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Fourier-transform Raman and infrared spectra and normal coordinate analysis of the triphenyl compounds and their methyl-, methoxy- and fluoro-substituted derivatives of arsenic, antimony and bismuth

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Abstract

The Fourier transform (FT)-Raman and infrared (IR) spectra of triphenyl-, perdeuterated triphenyl-, tris(2-methylphenyl)-, tris(3-methylphenyl)-, tris(2,4,6-trimethylphenyl)-, tris(2-methoxyphenyl)-, tris(3-methoxyphenyl)-, tris(3-fluorophenyl)- and tris(4-fluorophenyl)-arsine, -stibine and -bismuthine were measured in the range 3600–100 cm^{-1}. A normal coordinate analysis was performed for all substances using a modified valence force field. This leads to an unique force field for these compounds, where only the metal depending force constants vary noticeably. It was also possible to find a relationship between the chemical nature and the position of the different substituent and the metal–carbon stretching force constant. For all substances ^{1}H-NMR, ^{13}C-NMR and MS data were also given.

Keywords: FT Raman; FTIR; Arsine; Stibene; Bismuthine; Triphenyl; Normal coordinate analysis; Force constants

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1. Introduction

In 1995 we have published the Fourier transform (FT)-Raman and infrared spectra and the data of the normal coordinate analysis of triphenylbismuth and perdeuterated triphenylbismuth [1]. In recent times we have expanded the calculated modified force field to the homologous compounds triphenylarsine and triphenylstibine and their perdeuterated species. In order to investigate the metal–carbon stretching vibrations and force constants in detail further different substituted compounds were synthesized: tris(2-methylphenyl)-, tris(3-methylphenyl)-, tris(2,4,6-trimethylphenyl)-, tris(2-methoxyphenyl)-, tris(3-methoxyphenyl)-, tris(3-fluorophenyl)- and tris(4-fluoro phenyl)arsine, -stibine and -bismuthine.

Neither complete Raman- and infrared (IR) spectra data nor normal coordinate analysis of these species are known. Only few vibrational information is given [2–4]. Solely vibrational spectroscopic measurements of halogen substituted compounds were performed by van der

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Kelen and de Ketelaere [5,6]. They have suggested an assignment of the vibrational frequencies without model calculations.

Crystal structures are only known for the 2,4,6-trimethyl substituted species [7–10]. For the other investigated compounds the structure elements like bond distances and bond angles have been approached by comparison with similar molecules or other substituted phenyl derivatives [11–19].

The aim of this paper is to evaluate the FT Raman and infrared data of triphenyl compounds, their perdeuterated and methyl-, methoxy- and fluoro-substituted derivatives of arsenic, antimony and bismuth in order to perform a normal coordinate analysis of the complete molecules with C_1 symmetry using a modified valence force field. The calculated force field should establish the assignments of fundamental modes and supply a reasonable and transferable set of force constants especially the metal–carbon force constants which are dependent on the different substitution at the central metal atom.

2. Experimental

The FT-Raman and FT infrared spectra were recorded on Perkin-Elmer 1760 × spectrometer equipment. The 1.064 μm line of a Nd:YAG (Spectron Laser Systems) was used as exciting radiation for Raman spectra registration. The laser power at the samples was 400 mW. A semiconductor InGaAs detector operating at room temperature and additionally, an FTIR spectrometer (Perkin-Elmer 1700) was used in the range 500–100 cm^{-1} at a resolution of 2 cm^{-1}. Frequency accuracy was about ± 2 cm^{-1}. The NMR spectra were measured on a Bruker AM 400 NMR-spectrometer using TMS as internal standard and were reported as δ. Sample synthesis and spectroscopic preparation were carried out under an atmosphere of prepurified nitrogen. All substances were prepared by the Grignard reaction of MCl_3 with ArylMgBr in ether as reported previously [1,20,21]. Only in the case of tris(2,4,6-trimethylphenyl)metal the normal Grignard procedure was not successful. In this case 1,2-dibromethane was added to start the reaction.

$(C_6D_5)_3As$: m.p. 58°C; ^{2}H-NMR ($CHCl_3$): 7.19 (multiplett); ^{13}C-NMR ($CHCl_3$): 139.5; 133.6; 128.5; 128. MS: 321; 239; 235; 164; 160; 157 (100%); 82; 75; 54.

$(C_6D_5)_3Sb$: m.p. 48°C; ^{2}H-NMR ($CHCl_3$): 7.29; 7.18. ^{13}C-NMR ($CHCl_3$): 138.3; 136.1; 128.8; 128.5. MS: 369/367; 287/285; 283/281; 205/203 (100%); 164; 160; 82; 123/121; 54.

Tris(2-methylphenyl)arsine: m.p. 106°C; ^{1}H-NMR ($CDCl_3$): 7.16; 7.15; 6.96; 6.70; 2.34. ^{13}C-NMR ($CDCl_3$): 42.58; 137.48; 133.33; 129.93; 128.64; 126.34; 22.03. MS: 348 (100%); 257; 241; 180; 165; 139; 91; 77.

Tris(2-methylphenyl)stibine: m.p. 96°C; ^{1}H-NMR ($CDCl_3$): 7.18; 7.16; 6.95; 6.92; 2.40. ^{13}C-NMR ($CDCl_3$): 42.58; 137.48; 133.33; 129.93; 128.64; 126.34; 22.03. MS: 394; 303; 212; 181; 165; 152; 105; 91 (100%).

Tris(2-methylphenyl)bismuthine: m.p. 130°C; ^{1}H-NMR ($CDCl_3$): 7.48; 7.26; 7.20; 6.99; 2.37. ^{13}C-NMR ($CDCl_3$): 143.76; 138.69; 129.95; 128.71; 128.71; 26.39. MS: 482; 391; 300; 209 (100%); 181; 167; 91.

Tris(3-methylphenyl)arsine: m.p. 95°C; ^{1}H-NMR ($CDCl_3$): 7.14; 7.11; 7.07; 7.04; 2.23. ^{13}C-NMR ($CDCl_3$): 139.66; 138.12; 134.45; 130.70; 129.21; 21.47. MS: 348; 255; 241; 182; 166 (100%); 91.

Tris(3-methylphenyl)stibine: m.p. 65°C; ^{1}H-NMR ($CDCl_3$): 7.22; 7.15; 7.13; 7.07; 2.22. ^{13}C-NMR ($CDCl_3$): 138.37; 138.25; 136.98; 133.19; 129.37; 128.65; 21.47. MS: 394; 303; 212 (100%); 182; 167; 152; 91.

Tris(3-methylphenyl)bismuthine: m.p. 64°C; ^{1}H-NMR ($CDCl_3$): 7.31; 7.20; 7.16; 7.05; 2.23. ^{13}C-NMR ($CDCl_3$): 138.57; 138.24; 132.58; 128.95; 127.21; 21.47. MS: 482; 391; 300; 209 (100%); 165; 91.

Tris(2,4,6-trimethylphenyl)arsine: m.p. 169°C; ^{1}H-NMR ($CDCl_3$): 6.66; 2.26; 2.13. ^{13}C-NMR ($CDCl_3$): 142.83; 137.38; 135.86; 129.51; 23.44; 20.81. MS: 432 (100%); 313; 297; 282; 237; 221; 193; 178; 119; 105; 91; 77.

Tris(2,4,6-trimethylphenyl)stibine: m.p. 134°C; ^{1}H-NMR ($CDCl_3$): 6.99; 2.36; 2.31. ^{13}C-NMR ($CDCl_3$): 142.21; 140.74; 131.11; 130.91; 24.73; 21.04. MS: 478; 358; 320; 239; 164; 149; 136; 119; (100%) 105; 91; 77.

Tris(2,4,6-trimethylphenyl)bismuthine: m.p. 136°C; ^{1}H-NMR ($CDCl_3$): 6.95; 2.30; 2.25. ^{13}C-NMR ($CDCl_3$): 145.90; 137.23; 129.04; 27.78; 20.92. MS: 566; 447 (100%); 327; 237; 222; 209; 192; 119; 105; 91; 77.

Tris(2-methoxyphenyl)arsine: m.p. 198°C; ^{1}H-NMR ($CDCl_3$): 7.3; 6.88; 6.82; 6.71; 3.75. ^{13}C-NMR ($CDCl_3$): 62.01; 134.22; 129.89; 128.50; 121.27; 110.18; 55.72. MS: 396; 287; 273; 257; 214; 182 (100%); 168; 152; 107; 91.

Tris(2-methoxyphenyl)stibine: m.p. 185°C; ^{1}H-NMR ($CDCl_3$): 7.32; 7.12; 6.88; 6.82; 3.76. ^{13}C-NMR ($CDCl_3$): 162.78; 136.71; 130; 126.84; 121.85; 109.61; 55.63. MS: 442; 335; 305; 289; 228; 214; 168; 121; 107 (100%); 81.

Tris(2-methoxyphenyl)bismuthine: m.p. 165°C; ^{1}H-NMR ($CDCl_3$): 7.45; 7.31; 6.99; 6.87; 3.76. ^{13}C-NMR ($CDCl_3$): 159.84; 129.81; 128.15; 122.05; 114.20; 55.05. MS: 530; 423; 316 (100%); 209; 108; 77.

Tris(3-methoxyphenyl)arsine: m.p. 110°C; ^{1}H-NMR ($CDCl_3$): 7.17; 6.83; 6.82; 6.76; 3.64. ^{13}C-NMR ($CDCl_3$): 159.6; 140.82; 129.54; 126.01; 119; 114.09; 55.11. MS: 396; 287; 273; 257; 214 (100%); 182; 171; 139; 128; 107.

Tris(3-methoxyphenyl)stibine: m.p. 88°C; ^{1}H-NMR ($CDCl_3$): 7.18; 6.94; 6.92; 6.78; 3.64. ^{13}C-NMR ($CDCl_3$): 159.71; 139.29; 129.74; 128.5; 121.47; 114.3; 55.09. MS: 442; 335; 228; 214 (100%); 184; 171; 128; 107; 92; 77.

Tris(3-methoxyphenyl)bismuthine: m.p. 70°C; ^{1}H-NMR ($CDCl_3$): 7.18; 7.00; 6.99; 6.79; 3.64. ^{13}C-NMR ($CDCl_3$): 159.84; 129.81; 128.15; 122.05; 114.20; 55.05. MS: 530; 423; 316; 300; 209 (100%); 92; 77.

Tris(3-fluorophenyl)arsine: m.p. 40°C; ^{1}H-NMR ($CDCl_3$): 7.77 (multi); 7.22. ^{13}C-NMR ($CDCl_3$): 166.24; 136.21; 131.50; 131.35; 120.01; 114.53. MS: 360; 263; 245; 190; 170 (100%); 150; 95; 75.

Tris(3-fluorophenyl)stibine: m.p. 33°C; ^{1}H-NMR ($CDCl_3$): 7.82 (multi); 7.31. ^{13}C-NMR ($CDCl_3$): 165.24; 134.12; 132.61; 131.81; 114.99; 114.71. MS: 406; 311; 216 (100%); 190; 170; 140; 95; 75.

Tris(3-fluorophenyl)bismuthine: m.p. 69°C; ^{1}H-NMR ($CDCl_3$): 7.38; 7.36; 7.31; 6.91. ^{13}C-NMR ($CDCl_3$): 164.02; 157.31; 132.80; 132.07; 123.88; 115.17. MS: 494; 399; 304; 209 (100%) 95; 75.

Tris(4-fluorophenyl)arsine: m.p. 74°C; ^{1}H-NMR ($CDCl_3$): 7.20; 7.20. ^{13}C-NMR ($CDCl_3$): 163.41; 135.28; 134.63; 116.01. MS: 360; 263; 245; 190; 170 (100%); 150; 95; 75.

Tris(4-fluorophenyl)stibine: m.p. 91°C; ^{1}H-NMR ($CDCl_3$): 7.31; 6.95. ^{13}C-NMR ($CDCl_3$): 163.50; 132.94; 121.71; 116.23. MS: 406; 311; 216 (100%); 190; 170; 140; 95; 75.

Tris(4-fluorophenyl)bismuthine: m.p. 92°C; ^{1}H-NMR ($CDCl_3$): 7.64; 7.00. ^{13}C-NMR ($CDCl_3$): 162.85; 149.59; 139.14; 117.97. MS: 494; 399; 304; 209 (100%); 190; 96; 75.

3. Results and discussion

Normal coordinate analysis is carried out by a computer program developed in our research group, based on the program by Shimanouchi [22]. The program Prometheus© follows the GF-Matrix method according to Wilson et al. [23] and works on a normal PC under MS-Windows©. For each substituent the three homologous molecules with different metal central atoms (arsenic, antimony and bismuth) were calculated in one step. The vibrational problem was set up in internal coordinates, in-plane and out-of-plane vibrations were also calculated in one step.

3.1. Normal coordinate analysis

In the first step a model calculation was performed for the one phenyl ring system. After the optimisation of this molecular skeleton the complete molecules as three ring systems were calculated. It has been shown [1] that the normal coordinate analysis of the whole molecule leads to a triple degeneration of the normal vibrations which were calculated by the simplification of the one ring system. The calculated wave numbers and assignments for all molecules (except for the normal triphenyl species) are shown in Tables 1 and 2.

Because we are not able to make reliable infrared measurements < 100 cm^{-1} we have not listed the ring–metal–ring deformation and the skeletal torsion wave numbers and force constants. For the vibrations of the methoxy substi-

Table 1
Calculated vibrational frequencies of perdeuterated triphenyl and methyl-substituted compounds

Perdeuterated triphenyl-				Tris(2-methylphenyl)-				Tris(3-methylphenyl)-				Tris(2,4,6-trimethyl-phenyl)-			
Vibration[a]	AS	Sb	Bi	Vibration[a]	As	Sb	Bi	Vibration[a]	As	Sb	Bi	Vibration[a]	As	Sb	Bi
ν(CH)	2278	2279	2277	ν(CH)	3058	3058	3058	ν(CH)	3068	3069	3068	ν(CH)	3016	3016	3016
ν(CH)	2266	2266	2263	ν(CH)	3041	3041	3041	ν(CH)	3041	3042	3041	ν(CH)	3013	3013	3013
ν(CH)	2259	2260	2257	ν(CH)	3030	3030	3030	ν(CH)	3037	3038	3036	ν(CC)	1649	1652	1650
ν(CH)	2251	2250	2250	ν(CH)	3009	3009	3009	ν(CH)	3015	3015	3011	ν(CC)	1645	1648	1644
ν(CH)	2248	2245	2247	ν(CC)	1618	1619	1618	ν(CC)	1599	1598	1599	ν(CCH$_3$)	1461	1462	1461
ν(CC)	1534	1532	1528	ν(CC)	1560	1560	1559	ν(CC)	1570	1569	1567	ν(CC)	1437	1437	1437
ν(CC)	1527	1528	1526	δ(CCH)	1472	1472	1470	δ(CCH)	1484	1483	1482	ν(CC)	1413	1415	1414
δ(CCH)	1340	1333	1326	δ(CCH)	1439	1438	1437	ν(CC)	1421	1419	1416	ν(CC)	1276	1277	1275
δ(CCH)	1306	1306	1299	δ(CCH)	1292	1292	1292	δ(CCH)	1313	1313	1313	ν(CC)	1235	1235	1235
ν(CC)	1253	1251	1254	ν(CC)	1259	1259	1259	ν(CC)	1272	1270	1268	δ(CCH)	1185	1185	1185
δ(CCH)	1036	1034	1043	δ(CCH)	1233	1233	1232	ν(CC)	1255	1254	1253	δ(CCH)	1036	1035	1034
δ(CCH)	1032	1023	1021	δ(CCH)	1181	1181	1181	δ(CCH)	1174	1174	1174	ν(CCH$_3$)	998	998	995
δ(CCC)	947	947	954	ν(CC)	1106	1102	1099	ν(CC)	1070	1065	1063	ν(CC)	959	959	959
δ(CCH)	853	850	861	δ(CCC)	1058	1049	1038	ν(CC)	1062	1059	1052	γ(CH)	923	923	923
δ(CCH)	844	843	854	ν(CC)	1033	1033	1032	δ(CCC)	1037	1037	1036	γ(CH)	894	894	894
ν(CC)	810	816	812	γ(CH)	1004	1004	1004	γ(CH)	1011	1011	1011	γ(CM)	800	792	800
ν(CC)	795	792	794	γ(CH)	948	948	948	γ(CH)	930	930	930	γ(CCH$_3$)	593	592	593
γ(CH)	781	778	773	γ(CH)	864	864	864	γ(CH)	915	915	915	δ(CCCH$_3$)	561	561	560
γ(CH)	753	750	734	γ(CM)	797	797	796	ν(CC)	842	834	825	ν(CCH$_3$)	559	564	557
γ(CH)	729	726	724	δ(CCC)	755	752	750	γ(CH)	777	773	771	γ(CCH$_3$)	549	549	549
γ(CM)	685	682	688	γ(CH)	735	735	735	γ(CM)	713	706	702	δ(CCC)	530	522	519
γ(CH)	666	664	669	δ(CCC)	657	651	643	δ(CCC)	663	657	650	δ(CCC)	495	495	495
δ(CCC)	641	631	623	δ(CCC)	529	529	527	γ(CCH$_3$)	619	616	615	γ(CCH$_3$)	378	366	355
γ(CH)	527	525	530	γ(CCH$_3$)	455	454	454	δ(CCC)	520	520	520	δ(CCCH$_3$)	323	308	302
δ(CCC)	592	591	591	γ(CH)	443	443	443	δ(CCCH$_3$)	459	458	453	δ(CCCH$_3$)	290	290	290
τ(HCCH)	415	412	394	δ(CCCH$_3$)	413	411	408	γ(CH)	418	418	417	τ(HCCH)	251	251	251
τ(MCCH)	346	344	331	τ(HCCH)	287	275	263	ν(CM)	294	253	243	δ(CCCH$_3$)	195	195	195
δ(CCM)	324	275	246	ν(CM)	239	228	213	τ(HCCH)	253	243	223	ν(CM)	237	205	174
ν(CM)	226	214	208	δ(CCM)	167	168	165	δ(CCM)	221	202	183	δ(CCM)	170	161	147
τ(HCCH)	178	174	171	τ(HCCH)	155	155	155	τ(HCCH)	175	167	157	τ(HCCH)	102	96	92

[a] M, metal; ν, stretching vibration; δ, deformation; γ, out-of-plane deformation; τ, torsion.

Table 2
Calculated vibrational frequencies of the methoxy- and fluoro-substituted compounds

Tris(2-methoxyphenyl)-				Tris(3-methyoxphenyl)-				Tris(3-fluorophenyl)-				Tris(4-fluorophenyl)-			
Vibration[a]	As	Sb	Bi	Vibration[a]	As	Sb	Bi	Vibration[a]	As	Sb	Bi	Vibration[a]	As	Sb	Bi
ν(CH)	3052	3051	3051	ν(CH)	3054	3054	3054	ν(CH)	3036	3036	3036	ν(CH)	3031	3031	3031
ν(CH)	3022	3022	3022	ν(CH)	3033	3033	3033	ν(CH)	3015	3015	3016	ν(CH)	3018	3018	3018
ν(CH)	3004	3004	3004	ν(CH)	3031	3031	3031	ν(CH)	3013	3013	3013	ν(CH)	3010	3011	3011
ν(CH)	2991	2991	2991	ν(CH)	3012	3012	3012	ν(CH)	2994	2994	2994	ν(CH)	2999	2999	2999
ν(CC)	1601	1602	1601	ν(CC)	1611	1611	1611	ν(CC)	1632	1632	1631	ν(CC)	1646	1646	1645
ν(CC)	1577	1576	1575	ν(CC)	1570	1568	1567	ν(CC)	1576	1576	1575	ν(CC)	1577	1576	1575
δ(CCH)	1498	1497	1496	ν(CC)	1483	1481	1481	ν(CC)	1489	1488	1489	ν(CC)	1517	1515	1512
δ(CCH)	1434	1433	1431	ν(CC)	1419	1415	1414	ν(CC)	1427	1425	1424	δ(CCH)	1393	1392	1391
δ(CCH)	1302	1302	1302	δ(CCH)	1320	1320	1319	δ(CCH)	1333	1332	1331	δ(CCH)	1312	1311	1310
ν(CC)	1266	1264	1263	δ(CCH)	1305	1304	1303	δ(CCH)	1305	1304	1303	δ(CCH)	1309	1309	1308
δ(CCH)	1236	1235	1233	ν(CC)	1257	1256	1255	ν(CC)	1256	1255	1255	ν(CC)	1261	1260	1259
δ(CCH)	1181	1181	1181	δ(CCH)	1174	1174	1174	δ(CCH)	1174	1174	1174	δ(CCH)	1165	1165	1165
ν(CC)	1090	1086	1083	ν(CC)	1073	1065	1062	ν(CC)	1092	1088	1077	ν(CC)	1110	1110	1110
ν(CC)	1060	1050	1042	ν(CC)	1062	1061	1055	ν(CC)	1061	1061	1061	ν(CC)	1093	1069	1050
δ(CCC)	1021	1021	1015	δ(CCC)	1025	1024	1024	δ(CCC)	1017	1018	1019	γ(CH)	1025	1024	1022
γ(CH)	1003	1003	1003	γ(CH)	1013	1013	1013	γ(CH)	1011	1011	1011	δ(CCC)	1007	1007	1007
γ(CH)	968	967	968	γ(CH)	996	996	996	γ(CH)	937	937	937	γ(CH)	968	968	968
γ(CH)	908	905	907	γ(CH)	918	918	918	γ(CH)	905	906	905	γ(CH)	863	863	863
ν(OCH$_3$)	879	879	879	ν(OCH$_3$)	915	911	907	ν(CF)	861	859	847	ν(CF)	828	824	819
γ(CH)	861	859	860	γ(CH)	878	877	877	γ(CM)	777	793	782	γ(CH)	807	806	806
γ(CH)	755	752	753	ν(OCH$_3$)	814	811	806	γ(CH)	722	732	724	γ(CM)	760	755	749
ν(OCH$_3$)	718	715	712	γ(CH)	721	721	721	δ(CCC)	678	677	676	δ(CCC)	625	626	626
δ(CCC)	648	642	633	γ(CM)	708	696	689	γ(CF)	650	653	649	γ(CF)	614	612	611
γ(CM)	536	530	531	δ(CCC)	664	659	652	δ(CCC)	490	490	490	δ(CCC)	527	514	503
δ(CCC)	504	501	498	δ(CCC)	547	546	546	δ(CCF)	433	430	431	δ(CCF)	429	427	425
γ(CH)	451	448	448	γ(CH)	410	409	409	γ(CH)	405	405	399	γ(CH)	365	365	365
δ(CCM)	362	349	341	δ(CCM)	357	342	335	ν(CM)	293	245	225	τ(HCCH)	324	318	316
τ(HCCH)	288	273	273	ν(CM)	298	253	213	τ(HCCH)	234	234	234	ν(CM)	275	234	197
ν(CM)	275	245	207	τ(CCOCH$_3$)	282	290	290	τ(HCCH)	219	215	210	δ(CCM)	239	223	213
τ(HCCH)	169	158	155	τ(HCCH)	218	213	210	δ(CCM)	193	176	170	τ(HCCH)	119	113	110
δ(COCH$_3$)	78	63	55	δ(COCH$_3$)	113	96	87								
τ(CCOCH$_3$)	45	44	44	τ(CCOCH$_3$)	84	80	79								
δ(COCH$_3$)	44	43	37	δ(COCH$_3$)	75	69	59								

[a] M, metal; ν, stretching vibration; δ, deformation; γ, out-of-plane deformation; τ, torsion.

Table 3
Force constants set for the phenyl ring system

Force constant[a]	Value	Force constant[a]	Value
f_1 $\nu(M^b{-}C)$	c	f_{15} $\nu(C{-}C)/\nu(C{-}C)_o$	0.858
f_2 $\nu(C{-}C)$	6.538	f_{16} $\nu(C{-}C)/\nu(C{-}C)_m$	−0.300
f_3 $\nu(C{-}H)$	4.979	f_{17} $\nu(C{-}C)/\nu(C{-}C)_p$	0.423
f_4 $\delta(C{-}M{-}C)$	d	f_{18} $\nu(C{-}H)/\nu(C{-}C)$	0.034
f_5 $\delta(C{-}C{-}C)$	1.143	f_{19} $\nu(C{-}H)/\delta(C{-}C{-}H)$	−0.096
f_6 $\delta(C{-}C{-}{-}{-}M)$	c	f_{20} $\nu(C{-}C)/\delta(C{-}C{-}C)$	0.490
f_7 $\delta(C{-}C{-}H)$	0.501	f_{21} $\nu(C{-}C)/\delta(C{-}C{-}H)$	0.219
f_8 $\tau(C_2{-}M{-}C{-}C_2)$	0.484	f_{22} $\nu(M{-}C)/\delta(C{-}C{-}M)$	c
f_9 $\tau(H/C{-}C{-}C{-}C/H)_{o(Bi)}$	0.456	f_{23} $\delta(C{-}C{-}C)/\delta(C{-}C{-}C)$	0.094
f_{10} $\tau(H/C{-}C{-}C{-}C/H)_{m(Bi)}$	0.330	f_{24} $\delta(C{-}C{-}C)/\delta(C{-}C{-}H)$	0.058
f_{11} $\gamma(C_3{-}M)$ out-of-plane wag	c	f_{25} $\gamma(C_3{-}M)/\gamma(C_3{-}H)$	0.085
f_{12} $\gamma(C_3{-}H)$ out-of-plane wag	0.290	f_{26} $\gamma(C_3{-}H)/\gamma(C_3{-}H)$	0.029
f_{13} $\gamma(C_2H{-}C)$ out-of-plane wag	0.058	f_{27} $\tau(C_2{-}M{-}C{-}C_2)/\tau(H/C{-}C{-}C{-}C/H)$	0.030
f_{14} $\nu(C{-}H)/\nu(C{-}H)_o$	0.062	f_{28} $\tau(H/C{-}C{-}C{-}C/H)/\tau(H/C{-}C{-}C{-}C/H)$	0.065

[a] Force constant dimension: valence 10^2 N m^{-1}; deformation 10^{-18} N m; valence/valence 10^2 N m^{-1}; valence/deformation 10^{-8} N; deformation/deformation 10^{-18} N m.

[b] M = arsenic, antimony, bismuth.

[c] Values for the different molecules see Table 5.

[d] For the $\delta(C{-}M{-}C)$ force constant see text.

Table 4
Force constants for the different substituents

Force constant[a]		Force constant[a]	
Methyl-substituted derivates	Value	Fluorine-substituted derivates	Value
$\nu(C{-}CH_3)$	4.601	$\nu(C{-}F)$	6.198
$\delta(C{-}C{-}CH_3)$	0.804	$\delta(C{-}C{-}F)$	0.862
$\gamma(C_3{-}CH_3)$ out of plane wag	0.532	$\gamma(C_3{-}F)$ out of plane wag	0.615
$\nu(C{-}CH_3)/\delta(C{-}C{-}CH_3)$	0.132	$\nu(C{-}F)/\delta(C{-}C{-}F)$	0.005
Methoxy-substituted derivates			
$\nu(C{-}O)$	5.812	$\gamma(C_3{-}O)$ out-of-plane wag	0.854
$\nu(O{-}CH_3)$	6.310	$\tau(C/C{-}O{-}CH_3)$	0.547
$\delta(C{-}C{-}O)$	0.578	$\nu(C{-}O)/\delta(C{-}C{-}O)$	0.034
$\delta(C{-}O{-}CH_3)$	0.745	$\nu(O{-}CH_3)/\delta(C{-}O{-}CH_3)$	0.010

[a] Dimensions see Table 3.

tuted molecules the wave numbers < 100 cm^{-1} are given, but they were not used for the force constants calculations. Since we were mainly interested in the ring vibrations we have calculated the methyl group as a single point mass. The mean difference between the observed and the calculated wave numbers for the set of 27 substances is about 0.8%.

3.2. Force constants

The set of force constants of the ring system as the result of the normal coordinate analysis can be found in Table 3. These force constants are in good agreement with the corresponding set of force constants published for triphenylbismuth [1]. In Table 4 the force constants for the different

Table 5
Metal–carbon force constants

Substances	Force constants[a]			
Arsine	ν(As–C)	δ(C–C–As)	γ(C_3–As) out-of-plane	ν(As–C)/δ(C–C–As)
Triphenyl-	2.458	1.041	0.947	0.499
Tris(2-methylphenyl)-	2.397	1.247	1.153	0.705
Tris(3-methylphenyl)-	2.360	1.207	1.015	0.381
Tris(2,4,6-trimethylphenyl)-	2.242	1.014	0.960	0.888
Tris(2-methoxyphenyl)-	2.355	1.060	0.935	0.619
Tris(3-methoxyphenyl)-	2.601	1.023	0.987	0.524
Tris(3-fluorophenyl)-	2.894	0.795	0.972	0.412
Tris(4-fluorophenyl)-	2.522	1.104	1.001	0.563
Stibine	ν(Sb–C)	δ(C–C–Sb)	γ(C_3–Sb) out-of-plane	ν(Sb–C)/δ(C–C–Sb)
Triphenyl-	2.070	1.078	0.939	0.503
Tris(2-methylphenyl)-	2.001	1.284	1.145	0.709
Tris(3-methylphenyl)-	1.949	1.323	1.008	0.523
Tris(2,4,6-trimethylphenyl)-	1.885	1.080	0.960	0.857
Tris(2-methoxyphenyl)-	1.970	1.075	0.923	0.620
Tris(3-methoxyphenyl)-	2.234	0.978	0.984	0.517
Tris(3-fluorophenyl)-	2.580	0.814	1.108	0.510
Tris(4-fluorophenyl)-	2.134	1.143	0.994	0.567
Bismuthine	ν(Bi–C)	δ(C–C–Bi)	γ(C_3–Bi) out-of-plane	ν(Bi–C)/δ(C–C–Bi)
Triphenyl-	1.662	1.055	0.929	0.499
Tris(2-methylphenyl)-	1.601	1.261	1.135	0.705
Tris(3-methylphenyl)-	1.544	1.222	1.010	0.550
Tris(2,4,6-trimethylphenyl)-	1.480	1.091	0.929	0.724
Tris(2-methoxyphenyl)-	1.560	1.060	0.950	0.651
Tris(3-methoxyphenyl)-	1.822	0.987	1.001	0.499
Tris(3-fluorophenyl)-	2.161	0.900	1.052	0.563
Tris(4-fluorophenyl)-	1.726	1.186	0.984	0.569

[a] Dimensions see Table 3.

substituents are listed. But the main focus of our research lies in the force constants which are directly assigned to the metal–carbon bond. These force constants are affected by the nature and the position of the substituent (Table 5).

3.3. Metal–carbon stretching vibrations

With the exception of the substituents in 2 position fluorine- and methoxy substituents raise the metal–carbon force constants noticeably. In comparison with these substituents the methyl substituents decrease the metal–carbon force constant. The systematical comparison of all metal–carbon valence force constants for the investigated compounds is shown in Fig. 1. It can be seen that the difference between the force constants for arsenic, antimony and bismuth is about the same for the different substituents. The force constants for the triphenyl- and the perdeuterated-triphenyl species are identical as was shown for the triphenylbismuth [1].

As an example of the characteristic change of the carbon–metal force constant the FT-Raman spectra of perdeuterated triphenylstibine (Fig. 2) and tris(3-fluorophenyl)stibine are shown (Fig. 3). For two selected vibrations the LX-drawings are also illustrated (amplitude factor 50).

For the unsubstituted triphenylstibine compound the antimony–phenyl ring stretching vibra-

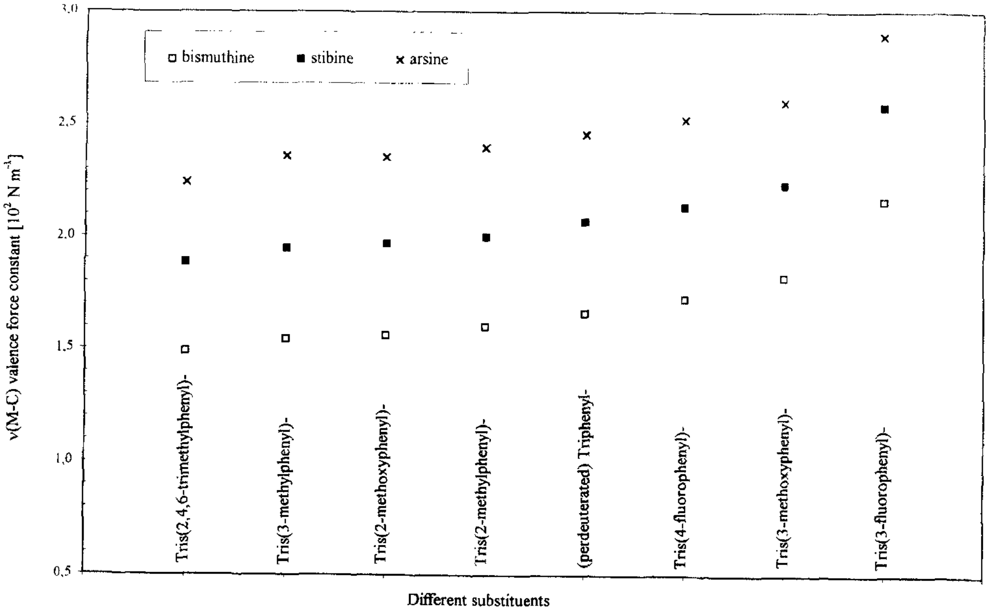

Fig. 1. Metal–carbon stretching force constants.

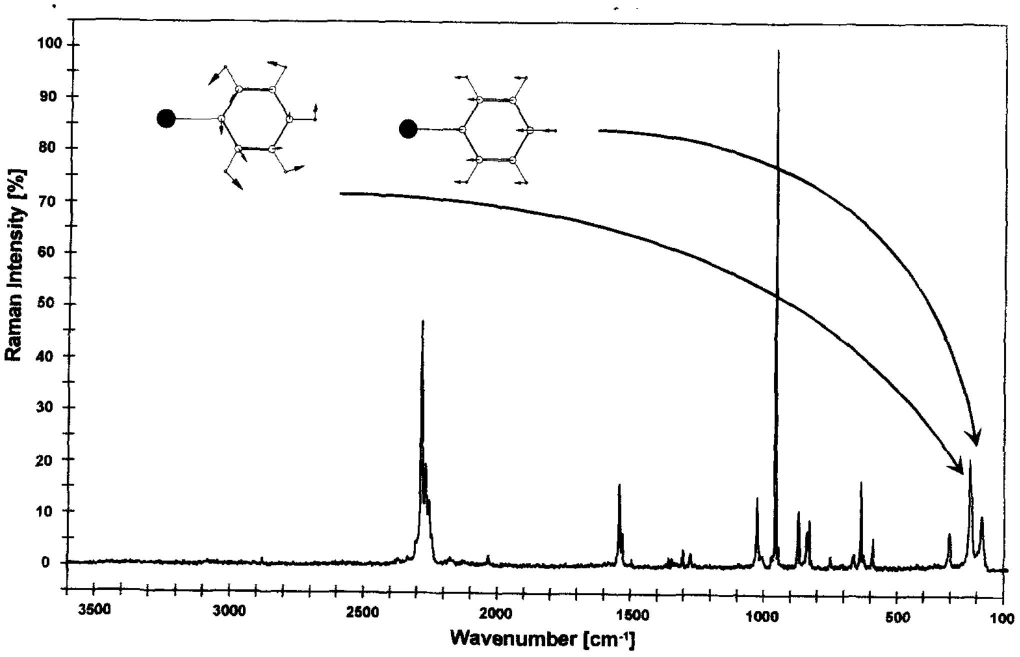

Fig. 2. FT-Raman spectrum of $(C_6D_5)_3Sb$ (KBr disc).

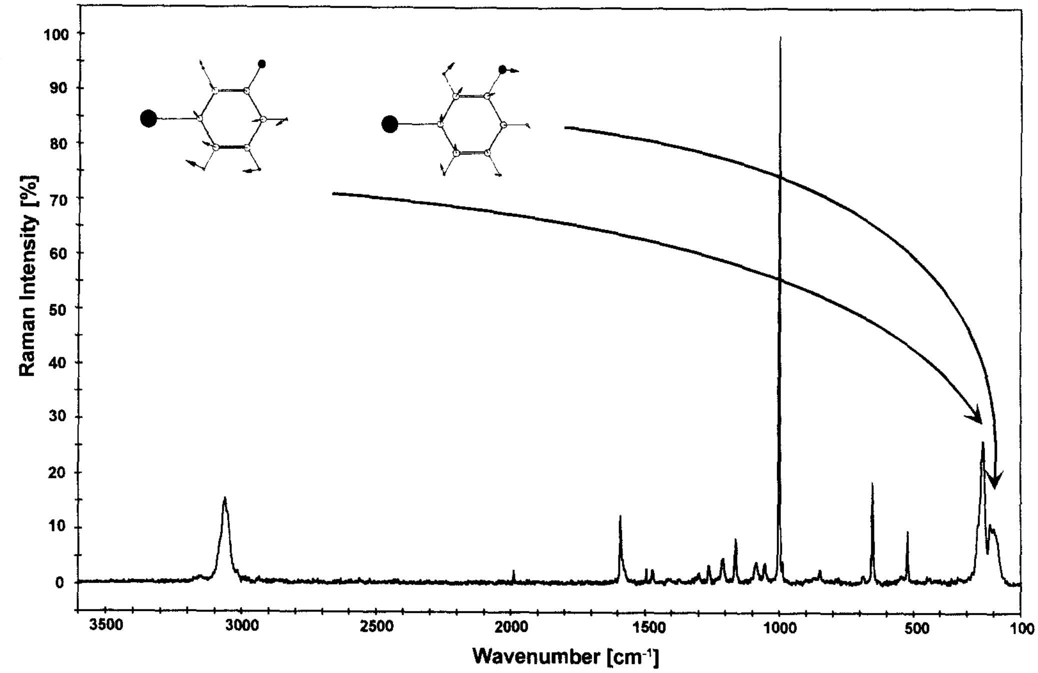

Fig. 3. FT-Raman spectrum of (m-$FC_6H_4)_3Sb$ (KBr disc).

tion can be found at 214 cm^{-1}. The antimony–carbon stretching vibration ($f(\nu(Sb–C)) = 2.07\ 10^2$ Nm^{-1}) shows a potential energy distribution with ν(Sb–C) (68), whereas the Sb–C–C deformation character is only 5%. Thus, this vibration mode can be interpreted as a characteristic stretching vibration, as shown in the LX-drawing (Fig. 2). The antimony–carbon deformation vibration at 275 cm^{-1} was calculated with a potential energy distribution with δ(C–C–Sb) (70) and ν(Sb–C) (4). In contrast to this, the antimony–carbon force constant for the 3-fluoro-substituted compound rises to 2.58 10^2 Nm^{-1} and the antimony–carbon stretching vibration should be found at higher wave numbers. Therefore, the Sb–C–C deformation mode should be shifted to a lower frequency because of the larger mass of the fluorine substituent. This effect can be observed in the FT-Raman spectrum of tris(3-fluorophenyl)stibine. The stretching vibration was found at 245 cm^{-1}. The potential energy distribution has been calculated with ν(Sb–C) (55) and δ(C–C–Sb) (15). For the deformation mode which can be observed at 215 cm^{-1} the calculation yields a potential energy distribution with δ(C–C–Sb) (70) and ν(Sb–C) (6).

References

[1] C. Ludwig, H.-J. Götze, Spectrochim. Acta Part A 51A (1995) 2019.
[2] G.B. Deacon, J.A. Jones, Aust. J. Chem. 16 (1963) 499.
[3] L.D. Pettit, D. Turner, Spectrochim. Acta Part A 24A (1968) 999.
[4] Y. Matano, M. Kinoshita, H. Suzuki, Bull. Chem. Soc. Jpn. 65 (12) (1992) 3504.
[5] R.F. de Ketelaere, G.P. van der Kelen, J. Organometal. Chem. 73 (1974) 251.
[6] F.T. Delbeke, R.F. de Ketelaere, G.P. van der Kelen, J. Organometal. Chem. 28 (1971) 225.
[7] M. Ates, H.J. Breunig, K.H. Ebert, R. Kaller, M. Dräger, U. Behrens, Z. Naturforsch. 47b (1992) 503.
[8] A.N. Sobolev, V.E. Zavodnik, V.K. Belsky, Proc. 3rd Int. Semin. on Crystal Chemistry and Coordinated Organometallic Compounds, Wroclaw, Poland, 1977, p. 149.
[9] A.N. Sobolev, I.P. Romm, V.K. Belsky, E.N. Guryanova, Koord. Khim. 6 (6) (1980) 945.
[10] A.N. Sobolev, I.P. Romm, N.Y. Chernikova, V.K. Belsky, E.N. Guryanova, J. Organometal. Chem. 219 (1981) 35.
[11] J. Trotter, Can. J. Chem. 41 (1963) 14.
[12] A.N. Sobolev, V.K. Belsky, Koord. Khim. 9 (2) (1983) 262.
[13] A.N. Sobolev, V.K. Belsky, J. Organomet. Chem. 214 (1983) 41.

[14] A.N. Sobolev, I.P. Romm, V.K. Belsky, E.N. Guryanova, J. Organomet. Chem. 179 (1979) 153.

[15] R. Graziani, G. Bombieri, L. Volponi, C. Panattoni, R.J.H. Clark, J. Chem. Soc. A (1969) 1236.

[16] N.L. Owen, R.E. Hester, Spectrochim. Acta Part A 25A (1969) 343.

[17] A. Schmuck, K. Seppelt, Chem. Ber. 122 (1989) 803.

[18] E.G. Claeys, G.P. van der Kelen, R.F. de Ketelaere, J. Mol. Struct. 40 (1977) 89.

[19] G. Fogarasi, A.G. Császár, Spectrochim. Acta Part A 44A (1988) 1067.

[20] P. Pfeiffer, Ber. Dtsch. Chem. Ges. 37 (1904) 4620.

[21] F.F. Blicke, U.O. Oakdale, F.D. Smith, J. Am. Soc. 53 (1931) 1025.

[22] T. Shimanouchi, Computer Programs for Normal Coordinate Treatment of Polyatomic Molecules by the University of Tokyo, Tokyo, 1968.

[23] E.B. Wilson, Jr., J.C. Decius, P.C. Cross, Molecular Vibrations, McGraw-Hill, New York, 1955.