Diode-Laser Spectroscopy in a Supersonic Free Jet: 1,1-Difluoroethylene at Low Temperature*

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The infrared spectrum of 1,1-Difluoroethylene has been measured in a supersonic free jet by diode-laser spectroscopy in the wavenumber region between 921 and 928 cm^{-1}. The low rotational temperature, 32(8) K, of the molecules in the jet simplified the spectrum substantially, allowing its identification in the band center region. Two different modes of jet-operation were used for the measurements: (1) a pulsed jet with a phase sensitive detection at the pulse frequency and (2) a continuous jet with frequency modulation of the diode-laser.

Introduction

1,1-Difluoroethylene ($C_2H_2F_2$, or DFE) is a heavy asymmetric top molecule with several low lying bending vibrations [1]. Therefore at room temperature the IR spectrum is very dense, confused, and consequently very complicated to assign. Most of these problems are alleviated in rotationally cooled spectra as produced in molecular beams.

In 1978 Duxbury and Herman [2] as well as Lafferty et al. [3] were able to identify some parts of the spectrum of the ν_4 and ν_9 band of DFE at room temperature. Duxbury used a CO_2 and an NO_2 laser while Lafferty employed a CO_2 laser simultaneously with a diode-laser. However, near the ν_4 band center at 926 cm^{-1} the spectrum is so dense that only few lines have actually been assigned. The aim of this work has been the observation of the spectrum in the wavelength region close to the ν_4 band center at very low rotational temperatures to obtain a secure assignment. Secondly, DFE serves as a beautiful example to demonstrate the power of the jet-method in greatly simplifying complex spectra.

At the achieved rotational temperature of 32(8) K, the recorded spectrum was essentially free from hot-band lines, leading to an assignment of most observed lines. The molecular constants determined by Lafferty et al. were found to have sufficient accuracy to reproduce the spectrum observed in the present study.

Experimental

The experimental arrangement has been discussed in our earlier work [4, 5]. The spectra were recorded in two modes of jet-operations: (i) in a pulsed molecular beam and (ii) in a continuous jet. The pulsed molecular jet was produced by a modified automobile valve (Bosch GmbH, West Germany) [4]. By switching the current of the magnetic valve, the molecules were injected into the vacuum chamber in a pulsed jet with a repetition rate of 82 Hz. The absorption signal was found to be an optimum at a pulse rate of 82 Hz.

For the continuously operated (cw) molecular jet a 5 kHz sinewave-frequency-modulated laser beam was produced and demodulated at 10 kHz to obtain second derivative spectra. The nozzle for the cw operation is a glass cylinder with a pin hole of about 0.1 mm diameter. The wall thickness is lower than 1 mm. Although both modes of jet operation yield in the present system comparable signal-to-noise ratios, it is noticed that the characteristic fringe features associated with diode laser spectroscopy, i.e. in the cw mode, is missing in the pulsed mode. The pulsed jet operation is therefore to be preferred.

Lines of HNCO [6] were used as wavelength calibration standard. Fringes of a germanium etalon (fringe spacing of about 0.016 cm^{-1}) provided a scale for calibration. The accuracy of the line positions thus measured is estimated to be about 0.0007 cm^{-1}.

Observations

1,1-Difluoroethylene is a near oblate asymmetric top with the asymmetry parameter $\varkappa = 0{,}793$. The spectra were recorded near the band center at

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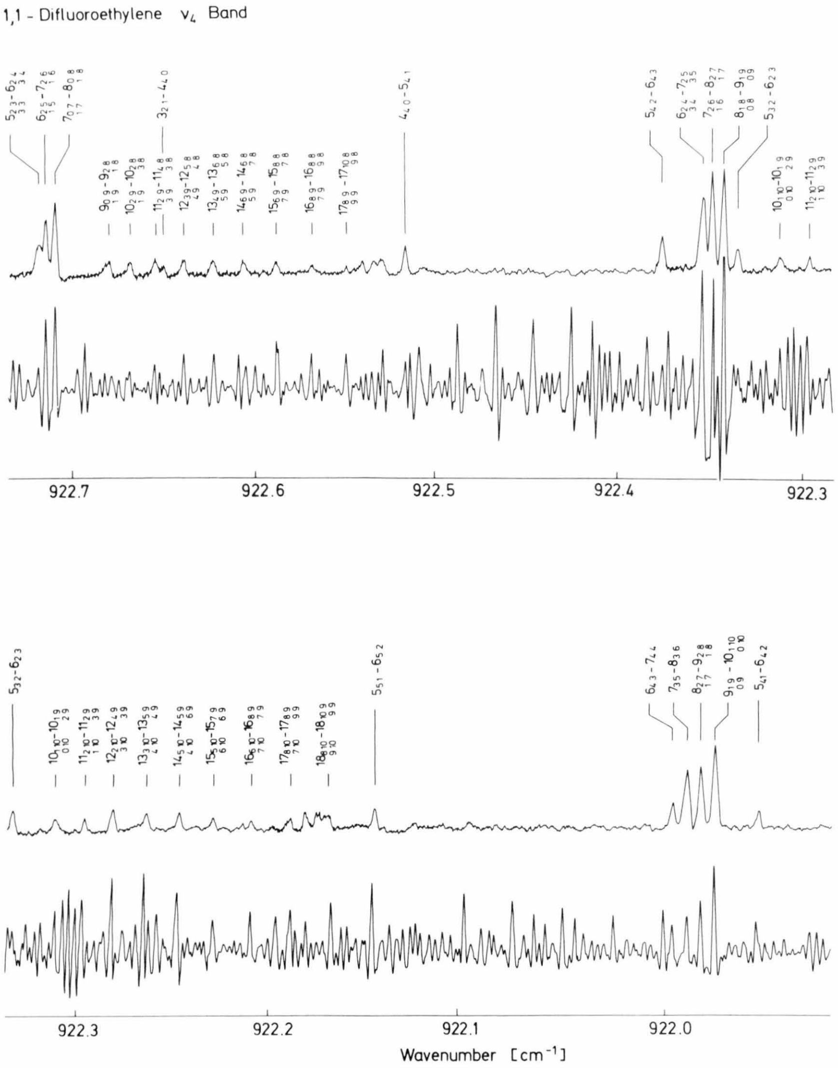

Fig. 1.

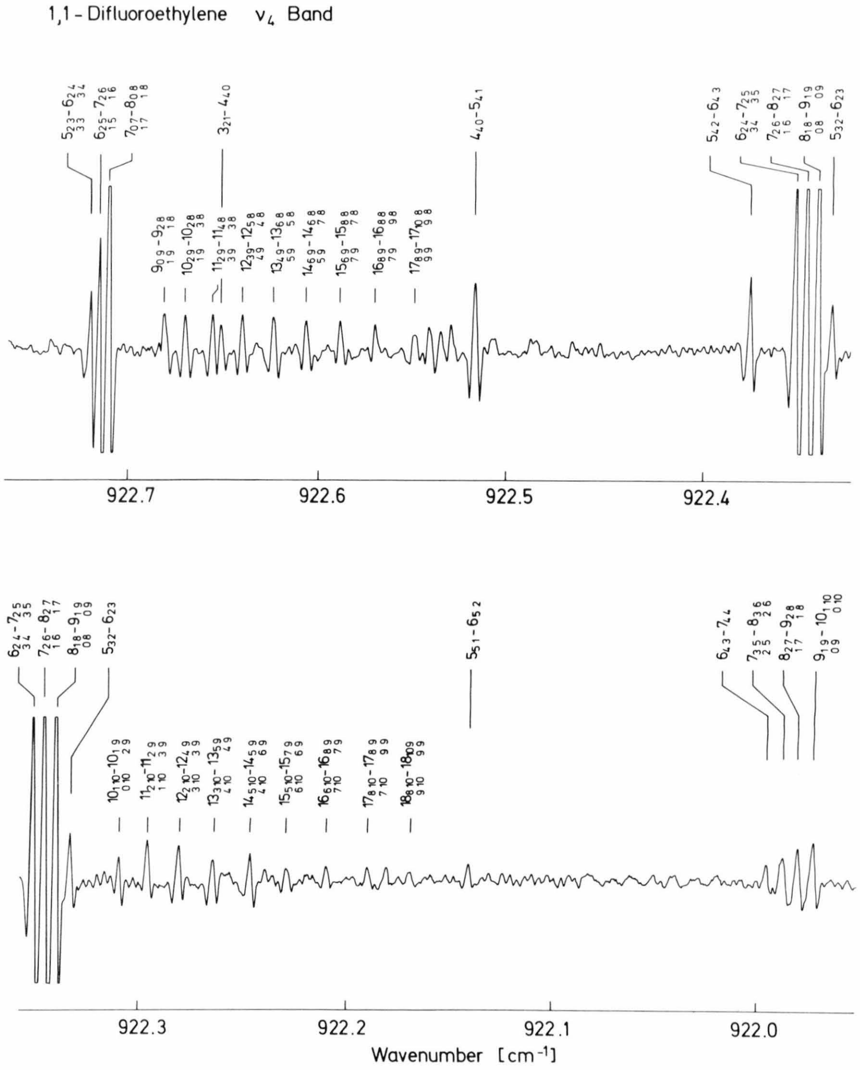

Fig. 2.

Fig. 1. Part of the spectrum of DFE. Upper trace: Jet spectrum observed with pulsed valve ($T_{\mathrm{rot}} = 32(8)$ K). Lower trace: Room temperature spectrum detected in the second derivative. In the jet spectrum the structures of the transitions of a Q-branch and a P-branch are clear. These structures are confused in the room temperature spectrum by the many hot-band lines.

Fig. 2. The spectrum of Fig. 1 observed in the cw molecular jet.

Table 1. Observed Transitions in cm^{-1} for the ν_4-Band of 1,1-Difluoroethylene.

J	k_a	$k_c - J$	k_a	k_c	obs.	O−C* $\times 10^{-4}$	J	k_a	$k_c - J$	k_a	k_c	obs.	O−C* $\times 10^{-4}$
6	4	2 − 7	4	3	921.5941	20	15	7	9 − 15	7	8	922.5845	3
10	0	10 − 11	0	11	921.6077	6	14	6	9 − 14	6	8	922.6025	1
10	1	10 − 11	1	11	921.6077	6	14	5	9 − 14	7	8	922.6025	1
9	1	8 − 10	1	9	921.6151	5	13	4	9 − 13	6	8	922.6198	0
9	2	8 − 10	2	9	921.6151	5	13	5	9 − 13	5	8	922.6198	0
8	3	6 − 9	3	7	921.6225	6	12	4	9 − 12	4	8	922.6377	14
8	2	6 − 9	2	7	921.6225	6	12	3	9 − 12	5	8	922.6377	14
7	3	4 − 8	3	5	921.6287	4	3	2	1 − 4	4	0	922.6490	14
7	4	4 − 8	4	5	921.6287	4	11	2	9 − 11	4	8	922.6537	18
5	4	1 − 6	4	2	921.9541	0	11	3	9 − 11	3	8	922.6537	18
9	1	9 − 10	1	10	921.9751	1	10	2	9 − 10	2	8	922.6675	11
9	0	9 − 10	0	10	921.9751	1	10	1	9 − 10	3	8	922.6675	11
8	2	7 − 9	2	8	921.9817	−1	9	0	9 − 9	2	8	922.6797	−1
8	1	7 − 9	1	8	921.9817	−1	9	1	9 − 9	1	8	922.6797	−1
7	2	5 − 8	2	6	921.9883	−1	6	1	6 − 7	1	7	923.0726	3
7	3	5 − 8	3	6	921.9883	−1	6	0	6 − 7	0	7	923.0726	3
6	4	3 − 7	4	4	921.9953	−5	5	1	4 − 6	1	5	923.0768	3
5	5	1 − 6	5	2	922.1364	10	5	2	4 − 6	2	5	923.0768	3
18	8	10 − 18	10	9	922.1644	14	4	3	2 − 5	3	3	923.0887	1
18	9	10 − 18	9	9	922.1644	14	11	6	5 − 11	6	6	927.6355	11
17	8	10 − 17	8	9	922.1866	20	11	7	5 − 11	5	6	927.6355	4
17	7	10 − 17	9	9	922.1866	20	15	14	2 − 15	12	3	927.6660	21
16	6	10 − 16	8	9	922.2056	2	9	4	5 − 9	4	6	927.6735	11
16	7	10 − 16	7	9	922.2056	2	3	2	1 − 2	2	0	927.6735	11
15	5	10 − 15	7	9	922.2265	10	9	5	5 − 9	3	6	927.6735	10
15	6	10 − 15	6	9	922.2265	10	8	3	5 − 8	3	6	927.6896	18
14	5	10 − 14	5	9	922.2456	10	8	4	5 − 8	2	6	927.6896	18
14	4	10 − 14	6	9	922.2456	10	7	2	5 − 7	2	6	927.7026	15
13	4	10 − 13	4	9	922.2636	9	7	3	5 − 7	1	6	927.7026	15
13	3	10 − 13	5	9	922.2636	9	5	1	5 − 4	1	4	927.7181	19
12	2	10 − 12	4	9	922.2809	11	5	0	5 − 4	0	4	927.7181	19
12	3	10 − 12	3	9	922.2809	11	4	2	3 − 3	2	2	927.7181	−9
11	2	10 − 11	2	9	922.2958	0	4	1	3 − 3	1	2	927.7286	15
11	1	10 − 11	3	9	922.2958	0	12	6	6 − 12	6	7	927.9794	3
5	3	2 − 6	3	3	922.3348	1	12	7	6 − 12	5	7	927.9794	3
8	1	8 − 9	1	9	922.3421	2	11	5	6 − 11	5	7	928.0001	5
8	0	8 − 9	0	9	922.3421	2	11	6	6 − 11	4	7	928.0001	5
7	2	6 − 8	2	7	922.3481	3	10	5	6 − 10	3	7	928.0188	7
7	1	6 − 8	1	7	922.3481	3	10	4	6 − 10	4	7	928.0188	7
6	2	4 − 7	2	5	922.3530	−3	4	3	2 − 3	3	1	928.0231	4
6	3	4 − 7	3	5	922.3530	−5	9	4	6 − 9	2	7	928.0353	7
5	4	2 − 6	4	3	922.3759	−1	9	3	6 − 9	3	7	928.0353	7
3	1	2 − 4	3	1	922.4511	−1	6	1	6 − 5	1	5	928.0669	10
4	4	0 − 5	4	1	922.5150	2	6	0	6 − 5	0	5	928.0669	10
16	8	9 − 16	8	8	922.5653	0	5	2	4 − 4	2	3	928.0734	10
16	7	9 − 16	9	8	922.5663	0	5	1	4 − 4	1	3	928.0743	5
15	6	9 − 15	8	8	922.5845	3	4	2	2 − 3	2	1	928.1170	7

* Calculated with molecular constants for 1,1-Difluoroethylene, determined by W. J. Lafferty et al. [3].

926 cm^{-1} for the ν_4 band, which is the CF$_2$-symmetric stretching vibration. Figure 1 shows part of a molecular jet spectrum and one taken at room temperature. The considerable simplification of the low temperature jet spectrum is evident. Practically no hot band transitions are excited under these conditions.

The lines of the jet spectrum were identified by a comparison between the calculated and the measured line positions and intensities based on the molecular constants determined by Lafferty et al. [3]. Most of the observed Q-branch lines are unresolved K-type doublets. For the P and R branches we have observed the expected splittings due to the K-type doubling.

The line width in the jet spectrum is 77 MHz and nearly twice as large as the theoretical Doppler width at room temperature. This suggests that the velocity component of the molecules in direction of the laser beam is almost twice as large as at room temperature.

Figure 2 shows the same part of the spectrum observed in the cw molecular jet. The lines are detected by the source modulation of the diode-laser. The typical line width was 111 MHz. This increase in the line width is due to broadening caused by the frequency modulation.

Table 1 presents the transitions which have been identified. The wavenumbers given in the table were all determined from the spectrum of the pulsed jet. Identification of additional ground state lines of high energy observed at room temperature was not possible with certainty due to the heavily confused spectra.

From the intensity distribution we found that the rotational temperature of the DFE in the jet is 32(8) K. Only transitions with low quantum numbers $J\,(J = 5 - 10)$ were used in estimating the rotational temperature because of the deviations from thermal equilibrium expected in the jet for high energy states [4]. The large error in the rotational temperature is presumably due to slight displacements of the optical path relative to the molecular beam during the measurements.

Discussion

The line positions predicted from the constants reported by Lafferty et al., together with an A-reduced Watsonian in I^r-representation [7], agreed so well with our measured values that a new fit was not warranted. In Table 1 the differences between observed and predicted values are listed in the column "O – C". A careful check of Table 1 reveals that the values in column "O – C" deviate systematically from zero. On the average the lines are blue shifted by an amount of $6.5 \times 10^{-4}\,\mathrm{cm}^{-1}$, which we consider to be a residual Doppler shift originating from a small deviation of the perpendicular alignment between the molecular jet axis and the laser axis [4].This observed shift is very small (comparable to the experimental uncertainty), and other effects such as calibration error could partly be responsible as well.

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