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This report describes absorption in the submillimeter region. Atmospheric effects on both lasers and broadband devices are considered. In addition, predictions are made as to the amount of absorption caused by battlefield activity.

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Foreword

This is the final contract report for the period from January 1979 to October 1979. The work reported was accomplished by D. H. Leslie and J. L. Manning of the Optical Sciences Division of Science Applications, Inc., for the Atmospheric Sciences Laboratory. The Principal Investigator for the program was G. D. Currie. The contract monitor was Dr. K. O. White.

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1. INTRODUCTION

The purpose of this report is to investigate properties of the atmosphere likely present in a land battlefield encounter, and to point out the impact of these properties which might affect the use of submillimeter wavelength electro-optic devices.

For the purposes of this report we define "submillimeter" to encompass the wavelength range 1 cm to .025 cm = 10 mm to 0.25 mm = 10^4 μm to 250 μm = 1 cm^{-1} to 40 cm^{-1}. The meaning of the term "submillimeter" should imply wavelength shorter than 1 mm. However, historically the term has included the spectroscopic region between coherent microwave sources, and thermal infrared sources. The frequency range contains an area of black magic materials: e.g. polyethylene windows, wire gratings, Rheststrahlen crystal filters, etc. For atmospheric sciences, the submillimeter is the region with wavelength beyond the 15 μm CO_2 vibration band. For spectroscopy, the region is studied with very large coarsely ruled diffraction gratings at the infrared side, and very high harmonics of crystal oscillators on the microwave side. The absorption by molecules in this region is almost completely due to transitions between rotational energy levels with no change in vibrational state.

micron

Much of the early work in this region was done by astronomers in their attempt to untangle the emission of stars, planets, etc., from the absorption of the earth's atmosphere. Water vapor is a strong absorber in this region. Because of the large amount of water along an atmospheric slant path, spectra from astronomical studies convey the impression that the atmosphere is virtually opaque to submillimeter radiation. Actually, although water absorption is strong, transmission is non zero in a number of window regions for moderate length horizontal paths.

The development of new sources of far infrared radiation has spurred military interest in the region. The main advantage of using a submillimeter source over a 10.6 μm source, for example for pointer-tracker, laser designation, or communication purposes, is the $1/\lambda^4$ long wavelength benefit in scattering from aerosols.[1] This translates to 43 db per frequency decade advantage for long wavelength sources. Likely situations where this advantage would apply are transmission through clouds, smokes, and snow. However, increased attenuation by atmospheric or battlefield gas could negate this advantage, and it is the purpose of this study to examine this possibility.

We review the subject of battlefield gases, estimate likely concentrations, and predict their effect on atmospheric transmission in the submillimeter windows.

2. SOURCES AND CONCENTRATIONS OF BATTLEFIELD GASES

A previous SAI study[2] has examined battlefield gas effects in the infrared region. In the infrared we are concerned with vibration-rotation transitions in molecules which can be non polar in their ground state. Almost all submillimeter absorption is due to pure rotation transitions in polar molecules, i.e., those having a permanent electrical dipole moment in their vibrational ground state. For this reason molecules which are significant absorbers in the infrared will not necessarily be significant submillimeter absorbers. An important example is methane: a gas likely present and significant in DF laser propagation through the atmosphere (due to absorption by ν_3 and $2\nu_4$ vibrations at 3.7 μm) but, never the less, not significant in the submillimeter. Its high degree of structural symmetry precludes a permanent dipole moment of any significance here. CO_2 is another molecule which plays a significant role in the infrared, but none in the submillimeter due to its lack of a permanent electric dipole moment. In the previous SAI study we predicted gas concentrations due to explosives, fires, and vehicle emissions. The details of these calculations are reported in reference 1 and are summarized here.

Most artillery payloads contain TNT, RDX, or HMX, or a combination of two of these compounds. These materials all belong to the CHNO family and the gaseous products are molecules containing C, H, N, and O atoms. Products of detonation for each of these explosives were calculated using the TIGER code,[3] which couples the thermodynamics and chemistry behind the shock wave following detonation. Diffusion and buoyancy models were applied to the gas cloud and showed that the cloud expanded to at least a 30 meter radius in a few minutes time and, for a temperature lapse rate corresponding to a very stable atmosphere, the center of the cloud rose to an altitude of 30 meters within a minute or so and then remained at that altitude. These are the conditions which cause the highest concentrations of the product gases, and hence are appropriate for a worst case estimate of battlefield atmospheric conditions.

Concentrations of the product gases were calculated by assuming an artillery barrage with one hit per 10 m by 10 m area per 30 minutes over a total area of 1 km^2, and assuming a 4 kg payload. The gases are contained below an altitude of 60 meters (30 meter buoyancy height plus a 30 meter radius). The concentrations in this 1 km by 1 km by 60 m volume are considered to be homogeneous. The resulting concentrations are shown in Table 1, along with the ambient concentrations of these gases. It should be noted that the concentrations in Table 1 represent fairly poor dispersion conditions.

The NH_3 concentration is somewhat uncertain. TIGER calculations must be truncated before ambient pressure and temperature are achieved because the reaction rates slow as the gas cools to a point where chemical equilibrium cannot be maintained: the real concentrations lag behind the equilibrium values. The NH_3 concentration is very sensitive to the pressure or temperature value where this truncation occurs. It should also be noted that Cook[4] predicts methyl alcohol from RDX and HCN from detonation of TNT, neither of which is predicted by TIGER.

Ozone and oxides of nitrogen are also formed in the high temperature and pressure environment of the explosive shock wave. For Tetryl, another CHNO explosive, we expect 2.2 moles of O_3 and 0.3 moles of NO per kilogram of explosive at 3 milliseconds after detonation. These amounts decrease by orders of magnitude on a time scale of 0.1 to 1 second, and ozone concentrations are not expected to be high on the battlefield.

TABLE 1. EXPLOSION PRODUCT VAPORS AND AMBIENT CONCENTRATIONS

	TIGER TNT	TIGER RDX	AMBIENT
CO	89 ppm	21 ppm	.075 ppm
H_2O	76	116	2×10^5
CO_2	125	131	330
CH_4	25	30	1.6
NH_3	0.6	0.9	---
HCN	1.5×10^{-4}	---	---

Many of the products of fires are hydrocarbons. Burning dry hay produces methyl alcohol (CH_3OH) and acetylene (C_2H_2); burning rubber produces ethylene (C_2H_4) and butadiene (C_4H_6); and ethylene also results from burning gasoline. Local concentrations may be high. An order of magnitude approximation shows that the combined concentration of ethylene and butadiene in the plume above burning rubber may be as high as 0.1 to 1% by volume.

Vehicle exhaust emissions include large amounts of CO_2 and H_2O and smaller amounts of CO, NO, aldehydes, and hydrocarbons such as ethylene. The CO_2 and H_2O emissions are not sufficient to cause a significant deviation from the ambient concentrations. CO from vehicles may be of the same order of magnitude as the background concentration, under poor dispersion conditions. Much of the NO emitted by vehicles is converted to NO_2 in the atmosphere; NO and NO_2 combined concentration is estimated at 50 ppb. Formaldehyde (CH_2O) is estimated at 2 ppb and ethylene (C_2H_4) at 0.25 ppb. All these estimates are for the 1 km^2 by 60 m volume discussed earlier. They assume one tank operating on a square kilometer for one hour, and so are easily scaled to longer times or higher vehicle densities.

3. ABSORPTION OF SUBMILLIMETER RADIATION

3.1 LINE STRENGTH AND SHAPE

The strength of an absorption line for a transition between two rotational states is given by[5]

$$S = \frac{8\pi^3}{3hc}\,\frac{n}{Q}\,g''\,\nu\,e^{-E''/kT}\,(1 - e^{-\nu/kT})\,|\mu|^2 \qquad (1)$$

where

n = number density of absorbing molecule
ν = transition frequency (cm^{-1})
g'' = lower state nuclear spin degeneracy
E'' = lower state energy
Q = partition function
μ = permanent electric dipole moment

The lower state energy of a diatomic is $BJ(J + 1)$, the upper state $B(J + 1)(J + 2)$ and hence the transition frequency for $E(J) \rightarrow E(J + 1)$ is simply $2B(J + 1)$. The diatomic recriprocal moment of interia in wavenumber units is denoted by $B = \frac{1}{4\pi hcI_B}$ where I_B is the moment of inertia about an axis perpendicular to the inter-nuclear axis. For a treatment of spectral details for molecules more complex then diatomics the reader is referred to reference 6. Symmetric top and asymmetric top spectra consist of many more lines and a less regular appearance.

In ags units the integrated line strength S' in equation (1) has units

$\frac{cm^{-1}}{molecule/cm^2} \times \frac{molecules}{cm^3} = cm^{-2}$. The absorption per unit length ("absorbance") of path depends on the spectral line width. The Lorentz line shape, normally used for infrared spectra, is not appropriate for the submillimeter where half widths can be the same order of magnitude as the transition frequency itself. The calculations in this report use the VanVleck-Weisskopf line shape (6):

$$k(\nu) = \frac{S}{\pi}\left(\frac{\nu}{\nu_o}\right)^2 \left\{\frac{\alpha}{(\nu - \nu_o)^2 + \alpha^2} + \frac{\alpha}{(\nu + \nu_o)^2 + \alpha^2}\right\}. \qquad (2)$$

where $k(\nu)$ is the absorption coefficient (cm^{-1}) at wavenumbers ν due to a line centered at ν_o with strength S (cm^{-2}) and half width α. The absorption at line center is then $k_{peak} \cong \frac{S}{\pi \alpha}$ for $2\nu_o >> \alpha$. At atmospheric pressure the line halfwidths (HWHM) are typically 0.05 - 0.15 cm^{-1} and we are considering $\nu_o > 1\ cm^{-1}$.

We will now apply equations (1) and (2) to some specific molecules to obtain their submillimeter spectra for a battlefield scenario.

3.2 SUBMILLIMETER ABSORPTION IN THE AMBIENT ATMOSPHERE

Atmospheric absorption in the submillimeter is dominated by water vapor. The only battlefield scenario possible where this would not be true is the polar environment where no water would be in the gas state. For comparison purposes, however, we present the submillimeter spectrum for a midlatitude summer atmosphere of 14.3 torr H_2O, and we give the absorbance in km^{-1}. Figures 1 and 2 present spectra based on line parameters from

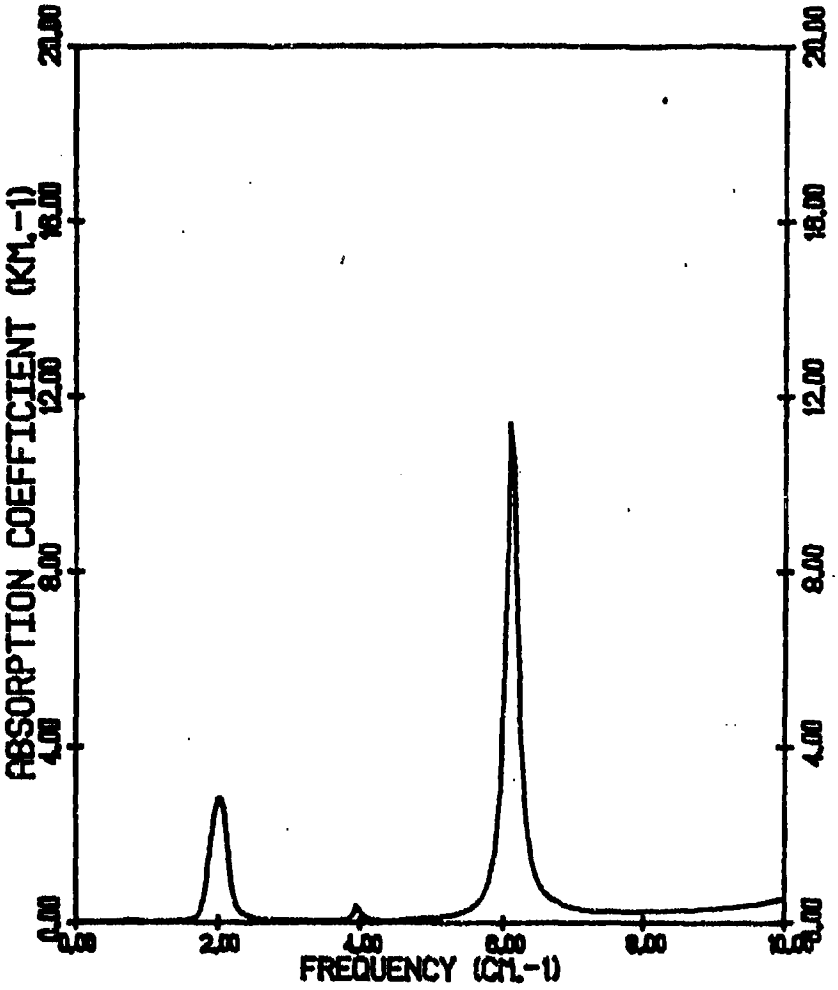

FIGURE 1. ABSORPTION BY MIDLATITUDE SUMMER ATMOSPHERE, 0 - 10 cm^{-1}.

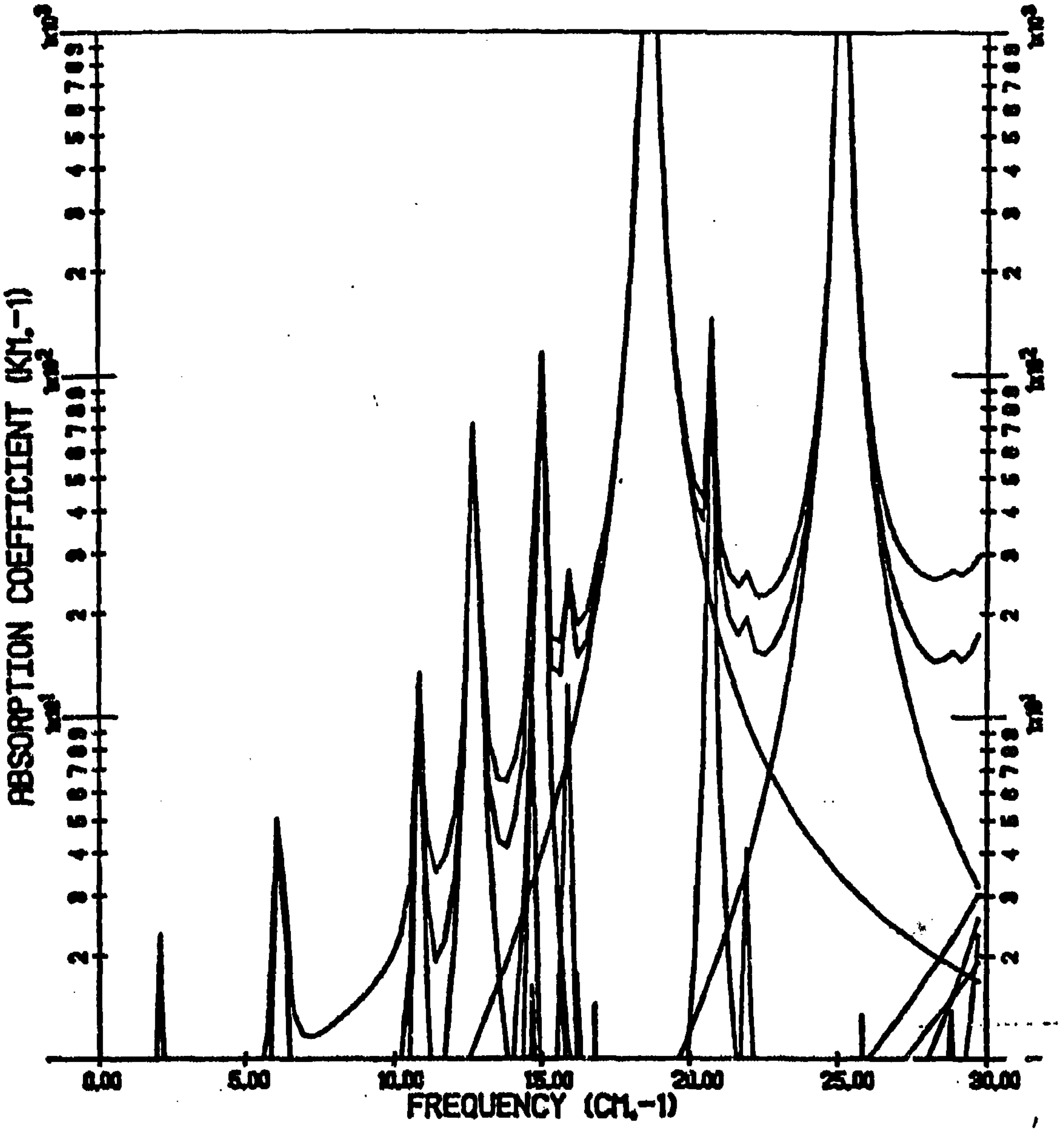

FIGURE 2. ABSORPTION BY MIDLATITUDE SUMMER ATMOSPHERE, 0 - 30 cm^{-1}. H_2O line parameters from reference 8.

the AFGL compilation (7). Absorption is comparatively low from 1 to 5 cm^{-1} with the exception of the feature at 2 cm^{-1} due to magnetic dipole absorption by diatomic oxygen. The line at 6 cm^{-1} is due to H_2O. A narrow band transmitter operating at exactly the H_2O absorption line frequency at 6.11 cm^{-1} would deliver only $e^{-5} = 0.7\%$ of its energy after traversing one kilometer of midlatitude atmosphere. A transmitter at 6.03 cm^{-1}, only one half width α away from ν_o, would deliver $e^{-2.5} = 8.2\%$ or over ten times the energy. This is a rather crude example of the need for accurate line parameters for both the trasmitter and absorbing medium. [The overshoot in Figure 1, responsible for the disagreement between figures 1 & 2 at 6 cm^{-1}, is an artifact of the plotting].

Figure 2 shows, in addition to absorption by individual lines, the sum of the wings of all the lines and an additional broad absorption - the continuum. The top most curve of Figure 2 represents the sum of these. Clearly the wings of the strong lines have an important contribution to the total ambient absorption, and are responsible for the residual absorption in the window regions between the line peaks. The strength of the peaks at 18 and 25 cm^{-1} represent 1/3 absorption lengths of less than one meter. The "window" regions at 22 and 27 cm^{-1} absorb at about 30 km^{-1}. Of course a reduction of water vapor partial pressure will reduce the absorption (almost) linearly. Nevertheless, it is against this very strong backdrop of ambient absoption that we wish to examine the absorptive effects of gases common to a land battlefield scenario.

3.3 ABSORPTION BY BATTLEFIELD GASES

Table 2 summarizes the battlefield gases expected due to high energy explosives, fires, and vehicles, along with predicted worst-case concentrations. The "submillimeter active" column relfects the presence or absence of a permanent electric dipole moment. The submillimeter spectra of some of these gases are not well documented.

TABLE 2. BATTLEFIELD GASES IN THE SUBMILLIMETER REGION

	NAME	SOURCE	WORST-CASE CONCENTRATION	SUBMILLIMETER ACTIVE?
CO	Carbon Monoxide	Explosives	89 ppm	yes
CH_4	Methane	Explosives	30 ppm	no
NH_3	Ammonia	Explosives	1 ppm	yes
HCN	Hydrogen Cyanide	Explosives? Vehicles?		yes
CH_3OH	Methyl Alcohol	Burning foliage		yes
C_2H_2	Acetylene	Burning foliage		no
C_2H_4	Ethylene	Burning foliage		no
C_4H_6	Butadiene	Burning rubber		yes
NO	Nitric Oxide	Vehicle exhaust	50 ppb	yes
NO_2	Nitrogen Dioxide	Vehicle exhaust		yes
CH_2O	Formaldehyde	Vehicle exhaust	0.25 ppb	yes

Figure 3 is the spectrum for CO from 0 to 40 cm^{-1}. The line parameters are from the AFGL compilation[6] and the plot is for 90 ppm of CO, approximately 90 times the ambient concentration.

Figure 4 plots absorption by 1 ppm of HCN. Although we do not predict significant concentrations of HCN, others have, as discussed in Section 2. We include its spectrum because it has the potential of affecting the HCN laser which operates at 29.71258 cm^{-1}.[9] The line strengths for HCN were calculated using

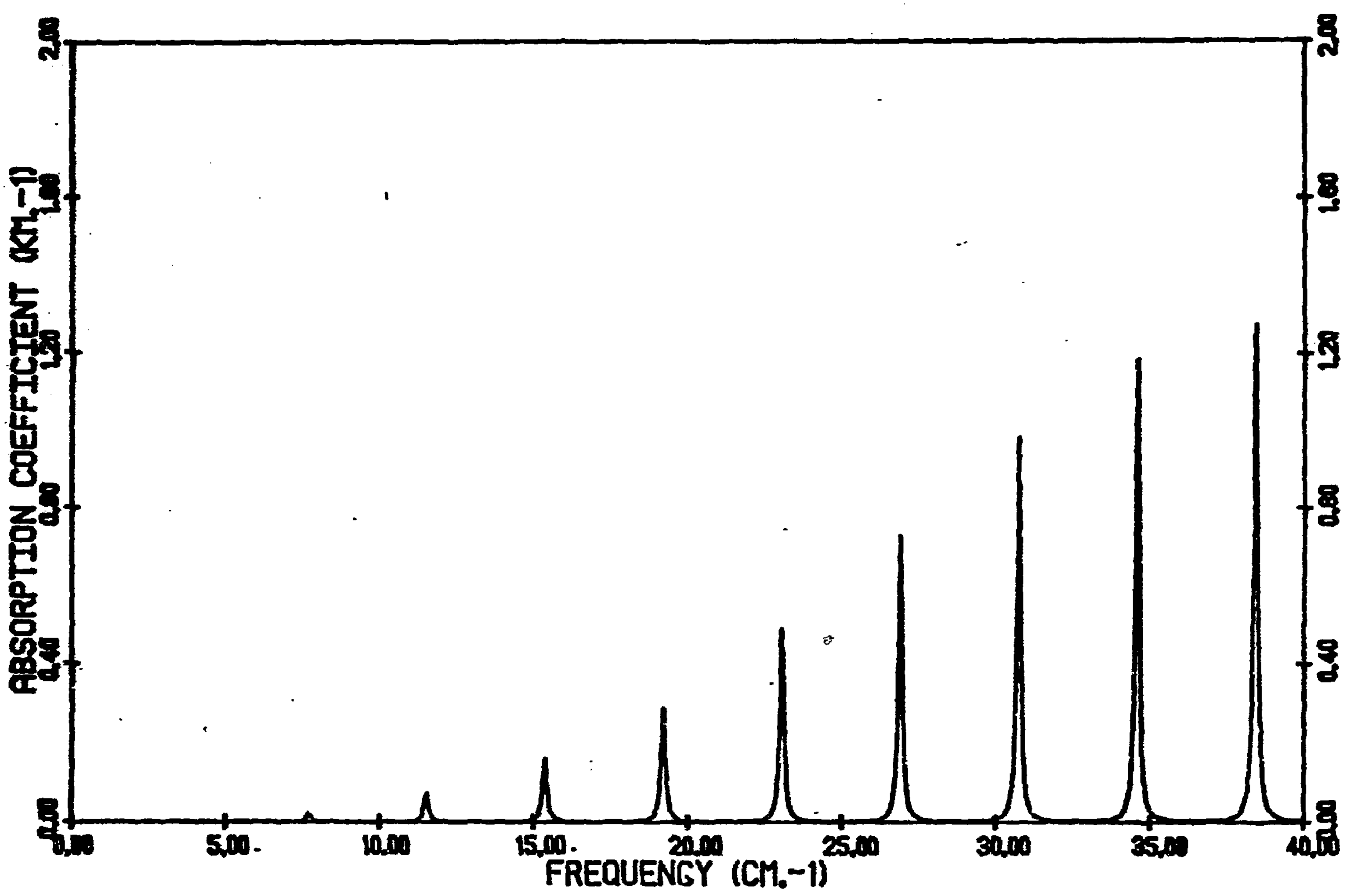

FIGURE 3. ABSORPTION BY 90 ppm of CO

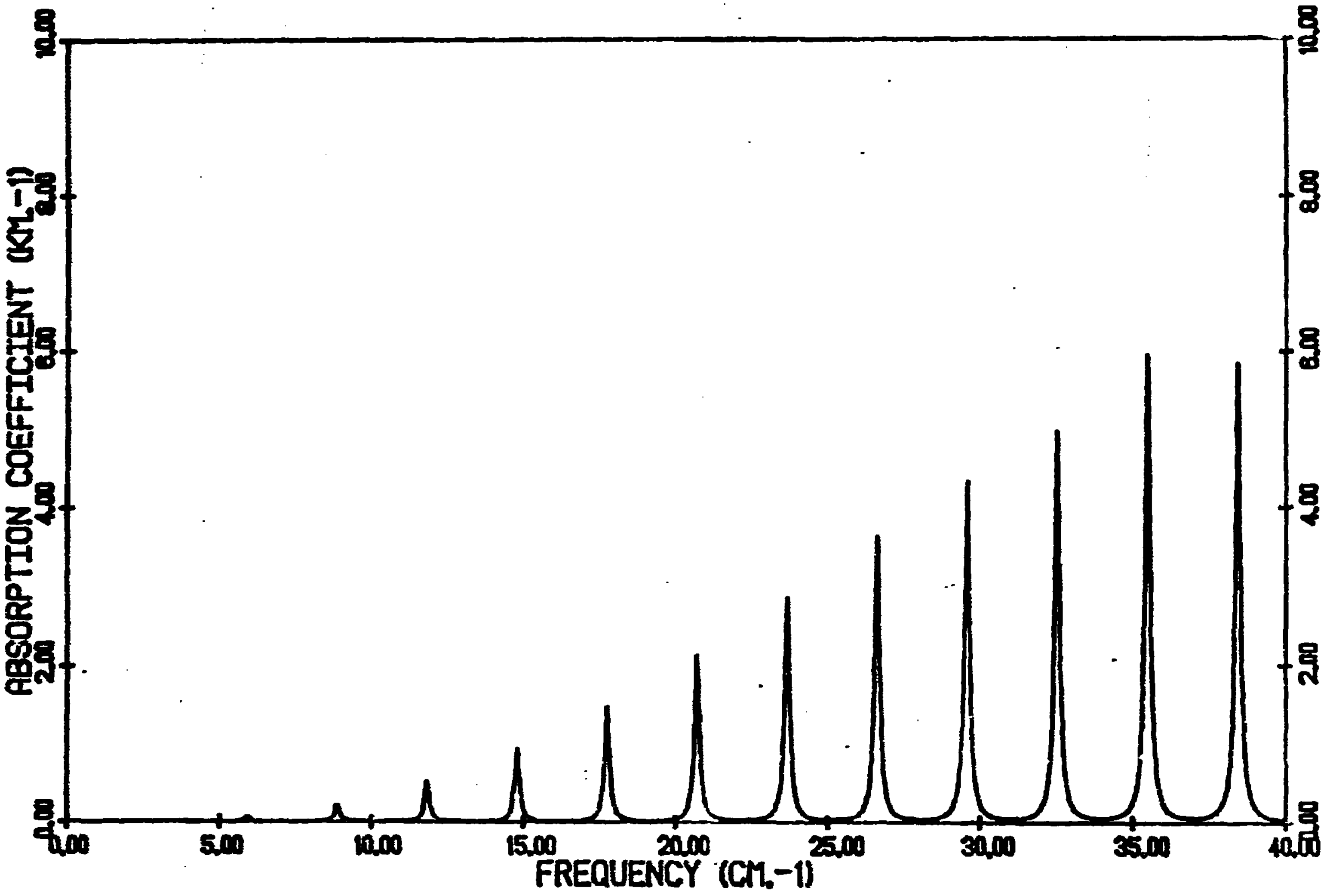

FIGURE 4. ABSORPTION BY 1 ppm OF HCN

equations 1 & 2 with B = 44.31597 GHz, and μ = 3.00 Debye (ref. 6 page 618). The line positions and strengths are summarized in Table 3. (d is assumed to be 0.10 cm^{-1}, and a small centrifugal distortion correction has been included in the frequency.) We remark that the HCN laser line does not line up exactly with the J9 → 10 absorption because the absorption is in the vibrational ground state where as the laser transition takes place in a highly excited vibrational state.

TABLE 3. CALCULATED ABSORPTION PARAMETERS FOR HCN

J" → J'	$\nu(cm^{-1})$	E"	$k^{*}_{max}(km^{-1}/ppm)$	S $(cm^{-1}/mol/cm^2)$
1 → 2	5.917	2.958	7.46 E-2	8.72 E-21
2 → 3	8.875	8.874	0.243	2.84 E-20
3 → 4	11.833	17.748	0.548	6.402 E-20
4 → 5	14.791	29.58	1.003	1.173 E-19
5 → 6	17.748	44.37	1.603	1.875 E-19
6 → 7	20.705	62.12	2.321	2.714 E-19
7 → 8	23.661	82.82	3.114	3.641 E-19
8 → 9	26.617	106.5	3.929	4.593 E-19
9 → 10	29.573	133.1	4.705	5.500 E-19
10 → 11	32.527	162.7	5.398	6.311 E-19
11 → 12	35.481	179.0	6.434	7.522 E-19
12 → 13	38.434	230.7	6.335	7.407 E-19

*assumes linewidth HWHM = .10 cm^{-1}

4. EFFECTS OF BATTLEFIELD GASES AT KEY WAVELENGTHS

A number of lasers operate in the submillimeter region. Table 4 lists a few of the stronger laser lines which occur in submillimeter windows. This list is by no means complete; reference 10 lists over 500 submillimeter lines of lasers pumped by CO_2 lasers.

Figure 5 shows a plot of H_2O absorption from 0 to 50 cm^{-1}, with the positions of the laser lines from Table 4. The transmission calculations in this figure are not highly accurate (they don't include induced emission and use the Lorentz line shape) but are sufficient for purposes of demonstration. The path for this calculations is one meter through the standard atmosphere concentration of water vapor (14.25 torr) and the figure demonstrates well the extreme magnitude of water vapor absorption in the submillimeter region.

The dominance of water vapor absorption over other ambient or battlefield generated gases is apparent from comparison of Figures 5 and 2. For the two laser lines between 8 and 9 cm^{-1}, the CH_3OH and CH_3CCH lines, we see from Figure 2 that the midlatitude summer water vapor concentration provides about 2 km^{-1} absorption, or 13.5% transmission over a 1 km path. Absorption due to other gases is orders of magnitude below this. The CH_3Br and CH_3CN lines between 13 and 14 cm^{-1} are in a small window between two H_2O lines, and H_2O contributes about 7 km^{-1} of absorption. Again, absorption from other gases is far less. The CH_3OH line is near an H_2O line and is not really well placed in the 22 cm^{-1} window. The HCOOH line has a good position in the 22 cm^{-1} window, and H_2O absorption is around 30 km^{-1}.

TABLE 4. SUBMILLIMETER LASER LINES NEAR ATMOSPHERIC TRANSMISSION WINDOWS

LASER	$\lambda(\mu)$	$\nu(cm^{-1})$	EXCITATION	PEAK POWER
NH_3	290.5	34.42	CO_2 10P(32)	0.8 kw
HCN	336.558	29.7126	electric discharge	0.6 W
HCOOH	433	23.1	CO_2 9R(32)	0.1 W
CH_3OH	471	21.2	CO_2 10R(38)	0.1 W
CH_3CN	713.7	14.01	CO_2 10P(32)	0.7 mW
CH_3Br	732	13.7	CO_2 10R(14)	0.4 mW
CH_3CCH	1175	8.51	CO_2 10P(44)	2.7 mW
CH_3OH	1217	8.22	CO_2 9P(16)	25 mW
$C^{13}H_3F$	1222	8.18	CO_2 9P(32)	2 mW

Data from references 9, 10, and 11.

The HCN laser line at 29.71 is in a good position in the 29 cm^{-1} window. Water vapor absorption, for the midlatitude summer sea level concentration, is about 30 km^{-1}, or 5% transmission through a 100 meter path. From Figure 4 we see that HCN has an absorption line at 29.57 cm^{-1}. A simple calculation using the parameters from Table 3 shows that 20 ppm of HCN are required to compete with water vapor absorption.

The NH_3 laser line at 34 cm^{-1} is beyond the scale of Figure 2. We can make a rough estimate of H_2O absorption from Figure 5, however. The transmittance is 89% for a one meter path, corresponding to absorption of about 120 km^{-1}.

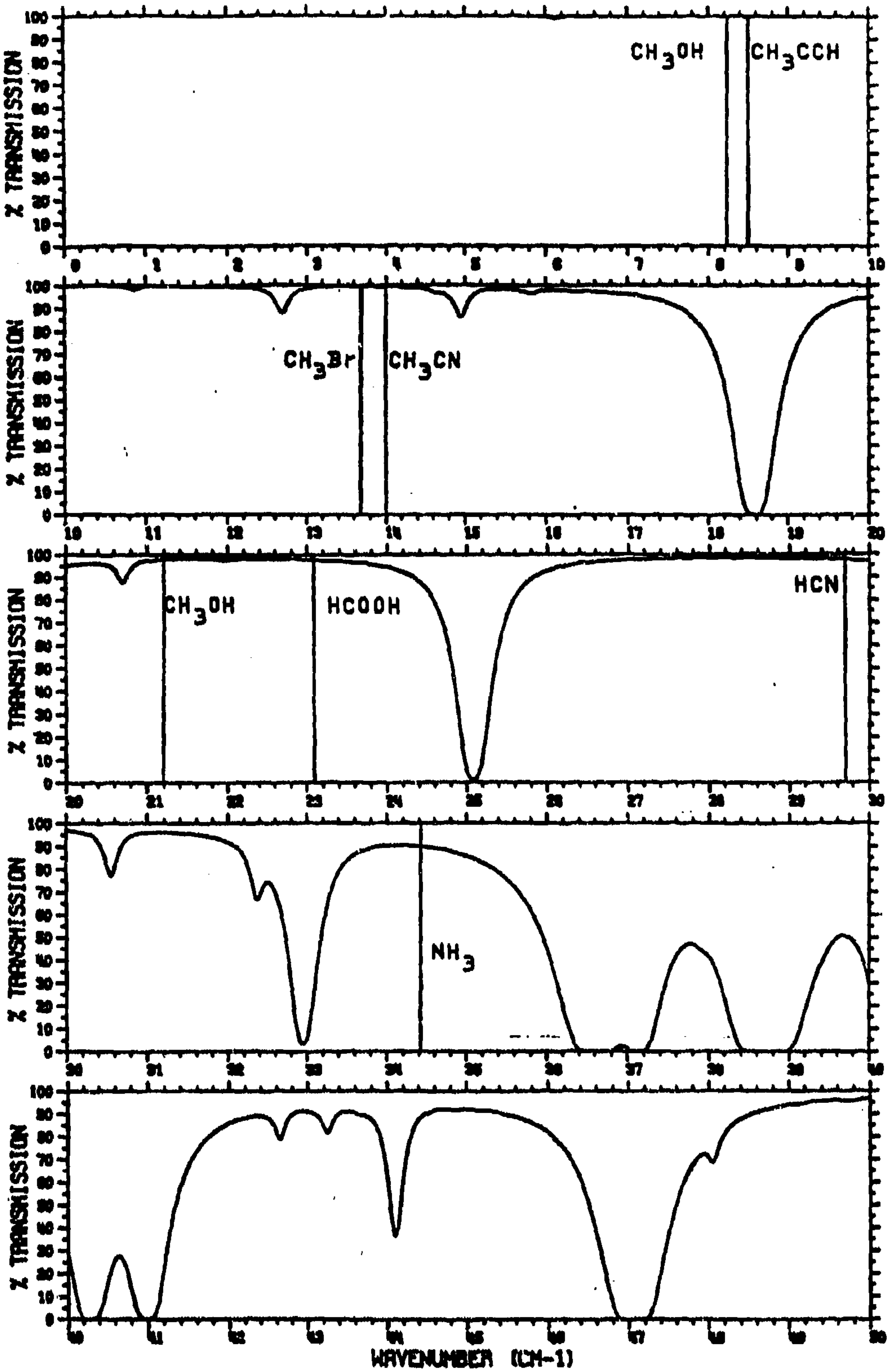

FIGURE 5. H_2O TRANSMISSION FOR A ONE METER PATH THROUGH A MIDLATITUDE SUMMER ATMOSPHERE, AND LASER FREQUENCIES IN THE SUBMILLIMETER WINDOWS.

Again, other gases cannot absorb within orders of magnitude of this value.

The 140, 94, and 35 GHz radar frequencies are also of interest (4.677, 3.133, and 1.167 cm^{-1}, respectively). These frequencies are relatively clear with 0.5 km^{-1} absorption or less due to atmospheric H_2O, and are not strongly affected by battlefield gases. Formaldehyde has three absorption lines near 140 GHz, and a high concentration of formaldehyde concentrations due to battlefield activity will not be high enough to have a significant effect. Appendix A outlines the calculation of the positions and strengths of these lines and discusses the merits of formaldehyde as a countermeasure for 140 GHz radiation.

5. CONCLUSIONS AND RECOMMENDATIONS

Absorption of submillimeter radiation is dominated by naturally occurring water vapor. This absorption is high even in the window regions, and for normal humidity conditions the applications of submillimeter radiation appear limited to short ranges, a few hundred meters at very most. Absorption is much less severe for the 35, 94, and 140 GHz regions.

Accurate prediction of submillimeter absorption by experimental battlefield gases is difficult because of a lack of data on the generation rates of some of the important battlefield gases, coupled with a lack of detailed submillimeter spectral information about these gases.

Theoretical studies can provide an excellent means of interpreting data and interpolating or extrapolating to make predictions for a range of conditions. Without some experimental data, a theoretical study can only speculate. While we believe that the work presented in this report is certainly better than speculation, the data base has some gaping holes. To obtain a thorough understanding of submillimeter absorption and the effects of battlefield activity on submillimeter radiation a program of combined theoretical and experimental work is needed. The work needed falls into four broad categories.

1. Modeling. Absorption should be modeled as a function of water vapor concentration for submillimeter windows or laser frequencies. The submillimeter spectrum of water is fairly well known and such a model would indicate the degree of usefulness of devices operating in the submillimeter. The effects of aerosols, both naturally occurring and battlefield induced, should also be modeled. The effects of snow have long been ignored.

2. Field Testing of Gas Sources. Experimental work is needed to determine the rates of combustion of battlefield materials - vegetation, diesel fuel, tires, perhaps a jeep. Chemical or spectroscopic analysis of air samples could provide information about what gases are emitted and at what rate, ideally in easily scaled units such as grams of product per gram of fuel per second. Controlled burning of a one acre hay field alone could provide a great deal of useful information. The work of Barrett et al.[12] along these lines is useful in the infrared, but their results are in units of infrared absorption coefficient per unit fuel mass per unit volume and product gas concentrations are not found. Their results therefore cannot be applied to the submillimeter. Their results for gram samples probably do not scale to acre magnitudes.

3. Gas Spectra. Although it presently appears that none of the battlefield generated gases can compete with water vapor in absorbing submillimeter radiation, lower humidity conditions might increase the relative importance of absorption by other gases. Testing in the field might also reveal other gases or higher concentrations than predicted. Calculations based on molecular parameters can predict the magnitude of absorption by these gases, but laser line absorption calculation requires accurate absorption line positions and strengths. Detailed calculation or laboratory experiments may be required to obtain the necessary line data.

4. Laser Field Tests. Lasers operating in the submillimeter windows should be tested under ambient atmospheric conditions and under conditions simulating the battlefield environment, such as above burning debris and in the vicinity of artillery explosions. A large scale land battle would indeed be difficult to model, or even to simulate. However, the effects of munition explosions, burning debris, etc., could be scaled up by using an outdoor White cell. A set of properly placed multipass mirrors could easily provide a 1 km path through a 50 meter square target area or fire area.

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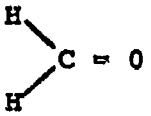
APPENDIX A
FORMALDEHYDE ABSORPTION AT 140 GHz

It is of interest to consider countermeasure absorption for 140 GHz radiation. Candidate gases should absorb strongly near 4.667 cm^{-1}. In this region of the spectrum, absorption is accomplished by transitions between closely spaced rotation energy levels of low angular momentum. For formaldehyde, CH_2O, three transitions in the $J:1 \rightarrow 2$ asymmetric rotor manifold absorb with total strength 0.6 km^{-1}/ppm.

Formaldehyde is a planar, nearly prolate asymmetric rotor with the following rotation constants:

$A = 9.408\ cm^{-1}$
$B = 1.296$
$C = 1.135$



Were it true that $B = C$, then CH_2O would be a prolate symmetric top and the analysis would be straightforward. However, the amount of asymmetry is described by:

$$b_p = \frac{C - B}{2A - B - C} = -0.00983.$$

A.1 TRANSITION FREQUENCIES

A rough estimate that CH_2O can absorb near 4.667 cm^{-1} is provided by the fact that 2B is very nearly an integer multiple of 4.667 cm^{-1}. It turns out that the asymmetry splitting shifts one absorption component almost to 4.667 cm^{-1}. Since CH_2O is very nearly a symmetric rotor we calculate the low J rotation levels from

$$E(J,K) = \frac{B+C}{2} J(J+1) + (A - \frac{B+C}{2}) w,$$

where

$$w = K^2 + c_1 b_p + c_2 b_p^2 + c_3 b_p^3 + \ldots,$$

and b_p is defined above. From reference 6 we obtain $c_1 = \pm 1$ for $J = 1$, and $c_1 = \pm 3$ for $J = 2$ of the $K = 1$ manifold; all other c's vanish for $K = 1$. The selection rules governing transitions 2 and 3 are $\Delta K_A = 0$, $\Delta K_C = \pm 1$, appropriate for an asymmetric rotor with electric dipole moment parallel to the axis of least moment of inertia (A). Of course the $K_A = 0$ levels are unsplit, and the selection rules in this case are $\Delta K = 0$ and $\Delta J = \pm 1$. Three transitions result which are close to 140 GHz (4.667 cm^{-1}):

$\nu_1 = 4.862$ $\quad 1_{01} \rightarrow 2_{02}$

$\nu_2 = 4.701$ $\quad 1_{11} \rightarrow 2_{12}$

$\nu_3 = 5.023$ $\quad 1_{10} \rightarrow 2_{11}$

Since at the low J,K quantum numbers centrifugal distortion is minimal, the above frequencies are accurate to 0.001 cm^{-1}. The energy level structure is given in Figure 6.

A2. ABSORPTION STRENGTH

Because CH_2O is very nearly a prolate symmetric top, and because we are dealing with undistorted states of low angular momentum, we can estimate the absorption strength of the above lines by using the symmetric rotor expression (reference 5):

$$\frac{\gamma}{N} = \frac{4\pi h f_v}{3c(kT)^2} \times \frac{S(I,K)}{4I^2 + 4I + 1} \times \left(\frac{\pi Ch}{kT}\right)^{1/2} \times \mu^2 \times \left(1 - \frac{K^2}{(J+1)^2}\right) \times g(\nu)$$

where

$$g(\nu) = \frac{\nu_o \nu^2 \Delta\nu}{(\nu - \nu_o)^2 + (\Delta\nu)^2} \quad \text{and} \quad \frac{S(I,K)}{4I^2 + 4I + 1} \approx 2$$

Using $\mu = 2.331$ Debye, $kT = 208\ \text{cm}^{-1}$, and some juggling of units we reduce the above to a more manageable form:

$$\gamma = 6.40 \times 10^{-4}\ f(J,K)\, g(\nu)\ \text{km}^{-1}/\text{ppm}$$

where

$$f(J,K) = \left(1 - \frac{K^2}{(J+1)^2}\right)$$

and the units of $g(\nu)$ are $(\text{cm}^{-1})^2$.

The γ for each line is now evaluated assuming an atmospherically broadened $\Delta\nu = 0.1\ \text{cm}^{-1}$ HWHM linewidth:

1. $\nu = 4.667$ $f(J,K) = 1.0$ $\gamma_1 = 0.141$
$\nu_o = 4.862$ $g(\nu) = 220.5$
$\Delta\nu = 0.1\ \mathrm{cm}^{-1}$

2. $\nu = 4.667$ $f(J,K) = 0.75$ $\gamma_2 = 0.441$
$\nu_o = 4.701$ $g(\nu) = 917.8$
$\Delta\nu = 0.1\ \mathrm{cm}^{-1}$

3. $\nu = 4.667$ $f(J,K) = 0.75$ $\gamma_3 = 0.038$
$\nu_o = 5.023$ $g(\nu) = 80.0$
$\Delta\nu = 0.1\ \mathrm{cm}^{-1}$

The total absorption at 140 GHz due to 1 ppm CH_2O is then $\gamma_1 + \gamma_2 + \gamma_3 = 0.62\ \mathrm{km}^{-1}$.

A.3. COUNTERMEASURE USE OF FORMALDEHYDE

Ambient H_2O absorption at 140 GHz for midlatitude summer conditions is 0.5 km^{-1}, the same order of magnitude as that provided by 1 ppm formaldehyde, or 0.62 km^{-1}. Since H_2CO boils at -21°C, it could be stored at high concentration in pressurized tanks, or in liquid solution with methanol. The molecular weight of formaldehyde is 30, roughly equal to the average molecular weight of air, and hence no settling out would occur as happens with smokes or fog oil. Dispersal of CH_2O from a helicopter, say, could easily be accomplished from pressure tanks.

It is of interest to calculate the quantity of formaldehyde needed to provide 20 dB/km attenuation (1% trans/km). For lack of a specific scenario we assume the CH_2O will be dispersed from a helicopter to fill a 20 m x 20 m x 1 km volume, or $4 \times 10^5\ \mathrm{m}^3$. 20 dB/km attenuation is equivalent to an absorption coefficient of 4.6 km^{-1} for a 1 km path. In the last section we calculated the absorption coefficient to be 0.62 km^{-1}/ppm, hence 7.5 ppm CH_2O uniformly mixed over a 1 km path would provide the required absorption. Certainly windy or turbulent weather conditions could require more CH_2O, but for the above scenario only 4.05 kg of formaldehyde would be required. One problem with formaldehyde is that it is highly toxic and could be lethal in sufficient quantity. It is also a suspected carcinogen of the lung[13].

What we have shown here is that small quantities (ppm) of a correctly chosen gas can strongly influence 140 GHz transmission through the atmosphere. It is important that the absorption line be as near as possible to the signal line center, within 0.05 cm^{-1} or less for example. Our discovery of the formaldehyde absorption line was quite accidental, and a great deal of searching will be required before a less toxic substitute can be found.

FIGURE 6. CH_2O LOW J,K ROTATION LEVELS