A-6 Ammonia Inversion

From Physics 191r

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INVERSION SPECTRUM OF AMMONIA

first experiment: yes

Contents

LEARNING GOALS

- Observe rotational states of the ammonia molecule.
- Study pressure broadening.
- Become familiar with vacuum techniques and microwave instrumentation.

INTRODUCTION

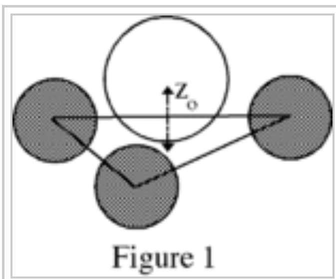

Figure 1. Ammonia molecule.

The structure of the ammonia molecule is pyramidal; three hydrogen atoms in an equilateral triangle form the base and a nitrogen atom is at the apex. The molecule can be described by a one-dimensional double potential well, z_0 being the distance of the nitrogen atom from the plane of the hydrogen atoms. See Figure 1. Let ψ_l and ψ_r be wavefunctions describing the lowest vibrational state of the nitrogen atom in the potential well to the left and right respectively of the barrier. If the barrier were infinitely high, the eigenvalues of ψ_l and ψ_r would be degenerate. However for ammonia, the barrier is unusually low and tunneling through the barrier is possible. Therefore ψ_l and ψ_r are not orthogonal; the states of definite energy are the symmetric and antisymmetric combinations of ψ_l and ψ_r.

For either eigenstate the two principal moments of inertia parallel to the plane of the hydrogen atoms are equal and therefore the molecule is categorized as a symmetric top. The rotational energy levels of an ideal rigid symmetric top molecule are characterized by two quantum numbers: **J** = total angular momentum and **K** = component of **J** along the axis of symmetry, which can take magnitudes from -J to +J. Transitions between the symmetric and antisymmetric states with Δ**J** = 0 and Δ**K** = 0 are the subject of this experiment. Qualitatively this is thought of as an inversion of the molecule about its center of mass.

At room temperature, $k_B T$ is on the order of the rotational energy level spacing; therefore many rotational states will be populated. Rotational motion adds a centrifugal term to the effective potential, further splitting the inversion states. The energy range for transitions between such inversion states is 22 to 26 GHz, suitable for study with microwave spectroscopy. This experiment therefore makes use of a microwave source, a waveguide, which can be filled with ammonia, and a detector, which measures the microwave power traversing the guide. As the frequency of the microwaves is swept, absorption lines are visible at energies of allowed transitions.

APPARATUS

- Gunn diode oscillator (Epsilon Lambda ELM B21M)
- Diode power supply (ELD101) and Sawtooth modulation supply
- Absorption cell (waveguide) and K-band microwave components
- Frequency absorption meter (Hewlett Packard K532A)
- Vacuum system with pressure gauges and NH3 gas manifold
- Oscilloscope and Signal Generator (General Radio 1001-A)

The apparatus is a simple absorption spectrometer in which a crystal detector (diode MA4E913) rectifies a microwave signal (tunable from 22.1 to 26.0 GHz) after it passes through the absorption cell. The detector crystals are fragile, rare and expensive. When installing a new crystal, avoid electrostatic discharge through it.[1] The microwave source is a Gunn diode oscillator (GDO), a solid state device operated in its negative impedance regime.[2] The frequency of the oscillator may be controlled in three ways: 1) mechanically tuning the size of the cavity[3] 2) applying a dc voltage to the varactor and 3) varying the diode bias voltage. These are used respectively as a coarse and a fine frequency adjustment and as a way to modulate the oscillator frequency so that the detected power may be viewed on an oscilloscope with the time base corresponding to microwave frequency. If a strong and narrow absorption line at frequency f_{abs} is present in the range of the frequency modulation of the GDO, a corresponding sharp main dip will be found when the detected voltage is displayed on the oscilloscope, swept synchronously with the microwave

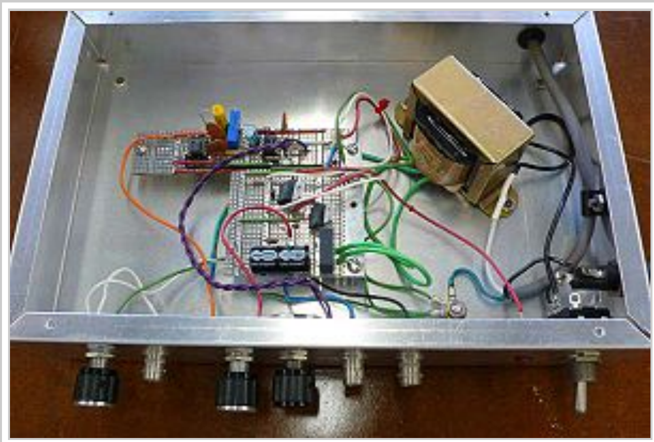

Figure 2. Sawtooth modulation box circuit.

Figure 3. Sawtooth modulation box panel.

source.

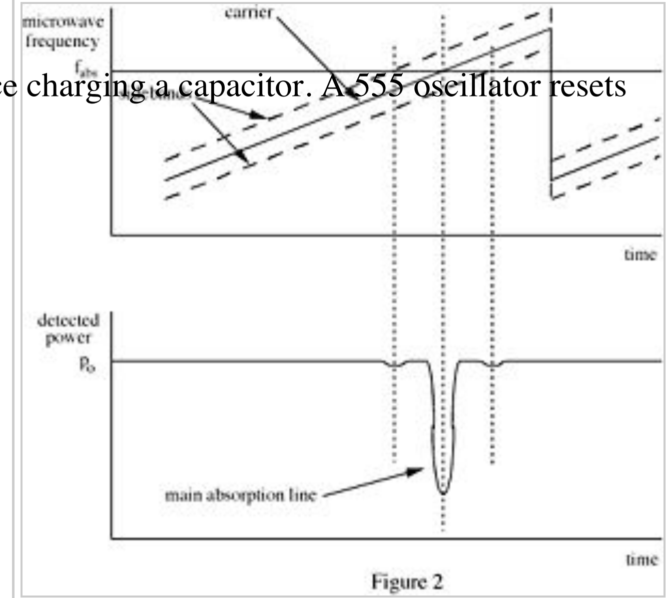

Figure 4. Modulation technique used to produce sidebands.

The sawtooth modulation signal is generated by a current source charging a capacitor. A 555 oscillator resets the capacitor voltage to zero when it reaches a threshold. A schematic diagram is available in the Bench Notes. The sawtooth output (Figure 3-1) amplitude is adjustable (Figure 3-2) from approximately 2 to 10 V. Frequency (Figure 3-3) varies from 5 Hz to 300 Hz however the sawtooth ramp becomes nonlinear at slow sweep speeds. A trigger pulse (Figure 3-4) (compliment of TTL) is used to trigger the oscilloscope. The same box provides a 0 to 15 V dc output (Figure 3-5) for the varactor tuning.

The microwave signal can be given a symmetrical pair of small modulation sidebands. For the sidebands to be present, the arm of the Magic T opposite that leading to the absorption cell must be terminated by a reflecting plunger, under which circumstances a wave is reflected from the plunger partly into the upper E-plane arm of the T. If the attenuator pad in that arm is set to introduce no attenuation, the wave impinges upon the modulator crystal, which can be driven directly from the signal generator. The microwave impedance of the crystal unit is made time dependent at the frequency set by the signal generator; therefore the wave reflected by the crystal is correspondingly modulated. A part of that wave is added to the wave that directly enters the branch of the T leading to the absorption cell. The relative phase of these waves depends upon the distance to the plunger in the other arm of the T and adjustment of it affects the display finally achieved. With a carrier wave and two sidebands incident on the detector crystal, a detected signal at the frequency of the signal generator, say 0.5 to 5.0 MHz is produced. A low pass filter in the preamplifier blocks that signal from the oscilloscope display. In the presence of sidebands, a small image of the main line should be found on each side of the main line at a frequency offset an amount just equal to the setting of the signal generator. See Figure 2. In practice the GDO power output, P_0 is not the same for all frequencies; this complicates measurement of line widths. The image lines may be moved relative to the strong main line by adjusting the modulation frequency. They may be used to calibrate the differential frequency scale of the display for measurement of hyperfine splitting intervals and line widths. Approximately the full signal from the attenuator-controlled output of the signal generator is required, i.e., the switch at 100 mV, the continuous knob near 2.0 and the “carrier” set around 0.5. Place the 150 Ω resistor (which is in a small Pomona box) in series with the diode to limit the current from the function generator.

The HP frequency meter is a cavity, which absorbs microwaves in a narrow band. If the band absorbed by the meter is within the frequency range generated by the GDO, a dip will appear in the oscilloscope display of microwave power vs. frequency. Changing the dimensions of the cavity changes its resonant frequency; this is accomplished by rotating the black cap of the meter. The intersection of the scale between the two red lines with the thin vertical black line gives the absorption frequency in GHz.

In order to inject ammonia gas into the waveguide, begin by evacuating the waveguide and gas handling apparatus.[4] Pressurize the flexible tube connected to the regulator to a few psi or less; close the valve to the regulator. Allow this ammonia to expand first into the small hexagonal pipe, then from the hexagonal pipe into the waveguide.

Two gauges are used to measure the pressure in the system: a thermocouple gauge and a capacitance manometer. The thermocouple gauge is useful in the pressure regime in which the thermal conductivity of a gas varies strongly with pressure. Current is passed through a filament to heat it and its temperature is measured with a thermocouple. Heat is conducted away from the filament by the surrounding gas, Therefore its temperature will be lower at higher pressures. A controller converts the voltage developed across the thermocouple to the corresponding pressure. Thermocouple gauges are generally calibrated for air, thus when measuring pressure of ammonia you will not get a correct reading. The thermocouple gauge should be thought of as a rough check of pressure. On the other hand pressure is independent of the type of gas so a device that directly measures pressure can give accurate readings. [5]. The sensor in the Baratron capacitance gauge is a sealed capacitor with one side a deformable diaphragm (like a drumhead); the other side of the diaphragm is a sealed vacuum. The pressure to be measured deforms the diaphragm, changing the capacitance which is calibrated in terms of pressure. For stability the controller contains a heater, which maintains a fixed temperature inside the Baratron head. Warm-up time is a few hours. Therefore if the controlling electronics are adjusted properly, the Baratron can make precise absolute pressure measurements in so far as the reference side of the capacitor contains a high vacuum. The measurement range of the gauge depends on the geometric dimensions of the capacitor; ours is designed to measure pressures lower than 1 Torr.

EXPERIMENTAL PROCEDURE

- The (J,K) = (3,3) line is the strongest absorption; it is expected at 23.870 GHz.[6] Measure the frequencies and relative intensities of as many absorption lines as possible. Compare to published values.
- Measure the offset of the first and second hyperfine structure satellites vs. J and K.
- Measure the width of an intense line as a function of pressure.

NOTES

1. ↑ Consult a staff member if you need to install a new crystal.
2. ↑ See Hobson (1974) and Gunn (1964) in the references for more information.
3. ↑ Never exceed the manufacturer's restrictions.
4. ↑ If you wish to evacuate the regulator, make sure that the ammonia bottle itself is valved off from the pump.
5. ↑ KS Baratron type 390HA.
6. ↑ See Townes and Schawlow for accepted frequencies and intensities of other lines.

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BENCH NOTES

- Baratron Head 390HA (http://www.fas.harvard.edu/~phys191r/Bench_Notes/A6/Baratron.pdf)
- Baratron 270 Signal Conditioner (http://www.fas.harvard.edu/~phys191r/Bench_Notes/A6/BaratronController.pdf)
- HP K532A Microwave Frequency Meter (http://www.fas.harvard.edu/~phys191r/Bench_Notes/D2/Frequencymeter.pdf)
- Epsilon Lambda ELD101 GDO Regulator (http://www.fas.harvard.edu/~phys191r/Bench_Notes/A6/GDOPwrsupply.pdf)
- Gunn Oscillator (http://www.fas.harvard.edu/~phys191r/Bench_Notes/A6/GunnOscillator.pdf)
- HP K870A Slide-Screw Tuner (http://www.fas.harvard.edu/~phys191r/Bench_Notes/A6/hptuner.pdf)
- MACOM Detector (http://www.fas.harvard.edu/~phys191r/Bench_Notes/A6/MACOMdetector.pdf)
- MACOM MA4E914 Sideband Mixer Diode (http://www.fas.harvard.edu/~phys191r/Bench_Notes/A6/ma4e914.pdf)
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- General Radio 1001A Signal Generator (http://www.fas.harvard.edu/~phys191r/Bench_Notes/A6/SignalGenerator.pdf)

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