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MICROWAVE DETECTION OF CHEMICAL AGENTS: A REVIEW

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RESEARCH DIRECTORATE

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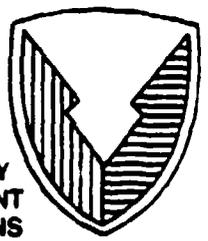
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This report represents an overview of microwave detection techniques and an analysis of their possible application to chemical agent point and remote sensing. Microwave rotational spectroscopy and millimeter wavelength radar are also discussed.

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PREFACE

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CONTENTS

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MICROWAVE DETECTION OF CHEMICAL AGENTS:
A REVIEW

1.   INTRODUCTION

        Since the first high resolution spectrum of ammonia was obtained in 1946,[1-3] microwave spectroscopy has been used successfully in applications ranging from molecular structure and conformation determinations to measurements of dipole moments.[4-7] However, the impact of microwave rotational spectroscopy (MRS) on organic and analytical chemistry has been relatively minor. This lack of general utility is understandable since the microwave spectra of large organic molecules are extremely complex and the absorption coefficients are relatively small compared to those found in the infrared (IR) and visible spectra. The requirement that spectra be obtained in the gas phase at millitorr pressures and the size and complexity of the microwave spectrometer have also limited the usefulness of MRS.

        Within the past 10 years, attempts have been made to find new analytical applications for microwave spectroscopy. Recent developments in solid state sources and resonant absorption cavities have resulted in considerable size reductions and the design and construction of portable microwave spectrometers.[8] Indications have also shown that microwave absorption may be a useful technique in analyzing molecules with molecular weights up to 200. In light of the recent technological advances, MRS needs to be reevaluated to determine if it can be used as an agent detection concept.

        In this report, MRS was studied and reevaluated. Emphasis was placed on microwave techniques used for air pollutant monitoring and analysis since this application is related most closely to the chemical agent detection problem (i.e., atmospheric detection of trace chemicals). Available, agent microwave data were reviewed and findings are presented herein. Finally, conclusions regarding the applicability of microwave absorption to chemical warfare (CW) agent detection have been drawn and are provided.

2.   DISCUSSION

2.1   Microwave Rotational Spectroscopy (MRS) Theory.

2.1.1   Introduction.

        Although a rigorous treatment of rotational spectroscopy theory is beyond the scope of this report, the following qualitative description will prove useful in understanding the various MRS applications presented in later sections. Detailed theoretical treatments of the subject can be found in References 9 and 10.

2.1.2   Transition Frequencies.

        As its name implies, MRS deals with transitions between molecular, rotational energy levels. The energy differences between these rotational states correspond to electromagnetic radiation in the microwave or millimeter region of the spectrum (Figure 1). Transitions are induced by the interaction of the molecule's permanent electric dipole moment with the electric vector of
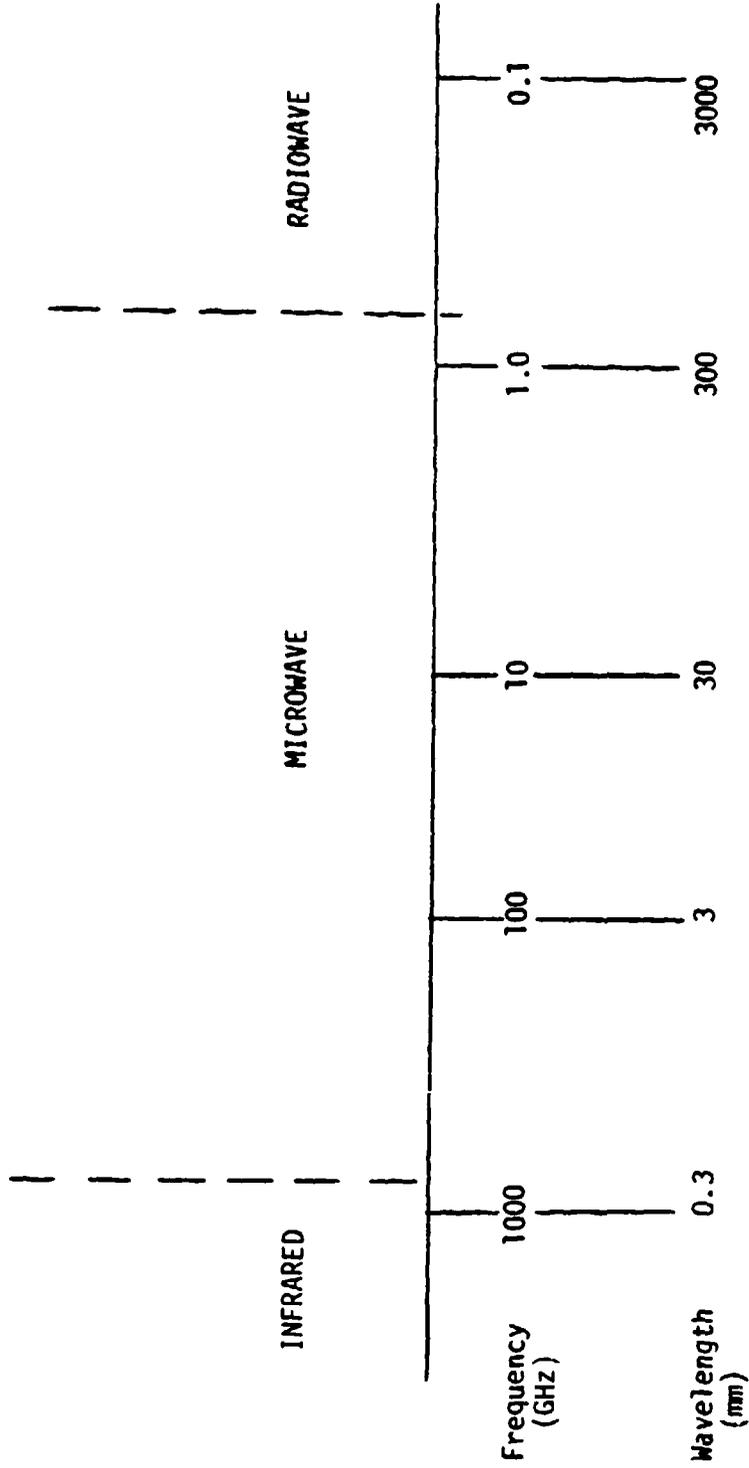
Figure 1. The Electromagnetic Spectrum

the microwave radiation. Transitions can also be induced in molecules that possess a permanent magnetic moment. The oxygen molecule is probably the most notable example of the latter.

Table 1 shows the classification of molecular rotars according to their principle moments of inertia; Ia, Ib, and Ic. A general expression for the rotational energy of an oblate symmetric rotar is simply

$$W/h = BJ(J+1) + (C-B)K^2 \tag{1}$$

where

$$A = B = h/(8\pi^2 Ib) \quad \text{and} \quad C = h/(8\pi^2 Ic) \tag{2}$$

J and K are, respectively, the principle quantum numbers for the total angular momentum and the projection of the total angular momentum onto the symmetry axis. Using the selection rules $\Delta J = \pm 1$ and $\Delta K = 0$, the transition frequency is found to be

$$\nu = \Delta W/h = 2B(J+1) \tag{3}$$

Therefore, in the rigid rotar approximation, the rotational spectrum consists of a series of absorption lines which are separated in frequency by 2B. Because B is inversely proportional to the moment of inertia, the absorption lines get closer together as the molecular weight and size increase. It is easy to verify that the spectrum of a prolate symmetric rotar $(A \neq B = C)$ is also described by Equation (3).

Table 1. Molecular Rotar Classifications

Rotar	Moments of Inertia	Example
Linear	$Ia \cong 0$, $Ib = Ic$	HC1, OCS
Sperical	$Ia = Ib = Ic$	CH_4
Prolate Symmetric	$Ib = Ic > Ia$	CH_3Br
Oblate Symmetric	$Ia = Ib < Ic$	C_6H_6
Asymmetric	$Ia \neq Ib \neq Ic$	H_2O

The asymmetric rotar case is significantly more complicated as K is no longer a "good" quantum number (since the dipole moment does not necessarily lie along the symmetry axis), and the degeneracies which greatly simplified the symmetric rotar spectrum no longer exist. A measure of the degree of molecular asymmetry is provided by Ray's parameter

$$K = (2B-A-C)/(A-C) \tag{4}$$

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which ranges from -1 for a prolate symmetric rotar to +1 for an oblate symmetric rotar. The rotational energy is given by

$$W/h = 1/2(A+C)J(J+1)+1/2(A-C)E_\tau \qquad (5)$$

where E_τ is a value to be determined for each rotational level and degree of asymmetry (i.e., value of Ray's parameter). The regularly spaced rotational levels of the symmetric rotar are now replaced by the very irregularly spaced states defined in Equation (5). This, along with a much more complex set of selection rules, serves to complicate greatly the rotational spectrum. A value of -0.834 for K has been calculated for GB.[11]

2.1.3   Absorption Intensities.

The absorption of microwave radiation follows the typical Beer's Law relationship

$$I = I_0 \exp(-\gamma l) \qquad (6)$$

where I_0 is the incident microwave intensity, l is the sample path length, and γ is the absorption coefficient. For small values of the product γl, the measured absorption ($\Delta I = I_0-I$) is approximately $I_0\gamma l$. Since γ is typically on the order of 10^{-6} to 10^{-8} cm^{-1}, the criterion of small γl is usually met.

An expression for the absorption coefficient is given by the Van Vleck-Weisskopf equation

$$\gamma = \frac{8\pi^2 Nf}{3\ CkT}\ (\mu_{ij})^2 v^2\ \frac{\Delta v}{(v-v_0)^2+(\Delta v)^2} \qquad (7)$$

where

N = number of molecules/milliliter

f = fraction of molecules in the lower energy state

k = Boltzmann constant

T = absolute temperature

μ_{ij} = the dipole matrix element connecting the upper and lower energy states

v_0 = the absorption line center

v = transition frequency

Δv = the half-width at half-maximum line width.

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The value of γ at the absorption maximum ($\nu = \nu_0$) is simply

$$\gamma_{max} = CN \nu_0^2 / \Delta\nu \qquad (8)$$

where C is constant for a particular compound and transition. Consequently, γ_{max} and the absorption intensity are proportional to the square of the transition frequency. The significance of this is that, assuming everything else remains constant, a microwave spectrometer will be more sensitive at higher frequencies. In reality, the sensitivity is limited by the availability of rotational lines and microwave sources in any frequency region. The typical frequency range for analytical microwave spectrometers is the R-band region from 26.5 to 40 GHz.

Quantitative analyses can also be performed using MRS. Although difficult to obtain, the integrated line intensity gives a direct measure of the molecular concentration. Because both N and γ are pressure dependent, a determination of the absorption maximum (and, therefore, γ_{max}) will not yield a concentration unless the concentration of absorbing gas is low and $\Delta\nu$ is determined predominantly by the background gas. In this case, $\Delta\nu$ remains constant and the signal strength is proportional to N. Concentrations can also be determined by generating a calibration curve of intensity versus concentration for the particular compound.

It should be stressed here that pressure or collision broadening is the major source of line broadening in microwave spectroscopy and is typically on the order of 5 to 25 KHz/mtorr. Therefore, microwave spectroscopy is performed solely in the gas phase at pressures generally of 1 to 100 mtorr. At atmospheric pressures, lines are broadened such that only a wide continuum absorbance is observed.

2.2 Applications of MRS to Qualitative and Quantitative Gas Analysis.

2.2.1 Introduction.

Within the past 10 years, interest has grown in analytical applications of microwave spectroscopy,[8,12-14] especially in the areas of pollutant monitoring[15-18] and gas mixture analysis.[19] MRS has certain inherent advantages over other spectroscopic techniques that make it attractive for these applications. One major advantage is the extremely high frequency resolution of gas phase microwave spectroscopy. Line widths of less than 100 kHz at a frequency of 50 GHz are typical. At this resolution (approximately 1 in 500,000), interferences are generally not a problem, and the assignment of 2 or 3 lines is sufficient for unambiguous identification of a particular compound. However, a theoretical study has indicated that, for a multicomponent sample, overlapping of lines will be prevalent, making identification of weakly absorbing compounds very difficult.[20]

In microwave spectroscopy, the integrated line intensity, and in some cases the maximum intensity, is directly proportional to the number density. Therefore, quantitative determination of any species may be obtained from the microwave spectrum. Because the spectra are taken at low pressures, MRS also

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has the advantage of requiring very small amounts of sample. For some strongly absorbing compounds, as little as 10^{-12} moles of sample may be required.[21]

Microwave spectroscopy also presents a number of drawbacks which may be critical in some instances. The requirement that spectra be obtained in the gas phase may be a problem for some samples. A more serious problem when considering a chemical agent detector is the increased spectral complexity and the decreased, individual line strengths that accompany the increase in molecular size. Because of this factor, very few large molecules have been analyzed by MRS. This drawback is thought to limit MRS to analysis of compounds that have fewer than 20 atoms or whose molecular weights are less than 200.[21] The limitation on a microwave detector may not be as severe since actual assignment of the lines is probably not necessary, and some overlap and broadening of absorption lines could be tolerated.

2.2.2   The Microwave Spectrometer.[4,8,9,14]

Certain general characteristics of microwave spectrometers will be reviewed here prior to discussing specific MRS applications. All microwave spectrometers are comprised of essentially four parts: a source of radiation, a sample cell, a detector, and a vacuum system. The microwave source used most often today is the Gunn-effect diode which is a doped crystal of gallium arsenide (GaAs). The Gunn diode has replaced the more conventional tube-type sources (e.g., the klystron and backward wave oscillator) because of its low noise, good reliability, and long life. Continuous microwave radiation emitted from the Gunn diode is monochromatic and electronically tunable over a 10 GHz range at a power level of over 20 mW.

From the source, the microwave energy is transmitted through a waveguide to the sample cell. High Q resonance cavities are frequently used as sample cells because of the large effective pathlengths obtained from multiple reflections through the cell. The Q of a cavity is defined as the electromagnetic energy in the cavity divided by the energy lost per cycle and is a measure of the cavity's efficiency in storing electromagnetic energy. The cavity resonance frequency (i.e., that frequency at which the cavity exhibits a maximum Q value) is dependent on the cavity dimensions and can be changed by altering the cell length. The source output frequency is coupled to the cavity resonance frequency and can actually be tuned mechanically over a few GHz by changing the cavity length. In practice, a feedback loop is established to change the cavity dimensions and to stabilize the microwave frequency. This kind of mechanical tuning allows source frequency stabilization to within one part in 100 million.

The silicon crystal diode is the most common microwave detector for spectroscopic applications and produces a direct current which is proportional to the incident power. The thermister and bolometer are used infrequently for some special applications.

Due to the extremely small microwave absorption coefficients (typically 10^{-4} to 10^{-7} cm^{-1}), the technique of Stark modulation is often used to enhance the signal-to-noise ratio in microwave spectroscopy. The Stark effect is a shift in absorption frequency which results from applying an external electric field to the sample. The Stark electric field is modulated at 100 to 1000 Hz, causing a modulation in the microwave absorption intensity as the transition frequency moves in and out of resonance with the microwave radiation.

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A narrow band amplifier is used to amplify only that component of the signal that is varying at the modulation frequency. Random fluctuations that are not being modulated at the Stark frequency are filtered out, resulting in a marked improvement in the signal-to-noise ratio.

Gas phase microwave spectroscopy also requires the use of a vacuum system for sample handling. The polar gases studied by MRS present the additional problem of adsorption onto the cell walls. Therefore, high vacuum techniques are necessary not only to prepare the sample, but also to maintain a clean system. A heated sample cell is employed sometimes to aid in driving off samples that have adsorbed to surfaces within the spectrometer.

2.2.3   Mixture Analysis.

Lawrence W. Hrubesh at Lawrence Livermore Laboratory has used MRS to analyze gas mixtures.[8,19] He has demonstrated a computer-controlled spectrometer capable of performing a complete quantitative analysis of a multicomponent gas sample in less than 7 min. A strictly qualitative analysis can be obtained in approximately 3 min from the same instrument. A sensitivity between 10 and 100 ppm was possible for most of the compounds investigated.

In computer memory, Hrubesh has stored the two strongest absorption lines in the 26.5 to 40.0 GHz region of over 120 compounds of interest. The slope of a linear calibration curve for each of the pure gases was also placed in the computer for use in quantitative determinations. Analysis of an unknown gas mixture begins with the synthesis of the strongest absorption frequency of cataloged compound number 1. The spectometer then signal averages for approximately 1 sec. If the signal-to-noise ratio is greater than or equal to 3:1, the second strongest absorption frequency of compound 1 is synthesized. If a signal-to-noise ratio of 2:1 is observed after 2 sec of integration, a positive identification for substance 1 is returned. This process continues for each of the compounds cataloged in the computer.

For a quantitative analysis, the computer resynthesizes the strongest absorption frequency of each positively identified compound. The computer then increases the microwave power from zero until an absorption maximum is reached. This maximum signal is used with the slope of the previously generated calibration curve to determine the partial pressure or volume percentage of the particular substance. The data obtained from analyzing a mixture of chloro-fluoro-hydrocarbons are shown in Table 2.

A somewhat different approach to mixture analysis is taken by White at NASA Langley Research Center.[8] His automated spectrometer operates in three modes beginning with a rapid scan of a specified frequency range. Any signal detected above a threshold level causes the spectrometer to switch to the second mode of operation. In this mode, the scan rate is reduced and the oscillator frequency is stopped at the approximate absorption maximum. After adjusting the gain to optimize the signal, the final measurement mode is initiated in which data points are collected every 0.01 MHz across the absorption line. Digital filtering and signal averaging are employed where appropriate. The spectrum obtained is used to calculate the center frequency, the line width, and the absorption coefficient which, in turn, are used to determine the concentrations of the species. After the entire frequency range has been scanned, to identify species, the positions of the strongest lines are compared to the

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line positions stored in computer memory. Cross checks are performed using the second and third lines of each identified compound. Such an analysis of an unknown mixture is very thorough and takes approximately 2 hr. White has used this computerized microwave spectrometer to compile a very extensive microwave line listing catalog of pure gases.[22-25]

Table 2. Chlorofluorohydrocarbon Mixture Analyzed by Hrubesh[8]

Gas #	Frequency (MHz)	% Volume	Name
18	39,860.2	0.7	Chlorobenzene
20	34,550.1	7.1	Chlorodifluoromethane
23	34,405.9	0.01	Chlorethylene
27	40,028.5	3.1	Chlortrifluoromethane
28	36,494.9	3.0	Dichlorodifluoromethane
38	35,902.9	2.9	Fluorobenzene
39	37,991.2	0.01	Fluoroethylene
76	39,452.4	0.08	Trichlorofluoromethane
		Remainder N_2	

2.2.4. Pollutant Monitoring and Portable Instruments.

Section 2.2.3 dealt with large research spectrometers designed to analyze a multicomponent gas mixture. An application that is perhaps more closely related to the problem of microwave detection of chemical agents is the use of MRS instruments for specific pollutant monitoring. In this case, the spectrometer "looks" for only one or a few atmospheric pollutants and ignores all other constituents. This application has met with success in some specific cases and has even led to the production of prototype portable systems for ammonia and formaldehyde detection.

Hiromichi Uehara and his co-workers at the Segami Chemical Research Center in Japan have been very active in the field of microwave detection of atmospheric pollutants.[26-29] These investigators have been successful in monitoring several gaseous species using single absorption peaks (Table 3). Using MRS, Uehara and Ijuuin were the first researchers to detect formaldehyde in situ in automobile exhaust. Acrolein was also monitored in the exhaust, but required that a preconcentration technique be used to obtain sufficient signal strengths for detection.

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Table 3. Examples of Pollutant Monitoring by MRS

Compound	Line Frequency (MHz)	Absorption Coefficient (cm^{-1})	Pressure (mtorr)	Concentration Detected (ppm)	Reference
Acrolein C_3H_4O	8902.2		200	5	27
Ammonia NH_3	23870.1	3.98×10^{-4}	4000-5000	10 (0.08 ppm is minimum detection limit with S/N=1)	26
Formaldehyde CH_2O	8884.87	3×10^{-6}	200	24 (0.2 ppm is minimum detected conc)	28

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Long-term stability of the microwave spectrometer is critical if the spectrometer is used as a pollutant monitor. A baseline drift of only 1% was achieved in an ammonia monitor built by Uehara by attaching the cavity to super invar rods (which have a low coefficient of thermal expansion) and placing the entire spectrometer in a temperature-controlled box. The mechanical rigidity afforded by these measures is important because the Gunn oscillator resonance frequency is dependent on the cavity dimensions.

In recent years, the advent of solid state microwave sources has made highly specialized, portable gas monitors possible. As early as 1974, Lawrence Hrubesh of the University of California Lawrence Livermore Laboratories (UCLLL) developed a formaldehyde monitor using a Gunn effect diode source and a resonant-cavity absorption cell.[8,21] This instrument which was built for the Environmental Protection Agency in Research Triangle Park, North Carolina, had the following requirements: (1) long-term stability, (2) automatic or unattended operation for long periods of time, (3) 0.030 ppm sensitivity, and (4) rapid response (90% of full-scale response in seconds). The low pressure cell of the microwave monitor was separated from the atmosphere by a dimethyl silicone membrane which permeated the polar formaldehyde more readily than the other atmospheric constituents. However, with this sampling technique, problems arose which led to extremely long response times. This problem, along with insufficient sensitivity for ambient formaldehyde, severely limited the monitor's usefulness. A subsequent design by UCLLL for an ammonia monitor placed the entire resonant cavity in an oven.[8,30] This modification eliminated the long response times caused by the gases adsorbing onto the surfaces of the spectrometer. A detection limit of 10 ppb of ammonia in air was achieved.

Varma and Hrubesh[8] express confidence that a hand-held "sniffer" type of microwave detector could be developed. Actually, this instrument would be a portable spectrometer capable of analyzing ambient air for a number of pollutants. A portable instrument weighing approximately 25 kg has already been developed by UCLLL for the National Institute for Occupational Safety and Health (NIOSH).[8,18] This instrument was designed to detect acetonitrile, acetaldehyde, acetone, carbonyl sulfide, ethanol, ethylene oxide, isopropyl alcohol, methanol, propylene oxide, and sulfur dioxide. Whether or not such a system would have sufficient sensitivity and selectivity for detecting large agent-type molecules is debatable. A complete assessment would require a knowledge of the microwave spectra of the agent as well as possible interfering compounds.

2.2.5. Trace Gas Radar.

The use of microwave radiation to detect gas seepages above natural gas or petroleum deposits has been proposed in two patents.[31,32] This technique has been used to detect both methane and propane gases in actual field tests. In this approach, a pulsed microwave signal is focused on the sampling volume, and the return or backscattered radiation is detected by a microwave receiver in a manner analogous to conventional radar. The receiver is tuned to a frequency offset from the transmitted microwave signal. This predetermined receiver frequency is characteristic of a particular gas, and along with the power and band shape, constitutes what is referred to as the microwave reradiation characteristic (MRC). For both methane and propane, the transmitted frequency used was 9.375 GHz while reradiation was detected at 9.361 GHz ($\Delta v = 14$ MHz) for the former and 9.355 GHz ($\Delta v = 20$ MHz) for the latter.

The underlying physical basis for this effect is not fully understood although it is suggested to be analogous to the resonance Raman effect with the incident radiation inducing a time-dependent polarizability in the molecule. This time-varying dipole then reradiates at some frequency offset from the incident frequency. Mobil Research and Development Corporation performed some laboratory experiments and field tests but failed to discover a satisfactory theoretical or empirical basis for the effect (written communication, J.J. Wise, Manager, Field Research Laboratory, Mobil Research and Development Corporation, December 1981). Since follow-up field tests were not successful in reproducing the earlier results either, Mobil canceled all further research in this area.

2.3   Chemical Agent Microwave Data.

2.3.1   Experimental Results.

All of the experimental studies on the microwave absorption of chemical agents were performed 20 to 30 years ago. A list of the available microwave rotational data is given in Table 4. As this table illustrates, the data are sparse and very contradictory. This dearth of spectral data is understandable since the molecular complexity and high toxicity of these compounds make them unattractive samples to most microwave spectroscopists. The exception is hydrogen cyanide (AC) whose simple molecular structure renders it highly amenable to microwave spectroscopic analysis. As a result, AC has been studied extensively and the microwave spectral data is essentially complete.[33]

Table 4 contains a number of discrepancies. For example, Armour Research[34] and Melpar[35] studied the same spectral region (22,000 to 25,600 MHz), but only the Melpar detected any absorption from GB. This is probably because Melpar cooled their sample to dry ice temperatures which resulted in a greater sensitivity because of an increase in the number of molecules in the ground vibrational state and in the population differences between the various rotational levels. However, it is unclear why Southern Research Institute,[36] under conditions similar to those reported by Melpar, observed no GB absorption in the frequency region from 18,000 to 40,000 MHz. It is possible that the Southern Research Institute spectrometer simply lacked the required sensitivity ($\gamma = 10^{-7}$ cm^{-1}) to detect the agent absorption.

2.3.2   Theoretical Treatments.

In July 1982, Geo-Centers, Inc. completed a 1-year theoretical evaluation of the use of microwave spectroscopy for chemical agent detection.[11] This study consisted of theoretical calculations of the microwave spectra of isopropyl methylphosphonofluoridate (GB), diisopropyl phosphonofluoridate (DFP), dimethyl methylphosphonate (DMMP), and diisopropyl methylphosphonate (DIMP). As a result of this work, McIlwain concluded that a microwave point detector is quite feasible and would have a sensitivity of approximately 0.1 ppm for GB; that a microwave point detector would be very insensitive to atmospheric and battlefield interferences; and that a dual-ended, nonspecific remote sensor for early warning is also possible using microwave absorption.

In calculating the microwave spectra, McIlwain had to make a number of assumptions and approximations because of the lack of molecular data on the compounds studied. For example, the molecular dipole moments were not available

Table 4. Chemical Agent Microwave Absorption Data

| Agent	Frequency Range (MHz)	Pressure (mtorr)	Temperature	Approximate Absorption Coefficient (α)	Reference
GA,GB	21,600 - 25,600	"reduced pressures"	probably room temperature	no absorption detected	34
GB	22,500 - 29,000	34 - 37	probably room temperature	10^{-9} - 10^{-7} cm^{-1}	37
GA,GB	18,000 - 40,000	4 - 76	probably room temperature	no absorption detected	36
GA	23,000 - 25,000 26,000 - 33,000 36,000 - 40,000 88,000 -115,000	7.6	room temperature	no absorption	35
GB	22,000 - 26,500 23,000 - 33,000 36,000 - 40,000 88,000 -115,000	38 7.6 7.6 7.6	-78.5 °C room temperature room temperature -78.5 °C	$< 10^{-6}$ cm^{-1} $< 10^{-7}$ cm^{-1} $< 10^{-7}$ cm^{-1} $< 10^{-5}$ cm^{-1}	35

and had to be calculated. The dipole calculated for GB was 1.57 D. Indications are that this is too low as other organophosphorous compounds have dipole moments of approximately 3 to 4 D (conversation with Wendel Shuley, III, Chemical Systems Laboratory,* January 1982). The Edgewood microwave study reported a GB dipole moment of 3.25 D although no source for this datum was given. Underestimating the dipole moment could cause an investigator to underestimate the agent absorption coefficient.

A particular molecular conformation had to be assumed in calculating the microwave frequencies. McIlwain chose the conformation which yielded the highest degree of hydrogen bonding. He also pointed out that if free rotations occur at room temperature around the phosphorus-oxygen (PO) bond, the calculated high resolution spectrum would be much more complex, and the individual line strengths would be reduced. In light of the number and magnitude of the approximations, the author stresses that the calculated spectra must also be considered only as rough approximations. Figures 2 to 4 are calculated spectra for GB obtained by Geo-Centers and illustrate the effects of pressure broadening on the absorption lines.

In 1983, Geo-Centers was awarded a follow-up, 3-year contract to substantiate experimentally the feasibility of a microwave agent detector, calculate microwave rotational spectra for other agent molecules, design and construct a breadboard microwave detector, and test and evaluate the breadboard prototype with simulant molecules.[38] As of the writing of this report, work was progressing on verifying the microwave spectral calculation method.

An Air Force study on the feasibility of microwave remote detection of CW agents was performed by Slater of Avco Everett Research Laboratory.[39] He investigated the ground clutter attenuation (GCA) and microwave acoustic detection concepts. The former scheme relies on the decrease in return signal from a topographical target due to the presence of an agent cloud in the beam path. A two wavelength DIAL type GCA system in which one frequency is tuned to an agent absorption maximum and another to an absorption minimum was also considered. In this approach, the second frequency is used to monitor normal atmospheric and ground clutter absorption and scattering variations that occur because of changing terrain, temperature, humidity, and/or pressure. The "on" and "off" return signals are subtracted, yielding a signal dependent only on the agent concentration. The DIAL-type experiment assumes that atmospheric and target absorption and backscatter are the same for λon and λoff. The smaller the difference ($\Delta\lambda = \lambda$on - λoff), the greater the chances are for this phenomenon to occur. However, the atmospheric pressure broadening of the microwave absorption lines makes it necessary to use a large $\Delta\lambda$ in order to achieve a significant difference in the agent absorption coefficients at λon and λoff. The result is that the wavelength variation in the atmospheric and target absorption and backscatter can give rise to a false signal which is indistinguishable from the agent signal, thus presenting a serious problem for the GCA microwave remote sensing technique.

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*The U.S. Army Chemical Research, Development and Engineering Center (CRDEC) was known as the U.S. Army Chemical Research and Development Center (CRDC) prior to March 1986 and as the Chemical Systems Laboratory (CSL) prior to July 1983.
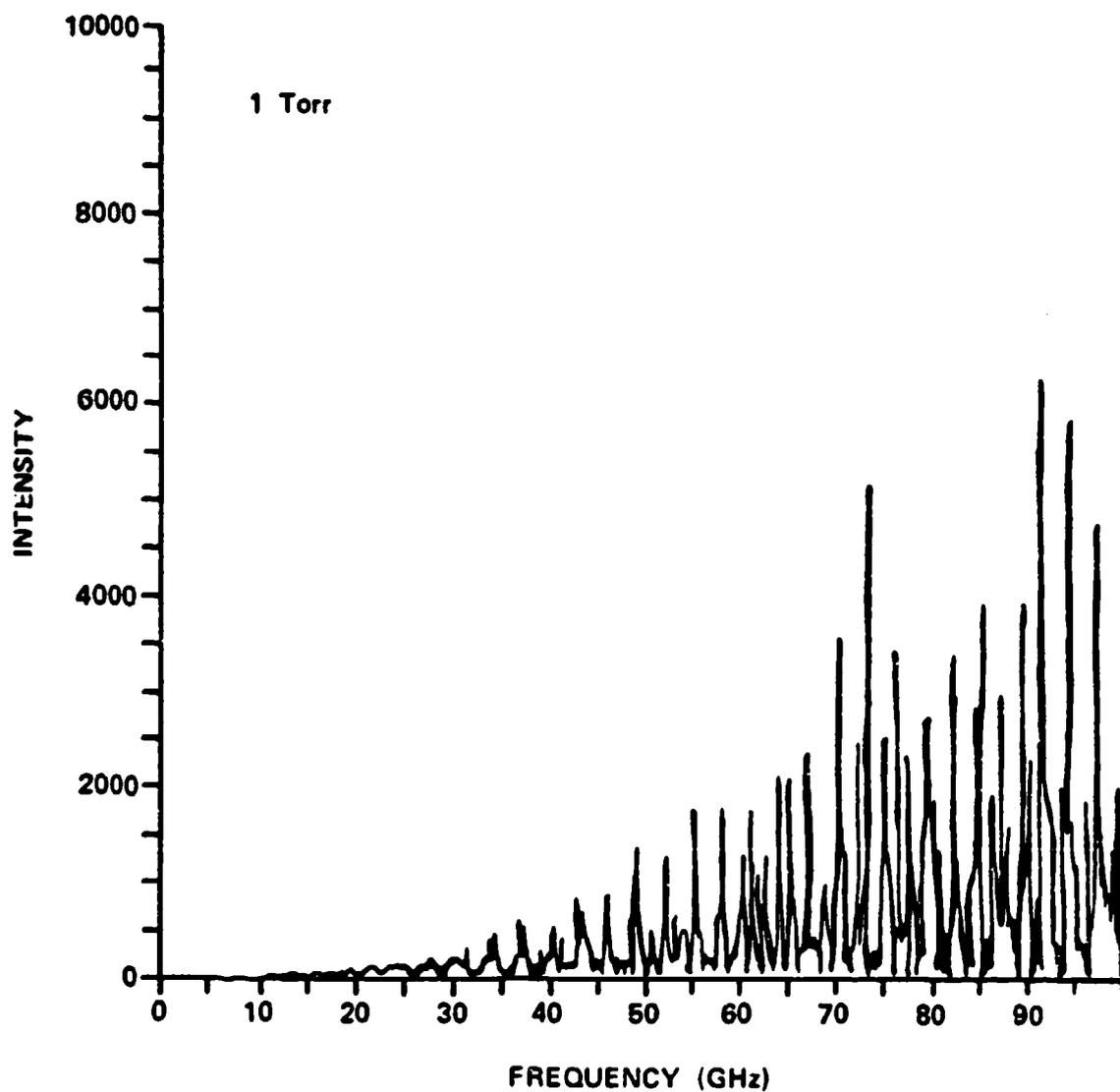
Source: Reference 38

Figure 2.   Calculated MRA Spectrum of GB.   Spectrum
            Represents 1 Torr of Pure GB

50 Torr

INTENSITY

FREQUENCY (GHz)
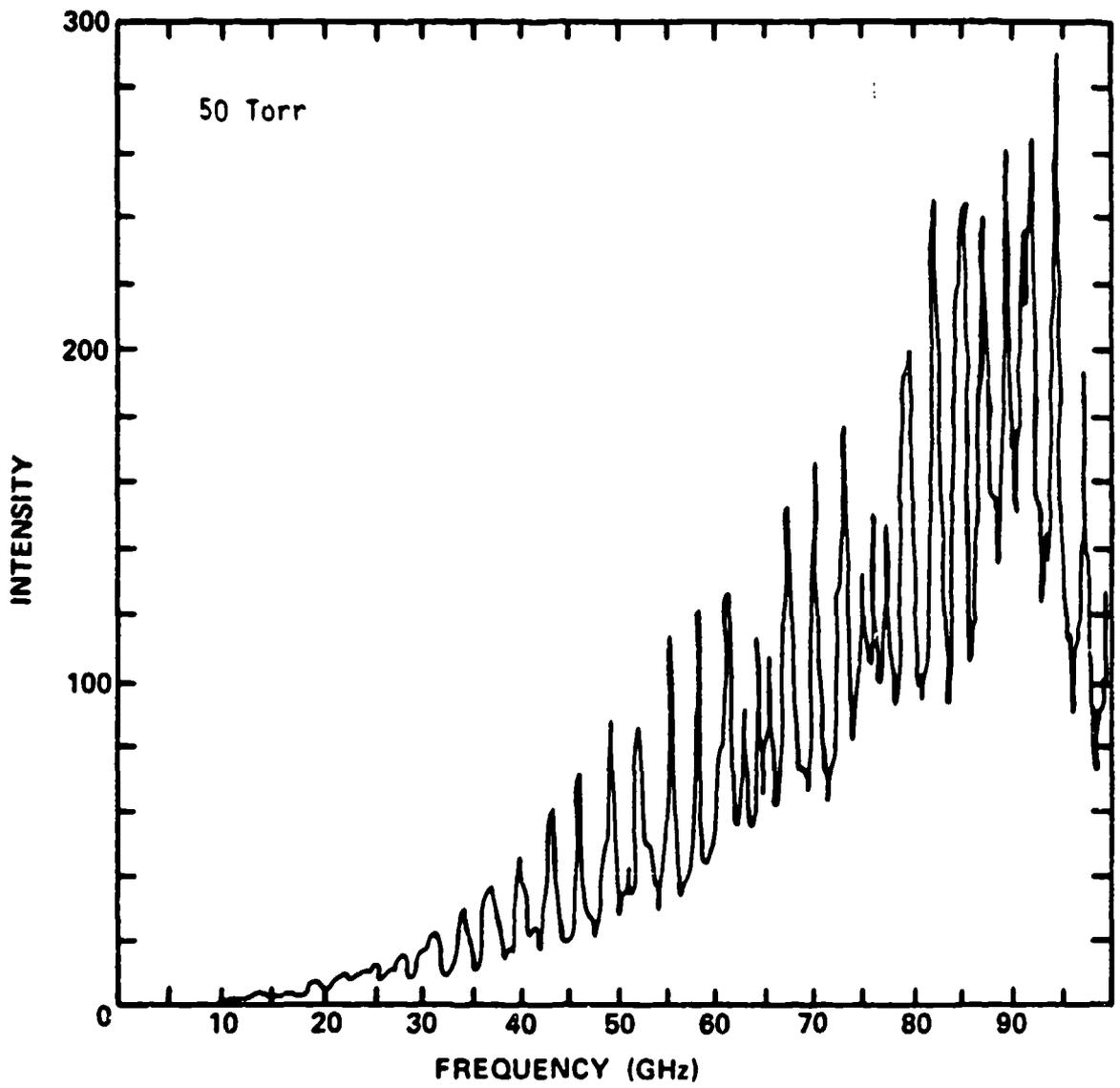
Source: Reference 38

Figure 3.   Calculated MRA Spectrum of GB.   Spectrum
            Represents 1 Torr GB Plus 49 Torr of Nitrogen
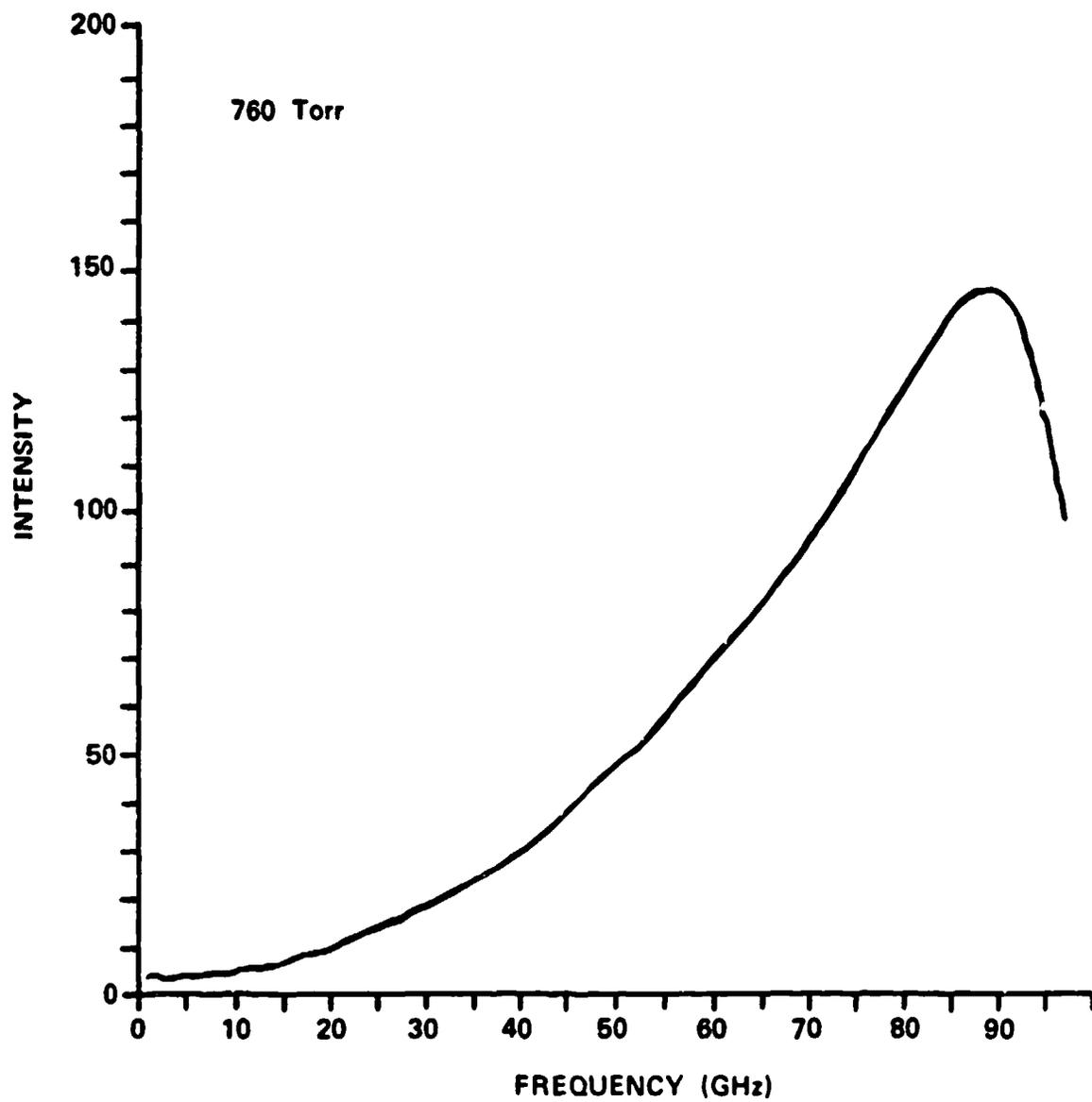
Source: Reference 38

Figure 4.   Calculated MRA Spectrum of GB.   Spectrum
Represents 1 Torr GB Plus 759 Torr of Nitrogen

The microwave acoustic concept appears to be even less promising. In this approach, the absorption of modulated microwave radiation generates a modulated pressure or sound wave in the agent cloud which is detected by a large area directional microphone. Slater's calculations indicate that this technique is not feasible for CW agent detection because of serious interfering noise problems and small signal strengths. He concludes that neither phase-sensitive detection nor signal averaging could improve the signal-to-noise ratio enough to render this a viable remote sensing scheme.

2.4   Microwave Radar Detection.

2.4.1   Introduction.

The previous sections of this report have dealt with the spectroscopic detection of gas-phase compounds. Microwave radiation can also be used to detect substances that are dispersed as aerosols or rains. In this case, the extinction and scattering are dependent upon the ratio of the particle size to the wavelength of the radiation as well as the complex refractive index of the chemical species. The solution to the problem of scattering and absorption by spherical particles is found in Mie theory which is covered extensively in a number of publications.[40-43] The results of Mie theory will be used in the following analysis of microwave remote detection.

2.4.2   The Radar Equation.

For short-pulse radar, the backscatter return power from volume-distributed incoherent scatterers at a range R is

$$P = \left[\frac{P_t \, G_0^2 \lambda_0 \beta_\theta \beta_\phi c \, t_\rho e^{-2\tau}}{32(4\pi R)^2} \right] \sigma_\nu \qquad \text{(reference 40)} \qquad (9)$$

where   P = peak transmitted power (W)

G = antenna gain (dimensionless)

R = range to scattering volume (m)

λ_0 = wavelength (m)

τ = total path attenuation (dB)

σ_ν = backscatter cross section per unit volume (m^{-1})

$\beta_{\theta,\phi}$ = half-power beam widths (rad)

τ_ρ = pulse length (s)

The total path attenuation τ is obtained by integrating the extinction coefficient of the atmosphere over the path from 0 to R:

$$\tau = \int_0^R \alpha_A \, dr$$

(10)

Multiplying Equation (9) by the two-way attenuation factor for the cloud itself $(e^{-2\alpha}r)$ and integrating the backscattered power over the length of the cloud (from R to R+ΔR) yields the relative backscatter return signal

$$S = \int_R^{R+\Delta R} P_r e^{-\alpha}r / P_t = C\sigma_v e^{-2\tau} \int_R^{R+\Delta R} e^{-2\alpha r} / r^2 dr$$

(11)

where the constant terms from Equation (9) have been collected in C. The integration is performed in the Appendix and the solution is

$$S = C\sigma_v e^{-2\tau} \left(e^{-2\alpha R} \left(\frac{1}{R} - \frac{e^{-2\alpha\Delta R}}{R+\Delta R} \right) - 2\alpha \left\{ \ln\left(\frac{R+\Delta R}{R} \right) + \sum_{n=1}^{\infty} \frac{(-2\alpha)^n}{n \times n!} \left[(R+\Delta R)^n - R^n \right] \right\} \right)$$

(12)

$$= C\sigma_v e^{-2\tau} E(\alpha)$$

The infinite series in Equation (12) converges so that $E(\alpha)$ and S decrease exponentially with increasing extinction coefficient (Figure 5). The plots in Figure 5 and all subsequent graphs were calculated assuming the range and range element were 500 and 50 m respectively.

The extinction coefficient for rain is a function of the precipitation rate (R_r in mm/hr) which in turn is related to the number of droplets per cubic meter (N_v) in the following manner:

$$\alpha_r = K1 R_r^b \quad (dB/Km)$$

(13)

and

$$R_r = 6\pi \times 10^{-4} \sum_{i=1}^{N_v} V_i di^3$$

where V_i is the terminal velocity, and di is the diameter of the ith droplet. K_1 and b are parameters determined by fitting calculated values of α for a

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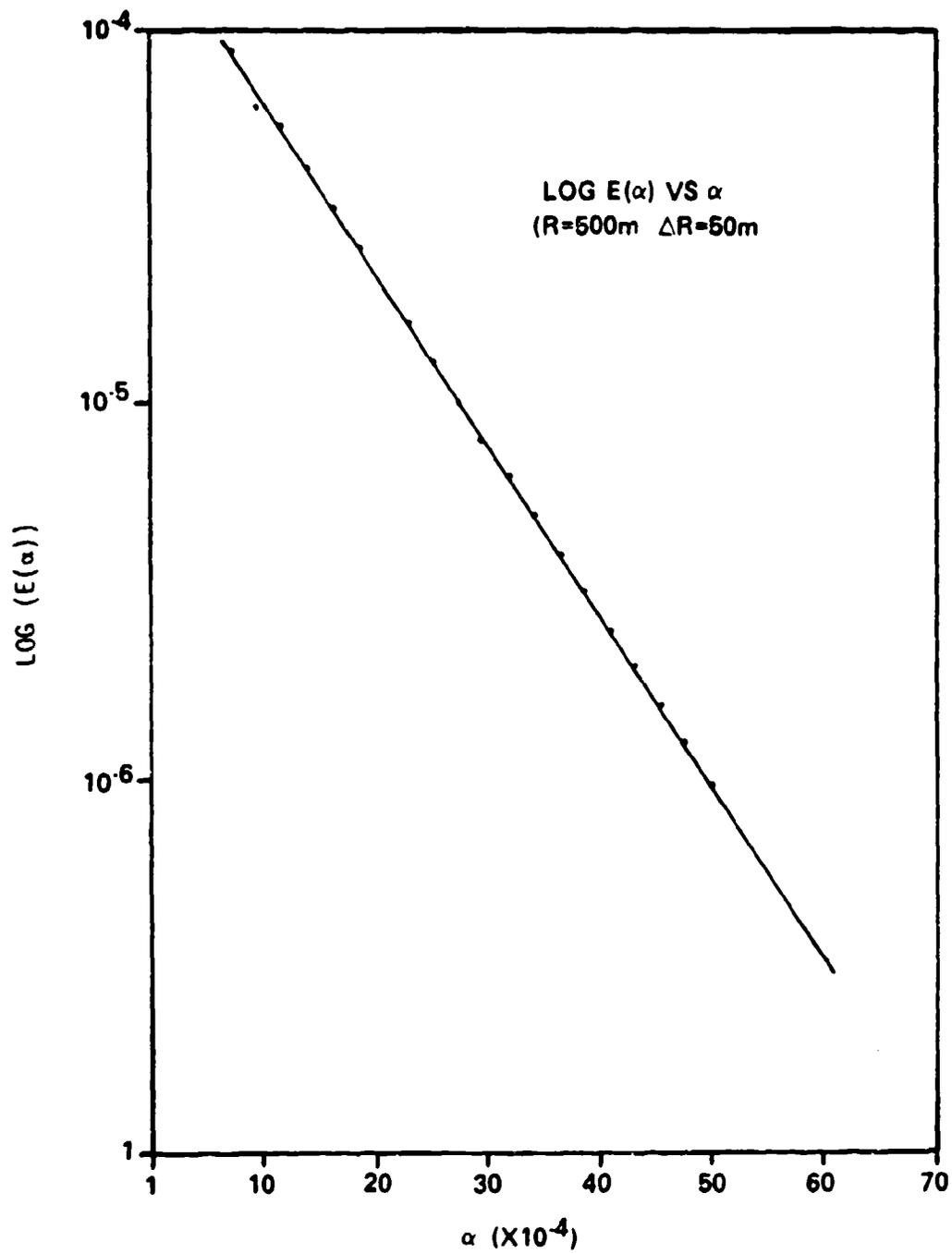
Figure 5. Plot of E(α) vs the Cloud Extinction Coefficient α

given size distribution and wavelength to Equation (13). If we assume a single droplet size rather than a distribution of sizes, Equation (13) h. r .:s

$$\alpha_r = K1(6\pi \times 10^{-4} \times N_v \times V \times d^3)^b \tag{14}$$

The analogous equation for clouds is

$$\alpha_c = K2 \times m_v \tag{15}$$

where m_v is the water or liquid content of the cloud, $K2 = 0.434 \times (6\pi/\lambda_0) \times Im(-k)$, $k = (\varepsilon_c-1)/(\varepsilon_c-2)$, and ε_c is the dielectric constant. For hydrometeor clouds, the water content or mass density in g/m^3 is

$$m_v = 10^6 \sum_{i=1}^{N_v} (4\pi/3) \times r_i^3$$

where the water density of 10^6 g/m^3 is used. This equation reduces to

$$m_v = 10^6 \times N_v \times (4\pi/3) \times r^3 \tag{16}$$

for a monodisperse cloud. Combining Equations (15) and (16), we get

$$\alpha_c = K2 \times 10^6 \times (4\pi/3) \times r^3 \times N_v \tag{17}$$

The backscatter coefficient can also be related to the number density using

$$\sigma_v = 10^{-10} \times (\pi^5/\lambda^4)_0 \times |k|^2 \times Z_r \tag{18}$$

where $Z_r = \sum_{i=1}^{N_v} d_i^6$ for rain and $Z_c = 4.8 \times 10^{-2} m_v^2$ or clouds.[44] Equation (18) is strickly valid only for the Rayleigh region where the index of refraction times the ratio of the particle cross sectional area to the wavelength of light is less than 0.5. Making this assumption and again using a single particle size, Equation (18) becomes

$$\sigma_{vr} = 10^{-10} \times (\pi^5/\lambda_0^4) \times |k|^2 \times d^6 \times N_v \tag{19}$$

for hydrometeor, rain and

$$\sigma_{vc} = 10^{-10} \times (\pi^5/\lambda_0^4) \times |k|^2 \times 4.8 \times 10^{-2} \times (10^6 \times (4\pi/3) \times r^3)^2 \times N_v^2$$

(20)

for hydrometeor clouds or aerosols.

Using the equations for α and σ, the radar return signal, S, can be plotted as a function of the number density as shown in Figures 6 through 8. For rain (Figure 6), the return signal increases for small N_v then drops as the increase in the extinction coefficient dominates the increase in backscatter coefficient. For hydrometeor clouds (Figures 7 and 8), the return signal increases over the range of realistic values of N_v. Figure 7 also illustrates the effect of K2 and α on the radar return. The effect of particle size on the return signal is shown in Figure 8. The purpose of these plots is to demonstrate the relative importance of particle size and attenuation coefficient on the return signal. The change in radar return that accompanies a change in molecular species (as reflected in α) is insignificant compared to that which accompanies a change in the particle radius.

2.4.3.   Chemical Agent Detection.

The radar technique is inherently lacking in chemical specificity because the predominant factors governing the backscatter return signal are the particle or droplet size and the cloud density or rainfall rate. This is a disadvantage for chemical agent detection where one would like to be able to distinguish between lethal and innocuous species. Possibly the thickened agent aerosols would be nonspherical and thus would have a different signature than the hydrometeors. In this case, the microwave radar would distinguish between naturally occurring and man-made aerosols, but still would not be chemical-agent specific.

3.   CONCLUSIONS

Some major advances in microwave spectroscopy have been made in the past 10 to 15 years with the advent of Gunn oscillator sources and resonance cavity cells. These advances have led to an increase in spectrometer sensitivity as well as a reduction in its size. Specialized systems for the detection of a single gas have also been constructed. The work being performed by Geo-Centers should determine whether MRS is applicable to chemical agent point sensing. A microwave rotational spectroscopic detector operating at low pressures would probably have good selectivity. Whether the detector would have sufficient sensitivity to detect chemical agents in the atmosphere needs to be determined.

A single-ended, MRS-based microwave system for chemical agent remote sensing does not appear to be feasible at this time. Primarily, this infeasibility is due to the small microwave absorption coefficients and the effects of atmospheric pressure broadening on the absorption lines. Microwave radar, however, could be useful as an early warning device which would signal the presence or release of an aerosol or rain. Qualitative and quantitative analysis of the threat could then be achieved by either an active or a passive IR system. The wide-area surveillance capability of radar makes it well suited for such an application.

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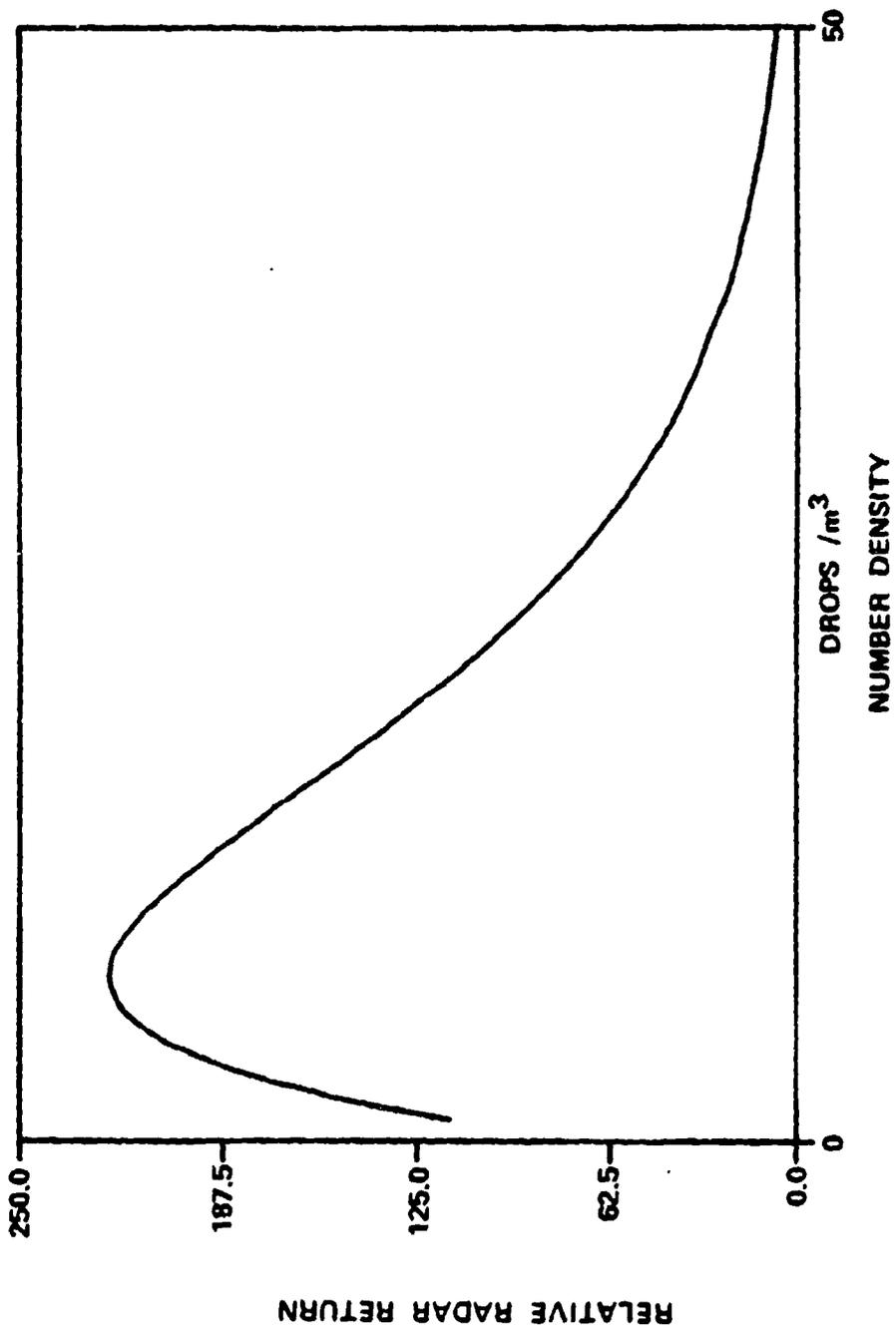
Figure 6. Relative Radar Return for Rain
(d=3mm, R=500m, ΔR=50m, λ=.86cm)
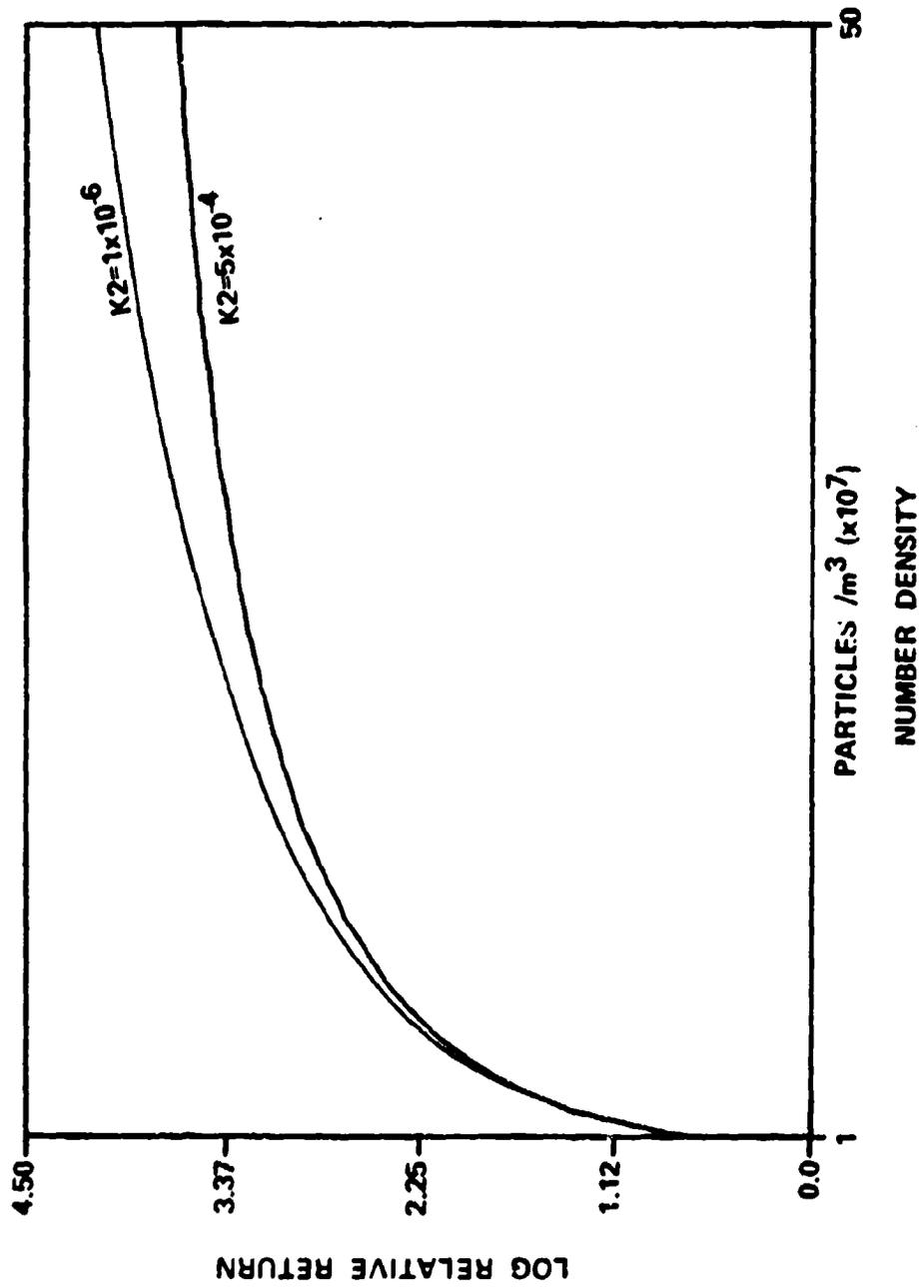
Figure 7. Relative Radar Return for Cloud
(r=20 μm, R=500m, ΔR=50m, λ=.86cm)
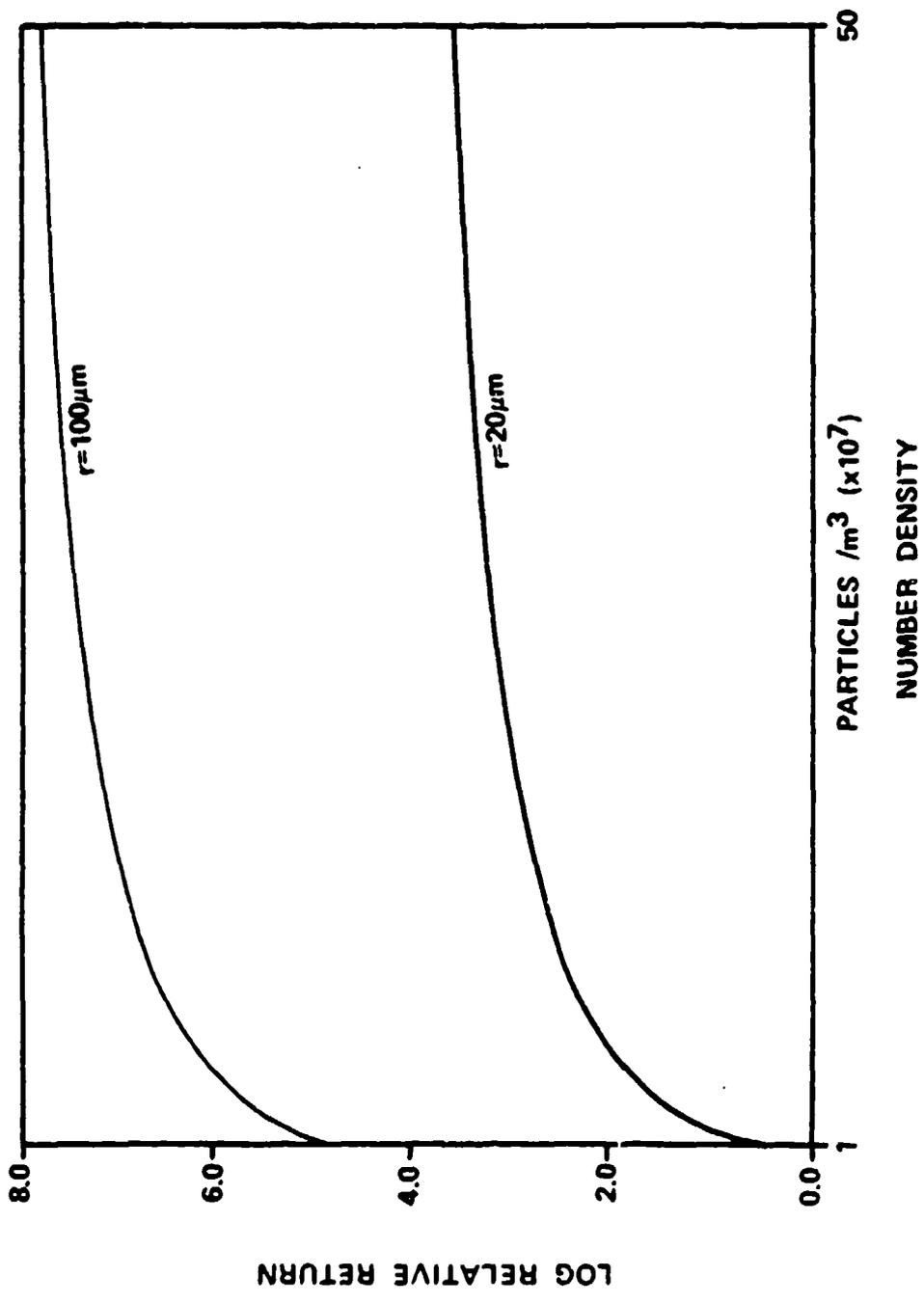
Figure 8. Relative Radar Return for Cloud
(R=500m, ΔR=50m, λ=.86cm)

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$$\text{Solution to } \int_{R}^{R+\Delta R} P_r/P_t \, dr$$

$$P_r/P_t = \Omega\sigma e^{-2r}/r^2$$

$$S = \int_{R}^{R+\Delta R} P_r P_t \, dr = \Omega\sigma \int_{R}^{R+\Delta R} e^{-2\alpha r}/r^2 \, dr$$

$$= \Omega\sigma \left< e^{-2\alpha r}/r \, \Big|_{R}^{R+\Delta R} - 2\alpha \int_{R}^{R+\Delta R} e^{-2\alpha r}/r \, dr \right>$$

$$= \Omega\sigma \left< -e^{-2\alpha r}/r - 2\alpha \times \left\{ \ln(r) + \sum_{n=1}^{\infty} [(-2\alpha)^n \times r^n/n \times n!] \right\} \right> \Big|_{R}^{R+\Delta R}$$

$$= \Omega\sigma \left< e^{-2\alpha R} \times [1/R - e^{-2\alpha\Delta R}(R+\Delta R)] - 2\alpha \times [\ln(R+\Delta R)/R] \right.$$

$$\left. \sum_{n=1}^{\infty} \{ (-2\alpha)^n/(n \times n!) \times [(R+\Delta R)^n - R^n] \} \right>$$

For typical values of $\alpha = 2 \times 10^{-3}$ m^{-1}, R = 500 m, and ΔR = 50 m;

$S = 2.24 \times 10^{-5}$ $\Omega\sigma$.

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