Normal coordinate analysis of isotactic polystyrene: 1. A force field for monosubstituted alkyl benzenes

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The normal modes for toluene, toluene D8, and ethyl benzene are calculated starting from a revised force field for benzene. A good agreement is obtained between calculated and observed frequencies.

INTRODUCTION

Isotactic polystyrene (IPS) has been the subject of numerous vibrational spectroscopic studies. However, a satisfactory interpretation of the entire spectrum has proved elusive for a number of reasons. Perhaps the most obvious difficulty is the size of the problem, the relatively large repeat unit results in a complicated spectrum. Initial attempts at interpretation concentrated on assigning the phenyl ring modes using monosubstituted alkyl benzenes as models[1]. Subsequently, assignments of conformationally sensitive backbone and mixed ring-backbone modes were made on the basis of studies of deuterated and partially deuterated polymers[2-5]. This work met with only limited success because of the change in the form of many normal modes upon deuteration. Jasse *et al.*[6-9] have recently studied a number of low molecular weight model compounds, paying particular attention to some of the conformationally sensitive modes below 600 cm^{-1}. However, some of the assignments used in these studies were based on the group frequencies of the phenyl ring, thus neglecting the possibility that such modes could mix with backbone vibrations. Furthermore, the assignment of infra-red bands and Raman lines to specific local conformations in model compounds may not be transferable to polymers, where conformationally sensitive modes are coupled along the chain.

A more precise understanding of the vibrational spectrum of IPS depends upon an accurate normal coordinate analysis of the polymer and should include the plotting of dispersion curves. Painter and Koenig[10] attempted a vibrational analysis but there are a number of limitations to their calculations. The low frequency vibrational spectrum of IPS had not at that time been published, so that this conformationally sensitive region of the spectrum was essentially ignored. Because of limitations on computer time, only the potential energy distribution of the A modes was reported and the dispersion curves were not calculated. However, a more serious deficiency has become apparent as a result of our attempts to determine a revised valence force field for benzene[11]. The valence force field applied to the vibrational analysis of polystyrene was similar to that defined by Lau and Snyder[12] for alkyl benzenes and includes the definition of an interaction force constant, $F_{R(X)\Phi(X)}$. The interaction is between the ring-methyl stretching coordinate $R(X)$ and a coordinate describing the in-plane bending of the same bond, $\Phi(X)$, and was refined to a significant value. However, in monosubstituted alkyl benzenes this force constant should be zero by symmetry, since a vertical mirror symmetry operation through the ring and alkyl group leaves the stretching coordinate $R(X)$ unchanged but reverses the direction of the bending coordinate. Finally, in the previous work all in-plane C–C–H bending coordinates of the ring were separately defined and because of the redundant coordinate at each carbon atom the definition of force constant interactions was confusing. In this communication we will report a valence force field for alkyl benzenes where these problems are taken into account. In the following paper this force field will be applied to IPS.

To make the force field generally applicable we have, as far as possible, used the force constant definitions of Snyder[13] for the alkyl portion of the molecule and a previously reported modified valence force field for benzene for the phenyl ring[11]. Interaction force constants between the ring and phenyl group were then defined and values determined by refining the observed and calculated frequencies.

CALCULATIONS

The normal vibrations were calculated on an IBM 370-168 computer using a program described by Boerio and Hannon[14,15] and modified by Holland-Moritz and Painter and Snyder[11]. The force field (F_R) is defined in terms of internal coordinates but the secular equation is transformed to a mass-weighted Cartesian coordinate description,

$$|D^T F_R D - \lambda I| = 0$$

where $D = BM^{-1/2}$. The B matrix relates the internal and Cartesian coordinates while M is a matrix of the masses of the atoms. The secular equation can be transformed to a block diagonal form using external symmetry

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coordinates. The Cartesian coordinates were calculated using bond lengths of C_{ring}–C_{ring}, C_{ring}–C_{alkyl}, C_{alkyl}–C_{alkyl}, C–H_{alkyl} and C–H_{ring} of 1.40, 1.51, 1.54, 1.09 and 1.084 Å respectively. Bond angles of 120° in the ring and tetrahedral angles in the alkyl group were defined. The internal coordinates are defined in *Figure 1*. The C–C–H angle bends, φ_i, were constructed as a combination $R_i(\varphi)$, defined as

$$R_i(\varphi) \doteq 1/\sqrt{2}(\varphi_1 - \varphi_2)$$

and so on around the ring. The $1/\sqrt{2}$ is a normalization factor. This definition simplifies the definition of interaction force constants, as discussed previously[11].

The force field was obtained by refining an initial set of calculated frequencies to the observed frequencies of the molecules, Toluene, D8 Toluene and ethyl benzene. The observed frequencies were those reported by Lau and Snyder[12]. For the convenience in the co-refinement the symmetry of both molecules was assumed to be C_s with a mirror perpendicular to the plane of the ring passing through the alkyl group. The initial group of interaction force constants were those defined by Lau and Snyder[12] with the exception of $F_{R(X)\Phi(X)}$, which was set equal to zero. Various force constants were included in a number of different refinements, but only those that appeared to have significant values were ultimately retained. In initial calculations we determined the ring-methyl stretch diagonal force constant, $K_{R(X)}$ to have a value of ~4.3, significantly smaller than that of a paraffin C–C single bond, 4.532 (ref. 13). However, because the ring-methyl bond has a slight double bond character (the bond length

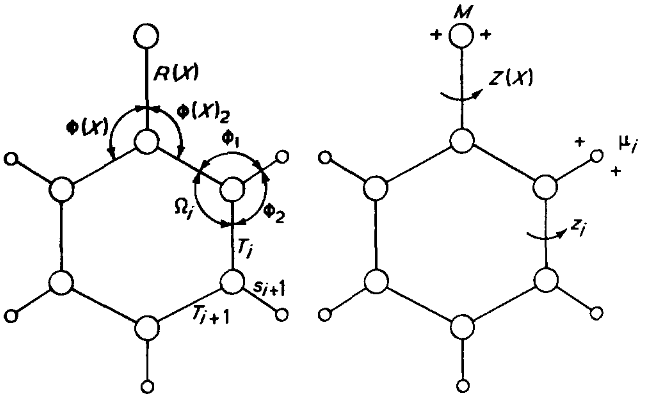

Figure 1 Internal coordinate definitions of a monosubstituted alkyl benzene

Table 1 Force constants for toluene and ethyl benzene

Force constants[a]	Coordinate involved	Φ_i	Disp.
Phenyl group, in plane			
K_T	T	7.0845	0.048
K_s	s	5.0220	
H_Ω	Ω	1.4612	
H_ϕ	ϕ	0.4956	
F^0_T	T_i, T_{i+1} (*ortho*)	0.6926	0.0368
F^m_T	T_i, T_{i+2} (*meta*)	−0.5104	0.0450
F^p_T	T_i, T_{i+3} (*para*)	0.6042	0.0511
$F^0_{T\phi}$	T_i, ϕ_i	−0.2714	
$F'^0_{T\phi}$	T_i, ϕ_{i+1}	0.2714	
$F^m_{T\phi}$	T_i, ϕ_{i+1}	−0.0568	
$F'^m_{T\phi}$	T_i, ϕ_{i+2}	0.0569	
$F^p_{T\phi}$	T_i, ϕ_{i-2}	0.1019	
$F'^p_{T\phi}$	T_i, ϕ_{i+3}	−0.1019	
$F_{T\Omega}$	T, Ω	0.3439	
F_{Ts}	T, s	−0.1150	
F^0_s	s_i, s_{i+1} (*ortho*)	0.0130	
F_Ω	Ω_i, Ω_{i+1} (*ortho*)	0.0847	
$F^0_{\Omega\phi}$	Ω_i, ϕ_{i-1}	−0.1005	
$F'^0_{\Omega\phi}$	Ω_i, ϕ_{i+1}	0.1009	
F^0_ϕ	ϕ_i, ϕ_{i+1} (*ortho*)	0.0126	
F^m_ϕ	ϕ_i, ϕ_{i+2} (*meta*)	−0.0007	
F^p_ϕ	ϕ_i, ϕ_{i+3} (*para*)	−0.0185	
Phenyl group, out of plane			
H_μ	μ	0.3239	
H_z	z	0.1190	
F^0_μ	μ_i, μ_{i+1} (*ortho*)	0.0184	
F^m_μ	μ_i, μ_{i+2} (*meta*)	−0.0235	
F^p_μ	μ_i, μ_{i+3} (*para*)	−0.0227	
F^0_z	z_i, z_{i+1} (*ortho*)	−0.0388	
$F_{z\mu}$	z_i, μ_i	0.0273	
$F'_{z\mu}$	z_i, μ_{i+1}	−0.0263	
Phenyl group—alkyl group interactions			
$K_{R(X)}$	$R(X)$	4.7455	0.0999
$H_{\Phi(X)}$	$\Phi(X)$	0.7165	0.0268
$H_{Z(X)}$	$Z(X)$	0.0100	
H_M	M	0.3829	0.0167
$F^0_{TR(X)}$	$T_{i-1}, R(X), T_{i-2}, R(X)$	0.1729	0.0704
$F^0_{\Omega\Phi(X)}$	$\Omega_i, \Phi(X)$	0.0758	0.1124
$F'^0_{\Omega\Phi(X)}$	$\Omega_{i-2}, \Phi(X)$	−0.0758	0.1124
$F_{T\Phi(X)}$	$T_{i-1}, \Phi(X)$	−0.3752	0.1092
$F'_{T\Phi(X)}$	$T_{i-2}, \Phi(X)$	0.3752	0.1092
$F_{\Omega R(X)}$	$\Omega_{i-1}, R(X)$	−0.5258	0.1031
$F^0_{\Omega R(X)}$	$\Omega_i, R(X), \Omega_{i-2}, R(X)$	0.1233	0.0807
Alkyl group			
K_r	r	4.6990	
K_d	d	4.5380	
K_R	R	4.5320	
H_α	α	0.539	
H_β	β	0.6180	
H_δ	δ	0.5330	
H_α	α	0.6630	
H_ω	ω	1.032	
F_r	r,r	0.032	
F_d	d,d	0.019	
F_R	R,R	0.083	
$F_{R\alpha}$	R,α	0.174	
$F'_{R\alpha}$	R,α	−0.097	
$F_{R\omega}$	R,ω	0.303	
F_β	β,β	−0.031	
F_α	α,α	−0.019	
F'_α	α,α	0.021	
$F_{\alpha\omega}$	α,ω	−0.022	
$f^t_{\alpha,\beta}$	$\bar{\alpha},\beta$	0.073	
$f^g_{\alpha\beta}$	α,β	−0.058	
$f'^t_{\alpha\beta}$	α,β	−0.009	
$f'^g_{\alpha\beta}$	α,β	−0.004	
$f^t_{\alpha\omega}$	α,ω	0.073	
$f^g_{\alpha\omega}$	α,ω	−0.064	
$F_{R(X)\alpha}$	$R(X),\alpha$ or $R(X),\beta$	0.1740	
$F'_{R(X)\alpha}$	$R(X),\alpha$	−0.0970	

[a] Force constant units: stretching constants, mdyn/Å; bending constants, mdyn Å/rad^2; stretch-bend interactions, mdyn/rad

Table 2 Observed and calculated frequencies and approximate potential energy distribution of toluene and ethyl benzene

Table 2a—Toluene A′

Frequency (cm^{-1})		
ν_{obs}	ν_{calc}	Potential energy distribution
3057	3062	K_s (98%)
3055	3049	K_s (98%)
3054	3038	K_s (99%)
2949	2964	K_r (100%)
2900	2876	K_r (98%)
1606	1597	K_T (93%), H_r (15%)
1497	1505	K_T (41%), H_ϕ (56%)
1450	1470	H_α (93%)
1380	1376	$K_{R(X)}$ (14%), H_α (45%), H_β (52%)
1211	1214	K_T (17%), H_ϕ (36%), $K_{R(X)}$ (26%)
1182	1161	K_T (13%), H_ϕ (73%), $K_{R(X)}$ (11%)
1041	1038	H_β (79%)
1030	1034	K_T (60%), H_r (12%), H_ϕ (20%)
1005	1009	K_T (25%), H_r (81%)
991	983	H_μ (97%), H_z (30%), F_z^0 (17%), $F_{z\mu}$ (−14%), $F'_{z\mu}$ (−14%)
898	908	H_μ (85%), H_z (22%)
788	787	K_T (29%), H_r (31%), H_ϕ (10%), $K_{R(X)}$ (35%)
732	735	H_μ (76%), H_M (13%)
698	700	H_μ (43%), H_z (27%), F_z^0 (17%)
522	521	K_T (11%), H_r (79%), H_ϕ (13%)
467	471	H_μ (11%), H_z (24%), H_M (48%)
220	209	H_μ (13%), H_z (49%), F_z^0 (16%), H_M (27%)

Table 2b—Toluene A″

Frequency (cm^{-1})		
ν_{obs}	ν_{calc}	Potential energy distribution
3056	3054	K_s (98%)
3055	3042	K_s (99%)
2951	2964	K_γ (100%)
1587	1590	K_T (94%), H_Ω (13%)
1468	1466	H_α (86%)
1445	1441	K_T (38%), H_ϕ (59%)
1316	1335	K_T (67%), H_ϕ (70%), F_T^0 (−13%), $F_{T\phi}^0$ (−11%), $F'^{0}_{T\phi}$ (−11%)
1286	1292	K_T (81%), H_ϕ (49%), F_T^0 (−14%), F_T^m (−11%)
1157	1160	K_T (28%), H_ϕ (74%), $F_{T\phi}^0$ (11%), $F'^{0}_{T\phi}$ (11%)
1084	1084	K_T (41%), H_ϕ (38%)
975	973	K_T (18%), H_β (72%)
967	968	H_μ (92%), H_z (28%), $F_{z\mu}$ (−12%), $F'_{z\mu}$ (−12%)
841	849	H_μ (81%), H_z (20%)
622	623	H_Ω (95%), H_ϕ (12%)
407	405	H_μ (18%), H_z (51%), F_z^0 (17%)
348	336	$H_{\Phi(X)}$ (95%)
44	105	H_Z (99%)

Table 2c—D8 Toluene A′

Frequency (cm^{-1})		
ν_{obs}	ν_{calc}	Potential energy distribution
2277	2288	K_s (93%)
2275	2277	K_s (93%)
2272	2264	K_s (95%)
2200	2212	K_r (99%)
2091	2073	K_r (96%)
1573	1579	K_T (91%), H_Ω (14%)
1389	1391	K_T (59%), H_Φ (24%), $K_{R(X)}$ (18%)
1175	1180	K_T (20%), H_Φ (12%), $K_{R(X)}$ (44%), H_α (13%), H_β (15%)
1051	1057	H_α (95%)
1036	1025	K_T (18%), H_Ω (19%), H_α (29%), H_β (34%)
963	957	K_T (30%), H_Ω (69%)
883	873	H_Ω (14%), H_ϕ (58%)
871	863	H_μ (40%), H_β (43%), H_M (24%)
841	825	K_T (22%), H_ϕ (61%)
812	808	H_μ (103%), H_β (12%)
718	724	H_μ (71%), H_z (12%), H_β (22%)
710	695	K_T (20%), H_Ω (25%), H_ϕ (37%), $K_{R(X)}$ (23%)
608	608	H_μ (15%), H_z (40%), F_z^0 (22%), H_M (11%)
548	541	H_μ (76%), H_z (20%)
490	482	H_Ω (71%), H_ϕ (18%)
403	406	H_μ (14%), H_z (31%), F_z^0 (10%), H_M (38%)
194	186	H_μ (10%), H_z (51%), F_z^0 (17%), H_M (26%)

Table 2d—D8 Toluene A″

Frequency (cm^{-1})		
ν_{obs}	ν_{calc}	Potential energy distribution
2275	2279	K_s (93%)
2273	2270	K_s (93%)
2204	2212	K_r (99%)
1549	1558	K_T (93%), H_Ω (10%)
1334	1320	K_T (116%), H_ϕ (22%), F_T^0 (−13%), $F_{T\phi}^0$ (−11%), $F'^{0}_{T\phi}$ (−11%)
1288	1279	K_r (123%), H_ϕ (15%), F_T^0 (−14%), F_T^m (−11%), F_T^p (−11%)
1046	1055	H_α (96%)
1044	1030	H_ϕ (89%)
862	842	H_ϕ (81%)
822	820	K_r (17%), H_ϕ (74%)
791	792	H_μ (105%), H_z (15%)
763	754	H_β (79%)
658	661	H_μ (81%), H_z (20%)
598	590	H_Ω (90%), H_ϕ (22%)
348	350	H_z (64%), F_z^0 (21%)
297	292	$H_{\Phi(X)}$ (90%)
32	75	H_z (99%)

is 1.51 Å compared with the usual value of 1.54 Å in aliphatic hydrocarbons) we would expect that the value of this force constant would be >4.532. We determined that the introduction of interaction force constant $F_{R(X)\Omega}$, which was not defined in previous work, significantly affected the magnitude of $K_{R(X)}$, allowing the calculation of a final value of 4.7455. This is intuitively satisfying in terms of the values of other C–C stretching force constants.

Other force constants which appear in our refinement but did not appear in the work of Lau and Snyder are $F_{\Phi(X)\Omega}$, $F'_{\Phi(X)\Omega}$, and $F^0_{\Phi(X)\Omega}$. These force constants refined to significant values and were retained while other interaction force constants (e.g. $F^m_{R(X)\Omega}$, $F_{R(\overset{m}{X})T}$, $F_{R(\overset{m}{X})\Omega}$, and $F_{\Phi(\overset{m}{X})T}$) did not refine to significant values and were therefore removed from the refinement.

RESULTS AND DISCUSSION

The final values of the force constants are presented in *Table 1*. A good fit between the observed and calculated frequencies was obtained by refining the ring-alkyl interaction force constants and the ring constants, K_T, F_T^0, F_T^m and F_T^p. All other force constants correspond to those determined for benzene[11] and the paraffins[13]. In the final analysis only fourteen force constants were included in the refinement.

The observed and calculated frequencies are listed in *Table 2*, together with the potential energy distribution for each mode. There is good agreement between the PED of

Table 2e—Ethyl benzene A′

Frequency (cm^{-1}) ν_{obs}	ν_{calc}	Potential energy distribution
3061	3062	K_s (98%)
3049	3049	K_s (98%)
3038	3038	K_s (99%)
2965	2965	K_r (100%)
2878	2877	K_r (97%)
2855	2855	K_d (98%)
1606	1597	K_T (93%), H_Ω (15%)
1500	1506	K_T (40%), H_ϕ (54%)
1467	1457	H_α (31%), H_δ (48%), H_γ (13%)
1455	1446	H_α (59%), H_δ (27%)
1378	1367	K_R (10%), H_α (46%), H_β (52%)
1310	1315	$K_{R(X)}$ (22%), K_R (14%), H_γ (71%)
1207	1213	K_T (15%), H_ϕ (33%), $K_{R(X)}$ (19%), H_γ (17%)
1179	1163	K_T (11%), H_ϕ (74%)
1065	1060	K_R (34%), H_β (41%)
1021	1034	K_T (59%), H_Ω (12%), H_ϕ (21%)
1003	1009	K_T (27%), H_Ω (77%)
990	983	H_μ (94%), H_z (29%), F_z^0 (17%), $F_{z\mu}$ (−14%), $F'_{z\mu}$ (−14%)
967	973	K_R (37%), H_β (20%), H_γ (13%)
904	913	H_μ (87%), H_z (21%)
771	771	K_T (10%), H_Ω (13%), H_μ (21%), $K_{R(X)}$ (19%), H_β (12%), H_M (12%)
749	753	K_T (11%), H_Ω (18%), H_μ (28%), $K_{R(X)}$ (16%), H_M (10%)
700	705	H_μ (63%), H_z (20%), F_z^0 (12%)
557	561	H_Ω (34%), H_μ (11%), H_ω (20%)
487	492	H_Ω (36%), H_z (12%), H_M (19%)
362	315	H_z (22%), H_ω (37%)
157	141	H_z (33%), H_ω (16%), H_M (37%)

Table 2f—Ethyl benzene A″

Frequency (cm^{-1}) ν_{obs}	ν_{calc}	Potential energy distribution
3055	3054	K_s (98%)
3043	3042	K_s (99%)
2965	2965	K_r (99%)
2918	2918	K_d (99%)
1589	1590	K_T (95%), H_Ω (13%)
1459	1449	H_α (91%)
1453	1443	K_T (39%), H_ϕ (61%)
1332	1337	K_T (79%), H_ϕ (63%), F_T^0 (−15%), F_T^{φ} (−11%), $F_{T\phi}^0$ (−13%), $F'^0_{T\phi}$ (−13%)
1310	1306	K_T (52%), H_ϕ (48%), H_γ (20%)
1245	1237	K_T (17%), H_ϕ (11%), H_β (15%), H_γ (50%)
1157	1159	K_T (29%), H_ϕ (72%), $F_{T\phi}^0$ (11%), $F'^0_{T\phi}$ (11%)
1072	1090	K_T (32%), H_ϕ (34%), H_γ (14%)
1033	1027	K_T (26%), H_β (25%), H_γ (39%)
975	968	H_μ (92%), H_z (28%), $F_{z\mu}$ (−12%), $F'_{z\mu}$ (−12%)
856	849	H_μ (81%), H_z (20%)
787	772	H_β (43%), H_γ (62%), $F_{\gamma\omega}$ (10%)
618	623	H_Ω (95%), H_ϕ (12%)
415	404	H_μ (18%), H_z (51%), F_z^0 (17%)
314	334	$H_{\Phi(X)}$ (83%), H_τ (12%)
219	187	$H_{\Phi(X)}$ (10%), H_τ (86%)
30	29	H_z (98%)

Toluene and Toluene D8 determined in these calculations and the PED determined by Lau and Snyder[12]. However, there is a minor discrepancy concerning the assignment of the 362 and 314 cm^{-1} bands of ethyl benzene. We calculate an A′ mode at 315 cm^{-1} and A″ mode at 334 cm^{-1}, similar to the calculated values of 308 and 339 cm^{-1} calculated by Lau and Snyder[12]. Our PED indicates these modes to be C–C–Me bend and C–Me bend, respectively. Lau and Snyder do not give a PED for ethyl benzene. These authors assign a mode at 308 cm^{-1} to the former and 360 cm^{-1} to the latter. However, Green[16] assigns a depolarized Raman line near 314 cm^{-1} to an A″ mode and a 365 cm^{-1} infra-red band to an A′ mode, reversing the assignments of Lau and Snyder. In the refinement we tried both assignments but could not force either frequency more than 10 cm^{-1} from their original value, even when the C–C–C bending constant H_ω was included in the iteration. In the final analysis both frequencies were given a 'confidence' of zero, thus removing them from the refinement. We presume that the addition of other interaction force constants would improve the fit of these two modes, but could also give misleading results. Certain interactions will be zero depending upon the symmetry properties of the molecule, which in turn depend upon the orientation of the ethyl group relative to the ring. In order to keep the result as general as possible we therefore decided not to include additional interactions involving the C–C–Me bend H_ω and the phenyl group.

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