Laser Spectroscopy of the ν_3 Band of Methyl Fluoride

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The ν_3 fundamental of CH_3F has been remeasured using a tunable diode laser and a waveguide CO_2 laser. Combination of this new measurement with earlier laser and microwave results has allowed us to obtain improved spectral parameters for both the ground and the $v_3=1$ excited state.

Introduction

Two papers have recently appeared in which it was attempted to determine the molecular constants of methyl fluoride (CH_3F) in the ground state and in the $v_3 = 1$ excited state [1, 2]. In both cases all constants could not be determined and assumptions had to be made concerning the values of some constants. As CH_3F is a very useful molecule for the calibration of a spectrometer (millimeter-wave Stark spectroscopy or diode laser spectroscopy) and for testing the performances of a new spectrometer, we have accurately measured many new transitions in the ν_3 fundamental using a tunable diode laser and a waveguide CO_2 laser. These new measurements in conjunction with earlier laser (laser-Stark [3, 4] and tunable side-band laser [1]) and microwave [5–10] results have allowed us to obtain improved values for the rotational and distortion constants, including all the sextic constants.

Observation

1. *Saturation Spectroscopy with a CO_2 Waveguide Laser*

Waveguide operation of CO_2 lasers allows a much wider frequency tuning range than is normally possible. An absorption cell was placed in the cavity of the waveguide laser, and when an absorption line fell within the tuning range of the laser, saturation resonances (inverted Lamb dips) were observed. Further experimental details are given elsewhere [11]. In order to enhance the sensitivity of the apparatus, Stark modulation of the absorption lines has been used. Accurate frequency measurements of the Lamb dip signals were performed by directly counting the frequency difference between the waveguide laser and a reference CO_2 laser. This latter laser is of conventional design and was frequency stabilized using the fluorescence detected Lamb dip technique [12].

The frequencies of the ${}^{Q}Q$ (12, 1) and ${}^{Q}Q$ (12, 2) lines are given in Table 1. The uncertainty is estimated to be roughly the halfwidth of the zerofield inverse Lamb dips.

The ${}^{Q}Q$ (12, 2) line frequency is in agreement with the previously reported value and about ten times more accurate [3, 4]. From our measurements we can see that the best frequency coincidence with the conventional CO_2 laser is with the ${}^{Q}Q$ (12, 2) line, which is only 38.1 MHz from its center. Submillimeter emissions can be obtained when pumping on either of the two lines ${}^{Q}Q$ (12, 1) and ${}^{Q}Q$ (12, 2), but C. W. pumping is able to generate only the 496.105 μm emission ($J = 13,\ K = 2 \rightarrow J = 12,\ K = 2$) line. This is in agreement with the fact that the ${}^{Q}Q$ (12, 2) is indeed closer to the CO_2 laser line center and is stronger than the ${}^{Q}Q$ (12, 1).

Additional lines of CH_3F were observed with the waveguide laser. One is about 60 MHz below the 9P(24) emission line center and could be the ${}^{Q}Q$ (22, 16). The ${}^{Q}R$ (4, 3) of ${}^{13}CH_3F$ has also been observed on the lower frequency side of the 9P(32) laser emission. A slight absorption occurs on the 9P(30) line and could be assigned to a hot band transition [4].

The ${}^{Q}Q$ (12, 3) has also been observed about 216 MHz above the 9P(20) laser line, but it was too close to the limit of the tuning range to get an accurate frequency measurement.

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Table 1. Observed transitions of the ν_3 band of CH_3F.

Sub band	K	ν_{obs} (GHz)[a]	o–c MHz
${}^QQ_K$ (1)	1	31 435.918 2	− 8.9
${}^QQ_K$ (2)	1	31 434.562 2	− 10.4
	2	31 346.696 2	− 8.4
${}^QQ_K$ (3)	1	31 432.539 2	− 1.7
${}^QP_K$ (1)	0	31 385.488 4	0.1
${}^QQ_K$ (12)	1	31 383.841 4[b]	0.7
	2	31 383.938 5[b]	− 0.7
	4	31 384.345 4	− 1.8
	5	31 384.675 4	7.1
	6	31 385.090 4	11.5
	7	31 385.600 4	9.8
	8	31 386.230 4	12.0
	9	31 386.993 4	12.0
	10	31 387.927 4	− 23.8
	12	31 390.362 4	− 0.79
${}^QQ_K$ (13)	3	31 375.286 4	− 25.5
	4	31 375.531 4	− 7.4
	5	31 375.829 4	− 12.3
	6	31 376.226 4	− 3.1
	7	31 376.718 4	+ 4.8
	8	31 377.320 4	+ 12.1
	9	31 378.043 4	+ 11.8
	11	31 379.968 4	+ 5.0
	12	31 381.237 4	− 3.7
${}^QQ_K$ (18)	3	31 321.314 5	1.8
	4	31 321.440 5	− 12.7
	5	31 321.653 5	9.9
	6	31 321.902 5	11.2
	7	31 322.201 5	− 3.8
	8	31 322.601 5	+ 4.7
	9	31 323.083 5	4.4
	10	31 323.667 5	− 1.0
	12	31 325.235 5	− 17.1
	13	31 326.299 5	− 5.3
	14	31 327.580 5	− 4.4

[a] Diode laser measurement, accuracy ~ 10 MHz, unless otherwise stated.

[b] Waveguide measurement, accuracy ~ 0.500 MHz.

2. Diode Laser Spectra

Spectroscopy has been performed with a Pb Salt diode laser from Laser Analytics. The diagram of the experimental set up will be given elsewhere. The emission frequency of the diode is calibrated by using varactor mixing with a stabilized CO_2 laser [13]. A microwave source (4—8 GHz) and/or RF sources (60—1050 GHz) were used to produce frequency markers on the CH_3F spectra. Frequency measurements were performed by displaying simultaneously the absorption spectra and the beatnote resulting from varactor mixing. Transition frequencies were determined by setting a beatnote on the line center via adjustment of the microwave or RF frequency. As for the inverted lamb dip measurements, absolute frequency measurements result from the knowledge of the fluorescence stabilized CO_2 reference laser frequency. However in this case the accuracy of the measurements was limited because of the Doppler widths of the absorption lines and because of the calibration of the microwave source. The frequencies of the lines are given in Table 1. The uncertainty is estimated to be 10 MHz although it could have been reduced by a direct measurement of the microwave frequency or by locking the diode frequency to the absorption lines. Most of the lines measured are complementary to previously measured spectra.

Analysis

The appropriate expression for the rotational energies in the vibrational ground state is [14]

$$\begin{aligned} E_0 = {} & (A_0 - B_0) K^2 + B_0 J (J+1) \\ & - D_0^J J^2 (J+1)^2 - D_0^{JK} J (J+1) K^2 \\ & - D_0^K K^4 + H_0^J J^3 (J+1)^3 \\ & + H_0^{JK} J^2 (J+1)^2 K^2 \\ & + H_0^{KJ} J (J+1) K^4 + H_0^K K^6 . \end{aligned}$$

For an accurate analysis of the $v_3 = 1$ excited state it is necessary to take into account the Coriolis interaction between the ν_3 and ν_6 fundamentals. To do this, we have to calculate the eigenvalues of small matrices whose maximal dimension is 3×3 and whose elements are [15]

$$\begin{aligned} H_{11} &= \langle v_3 = 0, v_6 = 1^+; J, K+1 \,|\, H \,|\, v_3 = 0, v_6 = 1^+; J, K+1 \rangle \\ &= \nu_6 + B_6 J (J+1) + (A_6 - B_6)(K+1)^2 - 2 A_e \zeta_6^Z (K+1); \end{aligned}$$

$$\begin{aligned} H_{22} = {} & \langle v_3 = 1, v_6 = 0; J, K \,|\, H \,|\, v_3 = 1, v_6 = 0; J, K \rangle = \nu_3 + B_3 J (J+1) \\ & + (A_3 - B_3) K^2 - D_3^J J^2 (J+1)^2 - D_3^{JK} J (J+1) K^2 \\ & - D_3^K K^4 + H_3^J J^3 (J+1)^3 + H_3^{JK} J^2 (J+1)^2 K^2 + H_3^{KJ} J (J+1) K^4 + H_3^K K^6 ; \end{aligned}$$

$$\begin{aligned} H_{33} &= \langle v_3 = 0, v_6 = 1^-; J, K-1 \,|\, H \,|\, v_3 = 0, v_6 = 1^-; J, K-1 \rangle \\ &= \nu_6 + B_6 J (J+1) + (A_6 - B_6)(K-1)^2 + 2 A_e \zeta_6^Z (K-1); \end{aligned}$$

Table 2. Molecular constants of CH_3F. Fixed parameters (cm^{-1}): $\nu_6 = 1182.67605^{a}$, $A_6 = 5.2006^{a}$, $B_6 = 0.8478838^{a}$, $A\zeta_6 = 1.5437^{a}$, $\zeta^{y}_{36} = 0.318^{b}$.

	Ground state		$v_3 = 1$		
ν_0			31 436 560.30	(62)	MHz
B	25 536.149 42	(70)	25 262.818 9	(197)	MHz
D_J	60.235 0	(308)	60.433	(201)	kHz
D_{JK}	439.418	(111)	400.34	(1.27)	kHz
H_J	0.879	(390)	3.64	(70)	Hz
H_{JK}	− 7.84	(5.47)	− 25.8	(6.6)	Hz
H_{KJ}	34.2	(21.2)	158.0	(20.9)	Hz
$A' - B' - (A'' - B'')$			− 18.513	(119)	MHz
$D'_K - D''_K$			18.67	(1.35)	kHz
$H'_K - H''_K$			− 66.2	(8.8)	Hz

^{a} Ref. [17], ^{b} Ref. [15].

$$H_{12} = -G_{36}\sqrt{(J-K)(J+K+1)};$$

$$H_{23} = G_{36}\sqrt{(J+K)(J-K+1)}$$

with $G_{36} = -\dfrac{\nu_3 + \nu_6}{\sqrt{2\nu_3\nu_6}} B_e \zeta^{y}_{36}$.

When $K = J : H_{22} = H_{12} = 0$ and when $K = -J : H_{33} = H_{13} = 0$.

The molecular constants of the ground state and the ν_3 fundamental are simultaneously fitted using a weighted least-squares program. As the Coriolis interaction is relatively weak, the constants of the ν_6 fundamental and the Coriolis interaction constant are constrained to their known values (Table 2). The input data are:

I) the newly observed transitions of the ν_3 band listed in Table 1;

II) the laser-Stark measurements of the ν_3 band [3, 4];

III) the tunable side-band laser measurements [1];

IV) the microwave transitions of both the ground state [5, 6] and the $v_3 = 1$ excited state [7, 8];

V) the submillimeter transitions of both the ground state [9] and the $v_3 = 1$ excited state [9, 10].

Eeach transition was weighed by the inverse square of its expected uncertainty.

Conclusion

Comparison of our B_0, D^J_0, D^{JK}_0 with those of Graner [16] shows a very good agreement. On the other hand, our ΔD^J, ΔD^{JK}, ΔD^K ($\Delta D = D_3 - D_0$) are much smaller than those of Refs. [1] or [2]. Moreover, Magerl et al. [1] did not treat the Coriolis interaction and Arimondo et al. [2] did not use the most recent measurements [4]. So it seems that our constants are more reliable. Our correlations are smaller than those indicated by Arimondo [2] (0.92 to 0.97 for D^J_0, H^J_0, ΔH^J) although we have determined more constants. Indeed all our correlation coefficients are smaller than 0.94, only two are greater than 0.9: $\varrho(H^{KJ}_0, H^{KJ}_3) = 0.923$ and $\varrho(B_3, D^J_3) = 0.937$. At this point, it is worth noting that the inclusion of the microwave data lowers the correlations significantly.

All the sextic constants of the $v_3 = 1$ state are determined for the first time, but, for the ground state, their uncertainty remains large. To improve them, it should be necessary to extend the measurements to higher J and higher K values, but it should then probably be necessary to analyze simultaneously the $v_6 = 1$ state.

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