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"NEAR ULTRAVIOLET EMISSION SPECTRUM OF m-DIFLUOROBENZENE"

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(*Received November 15, 1967 ; Resubmitted January 11, 1968*)

(Plate 2)

ABSTRACT. The emission spectrum of *m*-difluorobenzene molecule has been obtained by uncondensed transformer discharge through the flowing vapour of the compound. The spectrum lies in the region 2500-3000 Å and consists of about 90 bands. These bands have been analysed in terms of 240, 260, 336, 459, 510, 526, 736, 766, 1010, 1075, 1271, 1292, 1345, 1460, 3051 and 3096 cm^{-1} ground state fundamentals and 165, 189, 231, 381, 706, 970 and 1267 cm^{-1} as excited state fundamentals.

INTRODUCTION

m-Difluorobenzene is a disubstituted benzene wherein two fluorine atoms are substituted in 1 and 3 positions of the benzene ring as shown below :

It has been investigated by a number of workers. Herz (1943) studied the Raman spectrum of this compound. Ferguson *et al*, (1953) have recorded the infrared and Raman spectra of this compound and assuming C_{2v} point group for the molecule, classified various vibration frequencies in the four possible species. Later Green *et al*, (1963) revised the earlier assignments and reassigned modes of vibrations to the observed vibration frequencies.

The ultraviolet absorption spectrum in vapour phase has been investigated by Rao and Sponer (1952). They have recorded about 400 bands on a 3 meter Concave Grating Spectrograph and have analysed the bands in terms of 703, 740, 967 and 1269 cm^{-1} excited state frequencies. Frequency differences of 66 and 97 cm^{-1} have also been observed. They also studied the absorption spectrum of the substance in iso-octane solution and found the oscillator strength for the longest wavelength singlet-singlet absorption system, to be 0.0096.

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However, the emission spectrum of the substance has not been reported so far and therefore in the present study the emission spectrum of *m*-difluorobenzene has been recorded and a detailed analysis of the observed bands has been presented.

EXPERIMENTAL DETAILS AND RESULTS

The sample used in the present investigation was obtained from Eastman Kodak Company and was of white label quality. It was used without further purification.

The emission spectrum was obtained by employing an uncondensed transformer discharge through the flowing vapour of the substance in a π-type discharge tube of length 60 cms and diameter 2.2 cms. As the vapour pressure of the substance is high, a fine capillary tube was attached to the container of the liquid, which regulated the flow of the vapour in the discharge tube. When the discharge was started, a bluish white glow appeared which filled the entire cross-section of the tube. The voltage applied across the two electrodes of the discharge column was about 3500 volts. Due to discharge through the vapour of the substance a greasy substance was deposited on the inner walls of the discharge tube.

The spectrum was recorded on a Zeiss Q-24 Medium Quartz spectrograph. With a slit width of 30μ, the time of exposure varied from 1½ hours to 3½ hours to record the spectrum on Ilford N-40 plates. The bands were measured on a Hilger L-76 comparator.

The emission spectrum lies in the region 2500-3000Å and consists of about 90 bands. Most of these bands are sharp and are accompanied by companion bands which lie at intervals of 11 and 69 cm^{-1}. The intensity of the accompanying continuum which generally overlaps the emission bands of the substituted benzenes is very weak in the present case. The reason for this may be lesser dissociation of *m*-difluorobenzene molecules under the influence of electrical discharge. Three plates were measured and the mean of the three measurements were taken for the analysis. The accuracy of measurement is of the order of 5 cm^{-1} for sharp and strong bands and 8 cm^{-1} for weak and diffuse bands.

A typical spectrogram is reproduced in fig. 1(Plate 2). Table 1 gives the wave-numbers, estimated intensities and proposed assignments for the bands. In some cases alternative assignments have also been proposed but they are arranged in order of their probability. Table 2 gives a correlation between ground and excited state frequencies of the molecule.

DISCUSSION AND ANALYSIS

The molecule *m*-difluorobenzene belongs to C_{2v} point-group. The thirty vibrational modes are divided into : $11a_1$, $3a_2$,$10b_1$ and $6b_2$. The stretching and in-plane bending vibrations belong to a_1 and b_1 species and out-plane bending vibrations belong to the species a_2 and b_2. The electronic transition responsible for the present system is B_1-A_1 which corresponds to the forbidden transition $B_{2u}-A_{1g}$ of benzene.

The strong band of the system at 37910 cm^{-1} (2637.0Å) has been chosen as the 0-0 band. This selection of the 0-0 band is further supported by Rao and Sponer (1952), who have measured it at 2637.1Å.

The strong band of the system at 36900 cm^{-1} is at an interval of 1010 cm^{-1} from the 0-0 band. This frequency interval is taken as a ground state vibration of the molecule. The corresponding excited state frequency is 970 cm^{-1}. The ground state frequency 1010 cm^{-1} is in good agreement with the Raman frequency 1008 cm^{-1} which appears with strong intensity and has a depolarization ratio of 0.04. The second quantum of this ground state frequency is observed at 35883 cm^{-1} and the third quantum at 34896 cm^{-1}. The low depolarization ratio of this frequency in the Raman spectrum leads us to classify it as a totally symmetric vibration. This frequency quite likely involves ring breathing vibration corresponding to 992 cm^{-1} frequency of benzene. This assignment is further supported by the assignment of 997 cm^{-1} frequency in *m*-dichlorobenzene

Table 1

Emission bands of *m*-difluorobenzene

Wavenumber cm^{-1}	Intensity	Separation from 0-0 band cm^{-1}	Assignments
39177	1	1267	0+1267
38880	3	970	0+970
38829	1	918	0+519+381
38790	2	880	0+706+165
38616	4	706	0+706
38562	1	652	
38429	2	519	0+519
38386	1	476	
38291	1	381	0+381
38141	5	231	0+231
38099	2	189	0+189
38075	1	165	0+165
37910	10	0	0−0
37901	10	11	0−11
37841	10	69	0−69 ; 0−260+189
37804	2	106	0−106 ; 0−336+231

Table 1 (*Contd.*)

Wavenumber cm^{-1}	Intensity	Separation from 0-0 band cm^{-1}	Assignments
37777	1	133	0—133
37718	5	192	0—192 ; 0—133—69
37684	2	226	0—459+231
37670	1	240	0—240
37650	1	260	0—260
37574	6	336	0—336
37516	2	366	0+260—106
37479	1	431	0—240—133—69
37451	4	459	0—459
37400	4	510	0—510
37384	1	526	0—526 ; 0—459—69
37342	2	568	0—336—240 ; 0—459—106
37300	1	610	0—510—106 ; 0—336—260
37266	1	644	0—459—192
37185	1	725	0—725
37176	10	736	0—736
37163	10	746	0—736—11
37144	6	766	0—766
37109	6	801	0—459—336
37071	1	839	0—736—106 ; 0—510—336
37039	1	871	0—736—133 ; 0—526—336
36938	2	972	0—736—240
36900	10	1010	0—1010
36889	10	1021	0—1010—11
36835	6	1075	0—1075 ; 0—1010—69
36799	1	1111	0—1010—106
36768	1	1142	0—1010—133
36736	1	1174	0—1075—106
36703	4	1207	0—1010—133—69
36664	1	1246	0—736—510 ; 0—1010—240
36639	3	1271	0—1271
36619	6	1292	0—1292

Table 1 (*Contd.*)

Wavenumber cm⁻¹	Intensity	Separation from 0-0 band cm⁻¹	Assignments
36565	2	1345	0—1292—106
36450	1	1460	0—1460
36435	8	1475	0—1010—459 ; 0—2 × 736
36424	8	1486	0—1010—459—11 ; 0—2 × 736—11
36391	4	1519	0—1010—510
36367	4	1543	0—2 × 736—69
36259	1	1651	0—1010—510—133
36246	0	1664	0—1460—240
36206	0	1704	0—2 × 736—240
36163	8	1747	0—1010—736
36155	8	1755	0—1010—736—11
36102	3	1808	0—1075—736 ; 0—1010—736—69
36051	1	1859	0—1010—736—106
35987	2	1923	0—2 × 736—459
35911	1	1999	0—2 × 736—526
35883	3	2027	0—2 × 1010 ; 0—1292—736
35827	2	2083	0—736—1345
35703	1	2207	0—1460—736 ; 0—3 × 736
35649	1	2261	0—2 × 1010—240
35627	0	2283	0—2 × 1010—260
35556	1	2354	0—1010—1345
35541	0	2369	0—1075—1292
35487	0	2423	0—1075—1345
35432	1	2478	0—1010—1460
35374	0	2536	0—1460—1075
35354	1	2556	0—2 × 736—1075
35250	0	2660	0—1460—1292
35160	1	2750	0—2 × 1010—736
35097	1	2813	0—1460—1345
34896	1	3014	0—3 × 1010
34859	1	3051	0—3051
34814	1	3096	0—3096 ; 0—2 × 1010—1075
34642	1	3262	0—3051—226
34356	1	3554	0—3096—459
34137	0	3773	0—3096—736
33879	1	4031	0—4 × 1010
33795	1	4113	0—3096—1010

Table 2
Correlation between Ground and excited state Frequencies of m-Difluorobenzene

Ground State				Excited state	
Raman (cm^{-1}) (liquid)		Infrared (cm^{-1}) (liquid) Ferguson *et al.*	Emission (vapour) Present work	Emission (vapour) Present work	Assignments
Herz	Ferguson *et al.*				
232 (7) .76	235 (s) .84		240 (1)	165 (1)	C-C-C o.p.b.
248 (9) .76	251 (s) .83		260 (1)	189 2)	C-F o.p.b.
329 (1) dp ?	331 (w) .7		336 (6)	231 (5)	C-C-C i.p.b.
	459 (vw) dp	458 (s)	459 (4)	381 (1)	C-C-C o.p.b.
511 (5) .47	513 (s) .45	514 (s)	510 (4)		C-F o.p.b.
523 (6) .47	523 (s) .35	524 (s)	526 (1)		C-C-C i.p.b.
735 (15s) .16	736 (vs) .02	734 (s)	736 (10)	706 (4)	C-F i.p.b.
772 (1) dp ?	776 (w) .85	771 (vs)	766 (6)		C-F i.p.b.
1007 (15s) .06	1008 (vs) .04		1010 (10)	970 (3)	Ring breathing
1067 (4s)	1068 (m)	1068 (m)	1075 (10)		C-H i.p.b.
1254 (1s) .62	1259 (m)	1256 (w)	1271 (3)		C-F stret
1277 (7d) .11	1279 (s)	1271 (s)	1292 (8)	1267 (1)	C-F stret
1348 (0)	1339 (w)	1337 (vw)	1345 (2)		C-C stret.
	1454 (vw) P	1459 (m)	1460 (1)		C-C stret.
		3049 (vw)	3051 (1)		C-H stret.
3095 (5d) .38	3096 (m) .3	3086 (s)	3096 (1)		C-H stret.

stret.= stretching.

by Ghosh (1963), 998 cm^{-1} frequency in *m*-xylene by Singh (1957-58) and 996 cm^{-1} frequency in *m*-tolunitrile by Singh and Singh (1965), to the ring breathing mode.

The strong band **at** 36619 cm^{-1} involves the ground state frequency 1292 cm^{-1}. This frequency is correlated with the Raman frequency 1279 cm^{-1} which has a depolarization ratio of 0.08. The corresponding infrared frequency is 1277 cm^{-1} in liquid phase and 1294 cm^{-1} in vapour phase. Cooper (1954) who has studied the ultraviolet absorption of *p*-difluorobenzene in vapour phase has observed that the magnitude of C-F stretching frequency increases in vapour phase. In conformity with his observation, the ground state frequency 1292 cm^{-1} observed in the present case is assigned to C-F stretching mode. There is another ground state frequency 1271 cm^{-1} observed with medium weak intensity. This ground state frequency can be correlated with the Raman frequency 1259 cm^{-1} observed with medium intensity and infrared frequency 1256 cm^{-1} observed with weak intensity. In the present case we expect to observe two C-F stretching frequencies; therefore the ground state frequency 1271 cm^{-1} is assigned to the other C-F stretching mode.

Another strong band at 37170 cm^{-1} involves the ground state frequency 736 cm^{-1}. The second quantum of this frequency has been observed in a strong band at 36435 cm^{-1}. It also combines with almost all the other totally symmetric vibrations. In the excited state, we have observed a frequency 706 cm^{-1}. The ground state frequency 736 cm^{-1} may correspond to the excited state frequency 706 cm^{-1}. The Raman frequency 736 cm^{-1} that has appeared with strong intensity is correlated with the ground state frequency 736 cm^{-1}. It is suggested to be a totally symmetric vibration involving C-F in-plane bending mode.

The frequency 771 cm^{-1} appears with medium strong intensity in the emission spectrum. Usually C-H out-of-plane bending and C-F in-plane bending frequencies lie in this region but we believe that this frequency arises due to C-F in-plane bending mode and not due to C-H out-of-plane bending mode.

The two bands at 37574 and 37384 cm^{-1} which appear with strong and medium strong intensities respectively, are separated from the (0-0) band by 336 and 526 cm^{-1}. The ground state frequency 336 cm^{-1} is correlated with the Raman line 331.4 cm^{-1} which has a depolarization ratio of 0.7 and has been assigned as a_1 fundamental by Ferguson *et al* (1953). However, no overtone of this frequency has been observed but its intensity and combinability with other totally symmetric vibrations, lead us to place it in the category of totally symmetric vibrations. It, most likely, represents the a_1 component of the benzene degenerate vibration e_{2g} (606 cm^{-1}). The b_1 component of this vibration is represented by the ground state frequency 526 cm^{-1} which can be correlated with the Raman line 523 cm^{-1} having a depolarization ratio 0.35.

The ground state frequency 459 cm^{-1} is involved in a medium strong band at 37451 cm^{-1}. This ground state frequency is in good agreement with depolarized Raman frequency 459 cm^{-1} which appears weakly. The corresponding infrared frequency is 459 cm^{-1}. This non-totally symmetric frequency most probably corresponds to one of the components of the benzene vibration 404 $cm^{-1}(e_{2u})$. The other component has been identified at 240 cm^{-1} which is correlated with the depolarized Raman frequency 235 cm^{-1}.

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Indian Journal of Physics
Vol. 42. No 1.
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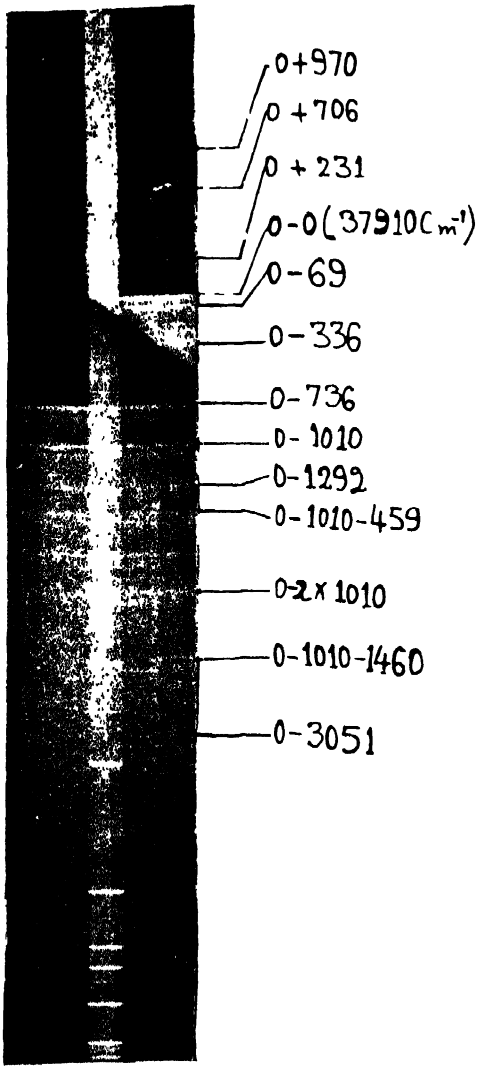

Fig 1. Emission spectrum of m-Difluorobenzene, photographed on Zeiss Q-24 Medium Quartz Spectrograph, slitwidth 30μ, time of exposure 2 hours.

Another ground state frequency 260 cm^{-1} is found to occur in a medium strong band at 37650 cm^{-1}. This ground state frequency is correlated with the Raman frequency 251 cm^{-1} which has a depolarization ratio 0.83. This is assigned to the C-F out-of-plane bending mode. Similar assignment was proposed for the frequency 252 cm^{-1} in *p*-difluorobenzene by Cooper (1954).

A ground state frequency of 1075 cm^{-1} is observed in a band at 36835 cm^{-1} which can be correlated with the Raman line 1068 and infrared frequency 1068 cm^{-1}. The low depolarization ratio of this Raman line, suggests it to belong to the totally symmetric species. It is assigned to C-H in-plane bending mode. Ghosh (1963) has assigned the frequency 1070 cm^{-1} in *m*-dichlorobenzene to a similar mode of vibration.

The ground state frequencies 1335 and 1460 cm^{-1} are correlated to the Raman lines 1339 and 1454 cm^{-1} and infrared frequencies 1337 and 1445 cm^{-1} respectively. These two frequencies represent C-C mode of vibration corresponding to 1310 and 1485 cm^{-1} frequencies of benzene.

The two bands at 34859 and 34814 cm^{-1} are found to involve the ground state frequencies 3051 and 3096 cm^{-1} respectively. They can be correlated with the infrared frequencies 3049 and 3086 cm^{-1} respectively. These are assigned to C-H stretching modes.

In addition to the above mentioned frequencies, difference frequencies of 69 and 106 cm^{-1} have also been observed. These are found to accompany almost all the strong bands. These may be attributed to the transitions $-69 = +189 -260$ and $-106 = +231-336$.

ACKNOWLEDGMENT

The authors are grateful to Prof. Nand Lal Singh for his valuable suggestions and criticisms during the course of the work.

REFERENCES

Coppor, C. D., 1954, *J. Chem. Phys.*, **22**, 503.

Ferguson, E. E., Collins, R. L., Nielson and Smith, D. C., 1953, *J. Chem. Phys.*, **21**, 1470.

Ghosh, D. K., 1963, *Ph. D. Thesis*, Banaras Hindu University, Varanasi.

Green, J. H. S., Kynstone, W. and Paisely, H. M., 1963, *J. Chem. Soc.*, p. 433.

Herz, E., 1943, *Monatsh. Chem.*, **74**, 160.

Rao, V. R. K. and Sponer, H., 1952, *Phys. Rev.*, **87**, 213A.

Singh, I. S., 1957-58, *J. Sci. Res. B.H.U.*, **8**(1), 19.

Singh, R. N. and Singh, S. N., 1965, *Ind. J. Pure & Appl. Phys.*, **3**, 101.