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A new model of the hydrogen and helium-broadened microwave opacity of ammonia based on extensive laboratory measurements

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ABSTRACT

Close to 2000 laboratory measurements of the microwave opacity and refractivity of gaseous NH_3 in an H_2/He atmosphere have been conducted in the 1.1–20 cm wavelength range (1.5–27 GHz) at pressures from 30 mbar to 12 bar and at temperatures from 184 to 450 K. The mole fraction of NH_3 ranged from 0.06 to 6% with some additional measurements of pure NH_3. The high accuracy of these results have enabled development of a new model for the opacity of NH_3 in a H_2/He atmosphere under jovian conditions. The model employs the Ben-Reuven lineshape applied to the published inversion line center frequencies and intensities of NH_3 (JPL Catalog—[Pickett, H.M., Poynter, R.L., Cohen, E.A., Delitsky, M.L., Pearson, J.C., Müller, H.S.P., 1998. J. Quant. Spectrosc. Radiat. Trans. 60, 883–890]) with empirically-fitted line parameters for H_2 and He broadening, and for the self-broadening of some previously unmeasured ammonia inversion lines. The new model for ammonia opacity will provide reliable results for temperatures from 150 to 500 K, at pressures up to 50 bar and at frequencies up to 40 GHz. These results directly impact the retrieval of jovian atmospheric constituent abundances from the Galileo Probe radio signal absorption measurements, from microwave emission measurements conducted with Earth-based radio telescopes and with the future NASA Juno mission, and studies of Saturn's atmosphere conducted with the Cassini Radio Science Experiment and the Cassini RADAR 2.1 cm passive radiometer.

1. Introduction

Understanding the microwave properties of ammonia (NH_3) has been of great interest both for application to microwave remote sensing techniques and for providing spectroscopic insight into the molecular structure of ammonia. The ammonia molecule is one of the strongest absorbers of microwave energy, primarily due to its inversion spectrum. Its large opacity has direct effect on the transmission of microwave radiation through outer planetary atmospheres, and its known precision has direct implications for the accuracy of various planetary microwave remote sensing measurements. The strong microwave absorption spectrum of ammonia has led to many laboratory measurements and models in the past seventy years. Unfortunately for spectroscopists, the polarity and symmetry of ammonia molecules gives them a strong tendency to adsorb or stick to various surfaces. This makes accurate knowledge of the mixing ratio of NH_3 in many experiments cumbersome and prone to added uncertainty, which has plagued many previous measurements and models. A new laboratory configuration and measurement procedure to account for molecular adsorption, described in Hanley and Steffes (2007), has been developed to allow the high-accuracy measurements and model described herein.

The microwave properties of gaseous ammonia were first measured in the laboratory by Cleeton and Williams (1934) from 7.5–30 GHz. They measured pure ammonia at a pressure near 1 bar, whereupon they detected a broad single line feature, due to pressure broadening and did not detect any individual NH_3 lines. Subsequent work was performed by Bleaney and Penrose (1946) who were able to resolve 18 lines between 20 and 26 GHz by measuring pressures of ammonia as low as 0.27 mbar and devised a formula for calculating NH_3 line frequencies based on quantum numbers. They concluded that NH_3, due to the strength of its dipole, exerts pressure broadening even at distances that do not correspond to direct collisions. By 1949 pure ammonia had been measured from 3.7 to 37 GHz and up to 6 atm of pressure (Bleaney and Loubser, 1950). One atmosphere of pure NH_3 was even measured up to 260 GHz by Nethercot et al. (1952). Many more measurements of pure ammonia were performed throughout the following decades by various researchers, culminating in the most extensive measurement to date of ammonia's inversion lines by Poynter and Kakar (1975). They measured the center frequencies of 119 lines up to $J = K = 16$ near 40 GHz for ammonia pressures of a few millibars and devised a 15-term exponential polynomial for calculating the center frequencies of other lines. These measurements along with

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many others have been incorporated into the largest and most current collection of NH_3 microwave transitions, the JPL line catalog by Pickett et al. (1998) and more recently Chen et al. (2006).

It was not long before experimenters began to measure the broadening effects of various foreign gases on the microwave lines of ammonia. Bleaney and Penrose (1948) measured the broadening effects of six gases, including H_2 and He by measuring the broadening of a single line ($J = 3$, $K = 3$), but did not make any acknowledgment of the adsorptive tendency of ammonia, making it possible that they were either not aware of it, or did not properly account for it in their measurements. Smith and Howard (1950) measured 15 different broadening gases and described how strongly ammonia adsorbed in their system. Unfortunately, they do not mention the corresponding desorption process of ammonia and how that could have affected their measurements. Potter et al. (1951) obtained results that differed significantly with those of Smith and Howard and the theory proposed by Anderson (1949), but did not present any hypothesis as to the discrepancy. Legan et al. (1965) performed a more thorough examination of both ammonia self-broadening and foreign gas broadening on 25 NH_3 resonant lines. The aforementioned measurements of the various broadening parameters fall over a fairly wide range and are well outside their respective stated uncertainties, hinting at the difficulty in accurately measuring them. Most of the early ammonia pressure-broadening experiments were limited to the pressures that could be produced in the laboratory, usually on the order of a few bars. Morris and Parsons (1970), however, were able to measure the broadening effects of H_2, He, N_2, and Ar on NH_3 up to pressures of nearly 700 bars by using a high-pressure vessel and gas compressor. Their measurements were only performed at room temperature and at one frequency (9.58 GHz) in a tunable resonant cavity. To date, the pressures at which these measurements of NH_3 were performed exceed those measured by other experimenters by nearly two orders of magnitude. Other measurements up to 6 bars by Steffes and Jenkins (1987) and an extensive set by Spilker (1990) up to 8 bars all suffer from improper characterization of the adsorption of ammonia in the test chambers. Adsorption, however, had no effect on the measurements of pure ammonia by Spilker (1993). Measurements of the hydrogen and helium broadening of the K_a-band (32–40 GHz) and W-band (94 GHz) opacities of ammonia have been made up to 2 bars of pressure and temperatures from 188 to 300 K (Joiner, 1991; Mohammed, 2005), but those too have large uncertainties due to adsorption. Recently, more accurate measurements of the full W-band (75–110 GHz) opacity of H_2/He-broadened NH_3 have been performed (Devaraj and Steffes, 2007).

The predominant lineshape used to describe early experimental results for the ammonia spectrum was that of Van Vleck and Weisskopf (1945). The Van Vleck–Weisskopf lineshape was shown to fit the ammonia spectrum well at low pressures where the individual lines had little overlap. Although the accuracy of the Van Vleck–Weisskopf lineshape had been questioned in the lower frequency tail of the spectrum, it was not until 1953 that it was measured and found to be too low by 40% at 2.8 GHz in 133 mbar of pure NH_3 (Birnbaum and Maryott, 1953). This led to the creation of new lineshapes (Anderson, 1949; Gross, 1955) with various modifications of the Van Vleck–Weisskopf theory. However, one that included the effects of increasing pressure on the molecular forces and resonant lineshapes of ammonia was not developed for over a decade (Ben-Reuven, 1966). Despite the work of Ben-Reuven, Goodman (1969) devised the first model for calculating NH_3 opacity in a H_2/He atmosphere using the Van Vleck–Weisskopf lineshape. Berge and Gulkis (1976) used the Ben-Reuven lineshape to fit the measurements of Morris and Parsons (1970) to a model for NH_3 opacity in a H_2/He atmosphere using an empirical correction factor and only the NH_3 inversion lines from Poynter and Kakar (1975). The Berge and Gulkis model became the predominant method for calculating opacity from ammonia throughout the microwave regime until the models of Spilker (1990) and Joiner (1991). De Pater and Massie (1985) recognized that the Berge and Gulkis model was inaccurate for millimeter waves due to the broadening effect of the rotational lines, namely those at 572, 1168, and 1215 GHz. There was also concern regarding the temperature dependence since that used in the Berge and Gulkis model was based on a single measurement. The Berge and Gulkis model was, however, shown to be accurate for pure ammonia at room temperature (Spilker, 1993). In 2005, de Pater et al. showed that a better understanding of the microwave opacities of NH_3 and water vapor (H_2O) would be necessary to achieve the results of remotely sensing H_2O concentrations in the deep jovian atmosphere as detailed in Janssen et al. (2005), thereby providing a strong impetus for this work.

In this paper we describe a new model for opacity of ammonia based on nearly 2000 laboratory measurements of the microwave opacity of NH_3 in an H_2/He atmosphere which have been conducted in the 1.1–20 cm wavelength range (1.5–27 GHz) across a wide range of temperatures and pressures, characteristic of those found in the atmospheres of Jupiter and Saturn. The new model for ammonia opacity derived from these measurements will provide reliable results for temperatures from 150 to 500 K, at pressures up to 50 Bars and at frequencies up to 40 GHz. These results directly impact the retrieval of jovian atmospheric constituent abundances from the Galileo Probe radio signal absorption measurements, from microwave emission measurements conducted with Earth-based radio telescopes and with the future NASA Juno mission, and studies of Saturn's atmosphere conducted with the Cassini Radio Science Experiment and the Cassini RADAR 2.1 cm passive radiometer.

2. Measurement theory

The method used to measure the microwave absorptivity of a gas is based on the lessening in the quality factor (Q) of a resonant mode of a cylindrical cavity in the presence of a lossy gas. This technique involves monitoring the changes in Q of different resonances of a cavity resonator in order to determine the refractive index and the absorption coefficient of an introduced gas or gas mixture (at those resonant frequencies). Described at length by Hanley and Steffes (2007), it has been successfully utilized for over one half of a century. The cavity resonator technique for measuring refractivity based on frequency shifts has had similar effectiveness, and is also described by Hanley and Steffes (2007). The cylindrical cavity resonators used in these experiments each consist of a section of cylindrical waveguide capped at both ends with resonant modes resulting from various standing-wave patterns. The Q of a resonance is a unitless quantity defined as

$$Q = \frac{2\pi f_0 \times \text{energy stored}}{\text{average power loss}} \tag{1}$$

(Matthaei et al., 1980), where f_0 is the frequency of the resonance and can be measured directly as the frequency divided by its half-power bandwidth or full width at half maximum (*FWHM*)

$$Q = \frac{f_0}{BW}. \tag{2}$$

The quality factor of a resonator loaded or filled with a test gas can be represented by

$$\frac{1}{Q^m_{\text{loaded}}} = \frac{1}{Q_{\text{gas}}} + \frac{1}{Q_{\text{vac}}} + \frac{1}{Q_{\text{ext1}}} + \frac{1}{Q_{\text{ext2}}} \tag{3}$$

(Matthaei et al., 1980), where Q^m_{loaded} is the measured quality factor of the gas filled resonator, Q_{gas} is the quality factor of the gas itself, Q_{vac} is the quality factor of the evacuated cavity resonator,