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## **Development of Laboratories for Teaching Chemical Principles using Radio Astronomy**

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Experimental exercises have been developed for undergraduate and graduate chemistry, astronomy, biology, and biochemistry students to teach basic principles in physical chemistry using the interstellar medium as the laboratory. Employing a radio telescope, in this case the Arizona Radio Observatory (ARO) 12m antenna, the physical and chemical properties of interstellar gas are investigated by measuring spectra of molecules such as HCO<sup>+</sup>, HCN, HC<sub>3</sub>N, CH<sub>3</sub>CN, and SiO in astronomical sources. For example, laboratory exercises have been created for graduate students with life sciences backgrounds that investigate the nature of organic chemistry in interstellar clouds. Additional laboratories are being developed to teach astronomy graduate and undergraduate students about practical aspects of molecular astrophysics and spectroscopy. Basic chemical principles are thus illustrated through an interesting, non-traditional approach.

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## Introduction

New techniques to illustrate basic chemical principles are valuable tools for the chemistry teacher, regardless of the level of instruction. The use of laboratory exercises exposes students to direct applications of these principles. Because chemistry encompasses a wide variety of fields, the traditional “bench experiments” approach is no longer the only avenue by which to introduce new concepts. Furthermore, the perpetuation of “traditional” labs can make the subject uninteresting

Here we describe a novel approach to the teaching of basic concepts of physical chemistry that falls under the category of chemical evolution. Laboratory exercises have been developed for undergraduate and graduate students that illustrate principles of gas-phase spectroscopy and kinetics using interstellar space as the “laboratory”. Observations at radio telescopes are used to measure high resolution spectra of molecules in a variety of astronomical objects. Not only can principles of spectroscopy be illustrated from these data, but concepts of detailed balance in quantum states, kinetic theory of gases, local thermodynamic equilibrium (LTE), and ion-molecule chemistry can also be taught.

In one laboratory exercise, students use a radio telescope to measure the emission spectra of selected molecules in astronomical sources, such as dense clouds and old stars. Molecular hyperfine structure, classical spectral patterns of linear and symmetric top species, and maser action are investigated. Another laboratory exercise was developed where students measure the rotational spectra of  $\text{HCO}^+$ ,  $\text{HCCCN}$ , and  $\text{CH}_3\text{CN}$  in the laboratory, and determine their unique spectroscopic properties. They then use their measurements to identify these molecules in interstellar gas.

## Radio Telescopes as Instruments of Chemical Education

Modern teaching laboratories in physical chemistry often use nuclear magnetic resonance (NMR), Fourier transform infrared instruments (FTIR), or ultraviolet-visible light spectrometers to illustrate scientific concepts and methods. Radio telescopes can also be employed in the same manner. However, instead of shining a form of light through a sample in a laboratory, these instruments collect radio waves emitted from gas clouds thousands of light years away. The experiments conducted with a radio telescope involve collecting radiation with optics and detectors, processing the information received through a spectrometer, and analyzing it with a computer interface, similar to any lab system. This information is then analyzed to assess the molecular content and concentrations, as in NMR and mass spectrometry.

Radio telescopes, however, are more complicated than the usual laboratory instrument. Furthermore, the signals of interest are far weaker than those in a laboratory setting by many orders of magnitude, on the order of  $10^{-19}$  Watts/m<sup>2</sup>. Therefore, the sensitivity and stability of the detectors on these telescopes must exceed that of normal laboratory instrumentation. The detection process consequently requires electronics that need to be fine-tuned to function at optimal performance.

Detection of radiation at radio telescopes is done using superconducting mixers, which are kept at 4.2 K with a closed-cycle helium refrigerator. Radiation from the sky,  $v_{\text{sky}}$ , is combined inside the mixer with a source of radiation at the telescope called the local oscillator (or  $v_{\text{LO}}$ ). This technique, called “heterodyne mixing” is needed because signals from space cannot be

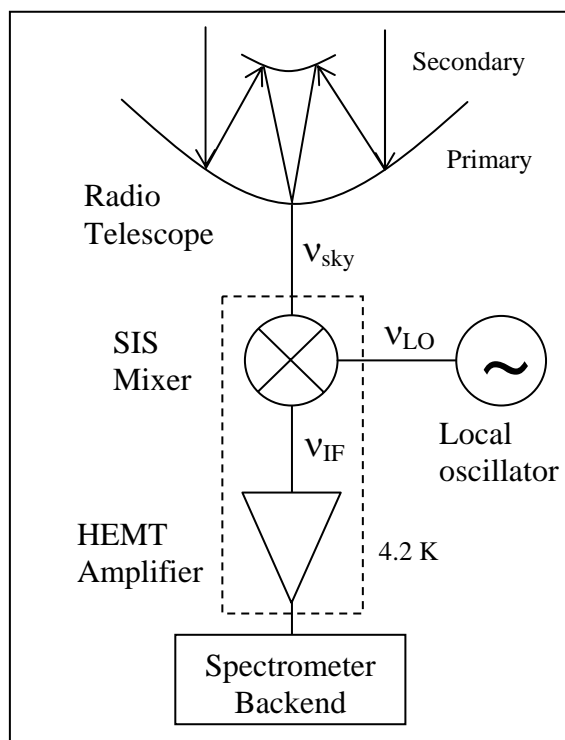


Figure 1. Schematic of the detection system at a radio telescope using an SIS (superconducting-insulating-superconducting) mixer and a HEMT (high electron mobility transistor) amplifier. Here  $v_{\text{sky}}$  is the sky frequency,  $v_{\text{LO}}$  is the local oscillator frequency, and  $v_{\text{IF}}$  is the intermediate frequency.

directly amplified due to a lack of low noise electronics; instead they are transformed to a lower frequency where they can be suitably amplified. The resulting signal, called the intermediate frequency or  $\nu_{\text{IF}}$ , where  $\nu_{\text{IF}} = \nu_{\text{sky}} - \nu_{\text{LO}}$ , is sent to a spectrometer backend where the data is separated as a function of frequency and stored in a computer. This process is illustrated graphically in Figure 1. Depending on the spectrometer backend, the spectral resolution can range from 30 kHz to 2 MHz and the bandwidth from 4 to 500 MHz. The data is displayed as a spectrum (i.e. signal as a function of frequency) with the intensity axis labeled in units of K, an artifact of early radio astronomy, where the signals were referenced to liquid nitrogen at 77 K. Signal averaging is done with specific data reduction programs that are available at the telescope, such as Unipops or Class, which can also be used to take out baselines and determine the spectral parameters such as line width and intensity.

On the practical side, most modern radio telescopes are under computer control. Tracking of an individual source is done by computer command. The data collected is automatically transferred and stored on computer disks, and the interface between the observer and the telescope is a menu driven system.

The telescope used in the laboratory exercises is the Arizona Radio Observatory 12m telescope on Kitt Peak, Arizona, see Plate 1. This instrument is a single dish radio telescope with a 12m diameter antenna. Because of its large diameter, the telescope can be used to study specific sources in the sky. The solid angle subtended by the telescope, or the beam size  $\theta$ , is related to the wavelength  $\lambda$  being observed by the relationship,  $\theta = 1.2\lambda/D$ , where  $D$  is the diameter of the antenna. The facility operates at wavelengths of 2 and 3 mm or from 65 to 180 GHz in frequency, and can be run 24 hours a day for 9 months of the year. Sky conditions can limit the use of the telescope, with clouds adding noise and rain, snow, or strong winds halting operations. Observers are allocated telescope time, similar to NMR use. However, due to high demand, a committee reviews the observing proposals for merit, with an emphasis on educational programs. The telescope can be used either on-site or remotely through the Internet, allowing observers from around the world to perform measurements. For the remote observing, users employ the same computer interface used at the telescope.

## **A General Laboratory on Molecular Astrophysics**

During this laboratory exercise, graduate students in astrochemistry and astronomy conducted several experiments involving observations using the 12m telescope. Different molecules were chosen to illustrate various concepts. The first exercise concerned HCCCN, cyanoacetylene. This molecule, a widespread interstellar species, has a simple spectrum with only one line per rotational

transition. Hence, the rotational spectrum can be accurately described by two spectroscopic constants  $B$  and  $D$ , see equation 1.

$$\nu = 2B(J + 1) - 4D(J + 1)^3 \quad (1)$$

Here  $\nu$  is the transition frequency,  $B$  is the rotational constant,  $D$  is the centrifugal distortion parameter, and  $J$  is the rotational quantum number. Students were first asked to calculate the frequencies of HCCCN based on these constants and equation 1. Three rotational transitions were chosen by the students to be measured at the telescope in the range of 72 to 163 GHz prior to the observations. This task allowed the students to actively participate in planning the observations. These frequencies were then used at the telescope to detect HCCCN towards a dense cloud, W51M, located approximately 23,000

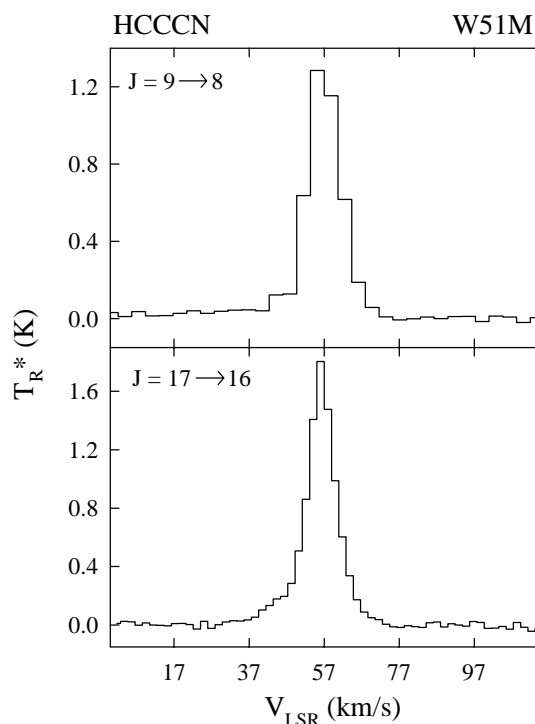


Figure 2. Spectra of the  $J = 9 \rightarrow 8$  (top panel) and  $J = 17 \rightarrow 16$  (bottom panel) transitions of HCCCN observed towards the molecular cloud W51M. Here  $T_R^*$  is the intensity (in K), and  $V_{LSR}$  is the source velocity with respect to the local standard of rest, which is directly related to the frequency via the Doppler relationship.

light years from Earth. All the transitions were readily observable; two are shown in Figure 2. This part of the exercise also gave the students an idea of the overall pattern of the rotational spectrum of a simple linear molecule.

The second exercise concerned a more complex species,  $\text{CH}_3\text{CN}$ . The  $J = 8 \rightarrow 7$  transition of this molecule near 147 GHz was observed towards W51M. The frequencies were provided to the students. In contrast to HCCCN, the spectrum of the  $\text{CH}_3\text{CN}$  molecule, or methyl cyanide, has many components per rotational transition. This species is a symmetric top molecule, and its geometry causes the spectrum to be split into multiple components labeled by the quantum number  $K$  ( $l$ ). These  $K$  components can range from  $K = 0$  up to the value where  $K$  equals the rotational quantum number  $J$ ; i.e.  $K = J$ . Thus, the observed  $J = 8 \rightarrow 7$  transition can have eight  $K$  components from  $K = 0$  to  $K = 7$ . The spectrum of this transition, recorded with the ARO 12m, is displayed in Figure 3. The  $K = 7$  component is blended with other emissions, but the other  $K$  components are visible. Other species are also present in the data, such as  $\text{CH}_3\text{OCH}_3$ . The relative intensities of the  $K$  components can be used to estimate the temperature

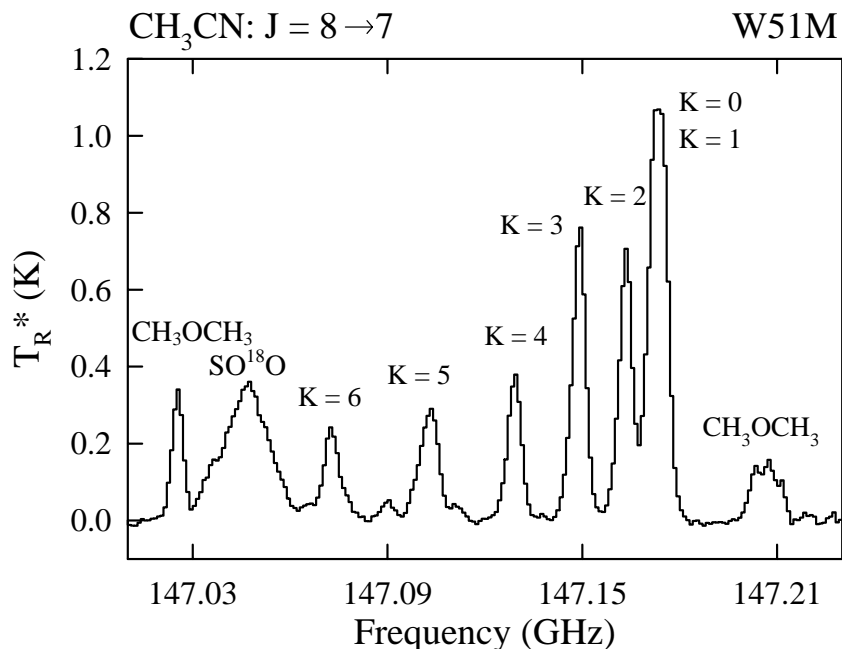


Figure 3. Spectrum of the  $J = 8 \rightarrow 7$  transition of  $\text{CH}_3\text{CN}$  observed towards the molecular cloud W51M using the ARO 12m telescope. The components of the symmetric top pattern are labeled with the quantum number  $K$ . Features due to  $\text{CH}_3\text{OCH}_3$  and  $\text{SO}^{18}\text{O}$  are also present in the bandpass.

of the molecular cloud W51M using a simple Boltzmann relationship, see below. CH<sub>3</sub>CN is a good thermometer because the  $K$  components lie across a range of energies, according to equation 2:

$$E_{\text{rot}} = BJ(J + I) + (A - B)K^2 \quad (2)$$

where  $A$  and  $B$  are the rotational constants of CH<sub>3</sub>CN. The parameter  $A$  is much larger than  $B$  ( $A = 158,099$  GHz and  $B = 9,188.9$  GHz) and thus the second part of equation 2 causes the separation between  $K$  components to quadratically increase in energy as  $K$  increases. Students were asked to calculate the gas kinetic temperature,  $T_{\text{kin}}$ , of W51M from the spectrum. The formula used is:

$$\frac{T(K)}{T(K')} = \frac{g(K)}{g(K')} \cdot \frac{J^2 - K^2}{J^2 - K'^2} \exp\left(\frac{-E_{\text{rot}}(K) + E_{\text{rot}}(K')}{kT_{\text{kin}}}\right) \quad (3)$$

where  $g(K)$  is a factor accounting for spin statistics in the molecule due to its 3-fold symmetry,  $g(K)$  is 2 for  $K = 3, 6, 9$ , etc. and 1 otherwise, and  $k$  is the Boltzmann constant.

The third part of the lab concerned the  $J = 1 \rightarrow 0$  transition of HCN near 88.6 GHz. This line was measured towards the cold, dark cloud L673 (2) and the molecular cloud M17-NW. The nitrogen nucleus has a spin of  $I(N) = 1$ ;  $I$  is the quantum number defining nuclear spin. An important spectroscopic effect of nuclear spin is quadrupole hyperfine structure. Consequently, the spectrum of the  $J = 1 \rightarrow 0$  transition is split into three hyperfine components, indicated by the quantum number  $F$  ( $F = J + I$ ), which provides a spectral fingerprint for HCN. In order of increasing frequency, these transitions are labeled:  $F = 1 \rightarrow 1$ ,  $F = 1 \rightarrow 2$ , and  $F = 1 \rightarrow 0$ . The intrinsic, or fundamental, intensity of the three hyperfine lines is determined by quantum mechanics, and should be related to the quantity  $(2F + 1)$ . Hence, the LTE intensity ratio should be on the order of 3:5:1. This ratio is evident in the spectrum of HCN towards M17-NW, see the top panel of Figure 4. The line marked U is an unknown feature. However, physical processes in the interstellar medium can change the observed intensities of the lines from the expected ratio. Opacity, or line trapping, can alter the LTE ratio, and this effect is evident in the observed spectrum of HCN towards L673, as seen in the bottom panel of Figure 5. The observed ratios of the HCN lines are approximately 1.1:1.8:1.0. Line trapping occurs when a species is very abundant and some of the radiation that is emitted by the molecule is continuously reabsorbed by the same species until it is lost to collisions. When such line trapping occurs, the molecule is said to be “optically thick”. This effect is described by the equation:  $T_{\text{R}} = T_{\text{ex}}(1 - e^{-\tau})$ , where  $T_{\text{R}}$  is the observed intensity,  $T_{\text{ex}}$  is the excitation temperature, and  $\tau$  is the optical depth parameter.

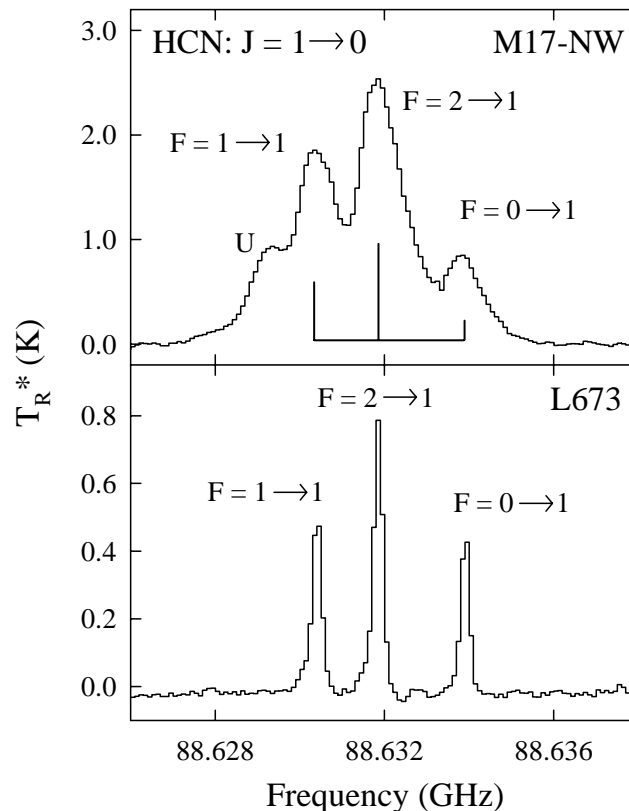


Figure 4. Spectra of the  $J = 1 \rightarrow 0$  transition of HCN observed towards the molecular clouds M17-NW (top panel) and L673 (bottom panel) using the ARO 12m telescope. The three quadrupole hyperfine components are labeled with the quantum number  $F$ , and their relative intensities (3:5:1) are indicated by the stick spectrum underneath the data in the top panel.

The frequencies of the observed hyperfine components were also used to estimate the quadrupole coupling constant for HCN. The splitting of the three components is related to the value of the quadrupole parameter,  $eQq$ , which is associated with the electric field gradient of the electrons across the nucleus with the quadrupole moment (3). The students measured the line frequencies, and calculated  $eQq$  using the following equation,

$$E_{eQq} = eQq \frac{\frac{3}{4}C(C+1) - I(I+1)J(J+1)}{2I(2I-1)(2J-1)(2J+3)} \quad (4)$$



where  $C = F(F + 1) - I(I + 1) - J(J + 1)$ , and  $F = J + I$ .

Finally, the students were asked to observe the  $J = 2 \rightarrow 1$  transition of SiO in its ground and first excited vibrational states,  $v = 0$  and  $v = 1$ , near 86.8 and 86.2 GHz, respectively, towards the star Chi Cygni, or Chi Cyg (4). The resulting spectra are shown in Figure 5. The intensity of the  $v = 0$  data is about 0.4 K (top panel); however, the  $v = 1$  line (bottom panel) shows much stronger emission near 9 K and a narrower line profile. These transitions were observed to illustrate maser emission in space. (A maser is a laser at microwave wavelengths.) The  $J = 2 \rightarrow 1$  transition in  $v = 1$  is pumped by infrared radiation emitted by the star, which creates a population inversion. Hence, maser action occurs for this line. The students calculated the vibrational temperature of SiO based on these two transitions. The result is a negative value ( $T_{\text{vib}} = -600$  K) – a nonphysical temperature indicating non-thermal emission from the  $v = 1$  state.

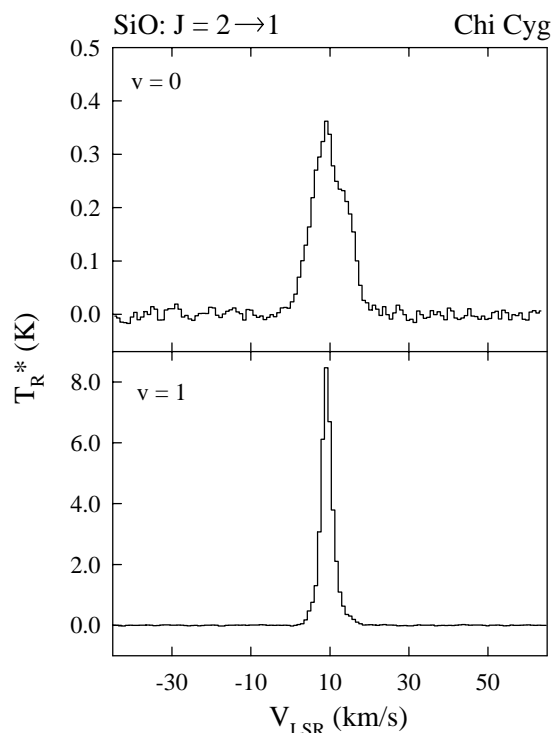


Figure 5. Spectrum of the  $J = 2 \rightarrow 1$  transition of SiO observed towards the star Chi Cygnus using the ARO 12m telescope, showing the  $v = 0$  transition near 82.8 GHz (top panel), and the  $v = 1$  line near 82.2 GHz (bottom panel). The line intensity of the  $v = 1$  transition indicates that this feature is a maser.

A handout describing the molecules and sources to be observed, as well as the procedure for the observations, was prepared and given to the students prior to the laboratory. The students analyzed the collected data, and were given accompanying questions and calculations. A picture of some of the students observing at the ARO 12m telescope is given in Plate 2.

### **A Laboratory in Applying Molecular Spectroscopy for the Detection of Interstellar Molecules**

Observations of molecular emission would not be possible without a priori knowledge of the spectral-line transition frequencies. Therefore, an exercise was prepared where students recorded the rotational spectrum of several known interstellar molecules in the laboratory, and took the resulting frequencies and spectroscopic constants to the ARO 12m and observed the same species in the interstellar medium. This laboratory was first developed for a mix of biology and astronomy graduate students. It is currently being remodeled as an exercise for chemistry graduate students taking an introductory spectroscopy course. The students used laboratory spectrometers already in place at the University of Arizona to first record rotational transitions of several molecules. The relatively simple systems  $\text{HCO}^+$  and  $\text{HCCCN}$  were used to demonstrate the steps involved in first identifying a molecule in the laboratory, fitting rotational constants to the measured frequencies, and accurately predicting the complete spectrum.

The spectrum of  $\text{HCO}^+$  was investigated initially using a millimeter/submillimeter spectrometer. This species is transient and requires exotic synthesis methods. It has to be produced in the gas phase from the reaction of CO and  $\text{H}_2$  in the presence of an AC discharge. For this section, the students were given the rotational constant of  $\text{HCO}^+$ ,  $B = 44,594.4 \text{ MHz}$  (5), and asked to calculate the frequency of the  $J = 2 \rightarrow 3$  transition near 267 GHz only using the  $B$  value (see equation 1). The spectrum of this transition of  $\text{HCO}^+$  was recorded, as shown in the bottom panel of Figure 6, and the calculated frequency was compared to the measured frequency. The difference is due to centrifugal distortion and this effect is taken into account by the constant  $D$ , see equation 1. The students then estimated the value of the  $D$  parameter and used that value to predict the frequency of the  $J = 3 \rightarrow 4$  transition of  $\text{HCO}^+$  near 356 GHz, using equation 1. The spectrum of this transition was measured and the frequency recorded. Both lines were then used to determine more accurate values of  $B$  and  $D$  for  $\text{HCO}^+$ .

As a second task, the students conducted measurements with a very high-resolution Fourier transform microwave (FTMW) spectrometer at the University of Arizona. This machine consists of a large resonant cavity created between two spherical mirrors. Molecules are introduced into the cavity in a supersonic

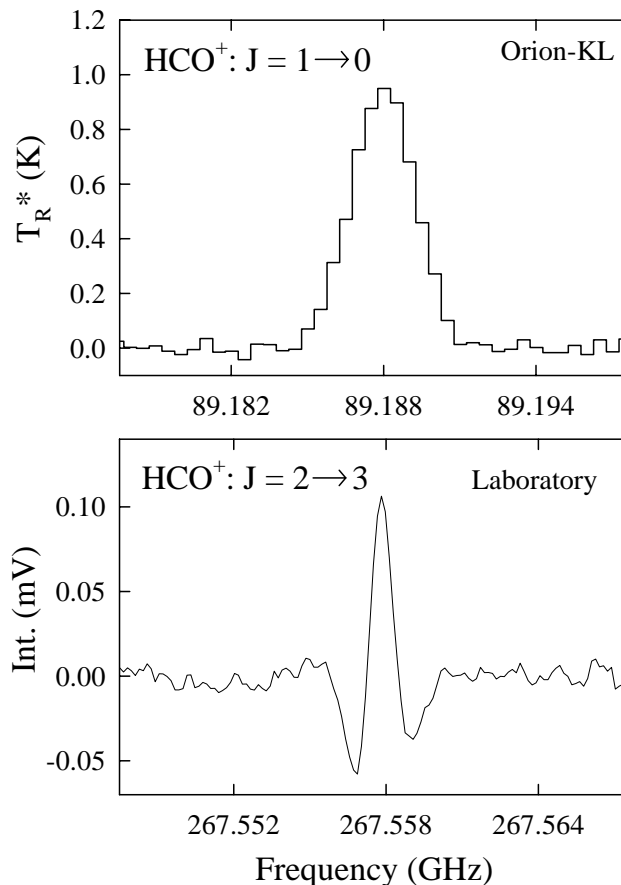


Figure 6. A combined lab/astronomical study of  $\text{HCO}^+$ . The  $J = 1 \rightarrow 0$  transition near 89 GHz was observed towards the molecular cloud Orion-KL, based in part on the  $J = 2 \rightarrow 3$  transition near 267 GHz that previously was recorded in the laboratory.

jet. Microwave pulses are then used to excite these molecules into a higher energy state, and they spontaneously decay over time. The emitted radiation is recorded as a function of time for each transition; i.e. a “free induction decay” (FID). The Fourier transform of the FID results in a frequency spectrum, similar to NMR. Each spectral line in this machine is split into two Doppler components due to the orientation of the supersonic jet source relative to the resonant cavity. A precision of better than 1 part in  $10^8$  is obtainable from this instrument.

This system was used to measure the spectrum of HCCCN, a highly reactive (sometimes explosive) gas that is not commercially available. Hence, it has to be synthesized by an exotic production method. HCCCN was made from a 0.75%:0.75% gas mixture of acetylene (C<sub>2</sub>H<sub>2</sub>) and cyanogen (NCCN) highly diluted in argon (98.5%) in the presence of a 900 V DC discharge. This mixture was pre-made for the students. The dilution in argon made it extremely safe. In this exercise, the students measured the two lowest lying rotational transitions ( $J = 1 \rightarrow 0$  and  $J = 2 \rightarrow 1$ ) of HCCCN using the FTMW spectrometer. HCCCN was introduced into the reaction chamber and pulses of microwave radiation at two specific frequencies were used to excite the two rotational transitions of interest. First, the  $J = 1 \rightarrow 0$  transition near 9 GHz was measured, followed by the  $J = 2 \rightarrow 1$  line near 18 GHz. These data were then used to determine the rotational constants,  $B$  and  $D$ . The  $J = 1 \rightarrow 0$  transition for this molecule is additionally split into three components due to electric quadrupole coupling. The splitting of the three lines was used to determine the spectroscopic constant  $eQq$  for HCCCN.

The students also measured the  $J = 2 \rightarrow 1$  transitions of the rare <sup>13</sup>C and <sup>15</sup>N isotopic species of HCCCN: H<sup>13</sup>CCCN, HC<sup>13</sup>CCN, HCC<sup>13</sup>CN, and HCCC<sup>15</sup>N in natural abundance. Despite the small change in mass resulting from using <sup>13</sup>C instead of <sup>12</sup>C or <sup>15</sup>N vs. <sup>14</sup>N, the frequency of the transitions and hence the rotational constants will vary considerably with each isotopically-substituted species. These data were consequently used to precisely determine the structure of HCCCN, which is shown in Figure 7. A spectrum of the  $J = 2 \rightarrow 1$  transition of HCC<sup>13</sup>CN is displayed in Figure 8.

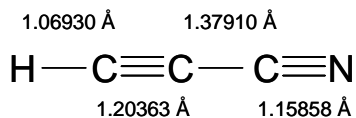


Figure 7. The HCCCN molecule showing the lengths of the four bonds.

Using the spectroscopic parameters for HCO<sup>+</sup> and HCCCN, the students then observed the  $J = 1 \rightarrow 0$  transition of HCO<sup>+</sup> and the  $J = 9 \rightarrow 8$  transition of HCCCN in the Orion molecular cloud. The spectrum recorded for HCO<sup>+</sup> is displayed in the top panel of Figure 6. These results demonstrated to the students that unusual species present in interstellar gas can be made under extreme conditions for fractions of seconds on Earth.

For the introductory spectroscopy course, the laboratory exercise will include measurements of the spectrum of CH<sub>3</sub>CN, methyl cyanide or acetonitrile, using a millimeter/submillimeter spectrometer. The  $J = 18 \rightarrow 19$  and  $19 \rightarrow 20$  transitions of CH<sub>3</sub>CN will be measured near 350 and 368 GHz. As stated earlier, this species is a symmetric top molecule and has several  $K$

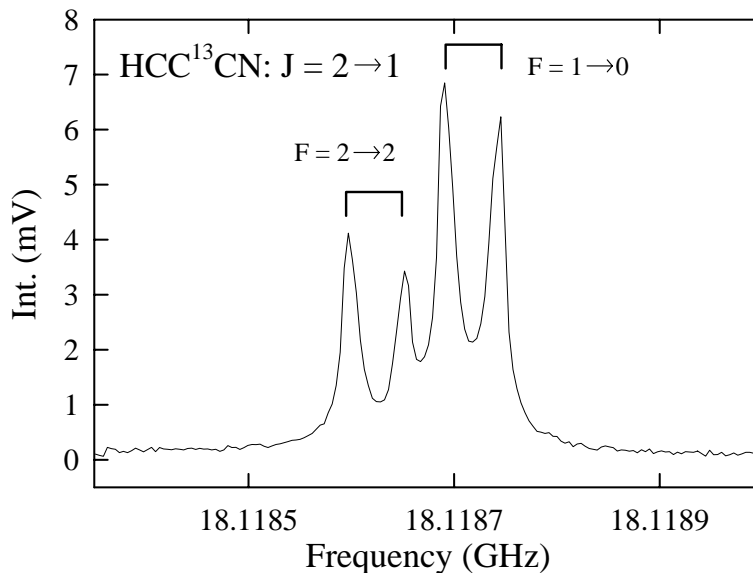


Figure 10. The  $J = 2 \rightarrow 1$  transition of  $\text{HCC}^{13}\text{CN}$  near 18 GHz showing two quadrupole hyperfine lines observed in the spectrum. Each component has a double peak profile due to the orientation of the molecular flow with respect to the microwave cavity.

components per rotational transition. The spacing between the lines starting at  $K = 0$  has a ratio of 1:3:5:7, etc. A sufficient frequency range will be scanned to cover up to  $K = 10$ . With these data, the students will be asked to determine the spectroscopic constants that characterize a symmetric top:  $B$ ,  $D_J$  and  $D_{JK}$ , using equation 6.

$$\nu = 2B(J + 1) - 4D_J(J + 1)^3 - 2D_{JK}(J + 1)K^2 \quad (6)$$

### Educational Level and Operational Modifications

A modified version of the spectroscopy exercise could be conducted for physical chemistry laboratory courses, and could even be simplified to be used for honors freshman chemistry labs. In order to obtain frequencies that are accessible with radio telescopes, measurements have to be conducted at microwave or millimeter wavelengths. Spectrometers that operate in this range are not readily available to physical chemistry teachers; however, a simple direct

absorption spectrometer can be constructed at microwave wavelengths. Microwave sources and detectors are commercially available. Microwave Gunn oscillator sources and room temperature detectors can be purchased for \$1000 each. A steel or glass cell, optics components, a Welch pump, and a pressure gauge are also needed and can be constructed or bought. Measurements of several known interstellar molecules, such as OCS, N<sub>2</sub>O, SO<sub>2</sub>, can be conducted with this simple instrument. Isotopic species of these molecules could also be studied in natural abundance for structure determinations.

The astrophysical version could be used for high school physics and astronomy classes for search and discover activities, in a simplified form. For elementary school, the concept of "space chemistry" can be illustrated by the many different types of species observed, such as N<sub>2</sub>H<sup>+</sup>, CCH, HC<sub>3</sub>N. Atomic emission from hydrogen H $\alpha$  lines also observed at radio telescopes can be used to exemplify the Bohr atom.

### Additional Resources

Resources with more information on laboratory rotational spectroscopy and radio astronomy are available. The Ziurys group maintains a website with information on rotational spectroscopy and links to other resources (6). The ARO website features descriptions of the 12m radio telescope and science conducted at millimeter wavelengths (7). Several books are available that describe rotational spectroscopy and radio astronomy in detail (e.g. 1,3,8).

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*Plate 1. The Arizona Radio Observatory (ARO) 12m telescope on Kitt Peak, Arizona was used for the laboratories.*



*Plate 2. Astronomy graduate students Marc-André Besel and Wiphu Rujopakarn observing at the ARO 12m telescope. Telescope operation and data processing are all conducted via computer interface.*