

# THE FLUORESCENCE AND EMISSION SPECTRA OF THE THREE ISOMERIC FLUORO-TOLUENES

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The near-ultra-violet fluorescence and emission spectra of the three isomeric fluoro-toluenes in the vapour phase were obtained and analysed in co-ordination with each other. The molecular vibrational frequencies obtained from this analysis are correlated with the values from Raman and near-ultra-violet absorption spectra. Possible assignments are also suggested.

The near ultra-violet absorption spectra of *o*-, *m*- and *p*-fluoro toluenes were studied by Cave and Thompson.<sup>1</sup> An analysis of *m*- and *p*-isomers was presented. Eight fundamentals were obtained in each of the two states in the *p*-compound, five in the upper state and six fundamentals in the lower state were obtained in the *m*-compound. For *o*-fluoro-toluene they only mentioned three possible fundamentals in the upper state and two in the lower state with uncertainties about the position of the (0, 0) band. The Raman spectra were studied by Kohlrausch<sup>2</sup> and Paulsen.<sup>3</sup> The infra-red spectra were studied by Thompson and Temple.<sup>4</sup> There appear to be no data available on the fluorescence or emission spectra of the vapour for these molecules. The results of our study are described below.

## EXPERIMENTAL

### FLUORESCENCE

The fluorescence tube is an all-quartz tube with a Pyrex graded seal similar to the one described by Sponer and Bass.<sup>5</sup> The cleaned tube is thoroughly degassed before the substance is introduced into it. The substance is sealed in the tube in vacuum after prolonged evacuation (solidifying the substance with a liquid-air bath). The set-up for fluorescence is essentially the same as that employed by Sponer and Bass except that no condensing lens is employed between the source and the window of the tube. Radiations from the quartz mercury arc and the silver spark were used for excitation purposes. Corex 9863 filter supplied by Corning Glass Works was used to cut out radiations below 2500 Å. Spectra were also taken without filters. A Hilger small quartz spectrograph with a dispersion of 36 Å/mm in the region 2840 Å and a medium quartz spectrograph with a dispersion of 12.6 Å/mm in the region 2800 Å were used to record the spectra on Ilford Selochrome and Special Rapid plates. The times of exposure varied between 30 and 150 h depending on the conditions of the experiment. The fluorescence was studied at the saturated vapour pressures corresponding to the temperature of the container (28° C).

The bands are measured by linear interpolation between two closely lying iron arc lines used as standards. Six settings are made for each measurement and the mean value was taken. The diffuse nature of the bands imparts a certain amount of error in the setting of the cross-wires and so wavelength data are given correct to the nearest Å. The wave-numbers also are corrected to the first 5 cm<sup>-1</sup>. From the nature of the bands we do not think that higher accuracy is possible.

### EMISSION

The emission spectra of the three isomers were excited by the ozonizer type of discharge. About 20,000 V are applied to the discharge tube from the secondary of a transformer. It is found that the vapour pressure for the excitation of the spectrum is critical. Both small quartz and medium quartz spectrophotometers were employed to photograph the spectra. The measurements are carried out and the data given on similar lines as for fluorescence.

## RESULTS

*p*-FLUORO-TOLUENE

## FLUORESCENCE SPECTRUM

It is found that silver spark and mercury arc are the most convenient sources of excitation. Spectra were taken with slit widths of 100 and 30 microns. Identical spectra were obtained with and without filters. Obtaining the spectra with the two sources of

TABLE 1.—*p*-FLUORO-TOLUENE; FLUORESCENCE BANDS

wave-lengths (Å)	intensity	wave-numbers (cm <sup>-1</sup> )	assignment
2703 <sup>a</sup> <sub>Hg</sub>	W.D.	36985	0 + 110
2709 <sub>Hg</sub>	W.	36905	0 + 30
	V.D.		
2717 <sup>a</sup>	W.D.	36800	0 - 75
2725 <sup>a</sup>	W	36680	
2738 <sup>a</sup>	M	36515	0 - 360
2761 <sup>a</sup> <sub>Hg</sub>	Str.	36205	0 - 670
2775 <sup>a</sup> *	V. Str.	36025	0 - 850
2782 <sup>a</sup> *	Str.	35935	0 - 850 - 90
	Sh.		
2792 <sup>a</sup> *	Str.	35805	0 - 1070
2798 <sup>a</sup> *	M	35730	0 - 1145
2806 <sup>a</sup> *	Str.	35620	0 - 1255
2810 <sup>*</sup> <sub>Hg</sub>	Str.	35575	0 - 1300
2824	W	35405	
2842 *	V. Str.	35175	0 - 2 × 850
2849 *	Str.	35095	0 - 2 × 850 - 90
	D.		
2859 *	M	34970	0 - 1070 - 850
2873 *	Str., Sh.	34795	0 - 850 - 1255
2880 *	M, V.D.	34710	0 - 1300 - 850
2901 <sup>*</sup> <sub>Hg</sub>	—	34460	
2911 *	W	34340	0 - 3 × 850
2920 <sub>Ag</sub>	W	34235	0 - 3 × 850 - 90
2930 <sub>Hg</sub>	W	34115	0 - 1070 - 2 × 850
2944 *	W	33960	0 - 1255 - 2 × 850
2950 <sup>*</sup> <sub>Hg</sub>	W	33890	0 - 1300 - 2 × 850
2974 <sub>Hg</sub>	W	33615	
2992 <sub>Hg</sub>	W	33410	0 - 4 × 850??
3008 <sub>Hg</sub>	W	33230	0 - 1255 - 3 × 850?
3046 <sup>*</sup> <sub>Hg</sub>	—	32825	0 - 670 - 4 × 850
3104	—	32210	0 - 1255 - 4 × 850

Bands marked Hg are excited only by a mercury arc.

Bands marked Ag are excited only by a silver spark.

Bands without any mark are excited by both sources.

Bands marked \* are common to fluorescence and ozonizer emission.

Bands marked *a* are observed in ultra-violet absorption also.

The (0, 0) band is assumed to be at 36875 cm<sup>-1</sup> in the above analysis.

Str., strong; M, medium; D, diffuse; Sh., sharp; W, weak; V, very.

excitation proved to be of great advantage in establishing the genuineness of the bands. Bands masked by atomic lines in one case are revealed in another. Bands obtained in both could be undoubtedly attributed to the fluorescence spectrum. In table 1 the wave-length, wave number, etc., of the fluorescence bands of *p*-fluoro-toluene are given.

The fluorescence bands start from 2700 Å and extend to the long wavelength side up to 3100 Å. The region between 2703-2770 Å is very weak. The bands from 2775 Å onwards are comparatively of a high intensity. The weakness of the earlier part may probably be due to self-absorption. (There is an unavoidable gap of about 3 mm

between the illuminated part of the vapour and the observation windows.) The stronger bands from 2775 Å appear to have a doublet structure which is less easily evident at higher wavelength. The intensity falls off rapidly from 2875 Å onwards.

## EMISSION SPECTRUM

The ozonizer discharge ran with a faint greenish tinge. Exposures of 4 h on Baby Quartz and 8 h on Medium Quartz instruments were found to record good spectra. The bands occur in the region 2723 to 3132 Å almost coincident with the region of fluorescence.

TABLE 2.—*p*-FLUORO-TOLUENE; OZONIZER EMISSION

wave-lengths (Å)	intensity	wave-numbers (cm <sup>-1</sup> )	assignment
2723	W	36715	
2734 <sup>a</sup>	W, D	36570	0 — 305
2744 <sup>a</sup>	M, D	36440	0 — 435
2759 <sup>a</sup>	—	36230	0 — 645
2765 <sup>a</sup>	—	36155	
2776 <sup>a</sup> , *	V. Str.	36015	0 — 860
2778 <sup>a</sup>	V.W.	35990	0 — 860 — 25
2782 <sup>a</sup> , *	W, D	35940	0 — 860 — 75
2792 <sup>a</sup> , *	M	35800	0 — 435 — 645
			0 — 1075
2800 <sup>a</sup> , *	W	35705	0 — 1170
2806 <sup>a</sup> , *	Str.	35625	0 — 1250
2810 <sup>*</sup>	W	35575	0 — 1300
			0 — 435 — 860
2826	W, V.D	35370	0 — 645 — 860
2842 *	Str.	35175	0 — 2 × 860
2848 *	W	35105	0 — 2 × 860 — 75
2861 *	W	34940	0 — 1075 — 860
2874 *	Str.	34785	0 — 1250 — 860
2881 *	M	34700	0 — 1300 — 860
2892	V.W, D	34570	0 — 2 × 1170
			0 — 645 — 2 × 860
2906	—	34405	0 — 2 × 1250
2911 *	—	34345	0 — 3 × 860
2929	V.W, D	34125	0 — 1075 — 2 × 860
2945 *	M	33945	0 — 1250 — 2 × 860
2950 *	—	33885	0 — 1300 — 2 × 860
2965	—	33720	0 — 645 — 3 × 860
2983	V.W, V.D	33515	0 — 4 × 860
3018	—	33120	0 — 1250 — 3 × 860
3043 *	V.W, V.D	32860	0 — 645 — 4 × 860
3061	—	32655	0 — 5 × 860
3083	—	32430	
3098	—	32265	0 — 1250 — 4 × 860
3132	—	31920	

Bands marked *a* are observed in ultra-violet absorption.

Bands marked \* are common to fluorescence and ozonizer emission.

The (0, 0) band is assumed to be at 36875 cm<sup>-1</sup>.

The intense part of the spectrum starts from 2775 and extends up to 2980 Å. Later, the bands gradually fade off. Four groups of bands are comparatively sharp and distinct (at 2775 Å, 2806 Å etc.). Bands on the longer wavelength side are broad and diffuse. The group at 2775 Å has a triplet structure while the one at 2806 Å has a doublet structure and the pattern repeats itself. About 32 bands have been measured in the emission picture. Table 2 gives the wavelength, intensity and wavenumber data of the bands.

## ANALYSIS

**Fluorescence.**—The absorption spectra, as interpreted by Cave and Thompson suggest that the (0, 0) band is at 36876 cm<sup>-1</sup>. If we assume 36875 cm<sup>-1</sup> (value corrected

to the nearest  $5\text{ cm}^{-1}$ ) as the position of the (0, 0) band in fluorescence, there are two bands on the short wavelength side of this frequency. These may be due to some ( $v'$ ,  $v''$ ) transitions. The experimental fact that the same spectra are obtained both with and without filters suggests the possibility of some smaller wavelengths than the (0, 0) band contributing to the excitation of the fluorescence, thus involving a few upper state fundamentals.

The first strong band is at about  $850\text{ cm}^{-1}$  to the long wavelength side of this (0, 0) band. Treating it as due to a fundamental we could trace its overtones up to  $3 \times 850$  with reasonable certainty. These bands show doublet structure. The long wavelength component of these bands is shifted by about  $90\text{ cm}^{-1}$  from the main band. Similar bands (shift  $96\text{ cm}^{-1}$ ) were found in absorption as well.

We find two more fundamentals  $1255\text{ cm}^{-1}$  and  $1300\text{ cm}^{-1}$  occurring in the analysis. Both fundamentals occur in combination with  $850$  and its overtones. Four more fundamentals  $360\text{ cm}^{-1}$ ,  $670\text{ cm}^{-1}$ ,  $1070\text{ cm}^{-1}$  and  $1145\text{ cm}^{-1}$  were found necessary to explain the other bands. Of the 29 observed bands, 26 could be interpreted. The deviations from observed values in certain bands are probably inevitable in view of the diffuseness of the bands.

#### EMISSION

A similar analysis was carried out for the emission bands. In this case, all bands are to the long wavelength of the (0, 0) band  $36875\text{ cm}^{-1}$ . Here again the prominent fundamental is  $860\text{ cm}^{-1}$ . The bands in these groups have a triplet structure, the components being shifted by 25 and  $75\text{ cm}^{-1}$  from the main band. The other observed

TABLE 3.—FUNDAMENTALS IN *p*-FLUORO-TOLUENE

Raman with $\rho$ values	infra-red	fluorescence	emission	u.v. absorption		assignment
				lower state	upper state	
			305	217 311	185	
344 (0.75)		360		337		
455 (0.35)			435	453	398	$\alpha_1$ type
642 (0.73)		670	645	641	584	$\beta_1$ „
824 (0.08)				825		
843 (0.08)	842	850	860	844	794	$\alpha_1$ „
—	1046	1070	1075	—	1014	$\alpha_1$ „
1157 (0.38)	1151	1145	1170	1156	1194?	$\alpha_1$ „
1217 (0.07)	1235	1255	1250	1240	1229	$\alpha_1$ „
				(authors)		
1295 (0.47)	1292	1300	1300		1247	$\alpha_1$ „
				—	(authors)	

fundamentals are 305, 435, 645, 1075, 1170, 1250 and  $1300\text{ cm}^{-1}$ . The fundamentals from various sources are given in table 3. Cave and Thompson in their work on the absorption spectra gave a list of the fundamentals they identified in both the states. On a study of the absorption, fluorescence, emission and Raman spectra, the correlation given in table 3 appears to be possible.

The molecule *p*-fluoro-toluene approximates to the point group  $C_{2v}$ . The electronic transition giving rise to the near ultra-violet absorption, emission and fluorescence spectra is of an allowed type.

In the Raman spectrum a line  $843\text{ cm}^{-1}$  is a very strong line with a very low depolarization factor (0.08). This fundamental is definitely of a totally symmetric type. In the absorption spectrum a prominent fundamental in the ground state is  $844\text{ cm}^{-1}$ . In the upper state such an outstanding fundamental is  $794\text{ cm}^{-1}$  (Cave and Thompson<sup>1</sup>). Similar fundamentals in fluorescence and emission spectra are 850 and  $860\text{ cm}^{-1}$ . Thus we correlated all the above values as due to one mode of vibration. It may probably be a C—CH<sub>3</sub> stretching or a C—C ring vibration. The frequencies 1046 (infra-red), 1070 (fluorescence), 1075 (emission) and 1014 (absorption, upper state) may represent a totally symmetric ring vibration.

Fluoro-toluenes may be expected to have two fundamentals in the region  $1250$ – $1350\text{ cm}^{-1}$ , one due to C—F stretching, another due to CH<sub>3</sub> bending. While it has not been easy to determine which particular frequency may correspond to which particular

vibrational mode the very observation of two such fundamentals is a support for the views we expressed on the  $\text{CH}_3$  bending frequencies in our earlier work on substituted anisoles.<sup>9</sup> In the emission and fluorescence spectra we could definitely observe two fundamentals 1250 and 1300  $\text{cm}^{-1}$ , and 1255 and 1300  $\text{cm}^{-1}$  respectively in *p*-fluoro-toluene. These could be correlated with the two observed fundamentals in the upper state 1229  $\text{cm}^{-1}$  (observed by Cave and Thompson) and 1247  $\text{cm}^{-1}$  (added by the authors). For possible additional fundamentals suggested by the authors in the absorption spectrum (from Thompson's data) reference may be made to table 3. The correlation with the Raman line is doubtful on account of the low intensity of 1295  $\text{cm}^{-1}$ . The one given in the table 3 is only a possibility.

In fluorescence and emission we have another fundamental, 670 and 645  $\text{cm}^{-1}$ . In absorption, the value is 641  $\text{cm}^{-1}$  in the lower state and 584  $\text{cm}^{-1}$  in the upper state. The corresponding Raman line 642  $\text{cm}^{-1}$  is of medium intensity with a fairly high depolarization factor 0.7. These factors suggest that the fundamental might be the  $\beta_1$  component of the 606  $E_g^+$  vibration in benzene. The  $\alpha_1$  component might be represented by the set of values 455 (Raman), 435 (emission) 453 (lower state) and 398  $\text{cm}^{-1}$  (upper state).

In the emission spectrum a low fundamental 305  $\text{cm}^{-1}$  was also observed. This might correspond to either 217 or 311  $\text{cm}^{-1}$  observed in absorption, probably the latter. Their nature is not clear. A similar fundamental is 360  $\text{cm}^{-1}$  in fluorescence. The values in ultra-violet absorption (lower state) and Raman spectra are 337  $\text{cm}^{-1}$  and 344  $\text{cm}^{-1}$  ( $\rho = 0.7$ ) respectively. We find in the emission spectrum two satellites for the main bands separated by 25 and 75  $\text{cm}^{-1}$ . In the fluorescence we have a corresponding value of 90  $\text{cm}^{-1}$ . These might represent the  $\nu'\nu''$  transition of some low lying non-totally symmetric vibrations (as for the satellites following the (0, 0) band and the main bands in absorption).

#### *m*-FLUORO-TOLUENE

##### FLUORESCENCE SPECTRUM

The fluorescence bands were obtained by excitation with mercury arc radiation. Spectra were taken with and without filters. The difference was only in the time of exposures. Spectra were taken with slit widths of 40 and 100 microns. The bands are

TABLE 4.—*m*-FLUORO-TOLUENE FLUORESCENCE BANDS: EXCITATION BY MERCURY ARC

wave-lengths (Å)	intensity	wave-numbers ( $\text{cm}^{-1}$ )	assignment
2663 <sup>a</sup>	W, D	37540	$\left\{ \begin{array}{l} 0 + 90 \\ 0 + 694 - 585 \end{array} \right.$
2684 <sup>a</sup>	—	37250	0 — 200
2694	W, D	37105	
2704	W	36975	0 — 585 + 90
2712	D	36865	0 — 585
2717	Str. V.D.	36790	0 — 750 + 90
2724 <sup>a</sup> , *	V. Str. Sh.	36700	0 — 750
2731*	Str. D	36605	0 — 750 — 90
2740*	W. V.D.	36485	
2747 <sup>a</sup> , *	Str.	36395	0 — 1055
2759	D	36230	0 — 1220
2767*	Str. D	36125	0 — 1325
2774	Str. D	36035	0 — 1325 — 90
2784	D	35915	0 — 2 × 750
2797	W, D	35745	
2808*	D	35595	0 — 750 — 1055
2827*	D	35370	0 — 750 — 1325
2844*	V.D	35150	0 — 3 × 750
2863	—	34915	
2886*	V.W, V.D	34635	0 — 2 × 750 — 1325
2908*	—	34385	0 — 4 × 750

Bands marked <sup>a</sup> are occurring in absorption also.

Bands marked \* are common to fluorescence and ozonizer emission.

The (0, 0) band is assumed to be at 37450  $\text{cm}^{-1}$ .

comparatively more diffuse than those of *p*-fluoro-toluene. About 21 bands could be measured. The strong region is between 2700 Å to 2840 Å consisting of 4 or 5 fairly strong groups of bands. The most intense band appears to be at 2767 Å. The fine slit pictures show a doublet structure for some of the bands. The weak region between 2663 Å and 2700 Å may possibly be the result of self-absorption. In table 4 wavelength, intensity, wavenumber and assignment are given.

#### EMISSION SPECTRUM

About 4 h and 8 to 10 h exposures were found necessary on the Small Quartz and Medium Quartz respectively to record good emission spectra. The greenish colour of the discharge is much fainter than that of *p*-fluoro-toluene. The bands extend from 2670 Å to 2951 Å.

TABLE 5.—*m*-FLUORO-TOLUENE; OZONIZER EMISSION

wave-lengths (Å)	intensity	wave-numbers (cm <sup>-1</sup> )	assignment
2670	weak band	37450	0, 0
2717*	W, D	36795	0 - 655
2725a, *	Str.	36690	0 - 760
2727	Str.	36665	0 - 760 - 25
2732*	M. D	36585	0 - 760 - 90
2740*	W, D	36490	0 - 760 - 2 × 90?
2745*	Str.	36415	0 - 1035
2748a, *	Str.	36385	0 - 1035 - 30
2752	W, D	36330	0 - 1035 - 90
2765*	Str.	36155	0 - 1295
2772	W	36070	{ 0 - 1295 - 90 0 - 1380
2781	Str.	35955	0 - 2 × 760
2786	W	35880	0 - 2 × 760 - 90
2803	Str. D	35660	0 - 760 - 1035
2808*	Str. D	35605	0 - 760 - 1035 - 90
2822	Str. V.D	35430	0 - 1295 - 760
2826*	M. D	35375	{ 0 - 1295 - 760 - 90 0 - 2 × 1035
2839	—	35215	
2845*	Str.	35140	{ 0 - 3 × 760 0 - 1295 - 1035
2851	D, V.W	35060	0 - 3 × 760 - 90
2860	W, V.D	34960	0 - 2 × 760 - 1035
2867	M	34865	0 - 2 × 760 - 1035 - 90
2882*	D	34685	0 - 2 × 760 - 1295
2899	—	34480	
2907*	—	34390	{ 0 - 4 × 760 0 - 1295 - 1035 - 760
2926	—	34170	{ 0 - 2 × 1035 - 1295 0 - 760 - 2 × 1295
2951	—	33880	0 - 2 × 760 - 2 × 1035

Bands marked *a* are occurring in absorption also.

Bands marked \* are common to fluorescence and ozonizer emission.

About 27 bands are observed. The earlier part of the spectrum has a doublet structure. The maximum intensity is in the region 2727 Å to 2900 Å. The first band at 37450 cm<sup>-1</sup> is about 19 cm<sup>-1</sup> to the violet of one of the three (0, 0) bands in absorption (37398, 37418 and 37431 cm<sup>-1</sup>) suggested by Cave and Thompson. Table 5 gives all the observed data on these bands.

#### ANALYSIS

*Emission.*—Assuming the position of the (0, 0) band to be at 37450 cm<sup>-1</sup> the first prominent band shifted by 760 cm<sup>-1</sup> may be taken as a fundamental in the ground state. Four overtones of this could be observed. Most of these have satellites shifted by

90  $\text{cm}^{-1}$  to the long wavelength side of the main bands. Other fundamentals are 1035 and 1295  $\text{cm}^{-1}$ . We find these fundamentals occurring in combination with the fundamental 760  $\text{cm}^{-1}$ . Another possible fundamental is probably 655  $\text{cm}^{-1}$  represented by a weak band. Its justification is only on comparison with *p*-fluoro-toluene where such a fundamental occurs. On the above lines, interpretation could be found for all the observed bands except two extremely doubtful bands.

#### FLUORESCENCE

In fluorescence, we have one band shifted by 90  $\text{cm}^{-1}$  to the violet of the (0, 0) band (cf. *p*-fluoro-toluene). The first prominent fundamental is 750  $\text{cm}^{-1}$  observed up to  $4 \times 750$ . The strongest band, however, is at 1325  $\text{cm}^{-1}$  which may also be treated as a fundamental. (It is, incidentally, equal to  $2 \times 660 \text{ cm}^{-1}$ .) Combinations of these fundamentals with 750 also are observed. Two prominent fundamentals are 585 and 660  $\text{cm}^{-1}$ . The various fundamentals from the various sources are tabulated in table 6.

TABLE 6.—FUNDAMENTALS IN *m*-FLUORO-TOLUENE

Raman	infra-red	fluorescence	emission	absorption		assignment
				lower state	upper state	
243		200?		184		} $\alpha_1$ type
527	532	585		253		
	685	660	655	520		
728	730	750	760	726	684	
1003	1004	1055	1035	1003	965	
1254	1255	1220	1295		1261	
1379	1376	1325	1380		1346	
					(authors)	

The molecule *m*-fluoro-toluene belongs to the point group  $C_s$ . The electronic transitions giving rise to the near ultra-violet absorption, fluorescence and emission spectra are of an allowed type. On a study of Raman, fluorescence, absorption and emission spectra the correlation given in table 6 appears to be plausible.

The most prominent fundamental in the fluorescence spectrum appears to be 750  $\text{cm}^{-1}$  which could be traced up to 3 overtones. (760 emission, 728 Raman, 730 infra-red, 726 and 684 u.-v. absorption.) Cave and Thompson point out the prominence of this upper state frequency (684). From the nature of the bands, this set of frequencies corresponds to the 843 (Raman), 842 (infra-red), 850 (fluorescence), 860 (emission), 844 (lower state) and 794 (upper state) in *p*-fluoro-toluene. The vibrational mode giving rise to these bands is most probably the same in the case of the two isomers. A C—CH<sub>3</sub> stretching mode or a C—C stretching vibration in the phenyl radical has been suggested as a possibility for this fundamental.

The next prominent fundamental is 1035  $\text{cm}^{-1}$  in emission and 1055  $\text{cm}^{-1}$  in fluorescence. The corresponding values of this frequency in Raman and infra-red are possibly 1003 and 1004  $\text{cm}^{-1}$  respectively. In the upper state the corresponding 965 fundamental is observed by Cave and Thompson to be the most outstanding fundamental in the whole spectrum. These fundamentals may be due to a C—C vibration in the phenyl radical.

The C—F stretching and CH<sub>3</sub> bending frequencies expected in the region 1250-1350  $\text{cm}^{-1}$  are again observed both in fluorescence and emission. In fluorescence the frequency 1325  $\text{cm}^{-1}$  is strong and conspicuous while the frequency 1220 is very weak and diffuse. Correspondingly, in the ozonizer emission, we have a frequency 1295 which is strong. It is possible that this might correspond to 1325 in fluorescence. However, it may also be taken as corresponding to 1220  $\text{cm}^{-1}$  in fluorescence in spite of the large deviation, in which case the weak band 1385 in emission may also be treated as a fundamental corresponding to 1325 in fluorescence. This kind of uncertainty of correlation is unavoidable from the nature of the bands. The Raman lines 1254 and 1379  $\text{cm}^{-1}$  justify the correlation chosen in table 6. In the upper state a fundamental 1346 could be taken from Thompson's data. A justification for this is that it interprets in accordance with the pattern some unexplained bands in absorption. It is again not easy to say which of the two in particular corresponds to C—F stretching or CH<sub>3</sub> bending. Assuming the correlation as given in table 6 we find a reversal of intensities between the two fundamentals.



However, the large intensity of  $1325\text{ cm}^{-1}$  in fluorescence may partly be due to the fact that  $1325$  is approximately equal to  $2 \times 660\text{ cm}^{-1}$  which is another fundamental.

In fluorescence and emission we have two frequencies  $660$  and  $655\text{ cm}^{-1}$ . In infra-red the corresponding value is  $685\text{ cm}^{-1}$ . The bands might represent one of the  $\alpha_1$  components of the  $E_g^+$  vibration in benzene. These bands and the other band in fluorescence  $585\text{ cm}^{-1}$  are very weak. In absorption we have a lower state frequency  $520\text{ cm}^{-1}$  corresponding to this  $585\text{ cm}^{-1}$  in fluorescence,  $527$  in Raman and  $532$  in infra-red.

#### *o*-FLUORO-TOLUENE

##### FLUORESCENCE SPECTRUM

The fluorescence spectrum of *o*-fluoro-toluene was investigated under similar conditions, using a mercury arc as the exciting radiation with and without filters. No discrete bands were obtained. A continuous patch in the region  $2700\text{--}3100\text{ \AA}$  was recorded, with an intensity maximum lying in the region  $2850\text{ \AA}$ .

The fluorescence spectrum of *o*-fluoro-toluene starts from about  $36690\text{ cm}^{-1}$  while the emission spectrum starts from  $37560\text{ cm}^{-1}$ . The difference between these two is about  $870\text{ cm}^{-1}$ . In fact the starting point of the fluorescence spectrum is very near the fundamental  $900\text{ cm}^{-1}$  in the emission spectrum. A possible conclusion from this is that the weak fluorescence in the intermediary region is self absorbed.

##### EMISSION

The ozonizer emission picture was also taken. Faint traces of bands could be observed in the region  $2660\text{ \AA}$  to  $2835\text{ \AA}$ , with a gradual fading towards longer wavelengths. About seven bands could be measured. The accuracy obtained is very low. Table 7 gives the wavelength, wavenumber data of these bands. The band at  $37560\text{ cm}^{-1}$  is possibly the (0, 0) band. This is about  $26\text{ cm}^{-1}$  to the long wavelength side of the probable (0, 0) band in absorption as suggested by Cave and Thompson.

TABLE 7.—*o*-FLUORO-TOLUENE; OZONIZER EMISSION

wave-lengths ( $\text{\AA}$ )	intensity	wave-numbers ( $\text{cm}^{-1}$ )	assignment
2661.7	—	37560	(0, 0) band
2689.2	—	37175	0 — 385
2727.0	Str.	36660	0 — 900
2744.7	W	36425	0 — 1135
2759.2	Str.	36230	0 — 1330
2778.2	W, V.D	35985	0 — 385 — 1135
2834.7	W. D	35265	0 — $2 \times 1135$

Among the seven observed emission bands, four fundamentals  $385$ ,  $900$ ,  $1135$  and  $1330\text{ cm}^{-1}$  could be assumed. Two other bands could be interpreted as combinations and overtones of these fundamentals, within the limits of accuracy possible.

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<sup>3</sup> Paulsen, *Monatsh.*, 1939, **72**, 244.

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