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Abstract

Calculations of the transition frequencies and absorption coefficients of microwave rotational transitions are given for a number of atmospheric pollutants and constituents. New measurements of the absorption coefficients are made in the vicinity of 70 GHz. The apparatus used in these measurements is briefly described. The calculated absorption coefficients are compared with these measurements and with existing measurements at other frequencies where available. Transitions with frequencies up to about 200 GHz are considered for the molecules and radicals SO_2, O_3, H_2O, NO_2, H_2S, H_2CO, NH_3, CO, OCS, N_2O, NO, OH, O_2, SO. Also discussed are criteria for the selection of appropriate transitions for the development of high sensitivity monitors to be used in air pollution and combustion research.

I. Introduction

Investigations of the use of microwave spectroscopy as a tool to aid in the detection and quantitative determination of gaseous pollutants and constituents have been pursued by a number of authors.(1,2,3) Several laboratory instruments have been designed for this purpose,(4,5) and a portable monitoring instrument for the detection of formaldehyde has been constructed.(6) Similar instruments for the detection of other species are presently under development in this laboratory.

Microwave rotational spectroscopy offers a number of advantages as a technique for pollution detection.(1,2) 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.(7) One can, in principle, 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.(8) Additionally, some form of modulation, such as Stark modulation, followed by frequency selective amplification and phase-sensitive detection is usually necessary.(9) Fortunately these techniques are for the most part well developed in the microwave region, making possible the detection of these very small signals.

Because of sensitivity limitations, it is important to select transitions for a given molecule which are as intense as possible. Theoretical calculations of rotational absorption coefficients (c.f. equation 11, 15 below) show that signal intensities increase rapidly with frequency. Therefore it is an advantage to operate the spectrometer at the highest possible frequency consistent with the availability of suitable microwave components.

For multicomponent detection it is important not only to determine the best single frequency for a given gas, but also to find suitable restricted intervals of frequencies appropriate to the simultaneous or sequential detection of a number of pollutants. This latter requirement follows because the sensitive spectrometers needed are normally tunable only over a small range of frequencies preselected at the time of design. For example, individual low noise klystron microwave sources in the millimeter wave region can be tuned only over a 10% frequency range and solid state sources in this region have even less bandwidth.(10) A knowledge of the absorption coefficients and frequencies of the various pollutant molecules is therefore necessary in order to select the most suitable frequency range.

Although calculations and measurements of the frequencies of molecular rotational transitions are readily found in the literature,(11) reliable information about the intensities of these transitions in many cases is not available. For this reason the absorption coefficients of a number of important pollutants and constituents were calculated and are reported here. Where available from the literature measured values are also given. Measurements were made in the 70 GHz region for a number of species (SO_2, H_2CO, NO_2, OCS) since values in this range are not available in the literature.

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 additional molecules important to specialized applications have well known spectra but have not been included.

In most cases the range of frequencies covered extends from a few gigahertz to 200 GHz and represents the approximate range for which device technology is reasonably well developed. In a few cases transitions at higher frequencies are included.

In the first portion of the paper the theoretical formulas and approximations used in the calculations are summarized. The methods used to measure the absorption coefficients are then presented. A discussion of the linewidths of the transitions is also given. Finally, the absorption coefficients and frequencies of the individual molecules are described. These are not arranged in order of their importance as pollutants but are grouped for convenience according to their molecular symmetry.

Included in the list are the potential pollutants SO_2, NO_2, H_2S, H_2CO, NH_3, CO, OCS and N_2O. H_2O and O_2 have been included because they are important components of the atmosphere and because of their potential as sources of interference in the detection of other constituents. Also discussed are the free radicals and transient species NO, O_3, SO, OH which play an important role in the chemical reactions associated with combustion and pollution processes. By measuring their concentrations, information about these reactions can be gained.

II. Calculation of Absorption Coefficients

The absorption of microwave energy by a gas may be expressed in terms of the absorption coefficient, $\gamma(\nu)$. For frequencies, ν near a resonant absorption centered at frequency ν_o, $\gamma(\nu)$ is given by$^{(12)}$

$$\gamma(\nu) = \frac{8\pi^3 Nf}{3ckT} |\mu_{ij}|^2 \nu^2 S(\nu,\nu_o) \qquad (1)$$

where $|\mu_{ij}|^2$ is the square of the dipole matrix element associated with the transition; N is the number of molecules per unit volume of the sample, and f is the fraction of these in the lower energy state of the transition. T is the absolute temperature and k is Boltzmann's constant. The normalized lineshape function $S(\nu,\nu_o)$ expresses the fact that the resonance has finite width.

At the pressures normally employed to observe microwave spectra (approximately 0.01 to 10 torr), the lineshape is Lorentzian and in the absence of power saturation may be written as

$$S(\nu,\nu_o) = \frac{1}{\pi}\left[\frac{\Delta\nu_L}{(\nu-\nu_o)^2+(\Delta\nu_L)^2}\right]. \qquad (2)$$

The linewidth, $\Delta\nu_L$, is caused by collisions between the molecules and is proportional to the pressure. Since the concentration, N is also proportional to the pressure, the peak absorption at resonance, $\gamma(\nu_o)$ obtained by combining equations (1) and (2), is pressure independent. It is therefore a convenient parameter to characterize the magnitude of absorption.

Under these conditions the peak absorption is given by[(12)]

$$\gamma_o = \frac{8\pi^2 \nu_o^2 |\mu_{ij}|^2 f}{3ckT} \left(\frac{N}{\Delta\nu_L} \right) . \qquad (3)$$

The ratio $N/\Delta\nu_L$ can be evaluated once the linewidth is known at a given pressure. If $(\Delta\nu)_1$, the linewidth (half width at half maximum) in MHz at one torr and 300 K is specified, we have

$$\frac{N}{\Delta\nu_L} = 3.219 \times 10^{10} \quad \frac{i_c}{(\Delta\nu)_1} \qquad (4)$$

where i_c is the isotopic concentration of the species responsible for the transition.

The fraction, f, of molecules in the lower energy state of the transition can be written as the product

$$f = f_v \, f_r \ . \qquad (5)$$

The fraction, f_v, of molecules in the vibrational state of interest can be calculated from the known fundamental vibrational frequencies, ω_i of degeneracy d_i. For the state v of energy, W_v

$$f_v = d_v e^{-W_v/kT} \prod_i [1 - \exp(-h\omega_i/kT)]^{d_i} \qquad (6)$$

where the product sum is the reciprocal of the vibrational partition function of the molecule. For the ground vibrational state normally observed, $W_v = 0$ and f_v is of the order of unity. The fraction, f_r of molecules in the lower rotational energy state can be expressed in terms of the rotational partition function, Q_r as

$$f_r = \frac{(2J+1) g_i e^{-W/kT}}{Q_r} \qquad (7)$$

where W is the energy of the lower state, $2J+1$ is the degeneracy associated with the principal rotational quantum number, and g_i is the degeneracy attributable to the "inner" quantum numbers which include contributions arising from possible inversion, internal rotations and the effects of nuclear spin statistics.

The above equations can be combined to yield

$$\gamma_o = 3.219 \times 10^{10} \frac{i_c}{(\Delta\nu)_1} \frac{8\pi^2\nu_o^2}{3ckT} \frac{f_v g_i (2J+1) |\mu_{ij}|^2 e^{-W/kT}}{Q_r} . \qquad (8)$$

The calculation of absorption coefficients for specific molecules using equation (8) depends upon the molecular symmetry. The appropriate formulas for the asymmetric top and linear molecules appearing in this report are described below.

Asymmetric Top Molecules

A number of molecules of interest are asymmetric top rotors with C_{2v} molecular symmetry. For these molecules the rotational states are identified by the quantum numbers $J(K_p,K_o)$ where J is the total rotational quantum number and K_p and K_o are pseudo-quantum numbers describing the projection of J on the symmetry axis for the limiting prolate and oblate symmetric tops respectively. The energy levels associated with these states cannot be obtained in closed form but can be calculated by a computer diagonalization of the rotational Hamiltonian. In order to obtain results of sufficient accuracy, it is necessary to include contributions to the Hamiltonian due to centrifugal distortion.(12)

In calculating the absorption coefficients it is convenient to define the line strength, S_{ij} for the transition

$$S^x_{ij} = \frac{(2J+1)\,|\mu_{ij}|^2}{\mu_x^2} \qquad (9)$$

where $x = a,b,c$ is the component of the dipole moment involved in the transition. The line strength can be calculated from the direction cosine matrix elements(12) evaluated using the wave functions of the states involved.

The rotational partition function can be written to sufficient accuracy using the semi-classical expression

$$Q_r = \frac{1}{\sigma}\sqrt{\frac{\pi}{ABC}\left(\frac{kT}{h}\right)^3} \quad . \qquad (10)$$

where for C_{2v} molecules the symmetry number $\sigma = 2$. A, B, and C are the rotational constants.

It is necessary to consider the effects of the nuclear spin statistics on the level populations. In the case of the molecules SO_2, O_3 and NO_2 the dipole moment, $\mu = \mu_b$ lies along the axis of intermediate moment of inertia which is also the symmetry axis of the molecule. Because of the zero nuclear spin of the two identical ^{16}O atoms, the total wave function must be symmetric under a 180° rotation about this axis. As a result only states of the form J(e,e) and J(o,o) are permitted, where e and o specify the parity of the pseudo-quantum numbers. The degeneracy factor, g_i in equation (8), is then unity for the permitted levels and zero for the rest.

In the case of H_2S and H_2O the dipole moment also lies along the axis of intermediate moment of inertia. However, the nuclear spin of ^1H is 1/2, requiring the total wave function to be antisymmetric under the above symmetry operation. Although all the rotational levels are permitted, the ratio of the number of symmetric nuclear wave functions to antisymmetric wave functions is 3:1. If equation (10) is used for the partition function, the appropriate weight factors then become $g_i = 1/4$ for the states (e,e) and (o,o) and $g_i = 3/4$ for the states (e,o) and (o,e).

The same weight factors apply to the case of H_2CO. However, the symmetry axis in this case is along the axis of least moment of inertia and $g_i = 1/4$ for the states (e,e) and (e,o) and $g_i = 3/4$ for the states (o,o) and (o,e) when used with equation (10).

After combining equations (8), (9) and (10) and substituting numerical values for the constants we have

$$\gamma_0 = 7.683 \times 10^{-14}\, i_c f_v \sqrt{ABC}\, g_i \mu^2 S_{ij}\, \frac{\nu_0^2}{T^{5/2} (\Delta\nu)_1}\, e^{-W/kT} \qquad (11)$$

where the dipole moment, μ is in Debye units (1D = 10^{-18} esu), and the transition frequency ν_0, the rotational constants A, B, C, and the line breadth $(\Delta\nu)_1$, are in MHz.

Linear Molecules

For diatomic and linear polyatomic molecules with $^1\Sigma$ electronic states in which the net electronic angular momentum is zero, the rotational transition frequencies for the ground vibrational state are given by(12)

$$\nu = 2B(J+1) - 4D(J+1)^3 \qquad (12)$$

where B and D are the rotational and centrifugal distortion parameters. The permitted dipole transitions obey the selection rule J → J+1. For these molecules the peak absorption coefficient in the pressure broadening regime (equation 8) can be expressed in the form(12)

$$\gamma_o = \frac{4\pi^2 N f_v h \mu^2 \nu_o^3}{3c(kT)^2 \Delta\nu_L} \left(1 - \frac{h\nu_o}{2kT}\right) \quad . \qquad (13)$$

After substitution of appropriate values for the constants we have

$$\gamma_o = 4.913 \times 10^{-12} \; \frac{f_v \mu^2 i_c \nu_o^3}{T^2 (\Delta\nu)_1} \left(1 - \frac{2.4 \times 10^{-5} \nu_o}{T}\right) \qquad (14)$$

where μ is the dipole moment in Debye units, and the transition frequency, ν_o and linewidth parameter, $(\Delta\nu)_1$ are expressed in MHz and MHz/torr respectively. The fraction, f_v of molecules in the vibrational state of interest (usually the ground state) is given by equation (6).

Because the diatomic molecules NO, OH, O_2 and SO have electronic ground states which are not Σ^1, their absorption coefficients cannot be calculated directly using the above equations. In these molecules the net electronic angular momentun couples to the rotational angular momentum to produce a fine-structure splitting of the rotational levels. The coupling is usually intermediate between Hund's cases (a) and (b), necessitating an exact calculation. The specific cases are discussed below.

Linewidths

Calculations of the linewidth parameter, $(\Delta\nu)_1$ appearing in equation (4) based on collisional models(9,13) are quite complex, and available only for a few cases of interest. Hence, if accurate absorption coefficients are desired, it is usually necessary to use experimentally determined values for $(\Delta\nu)_1$. Because of the limitations of the available data, in most of the calculations reported here, average values for $(\Delta\nu)_1$ were assumed for each molecule independent of the transition involved although variations of as much as 30% may occur for various transitions. If the actual linewidth for a given transition is known, however, the calculated absorption coefficient can easily be corrected by multiplying by the appropriate ratio. In some cases where no calculated or measured values were available estimated quantities were used.

It should be pointed out that the linewidth parameters given here are for the self-broadening case only in which the gas under study is present in a pure form. In mixtures of gases, collisions will occur with other constituents of the mixture, resulting in different linewidths. If the diluting mixture is primarily nitrogen or air, the resulting linewidths will usually be narrower than in the pure state. Calculations and/or measurements of linewidths for nitrogen and air diluted mixtures have been given for a number of gases including SO_2,(14,15) NO_2,(14) O_3,(16) N_2O,(13) and H_2O.(13)

Absorption Coefficient Measurements

Measurements of the absorption coefficients for the stronger transitions of several gases (NO_2, H_2CO, OCS) were made in the vicinity of 70 GHz in order to verify the calculated values. The apparatus used was similar to that previously described(17) for measurements of the absorption coefficients of sulfur dioxide and is shown in block diagrammatic form in Fig. 1. Microwave power supplied by an OKI 70V10A reflex klystron was transmitted through calibrated attenuators to a Fabry-Perot semi-confocal resonant cavity mounted in a vacuum chamber. A Baytron wafer-type crystal detector was used to monitor the output of the transmission cavity. The microwave frequencies were measured by zero-beating the 7th harmonic of a tunable, stabilized, X-band source with the OKI V-band klystron output. A counter directly measured the X-band source frequency. In addition, a diode modulator was used to provide a "fence" of marker frequencies on either side of the primary reference frequency.

The absorption coefficients were determined from the relationship(17)

$$\gamma = \frac{2\pi\nu_o}{cQ_o}\left[\sqrt{\frac{P_o}{P_1}} - 1\right] \qquad (15)$$

where ν_o is the frequency of the transition, c is the velocity of light, and Q_o is the loaded Q of the cavity without the gas absorption. P_1 and P_o represent respectively the peak output power of the cavity with and without the gas.

The quality factor, Q_o of the evacuated cavity, which was approximately 25,000, was measured by superimposing the frequency markers from the modulated X-band source on the 3dB down points of the cavity response curve. The power ratio, P_o/P_1, was determined by noting the change in setting of the calibrated precision attenuator necessary to maintain a constant detected output power with the chamber first filled with gas at a predetermined pressure and then evacuated. In this way uncertainties in the square law response of the detector were avoided. The pressure, which varied from 100 to 1000 mtorr depending on the particular gas, was measured with a calibrated capacitance manometer. In order to avoid saturation effects, the microwave power in the cavity was kept at a low level, normally less than 100 μW. The absorption coefficients were measured at a number of frequencies in the vicinity of each transition and the peak absorption, γ_o and linewidth parameter, $(\Delta\nu)_1$ were determined. The results for the specific gases measured are discussed below.

IV. Molecular Species

Sulfur Dioxide

Because of its comparatively large electric dipole moment ($\mu = 1.634$ D) and the large fractional abundance (94.5%) of its most common isotope, $^{32}S^{16}O_2$, sulfur dioxide is a strong absorber of energy in the microwave region.

The most extensive measurements of the microwave spectrum of $^{32}S^{16}O_2$ in its ground vibrational state are due to Steenbeckeliers$^{(18)}$ who interpreted them in terms of the Watson$^{(12)}$ theory of centrifugal distortion. Recently Lovas$^{(19)}$ reexamined all the available experimental data and obtained a 16 parameter fit to the spectrum using a form of the Watson rotational Hamiltonian given by Kirchhoff.$^{(20)}$ Using these parameters the present authors$^{(17)}$ have calculated the frequencies and absorption coefficients for all transitions up to rotational quantum number J = 50 for frequencies less than 200 GHz. The absorption coefficients were calculated for a room temperature value of 293 K (20°C) with the use of equation 11 and the statistical weights described above. An average value of 16 MHz/torr was used for the linewidth parameter, $(\Delta\nu)_1$.

The calculated absorption coefficients were compared$^{(17)}$ to existing measurements in the region 26-40 GHz and to new measurements in the vicinity of 70 GHz and were found to agree to within 5 to 10%. The frequencies and calculated and observed absorption coefficients are shown in Table 1. Only those transitions having the largest absorption coefficients within a given frequency interval are shown in the table.

Ozone

Although the electric dipole moment of ozone is smaller (μ = 0.532 D) than that of sulfur dioxide, the absorption lines are narrower. As a result the peak absorption coefficients for the two gases are comparable.

The microwave spectrum of $^{16}O_3$ has been studied extensively by Lichtenstein et al.(22) Using their parameters for the rotational Hamiltonian, the frequencies and absorption coefficients were calculated for T = 300 K and frequencies up to 200 GHz. The linewidths of several transitions have been measured by the above authors,(22) and the average value of 4.6 MHz/torr obtained was used in the present calculations. Similar calculations of the absorption coefficients have been given by Lichtenstein et al(22) and by Gora.(23) Calculations of the pressure broadened linewidths have been reported by Tejwani and Yeung.(16) No measurements of the absorption coefficients in this frequency range are available. The results obtained are shown in Table 2 where only the strongest transitions are shown.

Water Vapor

Because the rotational moments of inertia of the water molecule, $H_2{}^{16}O$, are so small, nearly all of the rotational transitions take place in the far infra-red. Only two transitions, the 6(1,6)-5(2,3) transition at about 22 GHz and the 3(1,3)-2(2,0) at about 183 GHz, occur in the accessible microwave region below 300 GHz. These two transitions are of considerable interest in studies of the atmospheric propagation of microwaves and have been investigated in detail. The absorption coefficients have been calculated, and in the case of the 22 GHz line, measured by Liebe.(24) His results for T = 300 K are shown in Table 3.

Nitrogen Dioxide

NO_2 is a light molecule with a very large A reciprocal moment of inertia. As a result relatively few rotational transitions take place in the accessible microwave region. For example, there are only five transitions below 60 GHz whereas there are 67 for SO_2. Because NO_2 is a free radical with a single unpaired electron, each rotational level is split into two levels by the coupling of the electronic spin magnetic moment and the magnetic moment generated through the molecular rotation. A further splitting of each of these occurs because of interactions with the moments of the ^{14}N (I=1) nucleus. The effect of these interactions is to produce a spectrum consisting of a large number of absorption lines in the vicinity of each rotational transition.

The microwave spectrum of NO_2 has been studied by Bird et al(25) and more precisely by Lees et al.(26) Recently Baron et al(27) measured the hyperfine transitions of the 5(1,5)-6(0,6) rotational transition near 70 GHz. With the use of a computer program that set up and diagonalized the full rotation-electron spin-nuclear spin Hamiltonian, they were able to compute the peak absorption coefficients for each of the hyperfine transitions. This has not yet been done for any of the other rotational transitions of NO_2. The relative intensities of the stronger hyperfine components, however, are expected(28) to be approximately the same for all rotational transitions. Thus their absorption coefficients can be estimated by multiplying the total coefficients as computed by equation (11) by the appropriate fraction. This was done for the strongest component with a fractional intensity of 20%. The results for the transitions occurring below 200 GHz are shown in Table 4. They were obtained using the values $T = 300$ K, $\mu = 0.316$ D, $f_v = 0.97$ and the experimental linewidth parameter, $(\Delta\nu)_1 = 4.0$ MHz/torr reported below.

To verify the calculated values and to establish the linewidth parameter, the absorption coefficient of the dominant hyperfine component near 70 GHz was measured using the apparatus described above. In order to increase the sensitivity of the apparatus to measure the expected small absorption coefficient, the Fabry-Perot cavity was modified by constructing a new flat mirror having smaller coupling holes and thinner irises. With this arrangement the cavity Q was increased to 46,000. In spite of this improvement the change in cavity response due to the gas absorption remained small, amounting to only 0.4 dB at the line center. As a result the uncertainty in the measurements was estimated to be about ±20%. The absorption coefficient measurements were made at a pressure of 1.0 torr and a temperature of 300 K using nitrogen dioxide gas supplied by Union Carbide, Linde division and having a purity of 99.5%.

The resulting peak absorption, γ_0 was 1.5 × 10^{-5} cm^{-1} and $(\Delta\nu)_1$ was 4.0 MHz/torr. Within the above uncertainty these results agree with those calculated.

It should be pointed out that because of Zeeman broadening of the absorption lines by the earth's magnetic field, the residual linewidth at low pressures has been observed(27) to be about 0.5 MHz HWHM. Since this is considerably broader than the Doppler width normally encountered, extrapolation of the results of Table 4 to low pressures should be treated with caution.

Hydrogen Sulfide

Hydrogen sulfide is an extremely light molecule. In fact only seven transitions have been observed at frequencies below 200 GHz. The available data on the microwave spectrum have recently been reviewed by Helminger et al.(29) Using their calculated values for the transition frequencies and line strengths, the peak absorption coefficients can easily be calculated using equation (11). The results for T = 300 K, dipole moment μ = 0.974 D and an assumed linewidth parameter of 15 MHz/torr are shown in Table 5. It should be noted that only the 1(1,0)-1(0,1) transition at 168.7 GHz is strong enough to be used conveniently for monitoring purposes. No measured absorption line intensities have been reported.

Formaldehyde

Formaldehyde has a large dipole moment ($\mu = 2.331$ D) and is a strong absorber in the microwave region. The microwave spectrum of H_2CO has been critically reviewed by Johnson et al.(30) Using equation (11) and the calculated frequencies and line strengths given by the above authors, the peak absorption coefficients were calculated for the most abundant isotope, $H_2{}^{12}C^{16}O$.

Measurements of the absorption coefficients and linewidths for two transitions occurring in the vicinity of 70 GHz were made using the apparatus described above. The formaldehyde gas was prepared by gently heating a solid sample of paraformaldehyde and passing the monomer through a drying tube containing anhydrous $CaSO_4$. The measurements were made at a pressure of 250 mtorr and a temperature of approximately 300 K. These results and some additional measurements made by White(31) using a calibrated Stark modulated spectrometer are shown in Table 6. The calculated values were obtained for T = 300 K using the observed linewidths for the measured transitions and an average value of 22 MHz/torr for the other transitions.

Ammonia

Because of its extremely small moment of inertia the lowest pure rotational absorption line of the symmetric top molecule NH_3 occurs at a frequency of approximately 572 GHz. Microwave absorption, however, occurs at lower frequencies due to an inversion oscillation of the nitrogen nucleus through the H_3 plane. The inversion transitions take place over a band of frequencies centered at about 23 GHz, with the individual frequencies depending upon the particular rotational state of quantum numbers J, K involved due to centrifugal distortion effects.

The peak absorption coefficients for T = 300 K have been calculated for most of the lines in the spectrum by Townes and Schawlow.(9) Measurements of the linewidths and absorption coefficients for a number of the stronger transitions have been reported by Bleaney and Penrose(32) and by White.(21) Their results and the calculated intensities, which are in good agreement, are shown in Table 7. The measured linewidths are, however, about 10-15% broader than reported by Legan et al.(32a)

Carbon Monoxide

Only two transitions of the relatively light molecule $^{12}C^{16}O$ exist below 300 GHz. Using the molecular parameters determined in a critical review of the spectrum by Lovas et al,(33) the absorption coefficients were calculated for a temperature of 300 K, using equation 14. An estimated value of 5 MHz/torr was used for the linewidth parameter. For carbon monoxide $f_v = 1.0$ at 300 K and $i_c = 0.987$. The calculated frequencies and absorption coefficients are shown in Table 8. In the only available measurement by

Britt et al,(34) values of 1.7×10^{-4} cm^{-1} and 4.25 MHz/torr were found for the absorption coefficient and linewidth respectively of the J = 0→1 transition.

Carbonyl Sulfide

Because of its stability, ease of handling and relatively intense microwave spectrum, carbonyl sulfide is often used as a calibration source in microwave spectroscopy experiments. In addition it has been used as a reactant in microwave studies of the free radical, SO.(35) Absorption coefficients and transition frequencies for the most abundant isotope $^{16}O^{12}C^{32}S$ were calculated for a temperature T=300 K using equation (14) and molecular constants given in Ref. (36). Values of 6.4 MHz/torr for the linewidth parameter and 0.828 for the fraction, f_v of molecules in the ground vibrational state were used. The results for frequencies up to 200 GHz are shown in Table 9.

Using the Fabry-Perot spectrometer described above and carbonyl sulfide gas with a stated purity of 97.5% supplied by the Matheson Company, measurements were made of the linewidth and absorption coefficients for the 5 → 6 transition of both $^{16}O^{12}C^{32}S$ and $^{16}O^{12}C^{34}S$. The results for these and several other measurements previously published(21,37,38) are shown in Table 10. As can be seen good agreement between the measured and calculated values is found.

Nitrous Oxide

Using equations (12) and (14) and assuming a temperature of 300 K, absorption coefficients and transition frequencies were computed for the ground vibrational state of the most abundant isotope, $^{14}N_2{}^{16}O$ of nitrous oxide. In the calculation the molecular constants, B and D were taken from Ref. (39) and the values $(\Delta\nu)_1 = 5$ MHz/torr and $f_v = 0.883$ were used for the linewidth and fractional occupation of the ground vibrational state. The results are shown in Table 11. A value of $\gamma_o = 2.5 \times 10^{-4}$ cm^{-1} was measured for the $J = 3 \rightarrow 4$ transition by Britt et al(34) in good agreement with the calculated value. At sufficiently low pressures the ^{14}N hyperfine structure extending over a range of about 0.75 MHz may be resolved. In this case the calculated intensities correspond to the total intensity of all hyperfine components.

Nitric Oxide

The nitric oxide molecule possesses an unpaired electron with orbital and spin angular momenta L=1 and S = 1/2, resulting in a $^2\Pi$ electronic ground state. The ground state is split by the spin-orbit interaction into a $^2\Pi_{1/2}$ level and a $^2\Pi_{3/2}$ level lying approximately 123 cm^{-1} above it. To a first approximation the molecular wave functions can be described by a Hund's case (a) representation in which both L and S are tightly coupled to the molecular axis. The projections Λ and Σ of L and S along the molecular axis then combine with the end-over-end rotational angular momentum of the molecule to form the total (exclusive of nuclear) angular momentum J. The observed microwave spectrum results from electric dipole transitions obeying the selection rule ΔJ = ±1. Because of interactions between the rotational and electronic motions of the molecule, both L and S are slightly decoupled from the molecular axis. This deviation from the ideal Hund's case (a) produces a shift in the rotational levels and a splitting (Λ-doubling) of the levels for each value of J. In NO the Λ-doubling is small, amounting to a few hundred MHz for the $^2\Pi_{1/2}$ level and less than 10 MHz for the $^2\Pi_{3/2}$ level. A further splitting of the rotational levels occurs because of hyperfine interactions involving the ^{14}N nucleus.

Accurate molecular parameters for interpreting the microwave spectrum were obtained by Gallagher and Johnson(40) for the $^2\Pi_{1/2}$ level and by Favero et al(41) for the $^2\Pi_{3/2}$ level. Although both levels are appreciably occupied T = 300 K, the stronger transitions come from the $^2\Pi_{1/2}$ level. The peak absorption coefficients for this level were calculated by Gallagher and Johnson(40) and more recently by Wacker et al.(42) Measurements of the linewidth parameters and absorption coefficients for the $^2\Pi_{1/2}$, J = 1/2 → 3/2 transitions were reported by French and Arnold.(43) The results of these observations and calculations are shown in Table 12. The calculated values are those obtained by Wacker et al(42) assuming $T = 300$ K and $(\Delta\nu)_1 = 2.8$ MHz/torr, the average linewidth reported by French and Arnold.

Hydroxyl Radical

The electronic ground state of the hydroxyl radical, OH is similar to that of nitric oxide. As in the case of NO the $^2\Pi$ ground state is split by spin-orbit coupling into $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ levels. In OH, however, the $^2\Pi_{1/2}$ level lies about 140 cm^{-1} above the $^2\Pi_{3/2}$ level. Because the rotational constant for OH is much larger than that of NO, the decoupling of the electronic orbital angular momentum is more pronounced. This leads to a large Λ-type doubling of each rotational level. Since the OH radical is so light its pure rotational spectrum lies in the far infrared. The observed spectrum in the microwave region results from direct transitions between the Λ-doublets. Each Λ-doubling transition is further split by hyperfine interactions with the ^{1}H ($I = 1/2$) nucleus. The hyperfine transitions obey the selection rule $\Delta F = 0, \pm 1$ where $F = J+1$. For the strongest transitions $\Delta F = 0$.

The microwave spectrum of OH was first investigated by Dousmanis et al(44) who fit the observed transition frequencies using the appropriate intermediate coupled wave functions. The molecular parameters have been summarized recently by Lovas and Tiemann(33) using the best available data. The peak absorption coefficients for a number of transitions in ^{16}OH were calculated by Wacker et al(42) assuming T = 300 K and a linewidth parameter $(\Delta\nu)_1$ = 8 MHz/torr reported by Dousmanis et al.(44) However, in measurements of the $^2\Pi_{3/2}$, J = 9/2, F = 4 → 4 and F = 5 → 5 transitions by Radford,(45) a value of only 3.75 MHz/torr was found for $(\Delta\nu)_1$. This variation in linewidth is probably due to the fact that the unstable OH radicals are never present in the absorption cell or cavity at 100% concentration. Hence the linewidth will depend upon the other constituents present. The frequencies and absorption coefficients assuming a linewidth of 5 MHz/torr are given in Table 13 for a number of transitions which have been observed.

Oxygen

Because of its symmetry, the homonuclear molecule $^{16}O_2$ has a zero permanent electric dipole moment. However, its $^3\Sigma$ electronic ground state contributes a net electronic spin S = 1, which couples with the end-over-end rotation to produce a molecular fine-structure splitting of the rotational energy levels. Magnetic dipole transitions between these levels lead to an absorption spectrum extending over a band of frequencies centered approximately at 60 GHz with an additional isolated line occurring at about 118.7 GHz. The dipole selection rules are $\Delta N = 0$, $\Delta J = \pm 1$ where N and J = N + S are the rotational and total angular momentum quantum numbers. The transition $J = N \pm 1 \rightarrow J = N$ can be identified by the line designation $N^{\pm}$. Other transitions in which $\Delta N \neq 0$ have been observed but occur at frequencies above 350 GHz.

Using the most recent values for the molecular constants, Liebe(46) has calculated the frequencies and absorption coefficients for the dipole transitions. The results for a number of representative transitions are shown in Table 14. A constant value of 1.80 MHz/torr for the linewidth parameter $(\Delta\nu)_1$ was used in calculating the absorption coefficients, although an approximate expression,

$$(\Delta\nu)_1^N = 1.98 - 0.023N \text{ MHz/torr}$$

has been given(47) to account for a dependence of $(\Delta\nu)_1$ on the quantum number N.

A careful measurement of the 9^+ transition at 61.15 GHz by Liebe(47) yielded the value 1.77 MHz/torr for $(\Delta\nu)_1$ and agreement to within less than 5% with the calculated absorption coefficient. This measurement and a number of other less precise results summarized in reference (46) are shown in Table 14.

It should be pointed out that the oxygen microwave spectrum is complicated by a Zeeman-splitting of each level into 2J+1 sub-levels by a static magnetic field. Even in the earth's field (∿0.5 gauss) the splitting(46) can amount to as much as 2 MHz, a resolvable effect at pressures below about 1 torr.

Sulfur Monoxide

The $^3\Sigma$ electronic ground state of the sulfur monoxide radical, SO is similar to that of oxygen. Each rotational level is split by interactions with the electronic spin (S=1) into a triplet with components designated by the total angular momentum quantum numbers $J = N-1, N, N+1$, where N is the rotational quantum number. The observed transitions are electric dipole with $\Delta J = 0, \pm 1$ and $\Delta N = \pm 1$.

The available data on the microwave spectrum of SO has been critically reviewed by Tiemann(48) who calculated the frequencies, line strengths and associated energy levels for all rotational transitions up to 350 GHz. Using these values the peak absorption coefficients for $^{32}S^{16}O$ were calculated for T = 300K and an assumed linewidth parameter of 15 MHz/torr. In performing the calculation, equation (8) and (9) were used with the classical expression, $Q_{class} = kT/hB$ for the rotational partition function replaced by the value $Q_r = 3\ Q_{class}$ to account(35) for the spin multiplicity, 2S+1. The results are shown in Table 15. No measurements of the absorption coefficients for SO have been reported.

V. Discussion

Calculations have been given of the microwave absorption coefficients of a number of polar molecules of interest to atmospheric pollution studies. The results are in most cases in good agreement with experimental data where available. As expected the absorption coefficients increase rapidly with frequency. This is particularly true for the Σ^1 linear molecules where the simple form of equation (13) applies. For asymmetric molecules a similar trend exists although the actual intensities depend dramatically on the specific states involved.

It is useful to consider possible ranges of frequencies where suitable transitions might be found for multi-component detection. With klystron sources operating in the vicinity of 70 GHz approximately 10% bandwidths are possible. In the range 67-73 GHz, for example, reasonably intense transitions are found for SO_2, NO_2, O_3, H_2CO and OCS. When these gases are diluted to low concentration in air or nitrogen, significantly narrower linewidths and therefore correspondingly larger absorption coefficients are found. Calculated and estimated values for the air broadened linewidths of the above molecules are shown in Table 16 where the corrected absorption coefficients are also given. If a spectrometer with an ultimate sensitivity of 5×10^{-11} cm^{-1} for a time constant of 10 seconds were available, detection limits ranging from less than 100 ppb for SO_2, H_2CO and OCS to about 3 ppm for NO_2 without preconcentration should be attainable.

Further increases in predicted sensitivity are of course possible at higher frequencies. However, these must be weighed carefully against the rapidly increasing technical difficulties inherent in high frequency spectrometer design.

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Table 1

Microwave Absorption Coefficients for SO_2

Transition		Frequency[a]	Calc.[b] Abs. Coef.	Meas.[c] Abs. Coef.	Meas.[c] Linewidth
Upper State	Lower State	MHz	cm^{-1}	cm^{-1}	MHz/Torr
22(5,17)	23(4,20)	12 132.5	3.4×10^{-6}		
24(4,20)	23(5,19)	22 482.5	1.2×10^{-5}		
17(2,16)	16(3,13)	28 858.0	1.7×10^{-5}	1.8×10^{-5}	18
26(6,20)	27(5,23)	34 097.8	1.9×10^{-5}	2.1×10^{-5}	18
15(4,12)	16(3,13)	38 518.3	3.3×10^{-5}	3.7×10^{-5}	19
14(2,12)	13(3,11)	47 913.4	7.0×10^{-5}		
2(1, 1)	2(0, 2)	53 528.9	1.2×10^{-4}		
4(1, 3)	4(0, 4)	59 224.9	2.6×10^{-4}		
6(1, 5)	6(0, 6)	68 972.1	4.6×10^{-4}	4.5×10^{-4}	15
14(4,10)	15(3,13)	69 464.1	9.7×10^{-5}	1.0×10^{-4}	19
6(0, 6)	5(1, 5)	72 758.2	2.8×10^{-4}	2.7×10^{-4}	14
8(1, 7)	8(0, 8)	83 688.1	7.3×10^{-4}		
18(5,13)	19(4,16)	91 550.5	2.0×10^{-4}		
7(3, 5)	8(2, 6)	97 702.4	1.4×10^{-4}		
10(1, 9)	10(0,10)	104 239.3	1.1×10^{-3}		
8(0, 8)	7(1, 7)	116 980.4	1.0×10^{-3}		
12(2,10)	12(1,11)	128 605.1	2.3×10^{-3}		
14(2,12)	14(1,13)	132 744.8	2.7×10^{-3}		
16(2,14)	16(1,15)	143 057.0	3.1×10^{-3}		
18(2,16)	18(1,17)	160 342.9	3.6×10^{-3}		
7(1, 7)	6(0, 6)	165 225.4	2.1×10^{-3}		
7(2, 6)	7(1, 7)	175 275.7	1.7×10^{-3}		
20(2,18)	20(1,19)	184 969.8	4.3×10^{-3}		
9(2, 8)	9(1, 9)	188 654.9	2.2×10^{-3}		
22(3,19)	22(2,20)	195 320.4	5.2×10^{-3}		

[a] Calculated frequencies from Ref. 17.

[b] Calculated absorption coefficients from Ref. 17 with T = 297 K, $\mu = 1.634$ D, $f_v = 0.917$, $i_c = 0.945$ and $(\Delta\nu)_1 = 16$ MHz/torr (except where measured).

[c] Measured values below 40 GHz, W. F. White, Ref. 21, above 40 GHz, Ref. 17.

Table 2

Microwave Absorption Coefficients for O_3

Transition		Frequency[a]	Calc.[b] Abs. Coef.
Upper State	Lower State	MHz	cm^{-1}
23(4,20)	24(3,21)	14 866.5	2.9×10^{-6}
18(3,15)	19(2,18)	23 859.5	9.0×10^{-6}
15(3,13)	16(2,14)	30 051.7	1.7×10^{-5}
18(2,16)	17(3,15)	37 832.4	2.8×10^{-5}
12(2,10)	13(1,13)	43 653.1	2.3×10^{-5}
7(2, 6)	8(1, 7)	53 688.1	4.5×10^{-5}
16(3,13)	17(2,16)	61 926.7	6.5×10^{-5}
6(0, 6)	5(1, 5)	67 356.2	1.5×10^{-4}
12(1,11)	11(2,10)	76 533.7	1.5×10^{-4}
2(1, 1)	2(0, 2)	96 228.4	2.8×10^{-4}
4(1, 3)	4(0, 4)	101 736.7	5.4×10^{-4}
6(1, 5)	6(0, 6)	110 835.9	8.4×10^{-4}
8(1, 7)	8(0, 8)	124 087.3	1.2×10^{-3}
19(4,16)	20(3,17)	136 860.2	2.8×10^{-4}
14(1,13)	13(2,12)	144 919.4	6.3×10^{-4}
12(1,11)	12(0,12)	165 784.4	2.2×10^{-3}
18(4,14)	19(3,17)	175 445.8	4.7×10^{-4}
10(0,10)	9(1, 9)	184 377.8	2.0×10^{-3}
14(1,13)	14(0,14)	195 430.2	2.8×10^{-3}

[a] Calculated using parameters from Ref. 22.

[b] Calculated absorption coefficients assuming T = 300 K, $\mu = 0.532$ D, $f_v = 0.954$, $i_c = 0.993$ and $(\Delta\nu)_1 = 4.6$ MHz/torr.

Table 3

Microwave Absorption Coefficients for H_2O[a]

Transition		Frequency	Calc. Abs. Coef.	Meas. Abs. Coef.	Meas. Linewidth
Upper State	Lower State	MHz	cm^{-1}	cm^{-1}	MHz/Torr
6(1,6)	5(2,3)	22 235.1	7.4×10^{-6}	7.2×10^{-6}	18
3(1,3)	2(2,0)	183 310.1	1.3×10^{-3}		19

[a] Data from Liebe, Ref. 24.

Table 4

Microwave Absorption Coefficients for NO_2

Transition		Frequency[a]	Calc. Abs. Coef.
Upper State	Lower State	MHz	cm^{-1}
7(1, 7)	8(0, 8)	15 539.3	1.1×10^{-6}
24(1,23)	23(2,22)	26 569.2	1.9×10^{-6}
21(2,20)	22(1,21)	39 247.3	4.1×10^{-6}
10(0,10)	9(1, 9)	40 661.4	9.5×10^{-6}
5(1, 5)	6(0, 6)	70 589.7	1.7×10^{-5}
37(3,35)	38(2,36)	81 100.0[b]	3.4×10^{-6}
12(0,12)	11(1,11)	98 100.0[b]	6.3×10^{-5}
19(2,18)	20(1,19)	103 900.0[b]	3.1×10^{-5}
32(2,30)	33(1,33)	118 200.0[b]	7.5×10^{-6}
3(1, 3)	4(0, 4)	124 474.6	3.4×10^{-5}
14(0,14)	13(1,13)	156 000.0[b]	1.7×10^{-4}
17(2,16)	18(1,17)	168 000.0[b]	8.3×10^{-5}
1(1, 1)	2(0, 2)	177 460.0	2.3×10^{-5}
24(2,22)	25(1,25)	188 000.0[b]	5.1×10^{-5}

[a] Measured frequencies from Ref. 25, 26, 27 except where noted.

[b] Approximate frequencies for unmeasured transitions estimated using a rigid rotor Hamiltonian.

[c] Calculated absorption coefficients are for the strongest hyperfine component only and were obtained by assuming this component to be 20% of the total absorption for the transition. Total absorption coefficients were calculated for $T = 300$ K, $\mu' = 0.316$ D, $f_v = 0.97$, $i_c = 0.99$, and $(\Delta\nu)_1 = 4$ MHz/torr.

Table 5

Microwave Absorption Coefficients for H_2S

Transition		Frequency[a]	Calc.[b] Abs. Coef.
Upper State	Lower State	MHz	cm^{-1}
3(3,1)	4(0,4)	35 028.0	5.7×10^{-8}
7(1,6)	6(4,3)	89 498.2	3.4×10^{-7}
4(2,2)	5(1,5)	119 664.5	5.2×10^{-7}
7(3,4)	8(2,7)	161 438.3	7.2×10^{-7}
1(1,0)	1(0,1)	168 762.8	1.0×10^{-2}
7(2,6)	6(3,3)	175 009.4	8.9×10^{-7}
7(4,4)	8(1,7)	185 100.0	3.1×10^{-7}

[a] Measured frequencies from Helminger, Ref. 29.

[b] Absorption coefficients calculated assuming $T = 300$ K, $\mu = 0.974$ D, $f_v = 1.0$, $i_c = 0.95$, and $(\Delta\nu)_1 = 15$ MHz/torr.

Table 6

Microwave Absorption Coefficients for H_2CO

Transition		Frequency	Calc. Abs. Coef.	Meas. Abs. Coef.	Meas. Linewidth
Upper State	Lower State	MHz	cm^{-1}	cm^{-1}	MHz/Torr
2(1, 1)	2(1, 2)	14 488.5	2.8×10^{-5}		
3(1, 2)	3(1, 3)	28 974.8	7.3×10^{-5}	8.1×10^{-5}	23
18(3,15)	18(3,16)	33 270.6	1.9×10^{-5}	2.0×10^{-5}	20
10(2, 8)	10(2, 9)	34 100.0	1.7×10^{-5}	1.9×10^{-5}	29
4(1, 3)	4(1, 4)	48 284.5	1.6×10^{-4}		
20(3,17)	20(3,18)	59 896.9	3.1×10^{-5}		
5(1, 4)	5(1, 5)	72 409.1	2.7×10^{-4}	2.6×10^{-4}	22
1(0, 1)	0(0, 0)	72 838.0	2.3×10^{-4}	2.3×10^{-4}	29
13(2,11)	13(2,12)	89 565.0	7.5×10^{-5}		
6(1, 5)	6(1, 6)	101 333.0	4.2×10^{-4}		
14(2,12)	14(2,13)	116 718.6	1.0×10^{-4}		
7(1, 6)	7(1, 7)	135 030.5	5.9×10^{-4}		
2(1, 2)	1(1, 1)	140 839.5	4.9×10^{-3}		
2(1, 1)	1(1, 0)	150 498.4	5.6×10^{-3}		
8(1, 7)	8(1, 8)	173 461.8	7.9×10^{-4}		
16(2,14)	16(2,15)	185 606.7	1.5×10^{-4}		

[a] Frequencies from Johnson et al, Ref. 30.

[b] Calculated using line strengths from Ref. 30 and T = 300 K, $\mu = 2.331$ D, $f_v = 0.99$, $i_c = 0.986$ and $(\Delta\nu)_1 = 22$ MHz/torr, except where measured.

[c] Measured values below 40 GHz, W. F. White, Ref. 31; above 40 GHz, this work.

Table 7

Microwave Absorption Coefficients for NH_3

Rotational Level	Frequency[a]	Calc.[a] Abs. Coef.	Meas.[b] Abs. Coef.	Meas.[b] Linewidth
J,K	MHz	cm^{-1}	cm^{-1}	MHz/Torr
6, 3	19 757.6	1.0×10^{-4}	1.0×10^{-4}	19
5, 2	20 371.5	5.4×10^{-5}	4.6×10^{-5}	16
6, 4	20 994.6	9.8×10^{-5}	9.7×10^{-5}	22
5, 3	21 285.3	2.3×10^{-4}	2.2×10^{-4}	20
7, 6	22 924.9	3.3×10^{-4}	3.0×10^{-4}	23
3, 3	23 870.1	8.0×10^{-4}	8.3×10^{-4}	27
6, 6	25 056.0	7.0×10^{-4}	6.4×10^{-4}	28
8, 8	26 518.9	2.1×10^{-4}	2.2×10^{-4}	28
10,10	28 604.7	9.4×10^{-5}	1.0×10^{-4}	28
11,11	29 914.6	5.7×10^{-5}	6.0×10^{-5}	28
12,12	31 425.0	6.5×10^{-5}	6.8×10^{-5}	28
13,13	33 157.0	1.8×10^{-5}	2.0×10^{-5}	27

[a] From C. H. Townes and A. L. Schawlow, Ref. 9. Calculated absorption coefficients have been adjusted to correspond to observed linewidth data.

[b] Measured data for frequencies below 26 GHz from Bleaney and Penrose, Ref. 32, and above 26 GHz from White, Ref. 21.

Table 8

Microwave Absorption Coefficients for CO

Transition	Frequency[a]	Calc.[b] Abs. Coef.
J+1 ← J	MHz	cm^{-1}
1 ← 0	115 271.2	2.1×10^{-4}
2 ← 1	230 538.0	1.6×10^{-3}

[a] Frequencies from Lovas, Ref. 33.

[b] Absorption coefficients calculated assuming $T = 300$ K, $\mu = 0.112$ D, $f_v = 0.995$, $i_c = 0.99$, and $(\Delta\nu)_1 = 5$ MHz/torr.

Table 9

Microwave Absorption Coefficients for OCS

Transition J+1 ← J	Frequency[a] MHz	Calc.[b] Abs. Coef. cm^{-1}
1 ← 0	12 163.0	6.1×10^{-6}
2 ← 1	24 325.9	4.9×10^{-5}
3 ← 2	36 488.8	1.7×10^{-4}
4 ← 3	48 651.6	3.8×10^{-4}
5 ← 4	60 814.3	7.6×10^{-4}
6 ← 5	72 976.8	1.3×10^{-3}
7 ← 6	85 139.1	2.1×10^{-3}
8 ← 7	97 301.2	3.1×10^{-3}
9 ← 8	109 463.1	4.4×10^{-3}
10 ← 9	121 624.6	6.0×10^{-3}
11 ← 10	133 785.9	8.1×10^{-3}
12 ← 11	145 946.8	1.0×10^{-2}
13 ← 12	158 107.4	1.3×10^{-2}
14 ← 13	170 267.5	1.6×10^{-2}
15 ← 14	182 427.2	2.0×10^{-2}
16 ← 15	194 586.4	2.5×10^{-2}

[a] Frequencies from Maki, Ref. 36.

[b] Absorption coefficients computed assuming $T = 300$ K, $\mu = 0.71515$ D, $f_v = 0.828$, $i_c = 0.937$ ($^{16}O^{12}C^{32}S$) and $(\Delta\nu)_1 = 6.4$ MHz/torr.

Table 10

Comparison of Measured and Calculated Absorption Coefficients for OCS

Species	Transition	Frequency	Calc. Abs. Coef.	Meas. Abs. Coef.	Meas. Linewidth
	J+1 ← J	MHz	cm^{-1}	cm^{-1}	MHz/Torr
$OC^{32}S$	2 ← 1[a]	24 325.9	5.1×10^{-5}	5.2×10^{-5}	6.1
$OC^{34}S$	2 ← 1[b]	23 731.3	2.1×10^{-6}	2.1×10^{-6}	6.4[c]
$OC^{32}S$	3 ← 2[d]	36 488.8	1.7×10^{-4}	2.0×10^{-4}	6.4
$OC^{34}S$	3 ← 2[d]	35 596.9	7.2×10^{-6}	7.9×10^{-6}	6.3
$OC^{32}S$	6 ← 5[e]	72 976.8	1.3×10^{-3}	1.2×10^{-3}	6.4
$OC^{34}S$	6 ← 5[e]	71 193.0	5.5×10^{-5}	5.6×10^{-5}	6.2

[a] Measured values from Gilbert, Ref. 37 T = 302 K.

[b] Measured values from Dymanus, Ref. 38 T = 297 K.

[c] Linewidth not measured. 6.4 MHz/torr assumed.

[d] Measured values from White, Ref. 21 T = 293 K.

[e] This work. T = 297 K.

Table 11

Microwave Absorption Coefficients for N_2O

Transition	Frequency[a]	Calc.[b] Abs. Coef.
$J+1 \leftarrow J$	MHz	cm^{-1}
$1 \leftarrow 0$	25 123.3	3.9×10^{-6}
$2 \leftarrow 1$	50 246.4	3.1×10^{-5}
$3 \leftarrow 2$	75 369.2	1.1×10^{-4}
$4 \leftarrow 3$	100 491.7	2.5×10^{-4}
$5 \leftarrow 4$	125 613.7	4.8×10^{-4}
$6 \leftarrow 5$	150 735.0	8.4×10^{-4}
$7 \leftarrow 6$	175 855.6	1.3×10^{-3}

[a] Pearson et al, Ref. 39.

[b] Absorption coefficients calculated assuming $T = 300$ K, $\mu = 0.1608$ D, $f_v = 0.883$, $i_c = 0.990$ ($^{14}N_2{}^{16}O$) and $(\Delta\nu)_1 = 5$ MHz/torr.

Table 12

Microwave Absorption Coefficients for NO

Transition			Frequency	Calc.[b] Abs. Coef.	Meas.[a] Abs. Coef.
Electronic	J+1 ← J	F+1 ← F	MHz	cm^{-1}	cm^{-1}
$^2\Pi^+_{1/2}$	3/2←1/2	5/2←3/2	150 176.3	2.3×10^{-4}	1.2×10^{4}
$^2\Pi^+_{1/2}$		3/2←1/2	150 198.5	8.8×10^{-5}	5.5×10^{-5}
$^2\Pi^-_{1/2}$		5/2←3/2	150 546.2	2.3×10^{-4}	1.3×10^{-4}
$^2\Pi^-_{1/2}$		3/2←1/2	150 644.1	8.8×10^{-5}	6.3×10^{-5}
$^2\Pi^+_{1/2}$	5/2←3/2	7/2←5/2	250 435.6	9.8×10^{-4}	
$^2\Pi^+_{1/2}$		5/2←3/2	250 439.2	6.4×10^{-4}	
$^2\Pi^-_{1/2}$		7/2←5/2	250 795.0	9.8×10^{-4}	
$^2\Pi^-_{1/2}$		5/2←3/2	250 814.6	6.4×10^{-4}	

[a] Measured values from French et al, Ref. 43.

[b] Calculated values from Wacker et al, Ref. 42, assuming T = 300 K and $(\Delta\nu)_1 = 2.8$ MHz/torr.

Table 13

Microwave Absorption Coefficients for OH

Transition			Frequency[a]	Calc.[b] Abs. Coef.
Electronic	J	F	MHz	cm^{-1}
$^2\Pi_{1/2}$	3/2	F = 1→1	7 761.7	5.9×10^{-6}
		F = 2→2	7 820.1	1.1×10^{-5}
	5/2	F = 2→2	8 135.9	3.5×10^{-6}
		F = 3→3	8 189.6	5.3×10^{-6}
$^2\Pi_{3/2}$	7/2	F = 3→3	13 434.6	6.7×10^{-5}
		F = 4→4	13 441.4	9.6×10^{-5}
	9/2	F = 4→4	23 817.6	8.5×10^{-5}
		F = 5→5	23 826.6	1.0×10^{-4}
	11/2	F = 5→5	36 983.5	6.4×10^{-5}
		F = 6→6	36 994.4	7.5×10^{-5}

[a] Frequencies obtained from Ref. 33.

[b] Calculated absorption coefficients from Ref. 42, assuming $(\Delta\nu)_1$ = 5 MHz/torr.

Table 14

Microwave Absorption Coefficients for O_2

Transition	Frequency[a]	Calc.[a] Abs. Coef.	Meas.[b] Abs. Coef.
$N^{\pm}$	MHz	cm^{-1}	cm^{-1}
35^-	50 987.3	1.9×10^{-8}	
31^-	52 021.2	1.1×10^{-7}	
27^-	53 066.8	5.0×10^{-7}	
23^-	54 130.0	1.8×10^{-6}	
15^-	56 363.4	1.1×10^{-5}	
9^-	58 323.9	2.1×10^{-5}	1.8×10^{-5}
3^+	58 446.6	1.3×10^{-5}	1.1×10^{-5}
5^+	59 591.0	1.9×10^{-5}	1.4×10^{-5}
9^+	61 150.6	2.3×10^{-5}	2.3×10^{-5}
3^-	62 486.3	1.4×10^{-5}	
17^+	63 568.5	1.0×10^{-5}	
21^+	64 678.9	4.4×10^{-6}	
25^+	65 764.7	1.5×10^{-6}	
29^+	66 836.7	3.9×10^{-7}	
33^+	67 900.7	8.0×10^{-8}	
37^+	68 960.1	1.3×10^{-8}	
1^-	118 750.3	1.6×10^{-5}	1.5×10^{-5}

[a] From Liebe, Ref. 46. Absorption coefficients calculated assuming T = 300 K and $(\Delta\nu)_1 = 1.80$ MHz/torr.

[b] Measured data summarized in Ref.46.

Table 15

Microwave Absorption Coefficients for SO

Transition	Frequency[a]	Calc.[b] Abs. Coef.
$J',N' \leftarrow J,N$	MHz	cm^{-1}
$1,2 \leftarrow 1,1$	13 043.7	2.8×10^{-5}
$1,0 \leftarrow 0,1$	30 001.6	1.0×10^{-4}
$2,3 \leftarrow 2,2$	36 201.8	1.1×10^{-4}
$2,1 \leftarrow 1,0$	62 931.8	9.1×10^{-4}
$3,4 \leftarrow 3,3$	66 034.9	2.3×10^{-4}
$2,2 \leftarrow 1,1$	86 094.0	1.3×10^{-3}
$3,2 \leftarrow 2,1$	99 299.9	3.4×10^{-3}
$4,5 \leftarrow 4,4$	100 029.6	3.8×10^{-4}
$2,3 \leftarrow 1,2$	109 252.1	2.0×10^{-3}
$3,3 \leftarrow 2,2$	129 138.9	5.0×10^{-3}
$5,6 \leftarrow 5,5$	136 634.9	5.3×10^{-4}
$4,3 \leftarrow 3,2$	138 178.6	8.7×10^{-3}
$3,4 \leftarrow 2,3$	158 971.8	7.6×10^{-3}
$4,4 \leftarrow 3,3$	172 181.3	1.2×10^{-2}
$6,7 \leftarrow 6,6$	174 929.3	6.7×10^{-4}
$5,4 \leftarrow 4,3$	178 605.2	1.8×10^{-2}

[a] Frequencies from Tiemann, Ref. 48.

[b] Absorption coefficients calculated as in text assuming $T = 300$ K, $\mu = 1.55$ D, $f_v = 1$, $i_c = 0.95$ and $(\Delta\nu)_1 = 15$ MHz/torr.

Table 16

Microwave Absorption by Air Diluted Gases at 70 GHz

Molecule	Transition		Frequency	Linewidth	Calc.[f] Abs.Coef.
	Upper	Lower	MHz	MHz/torr	cm^{-1}
SO_2	6(1,5)	6(0,6)	68 972.1	4.2[a]	1.6×10^{-3}
NO_2	5(1,5)	6(0,6)	70 589.7	4.0[b]	1.7×10^{-5}
O_3	6(0,6)	5(1,5)	67 356.2	2.3[c]	3.0×10^{-4}
H_2CO	5(1,4)	5(1,5)	72 409.1	7.0[d]	8.5×10^{-4}
OCS	6	5	72 976.8	4.1[e]	2.0×10^{-3}

[a] Calculated air-broadened value from G. D. T. Tejwani, University of Tennessee Research Report No. UTPA-ERAL-02, cited in Ref. 14.

[b] Calculated air-broadened linewidths for NO_2 were found to be approximately the same as for self-broadening, G. D. T. Tejwani, Ref. 14.

[c] Calculated value from G. D. T. Tejwani and E. S. Young, Ref. 16.

[d] Measured N_2-broadened value for 3(1,2)-3(1,3) transition, Srivastava et al, Ref. 49.

[e] Measured N_2-broadened value for 2-3 transition, Srivastava et al, Ref. 49.

[f] Absorption coefficients obtained by multiplying coefficient values obtained above by appropriate linewidth ratio.

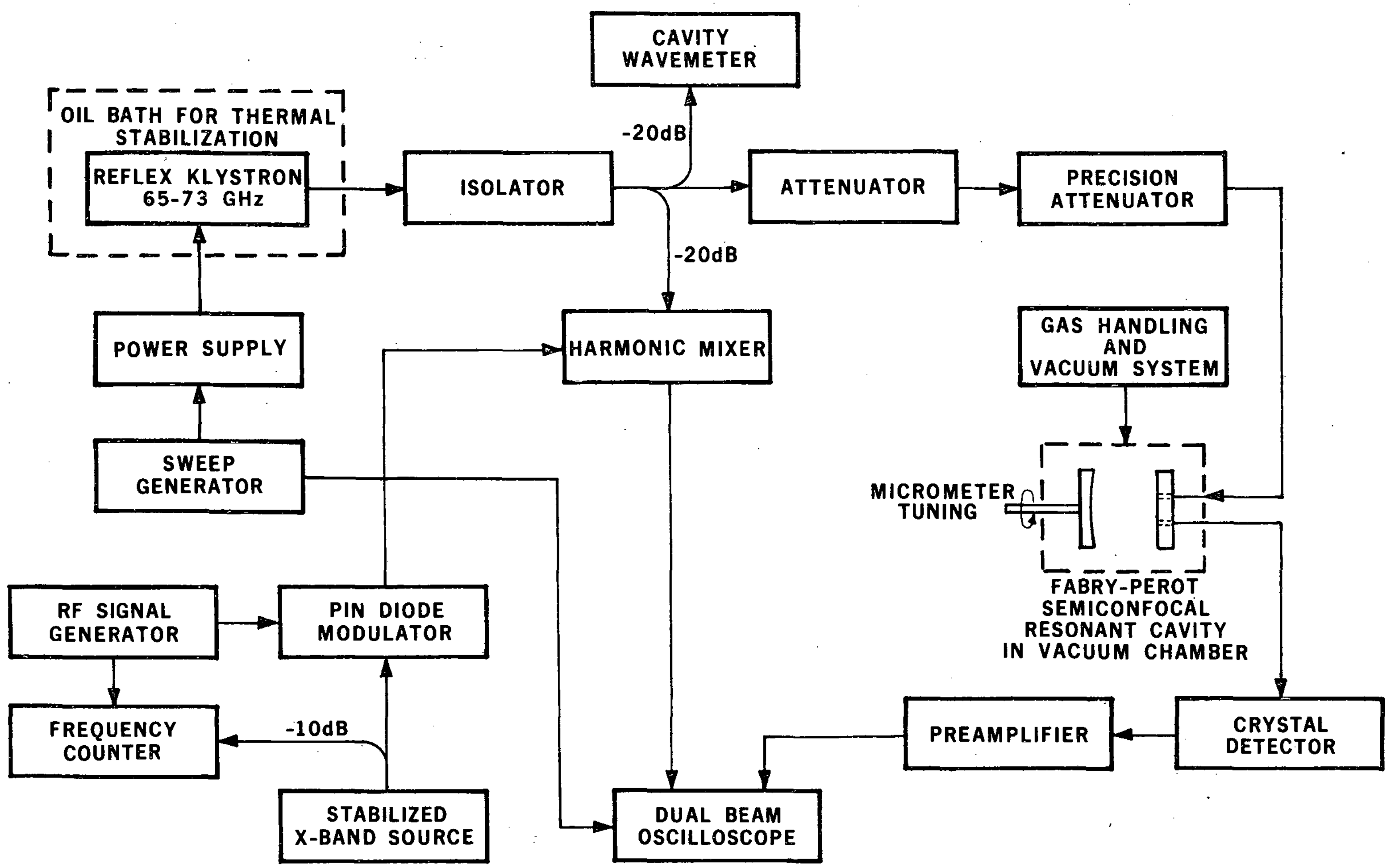

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Fig. 1. Block diagram of measurement apparatus.

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