Rotational isomerism in alkylgermane molecules (Alk = Bu^n, n-C_6H_{13}) according to Raman spectroscopy and quantum-chemistry results

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Temperature study of Raman spectra of alkylgermanes (Alk = Bu^n, n-C_6H_{13}) in liquid, polycrystalline, and glassy states was carried out. The spectra of liquid samples are complicated, because compounds exist as equilibrium mixtures of rotational isomers due to hindered rotation about C—C and Ge—C bonds. In crystals, only the most stable conformer persists, which results in simplification of the spectrum. Unlike n-hexylgermanes, n-butylgermanes crystallize on cooling with difficulties. Quantum-chemical calculations of the geometry and normal coordinate analysis of the possible conformers of the Bu^nGeH_3, Bu^nGeCl_3, and $Bu^n{}_2GeCl_2$ molecules were performed. The unusually large (~65 cm^{-1}) difference between the experimental ν(Ge—C) stretching frequencies of the *trans* and *gauche* conformers about the C—C bond nearest to the Ge atom is attributed to the difference in the electronic structure of these conformers, which is manifested in the differences in the Ge—C bond lengths, molecular geometry, and their force fields and, consequently, affects the mode frequencies and eigenvectors.

Key words: alkylgermanes, rotational isomerism, conformers, Raman spectroscopy, quantum-chemical calculations.

The last few decades have been marked by an enormous growth in the number of studies of a new type of conjugated organometallic high polymers, *viz.*, polydialkylmetallanes $[R_2M]_n$, whose homoatomic chains consist of M atoms (M = Si, Ge, or Sn).[1—7] These polymers exhibit unique electrooptical and electrophysical properties promising for industrial applications. However, these properties depend substantially on conformational ordering of both the main chain and side groups. Therefore, it is important to learn to determine the conformational state of alkyl groups in polydialkylmetallanes above and below the temperature of their thermochromic phase transitions. An approach proposed in our earlier studies[8,9] involves a comparison of the Raman spectra of the $[R_2M]_n$ polymer and the corresponding R_2MX_2 monomer, which requires a detailed examination of rotational isomerism in molecules of monomers. In the present study, this approach was applied to alkylgermanes (AG) as models of the corresponding poly(di-n-alkylgermanes).[2—4,10,11]

Earlier, we have thoroughly investigated rotational isomerism in alkyl derivatives of Ga,[12] As, Sb,[13] and Si[14,15] by vibrational spectroscopy. Analogous data for alkyl compounds of these and other main-group elements and metals were published in the literature.[16—19] In particular, the results of experimental research into rotational isomerism in various types of organosilicon compounds and the corresponding calculations of vibrational modes were reported.[18] Vibrational spectra of a series of organotin compounds Bu_xSnCl_{4-x} were studied in detail.[17] Analysis of these data led to a conclusion that Raman spectra of liquid samples of main-group element (El) compounds containing the Et group may reveal rotational isomerism about El—C bonds. This is manifested in the ν(El—C) skeletal stretching and δ(ElCC) bending modes, the frequency difference between the conformers being no larger than 15 cm^{-1}. An analogous phenomenon was observed even in crystalline high-molecular-weight poly(diethylsilane), which exhibits an order—disorder phase transition at ~35 °C accompanied by "defreezing" of rotational isomerism about Si—C bonds.[15]

If a molecule of a heteroorganic compound contains an n-propyl or longer n-alkyl substituent, the following unusual phenomenon is observed: the Raman spectra of liquid compounds exhibit two intense broad bands assigned to ν(El—C) stretching modes with substantially different (up to 100 cm^{-1}) frequencies. After crystalliza-

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tion of a sample, only one of these bands persists in the spectrum. Analysis of these results led to a conclusion[12,19] that this phenomenon is associated with the occurrence in the liquid phase of rotational isomerism in the El—C(1)—C(2)—R fragment due to hindered rotation about the C(1)—C(2) bond resulting in the appearance of *trans* (*anti*) and *gauche* conformers about this bond. Interestingly, the frequencies of the analogous *trans* (*T*) and *gauche* (*G*) conformers of *n*-alkanes[20—25] differ by only 15—20 cm^{-1}. Therefore, such a large frequency difference between two conformers of heteroorganic compounds of the above-mentioned type caused surprise and remained unexplained for a long time.

The aim of the present study was to experimentally investigate rotational isomerism by variable-temperature Raman spectroscopy for a new class of compounds, *viz.*, alkylgermanes, and theoretically examine this phenomenon using quantum-chemical calculations of geometric parameters and normal coordinate analysis of various conformers.

Results and Discussion

We measured the Raman spectra of five alkylgermanes, *viz.*, $Bu^n{}_4Ge$ (**1**), $Bu^n{}_2GeCl_2$ (**2**), $Bu^n{}_2GeBr_2$ (**3**), $(n\text{-}C_6H_{13})_2GeCl_2$ (**4**), and $(n\text{-}C_6H_{13})_2GeBr_2$ (**5**) (Figs. 1—6 and Tables 1 and 2), as well as the IR and Raman spectra of the cyclic trimer $[(n\text{-}C_6H_{13})_2GeO]_3$ (**6**) (Fig. 7).

The skeleton of molecule **1** (GeC_4) belongs to the local symmetry group T_d (if it is not lowered due to the nonequivalence of the *n*-butyl groups caused by rotational isomerism; see below). In this case, the 550—650 cm^{-1} region of the Raman spectrum of compound **1** should exhibit two lines corresponding to Ge—C stretching modes (ν(Ge—C)), *viz.*, an intense polarized line of A_1 symmetry and a less intense depolarized line of F_2 symmetry. The corresponding modes in the spectrum of Me_4Ge[19,26] have frequencies of 558 and 595 cm^{-1}. Similar patterns (two modes of A_1 and B_1 symmetry in the ν(Ge—C) region) should be observed in the Raman spectra of compounds **2—5** in the absence of rotational isomerism (see below). The C_2GeHal_2 fragment (Hal is halogen) common to these molecules has the local symmetry C_{2v}, and stretching modes of this fragments with frequencies lower than 700 cm^{-1} are easily interpretable based on analysis of the spectra of Me_2GeHal_2 [26] (see Table 1). An increase in the frequencies of ν^s(Ge—C) in the presence of halogen atoms in the molecules is quite understandable. It was demonstrated[27] that the frequency of the ν^s(Ge—C) stretching mode in the Raman spectra of AG is determined by the overall electronegativity of four substituents at the Ge atom.

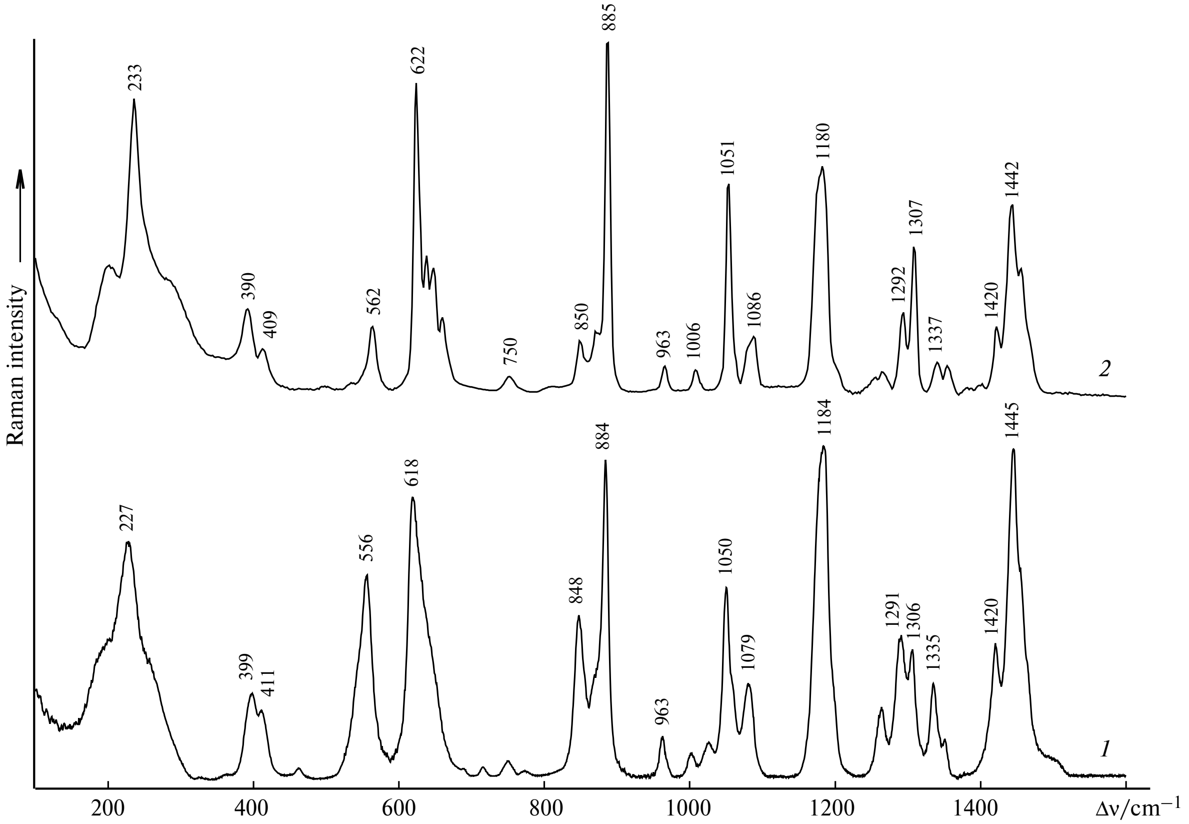


Fig. 1. Raman spectra of Bu_4Ge in the liquid (20 °C) (*1*) and glassy (−140 °C) (*2*) states.

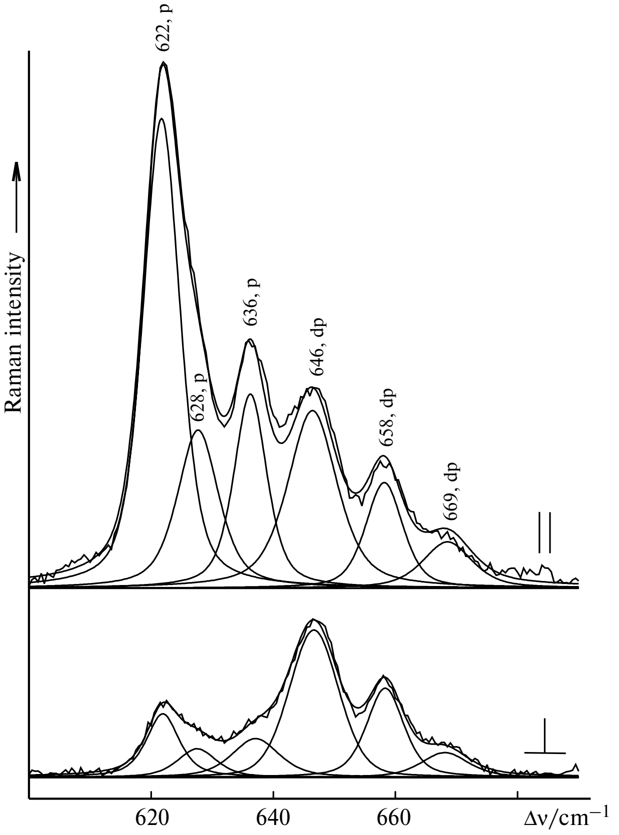
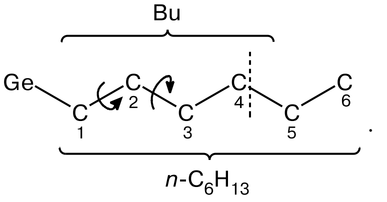


Fig. 2. Band corresponding to the ν(Ge—C) stretching modes of the *trans* conformers about the C(1)—C(2) bond in the Raman spectrum of glassy Bu_4Ge at –140 °C recorded using different polarizations of the laser beam and the corresponding curve fitting analysis.

However at room temperature, all known alkylgermanes are liquids and, consequently, they should exist as equilibrium mixtures of various conformers, which should lead to complication of the spectra.

Let us consider the isolated fragment



It is evident that not only conformational isomerism associated with hindered rotation about the C(1)—C(2) bond but also conformational isomerism about the C(2)—C(3) bond may occur in molecules containing *n*-butyl groups, *i.e.*, generally speaking, the following distinguishable conformers can exist: *TT*, *TG*, *GT*, *GG*, and *GG´*. Evidently, the number of conformational possibilities in the *n*-hexyl fragment is even larger due to hindered rotation about the C(3)—C(4) and C(4)—C(5) bonds. The fragment presented above is displayed in an all-*trans* conformation. In the presence of several alkyl groups in AG molecules, the above-mentioned conformers can, in principle, exist for each of these groups. In addition, there is a possibility of rotational isomerism due to hindered rotation about Ge—C bonds. All these facts can lead to a further complication of the spectral pattern. However, it is evident that certain conformers cannot occur due to steric hindrances.

It is noteworthy that the Raman spectra of Pr_4Ge[27] and compounds **1—6** recorded at 20 °C exhibit two intense broadened bands assigned to ν(Ge—C) with maxima in the regions of 555—585 and 620—655 cm^{-1} (see Table 2 and Figs. 1—7); the distance between these maxima reaches ~65 cm^{-1}. Evidently, the presence of these bands in the Raman spectra of liquid alkylgermanes is associated, like in the spectra of *n*-alkyl derivatives of other elements,[12,19] with the presence of *trans* and *gauche* conformers appeared due to hindered rotation about the C(1)—C(2) bond in the above-given fragment. Each band is broadened due to superposition of the lines belonging to the ν^s(Ge—C) and ν^{as}(Ge—C) modes of all corresponding conformers (see above).

For comparison, Table 2 gives the frequencies of the analogous bands in the Raman spectra of high-molecular-weight poly(dialkylgermanes) bearing the same alkyl substituents.[10,11] Analysis of the data listed in Table 2 leads to an important conclusion that in the side alkyl groups of these polymers, the *gauche* conformers about the C(1)—C(2) bond do not exist due, apparently, to steric hindrances.

Rotational isomerism can lead also to complication of the Raman spectra of liquid samples in the regions of 800—900 cm^{-1} (normal modes of complex eigenvector involving C—C stretching modes and various CH bending modes), 1000—1100 cm^{-1} (ν(C—C)), and 1250—1350 cm^{-1} (CH_2 wagging modes).[14,20,22,24] By analogy with the published data,[12—14] one would expect that only one, most stable, conformer will persist after crystallization. Hence, we examined the temperature dependence of the Raman spectra of compounds **1—4** on cooling.

Let us first consider the temperature evolution of the Raman spectrum of AG **1** (see Fig. 1), whose molecule is most symmetrical (and, in a first approximation, should have no conformers about the Ge—C bonds). A decrease in the temperature led to the glass transition (at about –120 °C) rather than to crystallization of compound **1**. This was not a surprise taking into account that compounds of other main-group metals containing *n*-butyl groups are prone to undergo the glass transition.[12] The glass transition of compound **1** can be judged not only from the external appearance of the sample but also from a series of spectral manifestations (the absence of a phonon spectrum in the low-frequency region, qualitative measurableness of the depolarization ratios of Raman lines even at –140 °C). A decrease in the temperature led

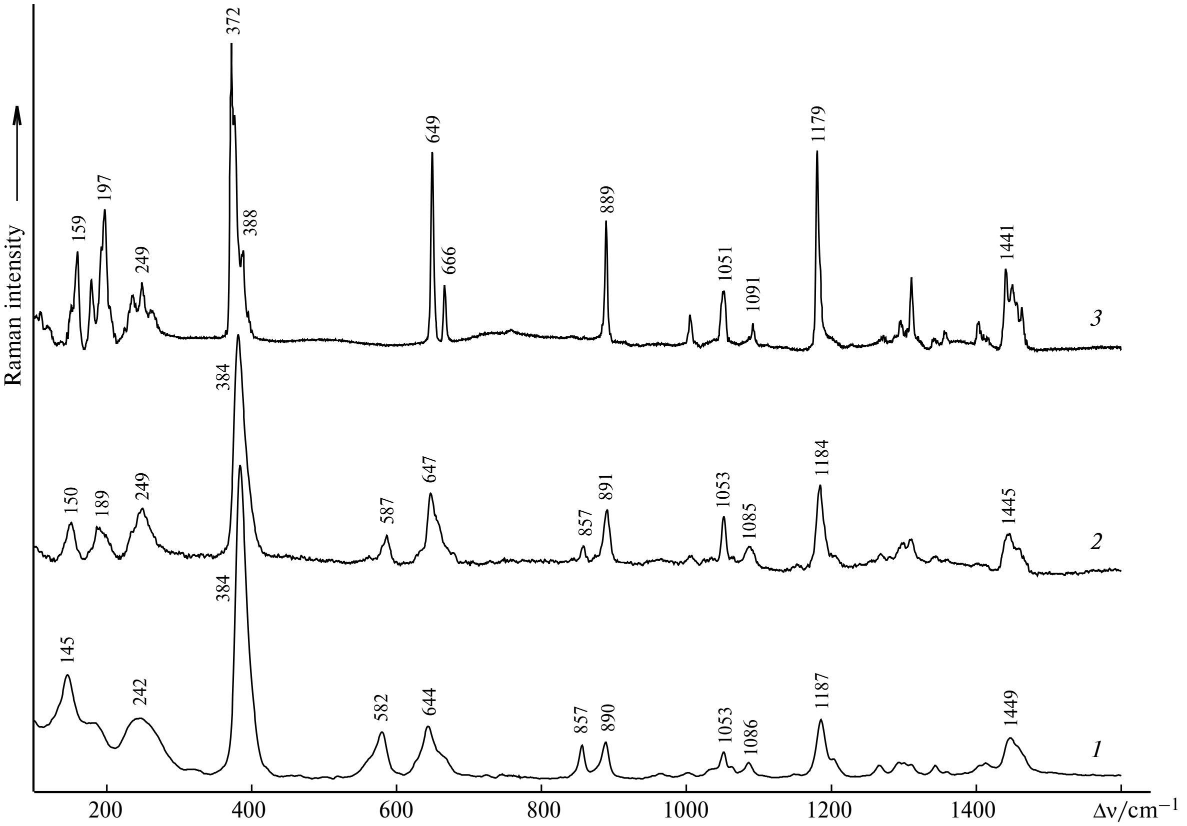


Fig. 3. Raman spectra of Bu_2GeCl_2 in the liquid (20 °C) (*1*), glassy (–170 °C) (*2*), and crystalline (–170 °C) (*3*) states.

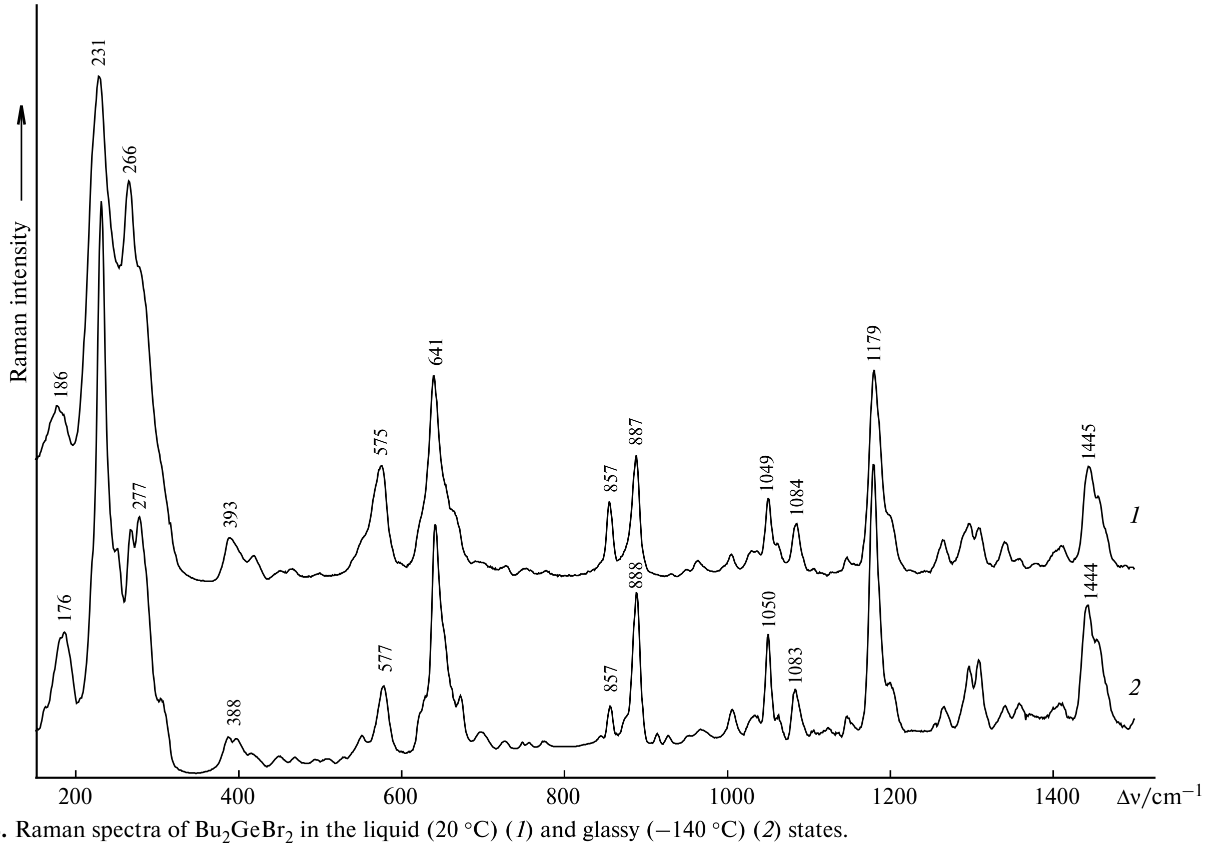


Fig. 4. Raman spectra of Bu_2GeBr_2 in the liquid (20 °C) (*1*) and glassy (–140 °C) (*2*) states.

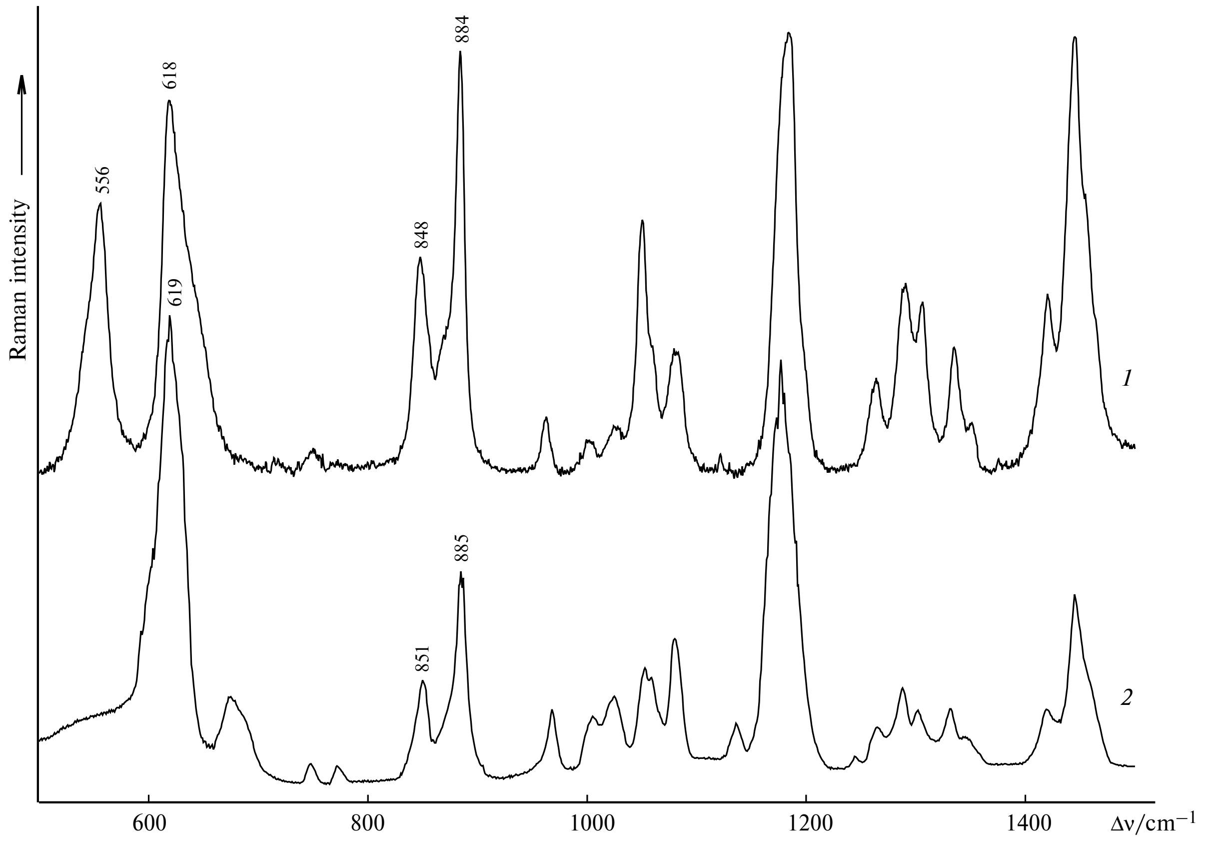


Fig. 5. Raman spectra of liquid Bu_4Ge (*1*) and the high-temperature phase of polygermane $[Bu_2Ge]_n$ (*2*) at 20 °C.

to a gradual decrease in the intensity of the band in the region of 560 cm^{-1}, where the ν^s(Ge—C) and ν^{as}(Ge—C) vibrational modes of all Bu groups in the *gauche* conformation about the C(1)—C(2) bond are situated. However, this band persisted even at −140 °C. Line narrowing on cooling revealed a fine structure of the band near 620 cm^{-1}, which is a superposition of the lines corresponding to ν^s(Ge—C) and ν^{as}(Ge—C) modes of all the *trans* conformers about the C(1)—C(2) bond. The frequency difference between the individual peaks was at most 15 cm^{-1}. Evidently, this structure is associated with rotational isomerism about the C(2)—C(3) bond, because

Table 1. Assignment of the modes for the C_2GeHal_2 fragment (Hal = Cl or Br) in the spectra of the Me_2GeHal_2 molecules and the *trans* conformers of Alk_2GeHal_2 molecules **2**—**5**

Symmetry species	Assignment	ν/cm^{-1}		ν/cm^{-1}, I_{RS}*			
		Me_2GeCl_2**	Me_2GeBr_2**	**2** (crystal)	**3** (glass)	**4** (crystal)	**5** (liquid)
A_1	ν(Ge—C)	596	589	649 s	641 s	655 s	641 s, br
	ν(Ge—Hal)	385	269	372 s	277 s	374 s	275 s
	δ(CGeC)	190	172	197 m	176 m	166 m	—
	δ(HalGeHal)	144	100	159 m	—	156 sh	—
B_1	ν(Ge—C)	642	635	666 m	653 sh	671 w	—
	γ(HalGeHal)	190	161	179 m	—	—	—
A_2	τ(HalGeHal)	190	148	150 w	—	—	—
B_2	ν(Ge—Hal)	402	293	388 sh	304 m	393 m	—
	ρ(HalGeHal)	163	172	159 m	—	—	—

* I_{RS} is the intensity of lines in the Raman spectrum.

** Lit. data[26]; the notations of the modes are given according to the lit. data[26]; the assignment of the bending modes is tentative.

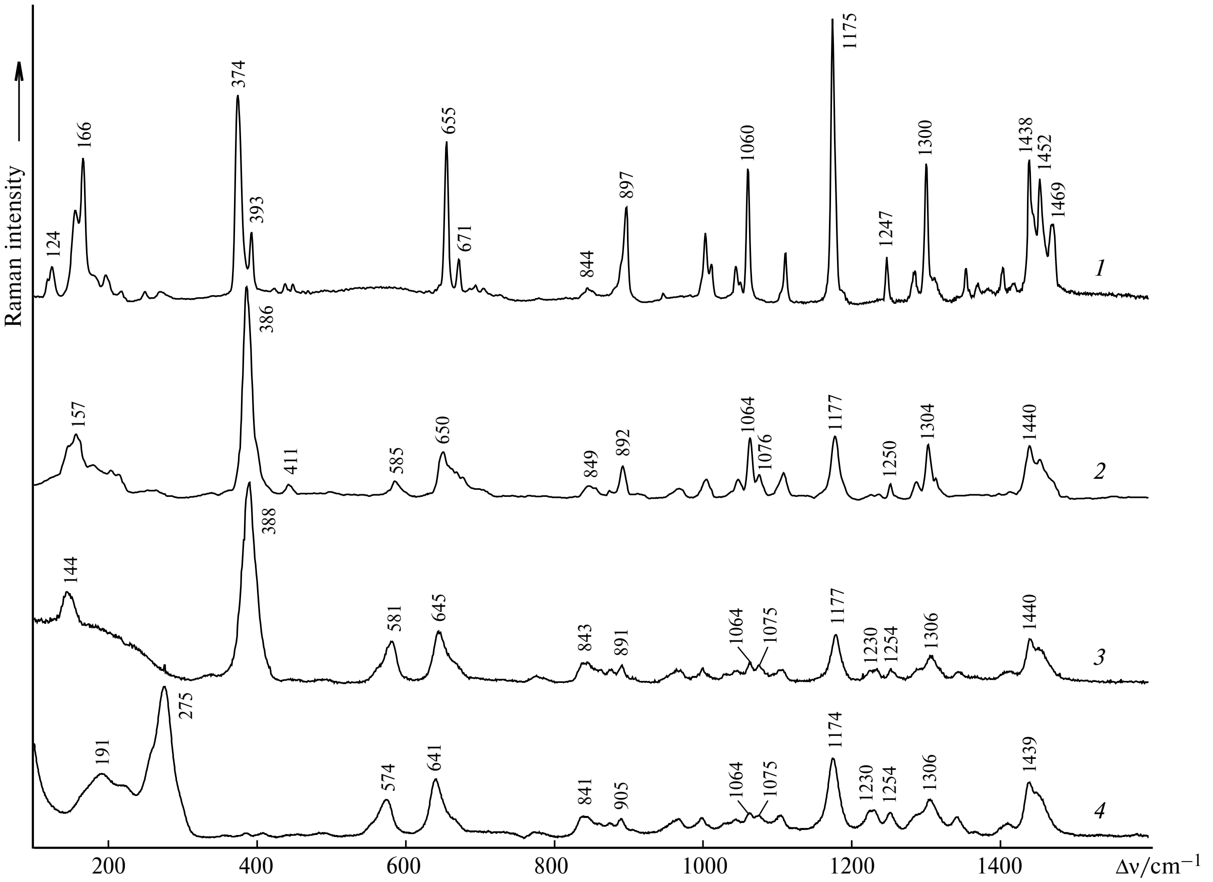


Fig. 6. Raman spectra of $(n\text{-}C_6H_{13})_2GeCl_2$ in the crystalline (–170 °C) (*1*), glassy (–170 °C) (*2*), and liquid (20 °C) (*3*) states and of liquid $(n\text{-}C_6H_{13})_2GeBr_2$ (20 °C) (*4*).

each *n*-butyl group in molecule **1** can adopt either the *TT* or *TG* conformation. The latter fact would lead to symmetry lowering of the GeC_4 skeleton from T_d to either C_{3v} (if three tails have identical conformations, whereas the fourth tail differs from them) or C_{2v} (if tails are identical in pairs). In these cases, spectral patterns may be further complicated due to splitting of the bands corresponding to degenerate modes and, in the latter case, also due to rotational isomerism about the Ge—C bonds.

Table 2. Frequencies of the maxima of broad bands of the ν(Ge—C) modes (see the text) in the Raman spectra of alkylgermanes and polygermanes of the $[Alk_2Ge]_n$ type

Compound	ν(Ge—C)/cm^{-1}	
	gauche conformer	*trans* conformer
Pr_4Ge* [27]	556	618
1*	556	618
$[Bu_2Ge]_n$ [11]	—	620
2*	587	647
3*	577	641
$[(n\text{-}C_6H_{13})_2Ge]_n$ [10]	—	624
4*	585	655
5*	574	641

* For a liquid sample.

Figure 2 shows complex line contours at ~620 cm^{-1} in the Raman spectrum of compound **1** measured at –140 °C (glass) at high resolution (<0.5 cm^{-1}) using different polarizations of the laser beam. The curve fitting analysis revealed three polarized (p) and three depolarized (dp) components. This indicates that at least three conformers are retained in the glassy sample of compound **1**. Presumably, the most intense pair of lines at 622 (p) and 646 (dp) cm^{-1} corresponds to the ν(Ge—C) modes of A_1 and F_2 symmetry of the most stable conformer of molecule **1** (all four *n*-butyl groups adopt the *TT* conformation; the molecular symmetry is T_d). Evidently, this conformer prevails in a mixture. A variety of conformational possibilities hinders an unambiguous assignment of two other conformers, whose symmetrical and antisymmetrical ν(Ge—C) modes are represented by pairs of lines at 628 (p)/658 (dp) cm^{-1} as well as at 636 (p)/669 (dp) cm^{-1}.

In molecules **2—5**, rotational isomerism can occur due to hindered rotation not only about the C—C bonds but also about the Ge—C bonds (Fig. 8).

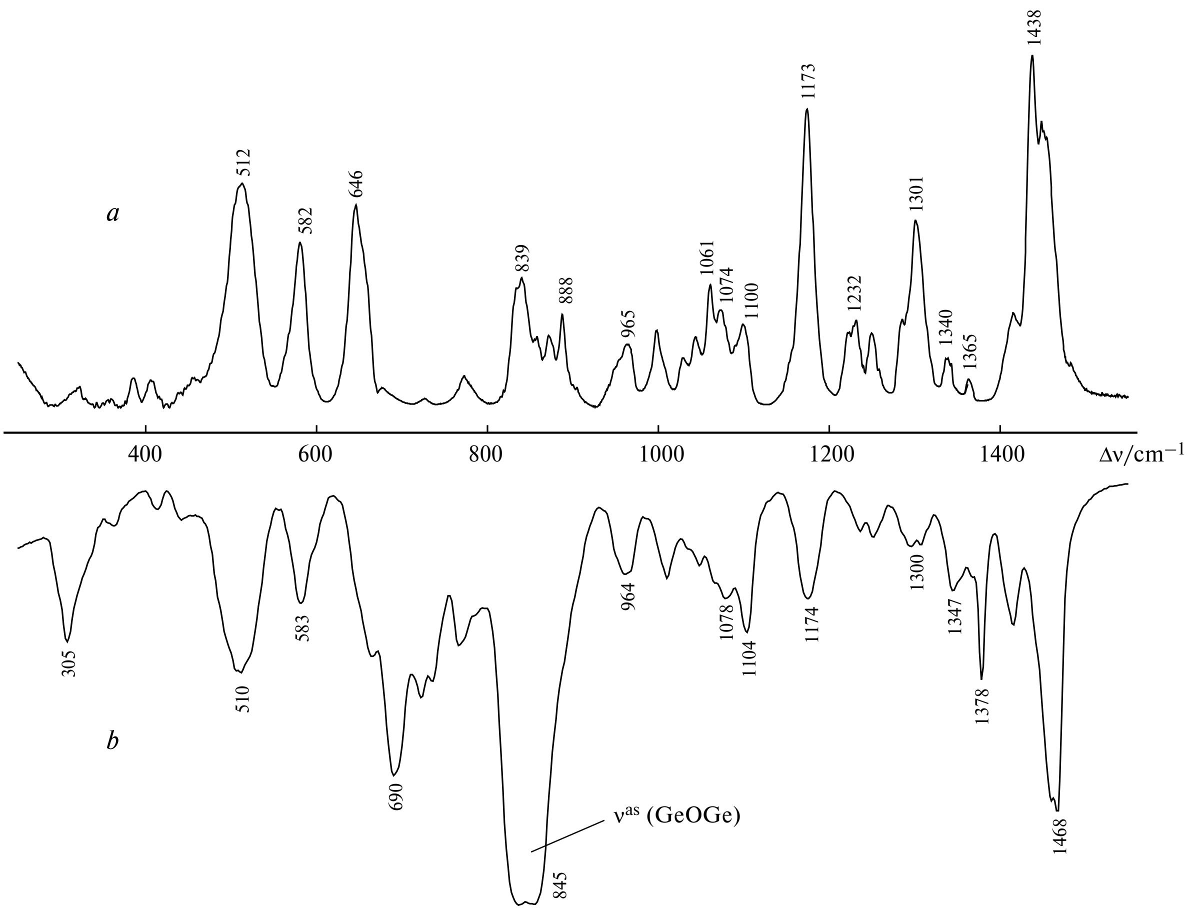


Fig. 7. Raman spectra (*a*) and IR spectra (*b*) of the liquid $[(n\text{-}C_6H_{13})_2GeO]_3$ compound at 20 °C.

The Raman spectra of compound **2** at 20 °C and at low temperature are shown in Fig. 3. Below −100 °C, this compound transforms, as a rule, into the glassy state. However, after numerous failures, we succeeded in crystallizing **2** by slowly varying the temperature about −100 °C. The spectrum of glassy AG **2** (see Fig. 3, curve *2*) shows the bands identical to those in the spectrum of the liquid sample, but they are somewhat narrower and their intensities are noticeably redistributed (pairs of bands at ~585/647 and 857/890 cm^{-1} are particularly illustrative). For instance, the intensity of the band at ~585 cm^{-1}, which belongs to the ν(Ge—C) modes of the *gauche* conformers about the C(1)—C(2) bond, decreases. Upon crystallization of the sample, the observed spectral pattern changes dramatically. The Raman spectrum (see Fig. 3, curve *3*) is substantially simplified, the bands are narrowed, and some of them corresponding to less stable conformers vanish. The band at ~585 cm^{-1} disappears. The band at 650 cm^{-1} corresponding to ν(Ge—C) of the *trans* conformers about the C(1)—C(2) bond is sharply narrowed and exhibits two clearly distinguishable narrow components corresponding to symmetrical (649 cm^{-1}) and antisymmetrical (666 cm^{-1}) ν(Ge—C) modes of the C—Ge—C fragment. The line at 857 cm^{-1} as well as a series of weak lines in the 1200—1400 cm^{-1} region disappear. Broad bands in the low-frequency region are split into a series of narrow lines. In the 100 cm^{-1} region, vibrational modes of the crystal lattice are manifested. The frequencies in the 800—1460 cm^{-1} region observed in the Raman spectrum of the crystalline sample of **2** are close to those in the spectrum of *trans*-butane.[20,23] Hence, it can be concluded that the *n*-butyl groups in crystalline AG **2** are ordered and adopt the *TT* conformation shown in the above-given scheme.

We failed to crystallize compound **3**. Cooling to −100 °C invariably led to its transition into the glassy state. Changes in the Raman spectrum of this compound on going from the liquid to the glassy state (see Fig. 4) are analogous to those observed for AG **2**.

Unlike compounds **2** and **3**, dihexyldichlorogermane **4**, like its silicon analog $(n\text{-}C_6H_{13})_2SiCl_2$,[14] readily crystallizes on cooling (transformation of **4** into the glassy state required very rapid cooling). Evidently, it is this hindrance to ordering of the Bu groups in butylsilanes

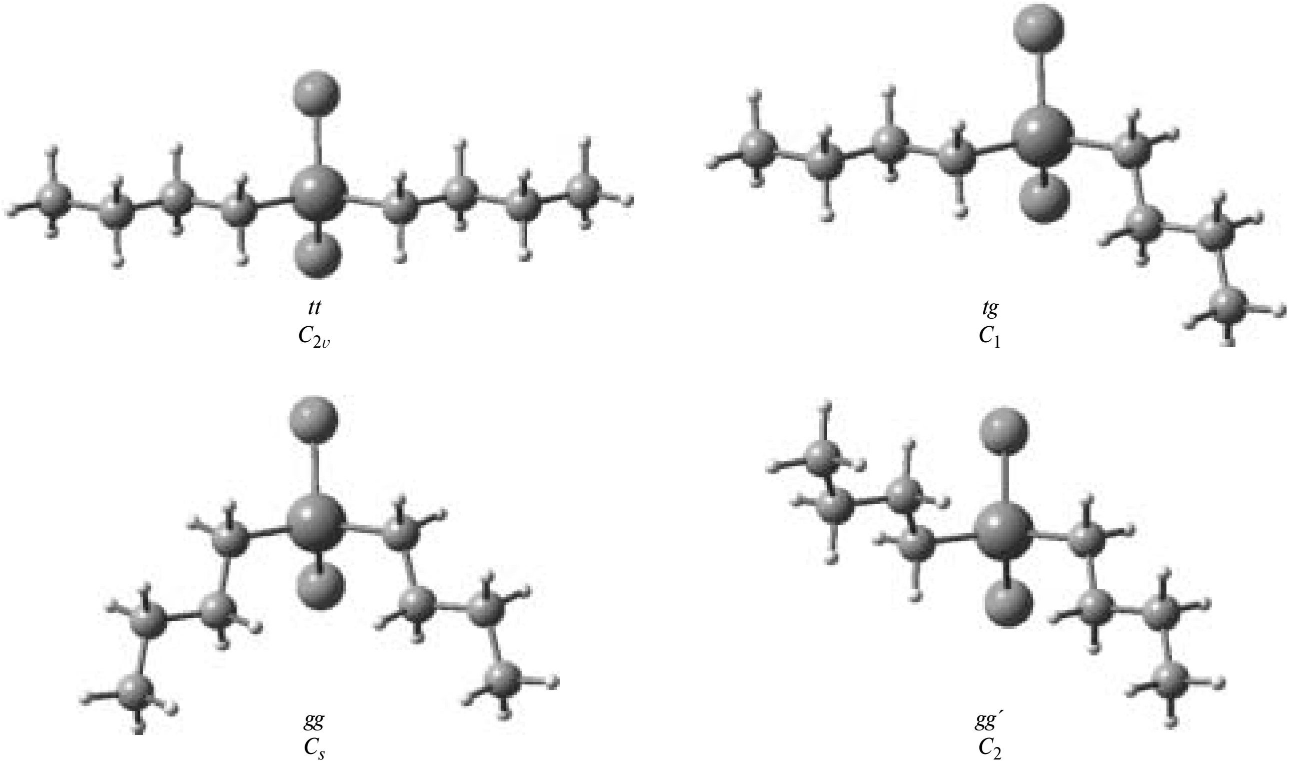

tt
C_{2v}
tg
C_1
gg
C_s
gg´
C_2

Fig. 8. Conformers (about the Ge—C bond) of the Bu_2GeCl_2 molecule for which quantum-chemical calculations were carried out (see the text).

and -germanes that is responsible for the difference in the nature of phase transitions of the corresponding polymers $[Bu_2M]_n$ and $[(n\text{-}C_6H_{13})_2M]_n$ (M = Si or Ge).[1,10,11]

An important result follows from a comparison of the Raman spectra of the liquid sample of **1** and the disordered high-temperature phase of poly(dibutylgermane) $[Bu_2Ge]_n$ [11] (see Fig. 5), which differ only in the region of ν(Ge—C) modes. As mentioned above, the absence of the band at ~560 cm^{-1} in the spectrum of the polymer indicates that the polymer does not form the *gauche* conformers about the C—C bond nearest to the germanium chain. At the same time, both spectra show a temperature-sensitive pair of lines at ~850/885 cm^{-1}. In each of these two spectra, the intensity of the lower-frequency line decreases on cooling. Upon crystallization of **2**, the line at ~850 cm^{-1} disappears. Apparently, this pair of lines is generated by rotational isomerism about the C(2)—C(3) bond, which was confirmed by calculations (see below). Thus, our data demonstrate that the ν(Ge—C) modes are sensitive to conformational isomerism about the C(1)—C(2) bond, whereas the vibrational modes in the region of 850—890 cm^{-1} to that about the C(2)—C(3) bond. This allows one to distinguish between the corresponding conformational types by Raman spectroscopy.

The results obtained upon cooling of compound **4** (see Fig. 6) are analogous to those observed for AG **2**. Upon crystallization, the spectrum of sample **4** exhibits an analogous temperature evolution in the region of ν(Ge—C) modes, that is, the disappearance of the band at ~580 cm^{-1} corresponding to the *gauche* conformers about the C(1)—C(2) bond and separation of two narrow lines (ν^s(Ge—C) = 655 cm^{-1} and ν^{as}(Ge—C) = 671 cm^{-1}) from the initially broad band of the *trans* conformers at 650 cm^{-1}. Let us also note the disappearance of the line at 1075 cm^{-1} diagnostic for the *gauche* conformations of *n*-alkanes starting from C_6. The degree of ordering of the long alkyl substituent is generally judged from the intensity ratio of the Raman lines at ~1060 (*trans*) and ~1080 cm^{-1} (*gauche*).[3b,14,20] The presence of only an intense line at 1060 cm^{-1} in the Raman spectrum of the crystalline sample of **4** is indicative of the all-*trans* conformation of the hexyl group. In the 900—1450 cm^{-1} region corresponding to internal modes of hexyl groups, the spectral pattern of crystalline **4** at 20 °C is identical to that of the $[(n\text{-}C_6H_{13})_2Ge]_n$ polymer,[10] which provides evidence for the same conformational state of the hexyl groups in these two compounds, *i.e.*, for ordering of the side chains in the $[(n\text{-}C_6H_{13})_2Ge]_n$ polymer below the phase transition temperature.

Figure 6 (curve *4*) also displays the Raman spectrum of liquid compound **5** at 20 °C. A comparison of the spectra of alkylgermanes **4** and **5** shows that the *n*-hexyl groups in the liquid phase of these compounds are in the same conformational state.

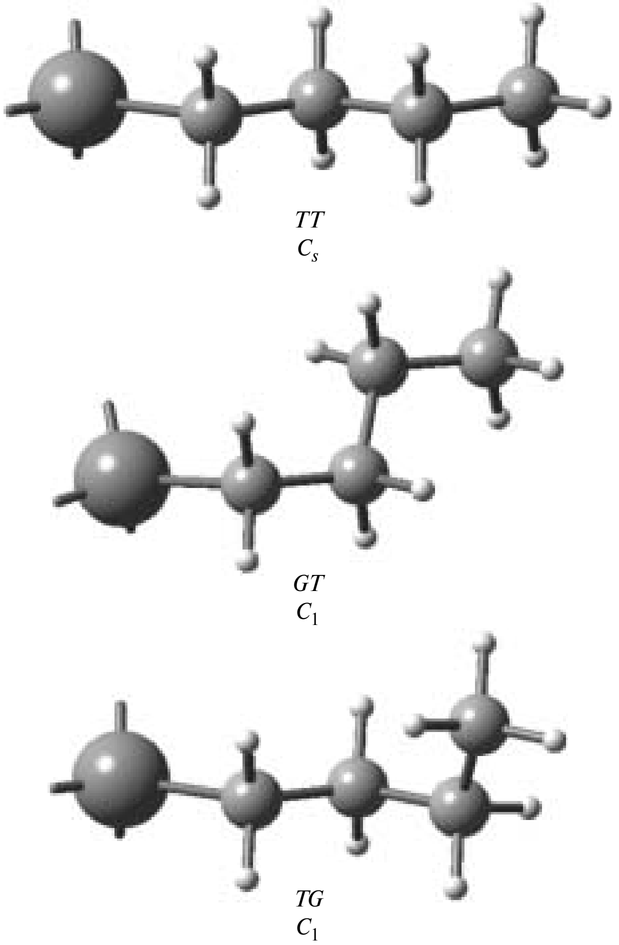
Table 3. Frequencies of the ν(El—C) modes in the Raman spectra of the *trans* and *gauche* conformers about the C(1)—C(2) bond of the main-group element (El) compounds Bu_xEl[12]

El	ν(El—C)/cm^{-1}	
	gauche conformer	*trans* conformer
Cl	653	722
Br	561	614
I	504	590
SH	653	739
Hg	505	602
Ga	520	600
In	495	583
Ge	557	620
Sn	499	585

Thus, we have demonstrated that rotational isomerism occurs in all alkylgermanes under study both in the liquid and glassy states, which results in complication of the spectral patterns, whereas only the most stable (all-*trans*) conformer persists in the crystalline phase at low temperature. Rotational isomerism about the C(1)—C(2) bond is responsible for the fact that the Raman spectra exhibit two broad bands belonging to ν(Ge—C) of the *trans* (*anti*) and *gauche* conformers; the difference between their frequencies for all alkylgermanes under study is ~65 cm^{-1}. The frequencies of the ν(El—C) modes for the analogous *trans* and *gauche* conformers of the *n*-butyl derivatives of other main-group elements are given in Table 3. The *trans* – *gauche* frequency difference varies from 65 to 97 cm^{-1}, depends on the position of El in the Periodic system, and tends to increase as El moves to the left and downward.

Such a large frequency difference between the ν(El—C) modes (see above) is difficult to explain, because no experimental method provides data for the less stable (*gauche*) conformer in the pure form. This problem can be solved using modern quantum-chemical methods, which allow one to theoretically estimate with high confidence the properties of "isolated" *gauche* conformers.

For this purpose, we examined various conformers of the AG molecules by quantum-chemical methods. To reveal the differences in the structure, energy, and vibrational spectra of the conformers about the C(1)—C(2) and C(2)—C(3) bonds, we optimized the geometry and carried out normal coordinate analysis for the most probable *TT*, *GT*, and *TG* conformers (see Fig. 9) of the model $BuGeH_3$ (**7**) and $BuGeCl_3$ molecules. The energy difference between the conformers of molecule **7** was also determined. The calculations were carried out by the DFT method at the B3LYP level of theory with the 6-311++G(d,p) basis set. Calculations for **7** were performed also by the semiempirical PM3 method.


TT
C_s

GT
C_1

TG
C_1

Fig. 9. Conformers of the $BuGeH_3$ and $BuGeCl_3$ molecules for which quantum-chemical calculations were carried out (see the text).

For molecule **7**, the calculated energy difference (B3LYP including the zero-point energy) is 1.0 kcal mol^{-1} between the *TT* and *GT* conformers and 0.9 kcal mol^{-1} between the *TT* and *TG* conformers, which is in good agreement with the common values[23,25] and is consistent with the observed equilibrium co-existence of these conformers at room temperature.

As expected, the results obtained by the semiempirical and DTF methods are somewhat different. However, they are, in principle, consistent with each other and show similar tendencies. In particular, both methods demonstrated that the calculated geometries of the *TT* conformers differ from those of the *GT* conformers (Table 4). The Ge—C bond in the *GT* conformers appeared noticeably longer than that in the *TT* conformers (for the corresponding conformers of the *n*-pentane molecule, analogous differences are insignificant[25]). There is also difference in the Ge(1)—C(2)—C angles. The calculated Ge(1)—C(2)—C(3)—C torsion angles in the *GT* conformers of molecules **7** and $BuGeCl_3$ noticeably deviate from

Table 4. Geometric parameters (bond lengths (*r*) and bond angles (ω)) for the *TT* and *GT* conformers of the $BuGeH_3$ and $BuGeCl_3$ molecules according to quantum-chemical calculations by the PM3 and B3LYP/6-311G(d,p) methods

Parameter	$BuGeH_3$				$BuGeCl_3$	
	PM3		B3LYP/6-311++G(d,p)		B3LYP/6-311G(d,p)	
	TT	*GT*	*TT*	*GT*	*TT*	*GT*
Bond			*r*/Å			
Ge—C(1)	1.956	1.964	1.978	1.982	1.956	1.964
C(1)—C(2)	1.500	1.502	1.535	1.537	1.534	1.534
C(2)—C(3)	1.523	1.522	1.535	1.534	1.536	1.533
Angle			ω/deg			
Ge(1)—C(2)—C	104.8	106.5	114.2	115.9	114.0	116.0
Ge(1)—C(2)—C(3)—C	180.0	69.1	179.0	65.8	180.0	66.7
C(1)—C(2)—C(3)—C(4)	180.0	175.4	179.0	177.1	180.0	176.0

the initial value of 60°. It should be noted that the analogous dihedral angles in the *gauche* conformer of *n*-butane[23] and the *GT* conformer of *n*-pentane[25] calculated by the *ab initio* method also differ from 60°, being 65.4° and 66.5°, respectively, which is consistent with our results for *n*-butylgermanes.

The differences in the geometry of the *TT* and *GT* conformers already suggest that the frequencies and eigenvectors of the normal modes involving the above-mentioned bonds and angles will also be unequal. Actually, the calculated frequency differences between the ν(Ge—C) normal modes for the *TT* and *GT* conformers were close to the experimental value: 70 cm^{-1} (PM3) and 56 cm^{-1} (B3LYP) for model **7**; 86 cm^{-1} for $BuGeCl_3$ (Table 5). In line with analysis of the experimental results, the calculations showed that the rotation about the C(2)—C(3) bond (*TG* conformer) affects the ν(Ge—C) mode frequencies to a much lesser extent compared to the rotation about the C(1)—C(2) bond, but it substantially influences the frequencies in the 850 cm^{-1} region.

For molecules of the *n*-Alk_2GeX_2 type, conformers associated with hindered rotation about the Ge—C bonds can arise (let us denote these conformers by *t* and *g* to distinguish them from the *T* and *G* conformers about C—C bonds). Manifestations of rotational isomerism of this type were revealed by performing analogous calculations (DFT/B3LYP method with the same basis set) on example of conformers of the Bu_2GeCl_2 molecule with the fixed *TT* conformation of both *n*-butyl groups (see Fig. 8). According to the results of calculations, the differences in the geometry for the most probable *tt* and *gt* conformers are insignificant, whereas the frequencies of the ν^s(Ge—C) modes for the *tt*, *gt*, *gg*, and *gg´* conformers differ by 8—13 cm^{-1}, which is consistent with the experimental data for molecule **1** in the glassy state.

Table 5. Frequencies of the ν(Ge—C) modes calculated for the *TT* and *TG* conformers of the $BuGeH_3$ and $BuGeCl_3$ molecules (without scaling)

Calculation method	ν(Ge—C)/cm^{-1}			
	$BuGeH_3$		$BuGeCl_3$	
	TT	*GT*	*TT*	*GT*
PM3	639	569	—	—
DFT B3LYP	669	613	654	568

The calculations of normal mode eigenvectors and potential energy distribution (PED) over the internal coordinates allowed us to refine the frequency assignment made on the basis of the experimental data (for molecules **1—6**, the bands with frequencies in the ranges of 620—650 and 560—580 cm^{-1} were assigned to the ν(Ge—C) stretching modes of the *TT* and *TG* conformers, respectively). The results of calculations for molecules **7**, $BuGeCl_3$ and **2** demonstrated that for all conformers, the vibration of the Ge—C bond does make the major contribution to the energies of these normal modes, *i.e.*, these normal modes are well-localized and may be reasonably called ν(Ge—C). However, the contributions of this coordinate are somewhat different for different conformers (from 62 to 76% in PED). The coordinates of angle changes, which make noticeable contributions to these normal modes, are also different. Therefore, the eigenvectors of the ν(Ge—C) (*trans*) and ν(Ge—C) (*gauche*) modes with frequencies of ~640 and ~570 cm^{-1}, respectively, are somewhat different.

The calculations confirmed the observed conformational sensitivity of the vibrational mode with a frequency in the region of 850—890 cm^{-1}. As in the spectra of *n*-hydrocarbons,[20,22,24] this mode is of complex eigenvector involving the C(2)—C(3) bond stretching coordinate and the rocking vibration of the Me group. This accounts for sensitivity of this mode to rotational isomerism about the C—C bond adjacent to the terminal Me group.

The results of calculations also explain the high intensity of the Raman line at ~1180 cm^{-1} (see Fig. 1—7), because this mode involves not only the H(1)—C(2)—C angle bending but also the ν(Ge—C) and δ(GeCH) coordinates with the participation of the Ge atom, whose polarizability is higher than that of the C and H atoms.

Thus, the large frequency difference between ν(Ge—C) of the *trans* and *gauche* conformers about the C(1)—C(2) bond, which is observed in the Raman spectra of alkylgermanes, is attributed primarily to the difference in their geometry, which inevitably leads to the difference in the force field. In particular, a noticeable elongation of the Ge—C bond in the *GT* conformer compared to that in the *TT* conformer results in a decrease in this bond force constant. Therefore, two conformers differ in the electronic structure. Obviously, the differences in the geometry and force field are reflected in the corresponding normal mode frequencies and eigenvectors.

Based on experience in comparison and analysis of the vibrational spectra of heteroorganic compounds containing various main-group elements, it can be said with confidence that principally the same results will be obtained in calculations of the *trans* and *gauche* conformers about the C(1)—C(2) bond of alkyl derivatives of other main-group elements starting with the second row. Therefore, quantum-chemical calculations were in this case not a fashion but appeared very useful, because they provided an insight into reasons for the unusually large frequency difference between the ν(El—C) modes of the conformers under consideration.

Experimental

The compounds were synthesized according to known procedures: Bu_4Ge,[28] Bu_2GeCl_2,[29] $(n\text{-}C_6H_{13})_2GeCl_2$,[3a] Bu_2GeBr_2,[3a] $(n\text{-}C_6H_{13})_2GeBr_2$,[3a] and $[(n\text{-}C_6H_{13})_2GeO]_3$.[3a] All compounds were characterized by ^1H and ^{13}C NMR spectroscopy and mass spectrometry.

Samples of **1—6** were subjected to high-vacuum microdistillation and sealed in capillaries just before Raman measurements.

The Raman spectra were recorded on a laser Raman T64000 spectrometer (Jobin Yvon) equipped with a highly sensitive CCD detector cooled with liquid nitrogen and on a U1000 instrument (Jobin Yvon) equipped with a cooled photomultiplier. The Raman spectra were excited with a 514.5-nm line of Spectra Physics 2020 and ILA-120 Carl Zeiss ion argon lasers; the laser power was 10—50 mW. The accuracy of the determination of the frequencies in the Raman spectra was ±1 cm^{-1}. The depolarization ratios of the Raman lines of liquid and glassy samples were estimated qualitatively.

To crystallize compounds **1—3** by cooling, numerous experiments were carried out using various temperature modes of cooling, annealing of samples, and addition of porcelain chips as additional crystallization centers. The temperature dependence of the Raman spectra was studied with the use of a 91-Arpajon cryostat (Meric); the temperature was measured using a platinum resistor (100 Ω). The temperature detector was mounted on a holder in the direct vicinity of the sample under study. The temperature was maintained within the prescribed range with accuracy of ±2 °C.

The IR spectra were measured on an M82 spectrometer (Carl Zeiss) and used for checking the sample purity. The absence of oxidative destruction products was judged from the absence of the IR absorption band at 850 cm^{-1} (ν^{as}(GeOGe) mode). This characteristic band is most intense in the IR spectrum, whereas its Raman intensity is low (see the spectra of compound **6** shown in Fig. 7).

Quantum-chemical calculations. Density functional theory calculations with the three-parameter functional B3LYP and the 6-311G(d,p) and 6-311++G(d,p) basis sets were carried out with the use of the Gaussian 98 program.[30] To determine the normal mode eigenvectors and calculate the potential energy distribution of the normal modes over the internal coordinates, the results were converted into the internal coordinates using the NCA-99 program.[31] The calculations according to the PM3 method were carried out using the HyperChem 5.01 program package.

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