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High-Resolution Spectroscopy of CF_2Cl_2 in a Molecular Jet

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Abstract. Absorption spectra of CF_2Cl_2 were recorded around 923 cm^{-1}, with a resolution of 50 MHz. The application of the molecular jet technique considerably simplifies the spectra as compared to room-temperature experiments. Rotational and vibrational temperatures were measured for CF_2Cl_2 pure and seeded in Ar or He. Molecular constants were obtained for the ν_6 vibrational band of the two most abundant chlorine isotopic species, as well as vibrational band origines for the $\nu_6 \pm \nu_4$ and the $\nu_6 \pm \nu_5$ hot-bands of the $CF_2{}^{35}Cl_2$ isotope.

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Several studies [1, 2] have been carried out to investigate the effect of fluorocarbons (freons) on the ozone concentration in the stratosphere. Large quantities of these freons (more than 500 million kg of $CFCl_3$ and CF_2Cl_2 per year), which are used as aerosol propellants and are also produced by refrigeration and plastic froam industries, are released in our atmosphere. These compounds have relatively long lifetimes in the troposphere (more than 50 years), due to their low reactivity. The chlorine atoms produced by the spontaneous photolysis of these freons may cause a depletion of the protective layer of ozone in the stratosphere.

Infrared spectroscopy is a very powerful method for detecting trace gases and one of the most important freons, CF_2Cl_2 has been investigated extensively [3–5]. Concentrations of CF_2Cl_2 in the stratosphere have been measured by balloon-borne grating spectrometers [6, 7] and by Fourier-transform spectrometers based on a mountain [8], borne by a balloon [1] or even located on a NASA Spacelab [9a].

It should be also mentioned that CF_2Cl_2 has been used for Carbon 13 isotopic enrichment [9b]. An accurate knowledge of the linear spectroscopy is necessary in order to understand the multiple photon excitation mechanisms involved in those experiments.

In relatively low resolution (0.1 cm^{-1}) studies the different vibrational bands of this molecule were characterized [10]. Even at low resolution the CF_2Cl_2 spectra are rather complicated, due to the presence of several overlapping chlorine isotopic bands. Spectral features belonging to the $CF_2{}^{35}Cl{}^{35}Cl$ isotopic species were identified unambiguously by using an isotopically enriched sample [11]. At room temperature two or three hot-bands from low-lying vibrational modes are intense enough to complicate the spectra even more.

The vibrorotational spectrum of this strongly asymmetric top molecule is not easy to interprete, especially at room temperature, when the Q-branches obscure a large part of the spectrum. Several overlapping spectra (due to isotopes and hot-bands) cause a line density of more than 1000 lines per cm^{-1} and even a

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resolution of 0.001 cm^{-1} is not sufficient to obtain spectroscopic constants from this room-temperature spectra. Microwave-infrared double resonance experiments [12–14] however, provided very detailed spectroscopic information for the fundamental ν_6 vibration and several hot-bands.

In the present experiment the large density of the room-temperature spectra was reduced by application of the molecular jet technique. The rotational cooling caused a narrowing of the Q-branches, so that *P* and *R* transitions became observable. Furthermore the vibrational cooling reduced the intensities of the hot-band transitions. Hot-band features could be recognized by comparing absorption spectra obtained for expansions of CF_2Cl_2 pure and CF_2Cl_2 seeded in Ar or He. Many transitions of the ν_6 fundamental could be resolved and assigned. Rotational constants for the vibrational excited state have been determined and are compared with the MW-ir double resonance results [12–14].

This work demonstrates that high-resolution so-called ir finger-print spectra can be obtained using the cooling properties of the molecular jet, even for rather complicated systems.

1. Experimental

CF_2Cl_2 pure or $12^1/_2$% seeded in Ar or He (stagnation pressure 1 bar) was expanded through a 300 μm diameter nozzle into a vacuum chamber pumped by a baffled 3000 l/s oil diffusion pump backed by a 1000 m^3/h roots pump and a 60 m^3/h rotary pump. A commercially available (Laser Technics model 203 LPV) molecular beam source was used to produce a pulsed molecular jet of 150–200 μs pulse duration with a repetition rate of about 125 Hz. The pressure in the vacuum chamber increased from 3×10^{-6} to $1\text{–}3 \times 10^{-4}$ Torr when the pulsed valve was switched on.

The infrared radiation from a Laser Analytics Inc. diode laser spectrometer (model SP 5000) (Fig. 1) was focused by a ZnSe ($f = 384$ mm) lens to a small focus (1 mm diameter) about 10–15 mm under the nozzle. A multi-pass system was mounted in the vacuum chamber to increase the absorption path length. This system consists of two concave aluminium reflectors (reflectivity = 97%, $f = 50$ mm) positioned 194 mm apart. Multiple reflection produces an elliptical or parabolical pattern [15] on both mirrors and a large number of small focal points in a small volume ($7 \times 1 \times 1$ mm^3). The outcoming laser beam is focused by a NaCl lens ($f = 50$ mm) on a HgCdTe detector. The fraction of the laser radiation which was absorbed by the molecular jet was typically less than 1% in a single-pass set-up. After mounting the multi-pass system, the absorbed fraction of the laser radiation increased a factor 15 to 20 for 20 passes. The signal of the HgCdTe detector is fed into a two channel Boxcar Integrator (EG & G PAR mod. 162). The gate (of 50 μs width) of the first channel coincides with the centre of the molecular jet pulse, the gate of the second channel (50 μs) is put 200 μs *before* the jet pulse. The difference-signal of the two channels is recorded on a two pens $X - Y$ recorder.

By means of a ZnSe beamsplitter about 10–15% of the laser radiation is directed through an absorption cell (15 cm long) containing 3 Torr of SiH_4 and focused on a second HgCdTe detector by a NaCl lens ($f = 50$ mm). A small chopper ($f = 1500$ Hz) allows phase-sensitive detection of the reference beam. The SiH_4 absorption spectrum has about 20–30 lines per cm^{-1} in the investigated frequency region (920–926 cm^{-1}) which are known with sufficient accuracy [16]. Our molecular jet spectra are recorded simultaneously with the SiH_4 spectra, while the diode laser current is varied linearly with the time (0.5×10^{-4} A/s). A third degree polynomial in the laser current was fitted through the known SiH_4 line frequencies and the obtained relation between laser current and frequency is used to calibrate the jet absorption spectra. The reproducibility of this method was tested by recording spectra of the same frequency region several times, performing each time the calibration procedure. The few NH_3 lines in this region were also recorded to check the accuracy of calibration. In all our measurements the reproducibility for each individual line of the molecular jet spectra was better than 0.003 cm^{-1} and the agreement with the NH_3 lines was good (0.002 cm^{-1}).

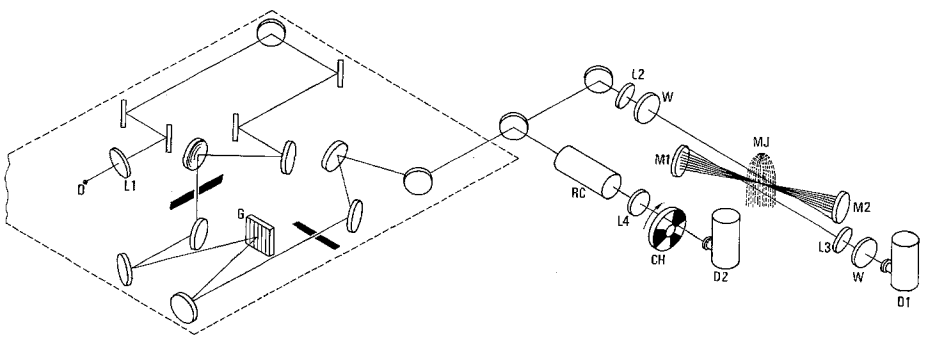

Fig. 1. Experimental set-up (D: diode, G: grating, W: window, D1, D2: HgCdTe detectors, L1–L4: lenses, RC: reference-cell, CH: mechanical chopper, MJ: molecular jet, M1 and M2 are the mirrors of the multipass system)

One of the advantages of the pulse jet technique is that slow laser amplitude fluctuations hardly effect the absorption signal during a scan, since we monitor the absorbed *fraction* of the laser radiation. In contrary, for absorption spectra obtained by modulating the laser radiation the transmission is measured and laser amplitude variations on the time scale of the scan limit the sensitivity. The minimum detectable absorption in our experiments was about 0.05% for strong diode laser modes. For weaker modes, the detector noise is the limiting factor.

The line width of the absorption lines observed in the molecular jet expansion was 50–65 MHz, due to both laser frequency fluctuations and Doppler broadening. We did not observe a significant difference in line width going from pure to seeded expansions (50 MHz for CF_2Cl_2 pure, 60 MHz for $12^1/_2\%$ CF_2Cl_2 in Ar and 65 MHz for $12^1/_2\%$ CF_2Cl_2 in He), which suggests that laser frequency fluctuations are mainly responsible for the observed width. This is confirmed by the fact that for some weak laser modes we observed a line width of about 100–150 MHz. The small contribution of the Doppler width indicates that most of the absorption occurs on the molecular beam axis, which is not so surprising considering the low back-ground pressure ($1–3 \times 10^{-4}$ Torr) and the large distance from the nozzle (10–15 mm).

2. Results and Discussion

2.1. Jet Cooling

In earlier experiments [18, 19] it has been shown that the rotational and vibrational cooling in a pure freon expansion is very moderate. Typically rotational temperatures of about 70 K and vibrational temperatures of 200 K can be achieved. To obtain a better cooling an Ar or He beam can be seeded with CF_2Cl_2. We compared the spectra obtained for a pure CF_2Cl_2 expansion to those of $12^1/_2\%$ of CF_2Cl_2 in He or Ar. The rotational temperature for the three different expansions were obtained from the width of the Q-branch at 921.8187(6) cm^{-1} belonging to the ν_6 fundamental of the $CF_2{}^{35}Cl^{37}Cl$ isotope (Fig. 2). Simulations of the spectra were computed (see Sect. 2.2) and compared to the experimental data and rotational temperatures were obtained for the seeded beams ($T_{rot} \simeq 15$ K) and for the pure beam ($T_{rot} \simeq 50$ K). For a rotational temperature of 15 K the rotational distribution has its maximum for $J = 10$ ($J_{max} \simeq 40$ for room temperature). Note that the width of the Q branches, which is proportional to $J(J+1)$ is reduced by a factor of $\simeq$15–20 with respect to a room temperature distribution.

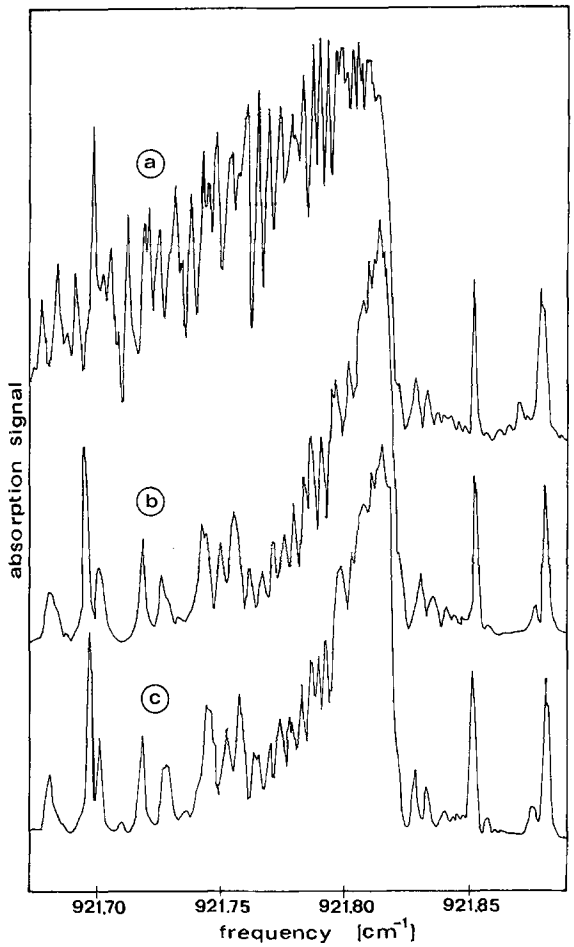

Fig. 2a–c. The Q branch of the ν_6 fundamental of $CF_2{}^{35}Cl^{37}Cl$ at 921.8187(6) cm^{-1}, recorded for a CF_2Cl_2 pure expansion (a), $12^1/_2\%$ CF_2Cl_2 in Ar (b), and $12^1/_2\%$ CF_2Cl_2 in He (c)

In order to estimate the vibrational temperature the intensity of the Q branch at 921.343(2) cm^{-1}, corresponding to the $\nu_6 \pm \nu_4$ hot-band of $CF_2{}^{35}Cl_2$ isotope (Fig. 3), was compared to nearby P transitions of the ν_6 fundamental of the $CF_2{}^{35}Cl^{35}Cl$. The vibrational cooling increased substantially for the He ($T_{vib} \simeq 100$ K) and Ar ($T_{vib} \simeq 125$ K) seeded beams with respect to the pure beam ($T_{vib} \simeq 200$ K). Note that this vibrational temperature reflects the population of the ν_4 vibrationally excited level with respect to the ground state. In a molecular-beam expansion the population of the different vibrational states can not be described by a Boltzmann distribution [17, 18]. The reason is that the relaxation from higher-energy vibrational levels to lower-energy levels involves often smaller energy transfers than relaxation of the lowest vibrational state to the ground state. As a result the vibrational temperature obtained from the intensity of the Q branch of the $\nu_6 \pm \nu_4$ hot-band predicts too high intensities for other hot-bands. The $\nu_6 \pm \nu_5$ hot-band,

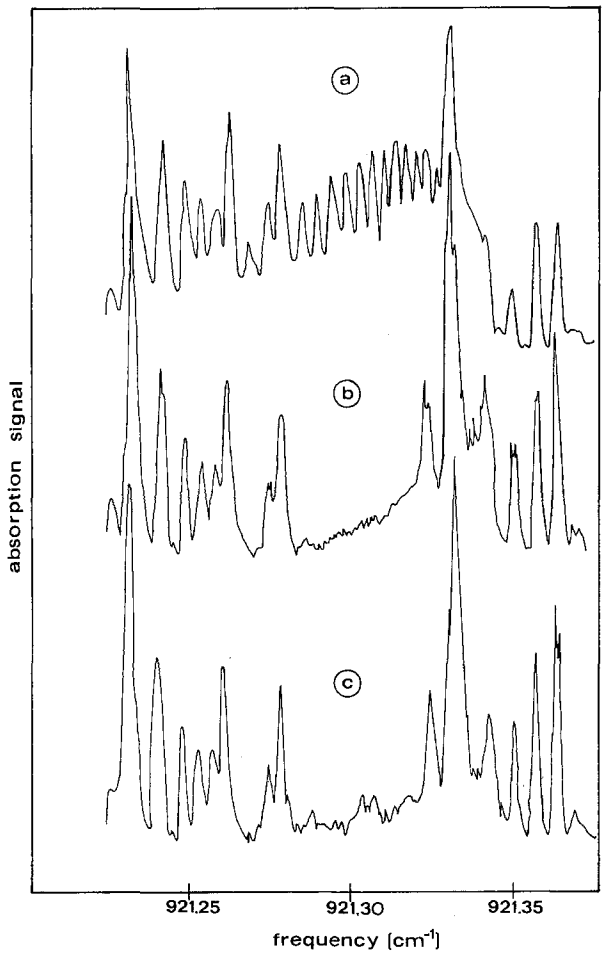

Fig. 3a–c. The Q branch of the $\nu_6 \pm \nu_4$ hot-band of $CF_2{}^{35}Cl_2$ at 921.343(2) cm^{-1}, recorded for a CF_2Cl_2 pure expansion (a), $12^1/_2$% CF_2Cl_2 in Ar (b), and $12^1/_2$% CF_2Cl_2 in He (c)

Table 1. Molecular constants for the ν_6 vibration of $CF_2{}^{35}Cl_2$

	This work	Ref. [12]
ν_0 [cm^{-1}]	923.2396(2)	923.23956(12)
ΔA [MHz]	− 3.38(5)	− 3.35(4)
ΔB [MHz]	− 7.76(4)	− 7.76(3)
ΔC [MHz]	− 7.93(3)	− 7.93(3)

Table 2. Molecular constants for the ν_6 vibration of $CF_2{}^{35}Cl^{37}Cl$

	This work	This work, ΔA fixed to value of [13, 14]	Ref. [13, 14]
ν_0 [cm^{-1}]	921.8194(3)	921.8187(6)	921.8192(3)
ΔA [MHz]	− 4.67(47)	− 2.52	− 2.52(3)
ΔB [MHz]	− 7.91(17)	− 8.10(16)	− 7.97(1)
ΔC [MHz]	− 8.92(31)	− 8.66(31)	− 8.54(1)

e.g., was only very weakly observed in the pure expansion, but not in the seeded beams, although its intensity should be at most a factor of two weaker than that of the $\nu_6 \pm \nu_4$ hot-band, assuming a Boltzmann distribution. The vibrational temperature for the CF_2Cl_2 pure expansion calculated from the intensity of the Q branch of the $\nu_6 \pm \nu_5$ hot-band at 922.698(5) cm^{-1} was 160 ± 20 K.

Neither of the two diodes we used had a laser mode in the frequency region between 916 and 920 cm^{-1}, preventing us to study the ν_6 fundamental of the $CF_2{}^{37}Cl_2$ and several hot-bands.

2.2. Molecular Constants

The CF_2Cl_2 molecule is a strongly asymmetric top ($\kappa = -0.57$) which makes its vibrorotational spectrum rather complicated. A computer program, using the rotational Hamiltonian of [19, 20], produced a simulation of the full absorption spectrum, including all the isotopes and hot-bands. In this case very accurate molecular constants were available [12–14] and the assignment of the measured spectra was quite straightforward. For the ν_6 fundamental of $CF_2{}^{35}Cl_2$ about 500 P and R transitions ($J \leqq 23$) could be assigned. A least squares best fit yielded values for vibrational origine and excited state rotational constants. The ground-state molecular constants, as well as the distortion constants of the excited state, were taken from [12–14] and were not varied, since our data were not accurate enough (± 90 MHz) to include them in the fit. The results of the fit agree perfectly with the ir–MW results of [12–14], as is shown in Table 1. A similar fit was performed for the ν_6 transition of the $CF_2{}^{35}Cl^{37}Cl$ isotope (110 P and R transitions with $J \leqq 9$ were assigned). The results of this fit are shown in Table 2. The agreement with the molecular constants of [13, 14] is good except for ΔA. Since in our spectra only transitions with low values for K_a and K_b occur, our fit is not very sensitive for the value of ΔA. Indeed, keeping ΔA fixed at the value of [13, 14] the χ-square value of our fit increased only 5%, and produced only small changes in the values of ν_0, ΔB, and ΔC (Table 2).

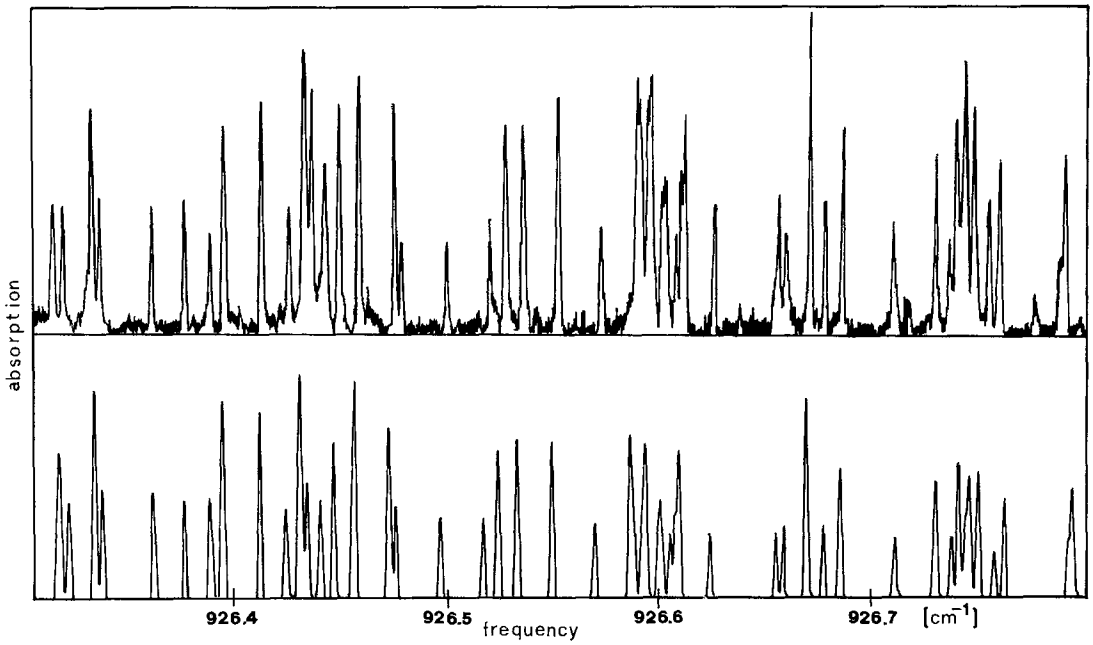

Fig. 4. A part of the experimental spectrum (upper panel) is compared with the corresponding simulated spectrum (lower panel). Note that in the experimental spectrum the horizontal axis is in reality the laser-current which is not exactly linearly proportional to the frequency

The standard deviation in our fits was 60 MHz for the $CF_2{}^{35}Cl_2$ data and 70 MHz for the $CF_2{}^{35}Cl^{37}Cl$ data. The agreement between measured and simulated spectra is illustrated in Fig. 4, which shows a piece of the *R* branch of the $CF_2{}^{35}Cl_2$ isotope.

For the two hot-bands essentially the *Q* branches were observed and only band origines were determined: 921.343(2) cm^{-1} for the $\nu_6 \pm \nu_4$ hot-band and 922.698(5) cm^{-1} for the $\nu_6 \pm \nu_5$ hot-band, both of the $CF_2{}^{35}Cl_2$ isotope.

3. Conclusions

High-resolution ir finger-print spectra of CF_2Cl_2 expanded in a molecular jet have been recorded. The spectroscopic constants obtained from these spectra are in excellent agreement with ir–MW double-resonance experiments [12–14]. The combination of diode laser spectroscopy and the cooling properties of a molecular jet is a very powerful technique to simplify spectra which are too complicated at room-temperature, due to the occurrence of hot-bands and rotational congestion. The availability of diodes in a vast frequency range makes this technique widely applicable.

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