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MICROWAVE SPECTROMETER FOR THE DETECTION
OF TRANSIENT GASEOUS SPECIES

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Microwave Spectrometer for the
Detection of Transient Gaseous Species

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Abstract

A microwave spectrometer and associated apparatus for the detection of unstable free radical species is described. The spectrometer, which operates over a frequency range from 66 to 73 GHz, consists of a tunable Fabry-Perot resonator followed by superheterodyne detection for high sensitivity at low power levels. The resonator tuning is accomplished by means of a computer controlled stepping motor and by a piezoelectric transducer which also permits the use of source modulation and phase sensitive detection at 100 Hz. The sensitivity of the spectrometer is adequate to permit the detection of rotational transitions with absorption coefficients as small as $2 \times 10^{-9} \text{ cm}^{-1}$.

The operation of the spectrometer is demonstrated by the detection of the two free radical species OH and SO. In the case of OH, a number of A-doubling transitions, previously unobserved, are reported.

1. Introduction

Free radical products and intermediaries have been extensively studied (1-4) in gas-phase reactions induced photochemically, thermally in flames, and by direct admixture of active species such as H and O atoms. In such studies it is important to determine the concentrations of the free radical species as a function of time after the initiation of the reaction. In

direct reactions (such as described in this report) a flow tube, in which the velocity of the flowing gas is known, is used to transform reaction time into a distance measured downstream from the reaction zone.

Measurements of the concentration of the free radical species have been made using a number of techniques including mass spectrometry (1,2), optical absorption or fluorescence (1,5) and gas phase electron spin resonance (ESR) (1,3).

Microwave spectroscopy as a technique for the measurement of free radical species is similar to gas phase ESR except that an electromagnet is not used to Zeeman tune a particular transition to the frequency of the spectrometer. Instead, the frequency of observation is chosen to correspond to a selected transition in zero field.

In the past we have developed (6,7) a spectrometer operating in the frequency range of 66-73 GHz for the detection of stable species of interest in environmental and energy research. The sensitivity of this spectrometer (8) is such that it can detect polar molecules with absorption coefficients as small as $2 \times 10^{-9} \text{ cm}^{-1}$ with a time constant of 1 second. For a molecule such as SO_2 this sensitivity corresponds to a detection limit of 1.2 ppm without preconcentration.

In this report, modifications of the spectrometer are described which make possible the detection of unstable species. Using this instrument we report the observation of a number of transitions of the free radicals OH and SO. As will be seen, the sensitivity of the spectrometer is sufficient to permit the observation of several OH A-doubling transitions previously unreported.

In the following section, the operation of the spectrometer is described. The design of the gas handling equipment and procedures used to generate the unstable species are also discussed. In section 3, measurements of the two species, OH and SO are reported, and in section 4, these results are compared to previous values available in the literature. A discussion of the intensities of the various absorption lines is given. Finally, an appendix is provided in which the absorption coefficients of the Λ -doubling transitions of OH are calculated.

2. Experimental Apparatus

2.1 Microwave Spectrometer

The free radical species were detected using a superheterodyne microwave spectrometer operating over a frequency range of 66-73 GHz. The operation of the spectrometer, which has been described in greater detail elsewhere (8) is illustrated by the block diagram in Fig. 1. The major components of the system include a Fabry-Perot microwave cavity absorption cell mounted in a vacuum enclosure, a signal oscillator, local oscillator, and low-noise receiver.

The Fabry-Perot transmission cavity (9,10a) serves as the gas absorption cell. It consists of two opposing mirrors 5 cm in diameter. One mirror is flat and contains two waveguide coupling ports. The other mirror is spherical with a curvature of 14.8 cm. The mirrors are mounted in a semi-confocal configuration with a spacing of approximately 7.4 cm. The cavity is tuned by moving the spherical mirror; a piezoelectric transducer provides fine tuning (6 MHz tuning range) and a stepping motor drive permits coarse tuning. The loaded Q of the cavity is approximately 67000.

The signal oscillator consists of a varactor tuned Gunn diode followed by a frequency doubler to yield up to 5 mW of microwave power at 70 GHz. The local oscillator, a klystron, is phase locked to the signal source with a 30 MHz offset frequency.

After passing through the cavity, the microwave signal is detected by the low-noise receiver (SSB NF = 11 dB). The output of the receiver, at 30 MHz, is further amplified and fed to a pair of 30 MHz phase detectors to yield a direct output, proportional to the gas absorption, and a quadrature output, proportional to the frequency difference between the cavity resonance and the signal oscillator. The latter signal is fed back to the varactor input of the Gunn diode thereby synchronizing the cavity frequency and the signal source.

The actual microwave frequency is determined by a frequency synthesizer controlled by a PDP 11/34 computer, via a CAMAC interface (10b). The output of the synthesizer is combined with a sample of the source oscillator frequency in a harmonic mixer. A narrow bandwidth discriminator tuned to 30 MHz converts the mixer output to a correction voltage which is fed to the piezoelectric transducer of the cavity. The spectrometer frequency is thereby maintained at the desired value for detection of the gas absorption signal.

To increase the system sensitivity, the gas absorption signal (at the direct output) is modulated and detected by a lock-in amplifier tuned to the modulation frequency. Two modulation schemes were investigated. In the first, the cavity and the source oscillator are source modulated at approximately 100 Hz with a deviation of about 0.2 MHz rms as shown in the block diagram, Fig. 1. Since the gas absorption occurs at a fixed frequency, the resultant signal at the output of the lock-in amplifier is approximately equal to the derivative of the gas absorption.

The second scheme investigated employed Zeeman modulation of the absorption lines. This method is applicable to free radical measurements because of the large magnetic interactions in these species. To produce the modulating field, the "field spinning" technique first described by Radford (11) and more recently employed by Destombes et al (12) was used. In this method sinusoidal modulation at a frequency $f/2$ is applied to two pairs of orthogonal Helmholtz coils surrounding the cavity. The two sets of Helmholtz coils are excited with a phase difference of $\pi/2$ thereby producing a rotating magnetic field of constant amplitude. The orientation of this field with respect to the microwave electric field is such that the $\pi(\Delta M = 0)$ and $\sigma(\Delta M = \pm 1)$ components of the transition are alternatively excited and detected by the lock-in amplifier tuned to a frequency f . The frequency f , was 25 kHz. The coils were also used to cancel out the earth's magnetic field, which, in the case of OH and SO, produced a significant broadening of the absorption lines at low pressure.

The computer system was programmed to sweep the microwave frequency over the desired range as described above, to collect and display the absorption signals and to control the cavity stepping motor. When desired, the signal-to-noise ratio could be improved by signal averaging a number of frequency scans.

2.2 Gas Handling and Radical Production

The free radicals OH (1) and SO (3) were generated using the gas phase chemical reactions:

The apparatus used to produce the radicals is shown in Fig. 2. A mixture of 5% H_2 (or 5% O_2) in Ar is passed through a calibrated flowmeter

(Matheson model 602 rotameter) to a quartz discharge tube. H (or O) atoms are produced by means of a microwave discharge cavity (ref. 13, cavity No. 5) powered by a diathermy machine at a frequency of 2450 MHz. The microwave power used ranged from 10 W to 60 W.

The H (O) atoms and Ar diluent pass into a mixing tube where NO_2 (OCS) measured by a second flowmeter (Matheson model 610 rotameter) is added through a moveable injector tube with a small pinhole at the end. The OH (SO) molecules produced are then pumped through the spectrometer cavity where they are detected. The total gas pressure in the cavity and mixing tube is measured by an MKS capacitance manometer.

To protect the radicals against decomposition by wall collisions, the glass components were carefully washed and rinsed with a dilute HF solution. The discharge tube was coated with a solution of boric acid and flame dried. The remainder of the glass surfaces were coated with a layer of halocarbon wax (14). A thin film of teflon particles (Fluoroglide, Chemplast Inc.) was sprayed on the spectrometer cavity mirrors.

By changing the position of the moveable injector with respect to the cavity, the reaction time before detection of the radicals could be varied. For a typical gas flow rate of 8.5 SCCM and a pressure of 0.06 torr, the flow velocity through the 13 mm I.D. mixing tube is approximately 1500 cm/sec. With a range of 13 cm for the injector, reaction delays up to about 8 msec could be obtained. In measurements of the flow rate of NO_2 , it is necessary to account for the dissociation equilibrium between NO_2 and its dimer N_2O_4 .

3. Free Radical Measurements

3.1 OH Measurements

The hydroxyl (OH) molecule (15) possesses an unpaired electron with orbital and spin angular momentum quantum numbers $L=1$ and $S=1/2$ resulting in a $^2\Pi$ electronic state.

The ground state is split by the spin-orbit interaction into a $^2\Pi_{3/2}$ level and a $^2\Pi_{1/2}$ level lying about 140 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 coupled to the molecular axis. The projections Λ and Σ of L and S along the molecular axis then combine with the rotational angular momentum of the molecule to form the total (exclusive of nuclear) angular momentum J. Because of the interactions between the rotational and electronic motions of the molecule, both L and S are somewhat decoupled from the molecular axis. This deviation from the ideal Hund's case (a) leads to a shift in the rotational levels and a splitting (Λ -doubling) of the levels for each value of J.

Because of the large rotational constant for OH, the pure rotational transitions lie in the near infrared and the observed spectrum in the microwave region is due to direct transitions between the Λ -doublets. Each Λ -doubling transition is further split by hyperfine interactions with the ^1H ($I = 1/2$) nucleus. The hyperfine transitions obey the selection rule $\Delta F = 0, \pm 1$, where $F = J + I$. For the strongest transitions, $\Delta F = 0$.

Because of the decomposition of the OH radicals following their production, the strongest signals are observed with the NO_2 injector located close to the spectrometer cavity. Most of the measurements were obtained with the injector located about 1 cm from the cavity entrance port.

Fig. 3 shows the $^2\Pi_{3/2}$, $J = 15/2$, $F = 8-8$ transition of ^1OH at a measured frequency of 70858.841 (20) MHz using source modulation at 93 Hz with a time constant of 1 sec. By applying an appropriate DC current to the two pairs of Helmholtz coils surrounding the cavity, the earth's magnetic field was cancelled thereby minimizing the linewidth. The observed signal-to-noise ratio is approximately 1000.

In Fig. 4 the same transition is shown for the isotopic species ^{18}OH observed in natural abundance. Because of the small amount (0.204%) of ^{18}O present, the signal observed is much weaker. Comparing the amplitudes of the two measurements, we find a ratio of 0.18% in reasonable agreement with the isotopic ratio. To improve the signal-to-noise ratio, the results obtained in Fig. 4 were obtained by the computer averaging of 25 scans followed by the subtraction of a small baseline error obtained with the H atom discharge turned off. The measured center frequency of the transition was 69910.546(50) MHz.

Measurements were made of the $F = 8-8$ transition of ^{16}OH using the "field spinning" Zeeman modulation technique. No difference in the measured microwave transition frequency was observed. However, it was difficult with the existing apparatus to obtain sufficient modulation amplitude to completely separate the π and σ components of the transition except at very low pressures, and to apply simultaneously the modulating and DC magnetic field compensation signals. The method was therefore abandoned in favor of the source modulation technique.

In addition to the two transitions described above, measurements were made of six other transitions in the same frequency region. The results are summarized in Table I. Of the eight transitions, only two have been observed previously. The results are further described in section 4.1.

3.2 SO Measurements

The $^3\Sigma$ electronic ground state of sulfur monoxide (16) 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. Each rotational level is split into 3 components designated by the total angular

momentum quantum numbers $J = N-1, N, N+1$, where N is the rotational quantum number. The electric dipole selection rules are $\Delta J = 0, \pm 1$ and $\Delta N = \pm 1$. In the present experiment the (3,4)-(3,3) transition is observed where the bracketed quantities refer to the J and N quantum numbers of the initial and final states.

As described above, SO was produced by the gas phase reaction of O atoms with OCS. Because the decomposition rate of the SO radicals is slower than their formation rate via the above reaction, the intensity of the SO signal increases as the injector is moved away from the spectrometer cavity.

Fig. 5 shows the observed signal for the (3,4)-(3,3) transition. The measured transition frequency is 66034.890 (50) MHz. Because of the large Zeeman effect, it is necessary to compensate for the earth's magnetic field.

4. Discussion

4.1 Spectroscopy of OH

The microwave spectrum and molecular constants of the OH molecule have recently been critically reviewed by Beaudet and Poynter (17). Using the best available frequency measurements and an appropriate Hamiltonian, they have computed the transition frequencies of all the lines observed in this report.

In Table I the measured frequencies (17a) obtained in this work are shown together with the calculated values reported by Beaudet and Poynter. The last column of the table shows the frequency difference between these two sets.

Of all the transitions reported here, only two, the $F = 7-7$ and $F = 8-8$ transitions of the $^2\Pi_{3/2}, J = 15/2$ state, have been measured previously (18) as shown in the third column of the table. Our measurements of these two

transitions are in fundamental agreement with these previous results although the frequency difference between them is slightly larger than the experimental uncertainties quoted. Comparable agreement with the calculated values is also obtained. For the weaker satellite transitions $F = 7-8$ and $F = 8-7$ not previously observed, agreement with the calculated values is obtained.

For the $^2\Pi_{1/2}$, $J = 19/2$, $F = 9-9$, and $F = 10-10$ transitions, the agreement with the calculated values is somewhat worse, the difference amounting to about 0.85 MHz. This is not too surprising since the highest frequency transitions previously observed (17) for the $^2\Pi_{1/2}$ electronic state were the $J = 13/2$, $F = 6-6$ and $F = 7-7$ transitions at 19.5 GHz. Because the molecular parameters were obtained from a fit of these lower J transitions, the calculated frequencies for $J = 19/2$ represent a significant extrapolation.

For ^{18}OH there is even less data available. The only transitions previously measured are for $J = 3/2$ and $J = 5/2$, the latter occurring at about 5.9 GHz. With so few data points available, it was necessary (17) to obtain many of the molecular parameters by isotopic scaling of the parameters for ^{16}OH . We find a difference of about 4.6 MHz between the observed and calculated frequencies.

4.2 Spectroscopy of SO

The microwave spectrum of SO has been reviewed recently by Tiemann (16). For the (3,4)-(3,3) transition, his calculated frequency is 66034.890(75) MHz in excellent agreement with the value 66034.895(50) MHz measured in this work. The result is also in agreement with the previously reported (19) measurement of 66034.94(20) MHz.

4.3 Intensities of Free Radical Transitions

The concentration of molecules produced in the microwave cavity can be determined by measuring the amplitude and linewidth of the microwave absorption signal. As described in reference 6 the change, ΔV in the voltage, V at the direct output of the spectrometer produced by the absorption is given by

$$\frac{\Delta V}{V} = \frac{c\gamma_0 Q_L}{2\pi\nu_0} \quad (3)$$

where Q_L is the cavity loaded Q , ν_0 is the frequency of the transition and γ_0 is the absorption coefficient.

Because the gas absorption is detected by means of source modulation followed by lock-in amplification at the modulation frequency, it is necessary to compute the effect of the modulation process on the observed signal. The calculation has been performed by Wahlquist (20) for the comparable case of a Lorentzian absorption line, Zeeman modulated by a sinusoidal magnetic field. A subroutine employing Wahlquist's analysis was incorporated in the computer program controlling the spectrometer and used to compare the calculated spectrum with the observed lineshape. The important parameters are the amplitude and linewidth of the observed signal, the rms amplitude of the modulation signal, the cavity Q and the absorption coefficient of the gas. The linewidth is determined by the product of the linewidth parameter $(\Delta\nu)_L$, and the measured gas pressure.

The method employed to compute the absorption coefficients for the OH Λ -doubling transitions is outlined in the appendix. The results for all the transitions observed in this report are summarized in Table II. In the table a temperature of 300 K and a pressure broadening linewidth parameter of 3.1 MHz/torr, comparable to that observed, is assumed. For ^{18}OH , the

absorption coefficients have been modified to account for the ratio (0.204%) of ^{18}O occurring in natural abundance. The absorption coefficient for the (3,4)-(3,3) transition of SO is given in Ref. 21. For a linewidth parameter of 5 MHz/torr and $T = 300$ K, we find $\gamma_0 = 6.9 \times 10^{-4} \text{ cm}^{-1}$.

In Fig. 6 is shown a comparison of a typical measurement of the OH $^2\pi_{3/2}$ $J = 15/2$, $F = 8-8$ transition and the theoretical curve derived by Wahlgvist. In calculating the theoretical curve, the following parameters were used: $\gamma_0 = 1.25 \times 10^{-4} \text{ cm}^{-1}$, $(\Delta\nu)_1 = 2.8$ MHz/torr, pressure = 0.120 torr, modulation amplitude = 0.139 MHz rms, $V = 8.5$ volts, and $Q_L = 67000$. The resulting concentration of OH radicals produced is 0.0064.

The concentration of radicals produced is a function of the operating parameters of the gas handling system, including the H_2 :Ar and NO_2 flow rates, the power applied to the discharge cavity, and the position of the NO_2 injector. For example, the concentration of OH radicals computed for the measurement shown in Fig. 3 is somewhat larger than that of Fig. 6, amounting to about 0.02.

The maximum concentration of OH radicals which can be produced by the present apparatus is limited by the 5% concentration of H_2 in the H_2 :Ar mixture used as a reactant. If all the H_2 molecules in this mixture were dissociated in the discharge cavity and all of the resulting H atoms survived to be converted to OH by reaction (1), then the maximum OH concentration would be 10%. The observed concentration is thus 8 to 20% of the theoretical maximum. A significant increase in the OH concentration would not be expected to result from an increase of the H_2 concentration in the supply gas since the recombination rate for the H atoms would then be larger.

The minimum concentration of OH that can be detected by the spectrometer using the $^2\pi_{3/2} J = 15/2, F = 8-8$ transition can be estimated from the calculated absorption coefficient and the minimum detectable absorption coefficient of $2 \times 10^{-9} \text{ cm}^{-1}$ previously reported for this spectrometer. With $\gamma_o = 1.2 \times 10^{-4}$ we have for the minimum concentration about 16 parts per million.

The concentration of SO molecules produced by the reaction of O atoms with OCS can be determined using the above analysis. For the data of Fig. 5, we find with $\gamma_o = 6.9 \times 10^{-6} \text{ cm}^{-1}$, $(\Delta\nu)_1 = 5 \text{ MHz/torr}$, pressure = 0.120 torr, modulation amplitude = 0.15 MHz, and $V = 8.07$ volts, a concentration of 0.0057. The absorption coefficient for SO is somewhat larger than that of OH, and the limiting detectable concentration for the given spectrometer sensitivity is about 3 parts per million.

5. Appendix: Intensities of OH Transitions

The peak absorption coefficient, γ_o for a microwave transition in the pressure broadening regime is given (21) by:

$$\gamma_o = 3.219 \times 10^{10} \frac{8\pi^2 \nu_o^2}{3ckT Q_r (\Delta\nu)_1} \frac{i_c f_v}{\mu^2 S_{ij}} \exp(-E/kT) \quad (\text{A1})$$

where ν_o is the transition frequency in MHz, $(\Delta\nu)_1$ is the linewidth parameter in MHz/torr, μ is the electric dipole moment in Debye units, S_{ij} is the line strength for the transition, E is the energy of the lower state, of the transition, i_c is the isotopic concentration, f_v is the fraction of molecules in the vibrational state involved, and T is the absolute temperature.

The rotational partition function, Q_r is given by the sum over all states of the energy function:

$$Q_r = \sum_J^{\infty} (2J + 1) \exp(-E/kT) \quad (\text{A2})$$

Because of the large rotational energies of the OH molecule, a reasonable approximation to Q_r can be obtained by summing over a finite number of terms. Since the Λ -doubling energy is much less than the rotational energy, we can write

$$Q_r = 2 \left\{ \sum_{J=1/2}^N (2J+1) \exp(-E_{1/2}(J)/kT) + \sum_{J=3/2}^N (2J+1) \exp(-E_{3/2}(J)/kT) \right\} \quad (A3)$$

where the energies $E_{1/2}$, $E_{3/2}$ are the rotational energies neglecting Λ -doubling, and the factor of 2 accounts for the two-fold degeneracy of each rotational level. The energy terms can be obtained from the computed values of Beaudet and Poynter (17) or calculated from the approximate expressions (15):

$$E_{1/2}(J) = a(J) + b(J) \quad \text{with } J = 1/2 + n, n = 0, 1, 2, \dots$$

$$E_{3/2}(J) = a(J) - b(J) \quad \text{with } J = 3/2 + n, n = 0, 1, 2, \dots$$

$$\text{where } a(J) = B[J(J+1) - 3/4]$$

$$\text{and } b(J) = B[(J+1/2)^2 + \lambda(\lambda-4)/4]^{1/2}$$

$$\text{with } B = 18.5509 \text{ cm}^{-1} \quad \text{and } \lambda = -7.48847 \quad (A4)$$

For $T = 300\text{K}$ (room temperature), the value $Q_r = 47.78$ is found using the above expressions and $Q_r = 48.95$ by summing over the energy values computed by Beaudet and Poynter.

The line strength, S_{ij} is defined in terms of the electric dipole matrix element $|u_{ij}|$

$$S_{ij} = (2J+1) |u_{ij}|^2 / \mu^2 \quad (A5)$$

where for OH the dipole moment μ is 1.6676 Debye units (22). Because of the nuclear spin, $I = 1/2$ of the H nucleus, each Λ -doubling transition is split into 4 hyperfine components of differing intensity. The line strength can be calculated (22) by first neglecting the hyperfine splitting. Then we have

$$S(J) = \frac{2J+1}{J(J+1)4X^2} \left\{ \frac{1}{2}(\pm X - 2 + \lambda) + \frac{3}{2}(\pm X + 2 - \lambda) \right\}^2 \quad (6)$$

where $X = [(2J+1)^2 + \lambda(\lambda-4)]^{1/2}$ and $\lambda = -7.48847$. The + sign is used for the $^2\Pi_{1/2}$ states, and the - sign for the $^2\Pi_{3/2}$ states.

When the hyperfine interaction is included, the expression for $S(J)$ must be multiplied by the hyperfine transition probabilities to yield for the case $\Delta F = 0$, where $F = J + I$ is the total angular momentum.

$$S(J,F) = \frac{(2F+1)[F(F+1)-I(I+1)+J(J+1)]^2}{8F(F+1)(2J+1)J(J+1)} S(J) \quad (A7)$$

For the case $\Delta F = 1$

$$S(J,F,F+1) = \frac{(F-I+J+1)(F+I-J+1)(I+J+F+2)(I+J-F)}{8(F+1)(2J+1)J(J+1)} \quad (A8)$$

The values computed for the line strengths from equations A6-A8 are in agreement to three significant figures with the values obtained by Beaudet and Poynter (17).

A computer program was written to compute the absorption coefficients for all transitions of interest using the line strengths of Eq. A6-A8 and the calculated transition frequencies and energy levels of Beaudet and Poynter. For the strongest transitions of each value, i.e. $F = J + \frac{1}{2}$, $\Delta F = 0$, the results are shown in Fig. 7. In the figure, values are given for various temperatures and an assumed linewidth parameter of 3.1 MHz/torr. Values for other transitions observed in our work are given in section 4 of the text.

The absorption coefficients for a number of OH transitions have been computed by Wacker et al (23). The results obtained here exceed their values by a factor of approximately three. A similar discrepancy has been noted previously by Radford (11).

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Table I
Frequencies of OH A-Doubling Transitions

Species	Transition	Previous ^a Measurements (MHz)	Calculated ^b Values (MHz)	New Measurements (MHz)	Difference ^c (MHz)
¹⁶ OH	² $\Pi_{3/2}$ J=15/2 F=7-7	70845.081	70845.048	70844.957(20)	-.091
	F=8-8	70858.930	70858.926	70858.841(20)	-.085
	F=7-8	-	70888.124	70887.994(50)	-.130
	F=8-7	-	70815.851	70815.805(50)	-.046
¹⁶ OH	² $\Pi_{1/2}$ J=19/2 F=9-9	-	66132.658	66133.521(30)	+.863
	F=10-10	-	66094.023	66094.850(30)	+.827
¹⁸ OH	² $\Pi_{3/2}$ J=15/2 F=7-7	-	69901.342	69896.714(50)	-4.628
	F=8-8	-	69915.174	69910.546(50)	-4.628

^aJ. L. Destombes, G. Journe1, C. Marliere and F. Rohart, C. R. Acad. Sci. Paris, Ser. B280, 809 (1975).

^bR. A. Beaudet and R. L. Poynter, J. Phys. Chem. Ref. Data, 7, 311 (1978).

^cMeasured value - calculated value.

Table II
Calculated Absorption Coefficients of OH Λ -Doubling Transitions

Species	Transition	Transition ^a Frequency (MHz)	Absorption ^b Coefficient (cm ⁻¹)
¹⁶ OH	² $\Pi_{3/2}$ J=15/2	F=7-7	1.00 x 10 ⁻⁴
		F=8-8	1.14 x 10 ⁻⁴
		F=7-8	8.44 x 10 ⁻⁷
		F=8-7	8.44 x 10 ⁻⁷
¹⁶ OH	² $\Pi_{1/2}$ J=19/2	F=9-9	1.99 x 10 ⁻⁷
		F=10-10	2.20 x 10 ⁻⁷
¹⁸ OH	² $\Pi_{3/2}$ J=15/2	F=7-7	2.04 x 10 ⁻⁷
		F=8-8	2.33 x 10 ⁻⁷

^aTransition frequencies as measured in this work

^bCalculated values assuming T = 300K and $(\Delta\nu)_1 = 3.1$ MHz/torr and, for ¹⁸OH, an isotopic concentration of 0.204%

Fig. 1 Block diagram of microwave spectrometer

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OH FREE RADICAL PRODUCTION

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Fig. 2 Apparatus for the production of OH free radicals. For SO the same apparatus is used with the NO₂ supply replaced by OCS and the H₂:Ar mixture replaced by O₂:Ar.

Fig. 3 Absorption signal for the $2\Pi_{3/2}$, $J = 15/2$,
 $F = 8-8$ transition of ^{16}OH at 70858.841(20) MHz.

Fig. 4 Absorption signal for the $2\Pi_{3/2}$, $J = 15/2$,
 $F = 8-8$ transition of ^{18}OH at 69910.546(50) MHz.

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Fig. 5 Absorption signal for the $(3,4)-(3,3)$ transition of SO at 66034.890(50) MHz.

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Fig. 6 Comparison of the measured (circles) absorption signal for OH and the theoretical calculation (solid line) assuming $\gamma_0 = 1.26 \times 10^{-4} \text{ cm}^{-1}$, $(\Delta\nu)_1 = 2.8 \text{ MHz/torr}$, pressure 0.120 torr, modulation amplitude = 0.139 MHz rms, $V = 8.5$ volts and $Q_L = 67000$. The concentration of OH radicals producing a fit is 0.0064.

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Fig. 7 Calculated absorption coefficients for the ${}^2\Pi_{1/2}$ Λ -doubling transitions of OH for $J = 1/2$ to $27/2$ and $F = J + 1/2$, $\Delta F = 0$. The results are obtained for a linewidth parameter of 3.1 MHz/torr and equilibrium temperatures of 300, 400, and 500 K.

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