Performance Characteristics of a Low Temperature Cell for Collisional Cooling Experiments

Christopher D. Ball, Frank C. De Lucia
The Ohio State University, Department of Physics
174 W. 18th Avenue, Columbus, OH 43210

Dipesh Risal, Alan Ruch, Hua Sheng
Franklin and Marshall College, Department of Physics and Astronomy
Lancaster, PA 17604-3003

Yilma Abebe, Paula A. Farina and Arlan W. Mantz*
Connecticut College, Department of Physics and Astronomy
270 Mohegan Avenue, New London, CT 06320

* Corresponding Author

ABSTRACT

We fabricated and tested a low temperature cell which is mounted directly on the second stage of a CTI-Cryogenics Model 22C CRYODYNE$^{(R)}$ CRYOCOOLER. The vacuum system consists of a room temperature vacuum shroud, a radiation shield maintained at 77K and the cell which is mounted directly to the second stage of the cryocooler. The ultimate cell temperature is 12.4 Kelvin, and the low temperature limit increases at a rate of 5.6 Kelvin/Watt. We achieve a cell temperature of 22 Kelvin under typical experimental conditions of approximately 29 milli Torr helium, slow flowing gas, and a heated injector. The absorption path length of the cell is 3.35 cm, and the window clear aperture is 1.27 cm. We performed a series of experiments in which we determined the translational temperatures of vibration-rotation transitions in the (1-0) band of CO for different cell temperatures. The results of our tests are discussed in this paper.

Keywords: collisional cooling, diode laser, molecular spectroscopy, diode laser, low temperature cell

2. INTRODUCTION

Molecular spectra recorded with molecules at reduced temperatures, but still in vapor phase, usually provide some simplifications when compared to spectra recorded for the same molecules at room temperature. For example, if the molecule is translationally cold, and if the gas pressure is sufficiently low, the Doppler line width[1] resulting from the random velocities of individual molecules will be reduced. Also, if the molecule is rotationally cold the rotational structure in the spectrum will be noticeably simplified at sufficiently high resolution, because only low lying molecular rotational states[2] are populated at the lowest temperatures. Finally, in the infrared spectral region vibrationally cold molecules will also exhibit spectra which have fewer vibrational features, again because only the lowest lying vibrational states are populated. Molecules with low lying bending vibrational states may or may not exhibit simplified structure, depending upon the energy associated with the vibrational level[2] and the gas temperature. For example, CO_2 vibrational rotational spectra at 20 Kelvin would be expected to exhibit a very simple spectrum because the lowest lying vibrational state is at 667 cm^{-1}, but C_3O_2 at the same temperature would not exhibit a simple spectrum because this molecule has a vibrational level at approximately 18 cm^{-1}.

Several techniques have been developed to study molecules at reduced temperatures. The use of a cell which is maintained at a low temperature by means of a refrigerant is normally limited by the vapor

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pressure of the gas being studied. This is not a very interesting technique for most gases, because the vapor pressure is very low or the gas sample freezes before reaching temperatures of 20 to 30 Kelvin. Supersonic free expansion jets[3-5] can provide low temperature molecular systems for spectroscopic study. The rotational temperature of the gas under investigation using supersonic jets may be as low as several Kelvin. Translational velocities which may be achieved using supersonic expansions correspond to room temperatures, so one must construct skimmers to collimate the beam and to filter undesirable velocity components in order to measure sub-Doppler line widths. This method has limited applicability in the infrared spectral region because of low number densities and limited absorption path lengths. However, Gough *et al* [6] were able to resolve NO hyperfine structure using a lead salt laser using a free expansion jet equipped with arrays of microchannel plate collimators.

De Lucia *et al* and Willey *et al*[7-14] developed the collisional cooling technique which they employ in the microwave spectral region. The important cell parameters include several centimeters of absorption path, low pressure, and very low temperatures (approximately 1.2 Kelvin is achieved by this group). The collisional cooling technique as described by De Lucia *et al* uses a helium buffer gas at pressures of tens of milliTorr with a gas kinetic temperature of one to several Kelvin to cool the analyte gas to low temperature through molecular collisions. The helium buffer gas is cooled through collisions with the cell walls which are maintained at these low temperatures through the continuous transfer of liquid helium coolant.

Recently the collisional cooling technique was extended to the infrared spectral region[15,16] where tunable diode lasers were used to study CH_3F and N_2O. The molecular translational temperatures determined from these measurements follow the expected $T^{1/2}$ dependence and the rotational temperatures were calculated from relative absorption strengths of successive rotational transitions. Both translational and rotational temperatures are essentially the same as the cell temperature. Fig. 1 is a drawing of the cell which was employed in reference 15.

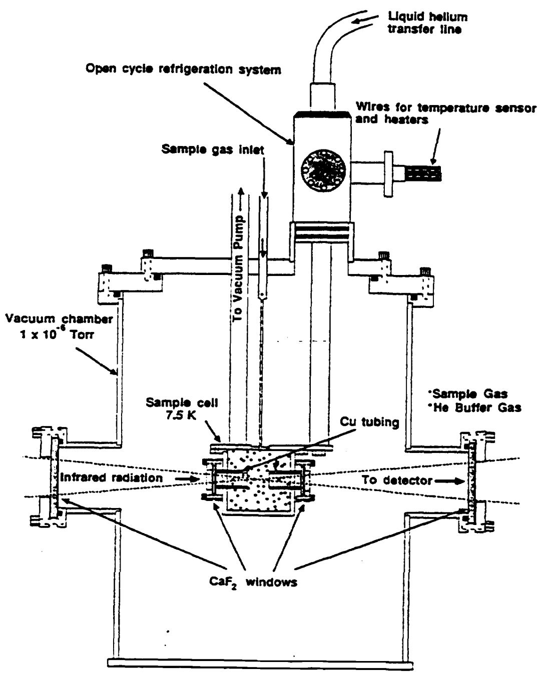

Figure 1: Schematic diagram, in cross section, of the low-temperature absorption cell as it was configured for the experiment described in reference 15. Calcium Fluoride windows replaced the usual microwave windows, and microwave waveguides were removed.

The results we are reporting were obtained from a collisional cooling cell which was designed and fabricated to operate at the cold second stage of a commercially available closed cycle helium refrigerator. This refrigerator has a second stage temperature limit of approximately 10 Kelvin with no thermal load[17].

3. CELL DESCRIPTION

The new cell and vacuum system are shown in Fig. 2. The cold finger of a CTI-Cryogenics Model 22C CRYODYNE(R) CRYOCOOLER is labeled **F**. A radiation cold shield, labeled **B**, is attached to the first stage of this cold finger. Holes are drilled in the radiation shield walls to permit the transmission of infrared radiation through the cell. The top of the radiation shield also has two clearance holes for the vacuum feedthroughs, labeled **D** and **E**, which are attached to the absorption cell. This radiation cold shield

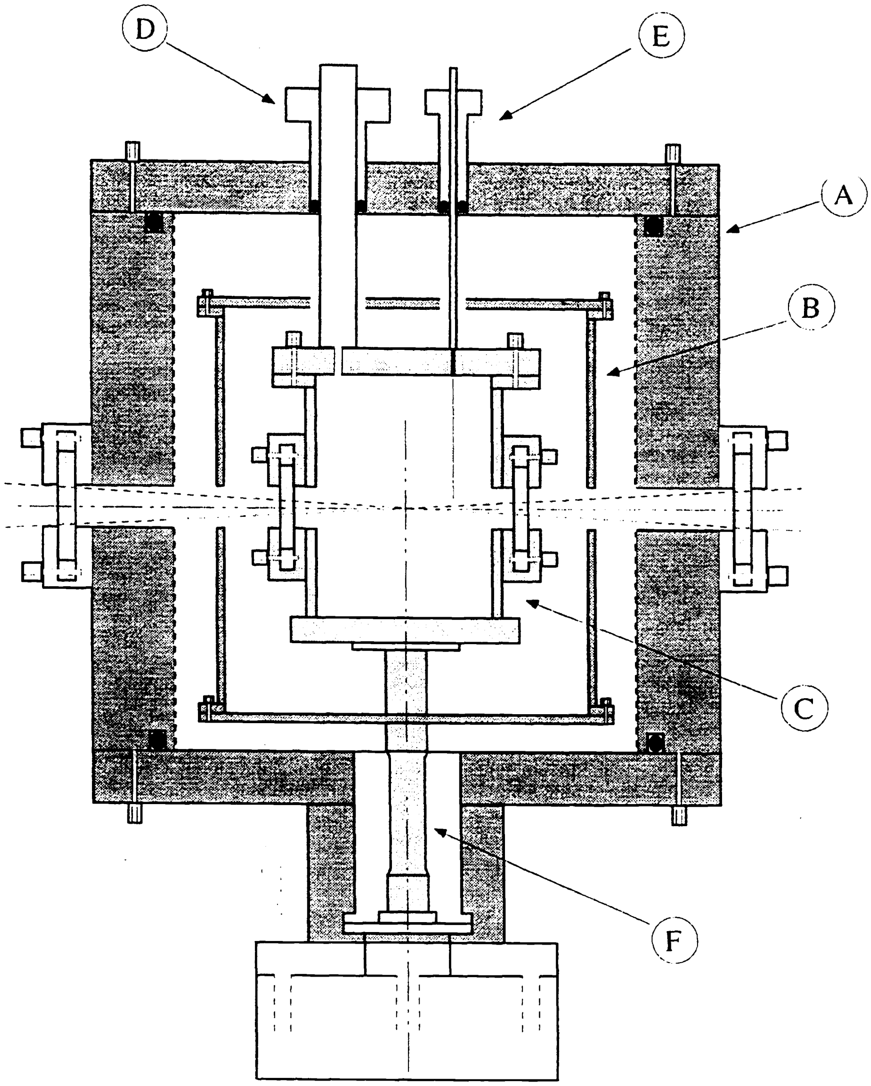

Figure 2: Schematic diagram, in cross section, of the low-temperature cell used for these experiments and described in detail in the text.

is maintained at approximately 77 Kelvin and is required if the refrigerator second stage is to achieve a minimum temperature of 10 Kelvin. The absorption cell, designated **C** , is mounted directly to the second stage of the refrigerator cold finger. The absorption cell is instrumented with a temperature sensor and a heater, so the cell temperature may be maintained at any temperature up to room temperature. The cell has an absorption path length of 3.35 cm. The window clear aperture is 1.27 cm, and the windows are bonded to the cell body to form a vacuum tight seal using indium gaskets. The top of the absorption cell is also bonded to the cell body using indium gaskets. These are the only seals in the absorption cell. The vacuum shroud for the collisional cooling cell is indicated by the letter **A.** This vacuum shroud is constructed using "O ring" vacuum seals at all places where pieces are joined, as shown in the figure. The cell evacuation port is labeled **D** in Fig 2. Through this port, helium gas is fed into the cell and the cell is evacuated. The tube is thin wall stainless steel (approximately 0.005 inch wall thickness) which is silver soldered to the top of the cell. Analyte gas is bled into the cell through the vacuum feedthrough which is labeled **E**. The gas fill tube is a thin wall (0.005 inch) small bore (100 micron diameter) stainless tube. The gas fill tube, or injector, is fed through the top of the cell where it is epoxied to maintain vacuum integrity. The last 2.5 centimeters of the injector inside the cell can be heated so the analyte gas does not freeze at the end of the fill tube.

The ultimate cell temperature with this design is 12.4 Kelvin. We applied different amounts of power to the ten ohm cell heater to establish the dependence of minimum cell temperature upon thermal load. The low temperature limit increases at a rate of 5.6 Kelvin/Watt. In a typical experiment with approximately 29 milliTorr of helium, slow flowing gas and a heated injector, the minimum cell temperature is 22 Kelvin.

The tunable diode laser system optical schematic, Fig. 3, shows the collisional cooling cell designated as the sample cell in the optical system. With the exception of this cell, the system shown in Fig. 3 is the system described by Balent and Mantz[18]. The laser was not actively stabilized during these experiments.

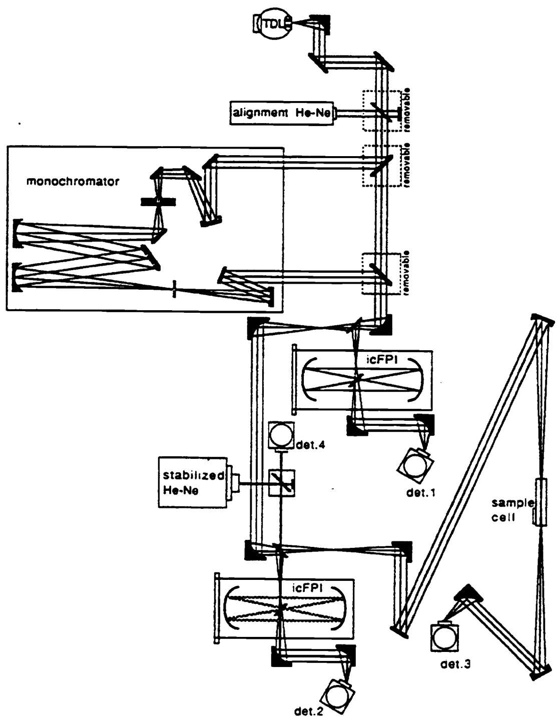

Figure 3: Optical schematic of the tunable diode laser spectrometer system used in these experiments. The cell shown in Fig. 2 replaces the sample cell in this figure.

4. SPECTROSCOPIC RESULTS

We used carbon monoxide for spectroscopic testing of the newly designed cold cell. Carbon monoxide was selected because a well characterized laser, which operates in the 4.7 micron region, was available, and the carbon monoxide fundamental band at 4.7 microns has strong absorption lines. Carbon monoxide also has a rather high vapor pressure at low temperatures. The vapor pressure of carbon monoxide at approximately 53 Kelvin is 1 Torr[19]. Because of this high low temperature vapor pressure collisional cooling experiments on carbon monoxide must be conducted at temperatures below approximately 12 Kelvin.

The Doppler width, $\Delta\nu_D$, of a molecular absorption line may be calculated from the relation[1]

$$\Delta\nu_D = 3.581 \times 10^{-7}\, \nu (T/M)^{1/2} \quad , \qquad (1)$$

where ν is the frequency of the observed transition (in cm^{-1}), T is the temperature of the sample gas in Kelvin, and M is the gram molecular weight of the molecule. We recorded absorption spectra for the R(2) and P(1) rotational transitions in the fundamental band of carbon monoxide at pressures in the range 0.120 to 0.048 Torr with cell temperatures between 300 Kelvin and the low temperature limit for these conditions of 38 Kelvin. A typical low temperature CO spectrum is shown in Fig. 4. Only pure carbon monoxide was used in these experiments.

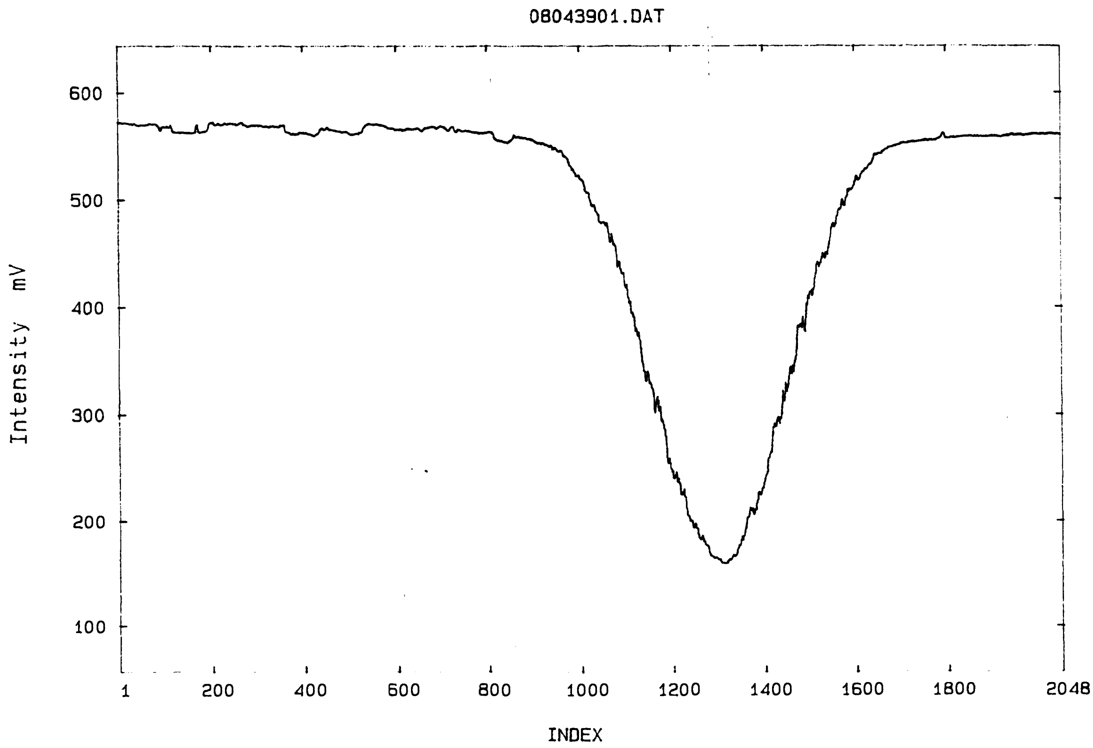

Figure 4: A typical low temperature spectrum of CO recorded using the low temperature cell described in this paper. The spectrum shows absorption by the P(5) line in the CO fundamental band. Cell temperature was 37 Kelvin, and gas pressure was 139 milliTorr.

The analysis of each recorded spectrum consists of least squares fitting the recorded line shape to a Voigt profile from which one obtains values for the Doppler and collisional line widths as well as the absorption line strength. Temperatures derived from the analyzed Doppler widths for the R(2) and P(1) lines were plotted as a function of the absorption cell temperature. These results are shown in Fig. 5 and Fig. 6 where a linear relation exists between the molecular gas temperature and the cell temperature. A careful analysis of the data suggests that the carbon monoxide temperatures are slightly higher, as much as 15 Kelvin for R(2) and 30 Kelvin for P(1), than the cell temperatures at the lower temperature limits.

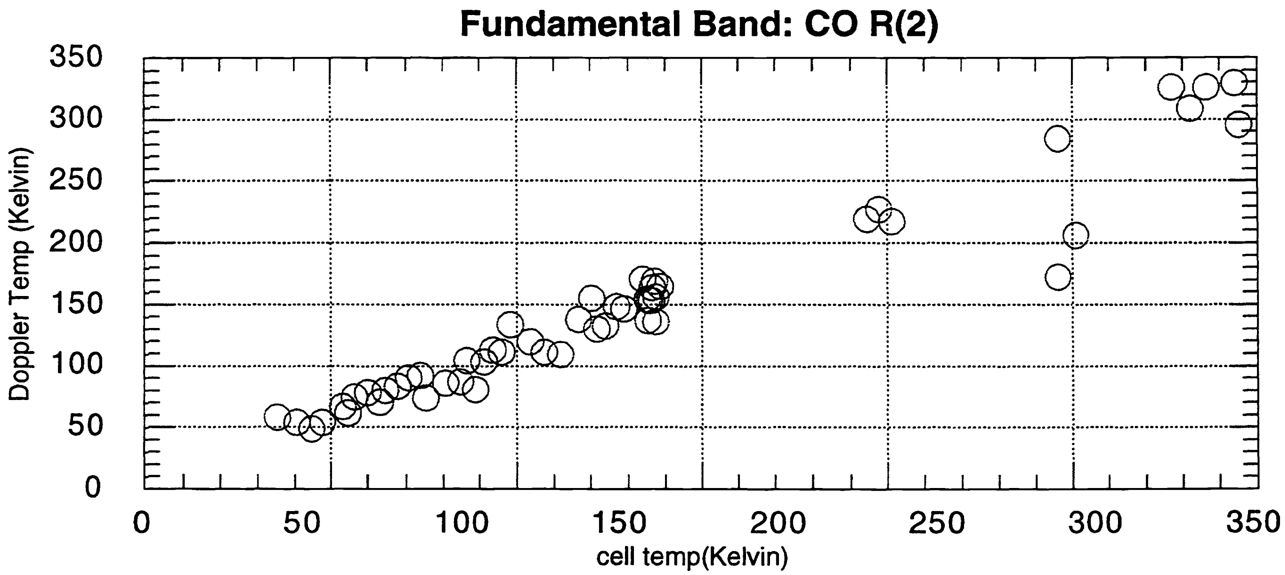

Figure 5: A plot of gas temperature calculated from the Doppler width for the R(2) line of CO versus cell temperature

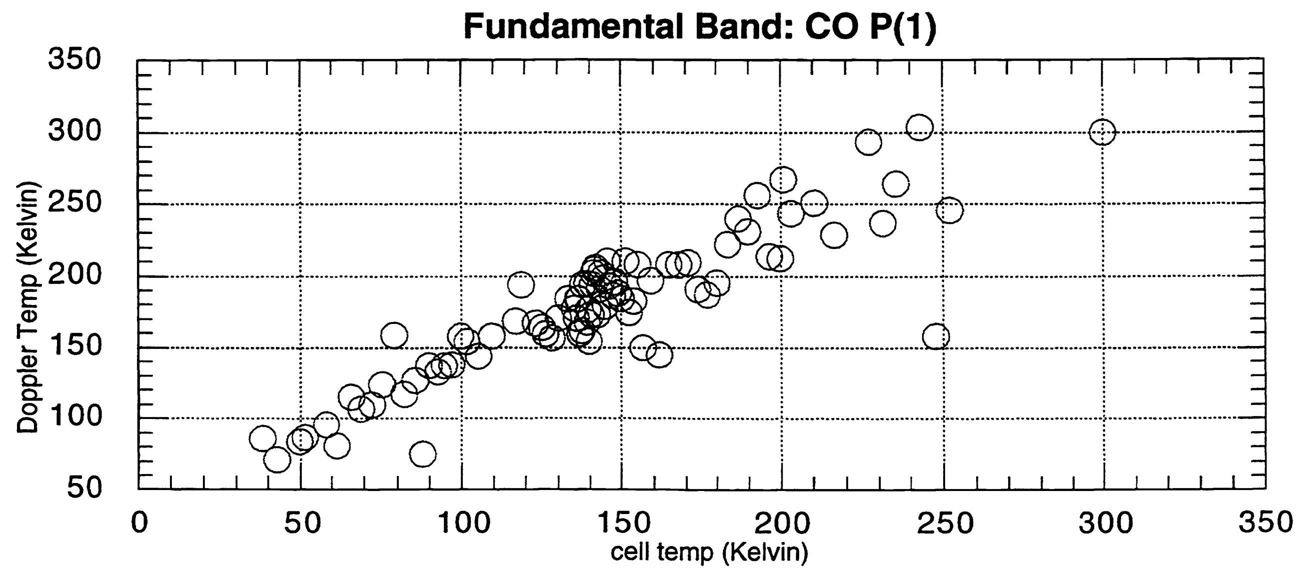

Figure 6: A plot of gas temperature calculated from the Doppler width for the P(1) line of CO versus cell temperature

The Lorentzian, or collisional components of the width are plotted for all data in Figs 7 and 8. At these low pressures the Lorentzian contribution to the line width is due mainly to the laser linewidth. The average value for the Lorentzian component for the P(1) line is 0.00033 cm^{-1} +/- 0.00013 cm^{-1}. This Lorentzian linewidth is consistent with the laser linewidth one would calculate from the laser tuning rate and the specifications for the current supply noise and the temperature controller closed loop stability.

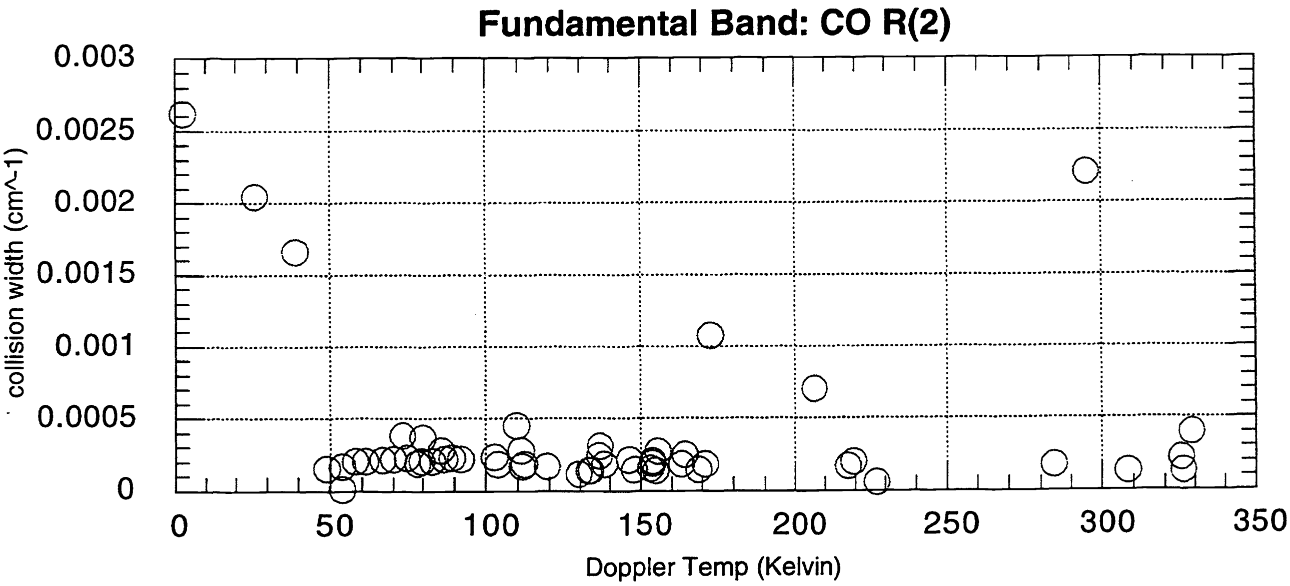

Figure 7: A plot of the Lorentzian, or collision, width for the R(2) line of CO versus Doppler temperature

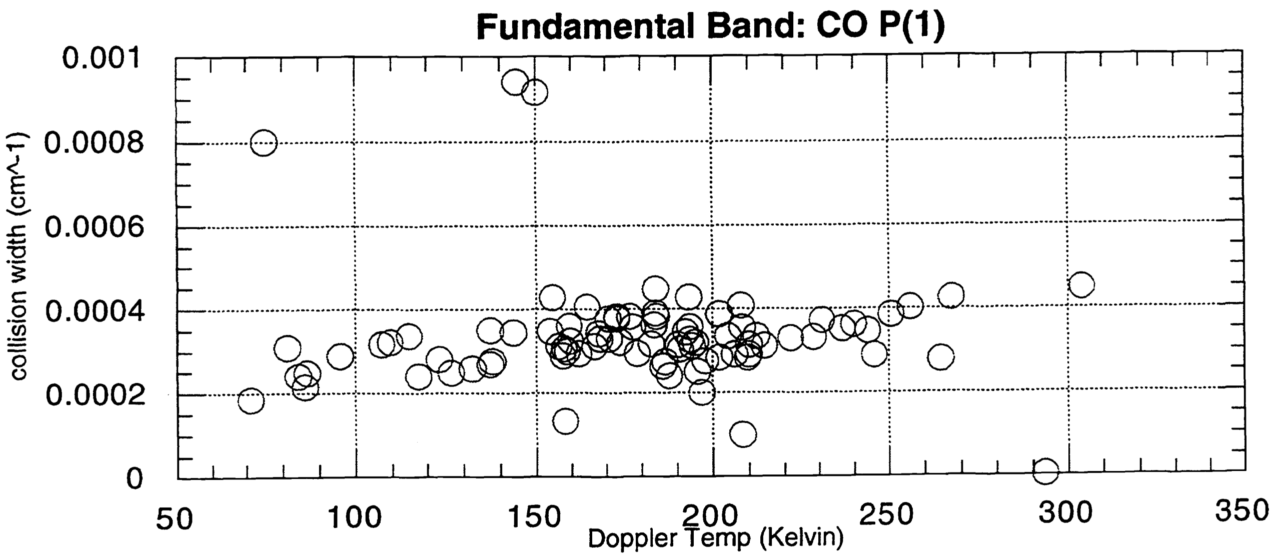

Figure 8: A plot of the Lorentzian, or collision, width for the P(1) line of CO versus Doppler temperature

5. CONCLUSIONS

The lowest cell temperature achieved with this configuration is 12.4 Kelvin. The present design permits operation of the cell under normal experimental conditions to temperatures as low as 38 Kelvin. We have also demonstrated that the cell is useful for recording low temperature spectra of gas samples which are maintained at any temperature within the range 300 to 38 Kelvin. These data suggest that the 38 Kelvin operational limit for the cell may result from an excessive thermal load imposed on the refrigerator by the design of the gas injector port. A small gas leak between the cell and the surrounding vacuum resulting from the epoxy connections on the cell would also contribute to an excessive heat load. On the basis of these test results we redesigned the vacuum feedthroughs using, wherever available, commercial vacuum fittings, silver soldered joints and longer thermal paths for the sample injector and helium supply line. First results on CO indicate that we can operate the redesigned cell at 10 to 12 Kelvin with normal gas loads. These new results will be communicated after more thorough testing and analysis of the new data.

6. ACKNOWLEDGMENTS

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