

# Zero-frequency refractivity of water vapor, comparison of Debye and van-Vleck Weisskopf theory

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**Abstract:** We show that the zero-frequency, refractivity of water vapor calculated by the van-Vleck Weisskopf theory via a summation over all the water lines from 22.2 GHz to 30 THz can explain all of the previous measurements from 0.5 MHz to microwave, mm-waves and THz frequencies. This result removes a long standing discrepancy in comparisons of measurements and theory, and is in excellent agreement with experiments.

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## Introduction

The propagation of electromagnetic waves in the atmosphere is strongly dependent on the relatively small (of the order of 0.0003) complex index of refraction  $n(\omega)$  of the atmosphere. Because the index is quite small, the refractivity term  $[n(\omega) - 1]$  is usually discussed. Even though water vapor is only one percent of the total atmosphere, at 50% relative humidity (RH) and 20°C, water vapor can account for more than 20% of the total atmosphere refractivity. The real part of the refractivity of water vapor is composed of two parts, a slowly-varying almost frequency-independent part, applicable from kHz to MHz to microwaves up to THz, into the infrared and the visible, and a strongly frequency-dependent part together with the strong absorption, due to the imaginary part, of the water vapor rotational resonance lines from 22.2 GHz to 30 THz. Measurements of the refractivity of water vapor have been made from 545 kHz [1] to microwave [2–5], mm-wave [6,7], far-infrared (THz) [8], infrared [9,10], and optical frequencies [11].

A recent experiment measured the essentially constant low-frequency refractivity of water vapor, by measuring the transit time shift of a THz pulse through a 138 m path length, as a function of RH of water vapor [12]. The time shift was measured to an accuracy of 0.1 ps, and the corresponding, essentially-constant refractivity from 0.1 to 0.9 THz was measured to be  $(n(0) - 1) = 70 \times 10^{-6} \pm 10\%$  at 10 g/m<sup>3</sup> water vapor density at 21 °C, for which  $(n(0) - 1)$  is the refractivity at zero frequency. These results were in acceptable agreement with earlier measurements [1–8]. Similar to the earlier MHz, microwave and mm-wave measurements [1–6], the  $(n(0) - 1)$  THz refractivity measurements were explained by a Debye type response [13,14], which considers only the permanent dipole moments of water vapor. van-Vleck Weisskopf lineshapes (v-VW) [15,16] were used to fit the rotational resonance lines of the water vapor. However, the extension of the Debye theory up to and beyond 50 GHz for the refractivity leads to a physical inconsistency with respect to the associated very large absorption predicted by Debye theory. Consequently, the low-frequency refractivity [12] was assigned to water dimers, trimers and clusters [17].

Here, we show that the previously neglected  $(n(0) - 1)$  low-frequency response of v-VW theory can explain the above physical inconsistency. Using both the JPL [18] and HITRAN [19] databases, to calculate  $(n(0) - 1)$ , the experimental results from 0.5 MHz to microwave,

mm-wave and THz (far-infrared) can be explained [1–8], and the associated absorption agrees with the measurements.

We can obtain mathematical agreement with Debye theory, if we set the fractional functions to 0.5 in the mathematics describing our calculations, corresponding to eliminating the rotational response. This is due to the mathematical consistency with the Debye theory as discussed in the v-VW original paper [15], and as described by Townes and Schawlow (T&S) [16]. However, the required uniform population of all the rotational ground states  $E_a$  to conform to the Debye theory would only be possible for a temperature high enough so that  $E_a/kT$  is significantly less than one. This extreme requirement shows that for water vapor, the use of Debye theory is a good approximation, but it is not physically correct.

The earlier experiments [1–6], assumed the validity of Debye theory, and then used the measured value of  $(n_o(0) - 1)$  to calculate the magnitude of electric dipole moment of the water molecule  $\mu = 1.839$  Debye.

An alternative to the early measurements of refractivity [1–6] to determine the dipole moment of water  $\mu$  is to measure the Stark splitting of the water vapor rotational lines [20–22], which is independent of the number density of water vapor molecules. The more recent Stark measurements at the frequencies of 22.235 GHz and 183.310 GHz [21,22], have obtained  $\mu = 1.848$  Debye. In addition, molecular beam electric resonance spectroscopy measurements [23,24], of the Stark splitting of the hyperfine lines in rotational states of  $H_2O$  have obtained  $\mu = 1.855$  Debye, which is considered to be the most accurate value. The JPL database uses  $\mu = 1.8546$  Debye, and the HITRAN database uses 1.855 Debye.

Here, we present the van-Vleck Weisskopf theory as the more physically correct theory for the refractivity, compared to Debye theory, to compare to the early, high quality refractivity measurements. We apply v-VW theory to these same precisely measured values and obtain an excellent fit to the early experiments [4–6], using the accepted value of the dipole moment  $\mu = 1.855$  Debye.

### Comparison of van-Vleck Weisskopf theory with Debye theory

The objective of this paper is to compare v-VW refractivity theory with Debye theory at zero frequency, in order to remove the fundamental absorption discrepancy between theory and experiment [12]. Consequently, we show that for the v-VW theory, in the limit as  $\omega$  approaches zero, the absorption coefficient  $\alpha(\omega)$  approaches zero, the phase  $\varphi(\omega) = \Delta k(\omega)L$  approaches zero, and the refractivity at zero frequency due to the electric dipole moment of water is given by

$$(n(0) - 1)_{v-VW} = c \cdot D \cdot \sum_j \frac{2A_j}{\pi\omega_j^2}. \quad (1)$$

where  $j$  refers to the water vapor resonance line with angular frequency  $\omega_j$ , and  $A_j$  gives the line strength [25,26]. The summation is to be taken over all of the spectral lines of water vapor from 22.3 THz up to 30 THz, as tabulated in the JPL and HITRAN databases [18,19]. This v-VW refractivity at zero frequency is not well known and was not used in the recent experimental comparison [25] of pulse reshaping to v-VW theory. This is because the zero frequency term only causes a pulse time shift, and consequently, has no effect on the observed pulse reshaping. We will show that the neglected low-frequency response of v-VW theory of Eq. (1) can describe all of the early measurements [1–8]. Initially, We will first describe the Debye theory as given in [12]. We will then describe the v-VW theory, and finally compare the two theories.

### Microwave and mm-wave Debye theory approach [12]

Previously, the low-frequency experimental results up to 100 GHz have been understood in terms of the Debye theory for a molecular vapor of permanent electric dipoles [1–6,13,14].

For low frequencies according to Debye theory, the dipole polarization of a vapor of water molecules will be in thermal equilibrium with an applied electric field of angular frequency  $\omega$  with the frequency-dependent, complex refractivity of [13,14],

$$(\tilde{n}(\omega) - 1)_D = \left( \frac{2\pi N_D \mu^2}{3kT} \right) / (1 + i\omega\tau). \quad (2)$$

where  $N_D$  is the number of molecules per cubic centimeter,  $\mu$  is the permanent electric dipole moment of the water molecule,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature, and  $\tau$  is the relaxation time required for the external field-induced orientations of the molecules to return to a random distribution after the field is removed. The Debye refractivity at zero frequency can be obtained from Eq. (2) as,

$$(n(0) - 1)_D = \frac{2\pi N_D \mu^2}{3kT}. \quad (3)$$

Using Eq. (3) with the following parameters [4–6]; water vapor density of  $10 \text{ g/m}^3$  at  $20^\circ\text{C}$  ( $T = 293 \text{ K}$ ), corresponding to  $N_D = 3.34 \times 10^{17}/\text{cm}^3$ ;  $\mu = 1.839 \text{ Debye} = 1.839 \times 10^{-18} \text{ StatC-cm}$ ; and  $k = 1.38 \times 10^{-16} \text{ [erg/}^\circ\text{K]}$ , gives the value of  $(n(0) - 1)_D = 58.5 \times 10^{-6}$ . In order to compare with the measurement  $(n(0) - 1) = 61.6 \times 10^{-6}$ , which has been adjusted to  $10 \text{ g/m}^3$  from  $10 \text{ mm of Hg}$ , we must calculate with the multiplicative component  $(n(0) - 1) = (1 + \bar{\epsilon})(n(0) - 1)_D$ . The  $\bar{\epsilon}$  term has been added to account for the atomic and electric response of the water molecule that is independent of the electric dipole moment [5]. For our case  $\bar{\epsilon} = 0.052$ , giving  $(n(0) - 1) = 61.5 \times 10^{-6}$ . This exceptional agreement is not surprising, because the early measurements assumed the validity of Eq. (3), and then the measured value of  $(n(0) - 1)$  was used to calculate the electric dipole moment of the water molecule. It should be noted, that using the considered to be correct value of  $\mu = 1.855 \text{ Debye}$ , the calculation gives  $62.6$ , in disagreement with the measurement.

Equation (2) can now be rewritten in the form below to enable simple comparison with the measurements.

$$(\tilde{n}(\omega) - 1)_D = \frac{(n(0) - 1)_D}{1 + i\omega\tau}. \quad (4)$$

The Debye refractivity can be rewritten in terms of the real and imaginary parts as

$$(\tilde{n}(\omega) - 1)_D = \frac{(n(0) - 1)_D}{1 + (\omega\tau)^2} - i \cdot \frac{(n(0) - 1)_D \cdot \omega\tau}{1 + (\omega\tau)^2}. \quad (5)$$

Initially, we are concerned with the real part of the Debye refractivity  $(n(0) - 1)_D / [1 + (\omega\tau)^2]$ , which falls off from the zero frequency as a Lorentzian with the half-width of  $\omega_{1/2} \tau = 1$ , equivalent to  $f_{1/2} = 1/(2\pi\tau)$ , where  $f$  is frequency. Note that there are only two parameters in the theory,  $(n(0) - 1)_D$  and  $\tau$ .

The Debye absorption coefficient is given by

$$\alpha_D(\omega) = \left( \frac{2\omega}{c} \right) \cdot \frac{(n(0) - 1)_D \cdot \omega\tau}{1 + (\omega\tau)^2}. \quad (6)$$

The real part of the Debye refractivity and the absorption can be rewritten in terms of their normalized frequency  $f/f_{1/2}$  dependence as,

$$(n(f) - 1)_D = (n(0) - 1)_D \cdot \left[ \frac{1}{1 + (f/f_{1/2})^2} \right]. \quad (7a)$$

$$\alpha_D(f) = \frac{4\pi f_{1/2}}{c} \cdot (n(0) - 1)_D \cdot \left[ \frac{(f/f_{1/2})^2}{1 + (f/f_{1/2})^2} \right]. \quad (7b)$$

The normalized frequency dependence in terms of  $(f/f_{1/2})$  for Eqs. (7a) and (7b) is shown in Fig. 1. The refractivity is described by the Lorentzian curve with a unity peak at zero frequency. The associated absorption is described by the product of  $(f/f_{1/2})^2$  and the Lorentzian. In the high frequency limit, the refractivity curve asymptotically approaches zero, while the absorption curve monotonically converges to unity. For example, with  $f_{1/2} = 200$  GHz (corresponding to  $\tau = 0.8$  ps), for the frequency  $f$  values of 50 GHz, 100 GHz, and 200 GHz, we obtain refractivity curve values of 0.94, 0.8 and 0.5, respectively, and the absorption curve values of 0.059, 0.2 and 0.5, respectively. Assuming a  $(n(0) - 1)_D$  refractivity value of  $58.5 \times 10^{-6}$ , from the refractivity curve we obtain  $58.5 \times 10^{-6} \times 0.94, 0.8,$  and  $0.5$  for 50, 100 and 200 GHz, respectively. Evaluating  $(4\pi/c) f_{1/2}(n(0) - 1)$  in Eq. (7b) to be  $0.490/\text{m}$ , we obtain from the absorption curve,  $0.490/\text{m} \times 0.059, 0.2$  and  $0.5$ , for 50, 100 and 200 GHz, respectively. The resulting absorption coefficients of  $28.9/\text{km}, 98/\text{km},$  and  $245/\text{km}$ , for 50, 100 and 200 GHz, respectively are all unphysically high and point out the inconsistency of the Debye theory. In addition, the value of  $f_{1/2} = 2000$  GHz required to fit the recent refractivity measurements [12] is much too large to assign to any known dephasing process.

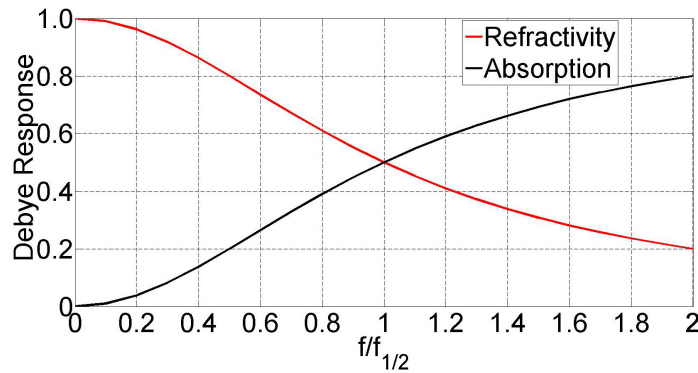


Fig. 1. The normalized frequency dependence  $(f/f_{1/2})$  for the Debye refractivity (upper curve at zero) and absorption (lower curve at zero). These curves describe the frequency dependence shown in brackets in Eqs. (7a) and (7b).

Here, it is important to note, that in contrast to water vapor, liquid water is well described by the standard Debye theory with a single relaxation time of 7.9 ps corresponding to  $f_{1/2} = 20.2$  GHz for frequencies of up to 100 GHz [27]. In order to describe recent THz-TDS measurements extending from 100 to 2000 GHz [28–30], a double Debye model with two relaxation times is required. The measurements are then well described by the two temperature dependent relaxation times of  $\tau_1 = 8.5$  ps and  $\tau_2 = 0.2$  ps (at 20 °C), corresponding to the  $f_{1/2}$  values of 18.9 GHz and 838 GHz, respectively [28–30].

### Van-Vleck Weisskopf lineshape theory

We have earlier fit our THz measurements of absorption and phase shift of water vapor [25], using the causal absorption and phase shift lineshapes of the v-VW theory [15,16,25], given below as

$$\alpha(\omega) = D \cdot \sum_j \frac{A_j}{\pi} \left( \frac{\omega}{\omega_j} \right)^2 \cdot \left[ \frac{\Delta\omega_j}{(\omega - \omega_j)^2 + (\Delta\omega_j/2)^2} + \frac{\Delta\omega_j}{(\omega + \omega_j)^2 + (\Delta\omega_j/2)^2} \right] \quad (8)$$

where  $j$  refers to the water vapor resonance line  $\omega_j$ ; here,  $j$  is only a summation index and has no relationship to the total angular momentum  $J$ . The corresponding change of the wave vector (phase) is given by

$$\Delta k(\omega) = D \cdot \sum_j 2 \frac{A_j}{\pi \omega_j} \left( \frac{\omega \omega_j}{\omega_j^2 - \omega^2} \right) \left[ 1 - \frac{\Delta\omega_j^2}{8\omega_j} \left( \frac{\omega}{\omega_j} \right) \cdot \left( \frac{\omega_j + \omega}{(\omega_j - \omega)^2 + (\Delta\omega_j/2)^2} - \frac{\omega_j - \omega}{(\omega_j + \omega)^2 + (\Delta\omega_j/2)^2} \right) \right] \quad (9)$$

For which

$$D = 10^{-18} \cdot \pi \cdot N, \quad (10)$$

with  $N$  equal to the number of molecules per cubic meter, to give  $\alpha(\omega)$  in units of inverse meters. The corresponding refractivity is given by

$$(n(\omega) - 1)_{v-1W} = \Delta k \lambda_0 / 2\pi = \Delta k (c / \omega). \quad (11)$$

The  $A_j$  line-strength values are from the JPL database in units of  $\text{nm}^2 \text{MHz}$  [18], for which  $\omega_j$  was summed up to 10 THz involving 1,305 lines [25]. The factor of  $10^{-18}$  in Eq. (10) converts the  $A_j$  cross-sections into  $\text{m}^2$ . The calculated absorption and phase  $\phi = \Delta kL$  agreed quite well with the measurements [25]. Consequently, a linear dispersion theory calculation showed excellent agreement with the measured reshaped THz output pulse [25].

### Comparison of $(n(0) - 1)$ of van-Vleck Weisskopf theory with Debye theory

In order to more easily compare with Debye theory, we present the  $A_j$  parameter from the JPL database [18], with notation similar to Townes and Schawlow [16], in more detail as

$$A_j = \left( \frac{8\pi^3}{3hc} \right) \cdot \frac{\nu_{ba}^x S_{ba} \mu_x^2 [e^{-E_a/kT} - e^{-E_b/kT}]}{Q_{rs}} \quad (12)$$

For which a summation is made over the internal states of  $E_a$ , the lower state of the transition  $\omega_j = 2\pi \nu_{ba}$  and  $E_b$ , the upper state.

The JPL rotational-spin partition function  $Q_{rs}$  is given by

$$Q_{rs} = \sum_j (2J + 1) e^{-E_a/kT}$$

where the index  $j$  sums over all the  $\omega_j$  resonance lines for which  $E_a$  designates the lower state. Equation (12) can be rewritten as,

$$A_j = \left( \frac{8\pi^3}{3hc} \right) \cdot \frac{\nu_{ba}^x S_{ba} \mu_x^2 (1 - e^{-(E_b - E_a)/kT}) e^{-E_a/kT}}{Q_{rs}}$$

and for frequencies up to 2 THz, an acceptable approximation is

$$A_j = \left( \frac{8\pi^3}{3hc} \right) \cdot \frac{\nu_{ba}^x S_{ba} \mu_x^2 (h\nu_{ba}/kT) e^{-E_a/kT}}{Q_{rs}}, \quad (13)$$

which is needed for convergence to Debye theory. The JPL and HITRAN databases do not make this approximation. Equation (13) reduces to

$$A_j = \left( \frac{2\pi}{3c} \right) \cdot \frac{\omega_{ba}^x S_{ba} \mu_x^2 (\omega_{ba}/kT) e^{-E_a/kT}}{Q_{rs}}. \quad (14)$$

$A_j$  can now be rewritten as

$$A_j = C_j \cdot \omega_j^2.$$

and we can rewrite Eq. (1) as

$$(n(0)-1)_{v-vW} = c \cdot D \cdot \sum_j \frac{2}{\pi} \cdot C_j. \quad (15)$$

for which

$$C_j = \left( \frac{2\pi}{3c} \right) \cdot \frac{S_{ba} \mu_x^2 e^{-E_a/kT}}{Q_{rs} kT}. \quad (16)$$

The remarkable result of Eq. (15) shows that for  $(n(0)-1)_{v-vW}$ , below 2 THz, there is no  $\omega_j$  dependence and no  $\Delta\omega_j$  linewidth dependence, due to the line symmetry about zero frequency of the v-VW theory. This significant situation only holds in the region for which  $h\nu_{ab} \ll kT$ , which is equivalent to  $\nu_{ab} \ll 5.7$  THz. Consequently, it is expected that this term is reduced for frequencies  $f$  above 2 THz.

In the following discussion the  $10^{-18}$  factor has been removed, because all the parameters and variables have their usual units. According to T&S in Eq. (4-28),  $^x S_{ba} \mu_x^2$  can be replaced by  $(2J+1) \mu_{ab}^2$ . With this substitution, Eq. (14) can be presented in more detail as

$$(n(0)-1)_{v-vW} = c \cdot \pi N \cdot \left( \frac{2}{\pi} \right) \cdot \sum_j \frac{(2\pi/3c)(2J+1) \mu_{ab}^2 e^{-E_a/kT}}{Q_{rs} kT}.$$

which can be reduced to

$$(n(0)-1)_{v-vW} = N \left( \frac{4\pi}{3kT} \right) \cdot \sum_j \frac{(2J+1) \mu_{ab}^2 e^{-E_a/kT}}{Q_{rs}}. \quad (17)$$

The index  $j$  sums over all the  $\omega_j$  resonance lines for which  $E_a$  designates the lower state. Townes and Schawlow write the fractional function  $f_a$  in their Eq. (4-25) as,

$$f_a = \frac{(2J+1) e^{-E_a/kT}}{Q_{rs}}. \quad (18)$$

which gives the fraction of the total number of molecules in the lower state of the two states of  $\omega_j$ . We can rewrite Eq. (17) as,

$$(n(0)-1)_{v-vW} = N \left( \frac{4\pi}{3kT} \right) \sum_j f_a \mu_{ab}^2. \quad (19)$$

for which  $\mu_{ab}$  is the dipole moment between the upper “b” and the lower “a” of the transition  $\omega_j$ . This important result shows concisely the difference between the van-Vleck Weisskopf and Debye theories. If all the  $E_a$  are set equal to zero, thereby, setting all the rotational lower  $E_a$  states to zero,  $f_a$  becomes  $f_a = 0.5$ , as in T&S Eq. (13-20). Using  $f_a = 0.5$ , Eq. (19) becomes

$$\left[ (n(0) - 1)_{v-VW} \right]_{Limit} = N \left( \frac{2\pi}{3kT} \right) \sum_j \mu_{ab}^2. \quad (20)$$

Townes and Schawlow [16], and van-Vleck and Weisskopf [15] have shown that

$$\sum_j \mu_{ab}^2 = \mu^2.$$

Thereby allowing Eq. (20) to be rewritten as,

$$\left[ (n(0) - 1)_{v-VW} \right]_{Limit} = \frac{2\pi N_D \mu^2}{3kT}. \quad (21)$$

which is identical to the Debye result for a vapor of permanent dipoles, and for which we have converted to number density/cm<sup>3</sup>.

With respect to the comparison of the  $(n(0) - 1)_{v-VW}$  with  $(n(0) - 1)_D$ , it is clear from Eqs. (19), (20) and (21) that the two results are significantly different from each other, because of the different fractional functions determined by the magnitude of  $E_a/kT$ . The required uniform population of all the ground states to conform to the Debye theory would only be achieved for a temperature high enough so that  $E_a/kT$  is significantly less than one.

This consideration shows that for water vapor the low frequency Debye theory may be a good approximation, but it is not physically correct. The difference can be demonstrated by calculations at the identical conditions and parameters:  $\mu = 1.855$  Debye,  $N = 3.340 \times 10^{17}/\text{cm}^3$  ( $10 \text{ g/m}^3$ ), and  $T = 300 \text{ K}$ . For this comparison  $(n(0) - 1)_D = 58.14 \times 10^{-6}$  and  $(n(0) - 1)_{v-VW} = 56.59 \times 10^{-6}$ , showing a difference of 2.56%, which would be very important in a dipole moment determination.

We now use the van-Vleck Weisskopf theory, as the more physically correct theory, to analyze the early very well done and accurate measurements [4–6]. Consequently, we compare our v-VW calculation to their measured value of  $(n(0) - 1)$  adjusted to be  $61.6 \times 10^{-6}$  for a water vapor density of  $10 \text{ g/m}^3$  (instead of  $10 \text{ mm Hg}$ ) corresponding to  $3.34 \times 10^{17}/\text{cm}^3$  and a temperature of  $20 \text{ }^\circ\text{C}$  ( $293 \text{ K}$ ). Calculating the v-VW zero-frequency refractivity for the same number density and using the JPL database for which  $T = 300 \text{ K}$ , we obtain  $56.69 \times 10^{-6}$ , which we adjust to  $293 \text{ K}$  by the factor 1.024 to give  $58.04 \times 10^{-6}$ , which must be multiplied by  $(1 + \bar{\epsilon})$  with  $\bar{\epsilon} = 0.052$  added to account for the atomic and electric response of the water molecule that is independent of the electric dipole moment [5], to give  $(n(0) - 1) = (1 + \bar{\epsilon}) (n(0) - 1)_{v-VW} = 61.06$  in excellent agreement with measurement. This agreement is better than would be achieved by Debye theory in the original paper [5], if they had used the established value of  $\mu = 1.855$  Debye.



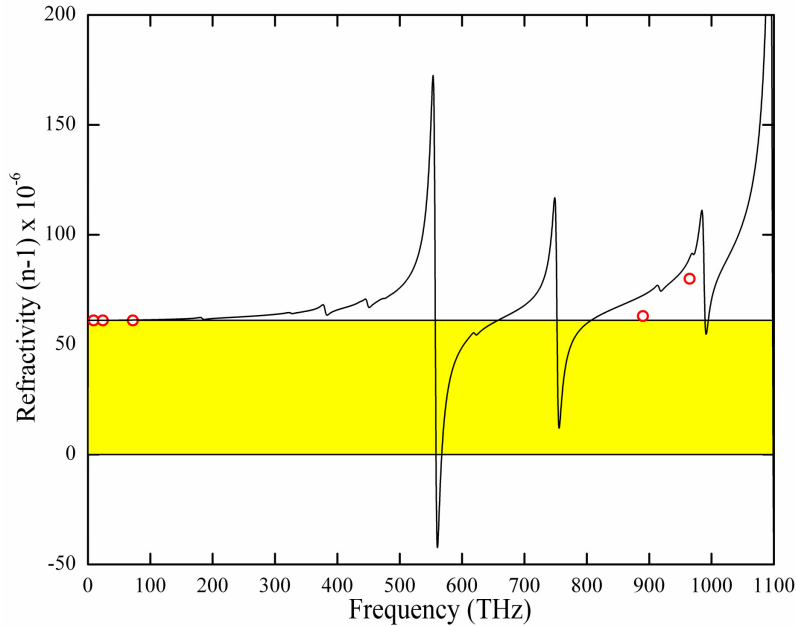


Fig. 2. Refractivity of water vapor at 20 °C and 10 g/m<sup>3</sup>, as calculated by the complete van-Vleck Weisskopf theory including the zero-frequency response, and the additional small term  $\bar{\delta}(n(0)-1)_{v,vw} = 3.02 \times 10^{-6}$  which describes the atomic and electric polarization of the water vapor, which is independent of the electric dipole moment. The measurements of [4–6] of  $61 \times 10^{-6}$  at 9.2, 24 and 72 GHz are indicated by the 3 open circles, respectively. The measurements of [8] are  $63$  and  $80 \times 10^{-6}$  for 890 and 965 GHz, respectively. The straight line at  $61.06 \times 10^{-6}$  marks the complete calculated value of  $(n(0) - 1)$ .

Figure 2 presents the complete v-VW refractivity of water vapor at 20 °C and 10 g/m<sup>3</sup>, which can be directly compared to Fig. 4 in [12], to demonstrate the now complete physical description of the previous physical inconsistency of the calculated refractivity. The entire frequency dependent  $(n(\omega) - 1)_{v,vw} + \bar{\delta}(n(0) - 1)_{v,vw}$  is shown from 0 to 1,100 GHz, and shows the slowly varying component of the refractivity starting from  $(n(0) - 1)$  together with the faster resonant response of the rotational transitions. Clearly, Fig. 2 shows that the use of Debye theory to describe microwave and mm-wave transmission measurements is not required. Excellent agreement is shown the early measurements [4–6,8], marked by the red circles

As a check on our results, we have also calculated the zero-frequency refractivity with the HITRAN database at 296 K, and obtained  $57.33 \times 10^{-6}$ , which was adjusted to 293 K, by the factor 1.010 to give  $57.92 \times 10^{-6}$ . This is relatively close agreement, considering that the JPL unadjusted value of  $56.69 \times 10^{-6}$  was adjusted to 293 K with the value of  $58.04 \times 10^{-6}$  involved the summation of 3085 lines up to 30 THz, and that the HITRAN calculation involved the summation of 8678 lines up to 30 THz, and shows the consistency and high accuracy of these two databases for water vapor.

As another check on our results we changed the extent of the frequency range for the summation over the water lines. For the same conditions as discussed above, the JPL calculations of  $(n(0) - 1) = 56.38 \times 10^{-6}$  for the summation up to 10 THz with 1305 lines, and  $(n(0) - 1) = 47.08 \times 10^{-6}$  up to 5 THz with 469 lines, and  $(n(0) - 1) = 18.72 \times 10^{-6}$  up to 2 THz with 144 lines.

The corresponding HITRAN calculation of  $(n(0) - 1) = 57.03 \times 10^{-6}$  for the summation up to 10 THz with 4843 lines, and  $(n(0) - 1) = 47.85 \times 10^{-6}$  up to 5 THz with 2671 lines, and  $(n(0) - 1) = 19.20 \times 10^{-6}$  up to 2 THz with 939 lines. The plots of  $(n(f) - 1)$  vs frequency

similar to Fig. 2 for all of these different JPL and HITRAN calculations scans are quite similar, only vertically displaced by their corresponding value of  $(n(0) - 1)$ .

### **Summary**

In summary, we have shown that the complete van-Vleck Weisskopf theory removes the previous physical inconsistency for low frequency, MHz, microwave, mm-waves and THz propagation of electromagnetic waves through the water vapor of the atmosphere. We have shown that the slowly varying component of the water vapor refractivity, previously explained by Debye theory, extends from zero-frequency up to more than 900 GHz, together with the more rapid response of the water vapor resonance lines and is well explained by v-VW theory, and with excellent agreement with experimental results.

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