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DETECTION AND MEASUREMENTS OF AIR POLLUTANTS AND CONSTITUENTS BY
MILLIMETER-WAVE MICROWAVE SPECTROSCOPY

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Branko Leskovar and William F. Kolbe*

The properties of millimeter-wave spectrometers as highly specific and sensitive experimental research tools for monitoring gaseous pollutants of interest in pollution research are presented. A spectrometer system operating at frequencies in the vicinity of 70 GHz and employing a semi-confocal Fabry-Perot resonator as the sample cell is described. The resonator is voltage tuned by means of a piezoelectric transducer which enables it to track the microwave source frequency. The operation and performance of the spectrometer are discussed and illustrated by measurements of diluted samples of sulfur dioxide. The noise from the microwave source, the absorption cell and the receiver, which ultimately limits the achievable sensitivity are discussed along with considerations for future sensitivity improvements.

Microwave rotational spectroscopy is a highly specific and sensitive experimental research method for investigating chemical kinetics and also for monitoring gaseous pollutants and other atmospheric constituents in the environment. The technique measures the absorption in the microwave region of the electromagnetic spectrum caused primarily by transitions between pure rotational states of gaseous molecules possessing permanent dipole moments. The physical process leading to absorption is the coupling of the electrical vector of the incident microwave radiation with the permanent dipole moment of the rotating molecule. As a technique for pollution detection microwave rotational spectroscopy offers a number of advantages. At the low pressures normally employed to observe rotational spectra, transition frequencies can usually be measured to a precision of 0.1 MHz or better. At a microwave frequency of 50 GHz, this precision corresponds to a resolution of at least 500,000:1. Thus the measurement of a single line usually suffices to determine the presence of a constituent in a mixture, and the measurement of 2 or 3 lines can make identification fairly certain. In principle, one can construct a single instrument capable of monitoring a number of different pollutants simply by tuning its operating frequency to appropriate values.

An important potential limitation to the performance of such an instrument is the system sensitivity or threshold detection limit. Rotational transitions involve exchanges of considerably smaller energy quanta than do molecular optical or infrared transitions, and population differences between states are smaller. Therefore, at the concentrations normally encountered in pollution studies, the net energy changes which must be detected are small, and fairly sophisticated detection schemes are required. Signal source stabilization and receiver design must be optimized in order to reduce noise contributions to a minimum. Additionally, some form of modulation, such as Stark modulation, followed by frequency selective amplification, phase-sensitive detection, and signal processing is usually necessary.

Previous investigations of this technique for pollutant monitoring have been restricted to the frequency region below 35 GHz.¹⁻³ Our calculations based on the modified Van Vleck-Weisskopf equation⁴ (Appendix) and measurements have shown that larger absorption coefficients and hence greater sensitivity can be obtained in the millimeter wave region above 35 GHz,⁵⁻⁶ with an optimized spectrometer using state-of-the-art components.⁷ As is shown in Figs. 1-6, suitable microwave transitions for sulfur dioxide, sulfur monoxide, nitrogen dioxide, ozone, formaldehyde and carbonyl sulfide are found in this frequency region. Specifically, calculations and measurements of the sulfur dioxide molecule show that the $^{32}\text{S}^{16}\text{O}_2$ transition at 68.9721 GHz, between the 6(1,5) - 6(0,6) levels, has a coefficient peak value of $\gamma_{\text{max}} = 4.5 \times 10^{-4} \text{ cm}^{-1}$. This amount is a factor of ten greater than for any transition between 8 GHz and 40 GHz.⁵ The pattern of absorption frequencies is a sensitive function of the exact structure and isotopic composition of a molecule. As molecules generally have different structural configurations, their rotational spectra offer distinctive information on their existence in a mixture. The list of molecules presented is not intended to be all-inclusive but is representative of some of the more important pollutants and atmospheric constituents. A large number of other molecules (some important to specialized applications) have well known spectra but have not been included.^{4,6} Since our findings indicate that it is advantageous to operate the spectrometer at as high a frequency as possible consistent with the availability of suitable microwave components, the spectrometer described in this report has been designed to operate in the vicinity of 70 GHz.

A block diagram of the spectrometer system is shown in Fig. 7. The system consists of the following major components: a signal oscillator, a local oscillator, a sample absorption cell, and a low-noise superheterodyne receiver.

The signal oscillator consists of a Hughes Model 4162H Gunn diode oscillator followed by a microwave

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isolator and a Spacekom Model DV-1 frequency doubler. With this combination up to approximately 5mW of microwave power is available over a band of frequencies in the vicinity of 70 GHz. Two Gunn diodes each with 1GHz mechanical and 100 MHz electrical (varactor) tuning provide coverage from 68.7 to 70.9 GHz and from 72.1 to 74.3 GHz, which permits the detection of several pollutant species. The Gunn diode is phase locked to the 76th harmonic of a reference signal at about 450 MHz. This signal is being produced by a General Radio Frequency Synthesizer Model 1062. The synthesizer can be swept over any frequency range of interest via a rear panel analog input. The phase locking is accomplished through the use of a Microwave System Model MOS-6/L frequency stabilizer.

The local oscillator signal is derived from an OKI 70V10A klystron immersed in an oil bath. A harmonic mixer and a Dymec DY-2650A stabilizer are used to phase lock the local oscillator to the second harmonic of the Gunn diode oscillator. Since the stabilizer uses a 30 MHz IF amplifier and phase detector, the local oscillator is offset 30 MHz from the signal oscillator. The 30 MHz reference is derived from the synthesizer master oscillator.

A semi-confocal Fabry-Perot transmission cavity is used as the sample absorption cell. Of the several possible configurations which fall under the category of Fabry-Perot resonators, the most attractive for stable, high-Q microwave operation is the semiconfocal geometry. This consists of a flat mirror facing a concave one, spaced as shown in Fig. 8. (The radius of curvature of the concave mirror is approximately twice the mirror spacing.) This geometry has the advantage that it is noncritical in alignment, is compact, and exhibits high Q. Resonances occur according to the relation

$$\frac{4d}{\gamma} = 2q + 1/2, \quad (q = 1, 2, 3, \dots) \quad (1)$$

where d is the mirror spacing, γ is the wave length of the radiation in the cavity, and q is the number of half-standing waves between the mirrors.^{8,9}

The Q of such a cavity is determined by reflection and diffraction losses as well as perturbations of the field structure by the coupling of energy into and out of the resonator. The primary design criterion is to generally minimize all losses. This policy was applied to the design described below, within the limits imposed by other system constraints.

The cavity desired was expected to be part of a working prototype high sensitivity spectrometer which eventually would be packaged as a portable air pollution detector. Therefore, the physical size of the entire spectrometer as well as the cavity size was limited. Mirrors were chosen primarily on the basis of compactness, having 5.08 cm diameters and a spacing of 7.43 cm. The spacing was such that diffraction losses could be assumed negligible compared to reflection losses.

To maximize the stability of the mirror surfaces, type 316 stainless steel 1.25 cm thick was used for the blanks. Optical quality grinding techniques produced surfaces true to a few wave lengths of sodium light on both mirrors. In order to provide high surface conductivity at microwave frequencies, 75 μ of silver was plated onto each mirror, followed by 1.5 μ of gold as a corrosion inhibitor. It was expected that the gold would be essentially transparent to 70 GHz microwave radiation, with the mirror surface exhibiting a conductivity characteristic of pure

silver.

In order to couple energy in and out of the cavity, two small holes were drilled in the surface of the plane mirror, and larger holes were bored from the rear to allow V-band wave guides to be positioned behind the small coupling holes as shown in Fig. 8.¹⁰ The positions of the input and output wave guides were made adjustable with respect to the irises, in order to allow the energy coupling to the cavity to be varied as desired. To minimize microwave losses in the coupling structure, the irises were made as thin as practicable.¹¹ For the value of 0.13 mm thickness chosen, adequate coupling was obtained with a hole diameter of 0.64 mm. The separation between an input and output coupling holes was 6.2 mm. Under these conditions a measured (loaded) Q of 42,000 and a minimum transmission loss of 22 dB were obtained.

The variable transmission loss of the cavity and coupling network is shown in Fig. 9 as a function of the distance (d_2 in Fig. 8) between the output wave

guide and the rear surface of the coupling iris. In obtaining this data, the input guide was positioned for maximum coupling. The quality factor, Q, of the cavity as measured at the output wave guide was nearly constant over the data range of Fig. 9.

The mirrors were mounted in a fixture which allowed their spacing to be adjusted while enclosed in a vacuum chamber. For fine adjustment of spacing, a cylindrical piezoelectric transducer 7.62 cm long and coated with a low vapor pressure epoxy was used as the mount for the concave mirror. The transducer was designed to provide about 10 μ of electrically-controlled tuning as compensation for thermal changes in the cavity and to allow it to track a frequency-swept and/or modulated microwave input. Experimental data demonstrating the slow-speed (thermal compensation) performance of the transducers and also their high-frequency response are shown in Figs. 10 and 11, respectively.

The tuning behavior of the cavity reflects mechanical resonances of the transducer-mirror structure, as expected. With an input voltage extending from about -800V to +800V, the piezoelectric transducer provides in excess of 10 MHz of continuous frequency tuning. This is more than adequate not only to compensate for thermal drifts of the cavity dimensions but also permit a frequency sweep through a gas absorption line. In normal operation the cavity resonant frequency is locked to the signal oscillator so that any frequency changes in the signal oscillator are automatically tracked by the cavity. This is accomplished by means of a feedback loop in which the quadrature component of the microwave receiver phase detector (described below) is amplified and fed back to the piezoelectric transducer. A Kepco Model BOP1000M operational power supply serves as a high voltage amplifier to drive the transducer. For calibration purposes, an unlocked mode is provided in which the cavity is not swept. Operation in this mode permits the receiver phase detectors to be adjusted and the Q of the cavity to be measured.

The low-noise microwave receiver is designed around a TRG Model V9125-2T mixed/preamplifier. According to specifications this unit has a single side band noise figure of 9.0 dB and an RF/IF conversion gain of 25 dB at the operating IF frequency of 30 MHz. The local oscillator power used is +3 dBm. The IF output of the receiver is further amplified by an RHG Inc. Model EST 3010 calibrated linear IF amplifier. After amplification, the signal is sent to two HP10514A phase detectors. The 30 MHz reference frequency from the

synthesizer is passed through a variable phase shifter, split into two components 90° apart in phase, and used to drive the two phase detectors. After an appropriate adjustment of the phase shifter, the two detected signals represent the in-phase and quadrature components of the cavity response function. At resonance the quadrature component is zero and, as described above, is used to control the cavity frequency. The in-phase component of the receiver signal is used to detect the changes in transmitted power thru the cavity resulting from the sample gas absorption.

Signal Detection

At high concentrations of the sample gas, the detected signal change is large enough to be observed directly as described in the next section. At low concentrations, however, it is advantageous to use some form of signal modulation and to employ a phase-sensitive, lock-in amplifier to extract the desired signal from the noise background.¹² As shown in the block diagram, Fig. 7, two different modulation schemes were implemented.

In the source modulation (FM) scheme, the signal oscillator frequency is varied by applying a modulating voltage at 33 Hz to the frequency synthesizer. The modulation rate must be low enough to permit the cavity tracking system to follow it. If the modulation depth is small compared to the absorption linewidth, the resulting signal, after amplification and phase detection, is approximately proportional to the derivative of the gas absorption line shape. The signal-to-noise ratio of the detected absorption can then be improved as desired by introducing a filter of sufficiently long time constant in the phase detector output.

In the second scheme a high voltage square wave at 19 KHz is used to Stark modulate the molecular transition frequency. In order to achieve the large electric field needed for this purpose, the spherical mirror is insulated and moved from the position shown in Fig. 8 to within 1 cm of the flat mirror. With this modification, electric fields of up to 1500 volts/cm can be obtained between the two mirrors. The switching of the Stark field between zero and its maximum value is accomplished by a pair of high voltage vacuum tubes operated sequentially in a pulsed mode. After phase detection and filtering in a lock-in amplifier, the resulting signal consists of an approximate reproduction of the original line shape unshifted in frequency and a series of Stark shifted peaks of the opposite polarity.

A Northern Scientific NS-636 multi-channel analyzer equipped with a signal adaptor is used to store and display the measured data and, if desired, to average a series of repetitive sweeps for further enhancement of the signal-to-noise ratio. A digital to analog converter connected to the analyzer address register is used to produce an analog voltage sweep of the frequency synthesizer over the region of interest. In order to avoid discontinuous frequency changes which would cause the signal oscillator phase lock loop to be broken, a triangular sweep is used.

Cavity Response and Stabilization

The conversion of the microwave signal as it passes through the cavity, the microwave receiver, the I.F. amplifier and the dual phase detectors is linear at each stage of conversion. If we express the equivalent voltage at the input of the cavity as

$$e_i(t) = E_i \cos \omega t \quad (2)$$

where ω is the microwave frequency, then at the output of the cavity we can write

$$e_o(t) = E_i [T_r(\delta) \cos \omega t + T_i(\delta) \sin \omega t] \quad (3)$$

where the cavity voltage transfer function $T(\delta)$ is given by

$$T_r(\delta) = \frac{1}{(Q_1 Q_2)^{1/2}} \cdot \frac{(1/Q_L)}{(1/Q_L)^2 + 4\delta^2} \quad (4a)$$

$$\text{and } T_i(\delta) = \frac{1}{(Q_1 Q_2)^{1/2}} \cdot \frac{2\delta}{(1/Q_L)^2 + 4\delta^2} \quad (4b)$$

In Eq. 4, Q_L is the loaded Q of the cavity, Q_1 , Q_2 are the Q factors associated with the input and output coupling ports of the cavity, and $\delta = (\omega - \omega_0)/\omega_0$ is the fractional frequency deviation of the microwave frequency from its resonant frequency ω_0 . In the microwave receiver the voltage $e_o(t)$ is converted to the IF frequency $\Omega/2\pi = 30$ MHz. If the conversion gain of the receiver and IF amplifier is denoted by K_r then at the input of the phase detectors we have

$$e(t) = K_r E_i [T_r(\delta) \cos \Omega t + T_i(\delta) \sin \Omega t]. \quad (5)$$

In the phase detector the signal $e(t)$ is mixed with the reference signal

$$e_r(t) = e_r \cos(\Omega t + \phi)$$

where ϕ is the phase of the reference. The mixing process is equivalent to a multiplication of the reference and signal to yield the output voltage V_d where, after filtering out components at frequency 2Ω ,

$$V_d = K_d K_r E_i [T_r(\delta) \cos \phi + T_i(\delta) \sin \phi] \quad (6)$$

and $K_d = e_r/2$ is the conversion loss of the phase detector. As described above the two phase detectors are driven by reference voltages 90° apart in phase. If we let the phase of the first detector, $\phi_1 = 0$ and the phase of the second detector, $\phi_2 = 90^\circ$ then we have for the two output voltages V_d and $V_{d'}$,

$$V_d = \frac{K_d K_r E_i}{(Q_1 Q_2)^{1/2}} \cdot \frac{(1/Q_L)}{(1/Q_L)^2 + 4\delta^2} \quad (7)$$

$$V_{d'} = -\frac{K_d K_r E_i}{(Q_1 Q_2)^{1/2}} \cdot \frac{2\delta}{(1/Q_L)^2 + 4\delta^2} \quad (8)$$

As described previously, stabilization and tracking of the microwave frequency by the cavity is accomplished by amplifying $V_{d'}$ and feeding it back to the piezoelectric transducer. Because of the electromechanical components (specifically the mass of the mirror and transducer) in the feedback loop it was necessary to roll off its frequency response with appropriate filters at frequencies above 30 Hz.

Fig. 12 shows the cavity signal V_d produced by sweeping over the frequency range from 68969.4 to 68975.1 GHz and displaying the results in the multi-channel analyzer. Because of the triangular frequency

sweep used, the cavity resonance is displayed twice in the figure. Curve (a) is the baseline produced with zero microwave power. Curve (b) shows the cavity response curve with the stabilization loop turned off, and curve (c) shows the cavity response with the stabilization loop turned on. Curve (d) shows the additional absorption produced by a sample of SO₂ gas with the cavity tracking. This is described in the next section.

Microwave Absorption by Concentrated SO₂

In order to demonstrate the detection of a gas absorption signal, the microwave cavity enclosure was filled with sulfur dioxide (SO₂) gas at a pressure of 0.023 torr. The microwave frequency was adjusted to sweep through the SO₂ 6(1,5)-6(0,6) transition at 68972.1 MHz. As measured previously, the absorption coefficient and linewidth parameter for this transition are $\gamma_{\max} = 4.5 \times 10^{-4} \text{ cm}^{-1}$ and $(\Delta\nu)_1 = 15 \text{ MHz/torr}$.⁵ At the operating pressure of 0.023 torr the expected linewidth (HWHM) is 0.34 MHz. The absorption curve for the transition is shown in Fig. 12, curve (d).

To calculate the magnitude of the absorption, we make use of the fact that the loaded Q_L of the cavity is reduced by the gas at its resonance to the value

$$Q_{Lg} = \frac{2\pi\nu_0 Q_L}{c\gamma_0 Q_L + 2\pi\nu_0} \quad (9)$$

where ν_0 is the transition frequency and c is the velocity of light. Eq. (9) is obtained by attributing to the gas a Q equal to

$$Q_g = 2\pi\nu_0 / c\gamma(\nu).$$

The relative change in the receiver detected voltage V_d (at the cavity resonance peak V_d is proportional to Q_L as in Eq. (7) is given by

$$\frac{\Delta V_d}{V_d} = \frac{V_{dg} - V_d}{V_d} = \frac{Q_{Lg} - Q_L}{Q_L} \quad (10)$$

For small absorption signals Q_g is much larger than Q_L and

$$\frac{\Delta V_d}{V_d} \approx -\frac{c\gamma(\nu)Q_L}{2\pi\nu_0} \quad (11)$$

For the measured Q_L = 46,000 and the parameters $\gamma_{\max}$, ν_0 of SO₂, Eq. (10) yields

$$\Delta V_d / V_d = -0.59$$

in good agreement with the value -0.61 obtained by measurement of Fig. 12. The (HWHM) linewidth is defined as the frequency deviation for which $\gamma(\nu)$ is equal to $\gamma_{\max}/2$. Repeating the calculation for $\gamma_{\max}/2$ yields a measured HWHM linewidth equal to 0.31 MHz in agreement with the calculated value above.

The accuracy of measurements of this kind is dependant upon the linearity of the receiver system, and the assumption that there is no saturation of the rotational transition by the measuring field. In the measurement illustrated above, the microwave power was reduced 3dB below the smallest value for which any

saturation could be detected.

Signal Detection using Source Modulation

The detection of gas absorption signals by the techniques outlined in the previous section is limited to strongly absorbing species. By signal averaging a series of repetitive sweeps through the absorption region the sensitivity can be increased, perhaps by a factor of 100 over that found in the above example. However, for weaker signals, it is necessary to use some form of modulation and to recover the signal with a phase-sensitive lock-in amplifier.

Source modulation, in which the source frequency is sinusoidally varied with a small amplitude while the average frequency of the source is swept slowly through the absorption region is a well known technique for extracting the resonance signal from the noise background. It is commonly used in measurements¹³ of linewidths of microwave transition.

In order to modulate the signal oscillator, a calibrated sinusoidal voltage was applied to the frequency synthesizer. Since the signal oscillator was phase locked at 70 GHz to the 152nd harmonic of the synthesizer, the actual modulation depth of the source could be readily determined. The cavity feedback loop was then enabled to permit the cavity to track the frequency excursions of the source. Because of the limited bandwidth of the cavity feedback loop, a low frequency of 33 Hz was chosen as the modulating frequency.

A sample of SO₂ gas diluted with N₂ gas to a concentration of 970 ppm (supplied and certified by Matheson Inc.) was introduced into the cavity at a pressure of 0.025 torr. The signal oscillator was then modulated at 33 Hz with a depth of 0.091 MHz RMS and the resulting signal phase detected with the lock-in amplifier and filtered with a time constant of 20 ms.

The detected signal is shown in Fig. 13. By turning off the modulation voltage and increasing the lock-in gain until the noise level was equal to the signal of Fig. 13, the signal-to-noise ratio (SNR) was determined to be equal to 20 for the time constant $\tau = 20 \text{ ms}$. Since the noise voltage is proportional to $\sqrt{(1/\tau)}$, the equivalent SNR for a 1 second time constant and a concentration of 970 ppm is 140. From Eq. 11 the detected signal ΔV_d is proportional to $\gamma_{\max}$ which in turn is proportional to the concentration of SO₂.

In order to relate the experimental data such as that shown in Fig. 13 to the actual gas absorption parameters $\gamma_{\max}$ and the linewidth $(\Delta\nu)_1$, it is necessary to compute the effect of the modulation process on the gas absorption signal. The calculation has been performed by Wahlquist¹⁴ for the comparable case of a Lorentzian absorption line, Zeeman modulated by a sinusoidal magnetic field. In the case of source modulation the important parameters are the amplitudes, ΔV_d of the Lorentzian absorption curve and the peak-to-peak amplitude, V_{pp} of the phase detected signal, and the respective linewidths $\Delta\nu$ and $\delta\nu$ of the two signals. Adapting Wahlquist's results, we find that the peak-to-peak detected signal V_{pp} and the detected linewidth $2\delta\nu$, are given by

$$V_{pp} = \Delta V_d K_a \gamma_{\max}^{\text{rms}} / \Delta\nu \quad (12)$$

and $2\delta\nu = 2K_b\Delta\nu$ (13)

the quantities K_a and K_b are plotted in Fig. 14 as a function of the ratio $v_{\text{mod}}^{\text{rms}}/\Delta\nu$ of the modulation amplitude to the Lorentzian HWHM linewidth. For small modulation depth the approximation $V_{\text{pp}} = 1.30 \Delta V_d v_{\text{mod}}^{\text{rms}}/\Delta\nu$ and $\delta\nu = \Delta\nu/\sqrt{3}$ can be used.

The validity of eqns. 12 and 13 in interpreting the measured data of Fig. 13 can be tested by first calculating the Lorentzian parameters of the absorbing gas. For a dilute mixture of SO_2 in N_2 Tejwani¹⁵ has calculated for the linewidth parameter $(\Delta\nu)_1 = 4.73 \text{ MHz/torr}$. Therefore $\gamma_{\text{max}} = 1.43 \times 10^{-3} \text{ C cm}^{-1}$ where $C \ll 1$ is the concentration of SO_2 in the mixture. For the given concentration of 970 ppm and pressure 0.025 torr the predicted values are $\gamma_{\text{max}} = 1.4 \times 10^{-6}$ and $\Delta\nu = 1.12 \text{ MHz}$. From Eq. 11 and the measured $Q_L = 46,000$ we have $\Delta V_d/V_d = 0.0045$. At the microwave power (approximately 0.3 μW at the input of the cavity) used, V_d was measured to be 0.093V yielding for ΔV_d the calculated value 419 μV at the Lorentzian peak.

At the modulation depth of 0.091 MHz rms we have $v_{\text{mod}}^{\text{rms}}/\Delta\nu = 0.76$ and from Fig. 14, $K_a = 0.84$ and $K_b = 1.00$. Eq. 12 and 13 then yield the results $V_{\text{pp}} = 266 \mu\text{V}$ and $2\delta\nu = 0.24 \text{ MHz}$. From Fig. 13 we obtain the measured values $2\delta\nu = 0.25 \text{ MHz}$ and $V_{\text{pp}} = 280 \mu\text{V}$ in good agreement with the predicted values.

The above calculation shows that it is possible to make absolute measurements of the gas absorption parameters, γ_{max} and $\Delta\nu$ using the technique of source modulation to enhance the signal-to-noise ratio. For routine measurements, an automated spectrometer programmed to fit the observed spectrum to the theoretical model would be highly desirable. In all measurements it is important to avoid saturation of the microwave signal or, if present, to account for it.

Signal Detection using Stark Modulation

Stark modulation, in which the molecular rotational transitions are repetitively shifted from their zero field positions by a zero-based square wave electric field, has the advantage over the source modulation method that only the molecular transitions are affected by the modulating field. Thus the baseline, in the absence of the absorbing gas, should be a straight line. This contrasts with the case of source modulation, where any variation with frequency of the power transmitted through the cavity will be detected as a spurious baseline signal and must be accounted for.

As described above, in order to obtain the large electric field needed, the flat mirror was insulated and moved to a position approximately 1 cm from the spherical mirror. The cavity was then filled with the 970 ppm SO_2 mixture described above. A Stark modulation amplitude of 1000V at a frequency of 19 kHz was used together with a lock-in amplifier time constant of 1.0 sec. The signal-to-noise ratio was found to be about 40 with the 1.0 sec time constant. This about two-to-three times worse than that observed with source modulation.

The principal reason that the sensitivity of the

Stark modulation scheme is less than that obtained with source modulation is that the loaded Q of the cavity is reduced significantly when the two mirrors are placed in close proximity.

The Q factor of the Stark modulation cavity was found to be only about 11,000. Since the absorption signal is proportional to Q, the reduction in signal amplitude is a factor of 4. This is partially offset by the somewhat decreased noise present at the higher modulation frequency used, and by the fact that the square wave modulation permits a larger percentage of the signal to be recovered after phase detection.

System Noise Characterization

The sensitivity of the spectrometer system is determined⁷ by the noise contributions of the signal source, the microwave cavity, and the receiver. In a modulated system, the noise frequencies of interest lie in a narrow band centered at the frequency of modulation. In order to characterize the performance of the spectrometer in greater detail, measurements of the total system noise were made using a narrow band wave analyzer tuned to various offset frequencies corresponding to possible choices of modulation. The measurements were repeated at different power levels to establish the dependence of the noise on the microwave power.

The power at the input coupling port of the cavity was determined using a square law diode detector calibrated with a TRG V980 calorimeter power meter. Three different power levels were established for the noise measurements, -35 dBm (0.31 μW), -25 dBm (3.1 μW) and -15 dBm (31 μW). The lowest power (-35 dBm) corresponds to that used in the measurements reported in the previous section.

An HP 302A wave analyzer was used to measure the noise output of the spectrometer system. A low noise amplifier connected between the spectrometer phase detector and the analyzer served to boost the output voltage V_d to a selected appropriate level. In all measurements, the receiver IF gain was adjusted to maintain the output voltage at the selected level. The wave analyzer output was calibrated by phase locking the local oscillator to an offset frequency differing from 30 MHz by about 20 Hz. The "carrier" power level recorded at this frequency was then used to normalize all successive measurements.

With the local oscillator restored to its offset of exactly 30 MHz and the cavity locked to the signal oscillator frequency, the noise-to-carrier ratio was measured for modulation frequencies from 33 Hz to 10 KHz and for the microwave power levels indicated above. The results are shown in Table 1. In the Table the power ratios are expressed in units of decibels RMS per Hz of bandwidth. The columns marked "Receiver Noise" were obtained in each case with zero microwave power and therefore represent the noise contribution of the microwave receiver alone. The measured receiver noise contribution is in agreement with the values calculated from the room temperature thermal noise power degraded by the receiver SSB noise figure of 9 dB.

The total noise measured at each power level includes contributions from the microwave source as well as from the receiver. At the lowest microwave power level the source noise and receiver noise are comparable, whereas at the two higher power levels the source noise is dominant. From the Table, it can be seen that there is no advantage to be gained from increasing the microwave power beyond -25 dBm. In fact, saturation of the

gas absorption at higher powers will actually cause the observed signal-to-noise ratio to deteriorate. There is an advantage in the use of higher modulation frequencies than 33 Hz. At -35 dBm input power and 10,000 Hz the improvement amounts to 4 dB at -25 dBm and 10,000 Hz it amounts to 8 dB.

However, the modulation frequency cannot be increased much above 33 Hz in the source modulation scheme because of the inertia of the cavity mirror and transducer. With Stark modulation, higher frequencies are possible, but the advantage is offset by a necessary reduction in cavity Q.

Conclusions

The measurements summarized in Table 1 show that the major contribution to the overall system noise comes from the noise generated by the source oscillator. The effect of source noise on the sensitivity of microwave spectrometers has been discussed by Strandberg¹⁶ and by Leskovar et al.⁷ As these authors have pointed out, two separate contributions are responsible for the total source noise reaching the microwave receiver. The first is AM noise which passes directly through the microwave cavity, and the second is FM or phase noise which is converted by the slope of the cavity response curve into AM noise before reaching the receiver. Our measurements to date indicate that it is the latter which is dominant.

In the present spectrometer, the source oscillator is phase locked to the 152nd harmonic of the frequency synthesizer. Within the bandwidth of the phase lock loop (50 KHz) the phase noise is determined by the spectral purity of the synthesizer signal degraded by 44 dB due to the multiplication factor of 152. The resulting noise, confirmed by our measurements, approaches closely the state-of-the-art for a phase locked oscillator.

Instead of phase locking the signal oscillator to the synthesizer, one can frequency lock it directly to the cavity. This can be accomplished by feeding the cavity discriminator output to the varactor tuning element of the Gunn oscillator. If the bandwidth of this feedback loop is larger than the modulation frequency used, the phase noise converted in the cavity will be reduced by a considerable factor. The necessary source modulation can then be obtained by driving the piezoelectric transducer with a modulating voltage. Finally, the cavity can be made to track the harmonic signal from the frequency synthesizer using a suitable discriminator to drive the piezoelectric transducer. The bandwidth of this feedback loop must be less than the modulation frequency to avoid interference between the two signals. With these modifications presently under development, the sensitivity of the spectrometer should be increased significantly.

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Appendix

The absorption of microwave energy by a gas may be expressed in terms of an absorption coefficient. The peak value of the absorption coefficient can be calculated from the modified Van Vleck-Weisskopf equation

$$\gamma_{\max} = A \frac{i_c}{(\Delta\nu)_1} \frac{8\pi^2 v_o^2}{3ckT} \frac{f_v g_i (2J+1) |\mu_{ij}|^2 e^{-W/kT}}{Q_r} \quad (14)$$

Where the constant $A = 3.219 \times 10^{10}$, i_c is the isotopic concentration of the species responsible for transition, $(\Delta\nu)_1$ is the bandwidth (half width at half maximum) in MHz at one torr and 300K, v_o is the resonant absorption frequency, c is the velocity of light, T is the absolute temperature and k is the Boltzmann's constant. The term $(2J+1)$ is the degeneracy associated with the principal rotational quantum number, g_i is the degeneracy attributable to the "inner" quantum numbers, $|\mu_{ij}|^2$ is the square of the dipole matrix element associated with the transition, W is the energy of the lower state, f_v is the fraction of molecules in the vibrational state of interest and Q_r is the rotational partition function. The calculation of absorption coefficients for specific molecules using equation (14) depends upon molecular symmetry. The rotational partition function Q_r can be defined to sufficient accuracy using the semi-classical expression

$$Q_r = \frac{1}{\sigma} \sqrt{\frac{\pi}{ABC}} \left(\frac{KT}{h} \right)^3 \quad (15)$$

For $^{32}\text{S}^{16}\text{O}_2$ the symmetry number, $\sigma = 2$ and $A = 60778.5553$ MHz, $B = 10317.9122$ MHz, and $C = 8799.6511$ are the rotational constants.

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TABLE 1. Noise to Carrier Ratio

Frequency (Hz)	Microwave Power Level		-25 dBm ⁽²⁾ (dB/Hz)	Receiver Noise (dB/Hz)	-15 dBm ⁽³⁾ (dB/Hz)	Receiver Noise (dB/Hz)
	-35 dBm ⁽¹⁾ (dB/Hz)	Receiver Noise (dB/Hz)				
33	-89	-96	- 93	-107	- 95	-115
100	-92	-96	- 95	-107	- 96	-116
200	-93	-96	- 96	-106	- 96	-116
500	-93	-96	- 98	-107	- 97	-116
1000	-93	-97	- 98	-107	- 97	-116
2000	-93	-97	- 99	-107	- 98	-116
5000	-93	-97	-100	-107	- 99	-116
10000	-93	-97	-101	-107	-101	-116

(1) IF gain 40 dB

(2) IF gain 30 dB

(3) IF gain 20 dB

Fig. 1 Absorption line intensities for SO₂ as a function of frequency.

Fig. 2 Absorption line intensities for SO as a function of frequency.

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Fig. 3 Absorption line intensities for NO_2 as a function of frequency.

Fig. 5 Absorption line intensities for H_2CO as a function of frequency.

Fig. 4 Absorption line intensities for O_3 as a function of frequency.

Fig. 6 Absorption line intensities for OCS as a function of frequency.

Fig. 7 Block diagram of microwave spectrometer system.

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Fig. 8 Cross sectional view of Fabry-Perot transmission cavity.

XBL 766-8142

XBL 766 8143

Fig. 9 Transmission loss of cavity as a function of output wave guide displacement.

XBL 766 8141

Fig. 11 Fabry-Perot cavity tuning in kHz peak-to-peak as a function of frequency of applied drive voltage. The drive voltage was maintained at a constant 10 V rms.

XBL 766 8140

Fig. 10 Piezoelectric tuning characteristics of cavity system. For the mirror separation given in Fig. 1, 1 MHz corresponds to a displacement of approximately 1.07 microns.

XBB 784-4399

Fig. 12 Spectrometer output showing (a) baseline with zero microwave power, (b) in-phase component of cavity response with cavity frequency fixed, (c) in-phase component with cavity tracking and (d) absorption signal for concentrated SO_2 .

Fig. 13 Detected absorption signal for 970 ppm SO_2 in N_2 using source modulation and a time constant of 20 ms. The calibration signal of 500 μV is referenced to the input of the lock-in amplifier.

XBB 701-280

XBL 704-0074

Fig. 14 Graph showing the lineshape parameters K_a and K_b plotted as a function of the ratio $v_{\text{mod}}^{\text{RMS}} / \Delta v$.

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