General Valence Force Field and Normal Coordinate Analysis of 1,3,5-Trisubstituted Benzenes

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The vibrational spectra of mesitylene and a complete assignment of the observed normal modes are presented and discussed together with literature data. A general valence force field suitable for different 1,3,5-trisubstituted benzenes was investigated and normal coordinate calculations for C_6H_5R (R = Me, Cl, Br) were performed. Good agreement between observed and calculated frequencies has been achieved. The force field together with force constants and potential energy distribution is presented. The complete set of the representations of the normal modes based on the calculated displacement vectors of the atoms is given.

1. Introduction

The vibrational spectra of benzene and its derivatives have been studied by a number of researchers in the past years[1]. Normal coordinate calculations (NCAs) of several molecules of this type were also performed[2-7]. Since most of the molecules have high symmetry the NCAs performed for them made use of symmetry adapted coordinates. This method is well established for free atomic rings, however, it does not work well for molecules coordinated on a metal atom with various ligands, because in this case the overall symmetry is very low. Within the scope of our investigations of half-sandwich complexes[8,9], we were interested to perform NCAs for the complete molecules without reducing the ring ligand to a point mass. In a first step towards this aim it was necessary to develop the NCA of free 1,3,5-trimethylbenzene (mesitylene) with internal coordinates. Since there were some discrepancies in the literature we have decided to reinvestigate also the vibrational analysis of mesitylene.

In this paper we first present the vibrational analysis of mesitylene. The polarized Raman and FT-IR spectra in the range from 100 cm⁻¹ to 3200 cm⁻¹

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and 400 cm^{-1} to 3200 cm^{-1}, respectively, with a complete assignment of the normal modes are given. Then, based on the assignments a modified general valence force field (MVFF) was set up and refined. The normal modes together with their representations are presented. The force field is then applied to the chloro and bromo derivatives. Our intention was to prove the general validity of the force field in applying it to various 1,3,5-trisubstituted benzenes. In this connection it is of interest whether the changed band positions of the halogeno derivatives are mainly caused by the mass effect. If there are no strong elec- tronic influences on the C-R bond by the halogeno atoms, the force field develo- ped for mesitylene should fit apart from small variations of the force constants.

2 Vibrational spectroscopy of mesitylene

Group symmetry considerations

In discussing the symmetry of mesitylene it is convenient to treat the skeletal modes of the ring separated from those of the methyl groups. Therefore, the ligands were first considered as point masses due to their free rotation around the C_{ring}-C_{Me} axis. The ring symmetry is then D_{3h} as it is for the halogeno derivatives. The 30 vibrational degrees of freedom are distributed amongst the symmetry species as:

$$4 \; A'_1 \; (Ra, \; p) + 3 \; A'_2 \; (i.a.) + 7 \; E' \; (IR; \; Ra, \; dp) + 3 \; A''_2 \; (IR) + 3 \; E'' \; (Ra, \; dp).$$

Caused by some influence of the methyl groups forbidden bands may though occur with weak intensities. The CH_3 groups have a local symmetry of C_{3v} and therefore give rise to two C-H stretch and three C-H deformation modes addi- tionally.

Vibrational spectra

Figure 1 shows the survey Raman ($I_{\|}$ and $I_{\perp}$) and FT-IR spectra of mesity- lene. The experimental conditions are described in detail in Ref. 9. The observed frequencies together with assignments are compiled in Table 1. The overtones and combination bands were not assigned explicitely. The frequencies for the skeletal modes of interest are given in Table 2 together with previous as- signments[10-13]

The band positions of the C-H stretching modes of the ring are expected with positions over 3000 cm^{-1} and polarized and depolarized intensities for the

symmetric and anti-symmetric C-H stretching mode, respectively. As it can be seen in Figure 2, there is a strong and polarized band at 3006 cm^{-1}, which can be assigned to the symmetric A$'_1$ vibration. The corresponding anti-symmetric vibration E' is of weaker intensity in the I$_{||}$ spectrum and is therefore hidden underneath the polarized mode. In the I$_\perp$ spectrum it can be detected at 3027 cm^{-1}. The assignments given in the literature except those of Ref. 13 must therefore be revised.

Further contestable band positions are those of the E'' modes. These are predicted to be active in Raman, but their assignments have been hithertho unsure because of very weak intensities. In our investigations they can be detected as bands with weak and medium intensity at 881 cm^{-1} and 225 cm^{-1}, respectively. Only one E'' band remains unassigned; its band position is calculated in this work.

Table 1--Observed wavnumbers of neat mesitylene at room temperature; Me, CH$_3$ group; vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad

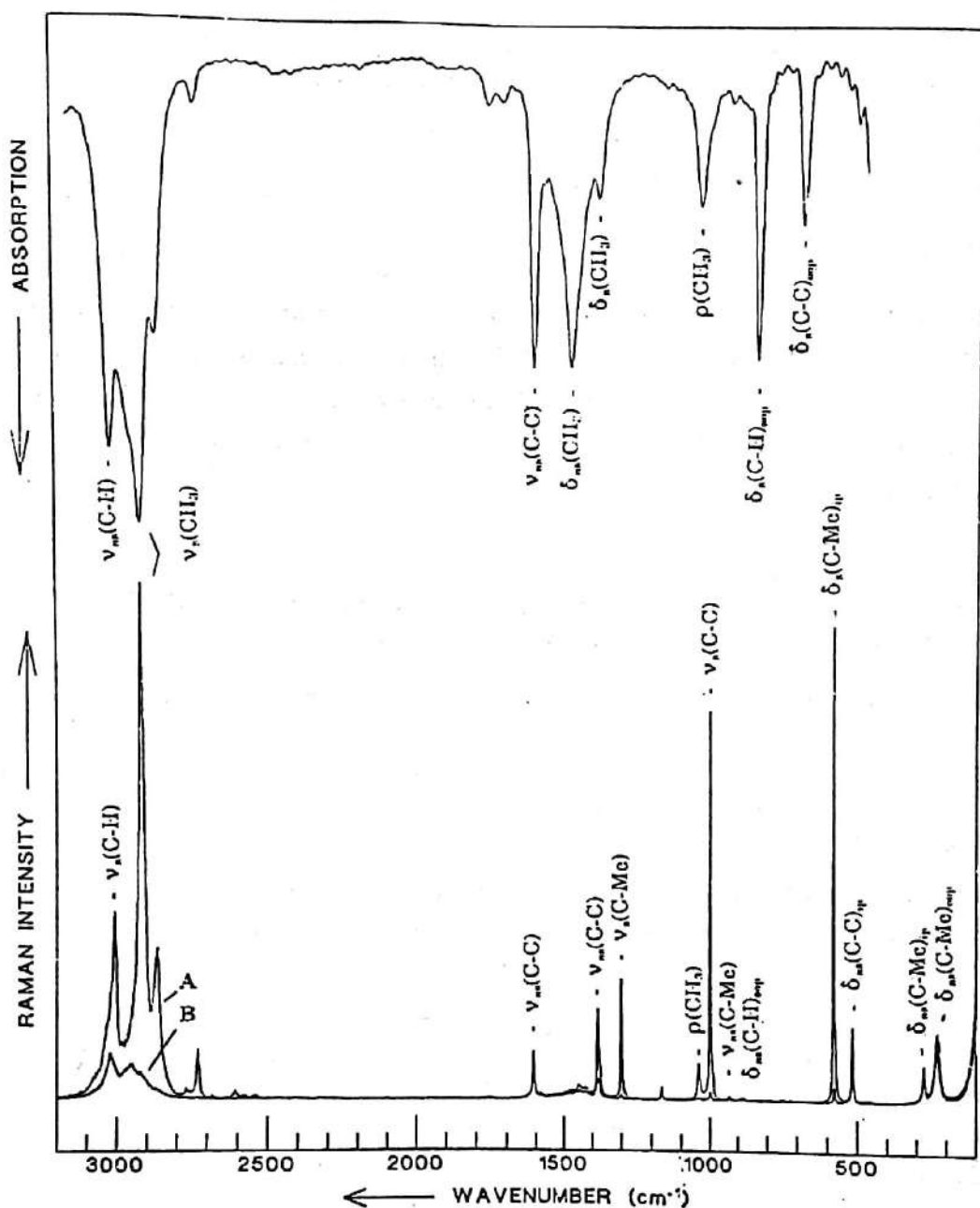| Raman / cm^{-1}	IR / cm^{-1}	assignment	Raman / cm^{-1}	IR / cm^{-1}	assignment
3074 w,sh			1247 vw		
3027 m,dp	3020 s	ν_{as}(C-H)	1207 vw		
3006 s,p		ν_s(C-H)	1166 m,dp		δ_{as}(C-H)$_{ip}$
2950 m,dp	2952 s,sh	ν_{as}(CH$_3$)	1038 m,p	1037 m	ρ(CH$_3$)
2915 vs,p	2918 vs	ν_s(CH$_3$)	998 vs,p	999 vw,sh	ν_s(C-C)
2868 m,p	2865 m		929 w,dp	927 w	ν_{as}(C-Me)
2769 vw,sh			881 w,dp		δ_{as}(C-H)$_{oop}$
2730 w,p		overtones	836 vw	837 s	δ_s(C-H)$_{oop}$
2679 vw,p		and	745 vw,p		
2606 w,p		combination	719 vw,p		
2576 vw,p		bands	687 vw	688 m	δ_s(C-C)$_{oop}$
2539 vw,p			648 vw,p		
1610 m,dp	1608 s	ν_{as}(C-C)	578 vs,p		δ_s(C-Me)
1580 vw,sh	1510 m,sh		555 w,sh		
1475 vw,sh	1473 s		515 m,dp		δ_{as}(C-C)$_{ip}$
1443 w,dp	1445 m,sh	δ_{as}(CH$_3$)	467 vw,br		
1422 w,dp			275 m,dp		δ_{as}(C-Me)$_{ip}$
1382 m,dp	1380 m	ν_{as}(C-C)	225 m,dp		δ_{as}(C-Me)$_{oop}$
1376 w,sh		δ_s(CH$_3$)	183 vw,dp		δ_s(C-Me)$_{oop}$
1301 s,p		ν_s(C-Me)			

Fig. 1. Survey Raman (A = $I_{||}$, B = $I_{\perp}$, lower spectra) and FT-IR (upper spectrum) of neat mesitylene at room temperature. Raman: excitation wavelength $\lambda_0 = 647.1$ nm, laser power P = 300 mW, slit width s = 2 cm^{-1}, FT-IR: resolution s = 2 cm^{-1}, number of scans n = 32.

Table 2--Observed skeletal modes of mesitylene (D_{3h}) and their symmetry assignments; data are given in wavenumbers

Symmetry	this work	Ref. 13	Ref. 11	Ref. 12	Ref. 10
A'_1	3006	3004	3020	-	$(3062)^a$
	1301	1299	1299	1295	1300
	998	998	997	998	998
	578	578	579	599	575
A'_2	$(1281)^b$	-	$(1290)^c$	-	$(1650)^c$
	$(1240)^b$	-	$(1260)^c$	-	$(1220)^c$
	$(308)^b$	$(381)^c$	$(495)^c$	-	$(390)^c$
E'	3027	3017	3017	-	$(3047)^a$
	1610	1608	1610	1609	1610
	1382	1374	1372	1380	1385
	1166	1163	1165	1167	1160
	929	928	930	-	930
	515	513	516	494	515
	275	274	275	278	230
A''_2	837	-	835	844	840
	688	-	686	690	690
	183	-	181	183	182
E''	881	-	880	882	847
	$(485)^b$	-	$(533)^c$	494	$(439)^d$
	225	-	224	232	275

a, derived from benzene; b, calculated value; c, suggested value; d, derived from m-xylene

The other band positions of symmetry type A'_1, E' and A''_2 are well established. They were detected with only small deviations by all researchers. The most difficult problem is the location of the incative modes with symmetry A'_2, for which only vague estimations and calculation values exist. Scherer et al.[14, 15] predicted the positions for bands with A'_2 symmetry at about 400 - 500 cm^{-1} and 1200 - 1300 cm^{-1}. We achieved the same regions of wavenumbers for the bands with A'_2 symmetry in our calculations (see Table 2).

3   Normal coordinate analysis

Structure parameters

Regular hexagons for the molecules were assumed. The bond lengths wre

taken from literature[16-18] as follows: the C-C bond, 1.41 Å for mesitylene and trichlorobenzene and 1.39 Å for tribromobenzene; the C-Me bond, 1.5 Å; the C-Cl bond, 1.69 Å; the C-Br bond, 1.84 Å; the C-H bond, 1.85 Å for all molecules. The methyl groups in mesitylene were substituted with point masses with m = 15 at the positions of the C-atoms.
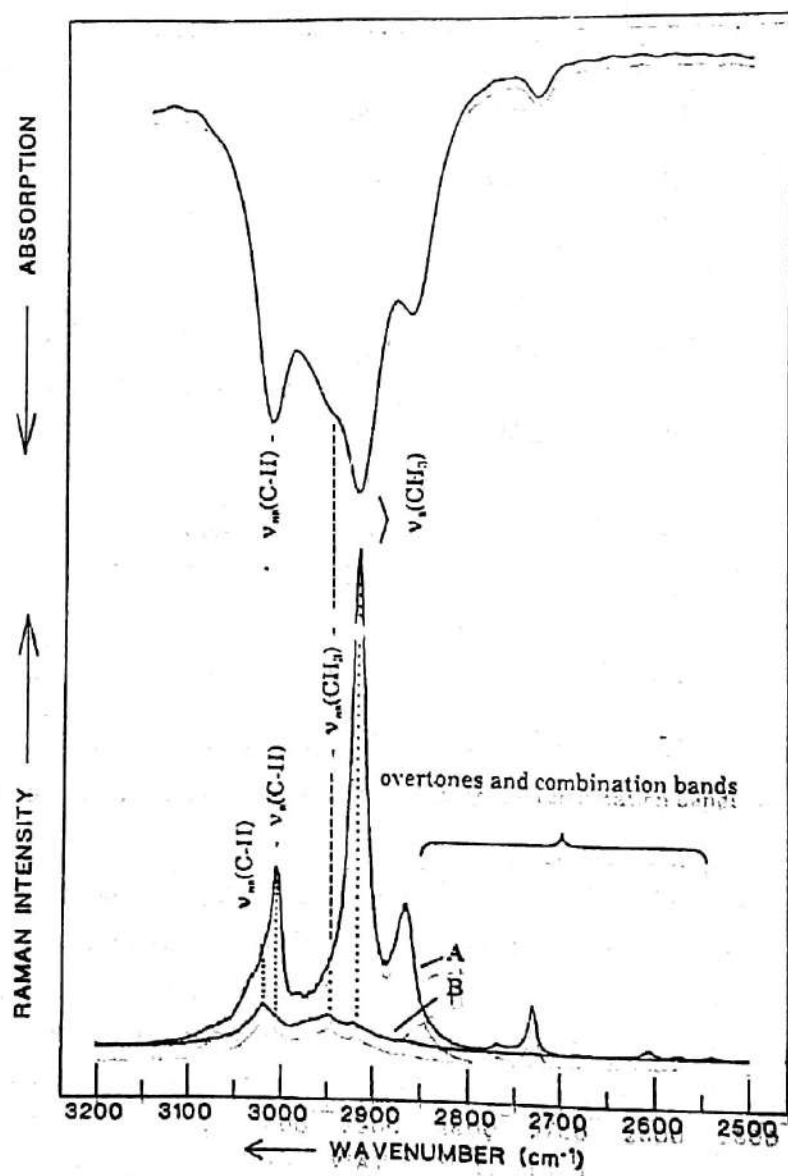

Fig. 2. Polarized (A) and depolarized (B) Raman spectra of neat mesitylene in the range of the C-H stretching vibrations at 3000 cm⁻¹.

Vibrational force field

Although most of the NCAs of mesitylene published in the literature hitherto worked with valence force fields (VFF) the results obtained had deviations up to 15 cm^{-1} of the calculated band positions compared to the observed ones. Data from calculations on benzene[19, 20] as a similar molecule could not be transferred to our calculatiosn for mesitylene. Benzene has a symmetry of D_{6h} and therefore a completely different valence force is necessary compared to a trisubstituted benzene ring with D_{3h} symmetry. The masses of R (R = Me, Cl, Br) in $C_6H_3R_3$ are distinctly larger than the masses of the H atoms in benzene (R = H) with additionally results in different force constants. Therefore we had to set up a completely new force field.

The defined internal coordinates are described in Figure 3. The letter s denotes the stretch coordinates. The greek lettes α - δ denote the in-plane deformation coordinates and ε and φ the out-of-plane deformation coordinates, whereas τ describes the torsion around the C-C axis. Thus, the molecule can be described by a force field with 42 diagonal elements including 12 stretch, 18 in-plane bend, 6 out-of-plane bend and 6 torsion coordinates. We first started with a simplified VFF without any off-diagonal elements. The force field was then refined by introducing the interaction force constants where necessary. The force constants were then refined by a fit alogrithm.
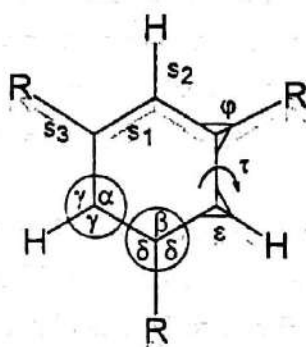

Fig. 3. Defined internal coordinates for 1,3,5-trisubstituted benzene;
s_1: stretch, s_2: C-H stretch, s_3: C-R stretch, α: C-C_H-C bend in-plane (i.p.), β: C-C_R-C bend i.p., γ: C-C-H bend i.p., δ: C-C-R bend i.p., ε: C-H bend out-of-plane (o.o.p), φ: C-R bend o.o.p., τ: C-C torsion.

To perform the NCA of the halogeno derivatives their masses instead of those of the methyl groups were used together with the changed bond distances and the optimized VFF of mesitylene. The assignments and band positions given in Refs. 11 and 14 were used for force constant refinement.

The normal coordinate calculations were performed by use of the FG matrix method of Wilson[21] and of a modified version of QCMP-067[22] and VIA[23]. The calculations were carried out on SPARC/2 workstation and displayed on a personal computer. The representations of the normal modes were drawn with a commercially available drawing program.

5   Results and discussion

The wavenumbers calculated for $R = CH_3$, Cl and Br are compiled in Tables 3 - 5, respectively, and compared with their ovserved values. The corresponding potential energy distribution (PED) of each normal mode is also given. The resulting force constants and their definitions are given in Table 6. Since there were only some of the representations of the normal modes presented in the literature[1] we have calculated and depicted the complete set of them; the in-plane and out-of-plane modes are shown in Figure 4. Note, that only the most intense displacement vectors are drawn by arrows.

As it can be seen from Tables 3 - 5, we achieved an excellent agreement between observed and calculated wavenumbers. With use of a force field with 42 diagonal elements and 132 off-diagonal elements represented by 35 force constants the 30 normal modes were calculated with deviations smaller than 1 cm^{-1} in all cases. The only inaccuracy are probably for the three A'_2, one E mode of mesitylene and some of the A''_2 modes of halogeno derivatives, as mentioned above. The band positions for the C-R out-of-plane deformation mode below 200 cm^{-1} of the halogeno derivates reported in the literature were only deduced from combination bands. Though their positions are almost unknown and they were not taken into account for the calculations and omitted in the tables. Therefore, the VFF had to be calculated without these data.

From the PED it can clearly be seen that the mass effect causes the changes of the band postions when substitution of the ligands from the "light" CH_3 up to the heavy bromine atom is done. Most of the force constants were only slightly changed which also supports the interpretation of a mass effect. The decrease of the C-R stretch force constant s_3 can be explained as a consequence of the change of the C-R bond distance from 1.50 Å to 1.84 Å.

The presented VFF has proven its general validity for 1,3,5-trisubstituted

benzenes. In slightly changed form we could use the present results also for half sandwich molecules with coordinated mesitylene[24]

in-plane modes

A_1', 998 cm⁻¹

E', 929 cm⁻¹

A_1', 578 cm⁻¹
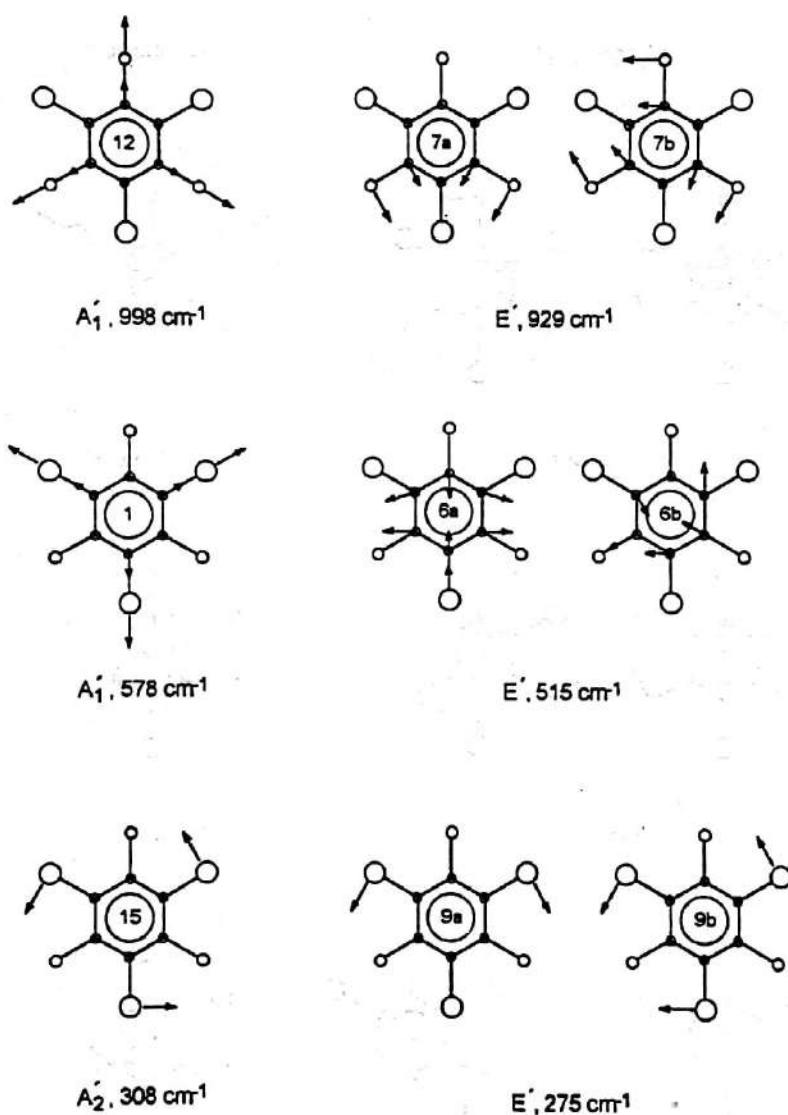
E', 515 cm⁻¹

A_2', 308 cm⁻¹

E', 275 cm⁻¹

Fig. 4. Representation of the normal modes of 1,3,5-trisubstituted benzenes, the numbering given inside the ring is according to Wilson's notation[21]
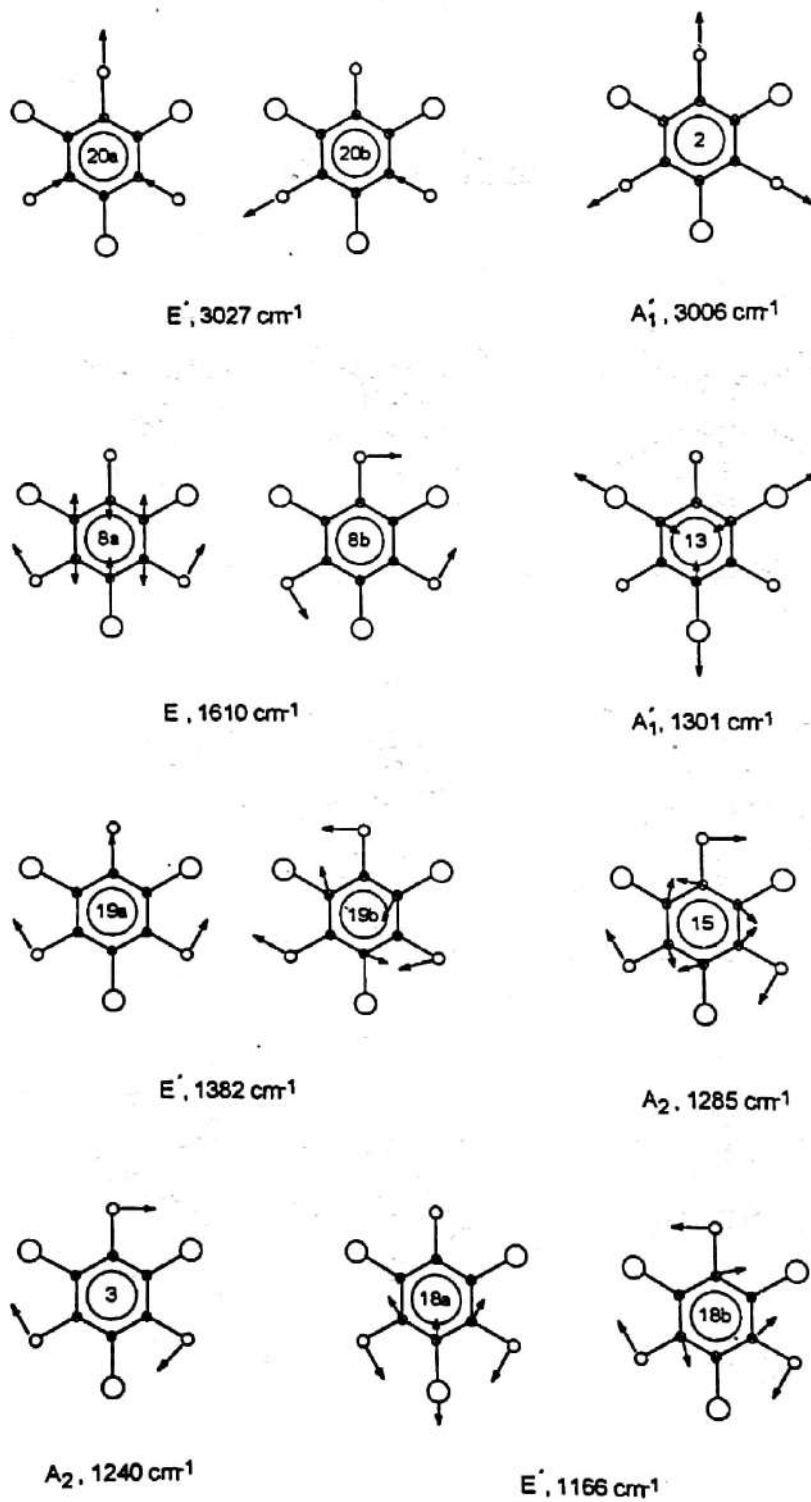
in-plane modes

E', 3027 cm⁻¹

A₁', 3006 cm⁻¹

E , 1610 cm⁻¹

A₁', 1301 cm⁻¹

E', 1382 cm⁻¹

A₂ , 1285 cm⁻¹

A₂ , 1240 cm⁻¹

E', 1166 cm⁻¹

Fig. 4. continued.

out-of-plane modes
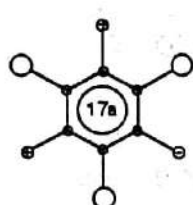
E", 881 cm⁻¹
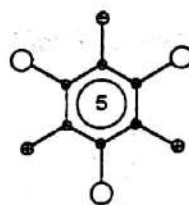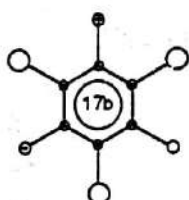
A₂", 837 cm⁻¹
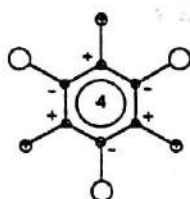
A₂", 688 cm⁻¹
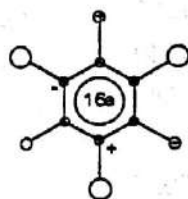
E", 485 cm⁻¹
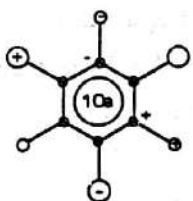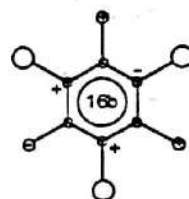
E", 225 cm⁻¹
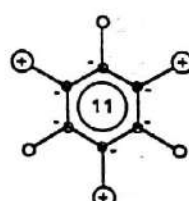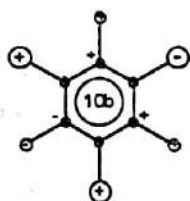
A₂", 183 cm⁻¹

—O = CH₃ group

—o = H atom

Fig. 4. continued.

Table 3--Observed and calculated wavenumbers of 1,3,5-trimethylbenzene and potential energy distribution (PED)

Symmetry	Observed / cm^{-1}	Calculated / cm^{-1}	PED / %[a]
A'_1	3006	3006	98 s_2
	1301	1301	59 s_3 + 24 β + 8 δ
	998	998	44 s_1 + 22 β + 12 s_2 + 9 δ + 6 s_3 + 5 α
	578	578	56 s_3 + 18 s_1 + 16 β + 5 δ
A'_2	-	1281	76 s_1 + 22 γ
	-	1240	72 γ + 22 s_1
	-	308	99 δ
E'	3027	3027	97 s_2
	1610	1610	36 s_1 + 24 s_3 + 11 β + 10 γ + 9 δ + 7 α
	1382	1382	37 s_1 + 21 γ + 15 δ + 13 s_2 + 7 s_3 + 5 α
	1166	1166	54 γ + 33 s_3 + 10 s_1
	929	929	55 s_1 + 24 s_3 + 14 γ
	515	515	48 s_1 + 16 β + 14 α + 13 δ
	275	275	80 δ + 10 s_2 + 8 s_1
A''_2	837	837	78 ε + 21 φ
	688	688	73 τ + 26 φ
	183	183	54 φ + 32 ε + 14 τ
E"	881	881	75 ε + 20 τ + 5 φ
	-	485	71 φ + 29 τ
	225	225	56 τ + 42 ε

[a] PED values below 5 % have been omitted

Table 4--Observed and calculated wavenumbers of 1,3,5-trichlorobenzene and potential energy distribution (PED)

Symmetry	Observed[a] / cm^{-1}	Calculated / cm^{-1}	PED / %[b]
A'_1	3084	3084	98 s_2
	1149	1149	48 s_3 + 30 s_1 + 8 β + 6 α
	997	997	30 β + 23 α + 16 δ + 14 s_1 + 9 s_3 + 5 γ
	379	379	73 s_3 + 11 s_1 + 6 β
A'_2	-	1326	87 s_1 + 11 γ
	-	1199	86 γ + 9 s_1 + 5 δ
	-	271	99 δ
E'	3086	3086	97 s_2
	1570	1570	49 s_1 + 10 β + 10 δ + 9 s_3 + 9 γ + 9 s_2 + 6 α
	1420	1420	46 s_1 + 20 γ + 15 δ + 8 s_3 + 6 s_2
	1098	1098	69 γ + 20 s_3 + 7 s_1
	816	816	46 s_1 + 39 s_3 + 7 γ
	429	429	38 s_1 + 17 β + 16 δ + 14 s_3 + 12 α
	190	190	82 δ + 9 s_1 + 8 s_2
A''_2	853	853	57 ϵ + 28 τ + 15 φ
	662	662	60 τ + 40 φ
	-	128	40 τ + 35 φ + 35 ϵ
E"	865	865	57 τ + 42 ϵ
	530	530	84 φ + 10 τ + 6 ϵ
	215	215	80 τ + 19 ϵ

[a] Refs. 11 and 14
[b] PED values below 5 % have been omitted

Table 5--Observed and calculated wavenumbers of 1,3,5-tribromobenzene and potential energy distribution (PED)

Symmetry	Observed[a] / cm^{-1}	Calculated / cm^{-1}	PED / %[b]
A'_1	3073	3073	98 s_2
	1115	1115	42 s_3 + 31 s_1 + 10 β + 8 α + 5 δ
	985	985	28 β + 23 α + 17 s_1 + 15 δ + 12 s_3 + 9 s_2 + 6 γ
	241	241	73 s_3 + 11 s_1 + 6 β
A'_2	-	1361	86 s_1 + 12 γ
	-	1233	87 γ + 9 s_1
	-	243	99 δ
E'	3090	3090	97 s_2
	1537	1537	48 s_1 + 12 γ + 10 β + 9 s_3 + 9 s_2 + 8 δ + 5 α
	1409	1408	45 s_1 + 25 γ + 14 δ + 7 s_2
	1099	1099	68 γ + 14 s_3 + 12 s_1
	742	742	51 s_1 + 36 s_3 + 5 α
	348	348	36 s_1 + 17 s_3 + 16 δ + 14 β + 11 α
	118	118	81 δ + 9 s_1 + 8 s_2
A''_2	849	849	59 ε + 33 τ + 8 φ
	-	678	49 τ + 47 φ
	-	104	41 φ + 31 ε + 18 τ
E''	870	870	51 τ + 48 ε
	509	509	79 φ + 16 τ + 5 ε
	193	193	85 τ + 12 ε

[a] Refs. 11 and 14
[b] PED values below 5 % have been omitted

Table 6--Internal coordinates (for definitions see Figure 3) and force constants for 1,3,5-trisubstituted benzene ($C_6H_3R_3$); values for stretches and their interactions are in mdyne$(Å)^{-1}$; for bendings, waggings and torsions and all interactions thereoff in mdyne$(Å)(rad)^{-2}$; and for interactions of stretches with bendings, waggings and torsions in mdyne$(rad)^{-1}$

force constant type	definition	R = CH_3	R = Cl	R = Br
diagonal				
C-C stretch	s_1	4.577	4.974	4.789
C-H stretch	s_2	4.608	4.867	4.864
C-R stretch	s_3	5.821	4.970	4.437
C-C_H-C bend i.p.	α	1.226	0.954	0.927
C-C_R-C bend i.p.	β	1.232	1.241	1.132
C-C-H bend i.p.	γ	0.449	0.414	0.440
C-C-R bend i.p.	δ	1.298	1.335	1.201
C-H bend o.o.p.	ε	0.392	0.162	0.182
C-R bend o.o.p.	φ	0.311	0.367	0.344
C-C torsion	τ	0.456	0.501	0.463
stretch / stretch interaction				
C-C stretch / C-C stretch (adjacent)	s_1s_1	0.829	0.939	0.889
C-C stretch / C-C stretch (adjacent)	s_1s_1'	0.433	0.472	0.630
C-C stretch / C-H stretch	s_1s_2	-0.436	-0.287	-0.321
C-C stretch / C-R stretch	s_1s_3	0.385	0.505	0.572
C-H stretch / C-H stretch	s_2s_2	0.018	0.026	0.005
C-H stretch / C-R stretch	s_2s_3	0.407	-0.457	-0.522
C-R stretch / C-R stretch	s_3s_3	-0.464	-0.440	-0.459
stretch / bend interaction				
C-C stretch / C-C_H-C bend i.p.	$s_1\alpha$	-0.569	-0.726	-0.819
C-C stretch / C-C_R-C bend i.p.	$s_1\beta$	-0.557	-0.695	-0.878
C-C stretch / C-C-H bend i.p.	$s_1\gamma$	0.199	0.155	0.166
C-C stretch / C-C-R bend i.p.	$s_1\delta$	-0.096	0.000	-0.088
C-H stretch / C-C-H bend i.p.	$s_2\alpha$	-0.168	-0.123	-0.123
C-H stretch / C-C-H bend i.p.	$s_2\gamma$	0.118	0.103	0.093
C-H stretch / C-C-R bend i.p.	$s_2\delta$	0.763	0 723	0.699
C-R stretch / C-C-H bend i.p.	$s_3\gamma$	-0.006	-0.060	-0.057
C-R stretch / C-C-R bend i.p.	$s_3\delta$	0.501	0.485	0.355
bend / bend interaction				
C-C_H-C bend i.p. / C-C_H-C bend i.p.	$\alpha\alpha$	-0.508	-0.469	-0.420
C-C_H-C bend i.p. / C-C_R-C bend i.p.	$\alpha\beta$	-0.109	-0.093	-0.093
C-C_R-C bend i.p. / C-C_R-C bend i.p.	$\beta\beta$	-0.149	-0.180	-0.157
C-C-H bend i.p. / C-C-H bend i.p.	$\gamma\gamma$	-0.014	-0.017	-0.016
C-C-R bend i.p. / C-C-R bend i.p.	$\delta\delta$	0.487	0.512	0.457
C-H bend o.o.p. / C-H bend o.o.p	$\varepsilon\varepsilon$	-0.038	0.018	0.004
C-C torsion / C-C torsion (adjacent)	$\tau\tau$	0.017	0.077	0.071
C-C torsion / C-C torsion (1 adjacent)	$\tau\tau'$	0.092	-0.002	0.020
C-C torsion / C-C torsion (2 adjacent)	$\tau\tau''$	-0.004	-0.008	-0.038

Acknowledgements

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