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Research Article

Detection of Ammonia in Liquids Using Millimeter Wave Spectroscopy

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Detection of ammonia plays a vital role for counter-bioterrorism applications. Using millimeter wave absorption measurements, ammonia dissolved in water solution is analyzed and compared to water-only solution. The inversion of ammonia molecule results in split rotational spectral lines and transitions of these lines can be detected. Two-port measurements were carried out with vector network analyzer and measurements revealed that ammonia presence can be identified, especially between 30–35 GHz.

1. Introduction

Millimeter and submillimeter range of electromagnetic spectrum offer many possibilities for detection and identification of chemical structures. In this range many atoms, molecules and crystals have sharp, strong spectral lines that are very helpful in identifying materials [1]. The principal class of spectra analyzed is the one that arises from the rotation spectra of gaseous molecules. Vibrational spectroscopy of solids and electronic resonances such as plasma oscillations, cyclotron resonance, and paramagnetic resonance can also be observed using this part of the electromagnetic spectrum [2].

Chemical structures exhibit unique absorption and emission spectra at millimeter waves. Emission and absorption lines that arise from particular arrangement of the molecule are mostly attributed to electric dipole moment arrangement of the molecule [3–5]. Especially, spectra of gaseous molecules present fundamental rotational frequencies. On the other hand, transitions between the vibrational states of the molecule are more radiative and these can be observed in the infrared and near infrared of visible region of the spectrum. Lower energy rotational states give rise to emissions at mm-wave region, but are mostly masked by emissions due to molecular interactions. In addition, at atmospheric pressures the mm-wave spectral lines are broadened making them difficult in identification of gaseous molecules.

Ammonia, NH_3, is an extremely important bulk chemical widely used in fertilizers, plastics, and explosives. Its detection plays a vital role for counter-terrorism measures. Gaseous detection of ammonia using pressurized waveguide section at Ka band was demonstrated in [6]. However, suggested measurement method is somewhat impractical, and the results showed only 0.5 dB attenuation compared to air only mixture. Infrared and Raman spectroscopy of ammonia in liquid [7–14] and detection of ammonia at interstellar space [15] have been analyzed extensively. Our goal in this study is to detect ammonia mixed in water utilizing mm-wave spectroscopy. Instead of passive, active detection method is used and promising results are obtained.

2. Material and Methods

Ammonia mixed in water with 25% concentration, reagent grade, was used as received. The measurement setup is shown in Figure 1. Agilent PNA-X type Network Analyzer was calibrated from 20 to 40 GHz with intermediate frequency at 1 kHz, number of calibration points set to 10,000, and power level to +5 dBm. Network Analyzer as a two-port device can simultaneously measure input reflection and transmission to the other port in terms of Scattering (S) parameters. In this configuration S_{21} represents signal received at port 2 when input signal is applied to port 1, with 50 Ohm port impedance. S_{21} is used as the main data for comparison

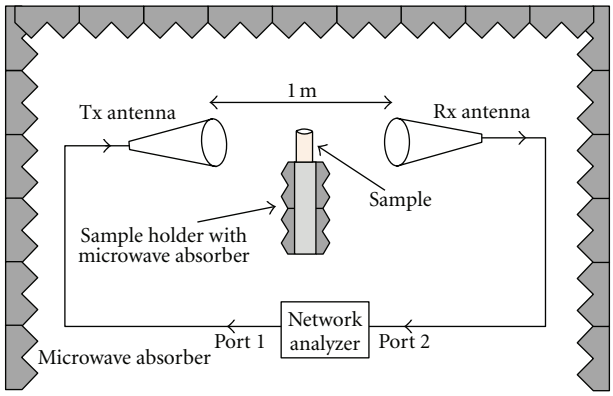

Figure 1: Measurement setup for samples.

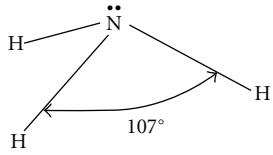

Figure 2: Ammonia molecule.

of detection. Wideband conical antennas were used for transmission and reception. Although the antennas were rated from 26.5 to 40 GHz, their port match and gain were found satisfactory starting from 23 GHz. Nevertheless, measurements were carried out relative to water-only sample, and basis of comparison were made with reference to that sample. Measurements were repeated several times to ensure that observed data was stable and not changing with time.

3. Results and Discussion

Ammonia molecule can be described as a near prolate top molecule. NH_3 molecule has a large dipole moment, and its geometry resembles a triangular pyramid as shown in Figure 2.

The electronic arrangement in nitrogen follows the octet rule and the four pairs of electrons (three bonding pairs and one non-bonding pair) repel each other, leading to the molecule's nonplanar geometry. The H–N–H bond angle of 107° is fairly close to the tetrahedral angle of 109.5°. The polarity of NH_3 molecules and their ability to form hydrogen bonds are the main reasons for high solubility of ammonia in water.

The molecular rotation energy of rigid symmetric is given as

$$E = \frac{L_x^2 + L_y^2}{2I_\perp} + \frac{L_z^2}{2I_\parallel}, \tag{1}$$

where angular momentums in respective coordinates are represented as L_x, L_y, and L_z, and the moment of inertia parallel to and perpendicular to z-axis are $I_\parallel$ and $I_\perp$,

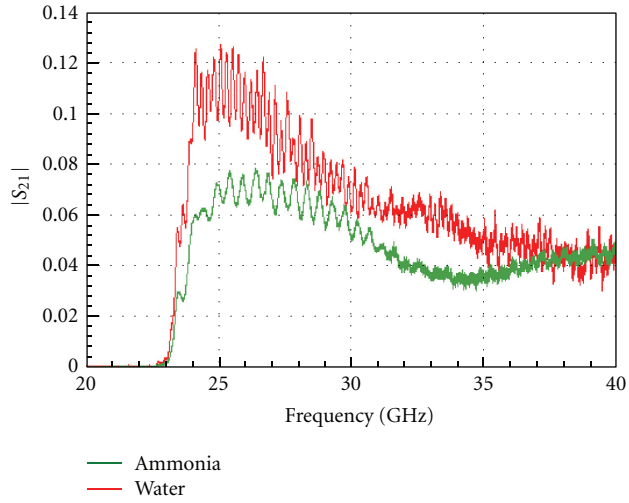

Figure 3: Transmission measurements of water-only and water-ammonia liquid solutions.

respectively. This can also be expressed in terms of total angular momentum L, where $L^2 = L_x^2 + L_y^2 + L_z^2$, as follows:

$$E = \frac{L^2}{2I_\perp} + \frac{L_z^2}{2I_\parallel}\left(\frac{1}{I_\parallel} - \frac{1}{I_\perp}\right). \tag{2}$$

The quantum mechanical expression for the energy is obtained by $L^2 = J(J+1)\hbar^2$ and $L_z^2 = K^2\hbar^2$, where $K = 0, \pm 1, \pm 2, \ldots, \pm J$ and $J = 0, 1, 2, \ldots$. Thus, allowed energy levels can be expressed as

$$\varepsilon_{J,K} = \frac{E_{J,K}}{hc} = \widetilde{B}J(J+1) + \left(\widetilde{A} - \widetilde{B}\right)K^2, \tag{3}$$

where

$$\widetilde{A} = \frac{\hbar}{4\pi c I_\parallel}, \qquad \widetilde{B} = \frac{\hbar}{4\pi c I_\perp}. \tag{4}$$

The selection rules for rotational spectra of symmetric top molecules are $\Delta J = \pm 1$ and $\Delta K = 0$, that is, the dipole moment of the molecule is oriented along the principal axis and an electromagnetic radiation can not affect the rotation of the molecule about its principal axis. Hence, the rotation is independent of K, and rotational changes about the symmetry axis do not produce rotational spectrum. The inversion of ammonia molecule causes the rotational line to break up and transitions occur between the split levels. The transitionally split energy levels can be approximated by [6]:

$$\varepsilon = \varepsilon_o + aJ(J+1) + (a-b)K^2, \tag{5}$$

where $\varepsilon_o = 23.787$, $a = -0.151$, and $(a - b) = 0.211$ GHz. Although approximate, the above equation is used to determine the J-K transition frequencies. Transition frequencies up to 40 GHz are shown in Table 1.

Measurement setup is used for water-only and water-ammonia liquid mixtures. Transmission measurement of S_{21} is recorded for both sample sets. Since the samples are in

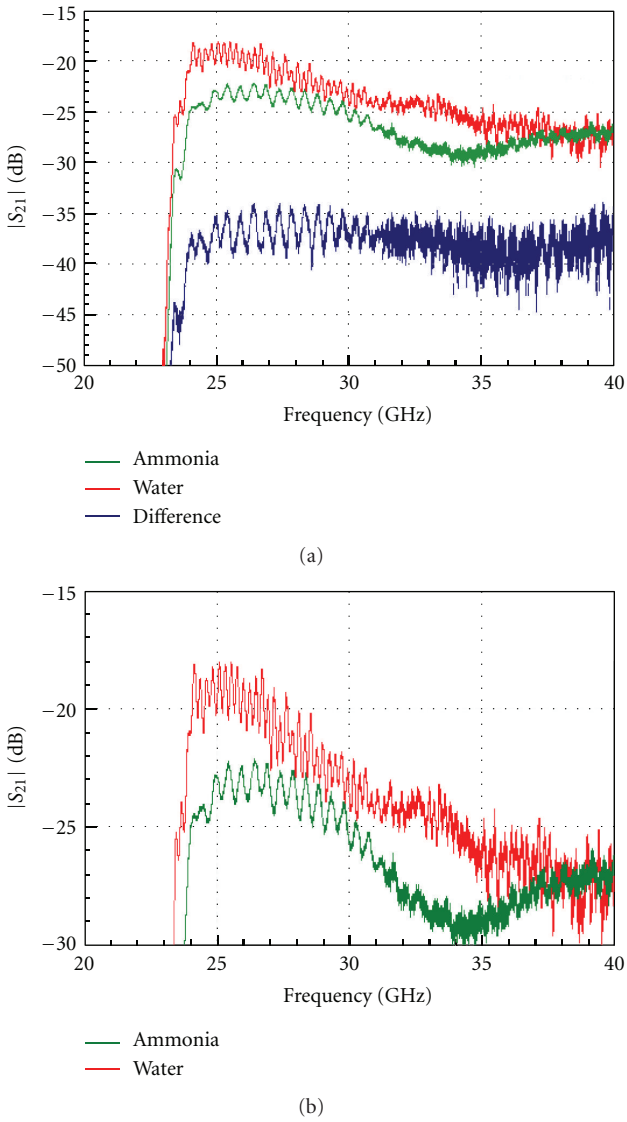

Figure 4: Logarithmic scale results of measurements: (a) larger scale with difference; (b) smaller scale for magnitude comparison.

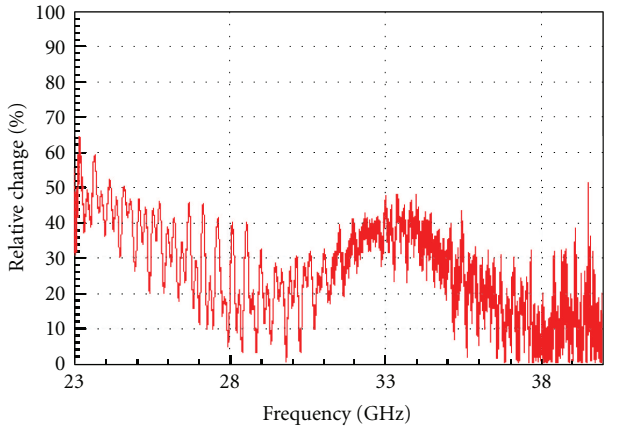

Figure 5: Relative percent change of ammonia-water sample with reference to water-only sample.

Table 1: NH_3 J-K transitions using approximate formula.

$J(K)$-$J(K)$	Freq (GHz)
2(1)-2(1)	23.092
8(7)-8(7)	23.254
1(1)-1(1)	23.696
9(8)-9(8)	23.701
3(3)-3(3)	23.874
4(4)-4(4)	24.143
10(9)-10(9)	24.268
5(5)-5(5)	24.532
11(10)-11(10)	24.955
6(6)-6(6)	25.041
7(7)-7(7)	25.67
12(11)-12(11)	25.762
8(8)-8(8)	26.419
13(12)-13(12)	26.689
9(9)-9(9)	27.288
14(13)-14(13)	27.736
10(10)-10(10)	28.277
15(14)-15(14)	28.903
11(11)-11(11)	29.386
16(15)-16(15)	30.19
12(12)-12(12)	30.615
17(16)-17(16)	31.597
13(13)-13(13)	31.964
18(17)-18(17)	33.124
14(14)-14(14)	33.433
19(18)-19(18)	34.771
15(15)-15(15)	32.022
20(19)-20(19)	36.538
16(16)-16(16)	36.731
21(20)-21(20)	38.425
17(17)-17(17)	38.56
18(18)-18(18)	40.509

the far field of receive and transmit antennas, and reflection from the samples are quite close to each other,one can infer absorption of samples directly from transmission measurements. Comparison of transmission measurements for both samples is shown in Figure 3.

It is observed that there is a considerable degradation of ammonia-water solution compared to water-only solution. The measurement result is also expressed in dB scale with $20\log(S_{21})$ conversion. The logarithmic scale results with larger and smaller scales are shown in Figure 4. The magnitude of difference between the two measurement results is also shown in Figure 4(a).

Especially between 30 and 35 GHz, the presence of ammonia can be easily distinguished, having almost 5 dB more attenuation than water-only solution. According to Table 1, J-K transitions of 18(17)-18(17), 14(14)-14(14), and 19(18)-19(18) fall into that band. We again stress the fact that an approximating function of the energy levels given in (5) was used in the calculation of these transitions in

gaseous ammonia, which would exhibit deviations in liquid ammonia. From 24 to 26.5 GHz, there is also a clear separation between the transmission measurements, however, the antennas are rated starting from 26.5 GHz, thus, we considered this band less reliable compared to 30–35 GHz band.

The relative percent change in received signal with respect to water-only sample is shown in Figure 5. This can be useful for a threshold detector in identifying ammonia presence since ammonia-water mixture has in excess of 25% relative percent change from 30 to 35 GHz.

4. Conclusion

Even though the measurements were carried out at atmospheric pressures and at room temperature, there is a clear difference between water-only and water-ammonia samples. The attenuation of water-ammonia solution is consistently higher than that of water-only solution. Therefore, it is possible to identify ammonia in water using millimeter wave measurements. When mixed with water, individual spectral lines of ammonia cannot be identified, but their effects on the millimeter wave response of the solution can be seen. These measurements reveal that ammonia in water can be distinguished without resorting to special equipment at millimeter waves. The concentration of ammonia in water was really high in our experiments. Although a small contamination of ammonia is a serious health hazard, its transportation in concentrated quantities for bioterrorism can be detected in millimeter wave range. Ammonia presence in air, of course, requires low atmospheric pressures due to broadened spectral lines. However, future research will concentrate on detection of ammonia in air.

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