On Measurement of Infrared Absorption at Low Temperatures

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Abstract: In order to measure the infrared absorption in vibration-rotation band of atmospheric constitutents at low temperatures, a new apparatus which provides the highly accurate measurements with simple operation, has been fabricated. This system can continuously change the temperature of the sample gas in the range of 80 to 400 K. Its availability was confirmed by taking the spectra of the 4.7 μ carbon monoxide band at various temperatures.

The imperfect mixing of sample mixtures and the effects which falsify the concentrations of uniform sample mixture in the low-temperature absorption cell, were examined by a gas chromatograph and their problems are discussed.

1. Introduction

The interest in radiative transfer and heat balances of planetary atmospheres has prompted many studies of infrared spectra of atmospheric constituents under controlled laboratory conditions. These studies have included the determination of total absorptance of vibration-rotation band and of molecular constants, but for complete charactarization of a band, it is necessary to know the strengths and half-widths of the individual absorption lines and their dependence on pressure and temperature. In particular, recent spectorscopic studies of the atomospheres of Mars, Jupiter and so forth, require information on these parameters at low temperatures for making valid estimates of the composition and temperature of their atmospheres. A detailed knowledge of those parameters also contributes to a currently important problem in molecular physics such as molecular structure and intermolecular forces. Nevertheless, a few measurements of these parameters at low temperatures have been made until now (Darnton and Margolis, 1973; Goldring and Benesh, 1962; Hoover and Williams, 1969; McMahon et al. 1972; Tubbs and Williams, 1972a, b,; Tubbs and Williams, 1973; Varanasi et al. 1973; Varanasi, 1975: Varanasi and Bangaru, 1975: Varanasi and Sarangi, 1975). The line strengths at low temperatures can be estimated from these values obtained at room temperatures by the use of theoretical relation (Herman and Wallis, 1955). However, the validity of the line-broadening theory such as Anderson-Tsao-Curnutte theory (Anderson, 1949: Tsao and Curnutte, 1962) at very low temperatures has not yet been verified by the sufficiently accurate measurements.

We have therefore intended to measure the line strengths and line half-widths of atmospheric constitutents at temperatures ranging from 80 to 400 K and a special apparatus have been constructed for this experiment. Although some apparatuses have already been offered for the same purpose, the advantage in our system comparing with these systems is that its operation is not only very simple but it provides

measurements with a high accuracy.

The purpose of this paper is to present details of the equipment and to discuss experimental procedures of absorption measurements at low temperatures.

2. Apparatus.

Figs. 1 and 2. show a block diagram and a photograph of the apparatus, respectively. Details of each part are described in order.
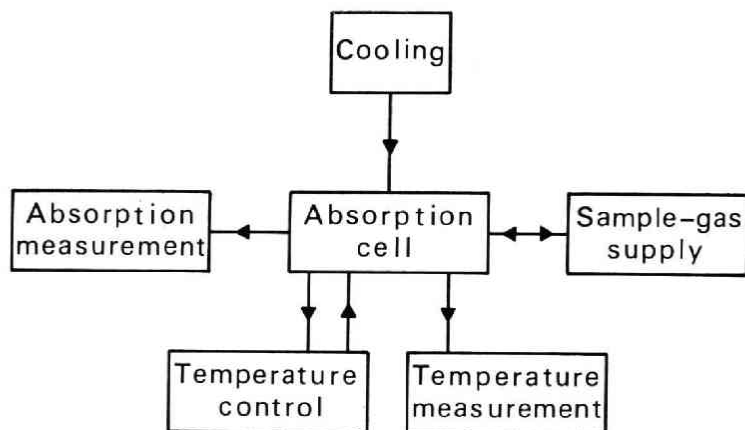

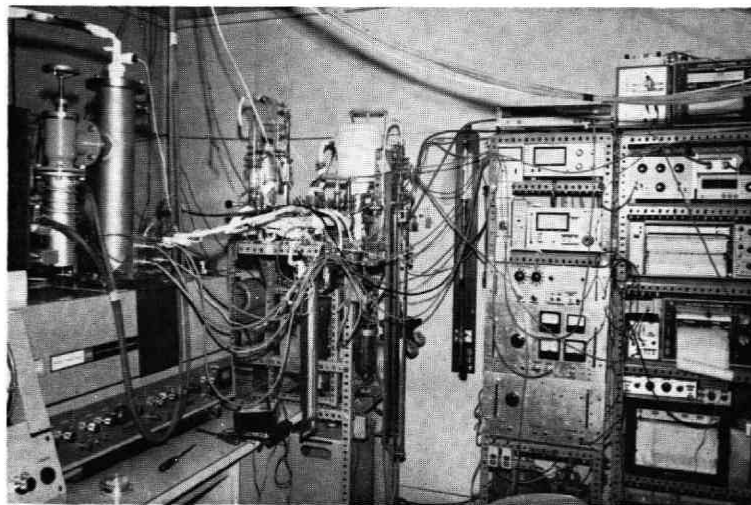Fig. 1, Block diagram of the apparatus for absorption measurements.

Fig. 2. Photograph of the apparatus.

(a) Spectrometer

The spectra are taken by a Hitachi-Perkin-Elmer 125 doublebeam grating spectrometer. A slave recorder attached to the spectrometer is used to magnify the wavenumber and absorptance coordinates.

The response linearity of detector-amplifier-recorder system is checked by inserting rapid rotating sector wheels in the sample beam. After carefull adjustments, uncertainties of spectral absorptance are confined to less than ± 0.004 over the full range of absorptance. The wavenumber calibration was made using the line positions of infrared active gases.

(b) *Sample-gas supply system*

Fig. 3 is a schematic diagram of sample-gas supply system. The portion surrounded by dashed line is a storage chamber in which sample gases are mixed according to demand. The chamber has a large volume of about 5.5 l to prevent the excessive decreases of total pressures when sample gases are introduced into the absorption cell. An oil free and vaccum tight diaphragm pump is attached to the chamber to accomplish a rapid mixing of gases. Pumping on the system is provided by an oil-diffusion pump with nitrogen-trap and pressures lower than 5×10^{-5} Torr are typical of the vaccum obtainable after the pumping for about 1 hour. Since its leak rates are observed to be less than 1×10^{-6} Torr. l/sec, pressure increases or decreases due to leakage are confirmed negligeble. Sample gases are introduced into the chamber through the buffer tank and needle valve from sample-gas cyliders. As ultra-high purity gases are available, an equipment for further purification is not installed on the way from sample-gas cyliders to the chamber.
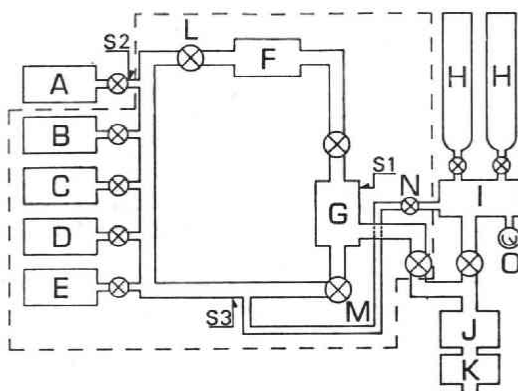

Fig. 3 Schematic diagram of sample-gas supply system.
A: absorption cell, B: precision mercury manometer, C: oil manometer, D: pirani vaccum gauge, E: ionization vaccum gauge, F: diaphragm pump, G: brass chamber, H: sample-gas cylinder, I: buffer tank, J: diffusion pump, K: pre-pump, L: cylider valve, M: butterfly valve, N: needle valve, O: burdon-type pressure gauge, $\otimes$: vaccum valve, S_1, S_2, S_3: Sampling points for gas analysis.

Pressure measurements in the range of 10 to 800 Torr are performed by a precision mercury manometer with an accuracy of ± 0.1 Torr. Pressures from 0.1 to 30 Torr are measured by an oil manometer with a precision of ± 0.05 Torr and lower pressures are measured with a pirani vaccum gauge or ionization vaccum gauge.

The chamber is wrapped with an insulating material in order to minimize the pressure changes induced by room-temperature fluctuations in the course of measurements. The temperature of sample gases is monitored by three thermistor-thermometers inserted into the chamber. These monitores indicate that temperature flucuations are always restrained to less than ± 0.3 K by the aid of air conditioner of the laboratory.

(c) Low-temperature absorption cell

Three low-temperature absorption cells with different lengths are made of copper to reduce temperature difference over the cell and to be cooled well.

The cross section of the absorption cell with path-length of 6 cm is depicted in Fig. 4. In the design shown in Fig. 4, sapphire windows (or other windows if desired) are used together with indium gaskets and end plates to seal the cell. The structure of the 1–cm absorption cell which is similar to that of the 6–cm absorption cell is not illustrated by a figure.
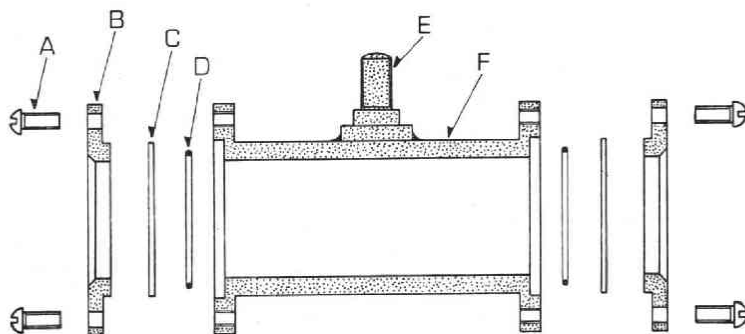

Fig. 4 Components of low-temperature gas cell with 6 cm in length for infrared-absorption studies.
A: screw, B: end plate, C: sapphire window, D: indium gasket, E: exterior screw to bring the cell into thermal contact with coolants, F: cell body.

Investigations of the absolute strength of the individual lines in vibration-rotation band at low temperatures need an absorption cell satisfying particularly the following requirements: (1) The cell must have a path length of the order of millimeter, (2) This path length must be uniform and known with the accuracy of about one percent. (3) The cell must be vaccum tight and cooled enough. The principal features of our shortest cell arrangements are shown in Fig. 5. An accurate spacer is sandwiched among two sapphire windows D, end plates C and I and tightened by screw J. This insert is slided snugly into the cell body and slight gaps between them are sealed by means of the end plate B and indium gasket. Small holes which are made in the end plate I for screw J, are also sealed with the end plate K and indium gaskets. Notched annular rings of a quartz or metal served as an adequate spacer. Whether or not this cell satisfys the requirement (2) depends on the flatness and parallelism of window plates and spacer. Therefore their both surfaces are polished thoroughly. Although
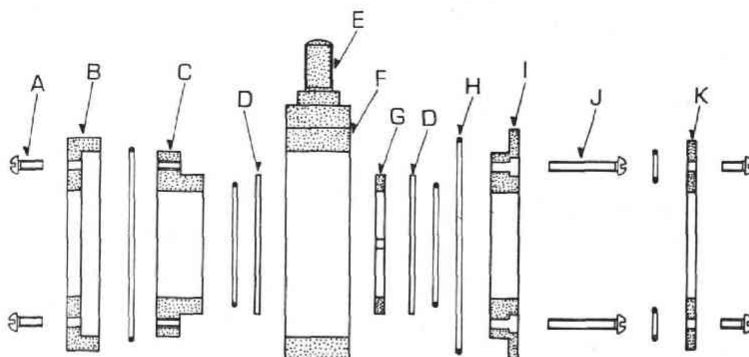
Fig. 5 Components of low-temperature gas cell with pathlength of mm order for infrared-absorption studies.

A: screw, B: end plate, C: end plate, D: sapphire window, E: exterior screw to bring the cell into thermal contact with coolants, F: cell body, G: spacer, H: indium gasket, I: end plate, J: screw, K: end plate.

this type of construction has no particular advantages for cells longer than about 1 cm, it would be useful for short cells as far as accurate and thin spacers are available.

Every cell body is equipped with cupro-nickel capillary through which sample gases can be introduced and has the small wells into which thermocouples can be inserted for temperature measurements. In the assembling of the cells, screws are tightened with a torque screw driver to reduce the strains on windows.

(d) Cryostat

The cells are cooled by a cryostat whose construction is shown schematically in Fig. 6. This cryostat is fabricated from stainless steel except copper bottom of inner tube to decrease gas emission, and its outer tube is equipped with $Ca F_2$ windows. An oil-diffusion pump is used to evacuate the region between inner and outer tubes to prevent the condensation of atmospheric water vapor on the windows and to lessen the evaporation of a coolant.

The cell suspended from the bottom of inner tube in the insulating vaccum of the cryostat is in thermal contact with contents in reservoir through a copper block.

When the probe inserted into reservoir, detects the change of coolants such as decrease in volume or increase in temperature, it sends warning signals. If liquid nitrogen serves as coolant, the probe supply an adequate amount of liquid nitrogen automatically from the external dewar to reservoir by operating its slave circuit.

Any one of liquid nitrogen, aceton-dry ice and water-ice is properly used as coolant according to the required temperature range.

(e) Temperature controller

Temperature of the cell is roughly controlled by choosing suitable material and cross-sectional area of the ring (see Fig. 6.). The finer control of temperature is
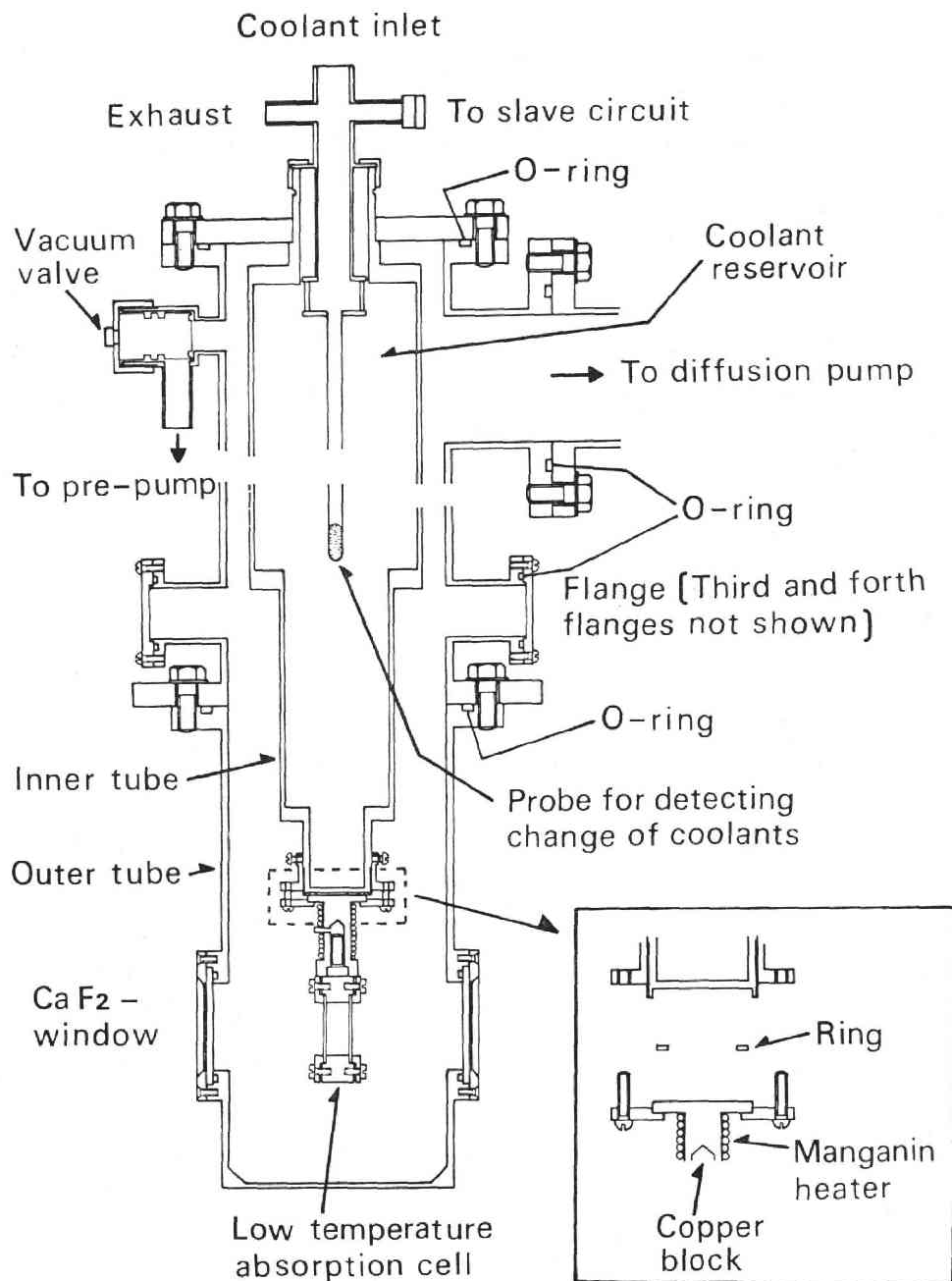
Coolant inlet

Exhaust   To slave circuit

                                 O-ring

Vacuum
valve   Coolant
                                         reservoir

                                 → To diffusion pump

To pre-pump

                                 O-ring

                                 Flange [Third and forth
                                 flanges not shown]

                                 O-ring

Inner tube

                                 Probe for detecting
                                 change of coolants
Outer tube

                                 Ring
Ca F₂ –
window

                                 Manganin
                                 heater

                                 Copper
Low temperature   block
absorption cell

Fig. 6   Cross section of the crystat for cooling the absorption cell.

attained by manganin heater wound onto a copper block (see Fig. 6.).   The electric
powers of heater are regulated with a temperature controller which operates efficiently
to minimize the differences between desired and actual temperatures.   Schematic
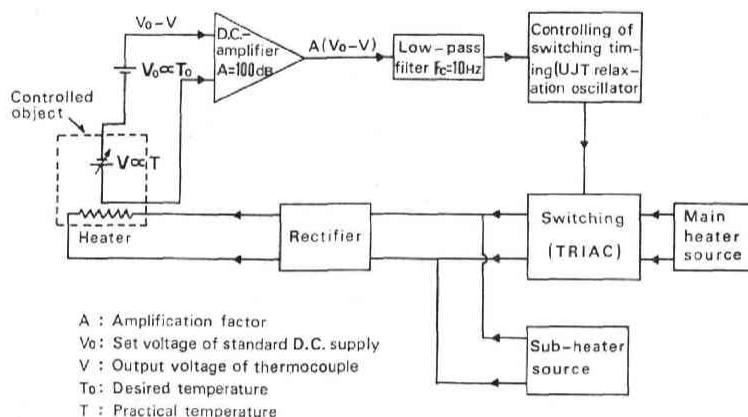
Fig. 7 Schematic diagram of TRIAC temperature controller.

diagram of this temperature controller is shown in Fig. 7. An input circuit is designed to accept resistance or voltage generating temperature sensors such as thermocouples, Pt sensors and thermistors. In the present work, the copper-constantan thermocouple is used as temperature sensor. The differential signal, V_0-V, between thermal voltage of a thermocouple, V, and set voltage of a standard D.C. supply, V_0, is magnified by a chopper type D.C. amplifier with amplification factor, A, of 100 dB. The output, $A(V_0$-V), is supplied to UJT (unijunction transistor) relaxation oscillator after passing through a low-pass filter which cut off the frequencies higher than 10 Hz. According to magnitude of A (V_0-V), the oscillator judges when TRIAC (Triode A.C. semiconductor switch) of the heater circuit should be turned on in half cycle of wave of A.C. voltage which is supplied to heater and furnishes a gate of TRIAC with a triger pulse at suitable time. Since the triger circuit and electric power source of heater circuit is synchronous and TRIAC is trigered at half of half cycle of A.C. wave when A (V_0-V)=0, above operations minimize the differencial voltage, V_0-V. Therefore the cell is automatically maintained in the region of the temperature which corresponds to the set voltage of standard D.C. supply.

The absolute temperature of the cell is determined from the voltage output of copper-constantan thermocouples embeded in the cell body. These thermocouples are thermally anchored to the lower part of copper block (see Fig. 6.) to reduce an influence of external heat flows on temperature measurements, and calibrated within ± 0.1 K by comparing with standard P_t-resistance thermometer in a constant temperature box. The voltage outputs are measured by means of potentiometric methods or digital voltage meters and their outputs are monitored by the recorders.

3. Results and discussion

The absorption measurements of foreign gas broadening require uniform mixtures as a sample. It is well known that pure gases, especially at elevated pressures and in complex systems, may diffuse so slowly as to require very long periods of time in order
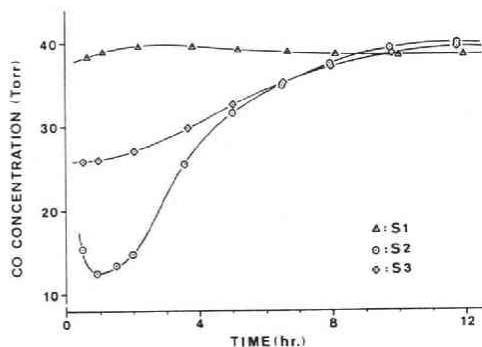
Fig. 8 Variations of CO concentrations.
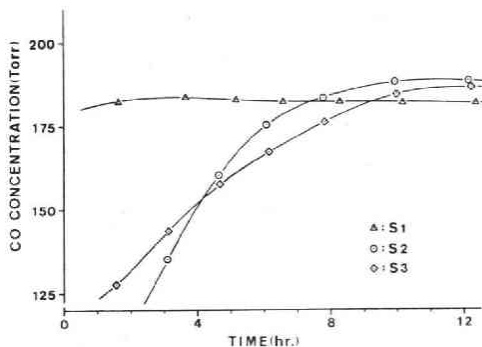P_{CO} in: 38.9 Torr, P_{tot}: 759.8 to 755.4
Torr, Temp: 24.8 ± 0.2 K.

Fig. 9 Variations of CO concentration
P_{CO} in: 182.8 Torr, P_{tot}: 760.9 to 757.8
Torr, Temp: 24.4 ± 0.2 K.

to make a uniform mixture.   Therefore the perfection of mixtures in our storage chamber was first checked by use of a gas chromatograph.   For example, when CO gas was introduced in the chamber without a diaphragm pump and total pressure of about 760 Torr obtained by the addition of N_2 gas, the variations of CO concentrations at three representative points, S_1, S_2, S_3 (see Fig. 3.) by diffusion are shown in Figs. 8 and 9.   Experimental errors in determination of CO concentrations are ± 0.5 Torr or less.   Since a small quantity of mixture, about 1 ml, was necessary for one gas analysis, influence of this sampling is almost negligible.   The mixtures would be perfect at the time when three curves in these figures coincide at the same concentrations.   It can be seen in these figures that our chamber wastes a very long time in order to mix gases perfectly and that the mixing of gases takes place more and more slowly with increase in CO concentration.   Accordingly, if the cell is connected to the storage chamber in the course of this slow mixing, significant concentration difference should be expected over long periods of time in that system.

In order to solve this difficulty, we adopted a method of mixing by diaphragm pump (see Fig. 3.); gases in the chamber are forced to circulate through the by-pass with using of diaphragm pump and to mix completely by means of the combined operations of butterfly valve and cylinder valve (see Fig. 3.).   The merit of this method is that rapid mixing can be achieved in a very short time period at room temperature.

Although uniform mixture can thus be obtained in the storage chamber, there still remain the possibilities that uniformity of gas mixture breaks in low-temperatur cell when the mixture is introduced into the cell.   Most probable cause of them is due to adsorption phenomenon; the composition of gas mixtures may be falsified by the occurence of selective adsorption on the wall of the cell, especially at low temperatures. For CO-N_2 mixtures, the actual CO concentrations in cooled cell were therefore analysed by a gas chromatograph at various conditions which will be employed in our absorption measurements.   From this analysis, we found that there are no appreciable differences of CO concentration between in the storage chamber and in the cell.   This means that the uniformity of the CO-N_2 mixtures is still maintained in the

A ; Sub-heater source on
B ; TRIAC controller on
　(Set voltage = 3583 μV)
C ; Set voltage → 3292 μV
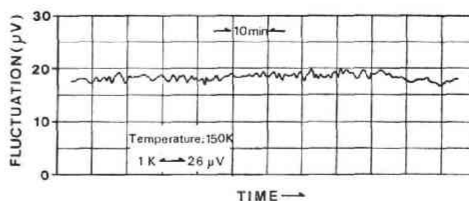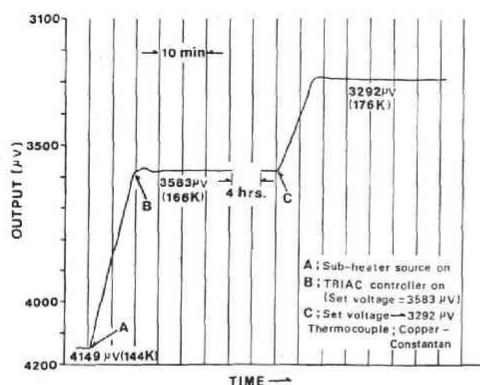Thermocouple ; Copper −
　　　　　　　　　Constantan

Fig. 11　Temperature flucutations of the cell
　　　　after magnification.

Fig. 10　Results of temperature control of the
　　　　cell.

colled cell as being in the storage chamber.

In general, since the obscure gas concentrations in the cell will inevtiably yield large errors for the results of absorption measurements and since the adsorption is highly selective in nature, it is necessary to check the ultimate composition of the mixture in the cell by means of gas chromatograph, mass spectrometer and so on.

With suitable coolants in the reservoir of cryostat, our cooling system could maintain the cell at desired temperatures for a long time within an accracy of ±0.3 K over a wide range of temperature. The temperature difference over the body of the cell is never exceed 0.2 K. For example, the results of 1-cm cell cooled by liquid nitrogen are shown in Figs. 10 and 11. Fig. 11 is a record of the temperature fluctuations after magnification. The cell is heated at first by the sub-heater source. When the temperature of the cell nearly reached the desired temperature (i.e. 166 k in this case), the sub-heater soruce is switched off and TRIAC temperature controller is on to regulate the temperature of the cell. In order to attain the steady state of temperature control quickly, the timing of the above exchange should properly be chosen as the temperature of the cell comes to the desired temperature smoothly. If we intend to change the temperature of the cell regulated at one temperature into some other temperature lying in a temperature range corresponding to the thermocouple's e.m.f. of ±400 μV, it can be performed easily and automatically by only resetting the voltage of standard D.C. supply (i.e. from 3583 μV to 3292 μV in the case of Fig. 10). The fluctuations and drifts of the temperature of the cell regulated by TRIAC temperature controller are very small and both less than ±0.1 K as shown in Fig. 11. In daytime, however, the drifts of the temperature of the cell are occasionally increased by the fluctuations of A.C. source. According to this effect, the final error in the regulation of the temperature of the cell becomes ±0.3 K at most. This value is accurate enough for almost all purpose of the absorption measurement, so no further improvements have been attempted.

The medium-high resolution spectra of the 4.7 μ carbon monoxide vibration-rotation band taken by the present apparatus are shown in Fig. 12. The spectrum A, B, C and D are that obtained at 300, 200, 150 and 100 K, respectively. The absorber thickness of each spectrum is restricted to 0.600 atm cm. From the figure we can
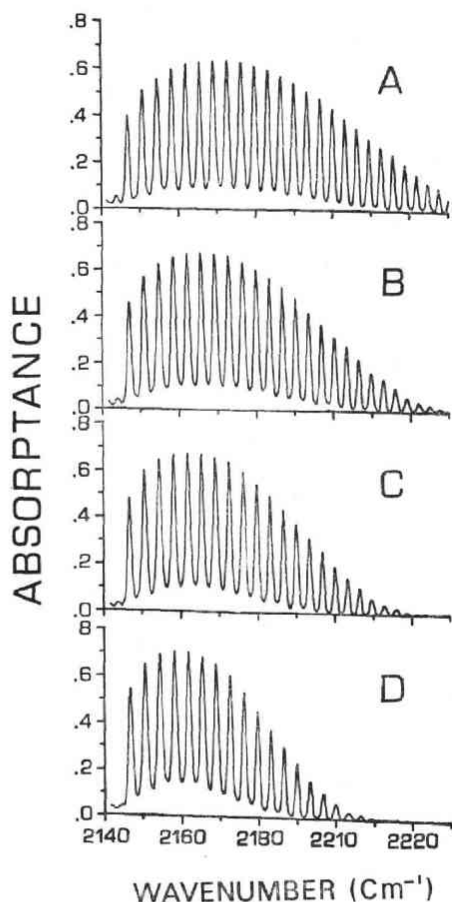
Fig. 12 Typical spectra obtained at various
temperatures by the present apparatus.

recognzie a remarkable temperature dependence of the band profile, which is mainly due to the temperature dependence of the rotational line strength.   As mentioned already, magnified spectra obtained by a slave recorder can be served for detailed analysises.

4.   Conclusions

The apparatus which is composed of spectrometer, sample-gas supply system, low-temperature absorption cell, cryostat and TRIAC temperature controller has been constructed in order to measure the infrared absorption in vibration-rotation band of atmospheric constitutents at the required temperatures in the range of 80 to 400 K.   Its availavility is comfirmed by obtaining the spectra of $4.7\,\mu$ carbon monoxide band at 300, 200, 150 and 100 K.   The gas chromatographical analysises show that the concentrations of the $CO-N_2$ mixture are not falsified by the selective adsorption on the wall of our cooled absorption cells under the condition which will be employed in our absorption measurements.

The specifications of the present apparatus are as follows.

1.   The uncertainties of spectral absorptance of our spectrometer is less than ± 0.004 over the full range of absorptance.

2.   Temperatures and pressures of sample gas can be measured with an accuracy of less than ± 0.1 K and ± 0.1 Torr, respectively.

3.   The low-temperature absorption cells with different lengths of 6 cm, 1 cm and of mm order are made of copper.   These cells are maintained at the required temperature ranging from 80 to 400 K for a long time within an accuracy of ± 0.3 K by the TRIAC temperature controller and cryostat with sutiable coolant.   The temperature difference over the body of the cell is smaller than 0.2 K.

4.   The perfect mixing of the sample gases is attained in a short period of time by forced circulation of the sample gases through the storage chamber.

Aoki for many helpful suggestions and encouragments during the course of this work.

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