Far-Infrared Laser Stark Spectroscopy of 1,1 Difluoroethylene

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ABSTRACT

The far-infrared laser Stark spectrum of 1,1 difluoroethylene (H₂C=CF₂) has been investigated with the 311 µm line of the hydrogen cyanide (HCN) laser. Numerous families of absorption lines have been observed for both parallel and perpendicular polarizations up to 60 000 V/cm. Three families of resonances have been identified as $J(K_{a},K_{c}) = 41(35,7) \leftarrow 40(33,8)$, $40(36,5) \leftarrow$ 39(34,6) and $43(35,8) \leftarrow 42(33,9)$. The Stark shift for the first two transitions can be adequately explained by quasi-first-order calculations, whereas the Stark shift for the third transition requires second-order corrections. The zero-field frequencies for these transitions have been experimentally determined and are reported with fractional uncertainties up to a few parts in 10^{6} .

INTRODUCTION

1,1 difluoroethylene, abbreviated here as 1,1–DFE, is a near oblate asymmetric-top molecule that has been the subject of numerous spectroscopic studies over the past several decades. The vibrational bands of 1,1–DFE were first investigated in 1945 [1] while its ground state rotational spectrum has been studied since 1957 [2]. This includes the detection of numerous coincidences between the absorption lines of 1,1–DFE and the 10.4 μ m and 337 μ m lines of the CO₂ and HCN lasers, respectively [3–8]. In addition, the high-resolution Fourier transform infrared (FTIR) spectra of 1,1–DFE were analyzed and accurate values of spectroscopic parameters have been obtained [9–12]. Zerbe-Foese *et al.* [13] investigated the pure rotational spectra of 1,1–DFE by double resonance modulation microwave (MW) spectroscopy in the 12 – 40 GHz range and by millimeter-wave (MMW) spectroscopy in the 90 – 260 GHz range. Combining the MMW data with previous MW, laser Stark and laser diode data, an optimized set of rotational parameters for this molecule was extracted [13]. The latest extension has been from the analysis of the FTIR bands of the v₁₁ and v₈ fundamentals [14]. Finally, along with its numerous spectroscopic investigations, 1,1–DFE has been used as a medium for the optically pumped molecular laser, producing 79 laser emissions in the farinfrared spanning from about 257 to 2070 μ m [15].

EXPERIMENTAL DETAILS

The HCN laser and Stark spectrometer system, along with the experimental procedures used in this study, have been described in detail in Refs. 16 and 17. Briefly, spectra were recorded by coupling the fixed-frequency FIR laser radiation, generated by the 311 μ m emission of the HCN laser ($v_{laser} = 964\ 313.4 \pm 1.0\ MHz$ [18]), into a Stark spectrometer with the molecular absorption monitored using a Golay cell detector. The spacing of the Stark plates was 0.051 508 \pm 0.000 05 cm [19] and electric fields up to 60 000 V/cm were used. The 1,1–DFE gas sample was obtained from the Union Carbide Company.

The theory of the Stark effect in 1,1–DFE has been described in detail elsewhere [8], with a brief overview given below. Consider a transition between two asymmetry doublets belonging to J^{I} and J^{II} for the near degenerate case.



Figure 1. Splitting of near degenerate energy levels due to the Stark effect. The near degenerate J^{I} and J^{II} energy levels are labeled as Δv^{I} and Δv^{II} , respectively. The Stark splitting of these energy levels are labeled as Δv^{I}_{U} ,

 $\Delta v_{\rm L}^{\rm I}$ and $\Delta v_{\rm U}^{\rm II}$, $\Delta v_{\rm L}^{\rm II}$, respectively.

The large, nearly first order Stark shifts for the upper and lower levels of J^I are given by

$$\Delta v_{\rm U}^{\rm I} = -\frac{\Delta v^{\rm I}}{2} + \frac{E_{J^{\rm I} \tau_{\rm I} \rm M}^{(2)} + E_{J^{\rm I} \tau_{\rm 2} \rm M}^{(2)}}{2} + \left[\left(\frac{\Delta v^{\rm I}}{2} + \frac{E_{J^{\rm I} \tau_{\rm I} \rm M}^{(2)} - E_{J^{\rm I} \tau_{\rm 2} \rm M}^{(2)}}{2} \right)^2 + \mu_{\tau_{\rm I} \tau_{\rm 2}}^2 \varepsilon^2 \right]^{1/2} \qquad \text{Eq. 1}$$

and

$$\Delta v_{\rm L}^{\rm I} = + \frac{\Delta v^{\rm I}}{2} + \frac{E_{\rm J^1 \tau_1 \rm M}^{(2)} + E_{\rm J^1 \tau_2 \rm M}^{(2)}}{2} - \left[\left(\frac{\Delta v^{\rm I}}{2} + \frac{E_{\rm J^1 \tau_1 \rm M}^{(2)} - E_{\rm J^1 \tau_2 \rm M}^{(2)}}{2} \right)^2 + \mu_{\tau_1 \tau_2}^2 \varepsilon^2 \right]^{1/2} \qquad \text{Eq. 2}$$

with similar expressions existing for the levels belonging to J^{II} . The transition dipole moment between the two levels is $\mu_{\tau_1\tau_2}^2$, calculated using the transition line strength parameter, λ ,

$$\mu_{\tau_{1}\tau_{2}}^{2} = \frac{\mu_{a}^{2} M^{2} \lambda(J\tau; J, \tau')}{J(J+1)(2J+1)}$$
Eq. 3

where μ_a is the *a* component of the electric dipole moment and M is the molecule's magnetic quantum number, relative to the ε field direction. The line strength parameters for *a*-type Q-branch transitions are quite small for prolate rotors but become relatively large for oblate asymmetric-top molecules, such as 1,1 DFE.

The second order Stark corrections (terms involving $E^{(2)}$) were calculated using Eq. 4, taking into account the interaction of nearby levels [20, 21], with the summation only including non-degenerate energy levels.

$$E_{J\tau M}^{(2)} = \mu_a^2 \varepsilon^2 \left[\frac{J^2 - M^2}{J(4J^2 - 1)} \sum_{\tau'} \frac{?(J\tau; J - 1, \tau')}{E_{J\tau} - E_{J - 1\tau'}} + \frac{M^2}{J(J + 1)(2J + 1)} \sum_{\tau'} \frac{?(J\tau; J, \tau')}{E_{J\tau} - E_{J\tau'}} \right]$$
$$+ \frac{(J + 1)^2 - M^2}{(J + 1)(2J + 1)(2J + 3)} \sum_{\tau'} \frac{?(J\tau; J + 1, \tau')}{E_{J\tau} - E_{J + 1\tau'}} \right] \qquad \text{Eq. 4}$$

RESULTS

The Stark spectra of 1,1–DFE were recorded in both parallel and perpendicular polarizations for electric fields up to 60 000 V/cm using the 311 μ m line of the HCN laser. In all, five families of resonances were observed. Although two series of absorption lines starting at 1 V and 12 V in the $\Delta M = 0$ (parallel polarization) Stark spectra have not been identified, over 92% of the lines observed in this work have been assigned to rotational transitions. From the detuning experiment [16], absorption lines for the first two assigned families of resonances were found to belong to transitions that were above the laser frequency while the third assigned family belonged to a transition whose frequency was below the laser frequency.

I. The $J(K_a, K_c) = 41(35, 7) \leftarrow 40(33, 8)$ Transition

A series of sharp narrow absorption lines were observed at low Stark voltages, starting at 153.6 V in the $\Delta M = 0$ spectrum. These absorption lines show a linear Stark effect (MV_M = constant) with increasing intensity as the Stark voltage is increased, indicating the absorption lines either belonged to a P or R branch transition [22]. From the predicted transition frequencies based on the available molecular constants, this transition has been assigned as $J(K_a, K_c) = 41(35,7) \leftarrow 40(33,8)$. The predicted frequency for this transition was 964 925.6 MHz, which is 612.2 MHz above the HCN laser frequency. The two sets of doublet levels involved for this transition are shown in Fig. 2.



Figure 2. Near degenerate energy levels involved in the $J(K_a, K_c) = 41(35,7) \leftarrow 40(33,8)$ transition.

The Stark shifts for each absorption line was calculated using the observed Stark voltages with Eqs. 1 – 4. The assigned quantum numbers, observed Stark voltages and calculated Stark shifts are listed in Table 1. The mean net Stark shift for this transition was calculated to be –610.0 MHz resulting in a transition frequency of $v_{tr} = 964\ 923.4$ MHz.

		Stark	Net Unner	Net Lower	Net Stark
M	M	Voltage (V)	Stark Shift	Stark Shift	Shift (MHz)
e	Ľ	0 ()	(MHz)	(MHz)	• • •
38	38	153.6	-686.89	-75.93	-610.96
37	37	157.8	-687.26	-75.99	-611.27
36	36	162.2	-687.42	-76.01	-611.41
35	35	166.8	-687.25	-75.99	-611.26
34	34	171.6	-686.04	-75.82	-610.22
33	33	176.8	-686.10	-75.83	-610.27
32	32	182.4	-686.59	-75.90	-610.69
31	31	188.2	-686.19	-75.84	-610.34
30	30	194.4	-685.85	-75.80	-610.05
29	29	200.9	-684.85	-75.66	-609.19
28	28	208.8	-688.56	-76.19	-612.36
27	27	216.5	-687.96	-76.11	-611.85
26	26	224.8	-687.91	-76.11	-611.80
25	25	233.5	-686.67	-75.93	-610.73
24	24	243.0	-685.75	-75.80	-609.94
23	23	253.8	-686.78	-75.96	-610.82
22	22	265.0	-685.11	-75.72	-609.39
21	21	278.1	-687.00	-76.00	-611.00
20	20	291.9	-686.69	-75.97	-610.73
19	19	307.6	-687.91	-76.15	-611.76
18	18	324.5	-687.03	-76.03	-610.99
17	17	343.7	-687.43	-76.11	-611.33
16	16	365.3	-687.53	-76.14	-611.40
15	15	389.7	-687.71	-76.18	-611.53
14	14	417.4	-687.15	-76.12	-611.03
13	13	449.3	-686.69	-76.08	-610.61
12	12	486.8	-686.59	-76.10	-610.49
11	11	530.8	-685.85	-76.04	-609.81
10	10	583.6	-685.07	-75.98	-609.08
9	9	648.3	-684.33	-75.96	-608.38
8	8	728.8	-683.12	-75.89	-607.23
41	40	141.9	-683.35	-71.81	-611.54
40	39	145.5	-683.78	-71.78	-612.00
39	38	149.1	-682.91	-71.57	-611.34
38	37	152.9	-682.11	-71.36	-610.75
37	36	157.1	-682.61	-71.33	-611.28
36	35	161.5	-682.89	-71.26	-611.63
35	34	165.9	-681.59	-70.96	-610.62
34	33	171.0	-682.37	-70.95	-611.42
33	32	176.0	-681.36	-70.69	-610.67
32	31	181.4	-680.84	-70.48	-610.36
31	30	187.2	-680.62	-70.31	-610.31
30	29	193.2	-679.38	-69.99	-609.40

Table 1. Observed Stark voltages and calculated Stark shifts for the $J(K_a, K_c) = 41(35.7) \leftarrow 40(33.8)$ transition of 1.1 Difluoroethylene

29	28	199.8	-679.12	-69.79	-609.33
28	27	207.0	-679.50	-69.67	-609.83
27	26	214.4	-678.27	-69.31	-608.95
26	25	222.7	-678.10	-69.09	-609.01
25	24	232.3	-681.28	-69.30	-611.98
24	23	241.9	-681.00	-69.03	-611.98
23	22	252.1	-679.76	-68.61	-611.15
22	21	263.4	-678.80	-68.21	-610.59
21	20	275.4	-676.83	-67.65	-609.18
20	19	289.2	-677.00	-67.34	-609.66
19	18	304.0	-675.63	-66.80	-608.83
18	17	320.7	-674.75	-66.29	-608.46
17	16	339.3	-674.01	-65.75	-608.26
16	15	360.8	-674.62	-65.33	-609.29
15	14	384.0	-672.38	-64.49	-607.89
14	13	411.1	-671.34	-63.73	-607.61
13	12	442.9	-671.78	-63.06	-608.72
12	11	479.2	-670.26	-62.04	-608.22
11	10	522.3	-669.11	-60.93	-608.18
10	9	573.2	-666.47	-59.46	-607.01
9	8	636.5	-665.52	-57.97	-607.55
8	7	715.5	-664.13	-56.12	-608.01
7	6	814.5	-659.37	-53.49	-605.89
6	5	947.4	-655.14	-50.34	-604.80
17	18	347.5	-699.06	-87.14	-611.91
15	16	395.0	-702.02	-88.96	-613.06
13	14	454.6	-698.85	-90.19	-608.66

II. The $J(K_a, K_c) = 40(36, 5) \leftarrow 39(34, 6)$ Transition

Another set of sharp absorption lines were observed to start at 352.1 V in the $\Delta M = 0$ spectrum. As before, the intensity of the observed absorption lines in the parallel polarization increased with increasing Stark voltage. From the detuning experiment and the variation in intensity of the observed absorption lines, these resonances were believed to belong to a P or R branch transition that was above the laser frequency. From the predicted transition frequencies, this transition was assigned to $J(K_{a,K_c}) = 40(36,5) \leftarrow 39(34,6)$, predicted with a frequency of 964 707.1 MHz. The assigned quantum numbers, observed Stark voltages and calculated Stark shifts for this transition are listed in Table 2.

$40(30,3) \leftarrow 39(34,0)$ transition of 1,1 Diffuoroethylene						
		Stark	Net Upper	Net Lower	Net Stark	
M_U	M_L	Voltage (V)	Stark Shift	Stark Shift	Shift (MHz)	
			(MHz)	(MHz)		
34	34	352.1	-3098.54	-2703.30	-395.24	
33	33	362.8	-3098.11	-2702.92	-395.19	
32	32	374.0	-3097.16	-2702.06	-395.10	
31	31	385.8	-3095.21	-2700.29	-394.92	
30	30	398.9	-3097.27	-2702.22	-395.05	
29	29	412.9	-3098.55	-2703.43	-395.11	
28	28	427.0	-3094.05	-2699.31	-394.74	
27	27	443.0	-3095.56	-2700.74	-394.82	
26	26	460.0	-3094.82	-2700.10	-394.72	

Table 2. Observed Stark voltages and calculated Stark shifts for the $J(K_a, K_c) = 40(36.5) \leftarrow 39(34.6)$ transition of 1.1 Difluoroethylene

25	25	478.2	-3093.74	-2699.16	-394.59
24	24	498.0	-3093.18	-2698.69	-394.49
23	23	519.6	-3092.49	-2698.11	-394.38
22	22	543.2	-3092.62	-2698.30	-394.32
21	21	569.2	-3093.02	-2698.76	-394.26
20	20	596.4	-3086.20	-2692.53	-393.66
19	19	628.3	-3088.97	-2695.21	-393.76
18	18	663.2	-3088.72	-2695.11	-393.61
17	17	702.3	-3088 92	-2695 45	-393.48
16	16	745.6	-3086 30	-2693 19	-393 10
15	15	794.3	-3082.24	-2689.65	-392.59
14	14	850.8	-3081.26	-2689.01	-392.25
13	13	916.9	-3083.36	-2691.28	-392.07
12	12	993.1	-3082.27	-2690.69	-391.58
11	11	1083 3	-3081.62	-2690.62	-391.00
10	10	1191.0	-3079.55	-2689.39	-390.15
9	9	1322.8	-3077.55	-2688.49	-389.06
8	8	1485 1	-3070 35	-2683 12	-387 23
		1.50.1	20,0.55	2000.12	207.20
40	39	228.1	-2359.09	-1964.83	-394.26
39	38	232.3	-2342.49	-1948.50	-393.99
38	37	237.5	-2333.59	-1939.04	-394.55
37	36	241.9	-2314.29	-1920.16	-394.13
36	35	247.1	-2300.19	-1905.90	-394.29
35	34	252.1	-2281.56	-1887.50	-394.06
34	33	257.9	-2267.40	-1873.05	-394.36
33	32	263.4	-2246.80	-1852.73	-394.06
32	31	269.8	-2231.70	-1837.27	-394.43
31	30	275.4	-2206.83	-1812.98	-393.85
30	29	282.4	-2189.97	-1795.75	-394.22
29	28	289.2	-2167.96	-1773.81	-394.15
28	27	296.6	-2146.78	-1752.50	-394.28
27	26	304.0	-2121.75	-1727.64	-394.11
26	25	312.1	-2096.92	-1702.83	-394.10
25	24	320.7	-2071.84	-1677.64	-394.20
24	23	329.5	-2043.53	-1649.43	-394.10
23	22	339.3	-2016.62	-1622.28	-394.34
22	21	349.5	-1986.90	-1592.45	-394.46
21	20	360.8	-1957.34	-1562.53	-394.81
20	19	371.6	-1919.87	-1525.42	-394.45
19	18	384.0	-1884.68	-1490.05	-394.63
18	17	396.2	-1842.11	-1447.93	-394.18
17	16	410.3	-1801.15	-1406.88	-394.27
16	15	424.5	-1753.73	-1359.86	-393.87
15	14	440.9	-1707.51	-1313.44	-394.07
14	13	458.6	-1657.12	-1262.93	-394.20
13	12	4/6.6	-1598.93	-1205.18	-393.76
12	10	49/.4	-1540.11	-1146.23	-393.88
11	10	519./	-14/4.40	-1080.75	-393./2
10	9	344.1 571.2	-1402.99	-1009.48	-373.31
9	0 7	5/1.2 602 1	-1324.89	-731.00 847.40	-373.24
0	6	636.5	-1240.03	-04/.49	_393.10
/	0	030.5	-1140.73	-/54.10	-392.03

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6	5	678.0	-1046.21	-653.13	-393.08
5	4	724.5	-930.44	-538.13	-392.30
4	3	783.8	-803.79	-411.96	-391.83
3	2	866.2	-664.20	-272.69	-391.52
2	1	1005.7	-511.25	-121.15	-390.10

The mean net Stark shift was calculated to be -393.6 MHz, giving a transition frequency of $v_{tr} = 964\ 707.0$ MHz. Although the second order Stark effect for these doublets was small, their contribution was larger than the second order Stark effect for the J(K_a,K_c) = 41(35,7) \leftarrow 40(33,8) transition. The larger second order contribution was expected since this transition was brought into resonance with the HCN laser emission at higher Stark fields.

III. The J(K_a,K_c) = $43(35,8) \leftarrow 42(33,9)$ Transition

A family of weak absorption lines was observed to start at 1031 V in the parallel polarization, with the intensities of these lines increasing with increasing Stark voltage. From the detuning experiment, these peaks were observed to belong to a transition that lay below the laser frequency. At higher Stark voltages, the pressure in the Stark cell had to be reduced to less than 20 mTorr. This significantly reduced the strength of the absorption lines making it difficult to distinguish them from noise. As a result, only four peaks were clearly observed in the $\Delta M = 0$ polarization. From the predicted transition frequencies, the absorption lines were assigned to the J(K_a,K_c) = 43(35,8) \leftarrow 42(33,9) transition, predicted at 963 436.6 MHz.

The observed Stark voltages, assigned quantum numbers, calculated first order, second order and net Stark shifts are listed in Table 3. The mean net Stark shift for this transition was 868.6 MHz, giving a transition frequency of $v_{tr} = 963\ 444.8\ MHz$. This transition shows a considerable amount of second order Stark effect, accounting for approximately 10% of the overall shift. Although there is some variation in the net Stark shifts, possibly due to second order Stark effects at higher electric fields, the experimentally determined transition frequency is in agreement with the frequency generated from the molecular constants.

	$45(55,8) \leftarrow 42(55,9)$ transition of 1,1 Diffuoroethylene					
		Stark	Net Upper	Net Lower	Net Stark	
M_U	M_L	Voltage (V)	Stark Shift	Stark Shift	Shift (MHz)	
			(MHz)	(MHz)		
35	35	1031.0	1119.91	250.65	869.26	
34	34	1060.6	1119.08	250.33	868.75	
33	33	1092.5	1119.10	250.20	868.90	
32	32	1126.8	1119.96	250.25	869.71	
43	42	832.9	1101.18	235.65	865.53	
42	41	852.8	1101.48	235.39	866.09	
41	40	873.2	1100.90	234.91	865.99	
40	39	895.1	1101.24	234.62	866.63	
39	38	917.7	1100.88	234.15	866.73	
38	37	942.0	1101.47	233.87	867.59	
37	36	967.2	1101.41	233.42	867.98	
36	35	993.9	1101.38	232.96	868.42	
35	34	1022.1	1101.55	232.51	869.04	
34	33	1052.0	1101.65	232.01	869.64	
33	32	1083.5	1101.39	231.40	869.99	
32	31	1116.7	1100.87	230.70	870.18	
31	30	1152.8	1101.62	230.23	871.40	
30	29	1190.9	1101.73	229.57	872.16	

Table 3.	Observed Stark voltages and calculated Stark shifts for the $J(K_{a},K_{c}) =$
	$43(35.8) \leftarrow 42(33.9)$ transition of 1.1 Diffuoroethylene

CONCLUSIONS

The laser Stark spectrum of 1,1–DFE has been studied using the 311 µm line of the HCN laser. The assigned transitions and their corresponding predicted and calculated frequencies are summarized in the Table 4. For the first two transitions, $J(K_a,K_c) = 41(35,7) \leftarrow 40(33,8)$ and $40(36,5) \leftarrow 39(34,6)$, the contribution from the second order Stark effect was small, on the order of a few MHz. This was as expected since the doublets involved in these transitions were nearly degenerate resulting in the quasi-first-order Stark effect accounting for the most of the shift. For the $J(K_a,K_c) = 43(35,8) \leftarrow 42(33,9)$ transition, the second order correction was quite significant, on the order of $\approx 10\%$ of the overall shift. Therefore, since the doublets involved in this transition were less degenerate than in the first two transitions, second order Stark effects became noticeable. The deviations present in the net Stark shift for the third transition may result from not including enough interacting levels to account for the second order effect, which plays an increasing role at greater electric fields.

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	Average Net	Experimental	Predicted			
Observed	Stark Shift	Transition	Transition			
Transition	(MHz)	Frequency (MHz)	Frequency			
			(MHz)			
$41(35,7) \leftarrow 40(33,8)$	-610.0	964 923.4 ± 2.5	964 925.6			
$40(36,5) \leftarrow 39(34,6)$	-393.6	964 707.0 \pm 2.1	964 707.1			
$43(35,8) \leftarrow 42(33,9)$	868.6	963 444.8 ± 8.5	963 436.6			

 Table 4. Predicted and calculated frequencies for transitions observed from 1,1

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