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HIGH RESOLUTION INFRARED SPECTROSCOPY OF PLANETARY MOLECULES USING DIODE LASERS AND FOURIER TRANSFORM SPECTROMETERS

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ABSTRACT

Modern observations of infrared molecular lines in planets are performed at spectral resolutions which are as high as those available in the laboratory. Analysis of such data requires laboratory measurements at the highest possible resolution, which also yield accurate line positions and intensities. For planetary purposes the spectrometer must be coupled to sample cells which can be reduced in temperature and varied in pressure. An approach which produces the full range of required molecular line parameters uses a combination of tunable diode lasers and Fourier transform spectrometers. The FTS provides broad spectral coverage and good calibration accuracy, while the diode laser can be used to study those regions which are not resolved by the FTS.

INTRODUCTION

The number of molecules known to be present in planetary atmospheres has grown tremendously in recent years. Ten planets and moons in the solar system have molecular atmospheres. These atmospheric bodies are listed in Table 1 (from Jennings, 1988). Spectra of the outer planets from the Voyager encounters show many molecular features, with Titan showing the greatest variety.
The Voyager Infrared Interferometer Spectrometer (IRIS) has provided high spatial resolution infrared spectra of the Jupiter, Saturn, Uranus, and Neptune systems. With the aid of laboratory spectra from our program, IRIS identified six molecular species in Titan's atmosphere which had not been seen on planets (Maquire et al. 1981, Kunde et al. 1981, Samuelson et al. 1983). Condensed phases of complex organics have also been identified on Titan (Khana et al. 1987).

Ground-based spectrometers now have spectral resolutions high enough to completely resolve molecular line profiles on planets. Several types of high resolution spectrometer are used for ground-based and airborne observations of planets. Infrared laser heterodyne receivers have produced spectra of narrow molecular features on Mars, Venus and Jupiter (Betz et al. 1976, Kostiuk et al. 1983). Fourier transform spectrometers have been operated on large telescopes at Mt. Palomar (Connes and Michel 1975) and Kitt Peak (Hall 1976, Wiedemann et al. 1989), as well as the KAO

TABLE 1.   MOLECULES IN THE SOLAR SYSTEM

OBJECT	MAJOR SPECIES	MINOR SPECIES
Venus	CO_2	H_2O, CO, HCl, HF
Earth	N_2, O_2	H_2O, CO_2, CH_4, NO, O_3, N_2O, CO, NH_3, HF, HCl...
Mars	CO_2	N_2, O_2, CO, H_2O, H_2, O_3, NO
Jupiter	H_2	NH_3, PH_3, CH_4, CH_3D, C_2H_6, C_2H_4, C_2H_2, H_2O, GeH_4, CO, HCN, HD
Io		SO_2
Saturn	H_2	NH_3, PH_3, CH_4, CH_3D, C_2H_6, C_2H_2, CO
Titan	N_2	H_2, CH_4, CH_3D, C_2H_2, C_2H_4, C_2H_6, C_3H_4, C_3H_8, C_4H_2, HCN, HC_3N, C_2N_2, CO_2, CO
Uranus	H_2	CH_4
Neptune	H_2	CH_4, C_2H_6
Triton	CH_4 (or N_2)	
Pluto	CH_4	
Sun		CO, C_2, CH, CN, NH, OH, MgH, CaH, TiO, SiH, ZrO, CoH, NiH, H_2O, H_2, SiO
Comets		C_2, C_3, CH, CN, CO, CS, NH, NH_2, OH, H_2O, S_2, HCN, CH_3CN, CO^+, CO_2^+, CH^+, H_2O^+, OH^+, N_2^+, CN^+

(Larson and Fink 1975). A Fabry-Perot spectrometer has observed molecules on Jupiter (Tokunaga et al. 1981, Drossart et al. 1986).

Our laboratory at Goddard Space Flight Center interacts closely with observational astronomers so that important infrared molecular problems can be identified and addressed early. The correct interpretation of a feature occurring in a planetary spectrum follows not only from information about the species which are known to be present, but also from knowledge of possible minor constituents which have spectra in the region of interest. Complete interpretation of planetary spectra requires knowledge of line frequencies and strengths, vibration-rotation constants, and line broadening coefficients (as functions of temperature). Laboratory determinations of these parameters must be continually refined to keep pace with the improving planetary results.

LABORATORY STUDIES RELATED TO PLANETARY OBSERVATIONS

Jovian C_2H_6 and C_2H_2

Our group has an ongoing program of observations of Jupiter in the 12-micron ethane band using our post-disperser coupled to the FTS at the Kitt Peak 4-meter telescope. An observed spectrum is shown in Figure 1. Prior to the observations we recorded a low temperature (140 K) laboratory spectrum of this ethane fundamental band with the 1-meter FTS located at the McMath telescope at Kitt Peak. The Jovian and laboratory spectra are compared in the figure. The features apparent in the Jovian spectrum are due to $^{12}C^{12}CH_6$. Elsewhere in the spectrum we have observed the RQ_0 Q-branch of $^{13}C^{12}CH_6$, which was not expected to be detectable. The detection of C-13 ethane, and the overall interpretation of the ethane spectra were greatly facilitated by the laboratory data.

During the same observations we measured acetylene line intensities near 755 cm^{-1} at various locations on the Jovian disk, including the "hot spot" identified by Caldwell et al. (1980). Our own laboratory spectra of acetylene, recorded with the 1-meter FTS, are being used to supply line strengths for the analysis of the Jovian data.

Support of Heterodyne Observations

Another observing technique which yields very high spectral resolution on planets is infrared heterodyning with CO_2 lasers. The Goddard Space Flight Center heterodyne receiver was used to detect narrow high-altitude emission lines from 12-micron ethane on Jupiter (Kostiuk et al. 1983). Before the search for this emission was begun a list was needed of precise frequencies for ethane transitions in the 12-micron band which would be within 0.1
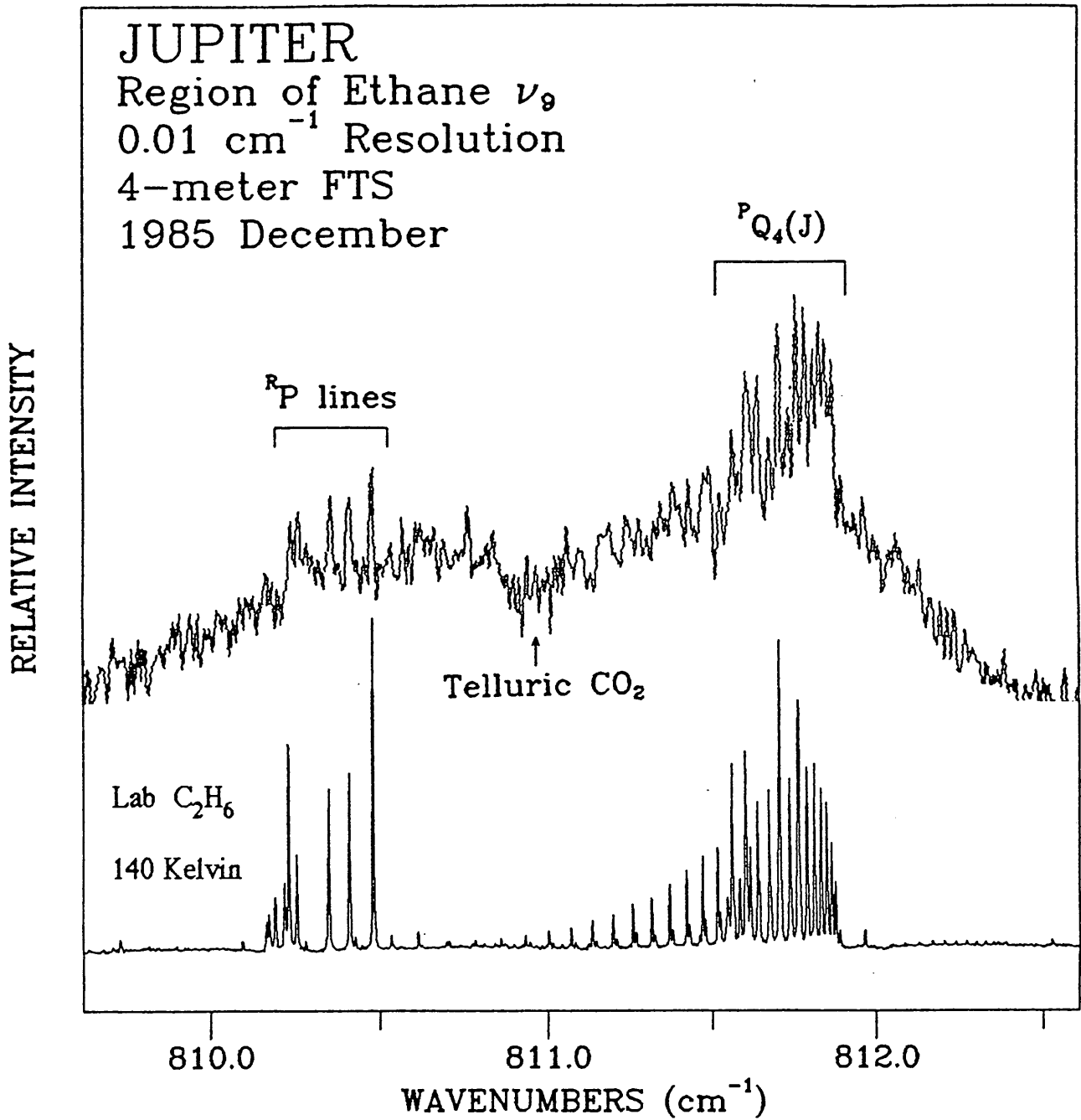
Figure 1. A portion of the high resolution FTS spectrum of
ethane in Jupiter compared with a laboratory
spectrum taken at 140 Kelvin (Jennings, 1988).

cm^{-1} of $^{14}CO_2$ laser lines at various geocentric source velocities, corresponding to dates on which the observations would take place. Ethane line intensities were also required to aid in choosing the strongest candidates for observation. This spectral information was derived from a combination of diode laser and FTS data for the 12-micron band. Thermal emission features due to the J=16 and 17 doublets, observed in the heterodyne spectra of Jupiter, are compared with diode laser spectra in Figure 2.

The 12-micron band of ethane is a prime candidate for study in the outer planets using high resolution instruments such as FTS and laser heterodyne spectrometers. We have published a laboratory analysis of this band (Susskind et al. 1982, Daunt et al. 1984). In that work Fourier transform spectra and diode laser spectra were combined to produce a complete characterization of the band. This culminated in a line atlas (Atakan et al. 1983) which is generally available to atmospheric modelers. Line broadening of ethane by hydrogen was measured at temperatures from 95 to 300 K (Halsey et al. 1988).

High Resolution Spectra of Hydrocarbons

Complex hydrocarbons gained a new degree of importance in planetary physics with the detection by Voyager of propane, diacetylene and methylacetylene on Titan (Maguire et al. 1981; Kunde et al. 1981). These added to the already known planetary hydrocarbons methane, acetylene, ethylene, and ethane. Because of the high line density in the infrared spectra of these molecules, very high spectral resolution is needed to resolve the rotational structure within bands when performing laboratory studies. It is important to completely resolve the line structure in these studies because only in this way can modeling of planetary spectra be correct in detail. Moreover, weaker hot band features which contribute to planetary spectra can only be studied by resolving the stronger main-band structure. High resolution laboratory spectra is, of course, also needed when individual line parameters (position, strength, broadening) are to be derived for use in high resolution observations of planets. We have devised a technique for double-passing the 1-meter FTS at Kitt Peak to improve its resolution to 0.0025 cm^{-1}. This was done in a simple manner (described in section 5.1) which retained the high quality of the spectra produced by this instrument. Spectra of many hydrocarbons (methane, methane-d, ethylene, ethane, propane, acetylene, methylacetylene, allene, and silane) were recorded for reference purposes, so that band structure and line parameters could be found when needed. These are supplemented with diode laser spectra in regions where doppler-limited resolution is required.

In addition to spectroscopy at mid-IR wavelengths, we have systematically studied the line intensities and pressure broadening parameters in the R-branch of $3\nu_3$ of methane near 1.1
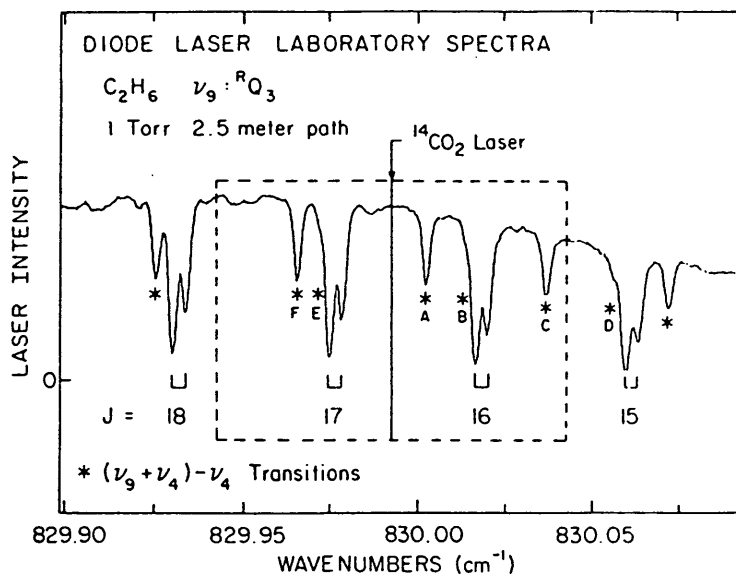
Figure 2a. Diode laser laboratory spectra in the region of $^R Q_3$ of ethane near 12 microns (Kostiuk et al. 1983).
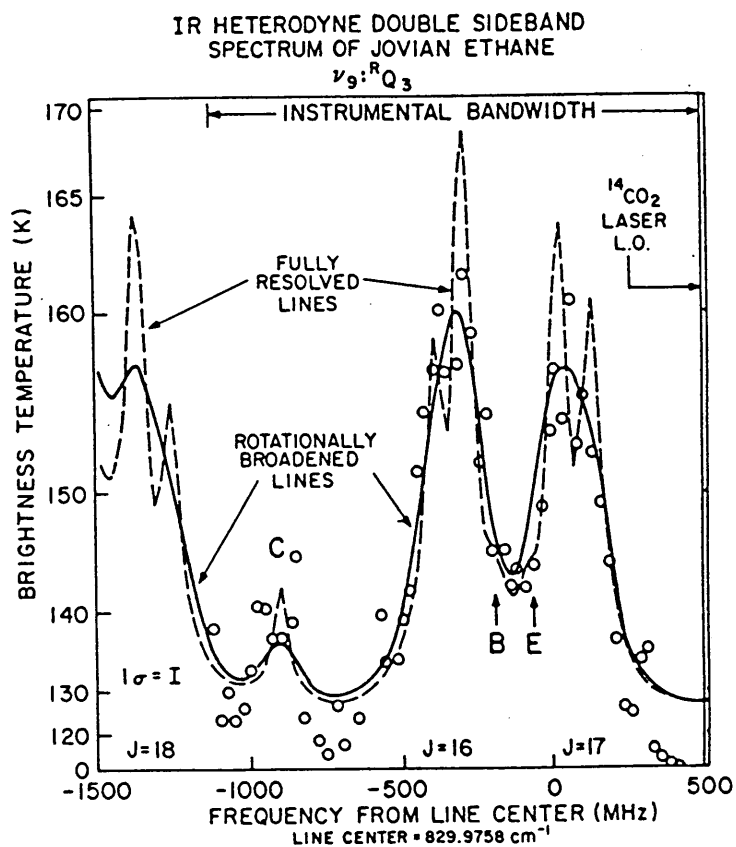

Figure 2b. Jovian stratospheric emission from ethane in the same region as Figure 2a, observed with the CO_2 laser heterodyne receiver (Kostiuk et al. 1983).

micron (Brault et al. 1981, Fox and Jennings 1985, Fox et al. 1988). These lines are important in that they can be observed on the outer planets using ground-based facilities. Broadening by hydrogen, helium, nitrogen and argon have been measured. We are new deriving pressure shifts of these lines, easily visible in the spectra (Fox and Jennings, 1989). This study has recently been extended to the v_3 band at 3 microns.

Temperature Dependence of Line Broadening

A goal of this laboratory program since its beginning has been to measure the line broadening parameters for planetary molecules as a function of temperature. This temperature dependence is especially important in predicting the profiles of molecular bands in the outer planets where the temperature is well below "room temeprature." Extrapolating broadening parameters from 300 K laboratory results to ~150 K planetary conditions can introduce significant errors.

We have designed and constructed a low temeprature sample cell (described in section 5.3) which can be operated at any temperature between 50 and 300 K. We have completed a diode laser study of line broadening in the 12-micron band of ethane as a function of temperature (Halsey et al. 1988), and the results of this work are shown in Figure 3. The broadening follows a 1/T law, which is a stronger dependence on temperature than was expected from hard-sphere collision theory. We also regularly use the 1-meter FTS at Kitt Peak to record temperature dependent spectra at 0.0025 cm^{-1} resolution. Molecules whose spectra have been recorded at low temperature so far in our program are methane, ethylene, ethane, and propane.

Hot Bands of Acetylene and Ethane

One would expect, at the low temepratures of the outer planets, that hot bands of gases would be absent in observed spectra. Hot bands arise from lower levels which are above the vibrational ground state of a molecule. It is now apparent at high resolution, however, that hot bands do contribute to observed spectra. In heterodyne spectra of the 12-micron v_9 band of ethane in Jupiter's stratosphere we found weak features due to $(v_9 + v_4) - v_4$. Drossart et al. (1985) detected $(v_4 + v_5) - v_5$ and $2v_5 - v_5$ lines of acetylene near 14 microns in the north "hot spot" region of Jupiter. Molecules such as ethane and acetylene which have low-lying vibrational states can have significant populations in these states even at temperatures around 150 K. Hot band lines are very sensitive probes of atmospheric temperature in regions of line formation.

We have now begun identifying and analyzing hot bands in the 12-micron region of ethane and the 14-micron region of acetylene. Spectra have been recorded of both gases using the 1-meter FTS at
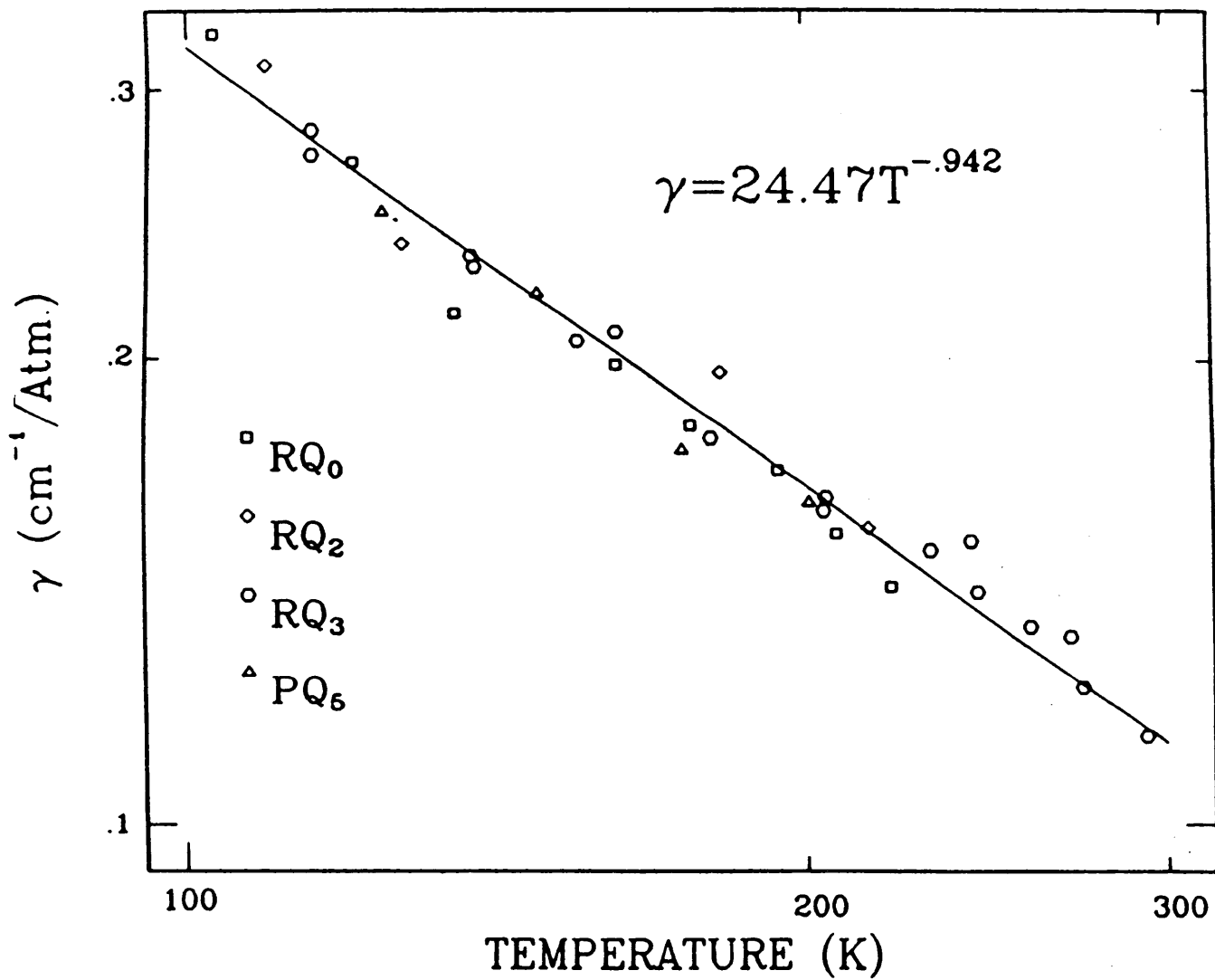
Figure 3. Temperature dependence of line broadening in the 12-micron
band of ethane due to hydrogen. Note the log-log plot.
(Halsey etal. 1988.)

Kitt Peak. We set the FTS up in double-pass configuration to give 0.0025 cm^{-1} resolution. The spectra were recorded with a variety of gas pressures and path lengths. From these spectra we identified seven hot bands in the v_5 region of acetylene and have identified the major $(v_4 + v_9)$-v_4 lines in ethane.

The 13-micron Spectrum of Propane

The 13-micron band of propane was identified by the Voyager 1 infrared spectrometer in the atmosphere of Titan (Maguire et al, 1981). Low resolution spectra were recorded by us for use in identifying propane in the Voyager spectra, and for deriving a band strength for the abundance determination.

Because of the complexity of the vibration-rotation structure in this band, very little laboratory work has been performed at high spectral resolution. It is important, however, to understand the detailed line structure in this region, because the band profile cannot be accurately modeled otherwise, and because the contributions from hot bands, which vary with temperature, cannot be predicted.

We have been pursuing an analysis of high resolution spectra of the 13-micron v_{21} band of propane in our laboratory. An assymetric-rotor analysis of this band has produced preliminary rotation-vibration constants. These have been made available to the Voyager IRIS team. The analysis is based on high resolution FTS data (0.0025 cm^{-1}) recorded at Kitt Peak at both room temperature and 175 K (see Figure 4), as well as diode laser spectra. Diode laser spectra have also been used to measure pressure broadening of lines in the 13-micron band due to H_2, N_2, and He (Figure 5).

INSTRUMENTATION

We use two types of spectrometers to perform high resolution spectroscopy. The 1-meter Fourier transform spectrometer of the National Solar Observatory at Kitt Peak is used to provide up to 0.0025 cm^{-1} resolution in the 1-20 micron range. A tunable diode laser spectrometer provides ~10^{-4} cm^{-1} resolution in the regions where the structure is not sufficiently resolved by the FTS.

Fourier Transform Spectroscopy

The high resolution FTS used in this work is operated by the National Solar Observatory and is a facility instrument at the McMath Solar Telescope at Kitt Peak. This 1-meter path difference interferometer can be operated in the single-sided interferogram mode with a resolution 0.005 cm^{-1}. The spectral coverage with several beamsplitters is from the ultraviolet to 20 microns

PROPANE at 175 and 296 Kelvin

v_{21} band   13.3 microns

Resolution : 0.0025 cm^{-1}

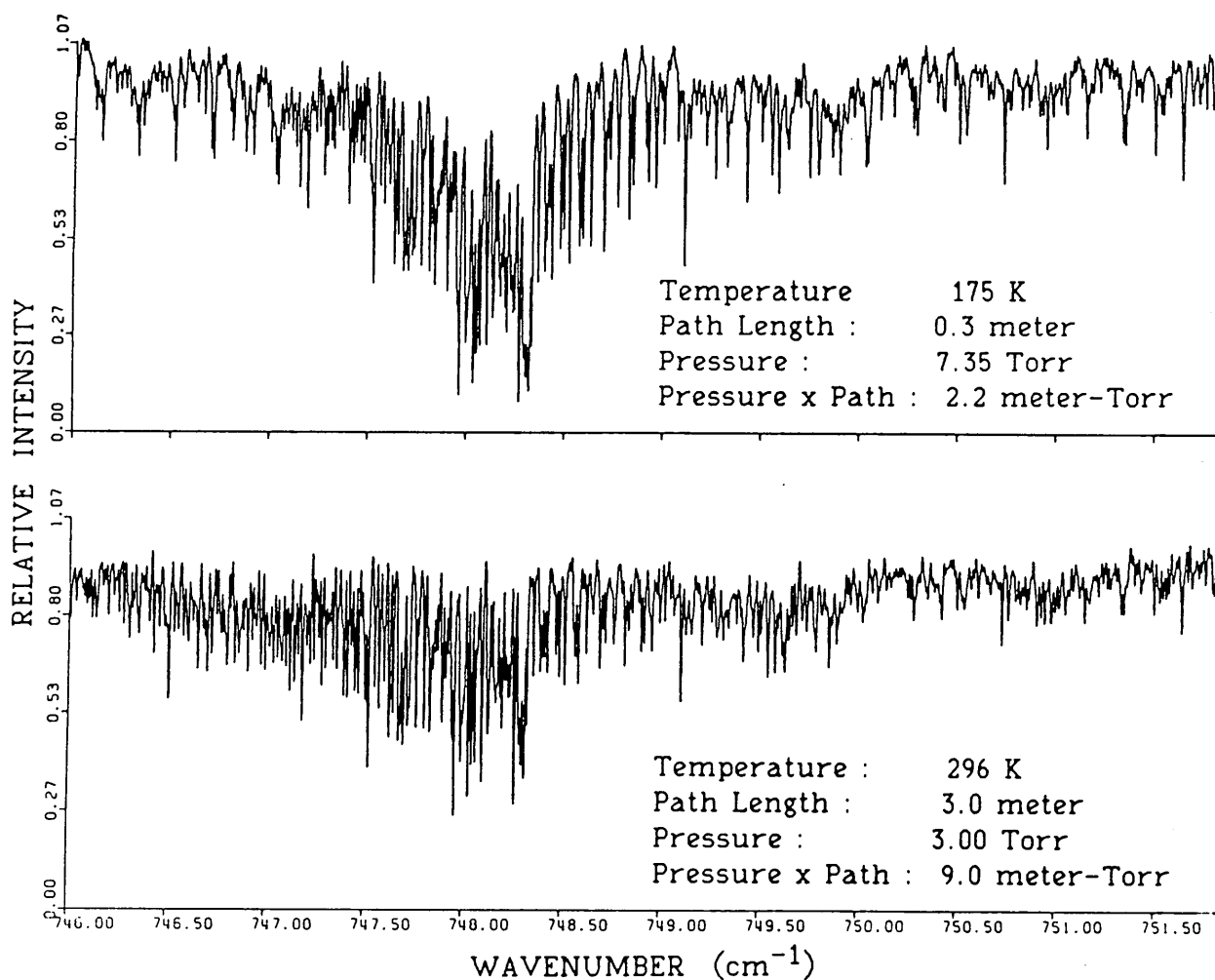Kitt Peak 1-meter FTS and Goddard Cryo-cell

Figure 4.   Comparison of the Q-branch region in the 13-micron band of
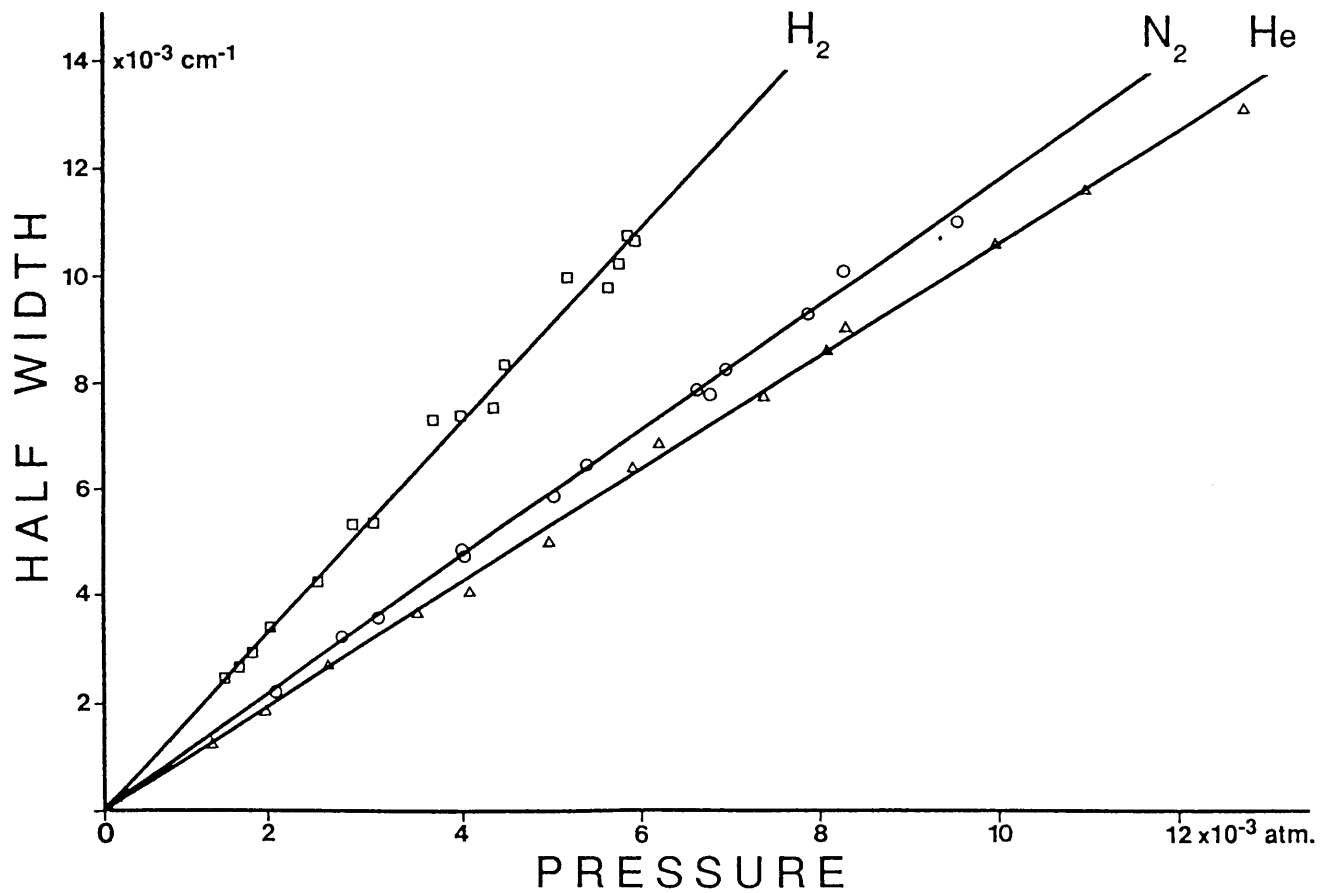propane at room temperature and at 175 K.

Figure 5.   Plots of the foreign-gas broadening widths (HWHM)
             as functions of pressure for propane broadened by
             hydrogen, nitrogen, and helium (Nadler and Jennings
             1989).

wavelength. Absolute calibration accuracy throughout this range exceeds 10^{-4} cm^{-1}. A variety of auxiliary equipment is available for laboratory spectroscopy using this instrument, including a 6-meter multiple traversal sample cell adjustable to 434 meters path.

The technique for double-passing the 1-meter FTS at Kitt Peak (Jennings, et al. 1985) is described by Figure 6. In conventional operation the instrument uses separated beamsplitter and recombiner, accepting radiation from two input ports and sending it to two output ports. The second input is not normally used for laboratory work with this instrument. To double the optical retardation of the instrument we place two mirrors and a compensator in the beams before the recombiner. These mirrors return the beams through the cat's-eyes to the beamsplitter and the modulated signal is detected at the second input. When single-sided interferograms are run the maximum optical retardation is 2 meters, yielding 0.0025 cm^{-1} resolution.
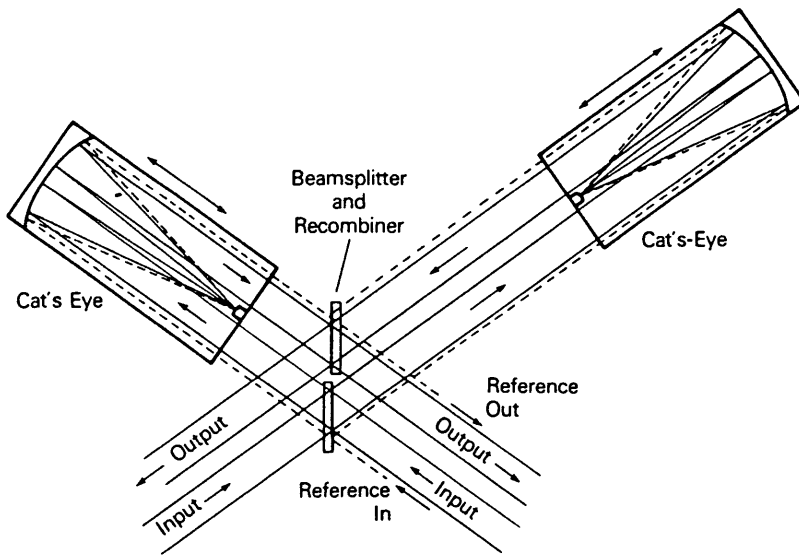
Diode Laser Spectroscopy

A schematic of the GSFC tunable diode laser spectrometer is shown in Figure 7. Th figure is taken from detailed desciptions of the spectrometer which have appeared in the literature (Jennings 1980, 1988). The instrument uses diode lasers manufactured by Laser Analytics which are mounted in a closed-cycle mechanical helium refrigerator. Coarse tuning of the laser frequency is accomplished by adjusting the refrigerator temperature in the range 9-80 K. The laser frequency is fine-tuned by sweeping the injection current. Devices have been invented in this laboratory for stabilizing the output frequency of diode lasers operated on methanical refrigerators (Jennings and Hillman 1977a,b).

The spectrometer is dual-beam, permitting sample spectra to be recorded simultaneously with either reference spectra or calibration etalon fringes. The optical beam is divided between two paths with either a rotating mirror chopper or wedged beamsplitter. Each path can accommodate a one-meter long absorption cell or combinations of etalons and cells. A multiple-traversal cell (up to 140 meters) can be inserted into one of the beam paths before the detector. The other beam is passed through an etalon to generate calibration fringes. Confocal etalons are used for calibrating the diode spectra; a 50 cm etalon produces fringes with 0.005 cm^{-1} spacing and 0.0001 cm^{-1} widths (Jennings 1984).

Data acquisition and recording is done using signal averaging. The diode laser is modulated at about 50 Hz and successive sweeps are averaged. The two detector signals are accumulated separately. For strong laser outputs the signal-to-noise can approach 10^4 after 30 seconds of accumulation. The advantage of signal averaging in this manner is that the diode mount

FTS Optical Schematic

A.) Dual-Beam Configuration
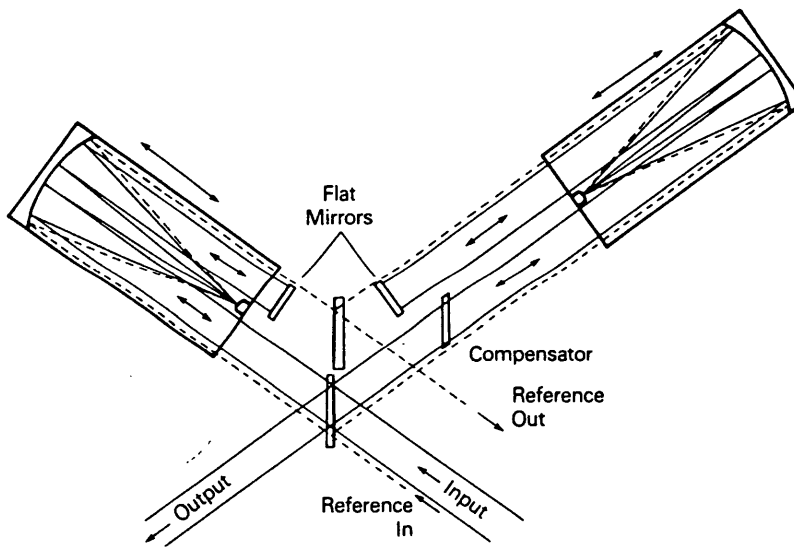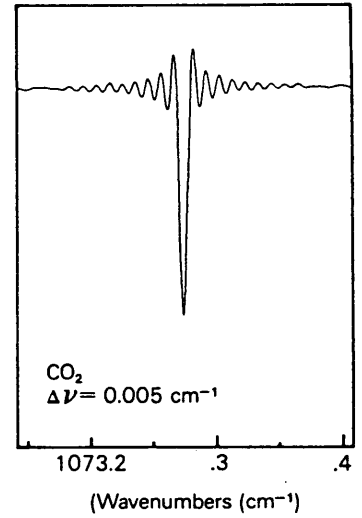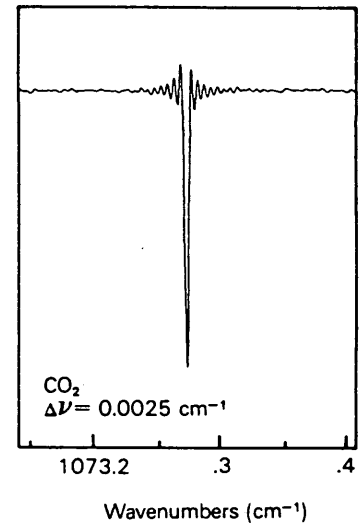

B.) Double-Pass Configuration

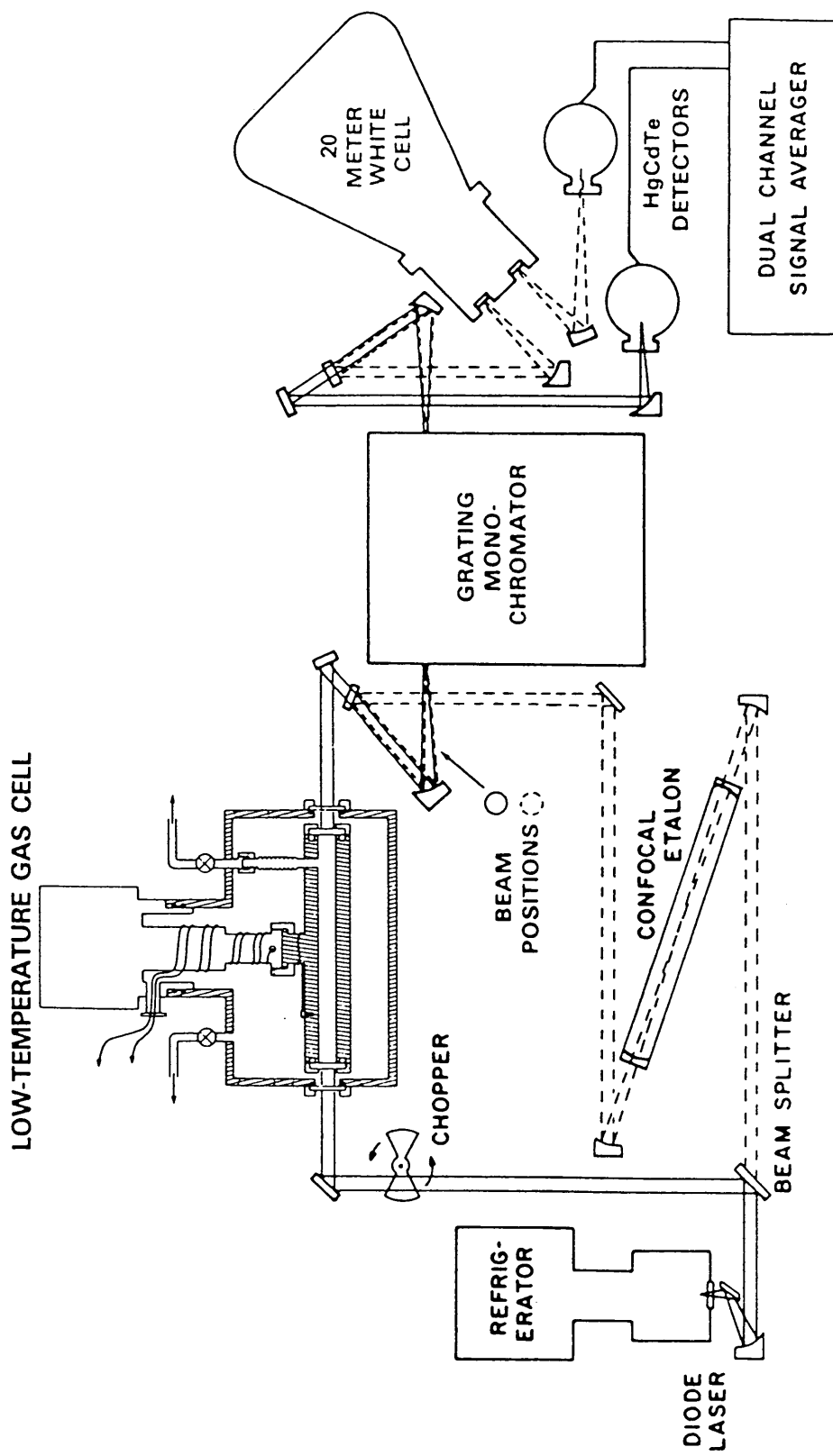Figure 6.   Single-pass (A) and double-pass (B) configurations of the 1-meter FTS at Kitt Peak (Jennings etal. 1985).

Figure 7. Schematic of the diode laser spectrometer.

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temperature reaches equilibrium with the average laser current and does not change during a scan. Temperature dependent variation of frequency sweep rate and laser output structure are thereby eliminated. Moreover, calibration fringe spacings in the spectrum do not vary. This eliminates a common source of calibration error.

We use deconvolution as a method for improving measurements of line positions and intensities when the Doppler linewidth causes blending in diode laser spectra (Halsey et al. 1985). In this manner were are able to remove the Doppler, Lorentz, and laser linewidths, making blended structure more visible. The final linewidth is less than 0.0003 cm^{-1}.

Temperature-Variable Sample Cell

We have constructed a low-temperature absorption cell which can be operated anywhere between 300 and 50 Kelvin. In this design a closed-cycle helium refrigerator is connected directly to a 30-cm long straight-path cell which is mounted inside a vacuum chamber. With ZnSe windows the cell can be used anywhere in the 0.6 to 20 micron range. The cell is described in detail by Halsey et al. (1988) and Jennings (1988). Figure 4 shows a portion of the Q-branch region in the 14-micron band of propane recorded at room temperature and at 175 K. Note the elimination of many lines at low temperature, simplifying the line structure.

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