Microwave and Millimeterwave Spectra of Difluoromethane: Centrifugal Distortion Analysis

L. Martinache, J. Burie, and J. Demaison
Laboratoire de Spectroscopie Hertzienne, Associé au C.N.R.S., Université de Lille I

I. Merke
Abteilung Chemische Physik, Institut für Physikalische Chemie der Universität Kiel

Z. Naturforsch. **42 a,** 846–848 (1987); received April 23, 1987

The rotational spectra of CH_2F_2, $v = 0$, $v_4 = 1$, $v_4 = 2$ and $^{13}CH_2F_2$, $v = 0$ have been reanalyzed. Accurate rotational and centrifugal distortion constants have been determined.

Difluoromethane (CH_2F_2) optically pumped by CO_2 lasers produces many powerful submillimeter continuous emissions. These emissions are reviewed in [1] and [2] where their frequencies are also listed. To be able to assign these emissions without ambiguity, it is necessary to know accurate ground state rotational energies. For this reason the ground state rotational spectrum was recently measured up to 800 GHz [3]. This work allowed us then to assign many submillimeter emissions [2]. But the v_4 mode lies only at 528.5 cm^{-1} [4], and some transitions from the ν_4 to the $\nu_4 + \nu_9$ combination band lead to FIR emission lines [1]. Moreover, $^{13}CH_2F_2$ is also a good lasing gas and 65 emissions have been recently measured [5]. So, it would be very useful to know the corresponding rotational spectra.

In this publication we present the analysis of the rotational spectra of $^{13}CH_2F_2$, $v = 0$; and $^{12}CH_2F_2$, $v_4 = 1$, $v_4 = 2$ as well as new data on the ground state. These spectra were previously measured in the centimeter wave range by Hirota [4]: up to $J = 20$ for $v_4 = 1$, up to $J = 7$ for $v_4 = 2$ and up to $J = 9$ for the ^{13}C isotopic species.

Difluoromethane was kindly provided by Prof. Lourtioz (Orsay) and was used without further treatment. $^{13}CH_2F_2$ was measured in natural abundance.

Table 1. Newly observed transitions of CH_2F_2 ($v = 0$), exp. in MHz, $e-c$ in kHz.

J	K_p	K_0 ←	J	K_p	K_0	exp. [MHz]	$e-c$ [kHz]
21	8	14	20	7	13	1003897.661	93
50	2	48	51	1	51	394573.884	−7
51	14	38	52	13	39	16291.985	9
55	15	41	56	14	42	15161.794	46
58	5	53	57	8	50	14792.738	−91
59	7	52	59	6	53	345864.047	−57
59	16	43	60	15	46	14185.926	125
62	11	51	61	12	50	358996.988	25

Table 2. Selection of newly observed transitions of $^{13}CH_2F_2$ ($v = 0$). A complete list of lines may be obtained upon request from the authors.

J	K_p	K_0 ←	J	K_p	K_0	exp. [MHz]	$e-c$ [kHz]
10	3	7	10	2	8	177713.365	4
18	1	17	18	0	18	211988.169	25
23	2	21	22	3	20	388741.838	39
28	1	27	28	0	28	373265.752	−19
29	7	23	28	8	20	15285.926	−7
31	3	28	31	2	29	265902.082	41
36	3	33	36	2	34	363743.563	58
36	13	24	37	12	25	206121.700	283
41	4	37	41	3	38	353334.834	12
41	6	36	40	7	33	345585.090	−142
41	7	35	40	8	32	271587.572	133
43	5	38	43	4	39	282593.992	−24
47	6	41	47	5	42	282662.239	−4

The millimeterwave lines were measured with a source-modulated spectrometer. A phase-stabilized klystron (65–75 GHz) supplies a harmonic generator with fundamental power. The radiation is then optically focused through a free space absorption cell and detected by a helium-cooled InSb bolometer. As radiation source a submillimeterwave C.S.F. B.W.O (350–400 GHz) was also used in fundamental mode. This allowed us to dramatically increase the sensitivity. The measurements were performed at room temperature and their accuracy is

---

Reprint requests to Dr. J. Demaison, U.F.R. de Physique, Université de Lille I, 59655 Villeneuve d'Ascq Cedex, France.

0932-0784 / 87 / 0800-0846 $ 01.30/0. – Please order a reprint rather than making your own copy.

Table 3. Selection of newly obsered transitions of CH_2F_2 in the $v_4 = 1$ state. A complete list may be obtained upon request from the authors.

J	K_p	K_0 ←	J	K_p	K_0	exp. [MHz]	$e - c$ [kHz]
25	0	25	24	1	24	467 522.969	− 35
27	2	25	27	1	26	283 079.843	− 37
32	3	29	33	2	32	16 842.778	29
33	4	29	33	3	30	214 596.711	− 1
41	3	38	41	2	39	447 821.758	− 48
41	5	36	41	4	37	255 940.441	19
43	4	40	43	3	41	494 775.412	− 12
45	3	42	45	2	43	516 391.312	− 20
47	17	30	48	16	33	345 889.288	185
48	5	44	48	4	45	513 037.482	163
51	10	41	50	11	40	198 340.400	13
54	11	43	53	12	42	176 702.385	114
56	6	50	56	5	51	388 753.655	24
60	7	53	60	6	54	358 335.322	73

Table 4. Selection of newly observed transitions of $CH_2 F_2$ in the $v_4 = 2$ state. A complete list may be obtained upon request from the authors.

J	K_p	K_0 ←	J	K_p	K_0	exp. [MHz]	$e - c$ [kHz]
6	2	5	6	1	6	134 555.200	128
15	3	13	15	2	14	219 392.685	431
16	5	12	16	4	13	356 979.359	409
20	1	19	20	0	20	246 382.662	− 339
21	1	20	20	2	19	388 750.569	− 52
21	2	19	21	1	20	178 676.605	− 148
22	2	21	22	1	22	293 898.872	240
24	4	21	24	3	22	297 354.392	197
26	3	23	26	2	24	183 382.793	− 6
33	5	29	33	4	30	371 056.644	7

Table 5. Molecular constants of difluoromethane[a].

	CH_2F_2			$^{13}CH_2F_2$
	$v = 0$	$v_4 = 1$	$v_4 = 2$	$v = 0$
A/MHz	49 142.87203 (230)	49 480.5939 (53)	49 815.6936 (161)	47 730.7563 (23)
B/MHz	10 604.82258 (53)	10 582.95888 (114)	10 561.0835 (35)	10 606.21792 (60)
C/MHz	9 249.75702 (49)	9 216.50731 (101)	9 181.4261 (38)	9 199.02313 (63)
Δ_J/kHz	11.16822 (32)	11.07003 (87)	11.0160 (61)	11.06133 (74)
Δ_{JK}/kHz	− 62.7228 (32)	− 62.4399 (88)	− 54.334 (77)	− 60.4405 (50)
Δ_K/kHz	627.1059 (84)	648.622 (26)	656.14 (68)	606.082 (32)
δ_J/kHz	2.151679 (55)	2.141288 (124)	2.1385 (37)	2.203878 (130)
δ_K/kHz	28.1661 (48)	30.6682 (129)	47.58 (33)	27.8714 (62)
Φ_J/Hz	0.015762 (61)	0.01513 (28)	0[c]	0.01482 (25)
Φ_{JK}/Hz	0.11470 (149)	0.149 (21)	32.46 (92)	0.1415 (67)
Φ_{KJ}/Hz	− 5.1257 (56)	− 5.427 (84)	− 242.7 (44)	− 5.237 (46)
Φ_K/Hz	26.507 (27)	28.384 (188)	0[c]	26.240 (197)
φ_J/Hz	0.0070197 (161)	0.006748 (102)	0.0626 (52)	0.007316 (54)
φ_{JK}/Hz	0.03200 (179)	0.0365 (170)	− 2.85 (64)	0[c]
φ_K/Hz	5.554 (48)	6.81 (79)	1 351 (36)	6.34 (28)
σ[b]/kHz	63	61	174	39
Number of lines	226	160	97	131

[a] A-reduction, representation I^r, the uncertainties shown in parentheses are in units of the last digit and are standard errors.
[b] Standard deviation of the fit.
[c] Fixed value.

between 30 and 200 kHz, depending mainly on the linewidth. This spectrometer is described elsewhere [6]. Some new centimeterwave lines were also measured with a microwave Fourier transform spectrometer [7−10]. The high sensitivity of this type of spectrometer was decisive to measure weak lines of high J. The spectrum was recorded at room temperature and at pressures below 20 mTorr.

The assignment was straightforward. First, an approximate spectrum was calculated using the experimental data of Hirota [4]. The higher J transitions were identified by the "bootstrap" method as described by Kirchhoff [11]. The newly measured transitions are listed in Tables 1 to 4. For $v_4 = 193$ new transitions with $J \leqq 60$ and $K \leqq 17$ have been measured up to 600 GHz. For $v_4 = 2$ the number of new measurements is 77 with $J \leqq 33$ and $K \leqq 5$ up to 400 GHz. For $^{13}CH_2F_2$, $v = 0$ the spectrum was also recorded up to 400 GHz, and 113 new lines were assigned with $J \leqq 47$ and $K \leqq 13$.

To derive the molecular constants from the experimental spectra a weighted least-squares program [12] based on the Hamiltonian of Watson [13] using the I^r representation in the A reduction was used. The data of Refs. [3] and [4] were also taken into account. The derived parameters are listed in Table 5.

For the ground state, the determined constants are nearly identical to those of [3], the biggest change being an improvement of their standard deviations, especially for φ_{JK}, which was the least well determined parameter. For the $v_4 = 1$ state, all the parameters are well determined except φ_{JK}, whose value is only two standard deviations, but it may be noted that the value found is very similar to that of the ground state and that its contribution is greater than 1 MHz for 8 lines, the biggest contribution being 4 MHz for the $60_{7,53} \leftarrow 60_{6,54}$ transition.

For the ^{13}C isotopomer, φ_{JK} could not be determined, so it was fixed at zero. An attempt to fix it at the ground state value slightly worsens the fit, and nearly no constants are affected (within one standard deviation), except δ_K, Φ_{JK}, φ_J and φ_K for which the variations are $2\,\sigma$, $4\,\sigma$, $3.7\,\sigma$ and $3\,\sigma$, respectively.

For the $\nu_4 = 2$ state Φ_J and Φ_K could not be determined. An attempt to fix them at the corresponding ground state values did not improve the quality of the fit and nearly no constants are affected. It may be noted that the centrifugal distortion constants of the $v_4 = 1$ state and of $^{13}CH_2F_2$, $v = 0$, are very similar to the corresponding ones of the ground state. On the other hand, the sextic constants of the $v_4 = 2$ state are completely different; in fact they have even not the expected order of magnitude. This could be explained by the fact that $2\,\nu_4$ is in Fermi resonance with ν_3. The effect of this resonance, although not noticeable on the rotational constants, may affect more strongly the centrifugal distortion constants, especially the sextic ones. Moreover, as the rotational spectrum of difluoromethane is relatively sparse, some lines could be assigned almost without ambiguity to the $v_4 = 2$ state, but they could not be included into the fit because they worsen it. This could be due to accidental local resonances.

Acknowledgements

This investigations has been supported in part by the Centre National de la Recherche Scientifique and by the EPR Nord/Pas-de-Calais.

I. M. acknowledges the funding of the Deutsche Forschungsgemeinschaft.

[1] E. J. Danielewicz, in: Review of IR-MM waves (K. J. Button, M. Inguscio, and F. Strumia, Eds.), p. 223, Plenum Press, New York 1984.

[2] J. C. Deroche, E. K. Benichou, G. Guelachvili, and J. Demaison, Intern. J. of IR-MM waves **7,** 1653 (1986).

[3] L. Martinache, D. Boucher, J. Demaison, and J. C. Deroche, J. Mol. Spectrosc. **119,** 225 (1986).

[4] E. Hirota, J. Mol. Spectrosc. **69,** 409 (1978).

[5] A. Scalabrin, J. Tomaselli, D. Pereira, E. C. C. Vasconcellos, K. M. Evenson, F. R. Petersen, L. Zink, and D. A. Jennings, Intern. J. of IR-MM waves **6,** 973 (1985).

[6] R. Bocquet, Thèse de 3è Cycle, Lille 1986.

[7] W. Stahl, G. Bestmann, H. Dreizler, U. Andersen, and R. Schwarz, Rev. Sci. Instrum. **56,** 1759 (1985).

[8] G. Bestmann, H. Dreizler, H. Mäder, and U. Andresen, Z. Naturforsch. **35 a,** 392 (1980).

[9] G. Bestmann and H. Dreizler, Z. Naturforsch. **37 a,** 58 (1984).

[10] G. Bestmann, H. Dreizler, E. Fliege, and W. Stahl, J. Mol. Struct. **97,** 215 (1983).

[11] W. H. Kirchhoff, J. Mol. Spectrosc. **41,** 333 (1972).

[12] Programs VT 28 and ZFAP 6, author V. Typke, Ulm.

[13] J. K. G. Watson, in: Vibrational Spectra and Structure (J. R. Durig, Ed.), Vol. 6, Chap. 1, eq. 68, Elsevier, Amsterdam 1977.