Atmospheric Water Vapor: A Nemesis for Millimeter Wave Propagation

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Millimeter waves offer an attractive way of solving unique system problems because of their ability to penetrate clouds, smog, dust or fog. This makes them a logical choice over electro-optical devices for adverse weather applications. Spectral lines of oxygen and water vapor ultimately limit the atmospheric transparency; hence, most applications operate between the absorption lines in four window regions (that is, 24 to 48, 72 to 110, 128 to 160, and 200 to 260 GHz). Observations have established the existence of excess water vapor absorption (EWA), which is most evident in these windows. Excess implies that the effect is not related to the known spectral properties of the water molecule. EWA is found to increase in nontrivial manner with humidity and the discrepancies can be as large as a factor of 10. Several groups (most notably at the Appleton Laboratory, UK), have gathered evidence of EWA from laboratory and field observations and brought forward hypotheses to account for the data. Qualitative explanations are based on the assumption that water molecules in moist air form larger molecules with a dimer being the first step in a series of stable species. Hydrogen bonding, ion attraction and attachment of the polar H₂O to foreign particles (aerosol growth) are the ordering forces considered in the clustering process. An assessment of the current EWA picture will be given and avenues of research attacks are discussed to solve the enigma in the quantitative description of the interaction between millimeter waves and moist air.

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I. INTRODUCTION

Atmospheric water in both vapor and liquid states is the major deterrent to an unrestricted exploitation of propagation of millimeter and, more so, of infrared wavelengths. For most applications, the operation of ground-based systems is limited to seven window regions W1 to W7, these being the gaps between molecular absorption lines and bands:

<table>
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<tr>
<th>Absorption Feature</th>
<th>Region</th>
<th>Window Range</th>
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<tr>
<td>22 GHz $\text{H}_2\text{O}$ line</td>
<td>W1</td>
<td>24 to 48 GHz</td>
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<td>60 GHz $\text{O}_2$ line complex</td>
<td>W2</td>
<td>70 to 115 GHz</td>
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<td>W6</td>
<td>20 to 38 THz</td>
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<td>W7</td>
<td>60 to 100 THz</td>
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The main attraction of millimeter wave systems is their ability to penetrate the somewhat opaque atmosphere (haze, fog, clouds, dust, smoke, light rain) under circumstances in which electro-optical and infrared systems normally fail. Accurate and detailed knowledge of atmospheric transmission is essential to an evaluation of the advantages of millimeter waves over the shorter wavelengths.

One objective of this paper is to focus attention on unsolved problems in the construction of a valid model for atmospheric millimeter wave transmission, subject to the following conditions: Frequency, $\nu = 10$ to 1000 GHz, with special emphasis on the EHF range, $\nu = 30$ to 300 GHz; altitude, $h = 0$ to 30 km; and relative humidity, $\text{RH} = 0$ to $\leq 100\%$. The radio engineer uses the optical term "clear" for moist, but unsaturated air ($\text{RH} < 100\%)$, and ignores haze conditions. Although many constituents contribute to the total atmospheric attenuation rate, $\alpha$ (dB/km), absorption in the window is dominated by water vapor and is of greatest concern for practical situations. At present, describing water vapor absorption mechanisms and relating them to measurable quantities is partly an empirical matter and lacks credibility in a general sense.

The following interaction effects between millimeter waves and air are well documented:
A) NEMESIS FOR MILLIMETER WAVE PROPAGATION

Case References
(a) Absorption line theory . . . 1, 4, 13, 31
(b) Moist air refraction . . . . 2, 5, 7, 47-50
(c) Water vapor absorption . . . 1, 3, 4, 7, 14, 16, 17, 24, 25
(d) Water vapor dispersion . . . 2, 4, 5, 7, 17, 62, 67
(e) Water vapor continuum
    absorption . . . . . . . 11, 12, 18, 21, 22, 24, 26, 31
(f) Oxygen absorption . . . . 15, 17, 19, 65
(g) Complete line parameter compilation for all atmospheric molecules . . . 110
    known as the AFGL Tape,
    HITRAN Model and FASCODE . 10, 14, 25, 29
(h) Scattering loss by particles 33, 32, 35-37
(i) Dielectric loss of water . . . 25, 27, 32, 102-106

Other physical effects, which have been taken into account in infrared transmission models (9), (20), and (23) are:
(k) Submicron aerosol particles . 38, 41, 42
(l) Growth of submicron
    particles in moist air . . . 35-37, 34

Of a more speculative nature are considerations of
(m) Water dimer (H₂O)₂ spectra . 6, 8, 21, 43, 58, 64, 66, 69, 81, 86, 89, 109
(n) Water cluster (H₂O)ₙ, n>2 . . . 21, 22, 44
(o) Water ion activity . . . . . 28, 45

The water polymer hypotheses have the inherent weakness that except for the dimer (43), neither definite structural observations have been made nor millimeter wave spectra calculated. In the cases (m) to (o), production and growth mechanisms (for example, ion-induced) as well as size and number density distributions have not been identified for the natural atmospheric environment.
Measured absorption in the windows W1 to W7 could provide clues for the understanding of which basic physical mechanisms are missing in current models. New instrumentation, such as the dispersion spectrometer (63,65) and the saturation hygrometer (107), might prove helpful in future investigations. Available experimental results on absolute attenuation rates, path transmittances, and thermal emission from laboratory (46-71) and field (73-101) observations in cloudless moist air are generally higher than values predicted on the basis of molecular absorption alone. It is a fact, even after allowing for difficulties in measuring the highly variable water content quantitatively, that the absorption by water vapor in the atmospheric transmission windows W1 to W7 is not completely understood.

Section II of this paper presents the framework for a radio path modeling scheme of which details, such as measurements and validation, have been published (15,17,19). The model serves as a basis for the definition and discussion, in Section IV, of the problem of excess water vapor absorption (EWA) in the light of experimental data. Section III is devoted to a brief presentation of relevant physical properties of atmospheric water vapor.

II. EHF RADIO PATH MODELING

Millimeter waves traveling through the cloudless (RH < 100%) atmosphere suffer both deterministic and random variations in amplitude and phase. Radiation is absorbed and refracted by gases and submicron particles. This interaction is modeled with the intent to predict the following frequency-dependent propagation effects: (a) absorptive loss of coherent radiation, (b) time of propagation between two points, (c) refractive ray-bending and ducting, (d) generation of incoherent noise, and (e) scintillations due to random fluctuations of the medium in space and time. The array of mathematical and empirical expressions used to compute these various effects is called the Propagation Model. Such a parameterization scheme depends foremost on spectroscopic information about kind and number density of absorber species and on their distribution within the path volume.

A. The Propagation Model

Complex refractivity N(ppm) is a convenient macroscopic measure of the interaction between millimeter wave radiation and the individual absorbers in moist air. A value of N accounts for the effectiveness and number density of a particular absorber population. Later these dependences are formulated in terms of measurable quantities. At this point, N is assumed to be known
and the basic relations that determine the electromagnetic behavior of a radio path are written down. The complex refractivity of a gaseous medium in ppm

\[ N = N_0 + D(V) + j N''(V) \]  

consists of three components; namely, the frequency independent refractivity \( N_0 \) plus various spectra of refractive dispersion \( D(V) \) and absorption \( N''(V) \). The atmosphere is characterized as a linear network with both passive and active properties. The amplitude and phase response of a plane radio wave traveling the distance \( L(km) \) and having an initial field strength \( E_0 \) is described by

\[ D = E_0 \exp (\Gamma L) \]  

where

\[ \Gamma = j(2\pi V/c)(1 + N \cdot 10^{-6}) \]  

is the propagation constant of the intervening medium, \( c \) being the speed of light. Usually, real and imaginary parts of \( N \) are separated and expressed as the power attenuation rate in dB/km

\[ \alpha = 0.1820vIM(n) \]  

and the phase delay rate in radian/km

\[ \varphi = 0.0209vRE(N) \]  

The frequency \( V \) is in gigahertz (GHz) throughout the paper.

The attenuation rate \( \alpha \) is the more familiar quantity in atmospheric wave propagation. The phase rate \( \varphi \) must be considered when it varies spatially (for example, radar pointing accuracy, long-baseline interferometry, maximum dish size for reflector antennas, etc.) or with frequency (for example, bandwidth limitations of a communication channel). Characteristics of short, horizontal radio paths may be approximated by an average value of \( N \). More general path geometries, such as a ground-to-satellite link, are treated by dividing the path into segments having quasi-constant \( N \)-values and summing. The cumulative behavior between the ray points \( s_1 \) and \( s_2 \) is expressed in dB by the total attenuation

\[ A = \int_{s_1}^{s_2} \alpha(s) \, ds \]  

or by the transmittance (multiply by \( 1/10 \log e + 0.023026 \) to convert dB to \( Np \)).
The medium becomes transparent when $T$ approaches one and, on the other hand, opaque for $T = 0$.

The total phase change for the same path is given in radians by

$$\phi = \int_{s_1}^{s_2} \varphi(s) \, ds \tag{8}$$

which translates into the travel-time in ns of the wave by

$$n = \frac{\phi}{2\pi v} \tag{9}$$

The path differential $ds$ is, in practice, an increment $\Delta s$ over which $N$ is quasi-constant, and depends upon the altitude, $h$; the starting angle, $\theta$, from the zenith in the case of a slant path; and refractive bending of the ray (Snell's law) due to gradients $\delta \omega / \delta s$ (19).

Absorption by the atmosphere causes emission spectra. Each unit of volume maintains thermal equilibrium with its environment via collisions; hence, the path element $ds$ radiates an equivalent blackbody emission $T(s) \alpha(s) \, ds$, which is reduced by the transmittance $\tau(s)$ along the path of observation. The resulting brightness temperature in K

$$T_B = 0.230 \int_{0}^{\infty} T(s) \alpha(s) \tau(s) \, ds \tag{10}$$

is either less than or equal to the ambient temperature $T$.

Equations (6), (8), and (10) constitute the key by which performance limitations of EHF systems operating over clear-air propagation paths may be evaluated. A transfer function exhibiting constant amplitude ($A = \text{constant}$), frequency-linear phase delay [$D(V) = 0$], and no noise ($T_B = 0$) implies ideal channel behavior. A broadband signal occupying a frequency interval $\Delta V$ is distorted by the deterministic spectra of $D(V)$ and $N''(V)$; in addition, $T_B$ imposes detection limitations. As a bonus, the emission spectra $T_B(V)$ afford opportunities to sense remotely the state of the atmosphere by passive radiometric means (for example, Refs. 39 and 40).

B. The EHF Refractivity of Moist Air

The physical state of moist air is described by
A NEMESIS FOR MILLIMETER WAVE PROPAGATION

\[
\begin{align*}
\text{dry air pressure (1 kPa = 10 mb)} & \quad P, \text{ kPa} \\
\text{relative inverse temperature (T in K)} & \quad t = 300/T \\
\text{water vapor partial pressure} & \quad e, \text{ kPa}
\end{align*}
\]

\[
N = 2.589 P t + (41.6 t + 2.39) e t
\]

(12)

Water vapor refractivity is about 16 times more effective, on a per molecule basis, than dry air in generating propagation phenomena such as delay, ray bending, ducting, scintillations, etc.

The dispersion contribution in ppm

\[
D(V) = \sum_i (S F')_i - 41.6 e t^2
\]

and the absorption spectrum in ppm

\[
N''(V) = \sum_i (S F'')_i + N'' + N''_X
\]

(14)

require further elaboration. Frequency-dependent molecular spectra are of two types:

1. Line spectra of absorption $SF''$ and of dispersive refraction $SF'$, having strength $S$ in units of kHz and shape factors $F'$ and $F''$ in units of GHz$^{-1}$; the sums over $i$ consider millimeter wave lines (see Tables 1 and 2) of O$_2$ ($i = 2$ to 45)$^2$ and H$_2$O ($i = 46$ to 74). Spectra of the trace gases O$_3$, CO, N$_2$O, SO$_2$, NH$_3$, etc. are neglected (10,17,29,31,110).

2. Continuum water vapor spectrum $N''_X$ due to far-wing contributions of very strong infrared lines. A third term, $N''_X$, which is not fully understood, was added to the absorption to account for contributions other than those of the rotational water vapor line spectrum (see Section IV).

Common to each spectroscopic feature is an intensity-against-frequency distribution function, the shapes $F'(V)$ and $F''(V)$.

For $h < 20$ km, the shape functions are (17)

\[
F' = \frac{(V - V_0) + YI}{(V - V_0)^2 + Y^2} + \frac{(V + V_0) + YI}{(V + V_0)^2 + Y^2}
\]

(15)

and

\[\text{The nonresonant oxygen spectrum, } i = l \text{ is discussed in Ref. 17.}\]
\begin{table}
\centering
\begin{tabular}{cccccccc}
\hline
Center frequency & Temperatures & Strength & Temperature & Width & Interference & Temperature & ID \\
\hline
\multicolumn{8}{l}{\text{TABLE 1. Data Base for } O_{16}^{16} \text{ Spectral Lines in Air up to 1000 GHz}} \\
\hline
\text{i} & \(v_0\) GHz & \(a_1\) kHz/kPa & nent \(a_2\) & \(a_3\) GHz/kPa & \(a_4\) kHz/kPa & nent \(a_5\) & \hline
1 & 0 & 3.070 & E-4 & -- & 5.6 & E-3 & -- & Nonresonant & \\
50.47360 & 0.940 & E-6 & 9.6900 & 8.60 & E-3 & 5.200 & E-6 & 1.79 & 37 & \\
50.98730 & 2.440 & E-6 & 8.6900 & 8.70 & E-3 & 5.500 & E-6 & 1.69 & 35 & \\
51.50302 & 6.040 & E-6 & 7.7400 & 8.90 & E-3 & 5.600 & E-6 & 1.77 & 33 & \\
52.02117 & 1.410 & E-5 & 6.8400 & 9.20 & E-3 & 5.500 & E-6 & 1.81 & 31 & \\
52.54223 & 3.080 & E-5 & 6.0000 & 9.40 & E-3 & 5.690 & E-6 & 1.79 & 29 & \\
53.06680 & 6.370 & E-5 & 5.2200 & 9.70 & E-3 & 5.280 & E-6 & 1.89 & 27 & \\
53.59572 & 1.240 & E-4 & 4.8600 & 10.00 & E-3 & 5.440 & E-6 & 1.83 & 25 & \\
54.12997 & 2.265 & E-4 & 3.8100 & 10.20 & E-3 & 4.800 & E-6 & 1.99 & 23 & \\
10 & 54.67116 & 3.893 & E-4 & 3.1900 & 10.50 & E-3 & 4.840 & E-6 & 1.90 & 21 & \\
55.22136 & 6.274 & E-4 & 2.6200 & 10.79 & E-3 & 4.170 & E-6 & 2.07 & 19 & \\
55.78380 & 9.471 & E-4 & 2.1150 & 11.10 & E-3 & 3.750 & E-6 & 2.07 & 17 & \\
56.26478 & 5.453 & E-4 & 0.0104 & 16.46 & E-3 & 7.740 & E-6 & 0.89 & D1b & 1 & \\
56.36339 & 1.335 & E-3 & 1.6550 & 11.44 & E-3 & 2.970 & E-6 & 2.29 & 15 & \\
15 & 56.96818 & 1.752 & E-3 & 1.2550 & 11.81 & E-3 & 2.120 & E-6 & 2.53 & 13 & \\
57.61249 & 2.125 & E-3 & 0.9100 & 12.21 & E-3 & 0.940 & E-6 & 3.76 & 11 & \\
58.32389 & 2.369 & E-3 & 0.6210 & 12.66 & E-3 & -0.550 & E-6 & -11.10 & 9 & D2 & 3 & \\
58.44660 & 1.447 & E-3 & 0.0827 & 14.49 & E-3 & 5.970 & E-6 & 0.79 & 7 & \\
59.16422 & 2.387 & E-3 & 0.3860 & 13.19 & E-3 & -2.440 & E-6 & 0.07 & 5 & D3 & 7 & \\
20 & 59.59098 & 2.097 & E-3 & 0.2070 & 13.60 & E-3 & 3.440 & E-6 & 0.49 & 5 & \\
60.30604 & 2.109 & E-3 & 0.2070 & 13.82 & E-3 & -4.350 & E-6 & 0.68 & 5 & D3 & 7 & \\
60.43478 & 2.444 & E-3 & 0.3860 & 12.97 & E-3 & 1.320 & E-6 & -1.20 & 7 & \\
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\end{tabular}
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<th>Temperature Exponential</th>
<th>Width</th>
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<th>ID</th>
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*aUnits: ppm/kPa

b_D denotes doublet
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<td>(10,13)</td>
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<td>481.49113</td>
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<td>2.810</td>
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<tr>
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<td>6.690</td>
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<td>(10,110)</td>
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<td>(10)</td>
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TABLE 2 (Continued)

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<th>Width</th>
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<td>$b_3$ GHz/kPa</td>
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<td>0.656</td>
<td>33.5</td>
<td>E-3</td>
<td>3</td>
</tr>
</tbody>
</table>

Plus 1809 additional lines up to 31 THz, of which 361 lines have strengths, $b_1 > 1000$. The strongest lines are at:

- 2774.100000
- 2023.000
- 0.208
- 29.5
- E-3
- 1
- 1
- 1
- 0
- Max. strength

- 6076.500000
- 2500.000
- 1.370
- 20.4
- E-3
- 3
- 3
- 0
- Max. attenuation

---

a Continued from Table 1.
b (1) denotes 1. vibrationally excited state.
- Stronger lines.
introducing the spectroscopic parameters of center frequency $V_0$, width $\gamma$, and overlap interference $I$. $F'$ and $F''$ are in units of 1/GHz.

For $h > 20$ km, only isolated resonant lines are present, spread over a megahertz frequency scale. Equations (15) and (16) reduce to Lorentzian shapes

$$F'_L = \frac{(V_0 - V)}{((V_0 - V)^2 + \gamma^2)}$$

and

$$F''_L = \frac{\gamma}{((V_0 - V)^2 + \gamma^2)}$$

where $F'_L$ and $F''_L$ are in units of 1/GHz. Peak dispersion at $V = V_0$ and maximum absorption at $V = V_0$ are given in ppm by

$$D_m = S/2\gamma$$

$$N''_m = S/\gamma$$

For $h > 40$ km, a further decrease in pressure converts the pressure-broadened Lorentzian into a Doppler-broadened Gaussian shape with a different width in kHz of

$$\gamma_D = 6.20 \frac{V_0}{m\bar{c}}$$

where $m$ is the molecular weight (e.g., $O_2$, $m = 32$, $t = 1$, $V_0 = 60$ GHz; $\gamma_D = 65.8$ kHz).

The convolution of Lorentzian and Gaussian shape functions is called the Voigt profile, which is governed by the parameter $\gamma/\gamma_D$. The Voigt profile is appropriate when this ratio falls in the range between $= 10$ and 0.1. Numerical evaluation of the height-dependent complex Voigt function requires considerable computational effort (19).

1. Microwave Spectrum of Oxygen ($O_2$-MS). The $O_2$ molecule has electronic, vibrational, and rotational energy levels with transitions causing spectral lines from the optical to the EHF range. The EHF lines are fine structure transitions between rotational triplet energy levels. All pertinent information on the $O_2$-MS is tabulated; that is, the line parameters have been reduced to five coefficients $a_1$ to $a_5$, which are listed in
Table I together with the center frequencies $\nu_0$ (17,19). Dependence on atmospheric properties is expressed by

\[ S = a_1 p t^3 \exp[a_2(1 - t)] \]  
\[ \gamma = a_3 (p + 1.3e) t^{0.9} \]  
\[ I = a_4 p t \]  

where $S$ and $\gamma$ are in kHz and GHz, respectively. Water vapor influences the $O_2$-MS through Eq. (22).

2. Microwave Spectrum of Water Vapor. From the AFGL line parameter compilation (10), 1838 $H_2O$ lines were read up to 31 THz when a maximum intensity ($\nu = \nu_0$) cutoff of $2 \times 10^{-3}$ dB/km (300 K) is applied. For the EHF range, 29 lines (see Table 2) must be considered explicitly and the remaining ones are lumped into a continuum far-wing contribution. An individual line is described by

\[ S_v = b_1 e t^{3.5} \exp[b_2(1 - t)] \]  
\[ \gamma_v = b_3(p + 4.80 e)t^{0.6} \]  
\[ I_v = 0 \]

where $S_v$ and $\gamma_v$ are in kHz and GHz, respectively.

3. Continuum Water Vapor Spectrum. The remaining 1809 (that is, 1838 - 29) $H_2O$ lines make far-wing contributions; they are fitted by (17)

\[ N'_v = 1.9 \times 10^{-5} p e t^4 (\nu/30) \]  

The continuum absorption $N'_v$ in ppm is of a magnitude and functional form that is similar to the empirical Gaut-Reifenstein expression (11)

\[ N'_v = 5.6 \times 10^{-5} p e t^{3.1} (\nu/30) \]  

which was introduced by Waters (31) and has proven useful to other workers (32,108). The far-wing contributions to refractivity of all rotational $H_2O$ lines yield with Eq. (12) in Eq. (13) the term $41.6 e t^2 (3,4,5)$. The contribution of the local lines, $i = 46$ to 74 to this value is in ppm

\[ \Sigma(SF'(\nu + 01))_i = 4.75 e t^3 \]
Very accurately measured refractivity can serve as a test for the low frequency response of theoretical line shapes applied to the rotational H₂O spectrum if one is sure of the spectroscopic database. A more detailed discussion of Eqs. (26) and (27) follows in Section IV.

4. Temperature Behavior. A closer look at the spectral line response aids in understanding the temperature dependence of EHF attenuation and phase dispersion rates in moist air. Line intensities are sensitive to temperature variations at various rates. The peak line intensities in ppm (Eq. (19)) are described by

\[
\begin{align*}
S/\gamma & = \left\{ \begin{array}{l}
0_2 \left[ \frac{a_1}{a_3} \left\{ \frac{\rho}{\rho + 1.3\rho} \right\} t^{2.1} \exp \left[ a_2 (1 - t) \right] \right] \\
H_2O \left[ \frac{b_1}{b_3} \left\{ \frac{s}{\rho + 4.8\rho} \right\} t^{2.9} \exp \left[ b_2 (1 - t) \right] \right]
\end{array} \right\} \\
(29)
\end{align*}
\]

The line intensities are independent of temperature when

\[
\begin{align*}
0_2 & : a_2 = 2.1 \ln \frac{t}{(t - 1)} \quad t = 1.1 \quad 1.3 \quad 1.5 \quad 2 \quad (see \ Table \ 1) \\
H_2O & : b_2 = 2.8 \ln \frac{t}{(t - 1)} \quad t = 2.76 \quad 2.54 \quad 2.35 \quad 2.02 \quad (see \ Table \ 2)
\end{align*}
\]

Lines with values lower than those prescribed by Eq. (30) increase in intensity when the temperature drops \(t > 1\) and vice versa. A useful approximation at a fixed frequency is given by

\[
\alpha(t) = \alpha(300 \text{ K}) t^y
\]

(31)

where the exponent \(y\) is obtained by fitting model data.

C. The Radio-Path Model

The path is assumed to be in a spherically stratified atmosphere in which each layer is homogeneous. The integral expressions (Eqs. (6), (8) and (10)) are evaluated by the layer-by-layer method (19,29) by using numerical integration techniques since closed-form solutions are lacking because of the complicated temperature height profile.

Mean conditions are modeled by the U.S. Standard Atmosphere 1976, and in situ data from radiosonde ascents can be programmed in directly. Whatever description of the atmosphere is employed, model or data, it is converted in the computer into n-layers.
each having an assigned set of values of \( p(h), e(h), t(h) \). Values for \( \alpha \) are calculated by using Eqs. (4), (14), (16) and (21) to (25) and for \( \phi \) by applying Eqs. (5), (12), (13), (15) and (21) to (25), by the standard line-by-line superposition (29) and adding the continuum Eq. (27).

The radio path is assumed to be a ray (that is, plane wave case), and the general procedure is to calculate the local \( N(h) \) for the programmed altitude grid reporting \( p, e, t \) and to store \( N_0, D(v), \) and \( N''(v) \) separately on file. The ray starts at a surface height \( h_0 \) with an elevation angle \( \theta \) and is guided through the inhomogeneous medium until it reaches the intended final height \( h_1 \). Refraction is most pronounced at the lowest heights and causes substantial ray bending when \( \theta \) is close to \( 0^\circ \) (tangential path); thus, many fine steps are required initially.

Modeling is introduced for the purpose of predicting the mean of EHF propagation effects and the limits of their variability from readily available climatological data bases. In order to apply such a tool in an optimum manner, it is important to consider the uncertainties in the spectroscopic data and the limitations imposed by the numerical calculation procedure.

D. Typical Examples

The examples presented in Figs. 1 to 7 almost speak for themselves. Figure 1 is a presentation of the complete rotational water vapor spectrum for a typical sea-level condition. It was calculated by using the AFGL Data Tape (10) rather than the EHF model given in sections B and C, and serves to demonstrate the very strong (over 6 orders of magnitude) absorption due to water vapor in the far-infrared that allows on the low frequency end just a few window ranges for transmission.

A more refined modeling result is depicted in Fig. 2. It displays at higher altitudes \((h = 16 \text{ km})\) spectral signatures of the trace gases \( \text{O}_2, \text{CO}, \text{N}_2\text{O} \), which are not included in the described model. At tropospheric heights \((h = 0 \text{ and } 4 \text{ km})\), only lines of \( \text{H}_2\text{O} \) and \( \text{O}_2 \) (see markings at bottom of figure) are important. The figure gives, in essence, a picture of atmospheric molecular absorption in the millimeter and submillimeter wavelength range. These computations by Burch and Clough (24) agree well with reported data and the presented model (Eqs. (27) and (41) of the water vapor continuum spectrum labeled \( C'_X \). The attenuation rate spans seven orders of magnitude over the frequency range \( \nu = 100 \) to \( 1000 \text{ GHz} \) and altitudes \( h = 0 \) to \( 16 \text{ km} \) where \( >99.5\% \) of the atmospheric water vapor is contained. The transparency in the window ranges W2 to W5, which are valleys between the absorption line peaks, is dominated by the water vapor continuum \( C'_X \). Figure 2 affirms the dominant role that
FIGURE 1. Attenuation rate \( \alpha \) at sea level \((h = 0 \text{ km}, e = 1.015 \text{ kPa})\) over the frequency range, \( \nu = 30 \text{ GHz} \) to \( 30 \text{ THz} \) displaying the envelope for maximum/minimum values of the rotational water vapor spectrum. Calculated by using the AFGL Tape (10).

![Graph showing attenuation rate against frequency](image)

**TABLE 1**. Attenuation rate \( \alpha \) at the altitudes, \( h = 0, 4, \text{ and } 16 \text{ km} \) over the frequency range, \( \nu = 100 \text{ GHz} \) to \( 1000 \text{ GHz} \). The following atmospheric conditions and trace molecular number densities \( M(m^{-2}) \) were used in the calculation (24):

<table>
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<th>( h, \text{km} )</th>
<th>( p, \text{kPa} )</th>
<th>( e, \text{Pa} )</th>
<th>( M(O_3) )</th>
<th>( M(\text{CO}) )</th>
<th>( M(\text{N}_2\text{O}) )</th>
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<tr>
<td>0</td>
<td>101.0</td>
<td>1.041</td>
<td>786.000</td>
<td>6.78E17</td>
<td>1.91E18</td>
</tr>
<tr>
<td>4</td>
<td>61.6</td>
<td>1.144</td>
<td>133.000</td>
<td>5.77E17</td>
<td>1.28E18</td>
</tr>
<tr>
<td>16</td>
<td>10.4</td>
<td>1.385</td>
<td>0.061</td>
<td>3.01E18</td>
<td>2.59E17</td>
</tr>
</tbody>
</table>

![Graph showing attenuation rate against frequency for different altitudes](image)
FIGURE 3. Attenuation rate $\alpha$ at the altitudes, $h = 0, 5, 10, 30$ km over the frequency range, $\nu = 45$ GHz to 125 GHz displaying band and line structure of the oxygen microwave spectrum.

FIGURE 4. Pure water vapor refractivity $N_0 + D(\nu)$ for $e = 1.705$ kPa over the frequency range, $\nu = 300$ GHz to 1000 GHz from measurements and calculation (67).
FIGURE 5. Zenith attenuation $A$ through the first 30 km of the U.S. Standard Atmosphere 1976 for dry (RH = 5%), moderate (50%), and humid (100%) air over the frequency range, $\nu = 30$ GHz to 300 GHz (EHF). The relative humidity RH was assumed to be constant for $h = 0$ km to 8 km (19). The experimental data are from Ref. 80 and Table 5.

FIGURE 6. Zenith phase dispersion $\Delta \Phi = \phi - \phi_0$ (Eq. (18)) for the same conditions specified in Fig. 5. The frequency-independent delay time due to $\phi_0[n_0(h)]$ is (Eq. (9)):

<table>
<thead>
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<th>RH, %</th>
<th>$5.000$</th>
<th>$50.000$</th>
<th>$100.000$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n, n_s$</td>
<td>$7.666$</td>
<td>$7.977$</td>
<td>$8.266$</td>
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</table>
water vapor absorption plays in atmospheric millimeter wave propagation, even at modest humidities (RH = 46% for h = 0).

A more detailed picture of molecular attenuation appears in Fig. 3. The oxygen microwave spectrum dominates in the ranges 50 to 70 GHz and 115 to 123 GHz. At levels close to the surface, the 60-GHz lines are merged into an unstructured band shape, the maximum intensity of which is pressure-proportional, until the lines separate (h > 15 km). Above 15 km, the shielding effect breaks down and radio channels with up to 400 MHz bandwidth can be accommodated between the lines. If there is a line close to the frequency of interest, isolated line behavior takes over. In the frequency-agile applications, it is possible to tune to a more or less constant shielding factor (for example, 0.5 dB/km) over the height range h = 0 to ≤ 30 km. Above h > 30 km, Zeeman splitting has to be considered in the frequency intervals ν0 ± 5 MHz until the O2 lines vanish above h > 100 km (19).

It is encouraging to the author to see experimentally verified results on millimeter wave water vapor refractivity expressed by N0 + D(ν), an example of which is presented in Fig. 4. After many careful measurements of microwave refractivity in the fifties and sixties (2,3,5,47-50,56), this marks a new start in a heretofore inaccessible frequency range. In comparison with conventional absorption spectroscopy, refractive dispersion measurements are superior for absolute intensity studies (15,57,65). An important result of Fig. 4 is the fact that the much stronger lines beyond
1000 GHz determine, by means of their far-wing intensity, most of the microwave refractivity $N_0$ (see Eq. (28)).

E. Cumulative Behavior

A standard example for an inhomogeneous medium is the one-way zenith response through the U.S. Standard Atmosphere 1976 (19). Figures 5 and 6 display the cumulative attenuation $\Delta$ and cumulative phase dispersion $\Delta\phi$, for which 48 height levels up to $h = 30$ km are summed. Except for the vicinity ($\nu_0 \pm 10$ MHz) of the $O_2$-MS lines, these curves represent the one-way zenith path behavior. Three humidity profiles $p(h)$ were used to model RH = 1, 50, and 100% in each of 26 height layers between $h = 0$ and 8 km. The RH drops rapidly below 1% above $h = 8$ km. The frequency range 55 to 65 GHz is opaque ($A > 30$ dB) for any system attempting to look through. The transmittance, Eq. (7) is measurable when the atmosphere is somewhat transparent ($A < 30$ dB), and it can be determined either by the absorption of a signal coming from the outside (sun emission, satellite beacon) or by the thermal emission originating predominately in 8 km thick layers. Frequencies around 57 and 63 GHz yield the maximum and minimum phase dispersion for the 60-GHz band, which is almost independent of the water vapor content. Actually, the foreign-gas broadening of the $O_2$-MS by water vapor (see Eq. (22)) reduces the attenuation slightly with increasing vapor pressure (see Fig. 5: $A(100\%) - A(5\%)$). Comparison of the total attenuation $A$ with measurements (see Table 5) yields reasonably good agreement when the empirical assumptions formulated by Eq. (27) are used in the calculation. The amount of water vapor absorption for a given atmospheric condition can be estimated, to some extent, if the surface vapor concentration $p_0$ is known.

The EHF thermal emission by $H_2O$, $O_2$, $O_3$ and CO was calculated by Waters by using Eqs. (10), (7) and (4) and the absorption coefficients given in Eq. (31). Calculations are shown in Fig. 7 both for no water vapor and for a total precipitable water vapor of 2 cm. The integral is evaluated for $h = 0$ to 60 km. Clear-sky emission varies primarily with the amount of water vapor. The calculations are for observations in the zenith direction from ground level. Cosmic radiation of $3$ K, which is incident on the atmosphere from the top, has been added to Eq. (10).

III. PHYSICAL PROPERTIES OF ATMOSPHERIC WATER VAPOR

The clear atmosphere appears in the EHF radio path modeling scheme only as a p-t-e (Section II, B) parameter system. The real atmosphere is an enormous theater of diverse but related and incessant activities (33). Water, endlessly changing its phases, is the main actor on this stage. On a global scale,
each year about 1 m of the ocean depth is evaporated, whereas the average water content of the atmosphere represents a depth of roughly 2 cm. Water vapor is rapidly exchanged causing it to be a patchy, capricious medium with parcels (scale sizes, 10 to 100 m), blobs (< 0.5 m) and strata (~ 1 m) of moisture that probably account for a fair share of the scatter and inconsistencies in millimeter-wave propagation data taken from field observations. The total integrated water vapor and liquid water in a vertical column can be detected with high time resolution (≤ 10 s) by ground-based radiometry in the microwave range (40). In relating millimeter-wave propagation and atmospheric water vapor, one has to be generally content to make predictions with no more than statistical certainty.

The fact that the three phases of water contribute to the weather cycle at the prevailing conditions (p-t-e) is most fundamentally a consequence of the molecular structure of H₂O. Water molecules tend to associate through hydrogen bonds having about one-tenth the strength of a molecular bond. Very schematically, in the solid phase four H-bonds form a rigid lattice; in the liquid phase, on the average, two H-bonds amalgamate chainlike links; and in the gaseous phase, a chance exists to associate singly H-bonded molecules to dimers (21,43, 44) or aggregate into clusters of preferred sizes (that is, 10 to 50 molecules) (22,28) under the influence of ion-activity (45). If further notice is taken that atmospheric air is never free from invisible particles having a variety of origins, chemical compositions, sizes, and affections for water vapor, then the radio engineer will almost despair at the prospects of ever putting order in the atmospheric pandemonium. The value of the interdisciplinary Workshop on Atmospheric Water Vapor for providing guidance with this task must be stressed.

A. Absolute Humidity

The amount of water vapor (that is, absolute humidity ρ) present in the atmosphere depends upon: (a) evaporation from surfaces; (b) transport by motions on various scales, mainly through the troposphere; (c) condensation-forming clouds and fog that causes precipitation fallout. The radio propagation engineer measures the amount of water vapor by means of an average concentration ρ, which varies at sea level between the extremes of 0.1 (dry, winter, polar) and 60 g/m³ (wet, summer, tropical). The height distribution is approximated from a known ground level ρ₀ by

\[ \rho = \rho_0 e^{-kt} \]

\[ 3 \text{The electron-rich end of } O \text{ in the polar molecule } H_2O \text{ attracts an electron-poor } H \text{ end of a neighbor } H_2O. \]
\[ p(h) = \rho_o \exp(-h/2 \text{ km}) \]  

(32)

and the most realistic measure for predictions is the total precipitable water vapor in cm \((10 \text{ g/m}^3/\text{km} = 1 \text{ cm})\).

\[ w = \int_{s_1}^{s_2} \rho(s) \, ds \approx 0.2 \rho_o \]  

(33)

The quantity \( w \) is measured, for example for a zenith path, with a microwave radiometer \((39,40)\). The variations of the dry air parameter \( p(h) \) and \( t(h) \) are described by standard height profiles and attention is called to the model of the U.S. Standard Atmosphere \((\text{for example, (33)})\). The number density for the atmospheric gases with constant volume mixing ratio \( (O_2, N_2, CO_2, \text{ noble gases; or referred to as dry air}) \) follows directly from the \( p-t \) combinations. Over the height range \( h = 0 \) to \( 16 \text{ km} \), the changes are for \( p \) from \( 101 \) to \( 10 \) kPa \((1 \text{ kPa} = 10 \text{ mb})\) and for \( t \) from \( 0.9 \) \((333 \text{ K})\) to \( 1.5 \) \((200 \text{ K})\). Ozone \( (O_3) \), besides water vapor, has a variable mixing ratio which is modeled separately. Examples of \( O_3 \) millimeter wave spectra are shown in Figs. 2 and 7 as reported by others.

Fractional fluctuations due to water vapor paths and turbulence are typically in the ranges

\[ \delta p = \pm 60\% \]

\[ \delta t = \pm 1\% \]

\[ \delta p = \pm 0.1\% \]  

(34)

Variability of humidity for a midlatitude location with a medium of \( 7.4 \text{ g/m}^3 \) is diurnally \( \pm 1.0 \), seasonally \( \pm 6.3 \), and locally \( \pm 1.2 \text{ g/m}^3 \).

1. **Molecular Quantities.** The molecular world of sea level air is very empty. The molecular radius \( r = 1.8 \times 10^{-4} \text{ \mu m} \), average spacing \( d \), and average distance \( \ell \) between collisions are in the ratios \( r : d : \ell = 1 : 18 : 320 \) \((33)\). Most of the time, a molecule is unperturbed by neighboring molecules. The number of dry air molecules per unit volume \( (\text{m}^{-3}) \) is

\[ M_d = 2.415 \times 10^{23} \text{ pt} \]  

(35)

\((\text{e.g.,} \ \ p = 101, \ t = 1 : M_d = 2.44 \times 10^{25})\).

Water vapor is an imperfect gas. From thermodynamic measurements, it is known that there are slightly more \( H_2O \) molecules
per unit volume than predicted by the ideal gas law. The correction is made by introducing the second virial coefficient \( B(t) \). The molecular number density of \( \text{H}_2\text{O} \) for a given vapor concentration (in g/m\(^3\))

\[
\rho = 7.219 \times 10^{-23} \text{ g/m}^3
\]  

follows from the relationship in m\(^3\)

\[
M_v = \left[ \frac{2.989}{\rho} \right]^{10^{-23}} + B(t) \right]^{-1} = 3.346 \times 10^{22}
\]  

(e.g., \( \rho = 10 : M_v = 3.35 \times 10^{23} \)). Very few values for \( B(t) \) have been reported (44,69):

<table>
<thead>
<tr>
<th>( t )</th>
<th>( T ), K</th>
<th>( B ), ( 10^{-27} \text{ m}^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>333</td>
<td>-2.8</td>
</tr>
<tr>
<td>1</td>
<td>300</td>
<td>-1.9</td>
</tr>
<tr>
<td>1.2</td>
<td>250</td>
<td>-0.9</td>
</tr>
</tbody>
</table>

The deviations from ideal behavior

\[
\varepsilon = \left[ \frac{M_v}{M_v^0} \right] (B = 0) - 1
\]  

are small, even at saturation (see Eq. (43)):

<table>
<thead>
<tr>
<th>( t )</th>
<th>( \rho ), g/m(^3)</th>
<th>( C ), ( 10^{-3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>130</td>
<td>12.3</td>
</tr>
<tr>
<td>1</td>
<td>25.5</td>
<td>1.6</td>
</tr>
<tr>
<td>1.2</td>
<td>0.82</td>
<td></td>
</tr>
<tr>
<td>0.82</td>
<td>0.03</td>
<td></td>
</tr>
</tbody>
</table>

The deviation \( \varepsilon \) led to the postulation of a dimer molecule \((\text{H}_2\text{O})_2\). The molecular structure (43) and the millimeter wave spectrum of the dimer (6,8,69) are well established; however, its number density under tropospheric conditions is not known.

The dimer number density is expected to depend strongly on temperature since the hydrogen bond strength is rather weak. Data which are suspected to be caused by a dimeric effect can be analyzed for their percent change-per-degree or for their power law \((tY)\) dependence to allow a positive identification.
A. Nemesis for Millimeter Wave Propagation

<table>
<thead>
<tr>
<th>Data</th>
<th>% Change/K</th>
<th>y</th>
<th>eV/molecule</th>
<th>kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-1.56</td>
<td>3.8</td>
<td>0.1</td>
<td>2.31</td>
</tr>
<tr>
<td></td>
<td>-2.54</td>
<td>7.7</td>
<td>0.2</td>
<td>4.60*</td>
</tr>
<tr>
<td></td>
<td>-3.78</td>
<td>11.6</td>
<td>0.3</td>
<td>6.90</td>
</tr>
<tr>
<td></td>
<td>-6.22</td>
<td>19.3</td>
<td>0.5</td>
<td>11.60</td>
</tr>
<tr>
<td></td>
<td>-12.10</td>
<td>39.0</td>
<td>1.0</td>
<td>23.10*</td>
</tr>
</tbody>
</table>

Bond strength is expressed in units of eV/molecule or kcal/mole and the value expected for a hydrogen bond lies between 3 and 5 kcal/mole. The dimer number density in \( m^{-3} \) was proposed to follow an expression (6)

\[
M_D = M_V^2 \cdot k(t) \tag{39}
\]

An approximate equation in \( m^3 \) for \( k(t) \) was derived from expressions given by Bohlander (69)

\[
k \approx 1.8 \times 10^{-27} t^{5.6} \tag{40}
\]

which when combined with Eqs. (37) and (39), yields in \( m^{-3} \)

\[
M_D = 2.0 \times 10^{18} \rho^2 t^{5.6} \tag{41}
\]

and for the fractional dimer concentration

\[
M_D/M_V = 6.1 \times 10^{-5} \rho t^{5.6} \tag{42}
\]

(for example, \( \rho = 20, t = 1 : M_D/M_V = 1.2 \times 10^{-3} \)).

Other estimates on the fractional dimer concentration \( M_D/M_V \) are reported in Ref. (21): 0.4 \( \times 10^{-3} \) for \( \rho = 20 \) assuming 5.4 kcal/mole; and in Ref. (44): 1.9 \( \times 10^{-3} \) at \( t = 1 \) and 0.95 \( \times 10^{-3} \) at \( t = 1.11 \), when extrapolated from saturated water vapor data taken over the range \( t = 0.77 \) to 0.84. These ratios \( M_D/M_V \) are close to values of \( \epsilon \) defined in Eq. (38).

B. Relative Humidity

The examples of atmospheric millimeter wave propagation (Figs. 1 to 7) showed clearly the dominant influence of water vapor. Some difficulties in predicting this influence obviously are related to the fact that water vapor is a vapor and not a gas. The first consequence of the vapor state is that a maximum concentration \( \rho_\text{sat} \) cannot be exceeded. A balance exists between two states called the saturation point. At saturation, the rate at which molecules evaporate from a plane surface (liquid or
solid) equals the rate of incoming condensing molecules. The saturation concentration over water for atmospheric conditions is fitted by

\[ p < p_s = 17.39 t^6 10^{(10-9.834t)} \]  

(43)

in g/m³ and is in a very rough approximation simply in g/m³

\[ p_s \approx 25 t^{-17} \]  

(44)

Equation (43) is programmed into the radio path model (Section II), which uses RH(h) information to calculate with t(h) the values e or p.

The saturation concentration defines relative humidity

\[ f = \frac{p}{p_s} \approx 0.04 t^{-17} = 0.28 e^{18} \leq 1 \]  

(45)

or, in the more familiar percent notation, RH - 100f ≤ 100%. The maximum vapor concentration varies over a wide range as a function of temperature.

<table>
<thead>
<tr>
<th>T, K</th>
<th>t</th>
<th>t^{-17}</th>
<th>( p_s (\text{true}) ) ( a )</th>
<th>( p_s ), Eq. 43</th>
<th>( p_s ), Eq. 44</th>
</tr>
</thead>
<tbody>
<tr>
<td>333.30</td>
<td>0.900</td>
<td>6.000</td>
<td>130.350</td>
<td>130.400</td>
<td>150</td>
</tr>
<tr>
<td>300.00</td>
<td>1.000</td>
<td>1.000</td>
<td>25.500</td>
<td>25.500</td>
<td>25</td>
</tr>
<tr>
<td>273.16</td>
<td>1.098</td>
<td>0.203</td>
<td>4.850</td>
<td>4.840</td>
<td>5</td>
</tr>
<tr>
<td>250.00</td>
<td>1.200</td>
<td>0.045</td>
<td>0.822</td>
<td>0.822</td>
<td>1</td>
</tr>
</tbody>
</table>

\( a \) Smithonian Hydrometric Table (see (33)).

\( b \) Triple Point

The interdependences between RH, p, w, and T are shown in Fig. 8. The humidity condition RH = 100% is a delicate balance point for phase changes. A drop in temperature by 1 K decreases the water vapor density of saturated air by about 6%. Energy is released during condensation which was stored in the random motion of \( H_2O \) molecules. One cubic meter of a forming cloud that converts 1 g of vapor into the liquid phase releases 2.5 kJ.

The latent heat release can generate electric fields. Depending upon the suddenness, the amount of cooling, and the water vapor supply, more or less violent updrafts (such as cumulonimbus clouds in thunderstorms) feed a turbulent air motion. Small aerosols are lofted into the upper region of a
A NEMESIS FOR MILLIMETER WAVE PROPAGATION

FIGURE 8. The amount of precipitable water vapor \( w \) in a radio path of length, \( L = 1 \) km and the corresponding homogeneous water vapor concentration \( \varrho \), both as a function of relative humidity \( RH \) for various temperatures \( T \). The temperature dependence of saturation water vapor pressure \( e_s \) and maximum vapor concentration \( \varrho_s (RH = 100\%) \) is:

\[
\begin{array}{ccc}
T, ^\circ C & e_s, kPa & \varrho_s, g/m^3 \\
-30 & 0.051 & 0.453 \\
-20 & 0.125 & 1.070 \\
-10 & 0.286 & 2.360 \\
0 & 0.611 & 4.840 \\
10 & 1.227 & 9.390 \\
20 & 2.337 & 17.270 \\
30 & 4.243 & 30.310 \\
40 & 7.378 & 51.020 \\
\end{array}
\]

The broken lines indicate schematically the range where water uptake by aerosol takes place (Fig. 9).

forming cloud while the larger, heavier ones remain suspended at lower levels. The small aerosols carry a positive charge, the lower levels take on a negative charge. The charge separation generates high electric field strengths and lightning discharges occur when a value of about 30 MV/m is reached. Even before, additional ions must be produced, which are suspected to have catalytic influence on the formation of homomolecular cluster \((H_2O)_n\) with \( n = 10 \) to 50 (28).

C. Submicron Hydrometeors

Atmospheric air is never free from invisible particles (aerosols) having a wide variety of origins, sizes, and chemical composition, and most importantly, having the ability to convert water vapor into submicron hydrometeors. To account for aerosol activity, one must follow the evolution of particle size spectra
FIGURE 9. Schematic size distribution of number density $N$ for equivalent spherical atmospheric particles from molecular to rain drop sizes, $r = 10^{-4}$ to $10^{4}$ μm (32,33,41).

and the attendant microphysical processes of mass transfer over many orders of magnitude in size ($r = 2 \times 10^{-6}$ to 1 cm) and number density ($N = 10^{23}$ to $1 \text{ m}^{-3}$). This problem of scale is sketched in Fig. 9 to illustrate the extent of the difficulties. The amount of relevant literature dealing with aerosols is overwhelming and the referenced material (33-45) is probably an incomplete selection in the search for nonmolecular millimeter wave absorbers in moist air.

Aerosol models start from dry particles, distributed over three distinct size ranges (Fig. 9) (35-38): $N$, nucleation mode; $A$, accumulation mode; $C$, coarse particle mode; and $X$, hypothetical submicron distribution required to explain EWA (see Section IV). Each mode is described by representative values of $a$.
log-normal distribution (22,43). A major process for the formation of the N-mode is the trace gas-to-particle conversion. Sulphur dioxide, for example, nucleates with water vapor to form sulfuric acid primary particles in large numbers (as high as $10^{15} \text{m}^{-3}$), which are rapidly (within ms) coagulated by Brownian motion into the N-mode (34). This mode may contain sizable mass concentrations, $\rho_A(N) \leq 20 \mu\text{g/m}^3$ (38), but more to the point, it presents an enormous surface area $S_A$ to the vapor phase and enables the aerosol to respond quickly to changes in relative humidity $\text{RH}$. Particle number density $N_A$ and total surface area $S_A$ for $1 \text{mg}$ of water distributed in spherical droplets of radius $r$ with $1 \text{m}$ are related as follows

<table>
<thead>
<tr>
<th>$r$, $\mu\text{m}$</th>
<th>$N_A$, molec/m$^3$</th>
<th>$S_A$, cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N 0.01</td>
<td>$2.4 \times 10^{14}$</td>
<td>3000</td>
</tr>
<tr>
<td>A 0.10</td>
<td>$2.4 \times 10^{11}$</td>
<td>300</td>
</tr>
<tr>
<td>C 1.00</td>
<td>$2.4 \times 10^{8}$</td>
<td>30</td>
</tr>
</tbody>
</table>

The mixture of gas and suspended particles is called an aerosol.

Solution droplets, such as $\text{H}_2\text{SO}_4$, are highly hygroscopic; that is, they adapt their size by taking up water if the RH in the ambient air is larger than the equilibrium RH over the droplet's surface. In a reverse situation, their size will shrink because of evaporation. Other hygroscopic agents are salt particles found in maritime (NaCl) as well as in urban (for example, $(\text{NH}_4)_2\text{SO}_4$) environments. These crystals undergo a sudden phase transition to become solution droplets at critical RH values (RH = 76% and 80% for NaCl and $(\text{NH}_4)_2\text{SO}_4$, respectively). The aqueous particles, or so-called hydrometeors, collect in stable, RH-dependent sizes predominantly in the A-mode. A third type of aerosol particle is relatively passive dust grains in sizes commensurate with the A and C modes. The solid matter accumulates a film of water on its surface. All the particle population is able to aggregate water (CN) but the small, hygroscopic parts of the CN (CCN) play the dominant role.

The total aerosol mass concentration in air with a humidity of $\rho = 1 \text{g/m}^3$ can range from $\rho_A = 1$ (clean air) to 400 $\mu\text{g/m}^3$ (polluted). At RH = 50%, an average mass loading of about 0.1 mg/m$^3$ has been deduced from data collected at 291 locations in the U.S. (38). Values between 0.5 (clean air) and 3 mg/m$^3$ (polluted) are reported for $\rho_A$ in cloud free aerosol (42).

Water vapor-to-liquid conversion becomes effective when RH exceeds 80%. An aerosol population can triple, even quadruple its dry state size, and thus lead to more than a hundred-fold increase in mass concentration. Since the average size stays below 1 $\mu\text{m}$, a more or less invisible cloud exists, optically
categorized in the atmosphere as haze. Optically active sizes (> 0.5 μm) in sufficient number are only produced if the limit RH = 100% is exceeded. In that case, the available amount of water (for example, that due to a sudden cooling of saturated air) is shared either by many (> 10^9) active particles (CCN) and small (r = 8 μm), uniform droplets form as fog or cloud, or by very few (< 10^8) and large (r > 100 μm), destabilizing droplets that produce rain.

The water uptake of aerosol has a theoretical foundation in the relationship between the ambient RH and the equilibrium radius of a particle. Hanel provided empirical data on the hydrometric activity of aerosol (35). He defined a mass growth factor g(f = RH) with respect to the dry mass concentration ρ_A and measured in the laboratory the equilibrium growth behavior of typical air samples. Two examples are depicted in Fig. 10. The accretion of water to particles is substantial when RH exceeds 80% and gives them almost pure water properties; that is, ρ_A(f > 0.8) = ρ_w. Two approximate expressions for g(f) can be formulated (35).

**FIGURE 10.** Water uptake [mass growth factor g(f = RH)] of two representative aerosol samples [maritime: NaCl; Continental: (NH₄)₂SO₄ + SiO₂] as a function of increasing and decreasing relative humidity RH (35).
A NEMESIS FOR MILLIMETER WAVE PROPAGATION

\[ g(f) \approx 4f^2 \quad (f < 0.8) \]  
(47)

and

\[ g(f) \approx \frac{1}{1-f} \quad (f < 0.95) \]  
(48)

if differences and hystereses in the growth behavior due to the
chemical makeup are disregarded. A detailed discussion of models
for growth factors can be found in Refs. 36 and 37.

By referring to radio path modeling, it is possible, at this
point, to formulate a path-integrated liquid water content in mm

\[ W = \int \rho_w \, ds = \int \rho^*_A \, g(f) \, ds \approx \int \rho^*_A / (1-f) \, ds \]  
(49)

The water content \( W \) increases at the expense of the precipitable
water vapor \( w \) defined by Eq. (33); hence, in cm

\[ w(f) = w(f=0) - W \]  
(50)

The amount of liquid water in moist air (RH \( \leq 100\% \)) is difficult
to measure. Several indirect methods have been developed. Three
more promising techniques are

1. The mass concentration \( \rho^*_A \) of a dried air sample is
determined by micro-weighing and available (35) empirical growth
factors \( g(f) \) are applied. For example, at RH = 99\%, the values
for \( g \) range between 65 and 120 and yield \( W = 0.013 \) to 0.024 mm
when \( \rho^*_A = 0.2 \, \text{mg/m}^3 \) over a path length \( L = 1 \, \text{km} \).

2. A passive, radiometric microwave method measures at two
(or more) difficult frequencies the sky noise \( T_B \) (see Eq. (10)
and Refs. 39 and 40). The brightness temperature \( T_B \) is converted
into zenith attenuation \( A \) (dB) by means of the spectroscopic data
base. Guiraud et al. (40) perfected the technique, which uses an
instrument operating at 20.6 and 31.65 GHz. The retrieval algo-
rithms for the simultaneous determination of water vapor and
water liquid content are adjusted to take into account a priori
statistics (that is, a representative radiosonde profile). For
example, the climatology of Oklahoma City yielded (40) in cm

\[ w = 6.22 \, A(20) - 2.72 \, A(31) - 0.01 \]

and in mm

\[ W = 1.30 \, A(31) - 0.53 \, A(20) - 0.001 \]  
(51)

The frequency 20.6 GHz is close to the 22 GHz vapor line (Table
2) and responds mainly to vapor; the frequency 31.65 GHz is
remote from the line and responds to the dielectric loss of water.
This instrument provides around-the-clock monitoring of \( w \) and \( W \).
A typical record over 7 consecutive days (Oklahoma City, April, h = 360 m, looking at zenith) displayed for each 24-hour period, the following extremes (40):

<table>
<thead>
<tr>
<th>Day</th>
<th>( W_{cm} )</th>
<th>( W_{mm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.5 to 1</td>
<td>0.01 to 0.02</td>
</tr>
<tr>
<td>2</td>
<td>1 to 2.6</td>
<td>0.02 to 0.5</td>
</tr>
<tr>
<td>3</td>
<td>2.4 to 0.8</td>
<td>0.02 to 2</td>
</tr>
<tr>
<td>4</td>
<td>1 to 2</td>
<td>0.03 to 1.5</td>
</tr>
<tr>
<td>5</td>
<td>0.5 to 1.2</td>
<td>0.1</td>
</tr>
<tr>
<td>6</td>
<td>0.8 to 1.3</td>
<td>0.1</td>
</tr>
<tr>
<td>7</td>
<td>2.4 to 4.2</td>
<td>0.1 to 1.5</td>
</tr>
</tbody>
</table>

The point of this example is that the low limits of \( W \) usually exceed the values that are obtained when using an average dry aerosol mass concentration and assumed \( g(f) \)-factors. The high limits of \( W \) are most likely due to visible clouds since their size range (\( r = 7 \) to \( 100 \mu m \)) contains the bulk of the water. Unfortunately, the data were not accompanied by notes providing information or meteorological or optical conditions. A similar, satellite-borne radiometer yields, over ocean surfaces with well-defined emission temperatures, the same information on \( w \) and \( W \) on a global scale (39).

3. The measurement of optical transmission gives insight into the average aerosol state. Both the optical (\( \lambda = 0.55 \mu m \)) attenuation rate \( \alpha_u \) and the visibility \( V = 20 \text{ dB}/\alpha_u \) are related to the liquid water content \( \rho_w \). In general, Mie scattering theory has to be applied in order to predict values of \( \alpha_u \) based on available size distributions and the complex refractive index of the particle material (23,33,35).

For the purpose of this paper, it is sufficient to bypass the elaborate, lengthy calculations and discuss the main features with the help of a simple empirical expression (27,37)

\[
\alpha_u \approx 300 \rho_w^{0.6} \quad \text{or} \quad V \approx 0.067/\rho_w^{0.6}
\]

(52)

where \( \alpha_u \) is in dB/km and \( V \) is in km. The relationships between \( \alpha_u \), \( V \), and the path-averaged water content \( \bar{w} \) are approximately:
Frequently, haze and fog conditions are described merely by stating the measured value of the visibility $V^*$ which, however, depends on the definition of the threshold value $[20 \text{ dB for } L = 1 \text{ km in Eq. (52)}]$. Nilsson performed detailed Mie calculations on five different aerosol models with the result that visibility $V$ (16 dB threshold) and relative humidity RH are related directly (23). The range of RH for these models is

<table>
<thead>
<tr>
<th>V, km</th>
<th>50</th>
<th>15</th>
<th>5</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>RH, %</td>
<td>20 to 73</td>
<td>84 to 95</td>
<td>96 to 99</td>
<td>98.7 to 99.7</td>
</tr>
</tbody>
</table>

In summary, the salient points of this section are:

1. The physical foundations for path-averaged water vapor $w$ (Eq. 33) and liquid water content $W$ (Eq. 49) were traced in measurable quantities. Both are expected to be the main source for millimeter wave absorption in moist air.

2. The number density $M$ of the major molecular absorbers was given for $O_2$ in Eq. (35), for $H_2O$ in Eq. (37), and for $(H_2O)_2$ in Eq. 41.

3. The water-vapor-to-water-droplet conversion in atmospheric aerosol and the associated scale problems were discussed to aid in the comprehension of the stages that a water molecule has to undergo before precipitating out of the atmosphere. The key role of relative humidity RH (Eqs. 43 to 48) in this process was underlined.

4. The interdependence between the optical properties (Eq. 52) of moist air and the liquid water content is not unique; it depends strongly on the aerosol size distribution.

IV. EXCESS WATER VAPOR ABSORPTION--EWA

Water vapor absorption (Eq. 14) in the millimeter wave windows stems from the fact that the intensity of the local millimeter wave lines $N_0^w = I_{SP}^w$ (Table 2) is insignificant and that two other absorption terms, $N_0^w$ and $N_0^w$, become dominant.
The far-wing response $N''_v$ of the rotational spectrum of $\text{H}_2\text{O}$ beyond 1000 GHz (Fig. 1) is estimated by applying the approximation $\gamma < \nu < \nu_o$ to the line shape $F''(\nu)$ (Eq. 16) and results in

$$F'' = 2\nu/\nu_o^3$$

where $F''$ is in units of 1/GHz. The $\text{H}_2\text{O}$ far-wing continuum of one line in ppm follows with Eqs. (24), (25), (53), and (11) as

$$N''_v = SF'' = C_\nu(1.50 \rho \nu^3 + \rho^2 t^2.1)$$

where

$$C_\nu = 0.184 b_1 b_3/\nu_o^3$$

For moist air, the $\rho^2$-term due to self-broadening is always smaller (< 20%) than the foreign gas-broadening term $\rho \nu$. The far-wing contribution of the strongest $\text{H}_2\text{O}$ line (Table 2: $\nu_o = 2774$ GHz, $C_\nu = 5.14 \times 10^{-10}$) is for an atmospheric condition described by $p = 100$ kPa, $t = 1.023$ (20°C), $\rho_B = 17.27$ g/m$^3$, at the frequency $\nu = 300$ GHz, $N''_v = 4.77 \times 10^{-4}$ ppm or $\alpha_v = 0.026$ dB/km, to which the $\rho^2$-contribution is 11%. The line center attenuation rate, in comparison, is $\alpha_m = 7.40 \times 10^5$ dB/km. Most certainly, line shape theory (Eq. 16) is overtaxed when it is applied to predict relative intensities in the far-wing over seven orders of magnitude.

An unspecified term $N''_v$ was added to Eq. (14) to account for discrepancies between predictions based on summing $N''_v$-terms (54) and measurements. The only certainty in the conflicting evidence for $N''_v$ is its correlation with atmospheric humidity. The abbreviation EWA (excess water vapor absorption) is used to describe $N''_v$. For simplicity's sake, different, mostly exponential temperature functions have been reduced to a power law $t^\gamma$ (Eq. 31). In this section, the exponents of physical ($\rho^\gamma$, $t^\gamma$) and frequency ($\nu^\gamma$) dependences are formulated for absorption models and compared with those for experimental data. This procedure appears to be one practical way of identifying a specific absorption mechanism, especially since EWA observations are not overwhelmingly consistent.

Two schools of thought have evolved to explain EWA:

1. A molecular approach searching for water polymers ($\text{H}_2\text{O}$) and their spectra in the atmosphere. Sizes of $n = 2$ (dimer) and $n = 3$ (cluster) are possibilities.

Jona already in 1919 had considered a water dimer to explain anomalous dielectric water vapor results.
2. Liquid water uptake by submicron aerosol particles under conditions of high relative humidity (RH > 85%) (9,20,23,25,30,35). Each conjecture is supported by some as well as contradicted by other bits and pieces of experimental evidence.

A. Definition of EWA

Window attenuation, both model and experimental, is fitted to expression in dB/km of the form

\[ \alpha = 0.182v^{x} = C p^{x} t^{y} (v/30)^{z} \]  

(56)

where \( x, y, z \) are the proper exponents of a particular absorption model.

The AFGL compilation lists 38,350 \( \text{H}_2\text{O} \) lines from 20 GHz to 331 THz (10) ordered in seven bands (14), of which 1809 rotational lines up to \( \nu = 13 \text{ THz} \) contribute to the millimeter wave continuum (17). A fit to these results yielded Eq. (26), which can be reformulated into Eq. (56). Magnitude and exponents for the line continuum are given in dB/km/g/m^3/kPa by

\[ C_{v} = 8.4 \times 10^{-6} \]  

and

\[ x_{v} = 1.2 \]  

\[ y_{v} = 3 \]  

\[ z_{v} = 2 \]  

(57)

These exponents are based on the molecular number density (Eq. 37) displaying the exponents \( x = 1 \) and \( y = 1 \). With Eqs. (56) and (57), it follows for the sample conditions above (\( \nu = 300, p = 100, D = 17, t = 1.023 \)) that \( \alpha_{v} = 2.75 \text{ dB/km} \).

The dimer spectrum is discussed in detail in Refs. 69 and 109. Absorption should follow dependencies given by Eq. (57), but modified for the dimer number density (Eq. 41). The response predicted in this fashion in dB/km/(g/m^3)^2 is

\[ C_{D} \approx \text{ (value of Table 4) } \]  

and

\[ x_{D} = 2 \]  

\[ y_{D} = 8 \]  

\[ z_{D} = \text{ values of Table 4} \]  

(58)
Aerosol liquid water attenuation is obtained from published dielectric data on bulk water (Fig. 13) yielding in dB/km in the Rayleigh approximation \[ \varepsilon' = (n'_w)^2 + (n''_w)^2, \varepsilon'' = 2n'_w n''_w \] (25, 30, 32).

\[ \alpha_A = 0.82 \nu P_w \frac{\varepsilon''}{\{(\varepsilon' + 2)^2 + (\varepsilon'')^2\}} \]

(59)

Another method of calculating the aerosol liquid water attenuation assumes that the medium has a refractive index \( n'_A = 1 \), and that the attenuation in bulk water is increased due to wavelength shortening \( \lambda'_w = \lambda_0/n'_w \). This allows to formulate

\[ \alpha_A = (\alpha_w/n'_w) (W/L) \]

(60)

Both methods have been applied to the latest dielectric data on water (106) producing somewhat different values (see Table 4). Frequency and temperature dependencies, when approximated using Eq. (60), follow in dB/mm from the rough data fit

\[ \alpha_w/n'_w = 24 \left( \nu/300 \right)^{0.65} t^{-6} \]

Now, if the liquid water content is estimated by Eqs. (49), (47), and (45), \( W = 6 \times 10^{-3} L \rho^2 \tau^{1.5} \rho'_A \), one obtains for the expected aerosol response in the form of Eq. (56) that

\[ X_A = 2 \]

\[ Y_A = 28 \]

\[ Z_A = 0.65 \]

(61)

In summary, millimeter wave window attenuation \( \alpha \) might very well be a combination of up to five different contributions:

\[ \alpha = \alpha_L (\text{local lines}) + \alpha_Y (\text{far-wings}) + \alpha_A + \alpha_D + \alpha_X (\text{cluster?}) \]

(62)

A parametric study of water vapor concentration \( \rho \) and temperature \( t \) dependencies could, in principle, reveal the following behavior in the attenuation rate:
### Table 1: Multiplication factor with respect to 300 K data

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>(g_s^3) (g/m³)</th>
<th>(\rho_s^2) (g/m²)</th>
<th>(t)</th>
<th>(t^3)</th>
<th>(t^8)</th>
<th>(t^{28})</th>
</tr>
</thead>
<tbody>
<tr>
<td>-20</td>
<td>1.07</td>
<td>1.15</td>
<td>1.185</td>
<td>1.664</td>
<td>3.890</td>
<td>116.00</td>
</tr>
<tr>
<td>-10</td>
<td>2.36</td>
<td>5.57</td>
<td>1.140</td>
<td>1.482</td>
<td>2.850</td>
<td>39.00</td>
</tr>
<tr>
<td>0</td>
<td>4.84</td>
<td>23.34</td>
<td>1.098</td>
<td>1.324</td>
<td>2.110</td>
<td>14.00</td>
</tr>
<tr>
<td>10</td>
<td>9.39</td>
<td>88.20</td>
<td>1.060</td>
<td>1.191</td>
<td>1.590</td>
<td>5.10</td>
</tr>
<tr>
<td>20</td>
<td>17.27</td>
<td>298.30</td>
<td>1.023</td>
<td>1.071</td>
<td>1.200</td>
<td>1.90</td>
</tr>
<tr>
<td>30</td>
<td>30.31</td>
<td>918.70</td>
<td>0.990</td>
<td>0.970</td>
<td>0.923</td>
<td>0.76</td>
</tr>
</tbody>
</table>

Data obeying \(x = 1\) and \(y = 3\) but displaying magnitudes different from \(C_V\) (Eq. 57) can be interpreted as failure of the line shape function (Eq. 16) to predict far-wing intensities. Discrepancies of this nature will be most pronounced for dispersion intensities (Eq. 15). Wing data of \(D(V)\) drop more gradually \((\propto 1/V)\) with decreasing frequency, and actually blend into the well-known refractivity \(N_0\) (Eq. 12) for \(V < 100 \text{ GHz}\), as seen in Fig. 4.

### B. Excess Water Vapor (EWA) Evidence from Laboratory Data

Laboratory measurements play an important role in verifying modeling schemes for EHF properties of moist air. Generally, all the spectroscopic parameters (> 200) entering into Eq (1) should be deduced from absolute intensity measurements under well controlled V-p-t-\(\phi\) conditions. By a judicious choice of the experimental variables, it is possible to investigate most parameters separately.

Numerous millimeter wave and infrared studies of water vapor and moist air have been reported. References 46 to 72 are selected for their bearing on the EWA problem. Evidence for EMA from these efforts is summarized in Table 3. It is not limited to absorption, but also shows up in dispersion spectra \(D(V)\) (63) and in refractivity \(N_0\)-studies (49, 52, 56, 63). The experiments are performed by various techniques. The radio path is simulated in an enclosure either for a single-transit or a multiple-reflection (resonator) passage. Detection sensitivity increases with path length. The transmitted energy can be a single frequency, a frequency pair for differential measurements, or a broadband (Fourier transform) signal. Main variables for an experiment are either frequency or pressure, the latter being...
<table>
<thead>
<tr>
<th>Frequency, GHz</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Foreign gas</th>
<th>x density, g/m³</th>
<th>Temperature, T, K</th>
<th>Path length or Resonator Q, x 10³</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>18-31</td>
<td>1.2</td>
<td></td>
<td></td>
<td>Air</td>
<td>0-40</td>
<td>318</td>
<td>800 (Q-box)</td>
<td>46</td>
</tr>
<tr>
<td>22</td>
<td>2</td>
<td></td>
<td></td>
<td>N₂</td>
<td>0-50</td>
<td>312</td>
<td>45</td>
<td>56</td>
</tr>
<tr>
<td>22,24</td>
<td>1.2</td>
<td></td>
<td></td>
<td>N₂</td>
<td>0-20</td>
<td>297</td>
<td>16</td>
<td>63</td>
</tr>
<tr>
<td>31,62</td>
<td>1.2</td>
<td>2,10</td>
<td>2</td>
<td>N₂</td>
<td>0-35</td>
<td>280-325</td>
<td>(&gt;100)</td>
<td>&gt;200 63</td>
</tr>
<tr>
<td>117-120</td>
<td>&gt;1</td>
<td></td>
<td></td>
<td>N₂</td>
<td>0-25</td>
<td>295</td>
<td>150</td>
<td>74</td>
</tr>
<tr>
<td>170-300</td>
<td>2</td>
<td></td>
<td></td>
<td>Air</td>
<td>0-20</td>
<td>295</td>
<td>100</td>
<td>53</td>
</tr>
<tr>
<td>213</td>
<td>2</td>
<td>4.26</td>
<td></td>
<td>N₂</td>
<td>0-60</td>
<td>270-320</td>
<td>(40) Q-box</td>
<td>66</td>
</tr>
<tr>
<td>210-300</td>
<td>2</td>
<td>&gt;10</td>
<td></td>
<td>N₂</td>
<td>3-6</td>
<td>273-333</td>
<td>28</td>
<td>58</td>
</tr>
<tr>
<td>450-960</td>
<td>1</td>
<td></td>
<td></td>
<td>N₂</td>
<td>1</td>
<td>295</td>
<td>2</td>
<td>59</td>
</tr>
<tr>
<td>890,965</td>
<td>1.2</td>
<td></td>
<td></td>
<td>N₂</td>
<td>0-35</td>
<td>293,323</td>
<td>10-60</td>
<td>58</td>
</tr>
<tr>
<td>300-1500</td>
<td>0.5</td>
<td></td>
<td></td>
<td>N₂, N₂₂</td>
<td>0-35</td>
<td>290-355</td>
<td>5-103</td>
<td>and Q-box 69</td>
</tr>
<tr>
<td>9-18 GHz</td>
<td>1.2</td>
<td></td>
<td></td>
<td>N₂, N₂₂</td>
<td>2-20</td>
<td>293-313</td>
<td>500</td>
<td>60</td>
</tr>
<tr>
<td>12-36 GHz</td>
<td>1.2</td>
<td>&gt;10</td>
<td></td>
<td>N₂, N₂₂</td>
<td>14</td>
<td>296-388</td>
<td>1185</td>
<td>54</td>
</tr>
<tr>
<td>14-27 GHz</td>
<td>1.2</td>
<td></td>
<td></td>
<td>N₂, N₂₂</td>
<td>0-20</td>
<td>289-301</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>21-38 GHz</td>
<td>1</td>
<td>5.5</td>
<td></td>
<td>N₂, N₂₂</td>
<td>14</td>
<td>298</td>
<td>21</td>
<td>68</td>
</tr>
</tbody>
</table>
A NEMESIS FOR MILLIMETER WAVE PROPAGATION

preferable for EWA studies. Gas mixture control and vacuum reference are laboratory advantages for absolute intensity studies.

Water vapor is recognized to be a medium that is difficult to control, even in the laboratory, due to its attractive force toward surfaces. The surface area of the laboratory enclosure replaces, in a way, the micro-surface of an atmospheric aerosol population. Water molecules do not ordinarily aggregate spontaneously, but water vapor becomes liquid water when wettable surfaces are present to retain the impinging molecules. A threshold of \( > 2 \times 10^{-5} \text{ cm}^{-1} \) in the surface-to-volume ratio is sufficient to form a continuous interface between vapor and liquid (38). This value is always exceeded in atmospheric air (see Eq. 46) as well as in a laboratory test chamber. An experimenter can select surface materials that, to a certain extent, passivate the attraction for water vapor. A systematic study was made of various surface coatings applied to an electropolished stainless steel (SS 304) cavity (3440 cm\(^3\) and 1265 cm\(^2\), S/V = 0.37 cm\(^{-1}\)) evacuated for > 24 hours to 10\(^{-4}\) torr and subjected to pure water vapor, \( e_0 = 2.40 \text{ kPa at 23.0°C} \). Results on the relative amount \( e/e_0 \) of water-uptake by the walls and the time response of the absorption (\( \eta_{Ad} \)) and desorption (\( \eta_{De} \)) process are as follows:

<table>
<thead>
<tr>
<th>Coating</th>
<th>( e/e_0,% )</th>
<th>No. (^b)</th>
<th>( \eta_{Ad},% )</th>
<th>( \eta_{De},% )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Teflon FEP120 (DuPont), 1 coat</td>
<td>-1.00</td>
<td>20</td>
<td>180</td>
<td>500</td>
</tr>
<tr>
<td>SS 304, electropolished</td>
<td>-1.50</td>
<td>30</td>
<td>150</td>
<td>400</td>
</tr>
<tr>
<td>HMDS(^a) silanizing</td>
<td>-1.35</td>
<td>27</td>
<td>190</td>
<td>750</td>
</tr>
<tr>
<td>Parylene C (Union Carbine)</td>
<td>-1.60</td>
<td>32</td>
<td>140</td>
<td>580</td>
</tr>
<tr>
<td>Silicone SR240 (GE)</td>
<td>-2.10</td>
<td>42</td>
<td>200</td>
<td>550</td>
</tr>
<tr>
<td>Teflon REPI20, 2 coats</td>
<td>-2.90</td>
<td>58</td>
<td>230</td>
<td>5500</td>
</tr>
<tr>
<td>Clear lacquer</td>
<td>-4.00</td>
<td>80</td>
<td>300</td>
<td>7200</td>
</tr>
<tr>
<td>60 GHz spectrometer cell,</td>
<td>-19.5(1)</td>
<td>102</td>
<td>2 hrs</td>
<td>5 hrs</td>
</tr>
<tr>
<td>untreated (63)</td>
<td>(S/V = 1.28 cm(^{-1}))</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Hexamethyldisilazane [(CH\(_3\)]_3Si\(^2\)NH

\(^b\)Number of molecular layers

The need for minimum S/V-ratios and judicious material selection for laboratory enclosures is clearly evident upon comparing the performance of one of the typical spectrometer cells with the preceding test. Water vapor surface effects have been recognized (52); yet, in many cases (46,49,56), they were excused as a possible source of error for the reported data. Work close to saturation requires a circulating gas-handling system with controlled mixing and continuously monitored RH levels (107). Additional sources of error are disturbances in thermodynamic
equilibrium: (a) the vapor heats up when injected into an evacuated cavity, (b) the absorption process releases heat and vice versa, (c) the ambient gas temperature is lowered during pump-down. All laboratory results on spectroscopic data ($N_2$, $D$, $N^+$) of water vapor should be seen in light of these comments. Some selected examples displaying EWA behavior are discussed in the following.

1. Moist Air Studies. Llewellyn-Jones et al. (66) investigated the temperature dependence of the frequency $\nu = 213$ GHz by studying moist nitrogen ($p = 93$ kPa) over the range $T = 270 - 320$ K. The attenuation (Eq. 62) for these conditions can be described by the empirical expression in dB/km

$$a = 0.22 p t^2 + 0.01 p^2 t^4 + 0.03 p^2 t^6$$ (63)

Close to saturation, the following values result from Eq. (63):

<table>
<thead>
<tr>
<th>T, K</th>
<th>$t$, $^\circ$C</th>
<th>$\rho$, g/m$^3$</th>
<th>$a$, dB/km</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>1.20</td>
<td>1</td>
<td>0.32 + 0.02 + 3.43 = 3.8</td>
</tr>
<tr>
<td>273</td>
<td>1.10</td>
<td>5</td>
<td>1.33 + 0.37 + 8.94 = 10.6</td>
</tr>
<tr>
<td>386</td>
<td>1.05</td>
<td>10</td>
<td>2.43 + 1.22 + 10.67 = 14.3</td>
</tr>
<tr>
<td>300</td>
<td>1.00</td>
<td>20</td>
<td>4.40 + 4.00 + 12.00 = 20.4</td>
</tr>
</tbody>
</table>

2. Pure Water Vapor Studies. In the case of self-broadening an exponent $x = 2$ (Eq. 54) is expected. Mrowinski (56) observed $c = 3 \times 10^{-4} p^2$ dB/km at $\nu_0 = 22.235$ GHz and $T = 39^\circ$C, in addition to the line absorption $c_x$. Measurements by Liebe (63) at 30.6 GHz and 61.2 GHz, $T = 300$ and 325 K yielded in dB/km

$$a = 4 \times 10^{-3} p t^2 (\nu/60)^2 + 8 \times 10^{-4} p^2 t (\nu/60)^2.5$$ (64)

The same experiment gave for the refractive dispersion (ppm),

$$D = N'(61.2) - N'(30.6),$$

the result

$$D = 2 \times 10^{-3} p t^8 + 1.2 \times 10^{-3} p^2 t^{16}$$ (65)

which is an average of the type of result exhibited in Fig. 11. The dispersion response resembles the water uptake curves (see Fig. 10) published by Hanel (35) and provided the impetus for the discussion presented in Section III.C.

Bohlender experimented extensively in the 100 GHz to 1000 GHz range and deduced from attenuation data, including results from other investigators, the component $c_\nu/p^2$ shown in Fig. 12 and listed in Table 4 (69,109). He also calculated (by theoretical
FIGURE 11. Dispersion D of pure water vapor measured with a spectrometer cell between the frequencies 61.2 and 30.6 GHz (63). A strong anomalous component is displayed exhibiting a condensation/evaporation hysteresis typical for water uptake activity (see Fig. 10).

means) the envelope of a rotational dimer spectrum, a fractional dimer concentration (Eq. 42) of $10^{-3}$ being assumed. The data fit between EWA and the dimer attenuation ($a/x$ in Table 4) is poor; the spectral shapes do not match. The fit is much improved if the aerosol attenuation rate (Eqs. 59 and 49) in dB/km

$$\alpha_a = (\alpha_w/n_w)\rho_w$$

(66)

is used in the comparison ($a/x$ in Table 4). Equation (66) assumes pure liquid water droplets of submicron size. Actually, based on this fit, it is possible to predict a liquid water concentration $\rho_w$ that is needed to reproduce the EWA data of Table 4; that is, in g/m$^3$

$$\rho_w = 1.1 \times 10^{-3} \rho^2$$

(67)

At this point, the reader might recollect the arguments that have been brought forward to formulate Eqs. (47), (49), (59), and (61). Millimeter wave attenuation by submicron hydrometeors is derived from Mie's scattering equations in the Rayleigh approximation (33). The refractive index and attenuation rate of bulk water are presented in Fig. 13 (102-106). The bulk water attenuation $\alpha_w$ is higher because of refractive wavelength shortening in the medium; hence, the division by $n_w$ is applied for the gaseous aerosol medium ($n' = 1$).
TABLE 4. The EWA Component $\alpha_x/\rho^2$ Reported in Refs. 69 and 109 Compared with the Water Dimer Spectrum $\alpha_p/\rho^2$ Calculated by Bohlander (69) and with the Aerosol Liquid Water Attenuation (a,b).

<table>
<thead>
<tr>
<th>Attenuation</th>
<th>Code</th>
<th>Frequency $\nu$, GHz</th>
<th>$T$, °C</th>
<th>Ref. Fig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_x/\rho^2$</td>
<td>x</td>
<td>100 200 300 400 500 600 700 800 900 1000</td>
<td>23 69 12</td>
<td></td>
</tr>
<tr>
<td>$\alpha_p/\rho^2$</td>
<td>c</td>
<td>4 10 18 45 50 40 25 15 11 7</td>
<td>23 69 12</td>
<td></td>
</tr>
<tr>
<td>$\alpha_A/\rho$</td>
<td>a</td>
<td>4 9 16 21 26 31 36 40 43 46</td>
<td>25 25, 22, 106</td>
<td></td>
</tr>
<tr>
<td>(Eq. 59) b</td>
<td></td>
<td>7 16 23 28 33 38 42 45 48 51</td>
<td>25 106</td>
<td></td>
</tr>
</tbody>
</table>

$H_2O$--Attenuation Rate

| Data | a/x | 0.84 0.88 0.88 0.89 0.90 0.91 0.90 0.92 0.92 |
| b/x | 0.47 0.62 0.66 0.70 0.74 0.78 0.80 0.83 0.84 |
| Fit: | c/x | 0.53 0.69 1.41 1.35 0.95 0.54 0.30 0.21 0.13 |

a) Units: $[dB/km/(g/m^3)]^2 \times 10^{-3}$.
b) Units: $dB/km/g/m^3$. 


FIGURE 12. Summary of reported frequency dependence for excess water vapor absorption, compared with a rotational dimer band spectrum \((M_p/M_v = 10^{-3})\) (69) and the absorption spectrum \(\alpha_A\) of liquid water in submicron hydrometeors (see Table 4).

FIGURE 13. Complex refractive index \(n_w\) and bulk attenuation rate \(\alpha_w\) of water as a function of frequency, \(\nu = 3\) GHz to 300 THz (composite from Refs. 102 to 106).
<table>
<thead>
<tr>
<th>ν, GHz</th>
<th>Model (19)</th>
<th>Field data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RH, %</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>α, dB/km</td>
</tr>
<tr>
<td>80.000</td>
<td>0.010</td>
<td>0.56</td>
</tr>
<tr>
<td>120.000</td>
<td>0.020</td>
<td>1.28</td>
</tr>
<tr>
<td>171.000</td>
<td>0.010</td>
<td>4.93</td>
</tr>
<tr>
<td>250.000</td>
<td>0.000</td>
<td>4.57</td>
</tr>
<tr>
<td>304.000</td>
<td>0.000</td>
<td>8.16</td>
</tr>
<tr>
<td>337.000</td>
<td>0.000</td>
<td>16.89</td>
</tr>
<tr>
<td>345.000</td>
<td>0.000</td>
<td>13.50</td>
</tr>
<tr>
<td>350.000</td>
<td>0.000</td>
<td>14.00</td>
</tr>
</tbody>
</table>

(b) Zenith Path from Sea Level

<table>
<thead>
<tr>
<th>ν, GHz</th>
<th>A_d, db</th>
<th>A, db</th>
<th>A_d, db</th>
<th>A, db</th>
<th>ρ_o</th>
<th>or²</th>
<th>w, cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.000</td>
<td>0.050</td>
<td>0.11</td>
<td>0.055</td>
<td>0.106</td>
<td>0.004α</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.000</td>
<td>0.050</td>
<td>0.11</td>
<td>0.046b(a)</td>
<td>0.085b(b)</td>
<td>0.003α</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20.600</td>
<td>0.090</td>
<td>0.56</td>
<td>0.11(2)</td>
<td>0.52(2)</td>
<td>0.10α</td>
<td>0.27(2)w</td>
<td>97</td>
</tr>
<tr>
<td>22.000</td>
<td>0.065</td>
<td>0.88</td>
<td>0.33(3)</td>
<td>1.150</td>
<td>0.07α</td>
<td></td>
<td>88</td>
</tr>
<tr>
<td>22.200</td>
<td>0.066</td>
<td>0.90</td>
<td>0.200</td>
<td>0.900</td>
<td>0.048(8)α</td>
<td></td>
<td>85</td>
</tr>
<tr>
<td>22.235</td>
<td>0.066</td>
<td>0.91</td>
<td>0.110</td>
<td>0.720</td>
<td>0.032w² - 0.026w</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td>31.700</td>
<td>0.120</td>
<td>0.35</td>
<td>0.13(2)</td>
<td>0.35(2)</td>
<td>0.032w² - 0.026w</td>
<td>91</td>
<td></td>
</tr>
<tr>
<td>35.000</td>
<td>0.150</td>
<td>0.39</td>
<td>0.168b(c)</td>
<td>0.300b(d)</td>
<td>0.010α</td>
<td></td>
<td></td>
</tr>
<tr>
<td>35.000</td>
<td>0.150</td>
<td>0.39</td>
<td>0.170</td>
<td>0.340</td>
<td>0.013(2)α</td>
<td></td>
<td></td>
</tr>
<tr>
<td>35.000</td>
<td>0.150</td>
<td>0.39</td>
<td>0.100</td>
<td>0.250</td>
<td>0.010α</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: (a), (b), (c), (d) represent different sources or calculations.

Ref. indicates the reference number for each model or calculation.
<table>
<thead>
<tr>
<th></th>
<th>36.000</th>
<th>80.000</th>
<th>90.000</th>
<th>91.000</th>
<th>95.000</th>
<th>110.000</th>
<th>111.000</th>
<th>118.000</th>
<th>123.000</th>
<th>150.000</th>
<th>210.000</th>
<th>225.000</th>
<th>230.000</th>
<th>230.000</th>
<th>240.000</th>
<th>240.000</th>
<th>300.000</th>
<th>345.000</th>
<th>411.000</th>
<th>667.000</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W_2$</td>
<td>0.160</td>
<td>0.450</td>
<td>0.250</td>
<td>0.240</td>
<td>0.220</td>
<td>0.450</td>
<td>0.470</td>
<td>1.210</td>
<td>1.110</td>
<td>0.100</td>
<td>0.070</td>
<td>0.050</td>
<td>0.050</td>
<td>0.050</td>
<td>0.040</td>
<td>0.020</td>
<td>0.010</td>
<td>104.00</td>
<td>150.00</td>
<td></td>
</tr>
<tr>
<td>$W_3$</td>
<td>0.41</td>
<td>1.37</td>
<td>1.38</td>
<td>1.40</td>
<td>1.48</td>
<td>2.10</td>
<td>2.20</td>
<td>1.10</td>
<td>3.29</td>
<td>3.62</td>
<td>7.63</td>
<td>7.64</td>
<td>7.82</td>
<td>7.82</td>
<td>8.32</td>
<td>17.40</td>
<td>31.00</td>
<td>104.00</td>
<td>150.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.15(2)</td>
<td>0.5(2)</td>
<td>0.170</td>
<td>0.320</td>
<td>0.41(4)</td>
<td>0.6(2)</td>
<td>0.97(17)</td>
<td>1.67(6)</td>
<td>3.340</td>
<td>0.28(25)</td>
<td>9.200</td>
<td>0.050</td>
<td>0.050</td>
<td>0.000</td>
<td>4.800</td>
<td>7.900</td>
<td>13.400</td>
<td>23.000</td>
<td>50.000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.640</td>
<td>1.400</td>
<td>0.940</td>
<td>1.510</td>
<td>1.500</td>
<td>2.180</td>
<td>2.400</td>
<td>3.400</td>
<td>1.19(14)</td>
<td>0.56(4)</td>
<td>0.72p</td>
<td>0.54(30)p</td>
<td>0.37(5)p</td>
<td>0.37(5)p</td>
<td>0.62p</td>
<td>1.05p</td>
<td>1.18(8)p</td>
<td>4p</td>
<td>12p</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.38(6)p + $b_2$</td>
<td>0.06(2)$p$</td>
<td>$0.2w + 0.06w^2$</td>
<td>$d_{AP} + b_2$</td>
<td>$0.35(2)w$</td>
<td>$0.17(3)p$</td>
<td>$0.45(14)w$</td>
<td>$0.56(4)w$</td>
<td>1.19(14)$w$</td>
<td>0.56(4)w</td>
<td>0.56(4)w</td>
<td>0.56(4)w</td>
<td>0.56(4)w</td>
<td>0.56(4)w</td>
<td>0.56(4)w</td>
<td>0.56(4)w</td>
<td>0.56(4)w</td>
<td>0.56(4)w</td>
<td>0.56(4)w</td>
<td>0.56(4)w</td>
</tr>
</tbody>
</table>

a. Digits in parenthesis give the Standard Deviation from the mean in terms of final listed digits.

b. Tangential path: (a) x 69, (b) x 173, (c) x 53, and (d) x 142 (Ref. 91).

c. $d_s = 12.8 \text{ g/m}^3$ or $w_s = 3.08 \text{ cm}$ and U.S. Standard Atmosphere 76.

d. $a, b$ - coefficient not given.
The refractivity $N_0 = 40.40 + \delta N_0$, when measured at 40°C and 21.4 GHz and 23.6 GHz (49,56,63) exhibited also the anomalies $\delta N_0$:

<table>
<thead>
<tr>
<th>RH, %</th>
<th>$\delta N_0$, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 85</td>
<td>0</td>
</tr>
<tr>
<td>91.0</td>
<td>0.3</td>
</tr>
<tr>
<td>94.0</td>
<td>0.8</td>
</tr>
<tr>
<td>97.0</td>
<td>1.5</td>
</tr>
<tr>
<td>98.0</td>
<td>1.8</td>
</tr>
<tr>
<td>99.0</td>
<td>2.5</td>
</tr>
</tbody>
</table>

### c. EWA Evidence from Field Measurements

Millimeter wave field measurements are carried out in three ways (37-101):

1. attenuation rate $\alpha$ (dB/km) for horizontal, line-of-sight paths;
2. total zenith attenuation $A$ (dB); and
3. sky noise $T_B$ (K), often employed to infer the $A$ value.

Most of the measurements are performed at single frequencies; a few were carried out in a broadband mode (Fourier transform technique) (86,90,93,98,101). Several difficulties plague field observations:

1. absolute calibration;
2. large scatter ($\pm 10\%$ to $\pm 30\%$) in data due to unspecified weather along the path;
3. scarceness of data at high humidities (RH > 90%);
4. lack of simultaneous recordings of the integrated water vapor $w$ (Eq. 33);
5. absence of data on integrated liquid water $W$ (Eq. 49) and visibility $V$ (Eq. 52) in cloud-free air; and
6. difficulty of fitting data empirically to surface-based meteorological variables.

Horizontal and zenith path data are summarized in Table 5 and compared with model calculations by using the U.S. Standard Atmosphere (19). As expected, the window (W1 to W5) absorption increases with the water vapor concentration $p$ or path-integrated water vapor $w$. It was observed earlier that measurements in the 100 GHz to 117 GHz range revealed considerably higher values of water vapor absorption than were predicted by H$_2$O line shape theory (73).

Generally, the absorption $A$ is divided into a dry contribution ($A_d$) and a wet term ($A_w$). The dry term is caused by oxygen absorption originating from a well-known spectroscopic data base (Section II); hence, in W1 to W3, it can serve as a check value.
A NEMESIS FOR MILLIMETER WAVE PROPAGATION

The wet term determines the transparency in all window ranges. Transparency is tightly coupled to humidity [that is, ρ, w, and W(RH)] causing various propagation limitations (for example, usable range L or minimum elevation angle θ) with increasing amounts of water vapor in the path volume. A typical case exists when weather conditions change from clear and dry to cloudy and wet. The water vapor absorption problem fades rapidly away above h > 3 km. It has become a standard practice to separate the wet term into two components: one proportional with ρ (monomer), the other with a ρ² (dimer) dependence. The first field results to support the dimer hypothesis were taken at 220 GHz (76).
Comparing these data with other available data in Table 5, one notices that in about half the cases a squared (x = 2) water vapor dependence improves the fit.

A horizontal path that operated at 182.9 GHz, close to the 183 GHz H₂O line (Table 2), exhibited differences in the water vapor proportionality depending upon clear or cloudy sky conditions. The difference, 3.90 compared with 4.20 dB/km, was reconciled when a temperature dependence of t² was assumed, which is about four times the t dependence for the 183 GHz line (Eq. 29: t²) (77). The same experiment produced at 171 GHz a relationship between attenuation rate ρ and concentration that becomes increasingly nonlinear when ρ > 10 g/m³. Measurements in W5 (330 GHz to 360 GHz) required a linear (x = 1, y = 2.3) and squared (x = 2, y = 11) water vapor term to fit the data (89).
Condensation effects were evident in recent W4 and W5 data (101). For the first time, the importance of relative humidity RH was recognized. An EMA contribution with x = 2 and y = 16 to 30 can be isolated and an increase of αw with beginning fog conditions was measured. Predicted attenuation rates in fog are in the range 3 to 15 dB/km for ν = 100 to 300 GHz, ρw = 1 g/m³ and T = 4°C (25). An independent measurement of water vapor w and liquid W contributions would be desirable.

Cumulative data taken through the total air mantle are more difficult to interpret for their phenomenological origins. In most cases, zenith attenuation A is correlated with the surface water vapor concentration ρ₀. Simultaneous measurements of the integrated vapor w, either by microwave (see Eq. 51) or infrared techniques (93) are rare. The maximum attenuation detectable in the EHF range is A ≈ 30 dB. The dry term A₀ of a slanted radio path follows the secant law A₀(90°)/sinθ, even for low angles (θ ≈ 10°); the wet term Aᵢ increases very rapidly below θ < 10° (91). A tangential path (θ = 0) traverses about 38 times the air mass at zenith but perhaps 100 times the water vapor content.

It seems certain that Aᵢ is a continuum spectrum (79,93,98, 108) and that earlier observations of spectral dimer features (81,86,90,64) were instrumental effects. To quote from Ref. 93:
"[EWA] shows no spectral features and scales with \( w \)." The frequency dependence of the empirical continuum spectrum (Eqs. 28 and 4) was \( z = 2 \). A fit of the \( \Lambda_v \) term between 15 GHz and 230 GHz (Table 5) yields in dB approximately
\[
\Lambda_v = 0.013 \rho_o (v/30)^{1.7}
\]
and the frequency dependence drops to \( z = 1.22 \) for window data taken between 140 GHz and 300 GHz (93).

Field data mostly serve the practical purpose of establishing an operational data base. Agreement with model calculations (Section II) is fair, when it is considered that the model makes use of Eq. (27) to describe the water vapor continuum. Either integrated vapor \( w \) or surface concentration \( \rho \) are useful predictors of millimeter wave window absorption (Table 5).

D. EWA Discussion

A water vapor continuum spectrum dominates the transmission behavior of atmospheric window ranges (W1 to W5: Figs. 1 to 3). Three absorption mechanisms have been parameterized to aid in identifying the respective relative contributions to the continuum. In the course of this paper, the following picture evolved:

<table>
<thead>
<tr>
<th>Far-</th>
<th>Aero-</th>
</tr>
</thead>
<tbody>
<tr>
<td>wing</td>
<td>Dimer</td>
</tr>
<tr>
<td>Eq.</td>
<td>Eq.</td>
</tr>
<tr>
<td>(57)</td>
<td>(58)</td>
</tr>
</tbody>
</table>

Relative magnitude \( C/C_v \)
- \( C/C_v = 1.0 \) EWA EWA 2 to 10 > 2
- \( C/C_v = 1.2 \) 2 2 1 + 2 1 + 2
- \( C/C_v = 3.0 \) 8 28.0 5.5, 10, 10, 11, > 10, 16 to 16, 26, 30
- \( C/C_v = 2.0 \) Fig. 0.8 1.5 to 1.2, 1.7, 12 2.5 2

The empirical expressions (Eqs. 62 to 68) merely organize experimental data; they are not found to be entirely satisfactory to uniquely support even one particular absorption scheme. At present it is difficult to relate EWA contributions quantitatively
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Results vary greatly from one experiment to the next, even under controlled laboratory conditions. EWA is most prevalent when RH > 90%; however, the best type of measurement has not yet been undertaken.

There are objections to both interpretations of EWA. Unclear problems with respect to the dimer are: (a) no direct physical evidence in the atmosphere; (b) no match to the frequency-envelope of a proposed spectrum (Table 4); and (c) no unique match to the temperature dependence. A promising EWA hypothesis is, at present, the vapor-to-liquid conversion of water by aerosol particles under conditions where RH ≤ 100%. Here the objections lie in the fact that invisible or haze clouds (see X-distribution in Fig. 9) must exist with liquid water concentrations close to those measured in fogs or clouds (for example, RH = 96%, T = 10°C, ρ = 9, and \(\rho_w = 0.1 \text{ g/m}^3\), by using Eq. (67)). Delogne raises the point that for the case of an inhomogeneous distribution of liquid aerosol water, the visibility V is improved due to the \(pV^2\)-dependence (Eq. 52) whereas millimeter waves respond just to the total water W (Eq. 49; Ref. 30).

Which explanation for EWA has the most merit can only be answered by additional, completely controlled experiments performed in the laboratory.

V. CONCLUDING REMARKS

The role that atmospheric water vapor plays in millimeter wave propagation was traced by means of data from modeling, laboratory, and field studies. The assumptions and approximations made, the reasoning used, the relative importance of various parameters, the limitations of available data, and the separation of water vapor and liquid water effects have been addressed. Molecular absorption due to oxygen is prominent in the 45 GHz to 125 GHz range (Fig. 3); water vapor dominates at higher frequencies, actually up to 30 THz (Figs. 1 and 2). Considering only molecular absorbers (H\(_2\)O and O\(_2\)) for a cloudless atmosphere leads invariably to discrepancies between predicted and measured attenuation rates. The problem is most apparent in the EHF window ranges. A horizontal path at sea level can experience, at 220 GHz for example, the following varying attenuation rates (32):

- Clear air 1.6 to 11.2 dB/km
- Fog 0.4 to 4.7 dB/km
- Rain (< 10 mm/hr) 1 to 7 dB/km

These values demonstrate the relative importance of understanding the clear air problem first. Clear air attenuation is related to atmospheric water vapor content; unfortunately, more than
two-thirds of this contribution is described only by empirical formulas that lack both physical insight and general applicability.

A reasonably concise model for the molecular absorption was presented in Section II and then applied to identify the magnitude and frequency and physical dependencies of the non-H$_2$O contribution to the available data body reported for laboratory and field experiments. The contribution is called EWA (excess water vapor absorption) and it was found the EWA exhibits in the millimeter wave range a continuum spectrum similar in frequency response to the dielectric loss spectrum of water. The search for liquid water in clear air led to the water-uptake phenomenon of aerosol particles, which grow rapidly in moist air with increasing RH. This problem has been addressed in the infrared (9,20,23) and deserves further study with respect to influences on millimeter waves.

Most of the evidence found in parameterizing EWA data supports a condensation phenomenon driven by relative humidity, RH: (a) the nonlinear pressure dependence (aerosol growth function), (b) the strong negative temperature dependence, (c) hysteresis effects when cycling the RH, (d) the governing variable is relative (RH) and not absolute (p) humidity, and (e) the failure of molecular approaches hypothesizing weakly bonded dimers but neither matching the spectral response nor the temperature dependence and number concentration necessary.

From a practical point of view, one is looking for invisible liquid water content in the range W = 0.02 to 0.2 mm when RH < 100%, which are normally known to exist under haze, cloud and fog conditions. But clouds and fog imply only larger, optically active (r > 1 μm) particle sizes. Should the condensation hypothesis have merit, then EWA can serve as a tracer to the otherwise not directly accessible world of atmospheric submicron particles. A systematic EWA study under controlled laboratory conditions of high humidity (RH = 90% to 99.9%) could reveal growth functions for particular aerosol ensembles and elucidate the various stages and time scales that H$_2$O molecules undergo in moist air until they become barely visible as clusters of > 10$^9$ molecules.

SYMBOLS AND ACRONYMS

**Acronyms**

- AFGL: Air Force Geophysical Laboratory
- CM: condensation nuclei
- CCN: cloud condensation nuclei
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D1-D4 02-MS doublets (Table 1)
EWA excess water vapor absorption
E18 computer short-form for 1018
EHF extreme high frequency range (30 to 300 GHz)
HITRAN high resolution transmission model developed by AFGL
H-bond molecular hydrogen bond
ID quantum number identification
IM imaginary part of
O2-MS oxygen microwave spectrum
RE real part of
W1-W7 atmospheric transmission windows

Symbols

a coefficient for fitting = c, Table 5
a1-a5 02-MS line coefficients, Eqs. (21) to (23) and Table 1
A total attenuation, Eq. (6), dB
b coefficient for fitting data = b2, Table 5
b1-b3 H2O line coefficients, Eqs. (24) and (25), Table 2
B(t) second virial coefficient, Eq. (37) m3
C speed of light, Eq. (3), km/s
d molecular spacing, Section III, m
D(v) dispersion spectrum, Eq. (13), ppm
e water vapor pressure, Eq. (11), kPa
E field strength, Eq. (2), V/m
f relative humidity RH, Eq. (45), 1
F' line shape for D(v), Eq. (15), GHz-1
F" line shape for N"(v), Eq. (16), GHz-1
g(f) aerosol mass growth factor, Eq. (47), 1
h altitude, Eq. (32), km
i running spectral line index, Tables 1 and 2
I interference coefficient, Eq. (23), 1
j = ±1, Eqs. (1) and (3)
k(t) dimer equilibrium factor, Eq. (39), m-3
L mean free path length, Section III, µm
m molecular mass, Eq. (20)
M molecular number density, Eq. (36), molec/m3
n refractive index, Fig. 13, 1
n' real part of n, Eq. (58), 1
n" imaginary part of n, Fig. 13, 1
N complex refractivity, Eq. (1), ppm
N0 frequency-independent part of N, Eq. (12), ppm
N'(v) refraction spectrum, Eq. (27), ppm
N"(v) absorption spectrum, Eq. (14), ppm
P dry air pressure, Eq. (12), kPa
p fluctuations of p, Eq. (34), kPa
Q resonator quality factor, Table 3, 1
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r aerosol particle radius, Eq. (35), μm
RH relative humidity, Eq. (45), %
s ray path length, Eq. (6), km
s₁, s₂ ray path coordinate, Eqs. (6) and (8)
ds path length increment, Eq. (6), km
S line strength, Eqs. (21) and (24), kHz
Sₘ aerosol surface area, Eq. (46), cm²
T 300/T, normalized inverse T, Eq. (11), 1
T temperature, Eq. (11), K
Tᵣ brightness temperature, Eq. (10), K
V visibility, Eq. (52), km
Vᵥ air volume containing water vapor, Section IV, cm³
W total precipitable water vapor, Eq. (33), cm
X concentration exponent (p), Eq. (53)
y temperature exponent (t), Eq. (53)
z frequency exponent (v), Eq. (53)
α attenuation rate, Eq. (4), dB/km
γ line width, Eq. (22), GHz
γ₀ Doppler line width, Eq. (20), kHz
Γ propagation constant, Eq. (3), 1
ε deviation from ideal gas behavior, Eq. (38), 1
η propagation delay time, Eq. (9), ns
η hav time constant for adsorption, Section IV.B., s
η hav time constant for desorption, Section IV.B., s
θ slant path angle, Section II, degree
λ optical wavelength, Section III, m
ν frequency, Eq. (3), GHz
ν₀ line resonance frequency, Eq. (15), GHz
ρ water vapor concentration, Eq. (36), g/m³
ρ path-averaged value of ρ, Eq. (52), g/m³
δρ fluctuations of ρ, Eq. (34), g/m³
φ phase rate, Eq. (5), rad/km
δ total phase delay, Eq. (8), rad
δ sum of, Eqs. (13) and (14)

Subscripts

A aerosol
D dimer
d dry
l absorption line
L Lorentzian
m maximum
n integer, cluster size
₀ initial value
s saturation
v water vapor
w liquid water
REFERENCES

Atmospheric Attenuation, Refraction, Dispersion, and Emission


Comprehensive Treatments


Selected Properties of Atmospheric Water


Laboratory Measurements

A NEMESIS FOR MILLIMETER WAVE PROPAGATION


Field Measurements

A NEMESIS FOR MILLIMETER WAVE PROPAGATION


Refractive Index of Water


Instrumentation


Additional References

