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Theoretical and calculational aspects of the radio refractive index of water vapor

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The radio refractive index is calculated by summing the refraction due to the infrared resonances of the water vapor monomer. Although this calculated refraction agrees well with measured values, its temperature dependence departs significantly from the measured variation with temperature. The rotational resonances of water vapor give a contribution to the radio refractive index that does not vary precisely as  $e/T^2$ ; theoretical reasons are given for this departure from the classical refraction by permanent dipoles.

INTRODUCTION

The radio refractive index equation of moist air is commonly given [e.g., Thayer, 1974] by

$$(n - 1) \times 10^6 = K_1(P_a/T)Z_a^{-1} + K_2(e/T)Z_w^{-1} + K_3(e/T^2)Z_w^{-1} \quad (1)$$

where  $n$  is refractive index,  $P_a$  is partial pressure of dry air,  $e$  is partial pressure of water vapor,  $T$  is absolute temperature, and  $Z_a$  and  $Z_w$  are small correction factors for nonideal gas behavior. The expressions  $(P_a/T)Z_a^{-1}$  and  $(e/T)Z_w^{-1}$  are proportional to the number densities of dry-air molecules and water vapor molecules, respectively. The compressibility factors  $Z_a$  and  $Z_w$  are given by Owens [1967]. The coefficients  $K_1$ ,  $K_2$ , and  $K_3$  are obtained by fitting data to this equation. This traditional fit to terms of the form  $e/T$  and  $e/T^2$  corresponds to the classical refraction by induced dipoles and permanent dipoles, respectively. We shall be concerned with the refraction caused by water vapor and hence with the corresponding coefficients  $K_2$  and  $K_3$ .

Each absorption resonance provides a nondispersive refraction at frequencies much lower than the resonance frequency. The electronic transitions at ultraviolet frequencies are the induced dipole type and hence provide refraction at optical frequencies that varies as  $P_a/T$  and  $e/T$ . Although pure vibrational transitions produce a radio frequency refraction

that varies as  $(e/T)$  [Van Vleck, 1927], the infrared vibrational-rotational transitions do not entirely fit either classical analogy, and Zhevakin and Naumov [1967a] show that these resonances contribute little to the refractive index at radio frequencies. The far-infrared rotational transitions of the water molecule are the permanent-dipole type and can be expected to provide a radio refraction that principally varies as  $e/T^2$ . However, Van Vleck [1932] shows that for the  $e/T^2$  dependence to be valid it is vital that no permanent-dipole rotational transitions involve energy changes of the order of the thermal energy  $K_B T$ , where  $K_B$  is the Boltzmann constant and  $T$  is the absolute temperature. Equivalently, there must be no transitions having resonance frequency  $\nu_i$  (in units  $\text{cm}^{-1}$ ) of the order of  $K_B T/hc$ , where  $h$  is Planck's constant and  $c$  is the speed of light in vacuum. Note that  $C \equiv K_B/hc = 0.695 \text{ cm}^{-1} \text{ K}^{-1}$ . One  $\text{cm}^{-1}$  is 30 GHz. For typical atmospheric temperatures between 250 K and 300 K, the frequency  $CT$  lies between 175 and 210  $\text{cm}^{-1}$  (5.25 THz and 6.3 THz). The rotational transitions of the water molecule certainly include strong resonances in and near this frequency interval. Thus there is theoretical expectation that the refractive index of water vapor may not be simply the sum of two terms behaving as  $e/T$  and  $e/T^2$ .

Thayer [1974] hypothesized that the radio refractive index equation would be more accurate if  $K_2$  were taken to have the same value as it does at optical frequencies. It is now clear that this is tantamount to assuming that the sum of refraction contributions from all the infrared water vapor resonances produces  $K_3$  but does not change  $K_2$ . We test this

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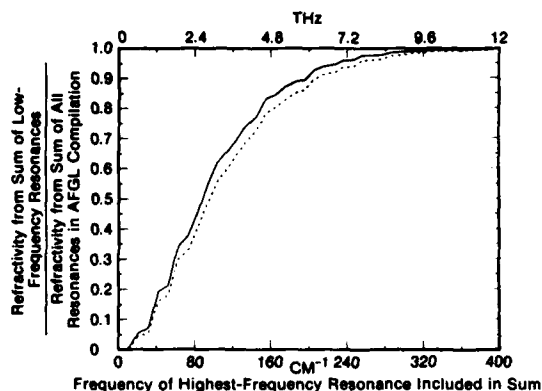


Fig. 1. The ratio of the radio refractivity contributed by all resonances having resonance frequency less than a value on the ordinate to the radio refractivity contributed by all infrared water vapor resonances. Solid curve corresponds to  $T = 273$  K while the dashed curve is for  $T = 333$  K.

hypothesis by calculating the sum of the contributions of infrared water vapor resonances to the refraction at radio frequencies.

#### CALCULATED REFRACTIVE INDEX

In principle, the refractive index can be calculated by summing the refraction contributions of all absorption resonances [Zhevakin and Naumov, 1967a, b; Birnbaum, 1953]. Birnbaum [1953] shows that for any sharp absorption resonance the Kramers-Kronig relationship implies a refraction in the far wings having a frequency dependence given by  $n_i \propto 1/(v_i^2 - v^2)$ , where  $n_i$  is the refractive index caused by the resonance labeled by the index  $i$ ,  $v$  is frequency, and  $v_i$  is the resonance frequency. This result applies for either  $v \ll v_i$  or  $v \gg v_i$ . Since this result applies to sharp absorption resonances in general, it certainly applies for any particular line shape model having a sharp absorption line shape (e.g., the Gross or Van Vleck-Weisskopf line shapes). Each resonance contributes a refraction  $n_i$  that is nondispersive in the limit of low electromagnetic frequency  $v \rightarrow 0$ ; each line contributes an amount [Hill and Clifford, 1981]

$$n_i = S_i Q / 2\pi^2 v_i^2 \quad (2)$$

where  $S_i$  is the integrated absorption strength of the resonance,  $v_i$  is its line frequency, and  $Q$  is the number density of absorbing molecules. Any particular line shape model that is sufficiently sharp in the sense of Birnbaum [1953] (e.g., the Gross or Van

Vleck-Weisskopf line shapes) must give equation (2). The strongest (largest  $S_i$ ) and lowest frequency (smallest  $v_i$ ) resonances contribute most. Therefore, although the strong water vapor resonances in the vicinity of the frequency  $CT$  may not give a temperature dependence behaving like  $e/T^2$ , the equally strong but lower frequency resonances may dominate the radio wave refraction and approximately restore this temperature dependence.

The line strength has temperature dependence arising from the partition function and the difference of two Boltzmann distributions. For the water molecule this temperature dependence is

$$S_i \propto T^{-3/2} [\exp(-E_i^L/CT) - \exp(-E_i^U/CT)] \quad (3)$$

where  $E_i^L$  and  $E_i^U$  are the values (in units  $\text{cm}^{-1}$ ) of the lower and upper state energies responsible for resonance  $i$  and  $C = 0.695 \text{ cm}^{-1} \text{ K}^{-1}$ .

We have calculated the radio frequency refraction of the infrared resonances of water vapor by summing the contributions of all water vapor lines in the Air Force Geophysics Laboratory (AFGL) line parameter compilation. This compilation extends from lines at radio frequencies to those in the visible. All water vapor lines are included in the sum; no lines have been excluded, no matter how weak or how high in line frequency. The calculation was performed for several humidities from 0% to 100% for each of many temperatures from  $-10^\circ\text{C}$  to  $63^\circ\text{C}$  and  $110^\circ\text{C}$  to  $250^\circ\text{C}$  and for total pressures of 0.2 atm, 0.8 atm, and 1.0 atm. As expected, for fixed temperature and humidity the refraction by water vapor was found to be independent of total pressure. Also as expected, the calculated refraction was proportional to the humidity. The Gross line shape having humidity and pressure-dependent line width was used, as by Hill *et al.* [1980]. This line shape gives (2) in the low-frequency limit. A 1-m radio wavelength was assumed; for such a low frequency there is no practical difference between the complete Gross formula and (2).

Suppose we begin summing the refraction with the lowest frequency in the line parameter compilation and proceed to include higher and higher frequency resonances. How does the refraction accrue as more resonances are included, and how high in frequency must we sum before the total refraction is approached? Figure 1 illustrates the answer by showing the ratio of the partial sum to the total sum. Although the graph only shows frequencies less than  $400 \text{ cm}^{-1}$  (i.e., 12 THz), the total sum includes all

lines from radio to visible frequencies. In principle, the curves in Figure 1 should step upward at the resonance frequency of each line; in fact, the curves are smoothed by plotting point to point at intervals of  $10 \text{ cm}^{-1}$ . Consider the proof by *Van Vleck* [1932] that rotational resonances should sum to provide a radio refraction that varies as  $(e/T^2)$ ; this proof requires neglecting  $0.5(v_i/CT)^2$  relative to unity. If  $0.5(v_i/CT)^2$  is less than 0.1, then  $v_i < 85 \text{ cm}^{-1}$  for  $T = 273 \text{ K}$ . Figure 1 shows that less than half of the radio refraction arises from rotational resonances satisfying  $0.5(v_i/CT)^2 < 0.1$ . Thus we should not be surprised if the radio refraction caused by rotational resonances does not vary precisely as  $(e/T^2)$ .

In a sense, a measurement of radio refractive index is an empirical sum of the refraction contributions of all the infrared and ultraviolet resonances. It is natural to treat our calculated refractive indexes as a simulated set of experimental data. Thus we do as the experimentalists have done; that is, we fit the calculated refraction to the form  $K_2(e/T)Z_w^{-1} + K_3(e/T^2)Z_w^{-1}$  as suggested by (1). This functional form fits the refraction very well; the rms error was only a few thousandths of one percent. The temperature range  $0^\circ\text{--}60^\circ\text{C}$  corresponds to that used in the experiments by *Boudouris* [1963]; fitting to this temperature range gave the following infrared contributions to  $K_2$  and  $K_3$ :

$$K_2 = 33.30 \pm 1 \text{ K/mbar} \quad (4)$$

$$K_3 = (3.5833 \pm 0.0032) \times 10^5 \text{ K}^2/\text{mbar} \quad (5)$$

Equations (4) and (5) result from the sum of all infrared resonances in the AFGL compilation. Note that the total value of  $K_2$  at radio frequencies is the sum of the above infrared contribution, 33.30 K/mbar, and the extrapolation to infinite wavelength of the empirically known value of  $K_2$  at optical frequencies,  $64.79 \pm 0.08 \text{ K/mbar}$  [*Thayer*, 1974]; the latter is caused by the ultraviolet electronic resonances of the water molecule.

We examined fitting the calculated refraction to several other temperature ranges. For the temperature range  $110^\circ\text{--}250^\circ\text{C}$ , which roughly corresponds to the higher temperature range of experiments reviewed by *Birnbaum and Chatterjee* [1952], we found that the infrared contribution to  $K_2$  is 2% larger than (4) and  $K_3$  is 0.1% smaller than (5). For the temperature range  $-10^\circ$  to  $40^\circ\text{C}$ , the infrared contribution to  $K_2$  is 2% larger than (4), and  $K_3$  is 0.05% smaller than (5). These deviations are within the error given in (4) and (5).

The choice of the estimated errors in (4) and (5) deserves explanation. Unlike experiments which have random variation, we are fitting to a smooth function of temperature. We must choose a nonstatistical measure of the error in  $K_2$  and  $K_3$ . Our choice is as follows: We first find the best fit that the computer can generate; then we make a small change in  $K_2$  and refit by changing only  $K_3$ , but not  $K_2$ . We continue to change  $K_2$  and refit  $K_3$  until the rms error in the refraction is twice the rms error of the best fit. The errors stated in (4) and (5) are the difference between the values of  $K_2$  and  $K_3$  from the best fit and those that double the rms error in the refraction. This definition of error gives a conservative estimate that accounts for the fact that a decrease in  $K_2$  can be approximately compensated by an increase in  $K_3$  and vice versa. If all the rms error in the fit to the refraction were blamed on only one of  $K_2$  or  $K_3$ , but not the other, then the errors would be only about one-tenth the errors stated in (4) and (5). The difference between minimizing rms error as opposed to minimizing percent rms error changes  $K_2$  and  $K_3$  by about one-tenth the error stated in (4) and (5). The error in the fitting is not caused by computer round-off; it is caused by the computed refraction having temperature dependence that is not adequately described by (1).

The line strengths are given to three decimal places in the line parameter compilation. By allowing increases in  $K_3$  to partially compensate for decreases in  $K_2$  (and vice versa), three significant figures in the calculated refraction imply errors in  $K_2$  and  $K_3$  that are about 10 times larger than those stated in (4) and (5). As will be seen in the discussion section, such large errors equal the experimental errors in  $K_2$  and  $K_3$ . Whether or not the three decimal places are all accurate is another question entirely.

We evaluate the relative contributions to  $K_2$  and  $K_3$  from the rotational resonances versus the vibrational-rotational resonances by separately calculating the refraction from all infrared resonances at frequencies in excess of  $1000 \text{ cm}^{-1}$  (corresponding to a  $10\text{-}\mu\text{m}$  wavelength) and separately for all resonances at frequencies less than  $1000 \text{ cm}^{-1}$ . The arbitrary boundary of  $1000 \text{ cm}^{-1}$ , which lies in the  $10\text{-}\mu\text{m}$  window, suffices to separate the radio refraction caused by the vibrational-rotational transitions at higher frequencies from the pure rotational transitions at lower frequencies. We find that nearly all of both  $K_2$  and  $K_3$  is caused by rotational resonances. The vibrational-rotational resonances produce only

TABLE I. Values of  $K_2$  and  $K_3$  for Radio Frequencies

	$K_2$	$K_3$
Boudouris	$72 \pm 10.5$	$(3.754 \pm 0.03) \times 10^5$
Birnbaum and Chatterjee	$71.4 \pm 5.8$	$(3.747 \pm 0.029) \times 10^5$
Thayer	$64.79 \pm 0.08$	$(3.776 \pm 0.004) \times 10^5$
Calculated	$98 \pm 1$	$(3.583 \pm 0.003) \times 10^5$

Values of  $K_2$  are in degrees Kelvin per millibar; values of  $K_3$  are in degrees Kelvin squared per millibar.

5.8% of the infrared contribution to  $K_2$  and decrease  $K_3$  by only 0.0009%. Specifically, for the fit to the temperature range  $0^\circ$ – $60^\circ\text{C}$ , the infrared water vapor resonances at  $\nu_i > 1000 \text{ cm}^{-1}$  give a contribution to  $K_2$  of  $1.92 \pm 0.02 \text{ K/mbar}$  and a contribution to  $K_3$  equal to  $-30.9 \pm 5 \text{ K}^2/\text{mbar}$ . Notice that the net refraction by these resonances is positive. We have no objection to a negative contribution to  $K_3$  because we do not force a classical interpretation on the refraction by the vibrational-rotational resonances.

We have investigated forcing the rotational resonances to contribute to only one term in (1). For the temperature range  $0^\circ$ – $60^\circ\text{C}$ , we fitted the calculated refraction from all resonances having  $\nu_i < 1000 \text{ cm}^{-1}$  to the form  $K'_3(e/T^p)$  and obtained

$$K'_3 = (3.1748 \pm 0.0083) \times 10^5 \text{ K}^p/\text{mbar} \quad (6)$$

$$p = 1.97421 \pm 0.00046 \quad (7)$$

The errors are defined analogous to the errors stated in (4) and (5). This one-term fit gave an rms error of a few thousandths of one percent in the refraction; this is roughly the same error as obtained by fitting with the two terms in (1). We fitted the calculated refraction from all resonances  $\nu_i > 1000 \text{ cm}^{-1}$  to the form  $K'_2(e/T^q)$  and obtained

$$K'_2 = 1.319 \pm 0.038 \text{ K}^q/\text{mbar} \quad (8)$$

$$q = 1.0565 \pm 0.0050 \quad (9)$$

This two-parameter, one-term fit gave a 0.02% rms error in the refraction caused by those resonances having  $\nu_i > 1000 \text{ cm}^{-1}$ . In comparison, the two-parameter, two-term fit in (1) gave 0.03% rms error.

#### DISCUSSION

Table I gives the values of  $K_2$  and  $K_3$  resulting from measurements by Boudouris [1963], the review of measurements, including their own, by Birnbaum

and Chatterjee [1952], the values reported by Thayer [1974], who assumed  $K_2$  equals its value at optical frequencies, and the calculations described in the previous section. Birnbaum and Chatterjee [1952] collected the  $K_2$  and  $K_3$  values from several experiments; they averaged the  $K_2$  values weighted inversely proportional to the square of the probable errors and averaged the  $K_3$  values by the same method. The values of  $K_2$  and  $K_3$  given by Smith and Weintraub [1953] are based on those by Birnbaum and Chatterjee [1952]. On the basis of their recent measurement of water vapor refraction, Liebe *et al.* [1977] give values of  $K_2$  and  $K_3$  that are nearly identical to those of Smith and Weintraub [1953]. The appendix discusses the significantly different values of  $K_2$  and  $K_3$  obtained by Hasegawa and Stokesberry [1975]. The experimental values of  $K_2$  and  $K_3$  seem consistent and well-represented by the upper two entries in Table I.

Now compare the experimental values in Table I (those of Boudouris and of Birnbaum and Chatterjee) with the calculated values. Similar to the calculations by Zhevakin and Naumov [1967a], our calculated refractive index is within a few percent of measured values. At  $-20^\circ\text{C}$ , the refractivity from our calculated values of  $K_2$  and  $K_3$  is 2.65% less than that obtained using the  $K_2$  and  $K_3$  values of Boudouris. This underestimate decreases with increasing temperature to 0.76% at  $260^\circ\text{C}$ . At  $20^\circ\text{C}$  our calculated  $K_2$  and  $K_3$  values give 2.4% less refractivity than  $K_2$  and  $K_3$  from Boudouris. For  $20^\circ\text{C}$ , Table 2 by Boudouris [1963] summarizes experimental error in refractivity for nine experiments; these errors average to 1.2%. This is one-half the discrepancy between calculated and measured refractivity at  $20^\circ\text{C}$ . However, the apportionment between the coefficients  $K_2$  and  $K_3$  differs from the measured results by several standard deviations. For instance, assuming that  $K_2$  has an average experimental standard deviation of 8 (see Table I), then the experimental value of  $K_2$  is 3.2 standard deviations smaller than its calculated value. Likewise, the experimental value of  $K_3$  is 5.7 standard deviations larger than its calculated value. Thus if one plots  $(n-1)/(e/T)$  as a function of  $T^{-1}$ , then the calculated curve (a straight line to excellent approximation) is significantly different from the measured curve because the slope  $K_3$  and intercept  $K_2$  of the straight line fits differ by many standard deviations. This is a genuine disagreement between theory and experiment.

One possible explanation for the discrepancy is

that the line parameter compilation is incorrect, in that  $S_i/v_i^2$  is inaccurate for some lines. Considering our previous comments (see the introduction) on *Van Vleck's* [1932] derivation, the rotational resonances most likely to provide a deviation from the  $K_3(e/T^2)$  dependence are those having frequencies near  $\nu_i \approx K_B T/hc \approx 190 \text{ cm}^{-1}$  (i.e., 5.7 THz). Since the term  $K_2(e/T)$  is much smaller than the  $K_3(e/T^2)$  term, even a small deviation from a  $1/T^2$  dependence by the rotational contribution will cause a large contribution to  $K_2$ .

A second possible explanation of the discrepancy is that water clusters contribute to the measured refraction, whereas we have only calculated the monomer contribution. In principle, it is possible to calculate the refraction contributed by a model absorption spectrum of the water dimer (the dimer absorption spectrum is given by *Bohlander* [1979]). However, it is not possible to calculate the refraction contributed by the broadband empirical excess absorption, for two reasons. First, the Kramers-Kronig relation is sensitive to the way in which this absorption decreases at high frequencies. Second, the excess absorption is defined as the measured absorption less the monomer absorption predicted with a particular line shape. To the extent that the tails of this particular monomer line shape are inaccurate, the excess absorption cannot be entirely attributed to water clusters; but one must accurately remove monomer absorption from the excess absorption because the refraction contribution of the monomer is fully accounted for in our calculations.

The discrepancy is not caused by our calculation using a 1-m radio wavelength (300 MHz) as opposed to the higher radio frequencies typically used in experiments (see Table 2 by *Boudouris* [1963]). The dispersion in  $(n-1) \times 10^6$  and  $A_T$  is shown graphically by *Hill and Clifford* [1981], where  $A_T \approx -K_3(e/T^2)$ ; thus the dispersion in  $A_T$  is a measure of that in  $K_3$ . The dispersion in  $K_2$  is easily calculated from that in  $(n-1) \times 10^6$  and  $K_3$ . From zero frequency to 60 GHz the graphs by *Hill and Clifford* [1981] imply that  $K_3$  increases by  $0.0096 \times 10^5 \text{ K}^2/\text{mbar}$  and  $K_2$  decreases by 1.6 K/mbar. These changes in  $K_2$  and  $K_3$  are considerably smaller than their experimental uncertainties.

Now consider Thayer's values of  $K_2$  and  $K_3$  in Table 1. Those values are based on his hypothesis that  $K_2$  should be the same at radio wavelengths as at visible wavelengths, namely  $K_2 = 64.79 \text{ K/mbar}$ . We have seen, however, that the infrared resonances

of water vapor are theoretically expected to give a contribution to  $K_2$ ; and the calculated values of  $K_2$  show that the infrared resonances of water vapor can give a significant contribution to  $K_2$  (namely a calculated contribution of 33.3 K/mbar in (4)). Thus Thayer's hypothesis is unfounded. We suggest that one should use the entirely empirical coefficients (e.g., those of *Boudouris* [1963]). Of course, the term  $K_2(e/T)$  is only needed for precise work. For most practical applications, this term may have its approximate value introduced into the  $K_3(e/T^2)$  term to yield the simpler radio refractive index equations discussed by *Smith and Weintraub* [1953] or *Bean and Dutton* [1966].

We conclude, quite opposite to the assumption by *Zhevakin and Naumov* [1967a], that the infrared contribution to  $K_2$  is dominated by the rotational resonances, not by the vibrational-rotational resonances. We noted in the introduction that the rotational resonances of water vapor need not provide a temperature dependence proportional to  $1/T^2$ . In fact, *Zhevakin and Naumov* [1967a] calculated the temperature dependence of radio refractive index caused by the rotational resonances; they obtained  $1/T^{1.97}$ . If one fits  $1/T^{1.97}$  to the form  $(K_2/T) + (K_3/T^2)$ , one obtains a value of  $K_2$  that is roughly the magnitude of the  $K_2$  contribution that we found from the rotational resonances. Thus the contribution of the rotational resonances to  $K_2$  is very sensitive to the deviation from  $1/T^2$  of their refractive temperature dependence.

One could force the rotational transitions to contribute to only one term in the radio refractive index equation by fitting their radio refraction to  $K'_3(e/T^p)$ . Then  $p$  would be close to, but not equal to, 2 (just as *Zhevakin and Naumov* [1967a] found  $p \sim 1.97$ ). Our fit to this functional form gives the  $K'_3$  and  $p$  values in (6) and (7). One would then likewise require that the vibrational-rotational transitions contribute to only one term by fitting their radio refraction contribution to  $K'_2(e/T^q)$ . Then  $q$  would be nearly, but not precisely, unity. Our fit gives the  $K'_2$  and  $q$  values in (8) and (9). We must view this type of fit to be in no fundamental sense superior to that in (1), and this fit obscures comparison of the calculated and measured refractive indexes. Since the rotational transitions do not provide  $K_3$  exclusively and the vibrational-rotational transitions do not contribute to  $K_2$  exclusively, we must view (1) as a low-order polynomial fit in inverse powers of  $T$  to a general function of temperature.

In fact, *Van Vleck* [1927] shows that the quantum mechanical correction to (1) has the form  $K_4(e/T^3) + K_5(e/T^4) + \dots$ . By including the term  $K_4(e/T^3)$  in (1) and using Van Vleck's expression for  $K_4$ , *Birnbaum and Chatterjee* [1952] (in their appendix) show that the value of  $K_2$  is reduced from its value deduced using (1) without the correction term. They show that this reduced value of  $K_2$  is less than the extrapolation to zero frequency of the optical-frequency value of  $K_2$ ; this is impossible since the (positive) infrared contribution to  $K_2$  must be added to its extrapolated optical value to obtain the radio frequency value of  $K_2$ . Since Van Vleck's derivation assumes that there are no strong resonances having energy changes of the order of the thermal energy  $K_B T$  and since we have seen in the introduction that the water molecule violates this assumption, it follows that Van Vleck's value for  $K_4$  should not be applied to water vapor and the discrepancy noted by *Birnbaum and Chatterjee* [1952] is removed.

Summing the refraction by absorption resonances can shed light on the radio refraction of dry air as well as water vapor. *Liebe* [1981] calculates refraction by oxygen resonances having resonance frequency less than 1000 GHz. These magnetic dipole transitions of molecular oxygen are expected to be the main contributors to the magnetic susceptibility of air at radio frequencies. *Liebe's* calculated refraction caused by these oxygen resonances accounts for three fourths of the observed magnetic susceptibility of air; reasons for the remaining difference in calculated versus observed susceptibility are unknown.

#### APPENDIX

*Hasegawa and Stokesberry* [1975] obtained values of  $K_2$  and  $K_3$  that are significantly different from those of *Boudouris* [1963] and *Birnbaum and Chatterjee* [1952]. *Hasegawa and Stokesberry* [1975] used the *Birnbaum-Chatterjee* method of averaging  $K_2$  and  $K_3$  from several different experiments. Unlike *Birnbaum and Chatterjee*, *Hasegawa and Stokesberry* included experiments that covered only very limited ranges in temperature, namely the two experiments by *Essen and Froome* [1951] and *Essen* [1953]. Because of their limited temperature range, *Essen and Froome* [1951] assumed  $K_2$  equal to its value at optical frequencies (an inaccurate assumption) and fitted only  $K_3$  to their data. Because of their small probable error, these two experiments

overwhelmingly dominated the average  $K_2$  and  $K_3$  determined by *Hasegawa and Stokesberry* [1975]. Because of the very limited temperature range of these two experiments and the inappropriate assumption regarding  $K_2$ , we feel that the average values of  $K_2$  and  $K_3$  of *Hasegawa and Stokesberry* are not accurate. It seems preferable, but perhaps impossible, to fit (1) to a compilation of available experimental values of refractivity, rather than to average the coefficients of fits made to each individual data set.

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