

Chem. 587
Homework Set 4
Spring 2007

I. Laboratory Measurements

This laboratory will give hands-on experience of measuring the rotational spectra of three interstellar molecules: HCO^+ , CH_3CN , and HCCCN . This exercise will illustrate: (i) the laboratory detection of formyl cation (HCO^+) (iii) the laboratory detection and effects of centrifugal distortion on CH_3CN (iii) the laboratory detection and structural analysis of cyanoacetylene (HCCCN).

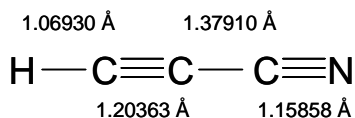
HCO^+ : Formyl cation is an important interstellar molecular ion. The production of HCO^+ is accomplished by the following reactions in an AC discharge:



Once formed, HCO^+ is very stable (does not readily react with H_2). Several transitions of this species will be measured in the laboratory, and its rotational constants will be determined.

CH_3CN : Methyl cyanide, or acetonitrile, is a common interstellar molecule and organic solvent. Unlike HCO^+ and HCCCN , this species is non-linear with the methyl hydrogens arranged symmetrically around the major axis of the molecule. This type of molecule is called a symmetric top, and has a unique pattern to its rotational spectrum. One transition of methyl cyanide will be measured, and the effects of the non-linearity of the molecule will be evaluated.

HCCCN : Cyanoacetylene, another widespread interstellar species, is a highly reactive (sometimes explosive) gas that is not commercially available. Hence, its laboratory study requires a somewhat exotic production method. HCCCN will be synthesized in a 0.5%:0.5% gas mixture of acetylene (C_2H_2) and cyanogen (NCCN) highly diluted in argon (99%) by a 900 V DC discharge. The discharge current (~50 mA) is strong enough to create highly reactive radicals and ions, which recombine into a number of products that are stabilized in the flowing gas as it expands in a near collision-free environment. One of the major products in the resultant gas stream is cyanoacetylene. It is estimated that only about 0.001 grams of HCCCN will be produced during the course of this exercise inside the confines of a very robust vacuum chamber—so there is no danger of exposure. Still, even with this miniscule amount of material, the spectrometer is sensitive enough to view its rare isotopic species containing, for example, ^{13}C , with high signal to noise (with the exception of deuterium) in natural abundance. HCCCN has the structure shown below. The numbers on the structure show the various bond lengths.



We will also prove that the structure above is precisely correct by measuring the frequencies of one rotational transition of several rare isotopic species (H^{13}CCCN , HC^{13}CCN , HCC^{13}CN).

Despite the small change in mass resulting from using ^{13}C instead of ^{12}C , or ^{15}N instead of ^{14}N , the frequency of the transitions and hence the rotational constants will vary considerably with each isotopically-substituted species. These data will show that the rotational constant of a given molecule is unique, despite minute changes in structure. This uniqueness is essential for the identification of interstellar molecules using their pure rotational spectrum. A more in-depth discussion of how small changes in mass affect the rotational spectrum is given in Appendix I.

Measurement of the Rotational Spectrum of Formyl Cation, HCO^+

In this activity, we will start with the known value of the rotational constant B for this molecule, HCO^+ , and predict the frequency of the $J = 2 \rightarrow 3$ transition. We will measure this transition frequency using a millimeter-wave direct absorption spectrometer. It will then be used to calculate the centrifugal distortion constant D . This constant will next be used to predict the frequency of the $J = 3 \rightarrow 4$ transition. Measurement of this second transition matching the frequencies in the new prediction will confirm the calculated constant.

Our search will begin by calculating approximate frequencies in the range of 260 to 300 GHz using the known rotational constant for HCO^+ of $B_{\text{HCO}^+} = 44594.4$ MHz. Remember, this frequency will not be exact because we are neglecting the effects of centrifugal distortion.

We will tune the spectrometer to that frequency and take a scan 100 MHz wide in frequency. After finding a feature, fit the feature to a Gaussian profile, and determined the exact frequency of the line. Use this frequency to calculate the distortion constant D .

With both B and D , calculate the frequency for the next transition up ($J = 3 \rightarrow 4$) and search for the transition. Repeating the process described above. The radiation source will have to be changed in order to produce the required frequency.

Measurement of the Rotational Spectrum of Methyl cyanide, CH_3CN

For this part, we will introduce a small quantity of acetonitrile, $\text{CH}_3\text{CN}_{(l)}$, into the spectrometer and measure the spectrum of one transition near 367 GHz. This species has several lines per rotational transition. The spacing between the lines starting at $K = 0$ goes as 1:3:5:7...

Start at 367.0 GHz and scan up in 100 MHz increments with scans 100 MHz wide to 367.8 GHz. This range will cover up to $K = 10$ for CH_3CN . Measure the frequencies of the features observed in the data. Also note the intensities of the individual peaks.

Measurement of the Rotational Spectrum of Cyanoacetylene, HCCCN

In this exercise, we will measure the two lowest lying rotational transitions ($J = 1 \rightarrow 0$ and $J = 2 \rightarrow 1$) of HCCCN using a very high resolution, pulsed-nozzle, Fourier transform microwave (FTMW) spectrometer. The relatively simple system of HCCCN will demonstrate the necessary steps involved in first identifying a molecule in the laboratory, fit rotational constants to the measured frequencies and accurately predict the complete spectrum of the molecule from only a couple of measurements in the laboratory.

HCCCN will be introduced into the reaction chamber and pulses of microwave radiation at two specific frequencies will be used to excite the two rotational transitions of interest. First, the $J = 1 \rightarrow 0$ transition near 9 GHz will be measured, followed by the $J = 2 \rightarrow 1$ line near 18 GHz. The emitted intensity will be recorded as a function of frequency for each transition, i.e. a free induction decay (FID) will be measured, and a fast Fourier transform will be taken to produce the molecular spectrum. A precision of better than 1 part in 10^7 should be obtainable from these data. It will then be used to determine the rotational constants, B and D.

The $J = 1 \rightarrow 0$ transition for this molecule is split into three lines by a perturbation. Known as electric quadrupole, this interaction is caused by the non-spherical nature of the nitrogen nucleus. The spectroscopic constant that describes this behavior is eQq .

Next measure the $J = 2 \rightarrow 1$ transition near 18 GHz of the rare ^{13}C isotopic species of HCCCN – H^{13}CCCN , HC^{13}CCN , and HCC^{13}CN .

II. Analysis

1. HCO⁺

- Knowing that the initial calculated frequency is incorrect, where would you expect the signal to be relative to the calculated frequency and why?
- What can you have concluded if there was no line present?
- Once we found the corresponding signal, why wasn't it EXACTLY as we calculated?
- With the two frequencies for HCO^+ , solve for the exact rotational constants.
- If you used the B value given and the value of D determined from just the lower frequency, and predicted the lines at much higher frequencies, what would happen and why?
- How would this affect a molecule whose spectrum was only measured at low frequency, when higher J transitions are extrapolated?

2. CH₃CN

- Estimate the value of D_{JK} for CH_3CN .
- Why don't all of the K components stack up on each other?

3. HCCCN

- Determine the structure of HCCCN from the data collected.
- Why doesn't the structure given in Section I with 5 decimal precision reproduce the frequencies well enough?
- Why does measuring the rotational spectrum allow us to overcome this?

d) Determine that value of eQq for the main isotopic species.

Useful constants and conversions:

$$1 \text{ Angstrom} = 10^{-10} \text{ meters}$$

$$1 \text{ amu} = 1.6605655 \times 10^{-27} \text{ kg}$$

$$h = 6.626176 \times 10^{-34} \text{ J s}$$

Appendix I

Relating Mass and Moments of Inertia

Here we will apply some of what was introduced in the Rotational Spectroscopy section of this document. First, we have to expand on a couple of the ideas presented earlier. The reduced mass used in Equation (1) is a convenient way to express the mass of the system in a time invariant frame. The part of the framework that satisfies this condition is the center of mass. However, since it is desirable to use an arbitrary coordinate system, we must first find the center of mass by solving:

$$\bar{r}_{center} = \frac{\sum m_n \bar{r}_n}{\sum m_n}, \quad (3)$$

where r_{center} is the center of mass of the system in the arbitrary coordinate frame. For instance, set the position of the hydrogen at (0, 0, 0) and the remainder of the atoms relative to that and solve for r_{center} . Since HCCCN is linear, only a single dimension is needed, which reduces the position vectors to scalars. Now transform the positions of each atom into the new coordinate system with the center of mass at the center with the following equation:

$$p_n = r_n - r_{center}, \quad (4)$$

where p_n are the new positions. With this new coordinate system, we can skip the reduced mass calculation and go straight for the moment of inertia by summing the contribution of each atom to the overall moment, I :

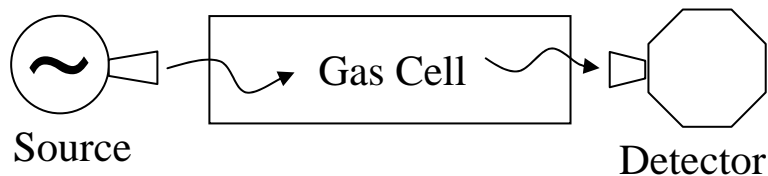
$$I = \sum m_n p_n^2. \quad (5)$$

Now, use Equation 3 to solve for the estimated rotational constant in either MHz or s^{-1} . The units for Equations 4 and 5 should be in Angstroms (or nanometers) and the units for Equation 6 should be in amu Angstrom² (or amu nm²). The following masses are needed for the calculation: $m_H = 1.00794$ amu, $m_C = 12.00000$ amu, and $m_N = 14.00674$ amu

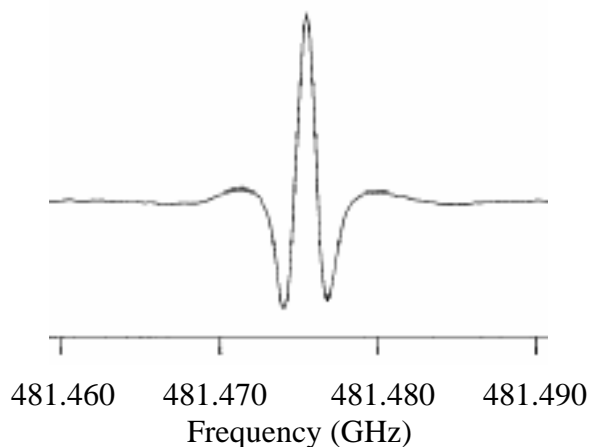
Appendix II

Millimeter-wave Direct Absorption Spectroscopy

A simplified block diagram of the direct absorption spectrometer is shown below in Figure 2. It consists of three basic parts: a tunable, stable source of mm radiation, a gas cell, and a detector. The radiation is focused through the gas cell and scanned in frequency. When a given frequency is coincident with a transition of a molecules contained in the cell, the radiation is absorbed. This absorption results in a decrease in power at the detector, hence the term, “direct absorption.”



The absorption results in a spectral line, as shown in Figure 3. The center of the line is at the exact transition frequency.



Appendix III Fourier Transform Microwave Spectroscopy

The FTMW system is a rather complicated instrument in itself, but its function is simple. It basically is used to measure the differences in rotational energy levels, or the frequencies of the transitions between the levels, as shown in Figure 1. It does this task by measuring a complicated process known as the “free induction decay” or FID. The Fourier transform of the FID creates a spectrum. The FID is created by interacting molecules trapped in a reaction chamber with a pulse of microwaves that have continuous frequency coverage over a small range. If any of the frequencies correspond to the energy difference between any two levels of the molecules, they will absorb the radiation and be excited to the higher level. After a short time period, the molecules will spontaneously jump back to the initial lower levels, and emit radiation corresponding to the frequency of that energy level difference. This radiation is detected by the spectrometer. The frequency is then increased and another pulse is shot into the molecules. Any emitted radiation is monitored. Then the frequency is increased again, a pulse is fired and so forth. Eventually a whole spectrum can be created over a large frequency range, and hence the exact frequencies of the rotational transitions are measured. Because the radiation used to excite the molecule is pulsed, it is also advantageous to pulse the molecules as well to synchronize the signal. Thus, a pulsed nozzle source for the molecules of interest is used.