High-Resolution Spectroscopy of CF$_2$Cl$_2$ in a Molecular Jet

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Abstract. Absorption spectra of CF$_2$Cl$_2$ 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$_2$Cl$_2$ pure and seeded in Ar or He. Molecular constants were obtained for the $v_6$ vibrational band of the two most abundant chlorine isotopic species, as well as vibrational band origins for the $v_6 \pm v_4$ and the $v_6 \pm v_5$ hot-bands of the CF$_2^{35}\text{Cl}_2$ 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 CFC$_3$ and CF$_2$Cl$_2$ per year), which are used as aerosol propellants and are also produced by refrigeration and plastic foamin 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$_2$Cl$_2$ has been investigated extensively [3–5]. Concentrations of CF$_2$Cl$_2$ 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 [9].

It should be also mentioned that CF$_2$Cl$_2$ 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$_2$Cl$_2$ spectra are rather complicated, due to the presence of several overlapping chlorine isotopic bands. Spectral features belonging to the CF$_2^{35}\text{Cl}^{35}\text{Cl}$ 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 interpret, 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
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 $v_6$ 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$_2$Cl$_2$ pure and CF$_2$Cl$_2$ seeded in Ar or He. Many transitions of the $v_6$ 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$_2$Cl$_2$ pure or 12.1/2% seeded in Ar or He (stagnation pressure 1 bar) was expanded through a 300 $\mu$m 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 $\mu$s pulse duration with a repetition rate of about 125 Hz. The pressure in the vacuum chamber increased from $3 \times 10^{-6}$ to $1-3 \times 10^{-4}$ 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 $\mu$s width) of the first channel coincides with the centre of the molecular jet pulse, the gate of the second channel (50$\mu$s) is put 200 $\mu$s 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 ($0.5 \times 10^{-4}$ 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)