Diode Laser Spectroscopy of the ν_3 Band of OF_2

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Portions of the ν_3, asymmetric stretch band of OF_2 have been measured under conditions of Doppler-limited resolution and the frequencies of 176 transitions measured with a nominal accuracy of 0.001 cm^{-1}. The remaining band constants were determined by constraining the ground state parameters to the values determined earlier and carring out a simultaneous fit of the existing infrared and $\nu_3 = 1$ microwave data. No evidence for the anticipated effects of weak Coriolis coupling for levels with $K_{-1} \leqq 16$ and $J \leqq 30$ was observed although such effects may present in levels with much higher quantum numbers.

Introduction

The analysis of the strongly interacting $\nu_1/2\nu_2$ Fermi diad of OF_2 centered near 920 cm^{-1} has been recently reported from this laboratory [1]. Perturbations of the spectra were observed which were considered to arise from a Coriolis interaction between the diad and the ν_3 fundamental which reported [3] to lie near 831 cm^{-1}. In an effort to characterize this effect further it was decided to carry out diode laser spetroscopy of the ν_3 band of OF_2, the results of which are the subject of the present paper.

Experimental

The diode-laser spectrometer was based on the cold-head assembly of Laser Analytics, and the measurements were carried out using a single diode from the same firm. Frequency differences were measured with a calibrated confocal etalon (free spectral range: 0.009811 cm^{-1}), and the absolute frequency was determined by accurately known absorption lines of ammonia [4]. The signals of OF_2 were observed using a multi-reflection cell with a pathlength of ca. 30 m.

Observations and Discussion

In accordance with expectation, the ν_3 band proves to be purely a-type and is much more intense than the $\nu_1/2\nu_2$ diad. Preliminary band constants were available from the microwave work of Morino and Saito [3] and the assignment process proceeded smoothly.

A section of the Q-branch spectrum near 828 cm^{-1} is shown in Figure 1. The usual form of such a branch is somewhat obscured in this case as a direct result of the relatively large α-constants in $\nu_3 = 1$. A total of 176 infrared frequencies for transitions with $J \leqq 30$ and $K_{-1} \leqq 16$ were accumulated, and these are shown in Table 1.

With the ground state rotational and distortion constants constrained at the values determined earlier [1, 2] the data of Table 1 were fitted with the 12 $\nu_3 = 1$ rotational transitions from reference [3] using Watson's A-reduced Hamiltonian [5]. The results obtained for the upper state constants and the band origin are shown in Table 2.

As can be seen from Table 1 all the transition frequencies measured are adequately fit by the standard semirigid rotor Hamiltonian. This leads to one to conclude that, at least for levels with $J = 30$ and $K_{-1} \leqq 16$, any Coriolis interaction with $\nu_1/2\nu_2$ must be negligible and can probably not explain the effects observed previously [1]. This indicates that the extraneous effect observed in $\nu_1/2\nu_2$ must have another source. In the case of the extraordinarily strong interaction present between $\nu_1 = 1$ and $\nu_2 = 2$ it was found necessary to extend the usual theory of Fermi resonance [1]. One possible explanation for the remaining effects in the diad spectrum is that the theory developed for this strong Fermi resonance condition is not adequate and must be extended still further.

The deviation of the distortion constant δ_K of the state $\nu_3 = 1$ from the value of the ground state (– 12.7 kHz) has the same magnitude but is of

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Table 1. Observed transitions (in cm^{-1}).

J'	K_-	K_+	J''	K_-	K_+	ν	Calc.-Obs.
2	0	2	3	0	3	826.6679	− 0.0005
3	0	3	4	0	4	825.9878	0.0007
5	0	5	4	0	4	831.9059	0.0015
6	0	6	5	0	5	832.5140	0.0001
7	0	7	6	0	6	833.1055	− 0.0006
20	0	20	21	0	21	813.9908	− 0.0005
28	0	28	29	0	29	807.6474	0.0003
29	0	29	30	0	30	806.8218	0.0001
2	1	1	3	1	2	826.5619	− 0.0002
3	1	2	4	1	3	825.8488	0.0008
3	1	3	4	1	4	826.0705	0.0004
5	1	4	4	1	3	832.0739	− 0.0013
5	1	5	4	1	4	831.7622	− 0.0001
6	1	6	5	1	5	832.3545	0.0005
6	1	5	5	1	4	832.7310	0.0002
7	1	7	6	1	6	832.9382	0.0004
9	1	9	9	1	8	825.7828	0.0003
19	1	18	20	1	19	814.1918	0.0003
20	1	20	21	1	21	813.9972	− 0.0006
28	1	27	29	1	28	807.1809	0.0002
29	1	29	30	1	30	806.8218	0.0004
2	2	0	3	2	1	826.5902	− 0.0006
3	2	2	4	2	3	825.9083	0.0008
3	2	1	4	2	2	825.8938	0.0005
5	2	3	4	2	2	831.9059	− 0.0003
5	2	4	4	2	3	831.8715	0.0004
6	2	5	5	2	4	832.5002	− 0.0001
6	2	4	5	2	3	832.5597	− 0.0005
7	2	6	6	2	5	833.1203	− 0.0001
18	2	16	19	2	17	814.5308	− 0.0003
19	2	17	20	2	18	813.7518	0.0001
19	2	18	20	2	19	814.2985	0.0000
27	2	25	28	2	26	807.4847	0.0004
28	2	26	29	2	27	806.6847	0.0006
28	2	27	29	2	28	807.1926	0.0002
3	3	1	4	3	2	825.8217	0.0011
5	3	2	4	3	1	831.7987	0.0011
6	3	3	5	3	2	832.4362	0.0000
7	3	5	6	3	4	833.0649	− 0.0003
7	3	4	6	3	3	833.0686	− 0.0003
18	3	15	19	3	16	814.5085	− 0.0005
19	3	16	20	3	17	813.6909	0.0001
19	3	17	20	3	18	813.9816	− 0.0006
27	3	24	28	3	25	807.0998	0.0006
27	3	25	28	3	26	807.6038	0.0003
28	3	26	29	3	27	806.7848	0.0004
6	4	2	5	4	1	832.3170	− 0.0001
7	4	3	6	4	2	832.9461	− 0.0002
18	4	14	19	4	15	814.5616	− 0.0006
18	4	15	19	4	16	814.6000	− 0.0007
19	4	15	20	4	16	813.7573	0.0000
19	4	16	20	4	17	813.8097	− 0.0001
23	4	20	23	4	19	826.1398	0.0000
27	4	24	28	4	25	807.3172	0.0002
27	4	23	28	4	24	807.0498	0.0002
7	5	2	6	5	1	832.7965	− 0.0007
18	5	13	19	5	14	814.4653	− 0.0003
18	5	14	19	5	15	814.4678	− 0.0003
19	5	14	20	5	15	813.6718	0.0012
19	5	15	20	5	16	813.6765	0.0003
20	5	15	20	5	16	827.0334	0.0005
20	5	16	20	5	15	827.0041	0.0004
21	5	17	21	5	16	826.8737	− 0.0003
21	5	16	21	5	17	826.9207	− 0.0002

Table 1 (continued)

J'	K_-	K_+	J''	K_-	K_+	ν	Calc.-Obs.
23	5	19	23	5	18	826.5820	− 0.0013
23	5	18	23	5	19	826.6947	− 0.0008
24	5	19	24	5	20	826.5862	− 0.0012
25	5	21	25	5	20	826.2339	− 0.0005
26	5	21	26	5	22	826.3929	− 0.0007
27	5	23	28	5	24	807.1394	0.0004
27	5	23	27	5	22	825.8057	− 0.0003
27	5	22	28	5	23	807.0865	0.0002
28	5	23	28	5	24	826.2638	− 0.0009
30	5	25	30	5	26	826.2457	− 0.0011
7	6	1	6	6	0	832.6139	0.0003
18	6	12	18	6	13	827.0611	0.0007
18	6	12	19	6	13	814.3018	0.0003
19	6	14	19	6	13	826.9484	− 0.0002
20	6	14	20	6	15	826.8306	− 0.0004
22	6	17	22	6	16	826.5750	− 0.0010
22	6	16	22	6	17	826.5781	− 0.0008
23	6	18	23	6	17	826.4386	− 0.0009
23	6	17	23	6	18	826.4437	− 0.0005
24	6	18	24	6	19	826.3057	− 0.0012
25	6	19	25	6	20	826.1619	− 0.0003
26	6	21	26	6	20	825.9920	− 0.0002
26	6	20	26	6	21	826.0154	− 0.0005
27	6	21	27	6	22	825.8656	− 0.0003
27	6	22	27	6	21	825.8298	− 0.0004
27	6	22	28	6	23	806.9833	0.0007
27	6	21	28	6	22	806.9784	0.0007
28	6	22	28	6	23	825.7147	− 0.0010
8	7	1	7	7	0	833.0231	− 0.0012
16	7	10	16	7	9	827.0551	0.0007
18	7	12	18	7	11	826.8453	0.0000
18	7	11	19	7	12	814.0981	− 0.0001
19	7	13	19	7	12	826.7318	− 0.0005
20	7	14	20	7	13	826.6119	− 0.0003
21	7	15	21	7	14	826.4868	− 0.0006
22	7	16	22	7	15	826.3557	− 0.0005
24	7	17	24	7	18	826.0769	− 0.0003
25	7	19	25	7	18	825.9291	− 0.0006
26	7	19	26	7	20	825.7763	− 0.0002
26	7	19	27	7	20	807.6293	0.0008
27	7	21	28	7	22	806.7941	0.0008
13	8	6	13	8	5	827.0808	0.0003
14	8	7	14	8	6	826.9956	0.0006
15	8	8	15	8	7	826.9052	0.0002
16	8	9	16	8	8	826.8087	0.0000
17	8	9	18	8	10	814.6378	− 0.0002
17	8	10	17	8	9	826.7063	− 0.0003
18	8	11	18	8	10	826.5980	− 0.0005
18	8	10	19	8	11	813.8574	0.0000
19	8	12	19	8	11	826.4833	− 0.0002
20	8	13	20	8	12	826.3630	− 0.0001
21	8	14	21	8	13	826.2372	− 0.0002
22	8	15	22	8	14	826.1056	− 0.0004
24	8	17	24	8	16	825.8237	0.0009
25	8	18	25	8	17	825.6759	− 0.0001
26	8	18	27	8	19	807.3980	0.0010
27	8	19	28	8	20	806.5639	0.0011
9	9	1	9	9	0	827.0808	0.0006
10	9	2	10	9	1	827.0198	0.0007
11	9	3	11	9	2	826.9532	0.0004
12	9	4	12	9	3	826.8806	0.0001
13	9	5	13	9	4	826.8019	− 0.0001
14	9	6	14	9	5	826.7170	− 0.0001
15	9	7	15	9	6	826.6262	− 0.0002

Table 1 (continued)

J'	K_-	K_+	J''	K_-	K_+	ν	Calc.-Obs.
16	9	8	16	9	7	826.5294	− 0.0002
17	9	8	18	9	9	814.3614	0.0000
17	9	9	17	9	8	826.4269	− 0.0005
18	9	10	18	9	9	826.3187	− 0.0010
19	9	11	19	9	10	926.2030	0.0001
20	9	12	20	9	11	826.0827	0.0000
21	9	13	21	9	12	825.9558	0.0006
22	9	14	22	9	13	825.8237	0.0005
23	9	15	23	9	14	825.6862	0.0001
26	9	17	27	9	18	807.1296	0.0003
10	10	1	10	10	0	826.7089	− 0.0005
11	10	2	11	10	1	826.6418	− 0.0002
12	10	3	12	10	2	826.5684	0.0003
13	10	4	13	10	3	826.4899	− 0.0001
14	10	5	14	10	4	826.4050	− 0.0001
15	10	6	15	10	5	826.3144	− 0.0003
16	10	7	16	10	6	826.2170	0.0002
17	10	7	18	10	8	814.0512	− 0.0002
17	10	8	17	10	7	826.1143	0.0001
18	10	9	18	10	8	826.0054	0.0002
19	10	10	19	10	9	825.8910	0.0000
21	10	12	21	10	11	825.6437	0.0002
25	10	15	26	10	16	807.6507	0.0007
26	10	16	27	10	17	806.8245	0.0005
11	11	1	11	11	0	826.2964	0.0003
12	11	2	12	11	1	826.2237	0.0002
13	11	3	13	11	2	826.1450	0.0001
14	11	4	14	11	3	826.0599	0.0004
15	11	5	15	11	4	825.9687	0.0007
16	11	6	16	11	5	825.8718	0.0008
16	11	5	17	11	6	814.4802	− 0.0003

Table 1 (continued)

J'	K_-	K_+	J''	K_-	K_+	ν	Calc.-Obs.
17	11	6	18	11	7	813.7068	0.0002
17	11	7	17	11	6	825.7697	0.0002
18	11	8	18	11	7	825.6611	0.0000
25	11	14	26	11	15	807.3109	0.0002
12	12	1	12	12	0	825.8454	0.0009
13	12	2	13	12	1	825.7667	0.0009
14	12	3	14	12	2	825.6826	0.0002
15	12	4	15	12	3	825.5915	0.0006
16	12	4	17	12	5	814.1023	− 0.0001
25	12	13	26	12	14	806.9360	0.0008
15	13	2	16	13	3	814.4579	− 0.0002
24	13	11	25	13	12	807.3478	0.0000
15	14	1	16	14	2	814.0140	− 0.0007
24	14	10	25	14	11	806.9054	0.0004
23	15	8	24	15	9	807.2435	− 0.0005
22	16	6	23	16	7	807.5414	− 0.0007
23	16	7	24	16	8	806.7345	− 0.0004
3	0	3	2	1	2	13796.2*	− 0.2
4	0	4	3	1	3	35877.0*	0.1
4	2	3	5	1	4	32375.0*	0.3
7	1	6	6	2	5	18108.0*	0.1
6	2	4	7	1	7	34753.1*	0.0
7	2	5	8	1	8	25096.7*	− 0.2
8	2	6	9	1	9	17661.5*	0.0
9	2	7	10	1	10	12679.6*	− 0.1
9	3	7	10	2	8	25998.7*	0.0
10	3	7	11	2	10	31931.2*	0.0
12	2	10	11	3	9	27242.7*	0.2
12	2	10	13	1	13	13967.9*	0.1

* = in MHz, rotational transition (0, 0, 1).

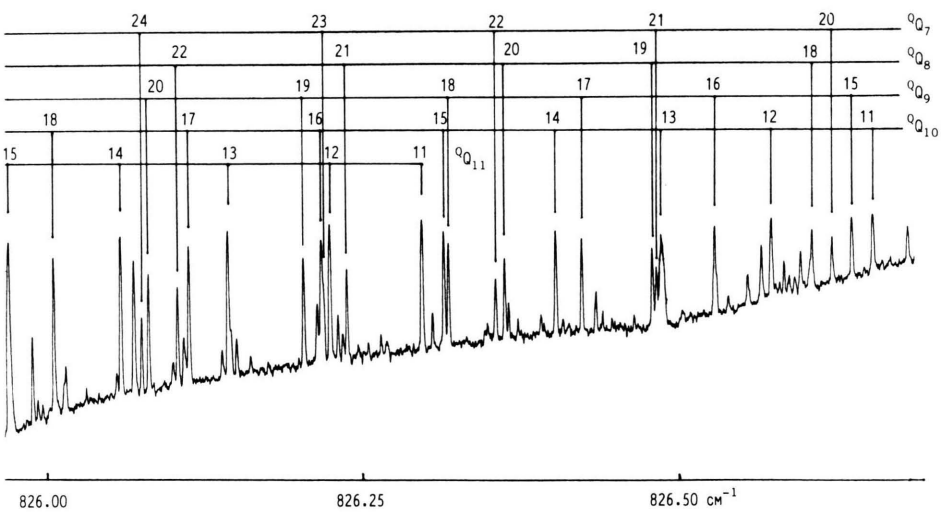

Fig. 1. A section of the a-type Q-branch spectrum of the ν_3 band of OF_2 near 828 cm^{-1} at Doppler-limited resolution. The usual structure of such a Q-branch is obscured by the effects of the relatively large α-constants in $\nu_3 = 1$. The individual assignments are indicated above the trace.

Table 2. Constants of the ν_3 band of OF_2.

		(0, 0, 0) *	(0, 0, 1)
ν_0	(cm^{-1})	0.0	828.6876(1)
A	(MHz)	58 782.54	58 197.72(5)
B	(MHz)	10 896.52	10 827.01(1)
C	(MHz)	9 167.26	9 052.05(1)
Δ_J	(kHz)	16.58	16.41(2)
Δ_{JK}	(kHz)	− 85.	− 91.1(1)
Δ_K	(kHz)	1 721.	1 722.1(3)
δ_J	(kHz)	3.542	3.917(6)
δ_K	(kHz)	64.7	52.(1)

The standard deviation is given in parenthesis.
* = from Reference [1, 2].

different sign from the difference between the mean value of δ_K of the perturbed states of the Fermi diad $\nu_1/2\nu_2$ and the ground state (11.3 kHz). This seems to indicate that the deviation of the δ_K constants is due to a very weak Coriolis coupling between the ν_3 band and the $\nu_1/2\nu_2$ Fermi diad.

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