LABORATORY MEASUREMENTS AND MODELING OF MICROWAVE ABSORPTION BY AMMONIA IN GAS MIXTURES APPLICABLE TO GIANT PLANET ATMOSPHERES

T.R. SPILKER
Stanford Center for Radar Astronomy, SEL Durand Bldg., Stanford, CA 94305-4055

Accurate knowledge of the microwave absorption behavior of ammonia is critical to the correct interpretation of radio astronomical and radio occultation data from the giant planets. Despite over 50 years of study, however, the microwave spectrum of ammonia has been a problem child in microwave spectroscopy, defying accurate characterization by a single general theory. Van Vleck-Weisskopf (VVW) theory[1] does well at pressures below about half a bar in a Jovian mixture but errs by as much as a factor of two at higher pressures[2]. A quantum mechanical treatment of the problem by Ben-Reuven[3] produced a formalism that worked well for pure gaseous ammonia but fared less well in mixtures[4,5]. Empirical modifications to the original Ben-Reuven formalism by Wrixon *et al.*[2] and Berge and Gulkis[6] improved its performance for mixtures resembling the atmospheres of giant planets, but newer data point to errors in their predictions that are considerably larger than the errors in radio occultation data.

New cavity resonator techniques developed at the Stanford Center for Radar Astronomy have allowed accurate laboratory measurements of the microwave absorptivity and refractivity spectra of gas mixtures containing trace amounts of ammonia in foreign gases, including hydrogen, helium, and a Jovian mixture of hydrogen and helium, over the entire range of temperatures, pressures, and frequencies currently available to our resonator-based spectrometer: 210 to 320 K, 1 to 8 atmospheres total pressure, and 9 to 18 GHz. The data point out sizable ranges of conditions where neither VVW nor modified Ben-Reuven formalisms yield accurate predictions, and strongly suggest that temperature dependences expressed in those formalisms are incorrect. They also indicate that the pressure range near one atmosphere (total pressure) involves fundamental change in the microwave absorption behavior of gaseous ammonia.

A parameterized version of the modified Ben-Reuven formalism of Berge and Gulkis[6] was optimized to fit the new data and that of other researchers[7,8]. Like other ammonia absorptivity prediction schemes this formalism is a summation of absorptivity contributions from individual inversion lines:

$$\alpha(f_0) = C \sum_J \sum_K A(J, K, \mathbf{m})\, F(J, K, \mathbf{m}, f_0)\ , \tag{1}$$

where $\alpha(f_0)$ is the absorption coefficient at frequency f_0, J and K are the rotational quantum numbers specifying individual absorption lines, $A(J, K, \mathbf{m})$ and $F(J, K, \mathbf{m}, f_0)$ are the line intensity and shape factors, respectively, and C is an empirical correction factor used by Berge and Gulkis to force a fit to the high pressure laboratory data of Morris and Parsons[7]. The vector $\mathbf{m}$ is a vector of the macroscopic conditions (*i.e.* temperature and the partial pressures of ammonia and all pertinent foreign gases in the mixture). In the Ben-Reuven line shape factor of Equation 1 these conditions are manifested in three parameters internal to F: γ, ζ, and δ. In the context of a Jovian mixture at moderate pressures the line shift parameter δ is insignificant[2] and is not treated in this analysis. The other parameters are the line broadening parameter γ and the coupling element ζ.

Using a mix of theoretical results and empirical data Berge and Gulkis give equations for γ and ζ of the forms:

$$\gamma(J,K,m) = G_{H_2}\left(\frac{300}{T}\right)^{\frac{2}{3}} P_{H_2} + G_{He}\left(\frac{300}{T}\right)^{\frac{2}{3}} P_{He} + G_{NH_3}\left(\frac{300}{T}\right)\gamma_0(J,K)\,P_{NH_3} \quad \text{GHz}, \tag{2}$$

$$\zeta(J,K,m) = Z_{H_2}\left(\frac{300}{T}\right)^{\frac{2}{3}} P_{H_2} + Z_{He}\left(\frac{300}{T}\right)^{\frac{2}{3}} P_{He} + Z_{NH_3}\left(\frac{300}{T}\right)\gamma_0(J,K)\,P_{NH_3} \quad \text{GHz}. \tag{3}$$

In these equations T is temperature in Kelvins, $\gamma_0(J, K)$ is the self-broadened line width in MHz/torr, P_i is the partial pressure of the gas species i, and G_i and Z_i are scaling coefficients for species i. In accord with the predictions of Ben-Reuven theory Berge and Gulkis used constants for the scaling coefficients: $G_{H2} = 2.318$, $G_{He} = 0.79$, $G_{NH3} = 0.75$, $Z_{H2} = 1.92$, $Z_{He} = 0.3$, $Z_{NH3} = 0.49$; these worked well with the Morris and Parsons data, taken at a single frequency and temperature. Data from this work, however, taken over a range of temperatures and at lower pressures, suggested these coefficient values may not be usable for all temperatures and pressures, an indication that the temperature and pressure dependences expressed in Equations 2 and 3 are not completely correct. The parameterized version of the formalism substituted free parameters for these coefficients and the Berge and Gulkis correction factor C, which is essentially unity for total pressures less than about 100 atmospheres. An optimization routine was implemented that would read the measured absorption spectrum of a specific gas mixture at a constant temperature and pressure, and adjust the values of the parameters to best fit those data. The design of the data set allowed separation of the seven-parameter optimization problem into three much simpler three-parameter problems.

Results of optimizations on data at varying temperatures and pressures allowed (in most cases) characterization of the variation of the parameters with temperature and pressure. Notably, as pressure decreased to one atmosphere the best-fit value of G_{H2} decreased significantly (to about a tenth the high pressure value) while the value of Z_{H2} more than doubled. As temperature decreased, the value of C also decreased, suggesting the temperature dependence of the Ben-Reuven intensity factor A (identical to the VVW intensity factor) is incorrect. Empirical expressions were derived for the variations of the parameters with macroscopic conditions. Incorporating these expressions into the formalism produced a new formalism that quite accurately fit the data.

Pure gaseous ammonia data by Bleaney and Loubser[8] yielded the values $G_{NH3} = 0.74$ and $Z_{NH3} = 0.50$, independent of pressure and in close agreement with Berge and Gulkis' values. Precise details of the pressure dependences of G_{He} and Z_{He} at the lowest pressures could not be characterized from the data of this work, but approximate temperature dependences were derived. Fortunately, like G_{NH3} and Z_{NH3}, these coefficients are relatively insignificant to the ultimate accuracy of the formalism. The critical coefficients are G_{H2} and Z_{H2}, for which more accurate characterizations could be made. An expression yielding G_{H2} directly from macroscopic conditions was derived, but finding an accurate expression for Z_{H2} was not possible with available data. However it was found that there was a close relation between G_{H2} and Z_{H2}, such that Z_{H2} could be calculated from the value of G_{H2}. The hydrogen broadening coefficient is given by:

$$G_{H_2} = 2.34\left[1 - \frac{2.157\,e^{-T/116.8}}{\left(e^{(9.022-T/20.3)} - 1 + P_{tot}\right)^{r}}\right] \quad , \quad \text{where } r = 8.79\,e^{-T/83} \ , \tag{4}$$

with P_{tot} the total pressure in atmospheres; the value of Z_{H2} is then calculated from G_{H2}:

$$Z_{H_2} = 5.7465 - 7.7644\,G_{H_2} + 9.1931\,G_{H_2}^{2} - 5.6816\,G_{H_2}^{3} + 1.2307\,G_{H_2}^{4} \ . \tag{5}$$

The expressions for the helium term coefficients are:

$$G_{He} = 0.46 + \frac{T}{3000} \quad , \quad Z_{He} = 0.28 - \frac{T}{1750} \ . \tag{6}$$

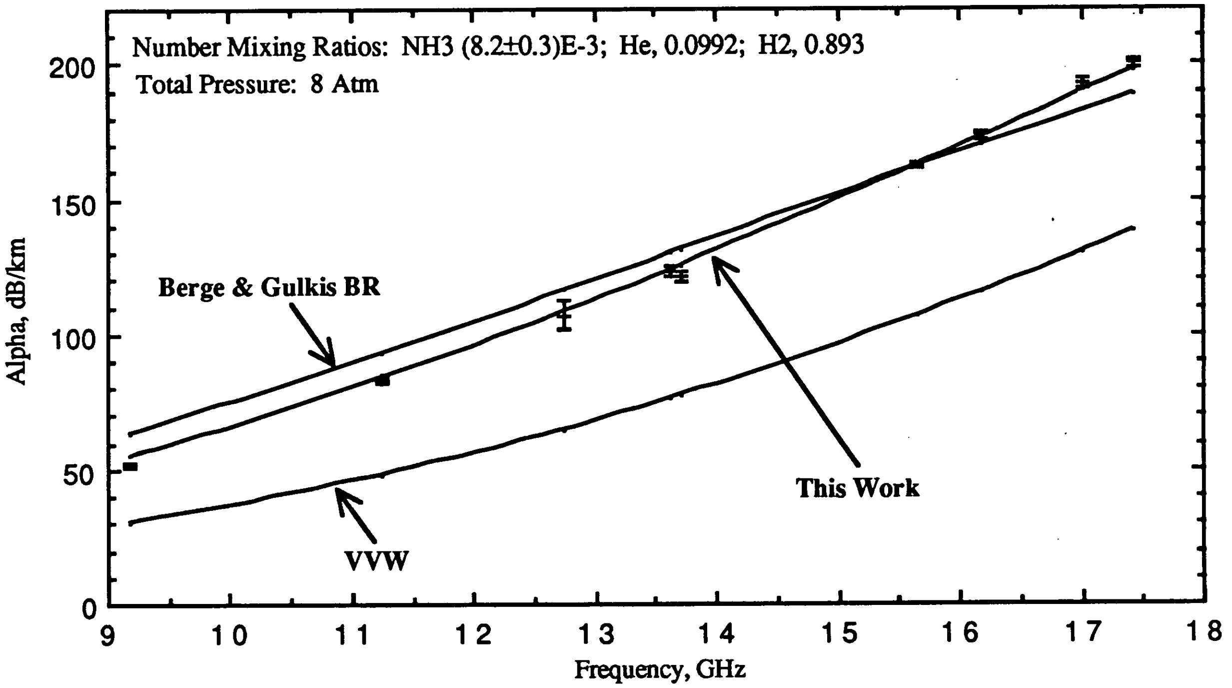
For P_{tot} less than about 10 bars, C is given by:

$$C = -0.33664 + \frac{T}{110.4} - \frac{T^2}{70{,}600} \ . \tag{7}$$

The new formalism produced by this method predicts ammonia absorptivity much more accurately than previous formalisms over a significant range of conditions. Figure 1 compares the predictions of three formalisms, Van Vleck-Weisskopf, Berge and Gulkis' Ben-Reuven, and the new formalism of this work, to laboratory data not used in generating the new formalism. Other laboratory data by Joiner *et al.*[9], and Steffes and Jenkins[10], indicate that it is accurate over a frequency range of at least 2 GHz (and possibly much lower) to 40 GHz. Figure 2 is a temperature-pressure diagram showing the relationship of the conditions represented in the data to the conditions observed in the atmospheres of the giant planets by Voyager spacecraft radio occultation experiments. The data are directly applicable to Jupiter at pressures greater than two bars, and to Saturn at pressures greater than about five bars. The Uranian and Neptunian atmospheres require extrapolation at all levels.

Due to the behavior of the expressions for G_{H2} and Z_{H2}, extrapolating this formalism to total pressures less than one bar is not possible. As has been done previously[2] a VVW formalism may be used for the lower pressures, although this will produce a discontinuity at one bar. One matching technique which would eliminate the discontinuity would involve using VVW below half a bar, where it is most accurate; linear interpolation (or a higher-order interpolation scheme) would be used between the VVW value at half a bar and the new formalism's value at one bar. Extrapolation in temperature more than 30 to 40 K beyond the data is considered risky, especially given

Absorptivity; (H2 + He) + NH3, 273 K



Absorptivity; (H2 + He) + NH3, 203 K

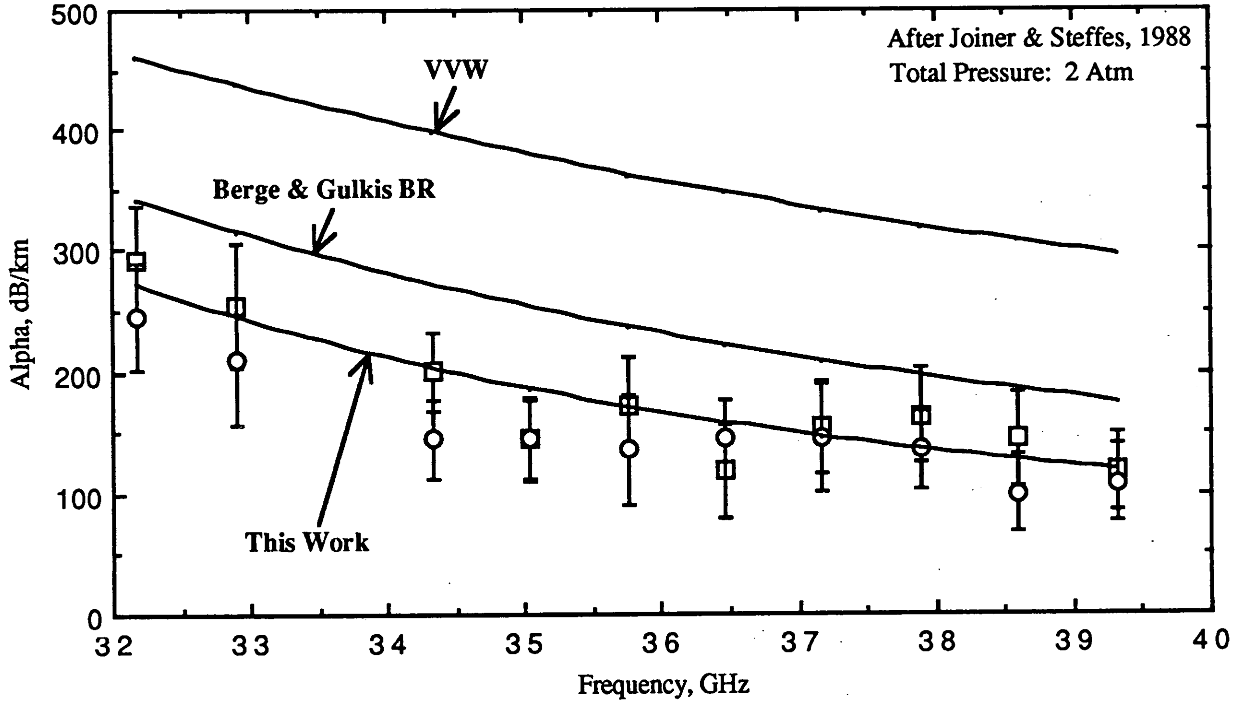


Figure 1: Predictions of the new formalism compared with laboratory data. Data in the upper graph were taken as part of this work but were not used in generating the formalism. Although the Berge and Gulkis formalism is reasonably accurate at this temperature its predicted frequency dependence is incorrect. Data in the lower graph are from Joiner *et al.*[9], and cover a frequency range considerably different from the data used in this work. These and other data indicate the new formalism is accurate over a frequency range of at least 2 to 40 GHz.

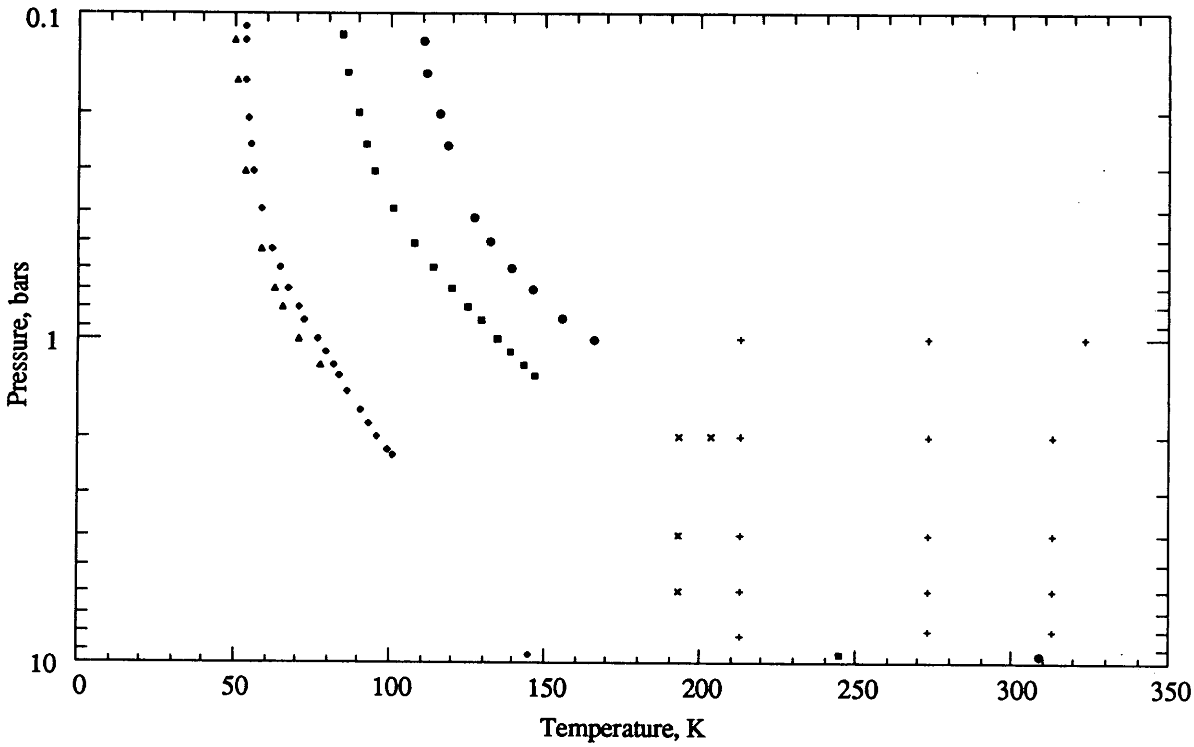


Figure 2: A comparison of the temperature and pressure ranges of laboratory data on microwave absorption by gas mixtures applicable to the atmospheres of giant planets, and conditions measured by the Voyager radio occultation experiments at Jupiter (circles), Saturn (squares), Uranus (diamonds), and Neptune (triangles). Values for Jupiter, Saturn, and Uranus at the bottom of the graph are extrapolations based on work by Lewis and Prinn[11]. The crosses represent data from this work; data from Joiner *et al.*[9], and Steffes and Jenkins[10] are marked with an "x."

the polynomial character of the expression for C, Equation 7. The data do indicate that the temperature dependence of the intensity factor is incorrect, such that absorptivities predicted by previous formalisms will be too high at low temperatures. Since this intensity factor is also used in VVW theory it may be necessary to use a modified VVW formalism in the matching scheme previously suggested.

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