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Low Frequency Vibrational Spectra of Triarylgermanium Pseudohalides

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Infrared spectra of arylgermanium derivatives in the low frequency region have attracted attention of only a few workers[1–3] in recent years. We synthesized some triarylgermanium pseudohalides (Aryl= C_6H_5, p-$CH_3C_6H_4$, pseudohalide=CN, NCO, NCS) and recorded their spectra as KBr discs in the region 650—250 cm^{-1} using a Perkin-Elmer Model 521 Spectrophotometer. The results and fundamental absorption frequencies along with their assignments are given. The characteristic vibrations of pseudohalide groups are identified at the expected positions and have been discussed together with the preparation and purification of the compounds.[4]

Some vibrations of the aromatic rings bonded to germanium atom fall in the recorded range of the spectra. Whiffen's nomenclature[5] has been used throughout to designate various modes of aromatic ring vibrations. A mass sensitive ring stretching vibration *t* has been observed in all the compounds in the range 370—270 cm^{-1}.[3] It is known[1,3] that when more than one aryl group is present in the molecule, a splitting of this absorption occurs giving rise to a lower component *t'*. Accordingly we have identified two distinct bands in triphenyl and tri-*p*-tolylgermanium compounds, the position of the absorption in the former being slightly towards lower frequency side than the latter. The two absorptions have been described by some earlier workers as asymmetric and symmetric phenyl-metal stretching.[2,6–8] The two other mass sensitive aromatic ring stretchings q and r lie above the reported range of the spectra. However, in triphenylgermanium derivatives they have been identified at 1095±1 cm^{-1} vs and 669±1 cm^{-1} w, while in corresponding *p*-tolyl derivatives they lie at 1088±1 cm^{-1} vs and 702±1 cm^{-1} w respectively.

The strongest absorption in the whole of the spectra is a mass-sensitive out-of-plane ring bending mode which appears as a doublet[6] separated by about 10 cm^{-1} and distinguished by y and y'. Apart from its slight sensitiveness to the mass of the substituent atom,[3] it appears to be dependent on the nature of the substitution of the benzene nucleus. We[9] have identified this absorption in a large number of aryltin compounds and have observed that *o*-, *m*- or *p*- substitution on the benzene ring produces an appreciable change in its position. Some earlier workers[10,11] have mistaken this absorption to be a tin-phenyl stretch. The two other mass sensitive ring deformations u and x are expected to lie below the recorded range of the spectra, although some workers[3,12] have preferred to call the lower component of t by the mode u.

TABLE 1. VIBRATIONAL FREQUENCIES OF TRIARYLGERMANIUM PSEUDOHALIDES

Assignment	$(C_6H_5)_3GeNCS$	$(C_6H_5)_3GeNCO$	$(C_6H_5)_3GeCN$	$(p\text{-}CH_3C_6H_4)_3$-GeNCS	$(p\text{-}CH_3C_6H_4)_3$-GeNCO	$(p\text{-}CH_3C_6H_4)_3$-GeCN
s	617 vw	622 w	614 sh	642 w	643 w	641 w
δ(NCO)		610 sh			606 sh	
CH_3-C_6H_5 rock.				592 s	594 s	595 s
y	471 sh	470 s	468 vs	500 s	500 s	500 s
y'	462 vs	462 vs	456 s	492 vs	492 vs	493 vs
δ(NCS)	478 sh			477 sh		
ν(Ge-NCO)		450 m			—	
Overtone of δ(Ge-CN)			438 m			437 m
w	390 vw	393 vw	390 vw	445 vw(b)	448 vw	447 vw
ν(Ge-NCS)	368 sh			374 sh		
t	340 vs(b)	338 s(b)	365 m	370 m	370 m	376 m
t'	272 w	285 w	276 w	328 m	327 m	327 m

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Out of the four mass insensitive ring deformations p, v, s and w only the last two occur in this region. Their position appears to be affected by the nature of the aryl group. An absorption of strong intensity consistently identified in the spectra of *p*-tolyl compounds at 592—595 cm^{-1} has tentatively been assigned to the CH_3-C_6H_5 rocking mode.