The precise determination of the carbohalide (including \text{CF}_2\text{Cl}_2) concentration in the atmosphere is presently of great importance because these gases may importantly contribute to the photochemistry of stratospheric ozone and affect the climate on a worldwide scale. The determination is difficult because the concentration of these admixtures in the atmosphere is extremely low (0.01-1 per $10^6$). Such low concentrations can be detected only with very advanced investigation techniques such as high-resolution spectroscopy and data processing with a computer.

Good results have been obtained when diode lasers were used for gas analysis because they are characterized by a combination of such properties as high resolving power ($\sim 10^{-6} \text{ cm}^{-1}$) and frequency tuning in a wide spectral interval (tens and hundreds of cm$^{-1}$). Spectrometers with diode lasers are characterized by fast response, are relatively simple in their design and operation, and provide high selectivity and precision of the measurements.

The authors of [1-3], who used diode lasers, obtained sections of the \text{CF}_2\text{Cl}_2 transmission spectra in the ranges 915-930 and 1155-1163 cm$^{-1}$ and determined the absorption coefficient, the coefficient of self-broadening of the lines, and the coefficient of collision-induced broadening of the individual lines. The authors of [2] have determined the sensitivity of absorption recordings in a single line; the sensitivity was 2 per $10^6$ with an optical path length of 1 m, i.e., the detection limit of the \text{CF}_2\text{Cl}_2 concentration could be 10 per $10^9$ with a 200-m-long optical cuvette.

But the data of [1-4] are incomplete and to date the sensitivity of the technique does not suffice for atmospheric measurements.

We studied in our work the $v_4$ band of \text{CF}_2\text{Cl}_2 in the range 915-930 cm$^{-1}$ because this band is characterized by highest integral absorption. Using the information of the entire spectrum recorded was the outstanding feature of our recording technique. In this way we obtained a substantial advantage over the technique of recording the absorption in a single line only. We obtained in our work the spectral dependence of the absorption coefficient of \text{CF}_2\text{Cl}_2. The data were processed on a computer with a correlation technique so that the coefficients of collision-induced broadening and self-broadening could be determined. The optimal recording conditions were analyzed. The sensitivity of the gas analyzer amounts to 50 per $10^6$ at an optical path length of 1 m.

Apparatus. Figure 1 depicts the optical scheme of the diode-laser spectrometer resembling that of [5]. The Pb$_x$Sn$_{1-x}$Se diode laser is operated in the periodic-pulsed mode at 10-77$^\circ$K (pulse length $\leq$10 msec; pulse repetition frequency $\sim$100 Hz).

Frequency scanning was performed by heating the $p-n$ junction of the laser in a pulse. The holder of the laser and the optical cryostat had been designed so that the radiation

![Optical scheme of the diode-laser spectrometer](image-url)
leaving from two opposite faces of the laser could be used. The optical scheme therefore has two identical arms. One arm is used for recording and includes a cuvette with the gas to be analyzed, a Fabry-Perot standard, a cuvette with a reference gas for absolute calibration, and a monochromator (when it is necessary to single out one mode only). The second arm is used for stabilizing the laser radiation frequency with the aid of an absorption line of the reference gas. CdHgTe photodetectors cooled with liquid nitrogen are used in both arms. The relative reproducibility of the tuned laser radiation frequency is better than $5 \times 10^{-5}$ cm$^{-1}$ from pulse to pulse [6]. An absolute frequency calibration was made with the absorption lines of NH$_3$, CO$_2$, and SF$_6$. The precision with which the position of the lines of the gas analyzed was determined is given by the precision of the frequency-scale calibration with the Fabry-Perot standard ($5 \times 10^{-4}$ cm$^{-1}$) and by the precision with which the frequencies of the lines of the reference gases are known.

Experimental Results. Figure 2 illustrates the operation of the spectrometer. Two cuvettes are inserted in the recording arm; one of the cuvettes was filled with NH$_3$ (Fig. 2a) and the absorption line of which was used for the absolute calibration of the frequency scale in this particular case. The second cuvette was filled with CF$_2$Cl$_2$ (Fig. 2b). A cuvette containing NH$_3$ was inserted in the stabilizing arm. One of the NH$_3$ absorption lines was used to stabilize the scanning cycles [6]. A relative calibration was made with the transmission spectra of a Fabry-Perot germanium standard having a free dispersion range of 0.049 cm$^{-1}$ (Fig. 2c).

The signal recorded (Fig. 2b) can be represented in the form

$$U(\nu) = U_0(\nu) e^{-\sigma(\nu)} = U_0(\nu) e^{-\kappa(\nu)PL},$$

where $U_0(\nu)$ denotes the transmission spectrum of the optical channel without a gas; $\sigma(\nu)$ denotes the spectrum of the optical density; $\kappa(\nu)$ denotes the spectrum of the absorption coefficient of the gas to be examined [in the general case, the coefficient depends upon the pressure of the buffer gas, i.e., $\kappa(\nu, P_{buff})$, in the particular case, $P_{buff} = 0$]; $P$ denotes the partial CF$_2$Cl$_2$ pressure; and $L$ denotes the length of the cuvette. When the data shown in Figs. 2a and 2b were processed with a computer, the $\kappa(\nu)$ values were obtained.

The spectra of the CF$_2$Cl$_2$ absorption coefficient obtained in this way are shown in Fig. 3. Resonance features on the background of a rather strong constant component can be recognized in each of the spectra. A similar structure, which is recognizable through the high density of the lines, has several causes, mainly the presence of various isotope forms of CF$_2$Cl$_2$ mixtures: (CF$_2^{35}$Cl$_2$;CF$_2^{33}$Cl$_2$;CF$_2^{37}$Cl$_2$;CF$_2^{35}$Cl$_2 = 9:6:1$). The spectra of these forms have a rather high line density and overlap; in addition, the basic transitions of the lines corresponding to hot bands are superimposed on the spectra. When the mixture under inspection is cooled to $\sim$130 K, the nonresonance absorption background associated with the hot bands can be considerably reduced (Fig. 4). This is accompanied by an enhancement of the resonance features by a factor of about 10 at the same pressures of the mixture. Reducing the temper-