

Inversion Spectrum of Ammonia

1. Background

This experiment is a beautiful realization of the quantum mechanical effects of the double well potential. The ammonia molecule is pyramidal shaped with the three hydrogen atoms forming the base and the nitrogen atom at the top as shown in Fig. 1. The nitrogen atom sees a double-well potential with one well on either side of the plane defined by the hydrogen atoms. Because the potential barrier, shown in Fig. 2, is finite, it is possible for the nitrogen atom to tunnel through the plane of the hydrogen atoms, thus “inverting” the molecule. The tunneling phenomenon results in a splitting of the ground state vibrational level of the nitrogen atom into two levels with different energies. The magnitude of this splitting depends on the rotational state of the molecule; at room temperature many different rotational states are occupied giving rise to the very rich “inversion spectrum” of the ammonia molecule. The goal in this experiment is to locate a number of lines (“line” in this situation means the frequency at which a transition from one state to another state occurs) in this spectrum, and to investigate several additional features of the transitions, namely hyperfine splitting and pressure broadening.

For the ammonia molecule there are different kinds of excitations above the ground state – rotational, vibrational, and electronic, listed in order of increasing energy. *In this experiment we are concerned with molecules in the ground vibrational and electronic states, but in various excited rotational states.* Each rotational state, specified by the rotational quantum numbers J and K , gives rise to a line in the inversion spectrum. (Lines are denoted by the values of J and K , e.g., 3, 3 for the line $J = K = 3$.) Lines in this spectrum are due to transitions between two different energy levels within the same rotational state, that is, **J and K remain unchanged in these transitions.**

Energy Levels

The values for the various parameters describing the ammonia molecule shown in Fig. 1 are: $\alpha = 67.97^\circ$, $\beta = 106.78^\circ$, $d = .1012$ nm and $z_0 = .038$ nm, where z_0 is the distance along the 3-fold axis of symmetry from the nitrogen atom to the plane defined by the hydrogen atoms. With $z_0 \approx .4d$, the molecule is considerably flatter than pictured.

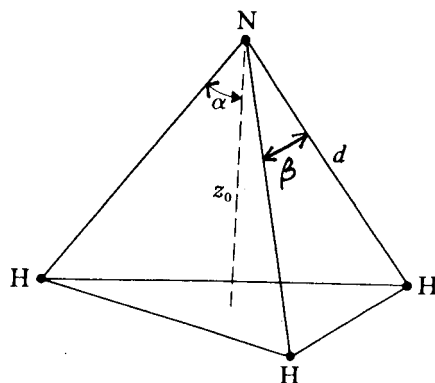


Fig. 1. Geometry of ammonia molecule.

As one might expect, the potential $V(z)$ experienced by the nitrogen atom in this double well is symmetric about the plane of the hydrogen atoms, $z = 0$, with $V(z) = V(-z)$. See Fig. 2. This potential is due to the Coulomb repulsion between the nitrogen nucleus and the three protons. Classically if the nitrogen atom is located in one of the wells and does not have sufficient energy to overcome the barrier or “hump” in the potential, it will be forever confined to that well. But quantum mechanically, after some length of time, there is a non-zero probability that the nitrogen atom will be located in the other well. This phenomenon is known as tunneling and is the result of the continuity of the wavefunction (solution to the Schrodinger equation) as it crosses the finite potential barrier. There are many manifestations of tunneling in nature, a prime example being nuclear decay.

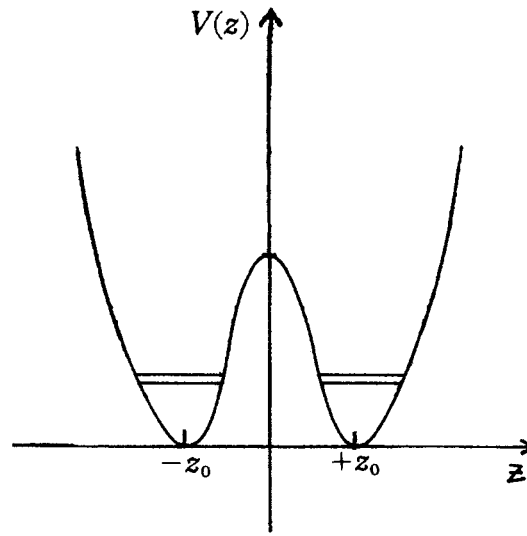


Fig. 2. Double-well potential experienced by nitrogen atom; equilibrium positions at $\pm z_0$.

For this case, we are interested in finding the energy eigenstates of the Schrodinger equation, or upon narrowing our focus, the energy eigenstates of the nitrogen atom. The energy eigenstates by definition have a well defined energy, and it is the energy difference between these eigenstates that is of interest here, as it is in many spectroscopy experiments.

First, let's consider the case if the potential barrier, located at $z = 0$, were infinite. At such a boundary the wavefunction must go to zero. The result for this case is that the wavefunction, ψ , is localized to either $z > 0$ (ψ_{up}) or $z < 0$ (ψ_{down}) and the nitrogen atom is confined to either one well or the other – the two wells are completely independent systems. Because the potential has the same form for $z > 0$ and $z < 0$, the wavefunctions for each well have identical form, as shown in Fig. 3a, and have the same characteristic energies or energy eigenvalues.

The case for a finite barrier is shown in Fig. 3b. The wavefunction in one well continues through the barrier and has non-zero amplitude in the other well. Now ψ_{up} and ψ_{down} represent wavefunctions where the nitrogen atom is predominantly localized above and below the plane $z = 0$, respectively. Such wavefunctions, predominantly localized in one well but spilling over into the other well, are solutions to the Schrodinger equation. However, they do not satisfy the requirement that energy eigenstates of this equation have definite parity when the potential V is symmetric [1]. In short, ψ_{up} and ψ_{down} do not satisfy the requirement that $\psi(z) = \pm\psi(-z)$. However, one can form linear combinations of ψ_{up} and ψ_{down} which do satisfy this requirement:

$$\Psi_{\text{odd}} = \left(\frac{1}{\sqrt{2}} \right) (\Psi_{\text{up}} - \Psi_{\text{down}}),$$

and

$$\Psi_{\text{even}} = \left(\frac{1}{\sqrt{2}} \right) (\Psi_{\text{up}} + \Psi_{\text{down}}).$$

These wavefunctions are pictured in Fig. 3c.

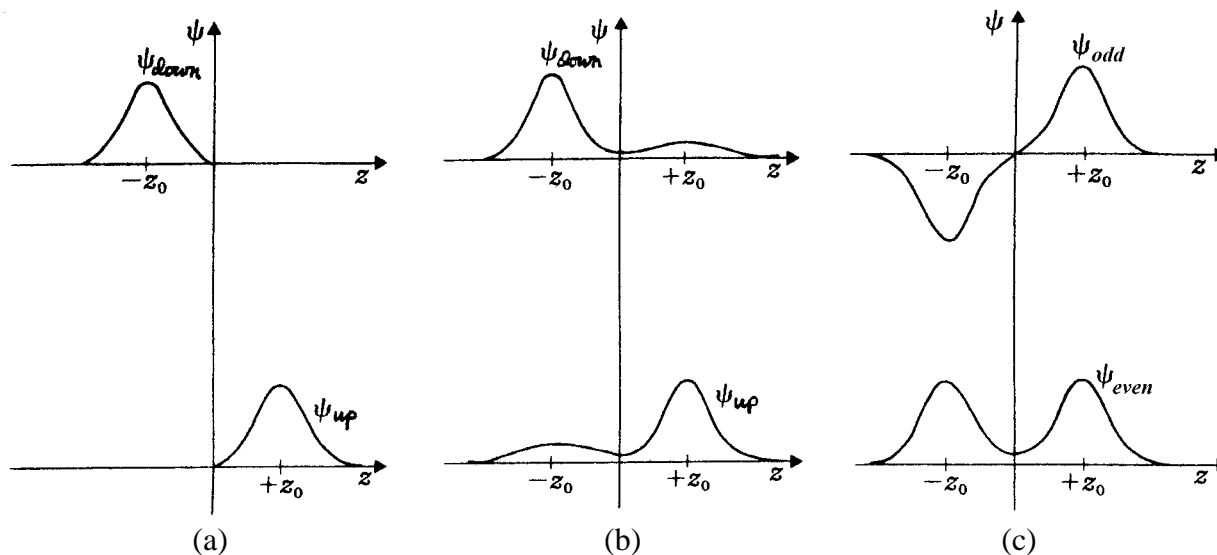


Fig. 3. Wavefunctions in a double-well potential. (a) Infinite barrier: wavefunctions are completely independent. (b) Finite barrier: wavefunctions spill over into adjacent well. (c) Correct energy eigenfunctions for the finite barrier case.

For ψ_{odd} , $\psi(z) = -\psi(-z)$ and for ψ_{even} , $\psi(z) = \psi(-z)$. ψ_{even} is said to have even symmetry and ψ_{odd} is said to have odd symmetry. ψ_{odd} and ψ_{even} are also mutually orthogonal, another requirement for energy eigenstates of the Schrodinger equation.

What about the energies associated with ψ_{odd} and ψ_{even} ? It turns out that ψ_{even} has lower energy than ψ_{odd} . Why this is the case can be inferred from considering what happens as the potential barrier is lowered from infinitely high to a finite value and finally to zero. For the infinite barrier, the wavefunctions ψ_{up} and ψ_{down} are the relevant wavefunctions and have identical energy eigenvalues, as mentioned earlier. For a finite barrier, ψ_{odd} and ψ_{even} are the relevant wavefunctions. As the potential barrier is lowered the amplitude of ψ_{even} in the barrier region becomes larger and larger. As the barrier goes to zero and the potential becomes a single well, ψ_{even} turns into a bell-shaped wavefunction representing the ground (vibrational) state of the system. Now let's consider ψ_{odd} for a finite barrier. As shown in Fig. 3c, ψ_{odd} has a node at $z = 0$. This remains true as the potential is lowered, and as the potential goes to zero, ψ_{odd} becomes the first excited (vibrational) state of the system as shown in Fig. 4. So we have gone from a situation with equal energies for an infinite potential barrier to the quite different energies associated with the ground and first excited vibrational states for no barrier. For the ammonia molecule in the ground vibrational state (and with small rotational angular momentum), the energy difference between the states ψ_{odd} and ψ_{even} is $h\nu \approx 9.8 \cdot 10^{-5}$ eV, corresponding to a frequency

of about 23.8 GHz. As we shall see later, this energy difference will vary depending on the rotational state of the molecule, making for a very rich spectrum.

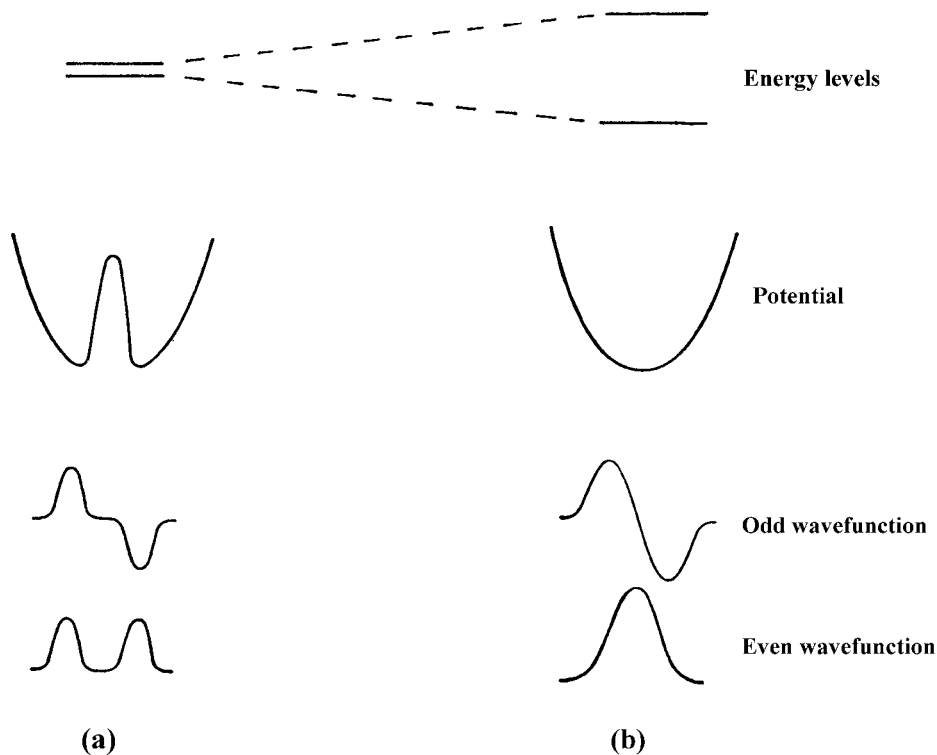


Fig. 4. Development of energy level splitting when the potential barrier is reduced. (a) With barrier present, wavefunctions have similar form and energy levels are closely spaced. (b) As barrier is reduced, wavefunctions take on distinctly different form and energy levels separate.

Where does “inversion” come from?

When a system like the NH_3 molecule is in a single state, e.g. ψ_{odd} or ψ_{even} , it is said to be in a stationary state. Such states are called stationary since any observable quantity associated with the state, energy for instance, does not vary with time. Stationary states can be expressed in the form

$$\Psi_{\text{E}}(\mathbf{r},t) = \psi(\mathbf{r})e^{-iEt/\hbar}$$

where E is the characteristic energy of the state. The complete expressions for ψ_{odd} and ψ_{even} are then

$$\Psi_{\text{odd}}(z,t) = \psi_{\text{odd}}(z)e^{-iE_1t/\hbar}$$

and

$$\Psi_{\text{even}}(z,t) = \psi_{\text{even}}(z)e^{-iE_2t/\hbar}$$

where E_1 and E_2 are the energies associated with ψ_{odd} and ψ_{even} , respectively. As stated earlier, the goal in this experiment is to measure the energy difference, $E_1 - E_2$. One can do this by shining electromagnetic radiation of frequency ν on a collection of NH_3 molecules where

$$h\nu = E_1 - E_2 = \Delta E.$$

When the NH_3 molecule is subject to such radiation, it is no longer uniquely in either the states $\Psi_{\text{odd}}(z,t)$ or $\Psi_{\text{even}}(z,t)$, but is in a state represented by a time dependent combination of Ψ_{odd} and Ψ_{even} . Application of time dependent perturbation theory yields the following expression for the wavefunction [2]:

$$\Psi(z,t) = \left(\frac{1}{\sqrt{2}} \right) [\psi_{\text{even}}(z) + \psi_{\text{odd}}(z)e^{-i2\pi\nu t}] e^{-iE_2t/\hbar}.$$

The expression has been constructed such that the nitrogen atom is most likely to be found above the plane of the hydrogen atoms ($z > 0$) at time $t = 0$. At time $t = 1/(2\nu)$ the nitrogen atom will most likely be found below the plane of the hydrogen atoms ($z < 0$), and at time $t = 1/\nu$ the nitrogen atom will again most likely be found above the plane of the hydrogen atoms. Thus ν is the frequency at which the position of the nitrogen atom inverts and then inverts again to return to its original position. Hence the name “inversion spectrum” is given to the collection of frequencies at which the inversion phenomenon occurs.

Features of the inversion spectrum

Before discussing the various features of the inversion spectrum, we will pause to describe how the experiment is performed so as to give some sense of the meaning of terms such as resonance, lines, linewidth, full width half maximum, and how these appear in terms of actual data output from the system. The output of a microwave source is connected to one end of a length of microwave waveguide with a detector located at the other end. Part of this waveguide is vacuum sealed and connected to a vacuum pump and gas handling system containing ammonia. See section II for a schematic of the system. The gas handling system and pump allow you to control the pressure of the ammonia in the system so as to be able to identify lines in the inversion spectrum (they go away when you pump the ammonia out of the system), and to observe effects like pressure broadening. The microwave source generates microwaves over a frequency span of adjustable range; typically the range is set somewhere between 10 and 50 MHz, depending on what you are trying to observe. When the output frequency sweeps through an inversion frequency (also called a resonance) for the ammonia molecule, some of the molecules absorb energy and that energy is removed from the microwaves propagating down the waveguide, thus reducing the detector output. The result of sweeping through a resonance is shown in Fig. 8 in section II. The signal would appear to be upside down since the detected power is reduced at a resonance, but it turns out that the output of the detector is of negative polarity with the result that increasing power is in the vertically downward direction. Hence a reduction in detected power results in a vertically upward deflection of the signal.

Fine structure

If the NH_3 molecule existed in only one state, the inversion spectrum would be very meager indeed, consisting of a single frequency. Fortunately, this spectrum is very rich, containing a large number of lines. Why is this so? It turns out that at room temperature (at which experiment is conducted) a large fraction of the ammonia molecules are in the ground vibrational state, but occupy many possible rotational states (which have much lower excitation energy than the vibrational states). The spacing

between the nitrogen atom and the hydrogen atoms determines the shape of the potential barrier, and this spacing depends on the rotational state of the molecule. Hence there is a different inversion energy or frequency for each rotational state of the molecule (remember, the energy difference between the two states, odd and even, depends on the shape of the potential barrier).

The total angular momentum of the molecule, P , is quantized and obeys the relation

$$P^2 = J(J + 1) \cdot \hbar^2$$

where J is zero or a positive integer and is known as the total angular momentum quantum number. The angular momentum is also quantized along the symmetry axis of the molecule, which for the NH_3 molecule is the previously denoted z axis. The component of the angular momentum along this axis is

$$P_z = K\hbar$$

where K is an integer between $-J$ and $+J$.

Let us consider qualitatively what happens to the shape of the molecule as J and K increase from zero. First consider a rotational state with $J > 0$ and $K = J$, i.e. a state where the angular momentum parallel the symmetry (z) axis is maximum. In this case the rotation tends to flatten out the pyramid and increase the distance between the hydrogen atoms. This lowers the potential barrier and thus increases the inversion frequency. (You may want to re-read the section discussing the energy difference between the two states Ψ_{odd} and Ψ_{even} as a function of barrier height.) Thus we can expect the inversion frequency to increase as $|K|$ increases, and it turns out the dependence goes as K^2 .

Now consider a rotational state with $J > 0$ and $K \ll J$. In this case there is a significant angular momentum component about an axis perpendicular to the symmetry axis. (Remember, the total amount of angular momentum is assumed constant, so if there is less along the z axis, there is more along an axis or axes perpendicular to the z axis.) The rotational motion now tends to elongate the pyramid and decrease the distance between the hydrogen atoms. The height of the potential barrier will thus increase and the inversion frequency will consequently decrease. Thus we can expect the inversion frequency to decrease as $[J(J+1) - K^2]$ as this quantity represents the square of the angular momentum perpendicular to the symmetry axis.

Combining these two effects we have

$$\nu_{\text{inversion}} = \nu_0 - c_1[J(J + 1) - K^2] + c_2K^2$$

where ν_0 , c_1 and c_2 are constants with c_1 and c_2 both positive.

While it is tempting to think of ν_0 as the inversion frequency of the ground state, $J = 0$, $K = 0$, the splitting of this state which would result in an inversion line is not permitted. The splitting is ruled out for all rotational states with $K = 0$ due to symmetry considerations related to the fact that the H nuclei (protons) are fermions, and as such the total wavefunction describing the molecule must change sign when two H nuclei are interchanged [3]. This requirement is verified experimentally since no inversion line for any state with $K = 0$ has been observed [4].

The above formula is a starting point for fitting the various lines in the NH_3 inversion spectrum as a function of J and K , and as such does not provide a good fit for the large number of lines in the this

spectrum. Empirical formulas using higher powers of $J(J + 1)$ and K^2 have been developed to better fit the spectrum and one such formula is [5]:

$$\nu_{\text{inversion}} \text{ (MHz)} = 23,787 - 151.3J(J + 1) + 211.0K^2 + .5503[J(J + 1)]^2 - 1.531J(J + 1)K^2 + 1.055K^4$$

This formula provides a good fit for smaller values of J and K (values $< \sim 6$), and you can use this for comparison purposes with the frequencies you measure in the laboratory. These lines, resulting from the various values of J and K , are called the “fine structure” of the inversion spectrum.

Hyperfine splitting

Are there lines in the inversion spectrum other than the fine structure lines? The answer is yes. Many of the lines have smaller satellite lines that are due to an interaction known as nuclear quadrupole splitting. The ^{14}N nucleus has a quadrupole moment resulting from a non-spherical charge density distribution within the nucleus. The quadrupole moment interacts with the second derivative of the electrostatic potential due to all the other charges in the molecule to produce an energy shift [6]:

$$\Delta E_{\text{quadrupole}} \sim eQ \frac{\partial^2 V}{\partial z^2}$$

where e is the magnitude of the electron charge, Q is the quadrupole moment of the nitrogen nucleus, V is the electrostatic potential at the site of the nucleus, and z is along the symmetry axis of the molecule. As it involves nuclear properties, transition lines arising from this interaction are part of the “hyperfine structure” of the inversion spectrum.

Just as the electrostatic potential creating the barrier between the two wells depends on the rotational state of the molecule, so does the second derivative of the potential at the site of the nitrogen nucleus. Lacking spherical symmetry, the orientation of the nucleus is also a factor in determining the quadrupole splitting. Combining these factors, the resulting expression for the splitting is [7]:

$$\Delta E_{\text{hyperfine}} = \Delta E_{\text{quadrupole}} = eQ \frac{\partial^2 V}{\partial z^2} \left[\frac{3K^2}{J(J + 1)} - 1 \right] \times \left[\frac{(3/4)C(C + 1) - I(I + 1)J(J + 1)}{2(2J + 3)(2J - 1)I(2I - 1)} \right]$$

where $C = F(F + 1) - I(I + 1) - J(J + 1)$. The quantity I is the nuclear spin, and for ^{14}N , $I = 1$. The quantity F is the total angular momentum, $\mathbf{F} = \mathbf{I} + \mathbf{J}$, with allowed values of F in this case being $F = J + 1, J, J - 1$. As previously mentioned, J and K remain unchanged for transitions in the inversion spectrum, but F can change and obeys the usual selection rules for electric dipole radiation, $\Delta F = 0, \pm 1$ [8]. How many transitions are possible? Consider a state like $J = K = 3$ where F can take on the values 4, 3, and 2. If $\Delta F = 0$, $\Delta E_{\text{hyperfine}} = 0$ and the transition line remains unshifted. For $\Delta F = +1$, the possible transitions are $F = 2 \rightarrow F = 3$, and $F = 3 \rightarrow F = 4$. For $\Delta F = -1$, the possible transitions are $F = 3 \rightarrow F = 2$, and $F = 4 \rightarrow F = 3$, making for a total of 5 transitions. The transitions where $\Delta F = \pm 1$ are the hyperfine lines and appear as pairs of satellite lines at frequencies above and below the main transition, $\Delta F = 0$.

The factor $eQ \frac{\partial^2 V}{\partial z^2}$ is called the quadrupole coupling constant. The units of Q are m^2 , so this factor clearly has units of energy. It is not possible to evaluate the factors Q and $\frac{\partial^2 V}{\partial z^2}$ separately in this experiment, and it is common practice to state the value of the product $eQ \frac{\partial^2 V}{\partial z^2}$, usually in terms of frequency. For the ammonia molecule the published value of $eQ \frac{\partial^2 V}{\partial z^2}$ is 4.08 MHz [9].

To calculate the hyperfine energy shift in terms of the quadrupole coupling constant, one needs to evaluate the above expression for the initial state and the final state and take the difference. Since I , J and K do not change, this calculation is easier than it appears as C is the only factor that changes.

Before leaving the topic of hyperfine structure, it should be mentioned that there are other hyperfine interactions besides quadrupole splitting. Both the nitrogen and hydrogen nuclei have magnetic moments, and these magnetic moments interact with each other and with the magnetic field arising from the rotation of the molecule [10]. These interactions result in energy shifts much smaller than the quadrupole splitting, and are manifested as very finely spaced lines within the main line and quadrupole satellites. Our apparatus is not capable of observing these finely spaced lines.

Linewidth

The lines you will observe in this experiment have a linewidth (frequency spread) that depends on a number of factors:

1. natural linewidth due to finite lifetime of the excited state;
2. Doppler broadening;
3. pressure broadening due to collisions between molecules;
4. saturation broadening;
5. broadening due to collisions with confining walls.

The natural linewidth for transitions in the 10 GHz frequency range is $\sim 10^{-5}$ Hz, which is negligible compared to other factors [11].

Doppler broadening results from a frequency shift in the radiation emitted by a source as the source moves toward or away from the detector (think train whistle). For Doppler broadening, $\Delta\nu = \nu_0(v/c)$ where ν_0 is the unshifted frequency of the transition, v is the velocity due to thermal motion and c is the speed of light. The velocities of the molecules obey the Boltzmann distribution, from which the value of v below can be used to derive the width of the transition at half maximum intensity (known as full width half maximum, or FWHM for short; see Fig. 4 Sec. II):

$$v = 2[(2kT \cdot \ln 2)/m]^{1/2}$$

where k is Boltzmann's constant, T is the absolute temperature and m is the mass of the molecule [12]. For an ammonia molecule at room temperature, $\Delta\nu/\nu \sim 10^{-6}$ (i.e. $\Delta\nu \approx$ tens of kHz for $\nu = 24$ GHz). This number turns out to be quite small compared to the effects of pressure broadening.

Pressure broadening is due to molecule-molecule collisions, which have the effect of reducing the lifetime of the excited state. From the uncertainty principle we know that

$$\Delta E \Delta t \geq \hbar$$

so if Δt , the time the molecule spends in the excited state, is reduced due to collisions with other molecules, the uncertainty in the energy, ΔE , of the excited state increases. This spread in the energy of the excited state is manifested as a spread in the linewidth associated with the transitions between the ground and excited states. The shape of the broadened line is Lorentzian with a frequency span, $\text{FWHM} = 1/(2\pi\tau)$, where τ is the mean time between collisions [13]. From the kinetic theory of gases we know that the mean time between collisions is inversely proportional to the density of the gas and thus inversely proportional to pressure, i.e., $\tau \sim 1/P$ where P is the gas pressure [14]. Substituting τ for Δt in the uncertainty relation,

$$\Delta E \tau \sim \Delta E(1/P) \approx \text{constant}$$

which yields

$$\Delta E \sim P$$

and we can thus expect the linewidth to be proportional to the gas pressure.

Pressure broadening is the dominant broadening mechanism in the ammonia inversion spectrum. The original measurement on this spectrum was performed with ammonia at atmospheric pressure; thus, the resultant broadening of a number of resonances was so large that the investigators saw only one line! [15]. The effects of pressure broadening are easy to observe in the experiment, as the pressure of the ammonia in the system can be varied by pumping the system down to the desired pressure after transferring ammonia from the storage reservoir. Indeed, to see the hyperfine lines due to quadrupole splitting, it is necessary to reduce the pressure in the system to several tens of millitorr or lower as they are located within several MHz of the center line. Note, however, the price to be paid in terms of reduced signal amplitude!

Different models of the collision process have been developed but they are lacking in sufficient detail to give exact theoretical predictions for linewidths. One theory which takes into account the rotational state of the molecule yields the result

$$\Delta\nu = 67.8P \left[\frac{K^2}{J(J+1)} \right]^{1/2} \text{ MHz/torr}$$

where $\Delta\nu$ is the FWHM and P is the pressure in torr [16].

Saturation effects are related to the intensity of the microwave radiation incident on the ammonia gas relative to the density of the gas. For high levels of microwave power and low gas densities, the

lifetime of the excited state is reduced, with a corresponding increase in the linewidth as discussed above. Radiation incident on a molecule that is already in the excited state can induce a transition to the ground state (indeed, this is the key principle on which lasers are based). If it is likely that such a radiation will be incident on the molecule before it has a chance to decay to the ground state, the lifetime of the excited state will be reduced. This situation is most likely to occur when the microwave power is high and the gas density is low. At higher pressures (typically above 100 millitorr) this effect is not important, given the power output of our microwave generator. But at low pressures (~ 10 millitorr), this effect can be noticeable, and an observable decrease in linewidth may result from lowering the microwave power.

Collisions between the molecules and the walls of the confining container also contribute to linewidth broadening. This effect is typically small for a system with cross-sectional dimensions on the order of a cm, as is the case for our apparatus. The linewidth due to this effect ≈ 10 kHz for the pressures at which you will be taking measurements [17].

The linewidth broadening contributions due to all the above-mentioned effects can be combined with the formula:

$$\Delta\nu_{\text{total}} = [\Delta\nu_1^2 + \Delta\nu_2^2 + \Delta\nu_3^2 + \dots]^{1/2}$$

where the $\Delta\nu$'s inside the brackets represent the individual contributions for each effect [18]. One states that the linewidths add in quadrature, just like noise.

References

1. R. Eisberg and R. Resnick, *Quantum Physics of Atoms, Molecules, Solids, Nuclei and Particles*, (Wiley, New York, 1985) p. 220.
2. C. Townes & A. Schawlow, *Microwave Spectroscopy*, (McGraw-Hill, New York, 1955) pp.67, 303.
3. Townes & Schawlow, pp. 69-71.
4. W. E. Good, Phys. Rev. 70, 213.
5. J. Simmons & W. Gordy, Phys. Rev. 73, 713.
6. Townes & Schawlow, pp. 131-136
7. Simmons & Gordy, Phys. Rev. 73, 713.
8. B. Bransden and C. Joachain, *Physics of Atoms and Molecules*, (Longman, London, 1983) p. 241.
9. J. Simmons & W. Gordy, Phys. Rev. 73, 713.
10. J. P. Gordon, Phys. Rev. 99, 1253.
11. Townes and Schawlow, p. 336.

12. Townes and Schawlow, p. 337.
13. Townes and Schawlow, p. 342.
14. F. Reif, *Statistical and Thermal Physics*, (McGraw-Hill, New York, 1965) p. 470.
15. C. E. Cleeton & N. H. Williams, *Phys. Rev.* 45, 234.
16. Townes and Schawlow, p. 353.
17. Townes and Schawlow, p. 374.
18. Townes and Schawlow, p. 375.

2. Preliminary Exercises and Measurement Possibilities

Preliminary Exercises

1. The rotational energy of the ammonia molecule is approximately equal to $P^2/2I$ where P is the total angular momentum of the molecule and I is the moment of inertia about the z axis. Since P is quantized with $|P| = [J(J + 1)]^{1/2}\hbar$, the above formula becomes $[J(J + 1)\hbar^2]/2I$. Using the information on the geometry of the ammonia molecule provided in Section I, calculate the moment of inertia about the z axis, and calculate several values for the rotational energy for $J \leq 10$. Compare these energies to kT for room temperature. Is it reasonable to expect these rotational levels to be significantly populated at room temperature? (The complete expression for rotational energy as a function of J and K can be found in Townes & Schawlow, p. 50.)
2. Calculate the full width half maximum for Doppler broadening at room temperature using the formula provided in Section I. Is $\Delta\nu_{\text{Doppler}}$ of the claimed magnitude?

Measurements

1. Locate 10 to 15 lines and compare the measured frequencies to published values. A table of measured frequencies from Townes and Schawlow is attached.
2. Use an expression like that given in Section I to fit your lines to a polynomial in terms of $J(J + 1)$ and K^2 . Compare the coefficients for your fit to those given in the Section I.
3. Measure the hyperfine splitting for several values of J , with $K = J$. Derive a value for the quadrupole coupling constant and compare it to the published value given in Section I.
4. Investigate linewidth as a function of pressure. These measurements cannot be strictly quantitative as the pressure gauge does not indicate absolute pressure, but a pressure that depends on the kind of gas in the system (the gauge is calibrated for air). However, it is possible to establish how the linewidth depends on pressure.

One needs to be careful with the pressure measurements. It is probably best to pump the system down and then close valve 3 to allow the pressure in the system to equilibrate. If the system is being pumped on, there may be pressure gradients across the system, making any pressure measurement suspect.

Rotational state		Frequency, Mc	Intensity, cm ⁻¹
J	K		
9	5	16,798.3	8.7 × 10 ⁻⁶
7	1	16,841.3	3.5 × 10 ⁻⁶
7	2	17,291.6	1.0 × 10 ⁻⁵
8	4	17,378.1	1.5 × 10 ⁻⁶
7	3	18,017.6	4.3 × 10 ⁻⁶
12	9	18,127.2	4.7 × 10 ⁻⁶
11	8	18,162.6	4.8 × 10 ⁻⁶
13	10	18,178.0	1.1 × 10 ⁻⁶
10	7	18,285.6	9.4 × 10 ⁻⁶
14	11	18,313.9	4.5 × 10 ⁻⁷
6	1	18,391.6	4.2 × 10 ⁻⁶
9	6	18,499.5	3.4 × 10 ⁻⁵
15	12	18,535.1	3.6 × 10 ⁻⁷
8	5	18,808.7	2.8 × 10 ⁻⁵
16	13	18,842.9	6.6 × 10 ⁻⁸
6	2	18,884.9	2.6 × 10 ⁻⁵
7	4	19,218.52	4.0 × 10 ⁻⁵
6	3	19,757.56	1.1 × 10 ⁻⁴
5	1	19,838.4	1.8 × 10 ⁻⁵
5	2	20,371.48	5.6 × 10 ⁻⁵
8	6	20,719.20	1.0 × 10 ⁻⁴
9	7	20,735.46	3.3 × 10 ⁻⁵
7	5	20,804.80	7.4 × 10 ⁻⁵
10	8	20,852.51	1.9 × 10 ⁻⁵
6	4	20,994.62	9.9 × 10 ⁻⁵
11	9	21,070.73	2.0 × 10 ⁻⁵
4	1	21,134.37	4.0 × 10 ⁻⁵
5	3	21,285.30	2.3 × 10 ⁻⁴
12	10	21,391.55	5.2 × 10 ⁻⁶
4	2	21,703.34	1.1 × 10 ⁻⁴
13	11	21,818.1	6.0 × 10 ⁻⁷
3	1	22,234.51	6.9 × 10 ⁻⁵
14	12	22,355	2.2 × 10 ⁻⁶
5	4	22,653.00	2.2 × 10 ⁻⁴
4	3	22,688.24	4.4 × 10 ⁻⁴
6	5	22,732.45	1.7 × 10 ⁻⁴
3	2	22,834.10	2.0 × 10 ⁻⁴
7	6	22,924.91	2.9 × 10 ⁻⁴
15	13	23,004	4.8 × 10 ⁻⁷
2	1	23,098.78	1.1 × 10 ⁻⁴

Rotational state		Frequency, Mc	Intensity, cm ⁻¹
J	K		
8	7	23,232.20	9.9 × 10 ⁻⁵
9	8	23,657.46	6.5 × 10 ⁻⁵
1	1	23,694.48	1.9 × 10 ⁻⁴
2	2	23,722.61	3.2 × 10 ⁻⁴
16	14	23,777.4	1.9 × 10 ⁻⁷
3	3	23,870.11	7.9 × 10 ⁻⁴
4	4	24,139.39	4.3 × 10 ⁻⁴
10	9	24,205.25	7.8 × 10 ⁻⁵
5	5	24,532.94	4.0 × 10 ⁻⁴
17	15	24,680.1	1.1 × 10 ⁻⁷
11	10	24,881.90	2.2 × 10 ⁻⁵
6	6	25,056.04	6.9 × 10 ⁻⁴
12	11	25,695.23	1.3 × 10 ⁻⁵
7	7	25,715.14	2.7 × 10 ⁻⁴
8	8	26,518.91	2.0 × 10 ⁻⁴
13	12	26,655.00	1.3 × 10 ⁻⁵
9	9	27,478.00	2.8 × 10 ⁻⁴
14	13	27,772.52	3.0 × 10 ⁻⁶
10	10	28,604.73	9.0 × 10 ⁻⁵
15	14	29,061.14	1.4 × 10 ⁻⁶
11	11	29,914.66	5.5 × 10 ⁻⁵
12	12	31,424.97	6.2 × 10 ⁻⁵
13	13	33,156.95	1.7 × 10 ⁻⁵
14	14	35,134.44	8.7 × 10 ⁻⁶
15	15	37,385.18	8.3 × 10 ⁻⁶
16	16	39,941.54	1.9 × 10 ⁻⁶

Table 1. Observed NH₃ inversion lines.
This table is from Townes and Shawlow, Table 12-3, pages 311-312.

3. Procedure and Instrumentation

The signals of interest in this experiment are very small, typically on the order of millivolts. To identify an ammonia inversion line and then adjust the electronic, mechanical and vacuum parameters of the system so as to achieve a good signal for that line is a tedious process, difficult to pursue in a completely systematic way. These notes are intended to help avoid some of the pitfalls in this process, and guide you in developing a technique for finding and clearly seeing the signal for a given line. To help get you going, a step-by-step procedure is provided for finding and clearly observing the 3,3 line and its associated hyperfine lines.

The lines in the ammonia inversion spectrum are observed by sweeping the output frequency of the microwave generator. When the frequency is swept through a resonance (inversion line), energy is removed from the microwaves propagating from the generator to the detector and the intensity of the detected signal is reduced. Because the output of the microwave detector is of negative polarity, increasing signal intensity is in the downward direction on the scope display, with the result that the inversion lines appear as positive going signals.

Microwave frequencies are measured with the HP 5351B Microwave Counter. The signal coming from the Wiltron 6653B Sweep Generator is divided into two parts by the small gray coupler, with approximately 95% of the power passing through to the waveguide part of the system and about 3% going to the counter (some power is dissipated in the coupler).

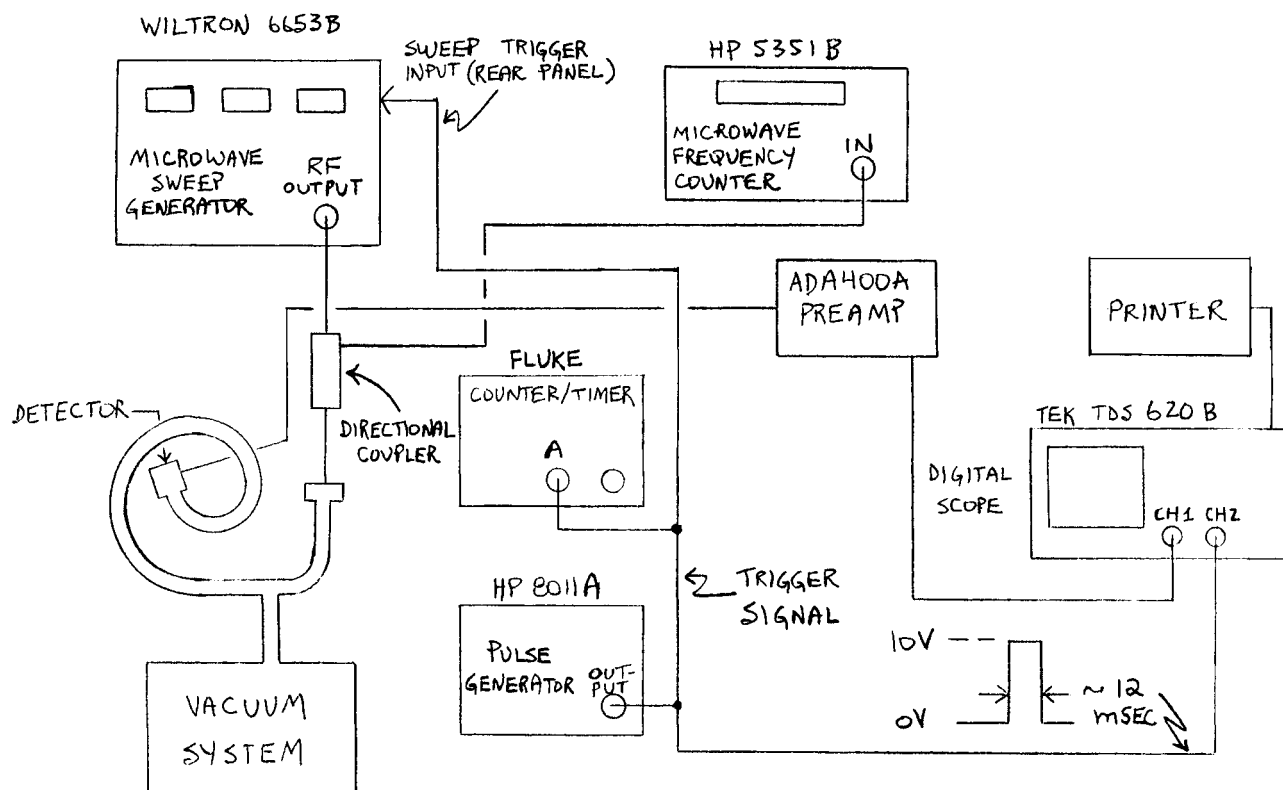


Fig. 5. setup of the microwave spectroscopy apparatus for measuring the ammonia inversion spectrum.

Procedure

1. If they have not already been turned on by the lab manager or TA, turn on the electronics (Wiltron 6653B Sweep Generator, HP 5351B Microwave Counter, HP 8011A Pulse Generator, Fluke Counter/Timer, and Tektronix Oscilloscope). The sweep generator and microwave counter require at least 1/2 hour to warm up and stabilize.

On to the vacuum system.

A comment on opening and closing the valves on the vacuum system:

To close a valve turn the handle clockwise until the O ring at the tip of the insert is in contact with the valve seat. This O ring forms an obvious dark ring when it contacts the glass, and this dark ring will spread slightly as the handle is further tightened to achieve closure of the valve. **Be careful not to over tighten these delicate valves** – a gentle touch is definitely in order. Also take care not to open any valve too far, as this may "break" the vacuum (allow air into the system). Both adjacent O rings on the barrel of the insert should remain in contact with the glass at all times. Typically, back out the valve insert no more than ~ 1/4 inch.

2. Check that the status of the valves on the system is as indicated below:

Valve 1 (vent valve): closed

Valve 2 (pump valve): closed

Valve 3 (system valve): open

Valve 4 (dosing valve): closed

Valve 5 (bulb valve): closed

3. Turn on the mechanical pump (switch is on the pump). If the liquid nitrogen dewar is in place around the cold trap, remove the dewar to make sure the trap is warm and that it gets pumped out at room temperature.

4. Open valve 2 to begin pumping on the vacuum system. After pumping on the system for about 10-20 minutes the pressure on the thermocouple gauge should read about 10 to 20 microns. When the pressure is in this range put the dewar in place around the cold trap and add liquid nitrogen to the dewar. (The TA can assist you in filling the gray 4 liter storage dewar with liquid nitrogen. As you conduct the experiment, check the level of liquid nitrogen in the dewar occasionally, and top it off as needed.) The cold trap is necessary to reduce the pressure and thereby the linewidth sufficiently to resolve the hyperfine lines associated with some of the inversion lines. After pumping on the system for 10 to 15 minutes with the cold trap in place, there will be very little ammonia in the system, and you will be able to observe the characteristics of the microwave system in the absence of ammonia.

The pressure in the vacuum system is measured by a thermocouple gauge. Such gauges do not measure absolute pressure; they measure the thermal conductivity of the gas in the system, and are

calibrated to read the pressure of air accurately. For other gases the pressure indicated can only be taken as an approximate measure of the absolute pressure. All references to pressure in these notes refer to the indicated pressure on the thermocouple gauge readout.

Now, back to the electronics.

5. Check that the period of the HP8011A pulse generator is about 55 milliseconds (measured by the Fluke Counter/Timer) and that the width of the negative going pulse is about 15 milliseconds (measured on the scope). The COMPL (complementary) and POS (positive) buttons on the 8011A should be in the depressed position. The pulse amplitude should be about 10 volts, and the output of the generator should be similar to that shown in Fig. 6 (upper trace).

A note on triggering: the output of the HP 8011A triggers both the microwave sweep generator and the oscilloscope. The sweep generator is triggered on a negative going edge; its rf output turns on and the frequency sweep begins about 15 milliseconds after this edge occurs. To better co-ordinate the microwave sweep and the scope display, the scope is triggered on a positive going edge about 15 milliseconds after the negative edge. This time interval is determined by the pulse width adjustment on the HP8011A. See Fig. 6.

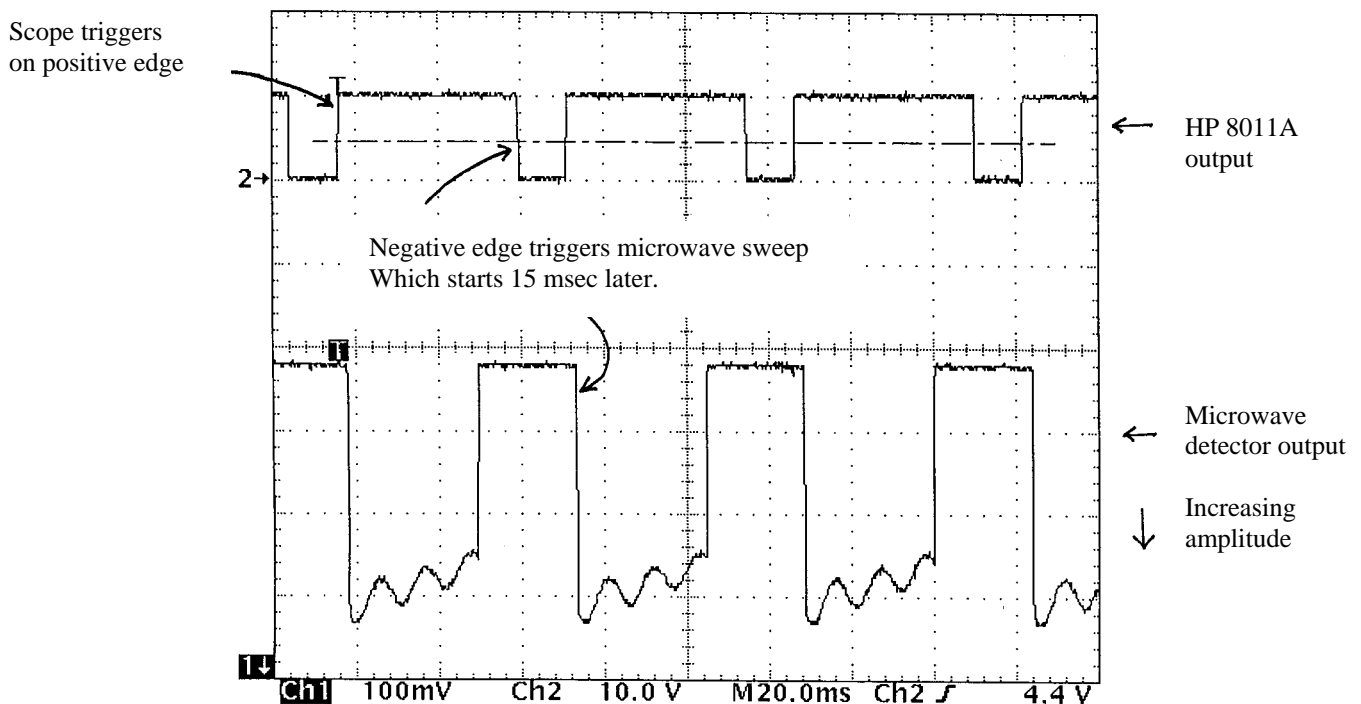


Fig.6. Scope traces showing relationship between pulse generator (upper trace) and detector output (lower trace). Center frequency = 23.880 GHz, $\Delta F = 50$ MHz, Pressure ≈ 0 microns.

6. Wiltron 6653B Sweep Generator: parameters like center frequency (CF), ΔF , power level, or sweep time on this unit can be changed in either of two ways: first push the button associated with the parameter to be changed and then either rotate the DECR \leftrightarrow INCR knob in the appropriate direction, or enter the desired numerical value on the DATA ENTRY keys and then press the appropriate units key to enter the value. Frequencies can be entered in units of MHz or GHz, but are always displayed in GHz. Similarly, times may be entered in milliseconds or seconds, but are always displayed in seconds. Note that the parameter selection buttons are located in the upper, dark gray area of the front panel.

Output power is displayed in dBm units; $\text{power(dBm)} = 10 \times \log(P/1\text{milliwatt})$. So 5 dBm power output corresponds to 3.16 milliwatts.

Settings for the 6653B Sweep Generator:

FREQ RANGE:	ΔF CF	(button in grey panel on the left side)
TRIGGER:	EXT OR SINGLE	(button in grey panel on the right side)
LEVELING:	INTERNAL	(button in grey panel on the right side)
RF ON	On	(adjacent indicator lamp on)
RETRACE RF	Off	(adjacent indicator lamp off)
Sweep time:	35 milliseconds	
Power Level:	+3.0 dBm	(push the Level button to check)
Center Frequency (CF):	23.880 Ghz	(23.874 in the HP freq. meter)
ΔF :	50 MHz	(<u>there is a significant difference between 50 MHz and larger ΔF's, as explained below</u>)

Use “clear entry” if you type in the wrong data.

In the ΔF CF mode, the output frequency of the 6653B is swept from $CF - \Delta F/2$ to $CF + \Delta F/2$. This mode is referred to as a centered range of sweep.

7. For the HP 5351B microwave frequency counter, the annunciators (downward pointing triangles) above the NORM and AUTO selections should be on. NORM refers to the frequency tracking rate setting (determines the counter's ability to follow a changing input frequency). In the AUTO mode, the counter will find the frequency automatically, whereas in the MANUAL mode it is necessary to manually enter a close estimate of the frequency being measured. To change a parameter such as resolution or sample rate, press the SET/ENTER button, the button associated with the parameter to be modified, the INC (increment) or DEC (decrement) button, and then finally the SET/ENTER button again. To set a numeric parameter, follow the same sequence with the buttons, except enter the appropriate value with the numbered buttons instead of using the INC or DEC buttons.

8. Oscilloscope settings:

Vertical gain:	100 mV/div (Ch 1), 10 V/div (Ch 2)
Horizontal:	10 msec/div
Trigger source:	Channel 2, positive slope

9. The detector output should be connected to the – input of the ADA400A preamplifier. Recommended preamplifier settings are:

– input:	DC coupled
+ input:	grounded
GAIN:	10
UPPER BANDWIDTH:	3 kHz
OFFSET:	ON. (The preamplifier offset can be very useful for adjusting the DC offset of the preamplifier output and thereby help keep the trace on the scope screen.)

10. Waveguide attenuator setting: .190" (smaller readings \Rightarrow greater attenuation for this device. For .190" the scale should show 3 major divisions between the 1 and 2, and the 15 should be aligned with the readout line.)

A stable trace something like that in Fig. 7, which shows one complete sweep of the 50 MHz frequency interval, should appear on the scope. If the trace for Channel 1 is not visible, change the vertical gain to 200 or 500 mV/div, and/or adjust the DC OFFSET on the preamp to get the trace on the screen.

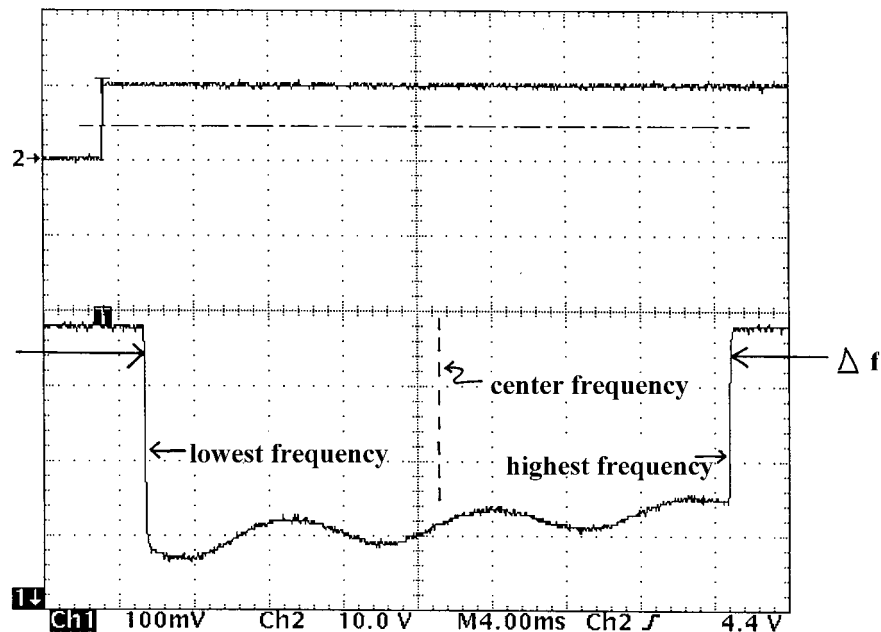


Fig. 7. Scope traces showing output of detector. CF = 23.880 GHz, ΔF = 50 MHz, $P \approx 0$ microns.

Note: all frequencies in the figures are those indicated on the Wiltron 6653B.

What you see in Fig. 7 is the amplitude of the signal at the detector as a function of frequency (x axis), and of the particular settings of the waveguide hardware (attenuator, E-H tuner, and detector tuner).

There was no significant amount of ammonia in the system (pressure \cong 0 microns) in Fig. 7. Fig. 6 shows several complete sweeps of the 50 MHz frequency interval.

A comment on tuning the microwave system:

There is a small, but not necessarily unique, range of E-H tuner, detector tuner and attenuator settings which will enable you to clearly see the signal from a particular inversion line. One can easily get into a loop of adjustment iterations which does not converge to a useful range of tuner settings. While it is instructive to initially run the tuner settings through a wide range to see the effect on the signal of interest, repeated large and random changes of the tuner settings may defeat attempts to find a suitable combination of settings. Making smaller adjustments, noting the effect of each adjustment, and developing a feel for how one adjustment affects another will help in finding and enhancing the signals observed in this experiment. When making these adjustments, please use a light touch on the hardware. In particular, **screwing the attenuator all the way down can damage it**, as the note on this device indicates.

11. Adjust the knobs on the E-H tuner, the detector tuner (red and green knobs), and the attenuator, and see how the detector output is affected by these various adjustments. These adjustments can help match impedances and cancel out reflections so as to make it easier to observe the signal.

12. Restore the attenuator setting to .190". Adjust the E-H tuner to best maximize the signal amplitude and flatness across the 50 MHz interval. Now adjust the red and green knobs on the detector tuner to again best maximize the signal amplitude and flatness over the frequency interval. (The knobs on the detector adjust a stub tuner, which affects the intensity of the microwave signal at the detector itself.) You should now be able to see a scope trace something like that in Fig. 8a. Note that the vertical sensitivity is now 20 mV/div.

It is important to minimize the amplitude variations over the swept frequency interval as large variations can tend to obscure any indication of the presence of an inversion line.

A comment on dosing the vacuum system with ammonia:

Before proceeding with the discussion of finding and observing ammonia inversion lines, a note on dosing the vacuum system with ammonia. The glass bulb on the vacuum system contains ammonium hydroxide, NH_4OH . Ammonia gas, NH_3 , evolves from the liquid (along with some water vapor). To admit ammonia to the microwave portion of the vacuum system, check that valve 4 is closed, open valve 5 **and then close it**. This allows a "high" pressure dose of ammonia into the glass tubing between valves 4 and 5. With valve 5 closed, open valve 4 to admit ammonia to the rest of the system. The pressure of ammonia in the system will be quite high and you will probably want to pump some of it out. It is possible to open valve 4 just slightly and bleed small amounts of ammonia into the system. This is a useful technique if you are looking at a line and want to increase the strength of the line by a small amount.

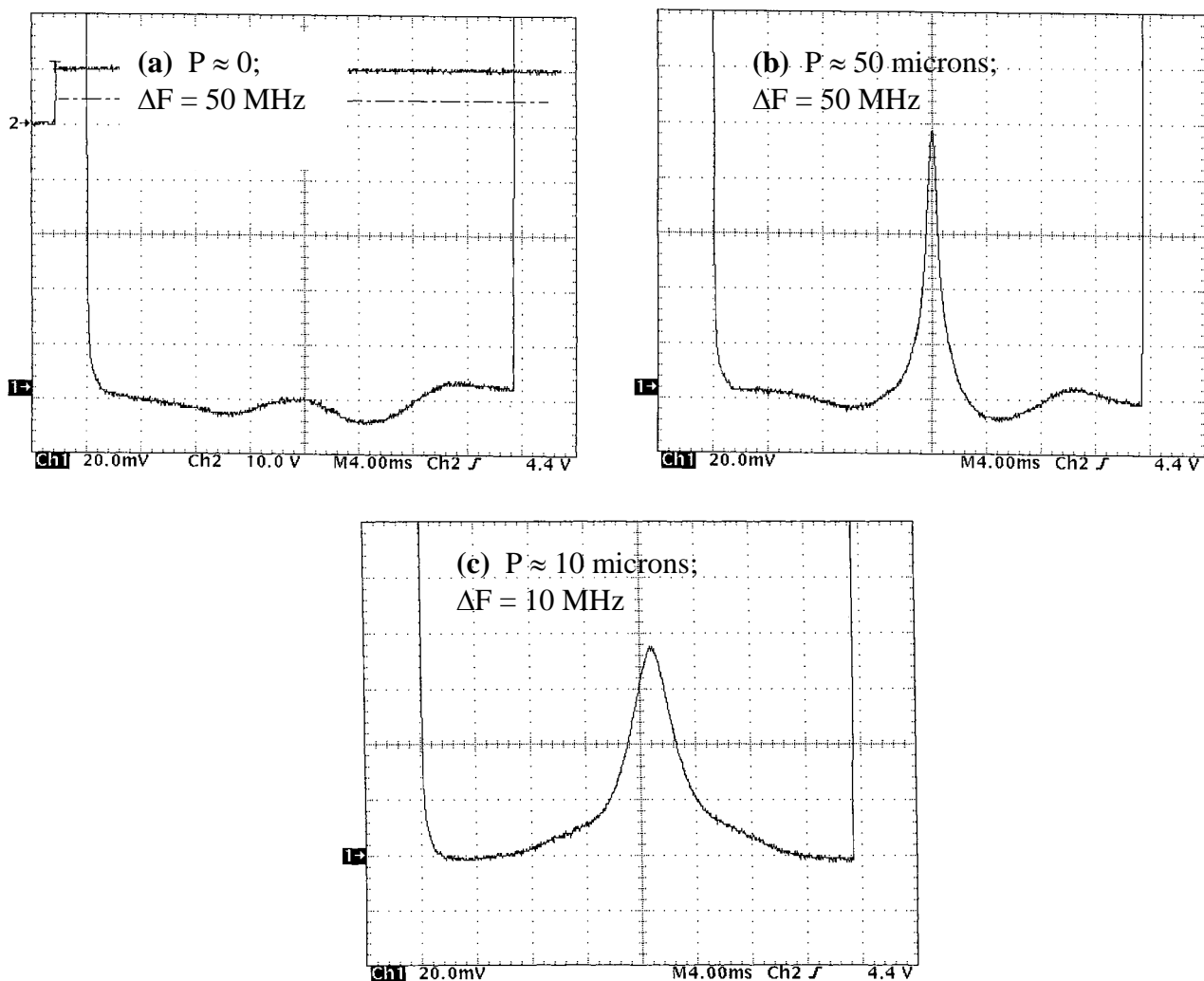


Fig. 8. Scope traces showing detector signal during dosing procedure. Note the pressures and frequency span in each trace. $CF=23.880 \text{ GHz}$ in all three traces.

CAUTION: NEVER pump directly on the liquid in the bulb (valves 4 & 5 should never be open at the same time). The ammonia will evolve from the liquid very vigorously, and the liquid in the bulb will cool rapidly which may cause the bulb to crack.

13. Having obtained a trace something like that in Fig. 8a, dose the system with ammonia (see above procedure). Pump the system out to about 50 microns. (At much higher pressures the inversion lines are so broad as to be difficult to see, and at much lower pressures the lines become so small as to be difficult to see.) There should now be an obvious bump/peak/irregularity in the scope trace. Fig. 8b shows an example of such a bump/peak. If you don't see any such thing after admitting ammonia to the system, check that the center frequency on the 6653B is 23.880 GHz, and that ΔF is set to 50 MHz. If these settings check out, adjust the E-H tuner to see if changing the tuning brings out the bump/peak/irregularity due the inversion line.

14. After observing the bump/peak/irregularity due to the inversion line, pump the system down until the pressure is 10-15 microns. This will reduce the amplitude of the line, and also cause it to narrow. Reduce ΔF to 10 MHz and, if necessary, re-center the peak on the scope display by adjusting the center

frequency. If the background is not level, adjustments of the E-H and/or detector tuners should help make it more level. Fig. 8c gives an indication of the shape of the 3,3 line under these conditions.

15. Resume pumping on the system. As the pressure drops, the hyperfine lines will become distinct as in Fig. 9a. To improve the signal to noise ratio, one can use the averaging feature (see ACQUIRE menu) of the scope. Fig. 9b shows an average of 8 sweeps, with the hyperfine lines clearly resolved.

The 3,3 line which you have been working with is one of the most intense lines in the ammonia inversion spectrum. Less intense lines (the 13,11 line has been observed with this system) are also quite observable, but the amount of care required to find and identify them is, of course, inversely proportional to the line intensity.

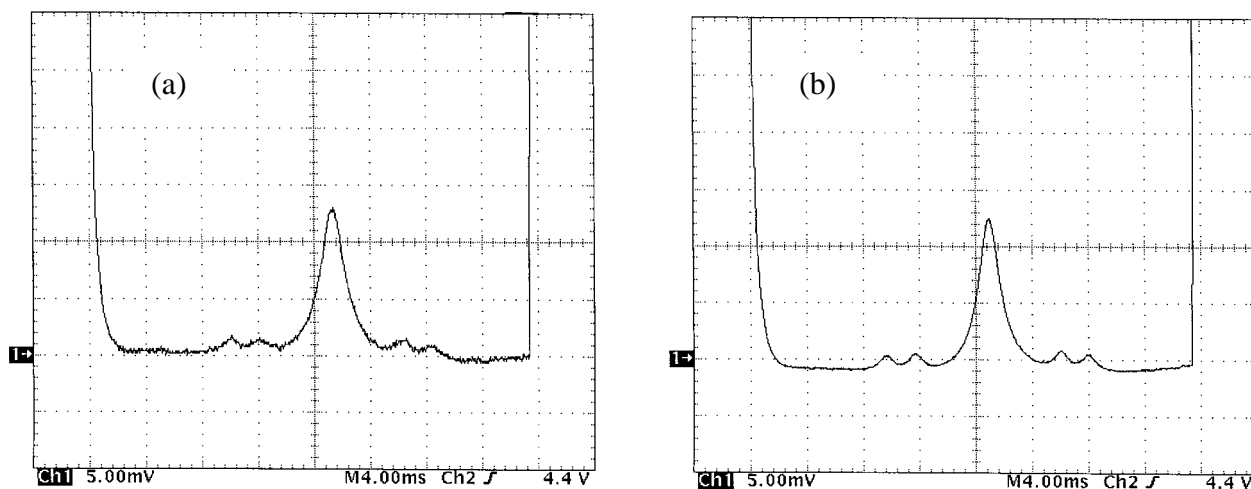


Fig. 9. Scope traces showing 3,3 line and hyperfine structure apparent at low pressure. CF = 23.880 GHz, $\Delta F = 10$ MHz, $P \approx 2$ microns. (a) Scope trace with single sweep. (b) Scope trace with average of 8 sweeps.

Frequency measurement:

Microwave frequencies are measured with the HP 5351B Microwave Counter. This counter can track a slowly varying frequency, but will not measure a frequency that is being swept many times a second (output of counter shows all zeroes). A way to measure the frequency of an ammonia line under observation is to put the 6653B Sweep Generator in manual sweep mode, and sweep over the entire ΔF range using the manual sweep adjust knob directly beneath the manual sweep button. By noting the low and high values of the frequency interval, one can deduce how the frequency varies across scope display. The center frequency of the swept frequency interval can be measured by putting the 6653B in the CW CF mode. A printout of the scope display can be generated for purposes of taking measurements with a ruler. This same technique can be used to determine the frequency spacing of the hyperfine lines.

While the HP 5351B is capable of measuring frequencies to the nearest Hz, the Wiltron 6653B is stable only to the nearest 10 to 100 kHz. So as not to have to look at lot of meaningless digits, the resolution of the HP 5351B is typically set at 10 kHz, with trailing digits suppressed.

In Summary:

The general procedure for finding and clearly displaying an inversion line is as follows. First adjust the center frequency and the ΔF interval (50 MHz or less recommended) on the Wiltron 6653B to cover a frequency range where you want to look for an inversion line. With the vacuum system pumped out, obtain a scope trace similar to Fig. 7. Admit some ammonia to the vacuum system. With the pressure in the system at 50 to 100 microns, look for any bump/peak/irregularity not present in the Fig. 7-like trace, the bump/peak in Fig. 8 being an obvious example. Adjust the waveguide hardware to enhance the contrast between the inversion line and background signal. Reduce ΔF and the system pressure, and further adjust the waveguide hardware to better bring out any details of interest associated with the line under observation.

Following this procedure should enable you to find and cleanly display the lines with hyperfine components. Finding and measuring the frequency of a line without worrying about any hyperfine components is not nearly as involved, as one does not have to flatten the background signal and reduce the pressure to narrow the linewidth.

If in the process of looking for or at the various lines in this spectrum, you are not sure whether the feature under observation is an ammonia inversion line or an artifact of the microwave system, you can pump the system out, which will reduce the magnitude of any signal due to an inversion line.

The $\Delta F \leq 50$ MHz situation:

It turns out that the Wiltron Sweep Generator has an idiosyncrasy related to the magnitude of ΔF . For values of $\Delta F \leq 50$ MHz, the center frequency indicated on the front panel of the 6653B is about 6-7 MHz higher than the actual output frequency (as measured by the HP 5351B). For values of $\Delta F > 50$ MHz, the indicated center frequency is about 80 MHz lower than the actual output frequency (again, as measured by the HP 5351B). Such a large error is a possible source of confusion, so setting $\Delta F \leq 50$ MHz may help simplify dealing with the sweep generator.

Shutting down the system:

When you are done taking measurements, pump the system to a pressure 10 microns or less, close valves 2 & 3, and then remove the liquid nitrogen dewar with the pump still running. Allow the cold trap to warm up completely (takes about 15 minutes) and then turn off the pump. Open valve 1 to let the trap and pump line up to atmospheric pressure. Close valve 1. Pour any remaining liquid nitrogen in the experiment dewar back into the storage dewar. Turn off all of the electronics.

NH3_Inversion_2004-ver2-1.doc
12/9/2004 3:26 PM