrument with water vapor, the sample inlet port of the instrument was connected to a dewpoint generator in the calibration laboratory of Michell Instruments (Cambridge, UK), as schematically shown in Fig. 8. The dry air was produced through a two-stage pretreatment of ambient air by means of compressor and dessicant dryer. The dry air was fed into the water vapor saturator via a water trap to bubble the liquid water in the saturator. The wet flow from the saturator was preset by a needle valve and mixed with the preset dry flow. The temperature of the dewpoint generator was maintained at a given value well above the required dewpoint output. By varying the flow rates, one can obtain various output dewpoints, hence the water concentrations. The device was calibrated in step of 10 °C from −60 to 20 °C tracable to the National Physical Laboratory. For generation of a dewpoint higher than 20 °C, the device was put into an oven where the temperature was raised well above the required dewpoint output and the required dewpoint was obtained by varying the flow rates while monitoring a Michell dewpoint meter connected at the exit of the generator. The instrument did not initially respond to
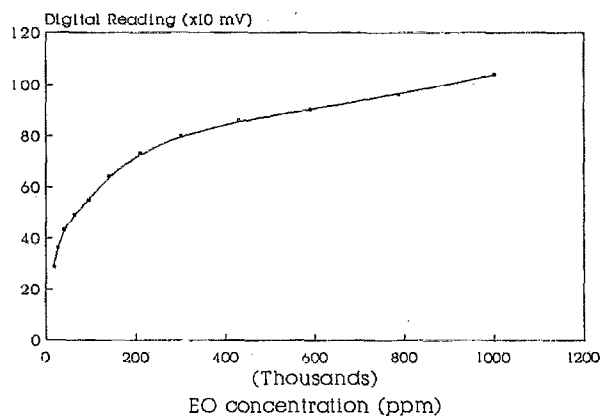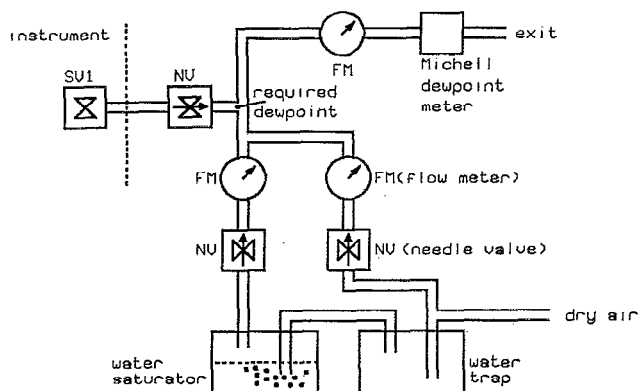

FIG. 7. Calibration curve for EO.

FIG. 8. Dewpoint generator for calibration of the spectrometer with water vapor.

FIG. 9. Calibration curve for water vapor.

changes in water vapor concentration at very low levels of below −40 °C dewpoint (127 ppm) but started to respond from level of −30 °C dewpoint (375 ppm) onwards. Since the gas sampling line in the instrument was trace heated up to 55 °C in order to avoid water condensation, the instrument was calibrated up to 50 °C dewpoint (138,736 ppm). Figure 9 shows the instrument response curve (output of lock-in amplifier 2) with respect to water concentration in the mixture.

As mentioned above, the instrument did not respond at concentrations of water vapor below −40 °C dewpoint (127 ppm) but had a relatively large residual output signal which was presumably due to water vapor adsorption on the surfaces of the gas cell from a previous sample ("gas memory" effect).[8] In order to test the detect limit of the instrument, the gas cell and its associated delivery ducts were heated up to 103 °C in order to reduce the "gas memory" effect and the gain of tuned amplifier 2 (see Fig. 3) was set to maximum. The sample inlet port of the instrument was connected to a compressed air supply line in our own laboratory which contained water vapor of −43.3 °C dewpoint (approximately 80 ppm) measured by a Michell dewpoint hygrometer. The gas sampling mode of the instrument was set such that with SV2 closed and SV3 opened (see Fig. 4), the SV1 was repeatedly pulsed open by applying a 0.1 s pulse voltage control signal to SV1 so that the pressure in the gas cell increased while SV1 was pulsed and then decreased. Each sampling cycle finished when the pressure as indicated by the Pirani gauge
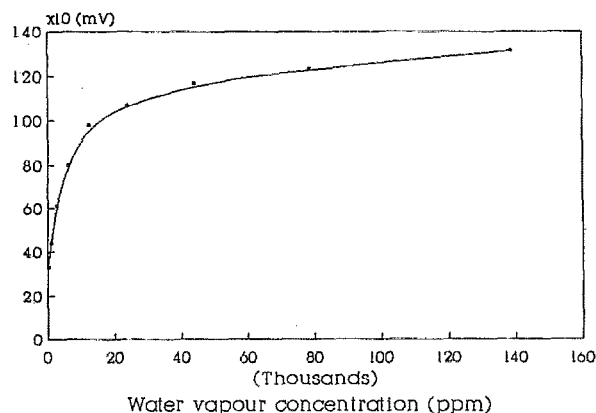
(see Fig. 4) reached approximately 0.1 mbar and at this point measurement took place. Figure 10 shows the real time outputment signal of lock-in amplifier 2 as recorded by a chart recorder. Knowing that the background noise $N \approx 20$ mV [see Fig. 10(a)], the signal $S \approx 350$ mV [see Fig. 10(b)], the water vapor concentration $C \approx 80$ ppm, the absorption coefficient of water vapor[1] $\alpha_{max} \approx 0.7 \times 10^{-5}$ cm^{-1} (at temperature of 103 °C), and the length of the waveguide gas cell $L \approx 50$ cm, the detect limit of the instrument was worked out[8] as (signal-to-noise ratio equal to 2) approximately 3×10^{-9} cm^{-1}, which is of the same order quoted for the Hewlett Packard spectrometer.[1]

V. DISCUSSION

Previous spectrometers have suffered from several disadvantages and limitations. If there is no means for measuring or locking the source frequency then quantitative measurements will be affected by many factors, e.g., pressure and composition of the gas mixture. The means for measuring and locking source frequency previously reported are either adversely affected by phase noise generated from the radiation source or involve frequency control systems which are overly complicated and costly and which result in measurement being time consuming. Also, they rely upon a relatively high value of Stark voltage which gives rise to an undesirable potential for arcing in the measurement cell and
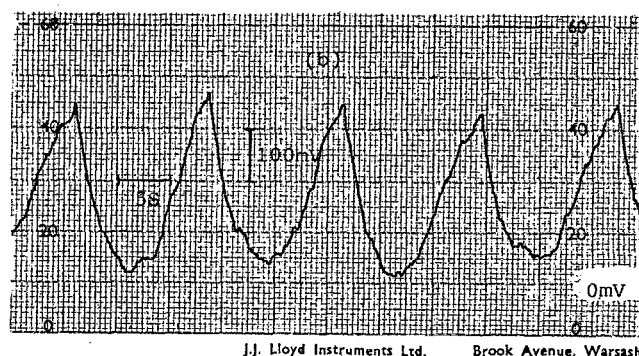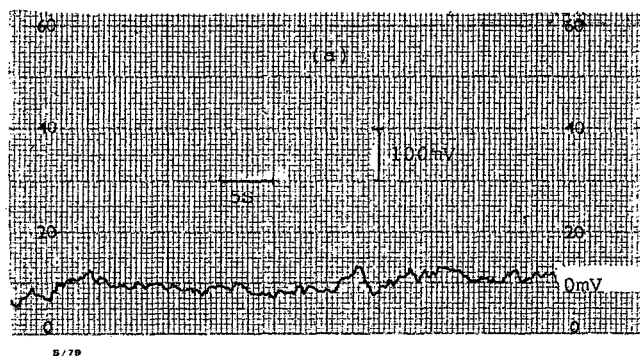

FIG. 10. Real time output signal of lock-in amplifier 2. (a) baseline, (b) signal.

also increases the probability of overlapping of adjacent absorption lines in a multicomponent gas mixture.

The technique reported here above is operated at relatively low Stark voltages obviating these potential adverse effects. It is particularly suited to quantitative measurement of analyte gases since unlike previous techniques where a slow scan through the absorption peak was necessary and resulted in phase noise from the radiation source proportional to $1/f$, in this technique the salient signal is obtained at a scanning frequency of 38 kHz with consequent benefits of reductions in noise and measurement time.

The calibration of the instrument for both ethylene oxide and water vapor was nonlinear (see Figs. 7 and 9). Various factors may contribute to the observed nonlinearity. The microwave power incident to the gas cell was set to approximately 1 mW. This power level was well above the range of power for which the crystal detector response is linear ("square low"[14]). The line-broadening effect due to the fact that the relaxation time of the molecules of the analyte gases is affected by the gas concentrations in a rather complex way[1,8] may, to a large extent, also contribute to the nonlinearity of the spectrometer. Finally, measurements take place while the gas cell is under low pressures (10^{-2}–1 mbar) backed by a mechanical rotary pump. Under such low pressures the pump oil vapor tends to come back to the gas cell to dilute the concentrations of the analyte gas thus affecting the output signal. The process of dilution is nonlinear with respect to gas concentration since the pumping speed is gas dependent[15] and this factor may also contribute to the nonlinearity of the spectrometer.

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