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High-Resolution Spectroscopy Measurements of the $^{12}CF_4$ $\nu_2 + \nu_4$ Band at 9 μm

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HIGH-RESOLUTION SPECTROSCOPY MEASUREMENTS OF THE $^{12}CF_4$ $\nu_2 + \nu_4$ BAND AT 9 μm

by

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ABSTRACT

Using a piezoelectic-translator-tuned cw CO_2 laser and a diode laser operating at 9 μm, many high-resolution spectra of the $\nu_2 + \nu_4$ band of $^{12}CF_4$ have been taken. Locations of absorption features within a few megahertz of several CO_2 lines used to pump a $^{12}CF_4$ 16-μm laser have been identified. Absorption coefficients of $^{12}CF_4$ under cooled conditions have been measured within the CO_2 low-pressure gain lines. Detailed, consecutive diode-laser measurements across the P, Q, and R branches of the $\nu_2 + \nu_4$ band, taken at low temperature to eliminate hot bands, have lead to tentative frequency assignments of the difficult spectrum of this molecule. Details of the frequency-assignment work will be presented in a later publication.

I. INTRODUCTION

Detailed high-resolution infrared absorption measurements at 9 μm on the $\nu_2 + \nu_4$ combination band of $^{12}CF_4$ using a diode laser and a piezoelectric-translator- (PZT-) tuned cw CO_2 laser have been made. Because this band, when pumped with some pulsed CO_2 laser lines in the 9-μm region, provides lasing from $\nu_2 + \nu_4 \rightarrow \nu_2$ at 16 μm, we attempted to identify the frequency offsets between several CO_2 pump lines and nearby CF_4 absorption features.

In addition, numerous consecutive diode-laser traces of most of the $^{12}CF_4$ P, Q, and R branches have been taken under cooled conditions ($T < -170°C$) to eliminate hot bands. The resulting spectral simplifications have made it possible to make frequency assignments in a first attempt at unraveling the spectrum of this complex molecule. Such assignment work is underway and will be published.

II. IDENTIFICATION OF ABSORPTION FEATURES NEAR CO_2 LASER PUMP LINES

Lasing in $^{12}CF_4$, optically pumped with a $^{12}C^{16}O_2$ laser, has been reported at various wavelengths in the 16-μm region.[1-8] In attempting to characterize in detail the mechanism of the 16-μm lasing, it is important to know the absorption coefficients and frequency displacement of $^{12}CF_4$ spectral features near CO_2 pump lines. We have measured the absorption of $^{12}CF_4$ at and around the centers of the 9R12 [9-μm band, R(12) line], 9R10, and 9R18 lines. The first gives rise to the strongest observed 16-μm transition at 615.06 cm^{-1} and the latter two to other weak laser lines. Measurements were made, both at room temperature and at an estimated $-172°C$, by absorption within the cw gain profiles of the $^{12}C^{16}O_2$ lines and by diode-laser spectroscopy.

The experimental arrangement for the cw CO_2 laser spectroscopy is conventional. We used a 160-cm-long, 2.5-cm-diam cell either in single or triple pass. The cw CO_2 laser was passively stabilized, and the gain profile was scanned with a PZT element of about 120-MHz scan range. Operating the CO_2 laser at pressures P of 1600 to 2270 Pa (12 to 17 torr), the width of the gain profile was 60 to 80 MHz and the power density in the CF_4 cell was usually less than 1 W/cm^2. The frequency scale was established from the length of travel of the PZT and from calibration against known features in the OsO_4 10-μm ν_3 band. The radiation was detected by a liquid-nitrogen-cooled HgCd:Te detector and recorded on an xy plotter after passing through a lock-in amplifier. Usually three scans were taken for each measurement, the first and last with a vacuum in the cell and the second with $^{12}CF_4$ at various pressures and temperatures in the cell. From the reproducibility of repeated measurements, we estimate the uncertainties to be ±20% in the absorption coefficients and 10% in the frequency-displacement measurement. Table I summarizes the results of absorption-coefficient and frequency-displacement measurements made with the cw CO_2 laser. The peak absorption in 9R12 is 20 to 30 MHz to the blue side of the CO_2 line center, which is 4 to 9 times higher than the absorption in 9R10 and 3 to 5 times higher than that in 9R18. For the 9R10 and 9R18 transitions, the absorption was constant over the CO_2 gain profile. Reference 1 gives a value of the absorption coefficient in 9R12 of 1.1 x 10^{-4} cm^{-1} · torr^{-1}, which contrasts with our value at line center of 4 to 6 x 10^{-4} cm^{-1} · torr^{-1}. The origin of the discrepancy is unknown, but may arise, in part, from the lack of precise laser stabilization in the earlier work.

Diode-laser absorption spectra were taken near several CO_2 pump lines and are shown in Figs. 1-7. (Note that, in all figures in this report, R(red) refers to the low-frequency side of the figure and B(blue) to the high-frequency side). Because of pen displacement on the dual chart recorder, the traces are offset from one another. A conventional diode-spectroscopy apparatus[4] in conjunction with the 160-cm cell was used for the measurements. Significant simplification of the spectrum was obtained by

TABLE I

WEAK SIGNAL ABSORPTION-COEFFICIENT (α) MEASUREMENTS OF $^{12}CF_4$ IN SOME $^{12}C^{16}O_2$ LINES AT ROOM TEMPERATURE AND −172°C

$^{12}C^{16}O_2$ Line 00^01-02^00 Transition	T (°C)	P (torr)	α Line Center[a] (cm^{-1} · torr^{-1})	α Peak (cm^{-1} · torr^{-1})	Frequency Displacement[b] (MHz)
R(10)	23	3-11	1.1 x 10^{-4}		
(1071.884 cm^{-1})	−172	15	1.2 x 10^{-4}		
R(12)	23	2.87	4.0 x 10^{-4}	8.1 x 10^{-4}	−34
(1073.278 cm^{-1})	23	5.90	3.8 x 10^{-4}	5.8 x 10^{-4}	−28
	23	11.4	3.6 x 10^{-4}	4.8 x 10^{-4}	−28
	−172	5.3	5.6 x 10^{-4}	9.1 x 10^{-4}	−18
	−172	6.5	4.7 x 10^{-4}	8.1 x 10^{-4}	−20
	−172	11.5	5.2 x 10^{-4}	6.0 x 10^{-4}	−18
R(18)	23	15	2.1 x 10^{-4}		
(1077.303 cm^{-1})	−172	16	1.3 x 10^{-4}		

[a] $\alpha = \ln(I_0/I)/PL$, where I_0 is the incident radiation, I is the transmitted radiation, P is the pressure, and L is the path length.

[b] $\alpha_{\text{Line Center}} = \alpha_{\text{Peak}}$.

cooling, as shown in Figs. 2 and 4, which also points out the importance of making absorption measurements at the same temperature that is being used during the optical pumping of the molecule. The diode spectra around 9R10 (Figs. 1 and 2) and 9R18 (Fig. 3) show no strong absorption features near CO_2 line centers; however, there is a strong $^{12}CF_4$ feature 29.5 ± 1.5 MHz to the blue of the 9R12 line center (Figs. 4 and 5). This value was determined from expanded traces by the use of etalon calibration. These results confirm those obtained by the CO_2 laser spectroscopy technique. In fact, the frequency-displacement measurement is probably more accurate by the diode method because the $^{12}CF_4$ line is just at the edge of the 9R12 gain profile, which makes its shift more difficult to measure accurately.

While performing the diode-laser experiments, we noticed two other near coincidences of isotopic CO_2 absorption lines with strong $^{12}CF_4$ features. These were 9R5 of $^{12}C^{16}O^{18}O$ (Fig. 6) and 9P14 of $^{12}C^{18}O_2$ (Fig. 7). Nearby strong $^{12}CF_4$ features are within 30 MHz of line center of those isotopic CO_2 lines. A more comprehensive search with a diode laser and a mixed-isotope CO_2 reference cell is necessary to determine all possible coincidences between CO_2 lines and CF_4 features.

Although the wide bandwidth of pulsed CO_2 lasers (~2 GHz) implies that many CF_4 features can be simultaneously pumped, we find a correlation between efficient 16-μm lasing and the proximity of a $^{12}CF_4$ feature to the CO_2 line center. This has been partially verified experimentally in that the use of a gain cell at 9R12 stabilizes the $^{12}CF_4$ 615-cm^{-1} output but provides no noticeable improvement when used on the 9R10 line and appears to reduce the gain in the 9R18 lines. Our results suggest that experiments should be carried out with the 9R12 pump line shifted about 30 MHz to the blue, into coincidence with the $^{12}CF_4$ feature. Such an experiment would help clarify saturation mechanisms, rotational hole filling, and performance improvements in $^{12}CF_4$ laser output.

III. FREQUENCY-ASSIGNMENT DIODE SPECTRA OF $^{12}CF_4$ P, Q, AND R BRANCHES

Consecutive overlapping diode-laser absorption traces have been made across most of the $\nu_2 + \nu_4$ P, Q, and R branches to illustrate which $^{12}CF_4$ lines are actually being pumped by a CO_2 laser and to help unravel the spectroscopy of this complex molecule. Because the number of traces covering all three branches is quite large, only a few of them are represented here. A complete discussion of the frequency assignments and determination of spectroscopic constants for this transition will be published later. Figures 8 and 9 show the $^{12}CF_4$ Q branch with the 9R2 $^{12}C^{16}O_2$ line at 1066.037 cm^{-1} serving as a frequency marker. Tentative $^{12}CF_4$ R-branch frequency assignments are shown by R(1), R(2), etc. (Fig. 9).

Figures 10-12 cover the R branch from R(2) through R(12). The dramatic increase in spectral complexity with increasing J is evident from the large number of fine-structure components. These features were impossible to sort out without cooling the gas to less than −170°C. The location of reference frequency marker lines from a mixed-isotope $^{12}C^{16}O^{18}O$ cell are indicated.[5-8]

Figures 13-19 cover the P branch to approximately P(14). As yet unassigned lines in the P branch are labeled P, Q, ..., X merely to provide continuity for the reader in looking from trace to trace. Structure here is considerably more complicated than in the R branch and may reflect the need for work at somewhat lower temperatures to insure that all hot bands are eliminated. Again reference lines from a reference cell are shown for frequency markers.

IV. SUMMARY

We have measured the spectrum of the $\nu_2 + \nu_4$ band of $^{12}CF_4$ at high resolution using both laser-diode and stabilized CO_2 laser absorption spectroscopy. Location of spectral features near several pump lines of the CO_2 laser have been determined within a few megahertz, and absorption coefficients for the features have been determined. Studies are underway on the complete analysis of the $\nu_2 + \nu_4$ band.

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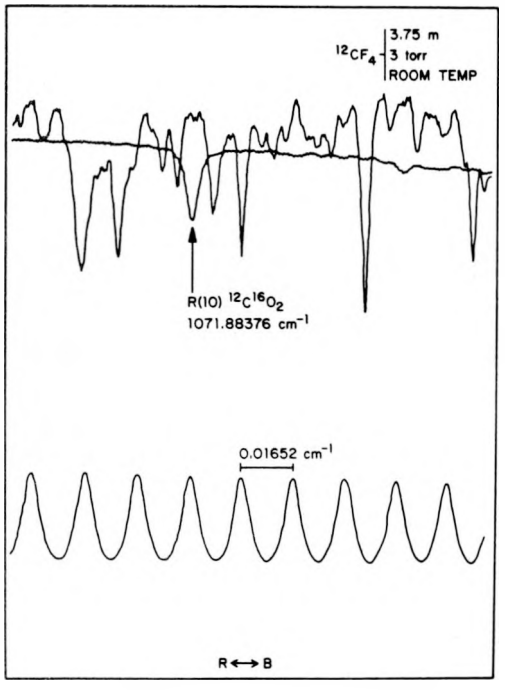

Fig. 1.
Location of the 9R10 $^{12}C^{16}O_2$ line relative to the $^{12}CF_4$ features.

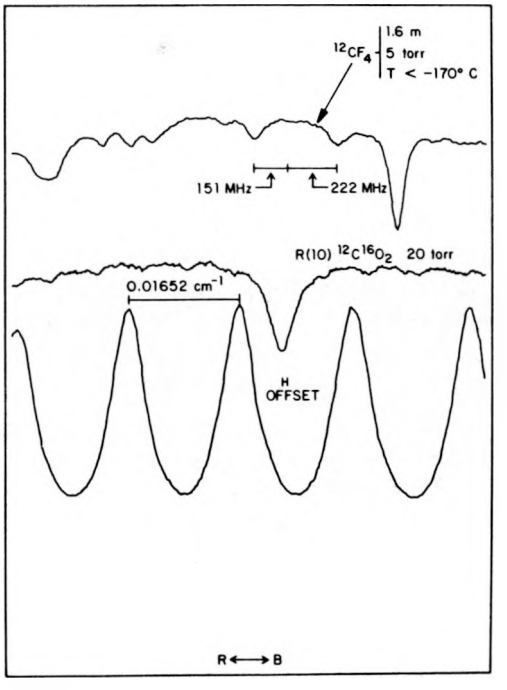

Fig. 2.
Measurement of the 9R10 $^{12}C^{16}O_2$ line relative to the $^{12}CF_4$ features. Note that the R(10) peak should be shifted to the right by the amount of offset shown.

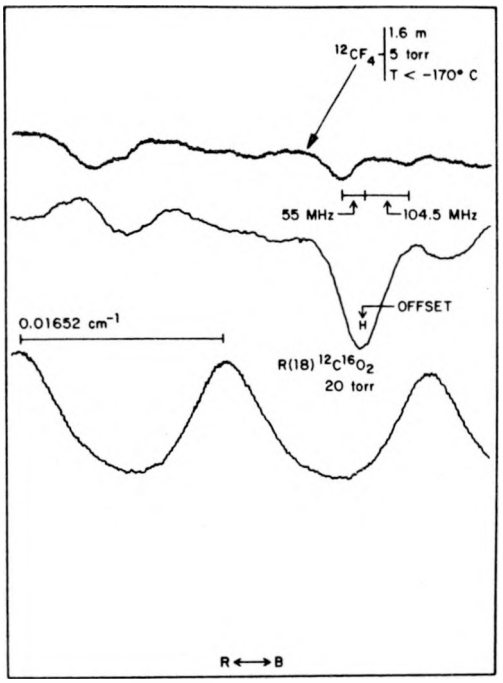

Fig. 3.
Measurement of the 9R18 $^{12}C^{16}O_2$ line relative to the $^{12}CF_4$ features. Note that the R(18) peak should be shifted to the right by the amount of offset shown.

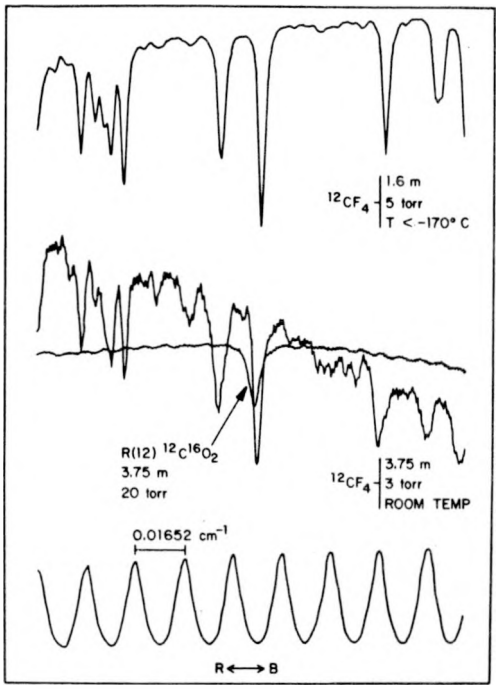

Fig. 4.
Location of the 9R12 $^{12}C^{16}O_2$ line relative to the $^{12}CF_4$ features.

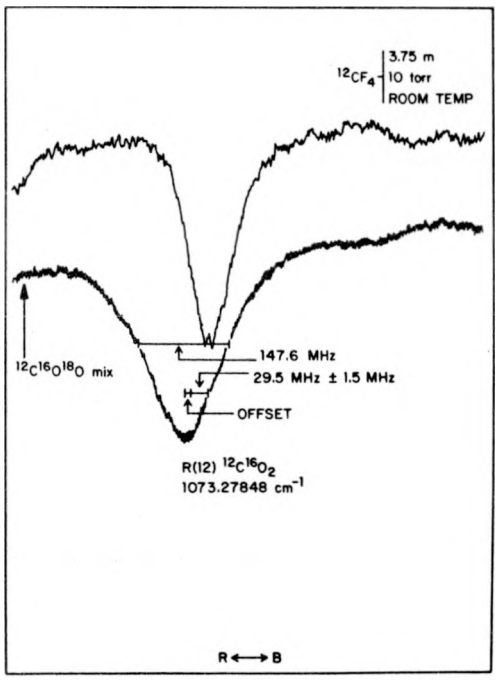

Fig. 5.
Measurement of the 9R12 $^{12}C^{16}O_2$ line relative to the $^{12}CF_4$ features. Note that the R(12) peak should be shifted to the right by the amount of offset shown.

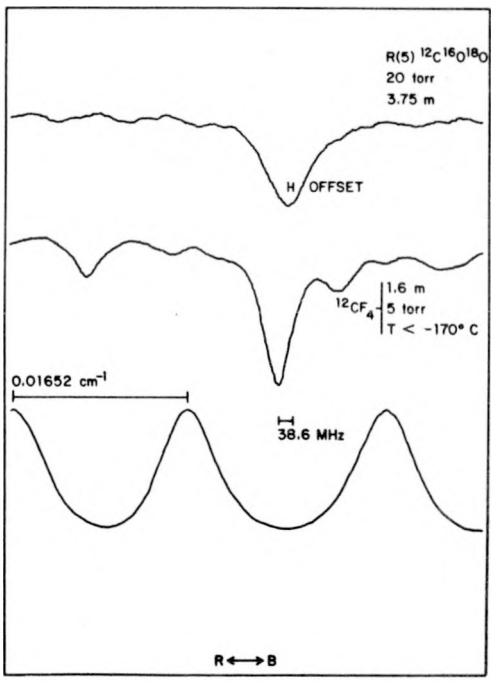

Fig. 6.
Measurement of the 9R5 $^{12}C^{16}O^{18}O$ line relative to the $^{12}CF_4$ features. Note that the R(5) peak should be shifted to the right by the amount of offset shown.

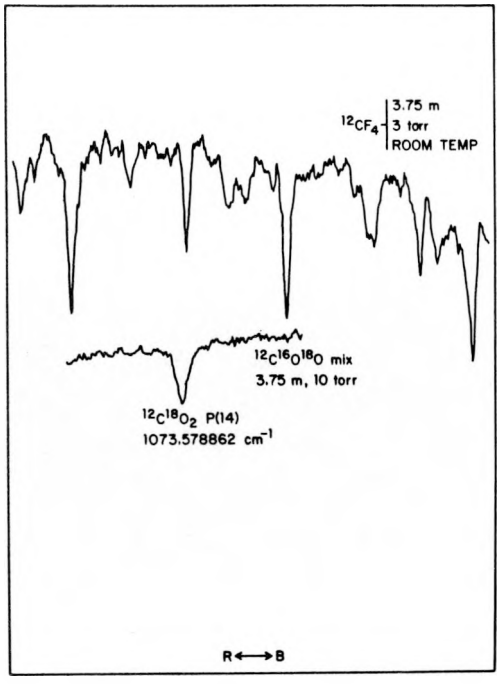

Fig. 7.
Location of the 9P14 $^{12}C^{18}O_2$ line relative to the $^{12}CF_4$ features.

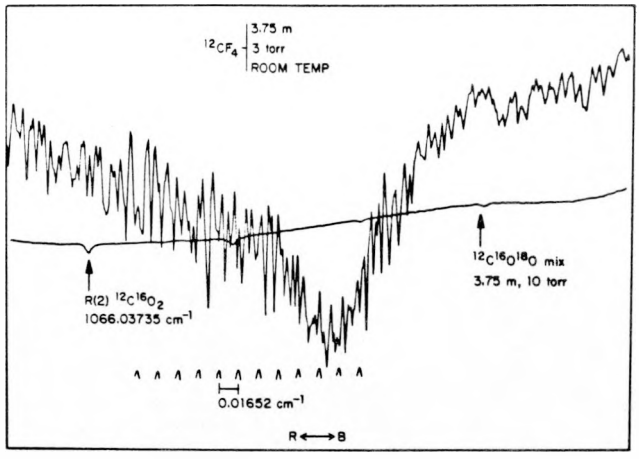

Fig. 8.
The Q branch of $^{12}CF_4$ with a 9R2 $^{12}C^{18}O_2$ frequency marker.

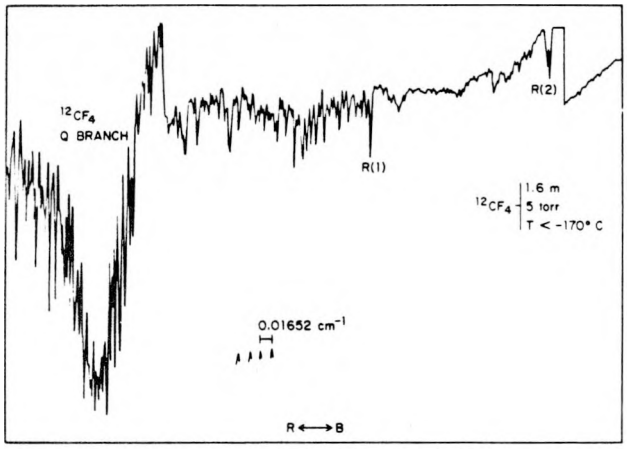

Fig. 9.
Beginnings of the $^{12}CF_4$ R branch.

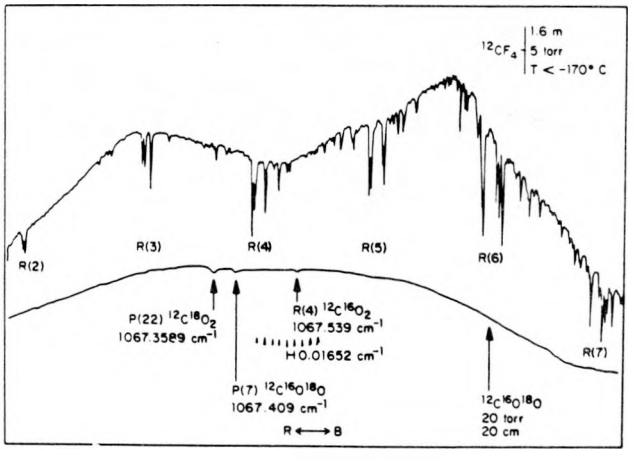

Fig. 10.
The $^{12}CF_4$ R(2) through R(7) lines with CO_2 frequency markers.

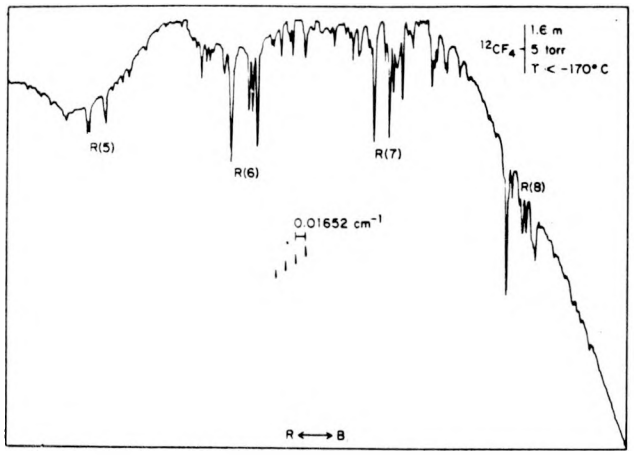

Fig. 11.
The $^{12}CF_4$ R(5) through R(8) lines.

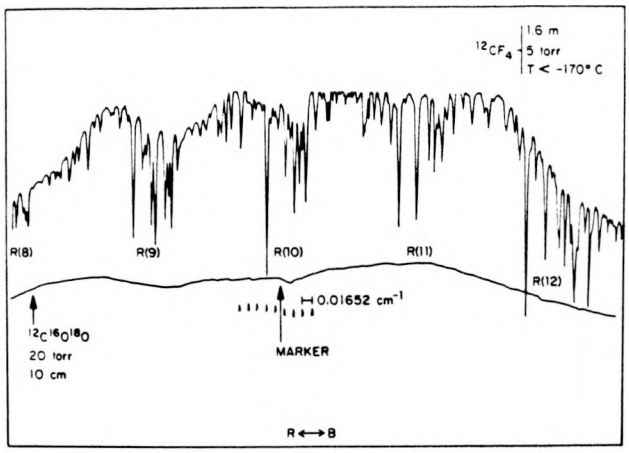

Fig. 12.
The $^{12}CF_4$ R(8) through R(12) lines with CO_2 frequency markers.

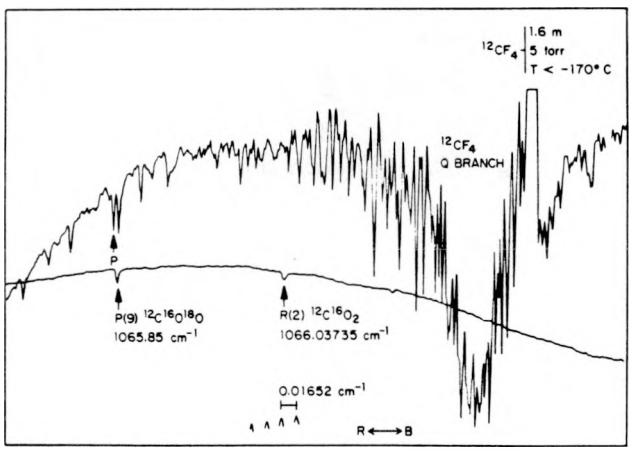

Fig. 13.
Beginnings of the $^{12}CF_4$ P branch.

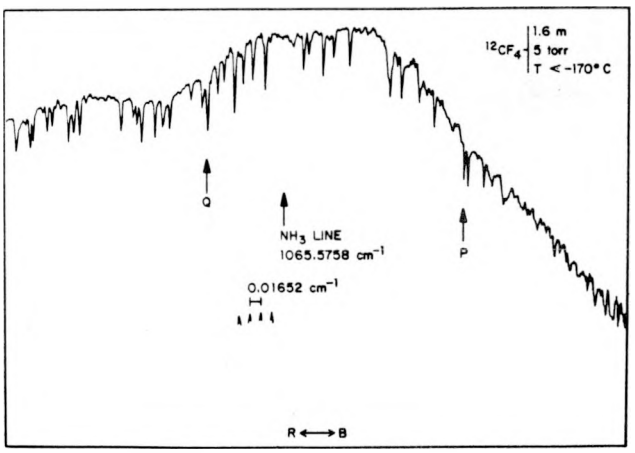

Fig. 14.
The $^{12}CF_4$ P-branch spectra with an NH_3 frequency marker.

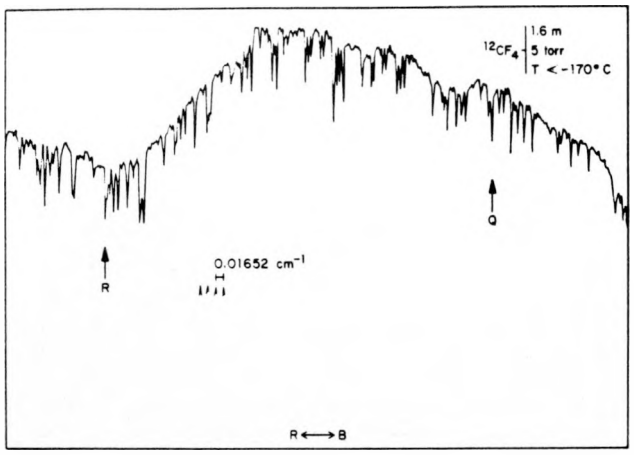

Fig. 15.
The $^{12}CF_4$ P-branch spectra.

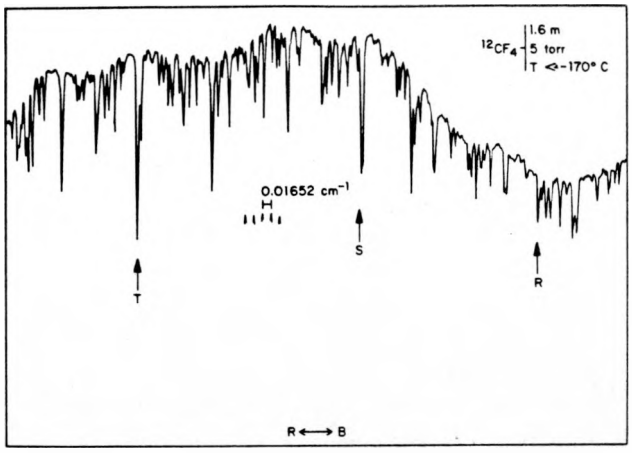

Fig. 16.
The $^{12}CF_4$ P-branch spectra.

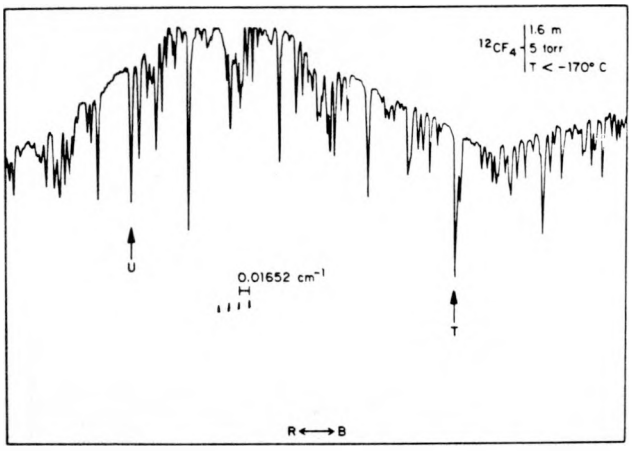

Fig. 17.
The $^{12}CF_4$ P-branch spectra.

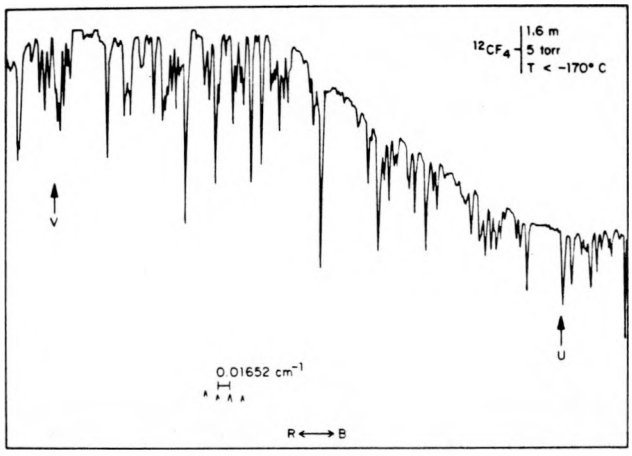

Fig. 18.
The $^{12}CF_4$ P-branch spectra.

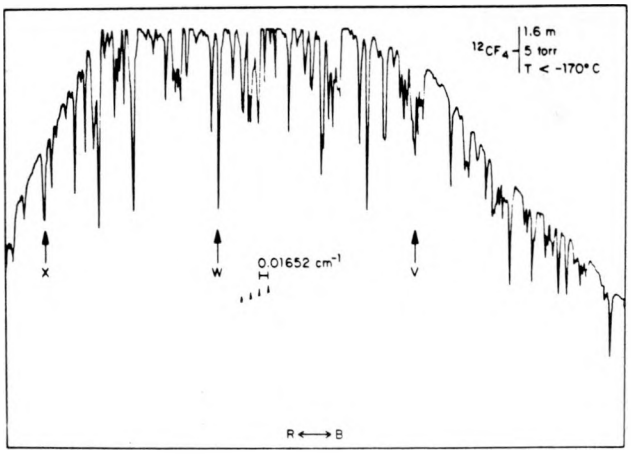

Fig. 19.
The $^{12}CF_4$ P-branch spectra.