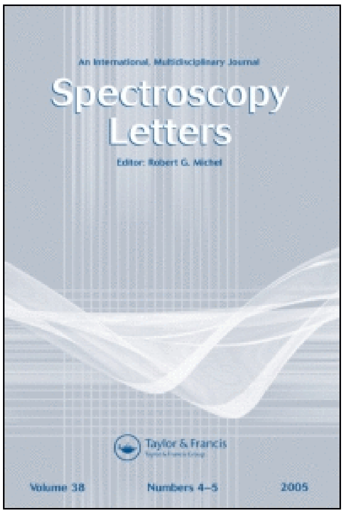

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VIBRATIONAL ANALYSIS OF THE 2665 A^{o} SYSTEM OF TOLUENE α-d_3

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Abstract

The vibrational analysis of the near ultraviolet spectrum of toluene α-d_3 molecule has been done. The (0,0) band has been assigned at 37515 cm^{-1} (2664.8 A). The observed bands have been interpreted in terms of the ground state fundamental frequencies 201, 305, 402, 500, 624, 759 & 1005 cm^{-1} and excited state frequencies 298, 316, 430, 528, 733, 930, 970

& 1130 cm^{-1}. The fundamentals determined from the infra red, Raman and electronic spectra of toluene and toluene α-d_3 molecules are correlated. The toluene and toluene α-d_3 molecules are assigned to C_{2v} point group in the ground electronic state. A non-planar geometrical configuration in the excited electronic state has been suggested to explain the intensity of some of the upper state fundamentals of low magnitude. An isotopic shift of 40 cm^{-1} has been found for the (0,0) band of toluene α-d_3 with respect to the normal toluene molecule.

INTRODUCTION

The electronic band system which appears in the wavelength region 2600–3000 A^{o} in benzene derivatives corresponds to the symmetry forbidden transition A_{1g}-B_{2u} of benzene. The role of a substituent group, which replaces one of the six hydrogen atoms of benzene, is to alter its high symmetry and hence to allow the transition. The intensity and shift in the spectra of a benzene derivative is interpreted in terms of inductive and mesomeric effects. In the derivatives exerting weak inductive and mesomeric effects, like -CH_3 group, the electronic spectra are expected to have more correspondence with the benzene molecule. Therefore, toluene molecule should exhibit the peculiarities of an allowed transition while still retaining some features of the forbidden 2600 A^{o} transition of benzene, which makes the vibrational assignment of electronic spectrum of toluene molecule quite interesting. The near ultraviolet spectra of toluene molecule was studied by Guisberg et al(3) while infrared spectrum of toluene and toluene α-d_3 by Wilmshurst and Bernstein(7). Tripathi et al(4,5) studied near ultraviolet spectra of a few derivatives of toluene. Lau and Snyder(1) have correlated Raman and infra red frequencies of toluene, toluene -d_8 and toluene α-d_3 molecules. The electronic spectra of only a few deuterated benzenes are reported, in literature. The present paper considers in detail the vibrational analysis of the electronic absorption spectrum of toluene α-d_3 molecule. The spectrum of this molecule is expected to show a close resemblance with that of normal toluene. The replacement of hydrogen atom by deuterium affects some of the fundamentals in the ground and excited electronic states. This helps in identifying the fundamentals sensitive to substitution (x-sensitive). The (0,0) band may also show a shift with respect to the parent molecule due to change in the difference of zero point energies in the two electronic states. We have determined several ground and excited state fundamental vibrational frequencies and their corresponding vibrational modes have been assigned taking help of the infra red and Raman spectra(1,2,3,6). Some of the fundamentals in the excited state have been chosen just to explain the difference frequencies and the symmetry of the toluene and toluene α-d_3 molecules in the upper electronic state is discussed in the light of the appreciable intensity of the bands involving these fundamentals.

<u>Experimental Procedure</u>:- A sample of toluene α-d_3 compound of high purity was procured from M/S Merck Sharp & Dohme, Canada and was used as such. The spectrum was photographed on Hilger medium quartz spectrograph using absorption path of 50 cm^{-1} long tube, at room temperature. The exposure time was varied from 20 minutes to one hour. The hydrogen lamps was used as a source of continuous energy and an iron arc for the recording the standard spectrum of iron to compare the spectrum of toluene α-d_3. Only a fraction of a drop of the compound, when inserted in the absorption column, results into sufficient quantity of vapours to cause the absorption of important bands. The weaker bands have been developed by increasing the amount of compound in the absorption column.

The band positions of the molecule corrected to the vacuum, their intensities and vibrational assignments are given in Table 1. In Table 2, the fundamental frequencies of toluene α-d_3 are compared with the frequencies reported in Raman and infra red spectra. These are also compared with the values for toluene and toluene α-d_1, molecules. The accuracy of our observations is ± 3 cm^{-1} for sharp bands and ± 5 cm^{-1} for diffused and weak bands. The purity of the toluene α-d_3 sample has been confirmed by non appearance of even the strongest bands of toluene in the spectrum of toluene α-d_3.

Results & Discussion:-

As pointed out in introduction the $-CH_3$ and $-CD_3$ substituent groups have a small perturbation effect on the orbitals of phenyl ring electrons. Therefore, the spectrum of toluene is expected to retain certain features of benzene spectrum as well as other features arising from the reduction of symmetry from D_{6h} to lower symmetry type. The (0,0) band is expected to appear with appreciable intensity. Sponer(3) has assigned a symmetry C_s and Ginsberg et al(3) C_{2v} to explain the electronic spectrum of toluene. Pitzer and Scott(3) considered symmetry C_{2v} to explain Raman spectrum of toluene and Lau and Snyder(1) in the analysis of Raman and infra red spectra of toluene, toluene α-d_3 and toluene $-d_8$. Our attempt is to verify these points from the vibrational analysis of toluene α-d_3 proposed here. If we assign C_{2v} point group to toluene α-d_3 molecule, the A_{1g} - B_{2u} transition of benzene will appear as A_1-B_2, the electronic moment lying in the plane of molecule and perpendicular to the $C-CD_3$ axis. The vibrations of symmetry type a_1, b_2 and a_2 are allowed to appear as 0-1 and 1-0 transitions. However only those vibrations which induce the electric moment in the direction of X- axis will be strong and as such the transitions accompanying the vibrations of symmetry type a_1 should have appreciable intensity while those accompanying b_2 and a_2 type of vibrations should be weaker. Since some features of C_6H_6 are expected to remain in the spectrum of toluene α-d_3,

Table 1

The assignment of observed frequencies of toluene α-d_3

Band position	Difference from (0,0)	Intensity		Assignment
		(i)	(ii)	
36129	-1386	vvw		0-1386
36302	-1213	*		0-1005-201, 0-1213
36382	-1133	*		0-1005-115
36425	-1090	*		0-1005-74
36510	-1005	w		0-1005
36548	- 964	vw		0-759-201
36590	- 925	*		0-624-305
36624	- 891	*		0-759-137
36682	- 833	*		0-759-74
36700	- 815	*		0-759-54
36723	- 792	w		0-759-36
36756	- 759	m		0-759
36783	- 732	vw		0-624-105
36793	- 722	w		0-624-93
36837	- 678	w		0-624-54
36852	- 663	vvw		0-624-36
36870	- 645	*		0-624-24
36891	- 624	m		0-624
36907	- 608	w		0-500-105
36926	- 589	m		0-500-93
36949	- 566	vvw		0-500-74
36964	- 551	w		0-500-54
36980	- 535	vvw		0-500-36
36996	- 519	*		0-500-22

Contd../-

37015	- 500	m		0-500
37061	- 454	vvw		0-402-54
37082	- 433	vw		0-402-36
37113	- 402	w		0-402, 0-2x201
37127	- 388	vvw		0-201-179
37142	- 373	vw		0-305-74
37164	- 351	m		0-305-54
37195	- 320	vw		0-201-115
37210	- 305	m		0-305, 0-201-105
37220	- 295	vvw		0-201-93
37241	- 274	s		0-201-74
37259	- 256	w		0-201-54
37279	- 236	vvw		0-2x115, or 0-201-36
37299	- 216	vw		0-2x105, 0-4x54
37314	- 201	vvw		0-201
37336	- 179	s	m	0-500+316, 0-179
37366	- 149		vvw	0-2x74
37378	- 137		w	0-448+316, 0-137
37400	- 115		vw	0-74-54
37410	- 105		w	0-402+298, 0-2x54
37422	- 93		vw	0-624+528, 0-93
37441	- 74		w	0-500+430, 0-74
37461	- 54		m	0-201+144, 0-54
37479	- 36		w	0-1005+970, 0-36
37491	- 24		vvw	0-759+733, 0-24
37515	---		vvs	(0,0) band
37550	35		vvw	0+144-105, 0+35
37569	54		*	0+144-93, 0+54

Contd../-

Table One (cont.)

37595	80	vw	0+144-74, 0+80
37624	109	m	0-144-36, 0-109
37659	144	m	0+147
37672	157	*	0+298-2x74
37688	173	w	0+144+35
37701	186	vvw	0+298-115
37732	217	w	0+298-74
37752	237	vw	0+298-54
37780	265	*	0+298-36
37796	281	vvw	0+316-36
37813	298	s	0+298, 0+2x147
37831	316	w	0+316
37849	334	vvw	0+430-93
37869	354	vvw	0+430-74
37886	371	vw	0+430-54
37903	388	m	0+430-36
37950	435	*	0+430
37967	452	w	0+528-74
37985	470	s	0+528-54
37999	484	w	0+528-36
38018	503	vvw	0+528-24
38043	528	vs	0+528
38064	549	w	0+733-179
38090	575	m	0+733-149, 0+430+144
38119	604	*	0+733-137
38135	620	*	0+733-115, 0+298+316
38149	634	vw	0+733-93, 0+2x316
38165	650	vvw	0+733-74

38191	676	w	0+733-54, 0+528+144
38218	703	vw	0+733-24
38248	733	m	0+733
38280	765	*	0+733+35
38315	800	vvw	0+930-137
38358	843	vw	0+733+109, 0+316+528
38398	883	w	0+930-54
38425	910	vvw	0+930-22
38445	930	m	0+930
38472	957	w	0+430+528
38480	970	s	0+930+35
38510	995	m	0+1130-137
38544	1029	vvw	0+1130-105
38560	1045	vw	0+1130-93
38578	1063	w	0+1130-74
38621	1106	w	0+1130-24
38645	1130	m	0+1130
38671	1156	w	0+528+733-105
38694	1179	*	0+528+733-93
38712	1197	*	0+733+528-74
38740	1225	m	0+733+528-36
38764	1249	vw	0+733+528-22
38783	1268	*	0+733+528
38809	1294	vvw	0+733+528+35
38832	1317	w	0+733+528+54
38863	1348	vvw	0+1130+298-74
38887	1372	w	0+1130+298-54
38920	1405	m	0+1130+298-22

Contd../-

Table One (cont.)

38944	1429	w	0+1130+298
38972	1457	m	0+2x733, 0+930+528
38997	1482	vvw	0+733+930-179
39013	1498	s	0+733+930-149
39034	1519	m	0+733+930-137
39056	1541	vw	0+733+930-115
39073	1558	m	0+733+930-105
39087	1572	*	0+733+930-93
39104	1589	vw	0+733+930-74
39118	1603	*	0+733+930-54
39136	1621	w	0+733+930-36
39152	1637	*	0+733+930-24
39173	1658	vw	0+733+930
39187	1672	w	0+733+970-36
39206	1691	*	0+733+970-24
39220	1705	m	0+733+970
39236	1721	w	0+930+970-179
39261	1746	m	0+930+970-149
39276	1761	vw	0+930+970-137
39299	1784	vw	0+930+970-115
39337	1822	w	0+930+970-74
39356	1841	vw	0+930+970-54
39390	1875	vvw	0+930+970-24
39421	1906	m	0+930+970
39445	1930	vw	0+930+970+35
39461	1946	w	0+2x970
39481	1966	*	0+970+2x528-54
39508	1993	vvw	0+970+2x528-24
39537	2022	*	0+970+2x528

39566	2051	vw	0+2x1130-201
39603	2088	*	0+2x1130-179
39628	2113	m	0+2x1130-137
39655	2140	*	0+2x1130-115
39676	2161	vvw	0+2x1130-105
39694	2179	*	0+2x1130-93
39709	2194	m	0+2x1130-74, 0+733+930+528
39725	2210	*	0+2x1130-54
39747	2232	vw	0+2x1130-22, 0+733+970+528
39772	2257	*	0+2x1130
39793	2278	vvw	0+930+2x733-115
39820	2305	w	0+930+2x733-94
39844	2329	vvw	0+930+970+430
39858	2343	w	0+2x733+930-54
39880	2365	vvw	0+2x733+930-36
39906	2391	m	0+2x733-930
39924	2409	vvw	0+930+970+528-24
39942	2427	m	0+930+970+528
39960	2445	vw	0+2x930+733-149
39972	2457	vvw	0+2x930+733-137
39989	2474	*	0+2x930+733-115
40012	2497	w	0+930x2+733-94
40034	2519	vvw	0+733+2x930-74
40053	2538	w	0+733+2x930-54
40066	2551	vw	0+733+2x930-36
40111	2596	vvw	0+733+2x930
40146	2631	w	0+930+970+733
40159	2644	vvw	0+3x930-149
40178	2663	*	0+3x930-137

Contd.../-

Table One (cont.)

40195	2680	m	0+3x930-115
40219	2704	vvw	0+3x930-74
40247	2732	w	0+3x930-54
40264	2749	vvw	0+3x930-36
40278	2763	*	0+3x930-24
40306	2791	m	0+3x930
40337	2822	vvw	0+3x930+35
40356	2841	w	0+3x930+54
40383	2868	vvw	0+3x930+80
40409	2894	w	0+3x930+109
40429	2914	*	0+2x733+930+528, 0+3x970
40461	2946	vvw	0+3x970+35
40491	2976	w	0+3x970+54
40507	2992	vvw	0+970x3+80
40531	3016	*	0+970x3+109
40541	3026	w	0+930+3x733-105
40561	3046	*	0+3x970+144
40586	3071	■	0+930+3x733-54
40602	3087	vw)	0+930+3x733-36
40613	3098	vvw)	
40648	3133	m	0+930+3x733
40672	3157	w	0+930+3x733+35
40698	3183	w	0+930+3x733+54
40714	3199	vvw	0+3x1130-201
40733	3218	vw	0+3x1130-179
40764	3249	vvw	0+733+930+3x528
40786	3271	w	0+3x1130-115
40819	3304	vvw	0+3x1130-74

40839	3324	vw	0+2x(733+930)
40869	3354	*	0+3x1130-36
40909	3394	*	0+3x1130
40942	3427	*	0+3x1130+35
40976	3461	*	0+3x1130+80
41037	3522	vvw	0+733+3x930
41060	3545	*	0+3x1130+157
41102	3587	*	0+3x1130+186
41127	3612	*	0+2x733+2x930+298
41171	3656	*	0+733x3+930+528
41206	3691	*	0+930+4x733-179
41231	3716	*	0+930+4x733-149
41288	3773	*	0+733+930+4x528
41301	3786	vw	0+930+4x733-74
41343	3828	vvw	0+930+4x733-36
41386	3871	*	0+930+4x733
41408	3893	*	0+733+528+3x930-149
41434	3919	*	0+733+528+3x930-137
41450	3935	*	0+733+528+3x930-115
41474	3959	vw	0+733+528+3x930-93
41497	3982	vvw	0+733+528+3x930-74
41523	4008	*	0+733+528+3x930-36
41551	4036	*	0+733+528+3x930-22
41569	4054	*	0+733+528+3x930
41584	4069	*	0+3x733+2x930
41614	4099	*	0+2x733+3x930-149

Contd../-

41644	4129	vvw	0+3x1130+733
41662	1457	*	0+2x733+3x930-93
41692	4177	*	0+2x733+3x930-74
41723	4208	*	0+3x930+2x733-54
41752	4237	*	0+2x733+3x930-24
41781	4266	*	0+2x733+3x930

v = very, s = strong, m = medium, w = weak.

Intensity (i) = at high vapour pressure, (ii) at low vapour pressure.

the components of 608 (e_{2g}) vibration of benzene should play a significant role towards the intensity of the spectrum and therefore, should appear strongly even if one of them belong to symmetry type b_2. The b_1 symmetry type which is not expected to appear as 0-1 or 1-0 transitions, may give rise to prominent bands in 1-1 transitions. If the tolueneα-d_3 molecule is classified to belong to C_s point group, all the vibrations of benzene are contained only in two symmetry classes i.e. a' & a'' and both of these are allowed, of course, a'' being much weaker than a' vibrations.

The entire band system of tolueneα-d_3 molecule covers the region 2767-2430 A°. Nearly 225 bands have been measured and analysed. The bands are sharp in general and degraded towards red. At the lower vapour pressure of the tolueneα-d_3

Table 2

Correlation of fundamentals of toluene α-d_3

Ground state fundamentals						Excited state fundamentals		
Toluene		Toluene α-d_3				Toluene	Toluene α-d_1	Toluene α-d_3 (present study)
I.R.	Raman	u.v.	I.R.	Raman	uv (present study)			
220	220	-	203	204	201	-	-	144 ?
-	313	-	308	308	305	-	-	298
407	-	-	406	405	402	-	-	316
522	523	514	499	499	500	456	454	430
622	624	620	622	622	624	528	526	528
788	788	785	760	758	759	751	743	733
1005	1005	1003	1003	1003	1005	932	935	930
						964	963	970
						1189	1180	1130

? = doubtful.

molecule, the strongest band appears at 37515 cm^{-1} (2664.8 A) on the higher wavelength side of the absorption spectrum. This band has been assigned as the (0,0) band. The position of (0,0) band of toluene has been reported at 37473 cm^{-1} by Sponer and 37478 cm^{-1} by Ginsberg et al.(3) Taking mean of the two values, ie , 37475 cm^{-1} as the position of (0,0) band for toluene molecule, a violet shift of 40 cm^{-1} is observed for toluene α-d_3 molecule, with respect to the normal toluene. Dwivedi et al(8) have reported (0,0) band position for toluene-α-d_1 at 37494 cm^{-1}, ie, a shift of 19 cm^{-1} towards violet end. Thus isotopic shift for toluene-α-d_3 is more than two times as compared to the toluene-α-d_1 molecule, which is as expected. The isotopic shift is obviously due to the change in the zero point energy of the ground and excited electronic states of the molecule.

An intense band appears at 37461 cm^{-1} at a separation of 54 cm^{-1} on the longer wavelength side of (0,0) band. This is a difference frequency, as none of the vibrations of benzene is expected to have this magnitude. The high intensity of this band indicates that this difference frequency should be explained as 1-1 transition of the vibrations of low magnitude. The lowest fundamental in the infra red and Raman spectra has been reported at 203 and 204 cm^{-1} respectively by Lau & Snyder(1). This frequency is depolarised and has been assigned to class b_1 by them. As discussed earlier, the vibrations of this class are not expected to participate in 0-1 and 1-0 transitions, and therefore, a band of appreciable intensity, at a separation of 203 cm^{-1} on higher wavelength side of the (0,0) band is not expected to appear. We have observed a very very weak band at a separation of 201 cm^{-1} on the higher wavelength side of the (0,0) band. The extremely weak intensity of a fundamental frequency of class b_1 justifies the classification of tolueneα-d_3 molecule to belong to C_{2v} point group in the ground state.

The next ground state fundamental in the ascending order of magnitude is reported at 308 cm^{-1} in infra red and Raman spectra. This frequency belongs to class b_2 as assigned by Lau & Snyder(1) and may appear as 0-1 or 1-0 transition in the near ultraviolet spectrum with weak intensity. We have obtained a medium intense band at frequency difference 305 cm^{-1} on the lower frequency side of the spectrum. This vibration belongs to $\overset{\frown}{\underset{\smile}{16}}$b vibration of benzene molecule. The difference frequency 54 cm^{-1} should find explanation in terms of any one of these two ground state fundamentals, i.e. 201 or 305 cm^{-1}, preferencially the lower one. If 1-1 transition of fundamental 201 cm^{-1} explains the difference frequency 54 cm^{-1}, its excited state counterpart should have a frequency 147 cm^{-1} with an extremely weak intensity, although its double miltiple may have appreciable intensity. In vibrational analysis, we find a band of medium intensity at a separation of 144 cm^{-1} on the shorter wavelength side of the (0,0) band. As there is no alternative explanation for the frequency

144 cm^{-1}, it can be assigned as an excited state fundamental. The occurance of a fundamental of b_1 class with medium intensity in the excited state indicates a possible departure of the molecules from C_{2v} symmetry in the excited state. This can happen due to nonplanarity of the geometrical configuration of the molecule in the excited state. No observed excited state frequency can be correlated with the ground state fundamental 305 cm^{-1} to explain 54 cm^{-1}. Moreover a transition starting from a vibrational level of frequency 201 cm^{-1} will be stronger than a transition starting from a vibration frequency 305 cm^{-1} due to Boltzmann factor.

The first prominent band on the shorter wavelength side of the (0,0) band has been measured at 37813 cm^{-1} and involves an excited state frequency 298 cm^{-1}. This can be explained as 2x147=294. However, an alternative assignment as an excited state fundamental has been prefered for this frequency. It can be correlated with one of the ground state fundamentals 305 or 402 cm^{-1}. The later fundamental has been measured at 406 cm^{-1} in infrared and at 405 cm^{-1} in Raman spectra(1) and is depolarised. It belongs to symmetry class a_2 and is related to the 16a vibration of Benzene. If one correlates the ground state fundamental 402 cm^{-1} with the excited state fundamental 298 cm^{-1}, a difference frequency 104 cm^{-1} is expected as a result of their 1-1 transition, which has been actually observed. If the frequency 298 cm^{-1} is not taken as fundamental, the ground state frequency 402 cm^{-1}

can also be explained as 2x201. Lau & Snyder(1) have justitied the fundamental nature of 402 cm^{-1} by theoritical calculations, and the same justification holds good in taking the frequency 298 cm^{-1} as a fundamental.

The next ground state frequency has been reported at 447 cm^{-1} in Raman spectrum which is polarised and belongs to symmetry class b_1. This frequency appears at 448 cm^{-1} in ~~in~~ infra-red spectrum as reported by Lau & Snyder(1). Its appearance as 0-1 transition in the electronic spectrum is not expected, but as pointed out ealier, its 1-1 transition may appear. We, therefore, correlate the frequency 316 cm^{-1} of excited state with this (448 cm^{-1}) frequency of ground state, and get an explanation for a medium intense band at 138 cm^{-1} (0-448+316=132) on the red side of the (0,0) band. The absence of a ground state frequency of 448 cm^{-1} (class b_1) in near ultraviolet is in the confirmity with C_{2v} symmetry of the molecule. However, if the excited state frequency 316 cm^{-1} represents a vibration of the same symmetry in the upper electronic state ~~state~~, its appearance with appreciable intensity in the electronic spectrum can only be explained on the basis of nonplanar geometrical configuration of the excited molecule.

In the electronic spectrum of benzene derivatives the components of the 608 (e_{2g}) vibrations of benzene are quite important. Ginsberg et al(3) have reported the frequency 514 (w) and 620 (w) as the ground state fundamentals 6a and 6b respectively in the normal toluene molecule. Dwivedi et al(8) have reported two ground state fundamentals at 519 and 632 cm^{-1} in tolueneα-d_1 molecule. Lau and Snyder(1) have assigned 6a vibration to a frequency 499 cm^{-1} observed in Raman as well as infra red spectra while 6b to a frequency 622 cm^{-1}. The former frequency is polarised and belongs to class a_1 while later is depolarised and related to b_2 symmetry class. Therefore, their appearance in the electronic spectrum of tolueneα-d_3 molecule is expected with appreciable intensity. We observe a medium intense band at 37015 cm^{-1}, ie, at a separation of 500 cm^{-1} from (0,0) band on the lower frequency side, and another an intense band at 36891 cm^{-1}, ie, a frequency separation 624 cm^{-1} on the same side. We can assign them as the ground state fundamentals 6a and 6b respectively. The 6a vibration has been assigned a value 456 cm^{-1} and 6b to 528 cm^{-1} in toluene in the B_2 state. An intense band at a frequency separation of 528 cm^{-1} on the higher frequency side of the (0,0) band has been obtained in the spectrum of tolueneα-d_3 and can be very safely considered as the 6b vibration in the B_2 electronic state. Its 1-1 transition appears at 97 cm^{-1} confirming the correlation. Hence we note that the 6b vibration has almost the same megnitude in toluene, tolueneα-d_1 and toluene α-d_3 molecules. It is not against expectations, since this (6b) vibration is independent of the substituent groups in monoderivatives of benzene. The 6a component in the excited state has been reported at 454 and 456 cm^{-1} for toluene(3) and toluene α-d_1 molecules(8) respectively. A medium intense band appears at a frequency difference 430 cm^{-1} and has been assigned as a fundamental, representing 6a mode in the upper electronic state. The 1-1 transition appears at 74 cm^{-1}. It is noted that 6a vibration has lower frequency in toluene α-d_3 compared to toluene in the A_1 as well as B_2 electronic states. This shows that the vibration is x-sensitive which is expected from the mode of this vibration in benzene.

The explanation for a difference frequency 179 cm^{-1} has been intriguing. A difference frequency of this magnitude has also been observed in toluene by Ginsberg et al(3), but no plausible explanation could be given by them. An attempt can be made to explain this frequency as a combination of the excited state fundamentals 316 cm^{-1} and the ground state fundamental 500 cm^{-1}. This transition can appear with appreciable intensity, as is the case, only when the molecule looses all its symmetry elements in the excited electronic state.

A very strong frequency appears in Raman spectrum of toluene α-d_3 at 758 cm^{-1} which is polarised, ie, totally symmetric and belongs to symmetry class a_1 as reported by Lau & Snyder(1). This frequency is observed at 760 cm^{-1} in infra-red spectrum, and has been correlated with b_{1u} 1010 cm^{-1} vibration of benzene ring. In case of toluene, it appears at 788 cm^{-1} in Raman and infrared spectra. We have found a medium intense band at 759 cm^{-1} on the lower frequency side of the (0,0) band which is assigned as fundamental. Its counterpart in the excited state is the frequency 733 cm^{-1} which will produce a very weak band at a separation 26 cm^{-1} on the red side of (0,0) band as a result of 1-1 transition. We find a very weak band at 24 cm^{-1} which confirms our correlation.

The highest ground state fundamental identified in ultra-violet ~~in~~ spectrum is 1005 cm^{-1}. This frequency appears at 1003 cm^{-1} in Raman and infrared and the ring characteristic of benzene is correlated with this. The frequency is polarised and totally symmetric as reported by Lau & Snyder$^{(1)}$. The excited state counterpart of this fundamental has been found at 930 cm^{-1}. The 993 (a_{1g}) and 1010 (b_{1u}) cm^{-1} vibrations of benzene intermix to result into a composit mode in benzene derivatives. We prefer to assign the fundamentals 759 (ES 733) cm^{-1} and 1005 (ES 930) cm^{-1} as the lower and upper components of the totally symmetric composite ring vibrations. The lower component is x-sensitive.

The C-CH$_3$ stretching frequency (7a) has been assigned a value 1211 cm^{-1} in infrared and Raman (polarised) spectra. Ginsberg et al$^{(3)}$ have reported it at 1212 cm^{-1} (vvw) in electronic spectrum of toluene. In toluene α-d$_3$ molecule a frequency 1184 cm^{-1} in infrared and 1182 cm^{-1} in Raman spectra has been observed. The counterpart of this frequency in the excited electronic state of toluene has been reported at 1189 cm^{-1}. Here again we expect a lower value for toluene α-d$_3$ molecule.

Therefore the excited fundamental 1130 cm^{-1} has been assigned to represent C-CD_3 (7a vibration) frequency .

Most of the bands in the absorption spectrum are assigned to result due to combination of the fundamentals as discussed earlier. The prominent bands have been analysed in terms of above discussed fundamentals and their overtones.(Table 1).

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