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THE ENERGY-LEVEL STRUCTURE OF THE CHD_2F FIR LASER

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Abstract—Extensive millimeter and submillimeter spectroscopic measurements have been combined with heterodyne measurements of the frequencies of optically-pumped FIR laser lines in CHD_2F. An analysis of these data and the known CO_2 laser pump frequencies provides an unambiguous assignment of the FIR laser lines and an accurate energy-level structure of both the ground and ν_6 excited state.

INTRODUCTION

The isotopes of methyl fluoride provide several of the most important optically-pumped FIR lasers.[1–4] Because of the orderly energy-level structure of symmetric top molecules, it has been possible to characterize the spectroscopic details of these lasers in a reasonably straightforward fashion. However, the isotopic substitution of one or two of the hydrogens makes the molecule an asymmetric rotor with a substantially more complex spectrum. Recently, one of us reported a number of new laser lines in optically-pumped CHD_2F[5] and measured the frequencies accurately by means of heterodyne techniques. In this paper, we report the measurement by means of millimeter and submillimeter spectroscopic techniques of 85 new transitions in the ground and ν_6 excited vibrational state. These data are then spectroscopically analyzed, along with the FIR laser frequencies to provide an accurate energy-level structure for this lasing species.

EXPERIMENTAL

We have previously discussed the experimental techniques that we have developed to provide continuously tunable coverage to frequencies above 1 THz.[6,7] The particular implementation of these techniques that was used in this experiment is discussed in a recent paper that describes the use of millimeter and submillimeter spectroscopic techniques to study energy transfer processes in optically-pumped FIR lasers.[8] Briefly, a 35 GHz klystron, phase-locked to a synthesizer, was used to drive a harmonic generator.[9] The output of this generator was matched into a 1 m long, 1 cm radius Cu cell which contained the CHD_2F at a pressure of about 20 mtorr. The output of the cell was focused into a 1.5 K InSb detector. The signal from the detector was digitized synchronously with the frequency sweep from the synthesizer.

THEORY

CHD_2F is a light, near-prolate asymmetric rotor with strong, symmetric-top-like, a-type transitions. In addition, there are much weaker c-type transitions. These are due to a small component of the dipole moment produced by the rotation of the molecular symmetry axis relative to the principal axes of the moment of inertia tensor.

We have previously discussed the application of Watson's reduced centrifugal distortion Hamiltonian to the analyses of a number of light asymmetric rotors,[10–12] including the closely related CH_2DF.[13] For the ground state of CHD_2F the Hamiltonian can be written as:

$$\mathcal{H} = 1/2(B+C)P^2 + [A - 1/2(B+C)][P_z^2 - b_p(P_x^2 - P_y^2)] - \Delta_J P^4 - \Delta_{JK}P^2P_z^2 - \Delta_K P_z^4 - 2\delta_J P^2(P_x^2 - P_y^2) - \delta_K[P_z^2(P_x^2 - P_y^2) + (P_x^2 - P_y^2)P_z^2] \quad (1)$$

where $b_p = (C - B)/(2A - B - C)$ is Wang's asymmetry parameter for a near-prolate top. For these near-symmetric-top species, the strong spectrum associated with the large component of the dipole moment along the a-axis connects only levels with the same value of K_p (the K quantum number in the prolate limit) and thus provides only second- and higher-order information about A, Δ_K and other constants that are coefficients of P_z^{2n}. Direct information about these spectral constants can

Table 1. Observed ground-state lines of CHD_2F(MHz)

Transition	Observed	Observed–calculated
3(1 2)–2(0 2)	207789.790	0.028
4(0 4)–3(0 3)	174621.710	0.027
4(1 4)–3(1 3)	172481.754	0.011
4(1 3)–3(1 2)	176962.270	0.007
4(2 3)–3(2 2)	174731.118	0.070
4(2 2)–3(2 1)	174859.143	0.008
4(1 3)–3(0 3)	253737.562	0.053
5(0 5)–4(0 4)	218173.968	−0.001
5(1 5)–4(1 4)	215571.790	0.009
5(1 4)–4(1 3)	221170.484	−0.010
5(2 4)–4(2 3)	218390.524	0.009
5(2 3)–4(2 2)	218646.325	−0.021
5(3 3)–4(3 2)	218448.047	−0.020
5(3 2)–4(3 1)	218449.932	−0.056
5(4 2)–4(4 1) 5(4 1)–4(4 0)	218413.863	0.002
6(0 6)–5(0 5)	261658.223	0.001
6(1 6)–5(1 5)	258642.076	0.017
6(1 5)–5(1 4)	265356.608	−0.062
6(2 5)–5(2 4)	262034.451	−0.013
6(2 4)–5(2 3)	262481.128	0.008
6(3 4)–5(3 3)	262143.230	0.034
6(3 3)–5(3 2)	262148.304	−0.011
6(4 3)–5(4 2) 6(4 2)–5(4 1)	262095.301	−0.018
6(5 2)–5(5 1) 6(5 1)–5(5 0)	262053.564	−0.021
7(0 7)–6(0 6)	305062.041	0.015
7(1 7)–6(1 6)	301689.098	−0.026
7(1 6)–6(1 5)	309515.900	0.021
7(2 6)–6(2 5)	305659.833	0.027
7(2 5)–6(2 4)	306371.784	0.006
7(3 5)–6(3 4)	305840.515	0.002
7(3 4)–6(3 3)	305851.957	−0.065
7(4 4)–6(4 3) 7(4 3)–6(4 2)	305776.037	−0.014
7(5 3)–6(5 2) 7(5 2)–6(5 1)	305722.458	−0.040
7(6 2)–6(6 1) 7(6 1)–6(6 0)	305669.808	−0.046
7(0 7)–6(1 5)	219251.249	0.022
8(0 8)–7(0 7)	348374.187	0.024
8(1 8)–7(1 7)	344709.746	−0.037
8(1 7)–7(1 6)	353642.864	−0.066
8(7 2)–7(7 1) 8(7 1)–7(7 0)	349258.300	0.099
8(0 8)–7(1 6)	258109.504	−0.008
8(2 6)–8(1 8)	243087.443	0.006
9(0 9)–8(0 8)	391585.245	0.045
9(1 9)–8(1 8)	387701.117	−0.020
9(1 8)–8(1 7)	397732.320	0.008
9(2 7)–9(1 9)	249733.722	0.020
11(2 10)–11(1 10)	184007.728	−0.016
13(2 12)–12(3 10)	196839.511	0.074
13(2 11)–12(3 9)	213009.571	−0.064
18(1 17)–18(1 18)	186372.769	−0.013
18(2 17)–18(1 17)	132181.396	−0.028
19(1 18)–19(1 19)	205820.878	0.009
20(1 19)–20(1 20)	225897.773	−0.004
20(4 17)–19(5 15)	216244.994	−0.061
20(4 16)–19(5 14)	216627.430	0.058

Table 2. Observed ν_6 excited state lines of CHD_2F (MHz)

Transition	Observed	Observed–calculated
4(0 4)–3(0 3)	173465.634	0.010
4(1 4)–3(1 3)	171770.005	−0.013
4(1 3)–3(1 2)	175282.918	0.033
4(2 3)–3(2 2)	173532.162	0.186
4(2 2)–3(2 1)	173609.816	0.037
4(3 2)–3(3 1) 4(3 1)–3(3 0)	173547.379	−0.051
5(0 5)–4(0 4)	216766.534	0.008
5(1 5)–4(1 4)	214690.853	0.023
5(1 4)–4(1 3)	219081.510	−0.033
5(2 4)–4(2 3)	216897.901	−0.017
5(2 3)–4(2 2)	217053.366	−0.062
5(3 3)–4(3 2)	216933.872	−0.072
5(3 2)–4(3 1)	216934.885	0.035
5(4 2)–4(4 1) 5(4 1)–4(4 0)	216915.868	−0.050
6(0 6)–5(0 5)	260023.952	−0.036
6(1 6)–5(1 5)	257597.359	−0.052
6(1 5)–5(1 4)	262865.202	−0.046
6(2 5)–5(2 4)	260252.482	−0.010
6(2 4)–5(2 3)	260524.333	0.020
6(3 4)–5(3 3)	260320.064	0.068
6(3 3)–5(3 2)	260322.435	0.022
6(4 3)–5(4 2) 6(4 2)–5(4 1)	260293.878	−0.066
6(5 2)–5(5 1) 6(5 1)–5(5 0)	260276.655	−0.029
7(0 7)–6(0 6)	303229.770	0.046
7(1 7)–6(1 6)	300487.133	−0.009
7(2 6)–6(2 5)	303593.413	−0.009
7(2 5)–6(2 4)	304027.486[a]	0.014
7(3 5)–6(3 4)	303705.244	−0.020
7(3 4)–6(3 3)	303710.710	0.007
7(4 4)–6(4 3) 7(4 3)–6(4 2)	303669.198	0.041
7(5 3)–6(5 2) 7(5 2)–6(5 1)	303645.972	0.045
8(2 6)–7(2 5)	347568.0[b]	0.495
9(6 4)–8(6 3) 9(6 3)–8(6 2)	390348.8[b]	1.280
10(6 5)–9(6 4) 10(6 4)–9(6 3)	433695.8[b]	1.236
17(7 11)–16(7 10) 17(7 10)–16(7 9)	736812.0[b]	0.637
18(7 12)–17(7 11) 18(7 11)–17(7 10)	780061.5[b]	−1.485

[a]Also measured by heterodyne techniques at 304027.5 MHz.[5]

[b]Reference (5), measured FIR laser frequency.

be obtained only by observation of the much weaker transitions that result from the component of the dipole moment perpendicular to the a-axis.

RESULTS AND ANALYSES

Initial estimates of the rotational parameters of CHD_2F in its ground vibrational state were obtained from the geometry calculated from the earlier work on CH_2DF.[13,14] From these predictions, the strong a-type lines of CHD_2F were easily found and assigned. Because the isotopic substitution destroys the symmetry of the molecule and rotates its geometrical symmetry axis from the principal axes of the moment of inertia tensor, weak c-type transitions could also be observed. In all, 54 pure rotational transitions of the ground state were measured in the region between 100 and 400 GHz. These measured frequencies are shown in Table 1. The pure rotational transitions in the ν_6 excited vibrational state are approx. 150 times weaker than ground-state lines. The initial predictions of these transition frequencies were obtained by use of an estimate of $B + C$ for the excited state that was calculated from an IR spectrum by Professor Eggers.[15] These predictions made possible rapid assignment of this spectrum. Table 2 shows the 31 observed microwave lines of this spectrum as well as the 5 laser frequencies used in our analysis that were measured by heterodyne techniques.

An initial analysis of the ν_6 microwave data provided unambiguous assignments for 6 of the 9 FIR laser lines that were measured by heterodyne techniques in Ref. (5). These assignments are consistent with those deduced by Eggers[16] from an analysis of the IR spectrum. However, our higher resolution allows us to assign the 347568.0 MHz line to the $8_{2,6}$–$7_{2,5}$ transition rather than to the $8_{2,7}$–$7_{2,6}$ transition which we predict at 346918.4 MHz. Our predictions also identify the FIR laser line at 304027.5 MHz as the cascade transition $7_{2,5}$–$6_{2,4}$. All of the other FIR laser lines are based on transitions that are degenerate to a very small fraction of a line width at both the FIR

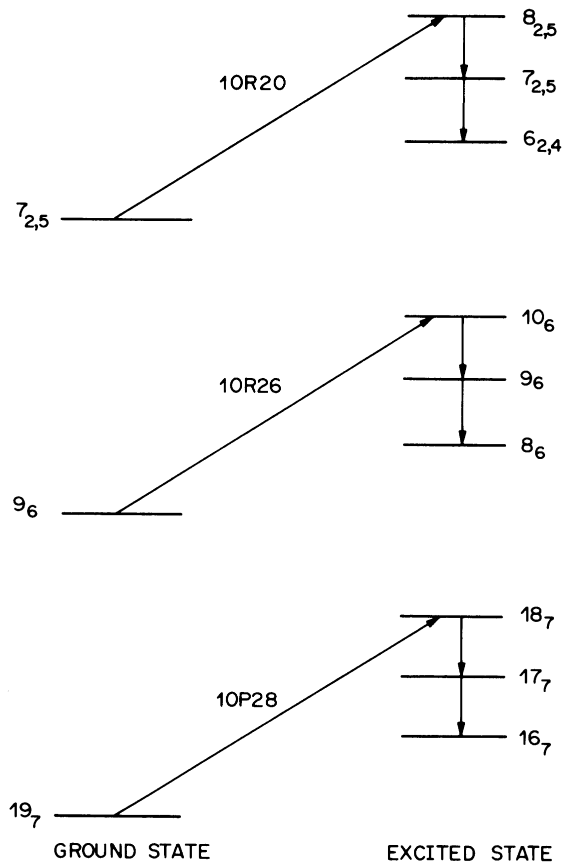

Fig. 1. Energy levels and laser transitions for the CHD_2F laser.

Table 3. Spectral constants of CHD_2F (MHz)

Constant	Ground state[a,b]	ν_6 Excited state[a,b]	
A	95207.015 (7)	96059.000	(10)
B	22405.599 (1)	22133.213	(45)
C	21284.478 (1)	21255.221	(45)
Δ_J	0.0411659 (96)	0.040259	(84)
Δ_{JK}	0.276159 (35)	0.17296	(119)
Δ_K	0.744936 (747)	1.50	(10)
δ_J	0.00195258 (66)	−0.000588	(92)
δ_K	0.150917 (234)	−0.054	(22)
$H_{JK} \cdot 10^4$	—	−0.451	(49)
$H_{KJ} \cdot 10^2$	—	0.1584	(96)
$L_{KKJ} \cdot 10^4$	—	0.119	(25)
r.m.s.	0.038	0.076[c]	

[a]The number of places retained is necessary to ensure that the constants reproduce the observed data.
[b]The numbers in parentheses are the standard deviations in terms of the last quoted place.
[c]From an analysis of the microwave data alone.

laser frequency and the pump frequency. Our predictions show this K-splitting to be less than 1 kHz in all cases.

Since the observed excited-state microwave lines and the measured FIR frequencies do not include any c-type lines, the A rotational constant cannot be determined directly. However, values for A and Δ_K can be obtained from a consideration of the entire optically-pumped FIR laser energy-level scheme, *including the known CO_2 laser pump frequencies*. Since the ground-state energy-level structure is well established by the microwave data, the CO_2 pump frequencies can be used to establish the difference in energy between levels with different K_p in ν_6. This is shown diagrammatically in Fig. 1. This is equivalent to the information obtained from the c-type transitions in the ground state. The decrease in accuracy in this information that is caused by unknown pump laser offsets, is at least partially offset by the higher K levels involved. Table 3 shows the results of this analysis. In the excited-state analysis, the value of Δ_K was held fixed and the remaining constants adjusted via a least-squares procedure to fit the data of Table 2. Δ_K was then adjusted so as to minimize the closure error in the loops which included the ground- and excited-state rotational energy-level structure and the CO_2 pump frequencies. The variation of this one parameter reduced the loop error for all of the loops to $\sim 0.001 \text{ cm}^{-1}$, a value comparable with the uncertainty in the laser pump offset. This calculation also predicts that the vibrational frequency of ν_6 is 964.504 cm^{-1}. In all of these calculations, the lines measured by microwave techniques were weighted 1000.

It should be noted that more constants are required to fit the ν_6 microwave data than are required to fit the ground-state data. Since the ground-state data are more extensive, we believe that this is due to small perturbation effects that are correlated with the higher-order distortion constants.

SUMMARY

The energy-level structure of CHD_2F that is important to the FIR optically-pumped laser has been calculated to high accuracy from a combination of millimeter and submillimeter microwave measurements, heterodyne measurements of the FIR laser frequencies and previously known CO_2 laser frequencies. Because the CO_2 laser frequencies were included in the analysis, the calculated levels not only predict strong pure rotational transitions accurately, but also predict pump frequencies.

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