Molecular structures of acetylene derivatives of tin
6.* Molecular structure of bis(trimethylstannyl)acetylene and analysis of vibrational spectra of its isotopomers by scaling of quantum-chemical force field

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The geometry and force fields of the bis(trimethylstannyl)acetylene molecule (a conformer with D_{3d} symmetry corresponding to a minimum of the total energy of the molecule) were calculated by the RHF and MP2(fc) methods. The effective core potential in SBK form with the optimized 31G* valence basis set was employed in the case of Sn atoms. The 6-31G** and 6-311G** basis sets were used for carbon and hydrogen atoms. Vibrational spectra of the light and perdeuterated isotopomers of bis(trimethylstannyl)acetylene were interpreted using the procedure of scaling the quantum-chemical force fields.

Key words: bis(trimethylstannyl)acetylene, molecular structure, *ab initio* quantum-chemical calculations, force field, scaling, vibrational spectra.

In our previous studies of the structure of various stannylacetylenes[1—7] by the electron diffraction method we failed to obtain reliable solutions of the problems under consideration, namely, to establish unambiguously how (i) the interaction between stannyl groups and the C≡C bond affects the molecular structure and (ii) the substituents influence the geometry of the Sn—C≡C fragment. When studying organotin compounds, solution of the inverse electron diffraction problem is often made difficult because a rather "short" diffraction pattern can be recorded experimentally owing to rapid damping of the scattering intensity.[2] Reliability of the molecular structure determination can be improved by using vibrational spectroscopy data for the structural analysis. The use of the root-mean-square (RMS) vibrational amplitudes, u_{ij}, fixed at the spectroscopic values makes it possible to reduce substantially the number of parameters to be refined while introduction of harmonic shrinkage corrections for internuclear distances, δ_{ij}, allows one to increase the symmetry of the molecular model.[8—14] In studies of bis(trimethylsilyl)acetylene (**1**)[15,16] we have shown that complete correspondence of the u_{ij} and δ_{ij} parameters obtained from spectroscopic calculations with the results of an electron diffraction experiment can be achieved by taking into account nonlinear relations between Cartesian and internal vibrational coordinates in the approximation described earlier.[12,13]

Establishment of adequate vibrational characteristics u_{ij} and δ_{ij} requires a reliably determined potential energy matrix, which can be obtained by solving the inverse spectral problem by scaling of the quantum-chemical force field. Refinement of a small set of scale factors which appear to be transferable for related molecules allows the experimental vibrational spectra to be interpreted unambiguously and the normal modes to be determined rigorously.[17—20] The results of quantum-chemical calculations of stannylacetylenes could serve as an objective basis for narrowing of the range of feasible solutions when analyzing both electron diffraction and spectroscopic data. However, no such time-consuming calculations have been carried out to date.

In this work, we use the results of *ab initio* quantum-chemical calculations of bis(trimethylstannyl)acetylene (**2**) in order to interpret the IR (35—4000 cm^{-1}) and Raman (50—3500 cm^{-1}) spectra of compound **2** and its perdeuterated isotopomer. The spectra were recorded[21] for either suspensions in Nujol or solutions of arbitrary concentration in cyclohexane and CCl_4. The spectral bands were assigned[21] without considering torsional motions of the stannyl and methyl groups. The authors[21] emphasized that they were not able to interpret unambiguously the spectra in the region below 200 cm^{-1} (the most important spectral region when calculating the u_{ij} and δ_{ij} parameters) using traditional approaches including normal coordinate analysis with the least-squares refinement of the force constants.

Calculation procedure

The geometry and harmonic force fields of molecule **2**, as well as the intensities of the bands in the IR spectra of compound **2**, were calculated for the conformer with D_{3d} symmetry, corresponding to the total energy minimum, by the restricted Hartree—Fock (RHF) method and with inclusion of

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electron correlation at the second-order level of Møller—Plesset perturbation theory (MP2) in the "frozen" core (fc) approximation. In this case, the fc approximation was applied only to the 1s orbitals of C atoms. The effective core potential (ECP) in the form proposed by Stevens, Basch, and Krauss (SBK) with the 31G* valence basis set optimized for this potential[23—25] was employed in the case of Sn atoms. The 6-311G** basis set (in a particular case, the 6-31G** basis set)[22] was used for carbon and hydrogen atoms.

In order to correlate the force constants of related molecules, the force constant matrices (in Cartesian coordinates) obtained from quantum-chemical calculations were transformed to the complete system of independent local-symmetry internal coordinates. The corresponding sets of internal vibrational coordinates have been discussed previously.[26] The scale factors, C_i, were introduced for groups of internal coordinates related by symmetry or local symmetry transformations. The quantum-chemical force constant matrices, F^{theor}, were modified using the diagonal matrices of the square roots of the scale factors according to the formula $F_{mn} = (C_m C_n)^{1/2} F_{mn}^{theor}$ by fitting the calculated frequencies to the experimental ones.[27] This congruent transformation leaves the most important characteristics of the initial force constant matrix unchanged. In solving the vibrational problem the Sn atomic weight was set to that of the most abundant (32.4%) Sn isotope (^{120}Sn, 119.9022).[28] Quantum-chemical calculations were carried out using the PC GAMESS version[29] of the GAMESS(US) program package.[30] Spectroscopic calculations were performed using the ANCO/SCAL/PERT[31,32] and SHRINK[12,13] program packages.

Structure of bis(trimethylstannyl)acetylene molecule and large-amplitude intramolecular motions

In Table 1, the calculated geometric parameters of the equilibrium conformation of bis(trimethylstannyl)acetylene molecule 2 (a conformer with D_{3d} symmetry, Fig. 1) are compared with the corresponding parameters of bis(trimethylsilyl)acetylene molecule **1**.[15] According to calculations, the C≡C bond in **2** should not be shorter than in **1** (*i.e.*, it should be 0.01—0.02 Å longer than that in the unsubstituted acetylene).[15,16] One should also expect a larger difference between the Sn—C(H$_3$) and Sn—C≡ bond lengths in molecule **2** compared to that between the Si—C(H$_3$) and Si—C≡

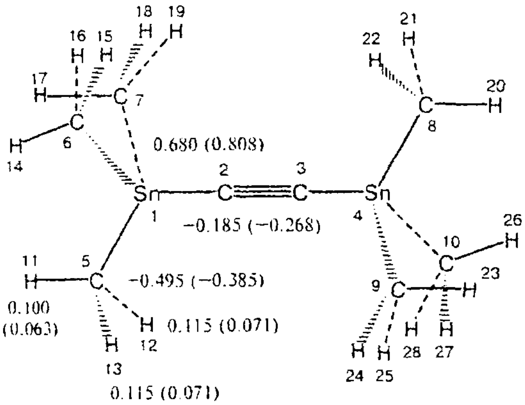

Fig. 1. Schematic view of bis(trimethylstannyl)acetylene molecule (a conformer with D_{3d} symmetry). Shown are the numbering of atoms and the charge distributions according to Mulliken and Löwdin (in parentheses) calculated in the MP2(fc)/6-311G** (Sn: SBK ECP) approximation for nonequivalent atoms of the linear fragment and for one of the equivalent Me groups.

Table 1. Geometric parameters of equilibrium D_{3d} conformations of bis(trimethylstannyl)acetylene (**2**) and bis(trimethylsilyl)acetylene (**1**) molecules calculated in different approximations

Parameter[a]	$(CH_3)_3SnC{\equiv}CSn(CH_3)_3$[b]			$(CH_3)_3SiC{\equiv}CSi(CH_3)_3$ [15]		
	RHF/6-31G**	RHF/6-311G**	MP2(fc)/6-311G**	RHF/6-31G**	RHF/6-311G**	MP2(fc)/6-311G**
Bond length, *r*/Å						
Sn—C(H$_3$)	2.1446	2.1395	2.1389	1.8877	1.8830	1.8776
Sn—C≡	2.0995	2.0991	2.0947	1.8577	1.8597	1.8451
C≡C	1.2069	1.2038	1.2421	1.2040	1.2010	1.2406
C—H(i.p.)	1.0852	1.0855	1.0930	1.0874	1.0879	1.0950
C—H(o.p.)	1.0844	1.0854	1.0923	1.0861	1.0866	1.0939
Bond angle, β/deg						
(H$_3$)C—Sn—C′(H$_3$)	111.0	111.0	111.0	110.4	110.6	110.6
(H$_3$)C—Sn—C≡	107.9	107.9	107.9	108.5	108.3	108.3
Sn—C—H(i.p.)	110.6	110.4	110.4	110.8	110.8	110.8
Sn—C—H(o.p.)	110.4	110.5	110.2	111.2	111.1	110.8
H(i.p.)—C—H(o.p.)	108.5	108.5	108.7	107.9	107.9	108.2
H(o.p.)—C—H′(o.p.)	108.4	108.4	108.6	107.8	107.8	108.0
Dihedral angle, τ/deg						
H(i.p.)CSnC≡	180.0	180.0	180.0	180.0	180.0	180.0
H(o.p.)CSnC≡	±59.9	±60.0	±59.9	±60.1	±60.0	±59.9
H(i.p.)CSnC(H$_3$)	±61.9	±62.0	±61.9	±61.2	±61.4	±61.5
H(o.p.)CSnC(H$_3$)	±58.1	±58.0	±58.2	±58.7	±58.6	±58.6
H(o.p.)CSnC′(H$_3$)	±178.0	±178.0	±178.0	±178.9	±178.6	±178.5
Total energy,						
−*E*/au	319.962758	320.015951	321.399296	891.330456	891.428502	892.824547

[a] Atoms labeled by "i.p." and "o.p." are situated in and out of the molecular symmetry plane, respectively.

[b] Calculations were carried out using the SBK effective core potential in the case of Sn atoms (see text).

bond lengths in **1** (0.04—0.05 Å *vs.* 0.02—0.03 Å,[15,16] respectively). The corresponding bond angles and dihedral angles in both molecules are nearly equal. The local symmetry of the methyl groups is very close to C_{3v} symmetry. The bond configurations at the Sn and C(Me) atoms are slightly distorted tetrahedra, flattened and elongated along the three-fold axis (Sn) and the three-fold pseudoaxis (C(Me)).

Internal rotations of the Me$_3$Sn groups in molecule **2** should be much more similar to free rotation than those of the Me$_3$Si groups in molecule **1**, for which the calculated barrier height appeared to be less than 10 cal mol^{-1}.[15,16] In particular, this is indicated by the fact that the force constant of the SnC$_3$ torsional vibration is by an order of magnitude smaller than that of the SiC$_3$ torsional vibration and is virtually equal to zero (Table 2).

Table 2. Force constants of bis(trimethylstannyl)acetylene molecule calculated (I) in the RHF and MP2(fc) approximations using the 6-311G** basis set (Sn: SBK ECP) and refined by scaling (II)[a] (in internal vibrational coordinates)

Force constant	RHF		MP2	
	I	II	I	II
C≡C str	**17.79**	**13.71**	**13.31**	**13.78**
/SnC≡ str	−0.09	−0.07	−0.04	−0.04
/SnC$_3$ s.str	0.03	0.02	0.01	0.01
/SnC$_3$ s.def	−0.05	−0.05	−0.03	−0.03
SnC≡ str	**2.59**	**2.36**	**2.46**	**2.35**
/SnC≡ str [b]	0.07	0.06	0.05	0.05
/SnC$_3$ s.str	0.11	0.10	0.09	0.09
/SnC$_3$ s.def	−0.22	−0.20	−0.17	−0.17
/SnC$_3$ s.def [b]	0.04	0.04	0.03	0.03
/CH$_3$ rock‖	0.04	0.04	0.04	0.04
SnC$_3$ s.str	**2.39**	**2.33**	**2.29**	**2.32**
/SnC$_3$ s.def	0.06	0.06	0.05	0.06
/CH$_3$ s.str	0.03	0.03	0.01	0.01
/CH$_3$ s.def	−0.13	−0.11	−0.12	−0.11
SnC$_3$ str A, **SnC$_3$ str B** *	**2.28**	**2.22**	**2.19**	**2.22**
/CH$_3$ s.def [c]	−0.13	−0.12	−0.13	−0.12
/CH$_3$ s.def [d]	0.07	0.06	0.06	0.06
/CH$_3$ rock⊥ [d]	±0.03	±0.02	±0.03	±0.03
*/CH$_3$ s.def [d]	±0.12	±0.10	±0.11	±0.10
*/CH$_3$ rock⊥ [c]	−0.03	−0.03	−0.03	−0.03
/SnC$_3$ def A */SnC$_3$ def B	−0.09	−0.09	−0.08	−0.09
/SnC$_3$ rock A */SnC$_3$ rock B	0.08	0.07	0.07	0.07
SnC$_3$ s.def	**0.63**	**0.61**	**0.53**	**0.61**
/SnC$_3$ s.def [b]	0.03	0.03	0.02	0.02
/CH$_3$ str A	−0.03	−0.02	−0.02	−0.03
/CH$_3$ rock‖	−0.14	−0.12	−0.13	−0.13
SnC$_3$ def A, **SnC$_3$ def B** *	**0.49**	**0.47**	**0.42**	**0.48**
/CH$_3$ str B	0.02	0.02	0.02	0.02
/CH$_3$ rock‖ [c]	0.03	0.03	0.03	0.03
/CH$_3$ rock⊥ [d]	±0.15	±0.13	±0.14	±0.14
*/CH$_3$ rock‖ [d]	±0.03	±0.02	±0.03	±0.03
*/CH$_3$ rock⊥ [c]	0.17	0.15	0.16	0.16
*/CH$_3$ rock⊥ [d]	±0.09	±0.08	±0.08	±0.08
/SnC$_3$ rock A */SnC$_3$ rock B	−0.09	−0.09	−0.08	−0.09
SnC$_3$ rock A, **SnC$_3$ rock B***	**0.57**	**0.54**	**0.47**	**0.54**
/CH$_3$ rock‖ [c]	0.12	0.10	0.11	0.11
/CH$_3$ rock‖ [d]	−0.06	−0.05	−0.05	−0.05
/CH$_3$ rock⊥ [d]	±0.03	±0.03	±0.03	±0.03
*/CH$_3$ rock‖ [d]	±0.10	±0.09	±0.09	±0.09
*/CH$_3$ rock⊥ [c]	−0.04	−0.03	−0.03	−0.03
/lb (*x*) */lb (*y*)	±0.06	±0.05	±0.05	±0.06
/lb (*x*) *b* */lb (*y*)*b*	±0.02	±0.01	±0.02	±0.02
CH$_3$ s.str	**5.80**	**4.98**	**5.48**	**4.93**
/CH$_3$ str A	−0.03	−0.03	−0.01	−0.01
/CH$_3$ s.def	0.17	0.14	0.16	0.14
CH$_3$ str A	**5.66**	**4.86**	**5.44**	**4.90**
/CH$_3$ def A	−0.16	−0.13	−0.16	−0.14
/CH$_3$ rock‖	0.11	0.09	0.11	0.10
CH$_3$ str B	**5.71**	**4.90**	**5.46**	**4.92**
/CH$_3$ def B	−0.16	−0.13	−0.15	−0.14
/CH$_3$ rock⊥	0.11	0.09	0.10	0.09
CH$_3$ s.def	**0.54**	**0.41**	**0.47**	**0.42**
CH$_3$ def A, **CH$_3$ def B** *	**0.64**	**0.51**	**0.56**	**0.51**
/CH$_3$ rock‖ */CH$_3$ rock⊥	0.03	0.02	0.03	0.03
CH$_3$ rock‖, **CH$_3$ rock⊥** *	**0.44**	**0.36**	**0.39**	**0.36**
lb (*x*), lb (*y*) *	**0.19**	**0.13**	**0.13**	**0.13**
/lb (*x*) [b] */lb (*y*) [b]	0.05	0.03	0.05	0.05
CH$_3$ s.tors	**0.02**	**0.02**	**0.02**	**0.02**
CH$_3$ tors A, **CH$_3$ tors B**	**0.02**	**0.02**	**0.02**	**0.02**
SnC$_3$ tors	**0.0003**	**0.0003**	**0.0001**	**0.0001**

[a] Notations of vibrations: str is stretching; def is bending of SnC$_3$ and CH$_3$ fragments; rock is rocking (‖ and ⊥ denote parallel and normal to the symmetry plane containing a given methyl group); lb is linear bending; tors is torsional (defined as the sum of the motions in the tetraatomic fragments); and s. is symmetric vibration; letters A and B denote degenerate vibrations. The numbering of atoms is shown in Fig. 1. For each coordinate, the diagonal force constant indicated in boldface print (one out of the two degenerate coordinates is asterisked) is followed by the force constants of interaction between this and other coordinates (slashed). The force constants of stretching vibrations and interactions between them are given in mdyn Å^{-1}, those of interactions between stretching and bending (including rocking and torsional) vibrations are given in mdyn, and those of all types of bending vibrations and interactions between them are given in mdyn Å. Listed are the force constants whose absolute values exceed 0.02 after scaling. The only exception is the SnC$_3$ tors force constant given with a precision of 1 significant digit.

[b] Interaction between vibrations in different Me$_3$Sn—C≡ fragments.

[c,d] The vibrations of the SnC$_3$ fragment are described with respect to the symmetry plane containing the interacting methyl group or with respect to one out of the other two symmetry planes, respectively.

Larger separation between the Me_3Sn groups in molecule **2** compared to that between the substituents at the acetylene fragment in molecule **1** rules out the possibility of steric interactions.

Even under standard conditions, the rotation of Me_3Sn groups can appear to be not the only large-amplitude motion in molecule **2**. The height of the barrier to internal rotation of the Me groups bonded to Sn atoms must be about halved as compared to that of the Me groups bonded to Si atoms, while the potential function of internal rotation is likely more flattened in the range of the angles of rotation (~60°) in which the function reaches its minimum and maximum values corresponding to staggered and eclipsed conformation, respectively. This conclusion can be drawn on the basis of experimental measurements of the barriers to internal rotation in $MeMH_3$ [33–36] and MMe_4 [37–41] (M = C, Si, Ge, Sn, Pb) molecules, which indicate a successive decrease in the barrier heights from 3—4 to 0.5 kcal mol^{-1} on going from hydrocarbons to Pb compounds. According to the data of vibrational spectroscopy studies[38] and elastic and quasielastic neutron scattering investigations,[39,40] the height of the barrier to internal rotation in solid $SnMe_4$ is 0.80(5) kcal mol^{-1}, which is 2.5 times lower than that in $SiMe_4$.

In addition, it has been supposed[42] that it is the large-amplitude bending vibrations of the M—C≡C—M linear fragment that are responsible for abnormally small values of the ${}^1J_{CC}$ spin-spin coupling constants for the C≡C bond in ${}^{13}C$ NMR spectra of several silyl- and stannylacetylenes.[43] The ${}^1J_{CC}$ values decrease substantially on going from mono- to disubstituted derivatives, the smallest values being close to those typical of the C=C bonds, which can be due to strong delocalization of the π-electron density of the C≡C bond. Originally, these results were considered as arguments in favor of nonlinearity of the M—C≡C—M (M = Si, Ge, Sn) fragments.[43] However, measurements of dielectric constants and refractive indices suggested that these fragments are linear. So the above-mentioned results[43] were attributed to a substantially flattened shape of the potential functions of corresponding bending vibrations.[42] Therefore, molecule **2** is likely a nonrigid system characterized by high intrinsic mobility.

The use of quantum-chemical force fields for interpretation of vibrational spectra of bis(trimethylstannyl)acetylene

Vibrational spectra of the light and perdeuterated isotopomers of **2** ($(CH_3)_3SnC{\equiv}CSn(CH_3)_3$ and $(CD_3)_3SnC{\equiv}CSn(CD_3)_3$, respectively)[21] were analyzed using the standard approach based on the approximation of small-amplitude harmonic vibrations assuming a D_{3d} molecular symmetry. The nonredundant set of local-symmetry internal coordinates used in this work is listed in Table 3.

The approximation of small-amplitude harmonic vibrations ignores free internal rotation of the Me_3Sn groups as well as the possibility for both the large-amplitude torsional motions of six methyl substituents and the large-amplitude bending vibrations of the Sn—C≡C—Sn linear fragment to occur. However, this approach has proved itself in the analysis of the vibrational spectra of compound **1**, in particular, because nearly free internal rotation of Me_3Si groups has no significant effect on the positions of the spectral bands of silylacetylenes.[15] One can expect that internal rotations also will have only little effect on the experimental spectra of compound **2**. Consideration of the linear fragment deformations in the framework of small-amplitude harmonic approximation also presented no difficulties in the spectral and electron diffraction studies of **1**.[15,16] Peculiarities of the effect of large-amplitude bending vibrations in the linear fragment on the molecular structure and spectra of **2** are hard to predict.

The unscaled quantum-chemical force constants of molecule **2** calculated in the RHF and MP2(fc) approximations, as well as their scaled modifications, are presented in Table 2 (the complete versions of the force fields are also available on request). Comparison of the RHF and MP2(fc) force fields shows that their general structure is independent of the calculation level. Not only do the corresponding off-diagonal force constants retain their signs, but are also in most cases very close in absolute values. The fact that the scaled force constants of both force fields virtually coincide can be evidence of unambiguous interpretation of the experimental spectra.

As for molecule **1**,[15] the calculated force fields of molecule **2** include a large number of relatively small interaction constants. Their absolute values very rarely reach 0.1—0.2 in the corresponding units (mdyn $Å^{-1}$, mdyn, and mdyn Å).* For both molecules, the force constants of (i) stretching and bending vibrations of the Me groups, (ii) interactions between these vibrations, and (iii) interactions of these vibrations with the framework vibrations are essentially transferable. However, for molecule **2** the force constants of the framework vibrations including the C≡C stretching and most of the interactions of these vibrations, as well as the force constants of torsional vibrations, are appreciably smaller.

It is difficult to compare the force constants of molecule **2** calculated in this work with the empirical force constants[21] because of the use of different sets of internal coordinates. Nevertheless, mention may be made of a number of essential distinctions. For instance, the empirical force constants of bending vibrations of Me groups (0.58 and 0.60 mdyn Å)[21] and, especially, of SnC_3 fragments (0.69 and 0.80 mdyn Å)[21] are substantially larger, whereas those of the C—H stretching vibration (4.735 mdyn $Å^{-1}$)[21] are somewhat smaller than the

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* These units correspond to the force constants of (i) stretching vibrations and interactions between them (mdyn $Å^{-1}$), (ii) interactions between stretching and bending (including rocking and torsional) vibrations (mdyn), and (iii) all types of bending vibrations and interactions between them (mdyn Å); 1 mdyn $Å^{-1}$ = 10^2 N m^{-1}, 1 mdyn = 10^{-8} N, and 1 mdyn Å = 10^{-18} N m.

Table 3. Nonredundant set of local-symmetry internal coordinates for bis(trimethylstannyl)acetylene (**2**) molecule[a]

Coordinate number	Coordinate notation	Instance of coordinate definition
1	C≡C str	C2C3 str
2, 3	SnC≡ str	Sn1C2 str
4, 5	SnC$_3$ s.str	(Sn1C5 str + Sn1C6 str + Sn1C7 str)/$\sqrt{3}$
6, 7	SnC$_3$ str A	(2 Sn1C5 str − Sn1C6 str − Sn1C7 str)/$\sqrt{6}$
8, 9	SnC$_3$ str B	(Sn1C6 str − Sn1C7 str)/$\sqrt{2}$
10, 11	SnC$_3$ s.def	(C6Sn1C7 bend + C5Sn1C6 bend + C5Sn1C7 bend − C5Sn1C2 bend − C7Sn1C2 bend − − C6Sn1C2 bend)/$\sqrt{6}$
12, 13	SnC$_3$ def A	(2 C6Sn1C7 bend − C5Sn1C6 bend − C5Sn1C7 bend)/$\sqrt{6}$
14, 15	SnC$_3$ def B	(C5Sn1C6 bend − C5Sn1C7 bend)/$\sqrt{2}$
16, 17	SnC$_3$ rock A	(2 C5Sn1C2 bend − C7Sn1C2 bend − C6Sn1C2 bend)/$\sqrt{6}$
18, 19	SnC$_3$ rock B	(C7Sn1C2 bend − C6Sn1C2 bend)/$\sqrt{2}$
20—25	CH$_3$ s.str	(C5H11 str + C5H12 str + C5H13 str)/$\sqrt{3}$
26—31	CH$_3$ str A	(2 C5H11 str − C5H12 str − C5H13 str)/$\sqrt{6}$
32—37	CH$_3$ str B	(C5H12 str − C5H13 str)/$\sqrt{2}$
38—43	CH$_3$ s.def	(H12C5H13 bend + H11C5H12 bend + H11C5H13 bend − Sn1C5H11 bend − − Sn1C5H13 bend − Sn1C5H12 bend)/$\sqrt{6}$
44—49	CH$_3$ def A	(2 H12C5H13 bend − H11C5H12 bend − H11C5H13 bend)/$\sqrt{6}$
50—55	CH$_3$ def B	(H11C5H12 bend − H11C5H13 bend)/$\sqrt{2}$
56—61	CH$_3$ rock$\parallel$	(2 Sn1C5H11 bend − Sn1C5H13 bend − Sn1C5H12 bend)/$\sqrt{6}$
62—67	CH$_3$ rock$\perp$	(Sn1C5H13 bend − Sn1C5H12 bend)/$\sqrt{2}$
68, 69	lb (*x*)	Sn1C2C3 lb in the *x*0*z* plane
70, 71	lb (*y*)	Sn1C2C3 lb in the *y*0*z* plane
72, 73	CH$_3$ s.tors	[(C$_3$)Sn1—C5(H$_3$) tors + (C$_3$)Sn1—C6(H$_3$) tors + (C$_3$)Sn1—C7(H$_3$) tors]/$\sqrt{3}$
74, 75	CH$_3$ tors A	[2 (C$_3$)Sn1—C5(H$_3$) tors − (C$_3$)Sn1—C6(H$_3$) tors − (C$_3$)Sn1—C7(H$_3$) tors]/$\sqrt{6}$
76, 77	CH$_3$ tors B	[(C$_3$)Sn1—C6(H$_3$) tors − (C$_3$)Sn1—C7(H$_3$) tors]/$\sqrt{2}$
78	SnC$_3$ tors	(C$_3$)Sn1···Sn4(C$_3$) tors

[a] For the notations of vibrations, see notes to Table 2.

corresponding parameters of the scaled quantum-chemical force fields. Originally, the force constants of Sn—C≡ and Sn—C(H$_3$) stretching vibrations were assumed to be equal and set to 2.33 mdyn Å^{-1}.[21] However, our calculations showed that these constants are different, though to a lesser extent than the corresponding parameters of molecule **1**.[15] The force constants of bending vibrations of the Sn—C≡C—Sn linear fragment are appreciably larger than the empirical values[21]; moreover, force constants corresponding to the interactions between these coordinates appear (see Table 2). Since the empirical force field[21] includes a much smaller number of force constants, the absolute values of some of them are forced to be strongly overestimated (*e.g.*, the force constant of the Sn—C(H$_3$) str/C—H str interaction, which is equal to −0.195 mdyn Å^{-1}).

In Table 4, the refined values of the scale factors for the force fields of molecule **2** obtained from solving the inverse spectral problems in the RHF and MP2(fc) approximations are compared with the scale factors found previously[15] for molecule **1**. The scale factors obtained for the MP2(fc) force field are close to unity. Appreciable decrease in the values of some scale factors calculated in the RHF approximation can be explained by inadequacy of this approach. Anharmonicity of vibrations also affects the magnitudes of scale factors. The RHF calculations of **1** were carried out in the standard 6-311G** basis set, whereas the SBK effective core potential (see above) was introduced for the Sn atoms in **2**. Nevertheless, comparison demonstrates very good agreement between the scale factors obtained for both molecules. Of prime importance is coincidence and, hence, good transferability of the scale factors corresponding to the stretching and bending vibrations in the SnC$_3$ and SiC$_3$ fragments (their values are close to unity). In addition, the scale factors corresponding to vibrations of the SiC$_3$ fragment are virtually independent of the basis set used in the Hartree—Fock calculations of the force field (see also Ref. 15). The scale factors for the force constants of the Me group in stannyl- and silylacetylenes are in excellent agreement with those found for Me fragments in different classes of compounds.[17—20]

As in the case of compound **1**,[15] introduction according to Dennison[44,45] of harmonizing corrections to experimental frequencies of nearly pure Me group stretching modes of the light and perdeuterated isotopomers of **2** makes the values of the scale factors of these vibrations much closer to unity (see Table 4). This improves agreement between the theoretical and experimental frequencies of both isotopomers, which is characterized by a mean error of 3.1 to 3.5 cm^{-1} (or 0.8 to 0.9%) compared to 6.1—6.9 cm^{-1} (or 1.0%) without frequency harmonization. The weak effect of harmonization on the relative errors is explained by the large contribution of discrepancies in the low-frequency region of the Raman spectra, in which the experimental data are somewhat less reliable (Tables 5 and 6). The quantum-

Table 4. Scale factors for the force fields of the bis(trimethylstannyl)acetylene molecule (**2**) calculated in the RHF and MP2(fc) approximations (the 6-311G** basis set, Sn: SBK ECP) and for the force field of the bis(trimethylsilyl)acetylene (**1**) molecule calculated in the RHF/6-311G** approximation

Vibration type[a]	Internal coordinate number [a]	Scale factor		
		RHF		MP2,
		2	**1** [15]	**2**
C≡C str	1	0.771	0.770	1.036
Sn(Si)—C≡ str	2, 3	0.910	0.944	0.953
Sn(Si)—C(H$_3$) str	4—9	0.973	0.944	1.013
Sn(Si)C$_3$ s.def	10, 11	0.961	0.960	1.139
Sn(Si)C$_3$ def	12—15	0.961	0.959	1.140
Sn(Si)C$_3$ rock	16—19	0.951	0.950	1.140
C—H str	20—37	0.858 (0.924)[b]	0.858 (0.924)[b]	0.901 (0.970)[b]
CH$_3$ s.def	38—43	0.769	0.777	0.897
CH$_3$ def	44—55	0.801	0.792	0.911
CH$_3$ rock	56—67	0.816	0.790	0.921
Sn(Si)—C≡C lb	68—71	0.690	0.690	1.000
CH$_3$ tors	72—77	1.100	1.100	1.000
Sn(Si)C$_3$ tors	78	1.000[c]	1.000[c]	1.000[c]

[a] See Tables 2 and 3.

[b] Scale factors obtained after introduction of harmonizing corrections to experimental frequencies of stretching vibrations of Me groups are given in parentheses (see text); other scale factors remained unchanged after refinement for compound **2** and were reproduced with an accuracy of 0.001—0.002 for compound **1**.

[c] Fixed.

Table 5. Vibrational frequencies (ν) and IR band intensities (*I*) calculated in the MP2(fc)/6-311G** (Sn: SBK ECP) approximation and band assignment in the experimental spectra of $(CH_3)_3SnC{\equiv}CSn(CH_3)_3$ (**2**) based on the scaled quantum-chemical force field[a]

Symmetry type	Vibration number	MP2 calculations		Experiment,[21] ν^b/cm^{-1}		Scaling of MP2 force field	
		ν/cm^{-1}	I/D^2 (amu)$^{-1}$ Å^{-2}	IR[c]	Raman[c]	ν^b/cm^{-1}	Potential energy distribution (%)
A_{1g}	1	3179	0.0	—	2987 (w dp) [3112]	3017 [3131]	CH$_3$ str A (99)
	2	3077	0.0	—	2920 wm p [3042]	2921 [3031]	CH$_3$ s.str (99)
	3	2036	0.0	—	2065 mw p	2065	C≡C str (91)
	4	1489	0.0	—	—	1421	CH$_3$ def A (96)
	5	1272	0.0	—	1205 mw p	1204	CH$_3$ s.def (96)
	6	811	0.0	—	—	784	CH$_3$ rock∥ (90)
	7	517	0.0	—	520 vs p	520	SnC$_3$ s.str (99)
	8	189	0.0	—	175 sh	189	SnC≡ str (48) SnC$_3$ s.def (35) CH$_3$ rock∥ (12)
	9	119	0.0	—	140 sh	123	SnC$_3$ s.def (50) SnC≡ str (25) CH$_3$ rock∥ (20)
A_{1u}	10	3183	0.0	—	—	3021 [3136]	CH$_3$ str B (99)
	11	1472	0.0	—	—	1406	CH$_3$ def B (96)
	12	688	0.0	—	—	660	CH$_3$ rock⊥ (95)
	13	103	0.0	—	—	104	CH$_3$ s.tors (98)
	14	3	0.0	—	—	2	SnC$_3$ tors (99)
A_{2g}	15	3183	0.0	—	—	3021 [3136]	CH$_3$ str B (99)
	16	1473	0.0	—	—	1406	CH$_3$ def B (96)
	17	688	0.0	—	—	660	CH$_3$ rock⊥ (95)
	18	104	0.0	—	—	103	CH$_3$ s.tors (98)
A_{2u}	19	3179	1.33	2995 m [3120]	—	3017 [3131]	CH$_3$ str A (99)
	20	3077	0.40	2920 m [3042]	—	2921 [3031]	CH$_3$ s.str (99)
	21	1488	0.22	1410 w	—	1421	CH$_3$ def A (96)

(*to be continued*)

Table 5. (*continued*)

Symmetry type	Vibration number	MP2 calculations		Experiment,[21] ν^b/cm^{-1}		Scaling of MP2 force field	
		ν/cm^{-1}	$I/D^2\,(amu)^{-1}\,Å^{-2}$	IR[c]	Raman[c]	ν^b/cm^{-1}	Potential energy distribution (%)
	22	1271	0.08	1193 (wm)	—	1204	CH_3 s.def (96)
	23	801	5.54	770 vs	—	774	CH_3 rock$\parallel$ (90)
	24	606	7.01	595 vs	—	591	SnC≡ str (98)
	25	515	0.48	517 m	—	518	SnC_3 s.str (99)
	26	140	0.44	146 ms	—	149	SnC_3 s.def (74) CH_3 rock$\parallel$ (24)
E_g	27	3184	0.0	—	—	3022 [3136]	CH_3 str B (99)
	28	3178	0.0	—	2987 w dp [3112]	3017 [3131]	CH_3 str A (99)
	29	3077	0.0	—	2920(wm p) [3042]	2921 [3031]	CH_3 s.str (99)
	30	1482	0.0	—	—	1415	CH_3 def B (82)
	31	1477	0.0	—	—	1410	CH_3 def A (82)
	32	1263	0.0	—	1195 wm dp	1197	CH_3 s.def (95)
	33	806	0.0	—	—	779	CH_3 rock$\perp$ (84)
	34	739	0.0	—	—	712	CH_3 rock$\parallel$ (85)
	35	535	0.0	—	540 m dp	538	SnC_3 str A, SnC_3 str B (99)
	36	295	0.0	—	—	301	lb (x), lb (y) (65) SnC_3 rock A, SnC_3 rock B (24)
	37	136	0.0	—	150 s dp	144	SnC_3 def A, SnC_3 def B (72) CH_3 rock$\perp$ (23)
	38	108	0.0	—	100 s dp	109	CH_3 tors A, CH_3 tors B (89)
	39	78	0.0	—	100 s dp	81	lb (x), lb (y) (40) SnC_3 rock A, SnC_3 rock B (37)
E_u	40	3184	0.99	2995 m [3120]	—	3022 [3136]	CH_3 str B (99)
	41	3178	0.07	2995 m [3120]	—	3017 [3131]	CH_3 str A (99)
	42	3077	1.05	2920 m [3042]	—	2921 [3031]	CH_3 s.str (99)
	43	1481	0.28	1410 w	—	1414	CH_3 def B (86)
	44	1477	0.01	1410 w	—	1410	CH_3 def A (86)
	45	1263	0.87	1193 wm	—	1197	CH_3 s.def (95)
	46	807	3.75	770 vs	—	779	CH_3 rock$\perp$ (85)
	47	741	3.31	726 m	—	714	CH_3 rock$\parallel$ (86)
	48	536	2.60	538 vs	—	539	SnC_3 str A, SnC_3 str B (98)
	49	207	1.54	212 ms	—	218	SnC_3 rock A, SnC_3 rock B (69) CH_3 rock$\parallel$ (16)
	50	135	0.13	146 (ms)	—	143	SnC_3 def A, SnC_3 def B (70) CH_3 rock$\perp$ (21)
	51	108	0.0002	—	—	108	CH_3 tors A, CH_3 tors B (96)
	52	34	0.03	—	—	35	lb (x), lb (y) (68) SnC_3 rock A, SnC_3 rock B (28)

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[a] See Tables 2 and 3.

[b] "Harmonized" experimental frequencies of stretching vibrations of methyl groups and theoretical frequencies that changed after scaling with the use of the harmonized frequencies are given in square brackets. (The absence of bracketed values indicates insignificance of harmonization corrections.) The characteristics of the bands that overlap with more intense bands are given in parentheses.

[c] The following notations are used: w, m, s are weak, medium, and strong bands; v is very; sh is shoulder; and p and dp denote polarized and depolarized lines, respectively.

chemical estimates are in good agreement with the experimental intensities of the IR bands (see Table 5).

The distribution of normal vibrational modes of molecule **2** over the irreducible representations of the D_{3d} point symmetry group has the form:

$$\Gamma_{3N-6} = 9\,A_{1g} + 5\,A_{1u} + 4\,A_{2g} + 8\,A_{2u} + 13\,E_g + 13\,E_u.$$

Vibrations active only in the Raman spectra include the A_{1g} (polarized) and E_g (depolarized) modes (Fig. 2). The IR bands (Fig. 3) correspond to A_{2u} and E_u modes. The A_{1u} and A_{2g} modes are optically inactive and are not observed in the spectra. In particular, one of the A_{1u} modes corresponds to torsional motion of the trimethylstannyl groups. According to our calculations, its frequency is 1—2 cm^{-1} (ν_{14}, see Tables 5 and 6), which is lower than in the case of molecule **1**.[15]

Nearly pure modes correspond to most of the bands in the spectra of the light isotopomer (see Table 5). The exceptions are several modes corresponding to the Raman bands in the frequency region below 200 cm^{-1} (the ν_8, ν_9, and ν_{39} bands in Table 5). In the spectra of the perdeuterated isotopomer (see Table 6), mixed are the analogous modes and those corresponding to the ν_{38} Raman band and to the ν_{23} and ν_{24} IR bands. The last two A_{2u} modes are mixtures of the CD_3 rocking and SnC≡ stretching vibrations. In these cases, the traditional classification, according to which each frequency corresponds to a particular bond or atomic group vibration, is arbitrary and inefficient.

The spectral analysis carried out in this work made it possible to interpret the experimental bands in the low-frequency regions of the IR and Raman spectra of the light and perdeuterated isotopomers of compound **2**. Previously,[21] this presented some difficulties. In particular, we showed that the A_{1g} mode with predominant contribution of the totally symmetric bending vibration of the SnC_3 fragment in the Raman spectrum of the light isotopomer of compound **2** must correspond to a band whose frequency is higher than that suggested originally.[21] The previously unassigned shoulder at 140 cm^{-1} (ν_9, see Table 5, Fig. 2) is well suited to correspondence in this case. The ν_9 band in the Raman spectrum of the perdeuterated isotopomer can overlap with the intense depolarized bands at 125 or 90 cm^{-1}. The previously unassigned depolarized Raman bands at 150 and 125 cm^{-1} in the spectra of the light and perdeuterated isotopomers, respectively, correspond to degenerate SnC_3 bending vibrations (E_g, ν_{37}, see Tables 5 and 6, Fig. 2). In turn, intense depolarized bands at 100 cm^{-1} for $(CH_3)_3SnC{\equiv}CSn(CH_3)_3$ and at 90 cm^{-1} for $(CD_3)_3SnC{\equiv}CSn(CD_3)_3$ formerly assigned[21] to the ν_9 mode

Table 6. Experimental vibrational frequencies (ν/cm^{-1}), those calculated in the MP2(fc)/6-311G** (Sn: SBK ECP) approximation (ν/cm^{-1}), and band assignment in the experimental spectra of $(CD_3)_3SnC{\equiv}CSn(CD_3)_3$ based on the scaled quantum-chemical force field

Symmetry type	Vibration number	MP2 calculations, ν/cm^{-1}	Experiment[21]		Scaling of MP2 force field	
			IR	Raman	ν/cm^{-1}	Potential energy distribution (%)
A_{1g}	1	2354	—	2245 [2314]	2234 [2318]	CD_3 str A (99)
	2	2206	—	2125 s p [2189]	2094 [2173]	CD_3 s.str (99)
	3	2036	—	2065 m p	2065	C≡C str (91)
	4	1075	—	—	1026	CD_3 def A (97)
	5	980	—	935 s p	932	CD_3 s.def (89)
	6	628	—	—	610	CD_3 rock‖ (92)
	7	469	—	465 vs p	472	SnC_3 s.str (95)
	8	182	—	—	181	SnC≡ str (58) SnC_3 s.def (25)
	9	105	—	125 (s dp)	109	SnC_3 s.def (55) CD_3 rock‖ (25) SnC≡ str (15)
A_{1u}	10	2357	—	—	2237 [2321]	CD_3 str B (99)
	11	1066	—	—	1018	CD_3 def B (98)
	12	513	—	—	492	CD_3 rock⊥ (97)
	13	73	—	—	73	CD_3 s.tors (98)
	14	1	—	—	1	SnC_3 tors (99)
A_{2g}	15	2357	—	—	2237 [2321]	CD_3 str B (99)
	16	1066	—	—	1018	CD_3 def B (98)
	17	513	—	—	492	CD_3 rock⊥ (97)
	18	73	—	—	73	CD_3 s.tors (98)

(*to be continued*)

Table 6. (*continued*)

Symmetry type	Vibration number	MP2 calculations, ν/cm^{-1}	Experiment[21]		Scaling of MP2 force field	
			IR	Raman	ν/cm^{-1}	Potential energy distribution (%)
A$_{2u}$	19	2354	2240 w [2309]	—	2234 [2318]	CD$_3$ str A (99)
	20	2206	2120 mw [2183]	—	2094 [2173]	CD$_3$ s.str (99)
	21	1075	1025 mw	—	1026	CD$_3$ def A (97)
	22	980	925 m	—	932	CD$_3$ s.def (89)
	23	627	600 sh	—	609	CD$_3$ rock$\parallel$ (54) SnC$\equiv$ str (42)
	24	598	580 vs	—	582	SnC$\equiv$ str (65) CD$_3$ rock$\parallel$ (31)
	25	467	470 w	—	469	SnC$_3$ s.str (95)
	26	123	130 ms	—	130	SnC$_3$ s.def (70) CD$_3$ rock$\parallel$ (27)
E$_g$	27	2357	—	2245 [2314]	2238 [2322]	CD$_3$ str B (98)
	28	2353	—	2245 [2314]	2234 [2318]	CD$_3$ str A (98)
	29	2206	—	2125 (s p) [2189]	2094 [2173]	CD$_3$ s.str (99)
	30	1071	—	—	1022	CD$_3$ def B (76) CD$_3$ def A (21)
	31	1069	—	—	1020	CD$_3$ def A (76) CD$_3$ def B (21)
	32	981	—	935 (s p)	934	CD$_3$ s.def (88)
	33	620	—	—	601	CD$_3$ rock$\perp$ (87)
	34	564	—	—	546	CD$_3$ rock$\parallel$ (85)
	35	487	—	490 m dp	487	SnC$_3$ str A, SnC$_3$ str B (91)
	36	289	—	—	294	lb (x), lb (y) (64) SnC$_3$ rock A, SnC$_3$ rock B (21)
	37	118	—	125 s dp	125	SnC$_3$ def A, SnC$_3$ def B (69) CD$_3$ rock$\perp$ (27)
	38	80	—	90 m dp	81	CD$_3$ tors A, CD$_3$ tors B (46) SnC$_3$ rock A, SnC$_3$ rock B (26) lb (x), lb (y) (18)
	39	68	—	90 m dp	69	lb (x), lb (y) (32) SnC$_3$ rock A, SnC$_3$ rock B (28) CD$_3$ tors A, CD$_3$ tors B (28)
E$_u$	40	2357	2240 w [2309]	—	2238 [2322]	CD$_3$ str B (98)
	41	2353	2240 w [2309]	—	2234 [2318]	CD$_3$ str A (98)
	42	2206	2120 mw [2183]	—	2094 [2173]	CD$_3$ s.str (99)
	43	1071	1025 mw	—	1022	CD$_3$ def B (82)
	44	1069	1025 mw	—	1021	CD$_3$ def A (82)
	45	981	925 m	—	934	CD$_3$ s.def (88)
	46	621	600 sh	—	602	CD$_3$ rock$\perp$ (88)
	47	564	550 wm	—	546	CD$_3$ rock$\parallel$ (88)
	48	487	490 ms	—	488	SnC$_3$ str A, SnC$_3$ str B (90)
	49	199	210 ms	—	208	SnC$_3$ rock A, SnC$_3$ rock B (63) CD$_3$ rock$\parallel$ (21)
	50	117	130 ms	—	124	SnC$_3$ def A, SnC$_3$ def B (67) CD$_3$ rock$\perp$ (24)
	51	77	—	—	77	CD$_3$ tors A, CD$_3$ tors B (96)
	52	31	—	—	31	lb (x), lb (y) (66) SnC$_3$ rock A, SnC$_3$ rock B (29)

Note. For the notations, see notes^{a-e} to Table 5.

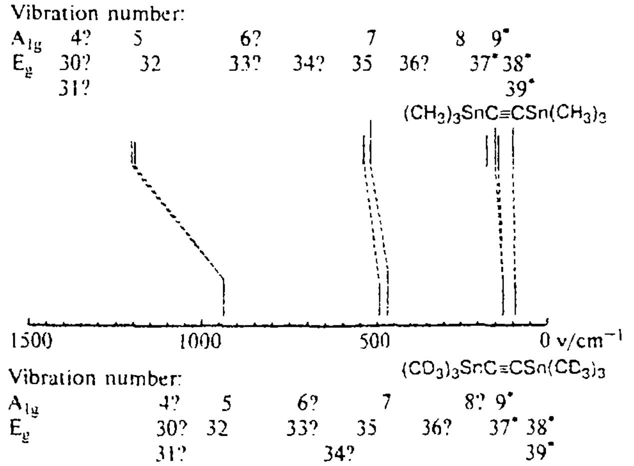

Fig. 2. Band diagram of experimental Raman spectra of $(CH_3)_3SnC{\equiv}CSn(CH_3)_3$ and $(CD_3)_3SnC{\equiv}CSn(CD_3)_3$ molecules corresponding to active (A_{1g} and E_g) modes in the frequency region below 1500 cm^{-1}. Asterisked are the numbers of reassigned bands (see Tables 5 and 6).

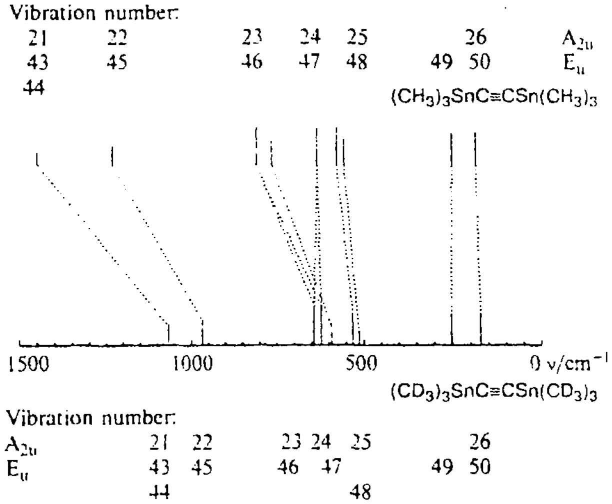

Fig. 3. Band diagram of experimental IR spectra vibrations of $(CH_3)_3SnC{\equiv}CSn(CH_3)_3$ and $(CD_3)_3SnC{\equiv}CSn(CD_3)_3$ molecules corresponding to active (A_{2u} and E_u) modes in the frequency region below 1500 cm^{-1}.

must correspond to E_g type modes. In the case of the light isotopomer these are two modes with close frequencies (ν_{38} and ν_{39}). The former corresponds to a pure Me group torsional mode, whereas the latter includes contributions of bending vibrations of the Sn—C≡C—Sn chain and rocking vibrations of the SnC_3 fragment. In the Raman spectrum of the perdeuterated isotopomer, the ν_{38} and ν_{39} bands correspond to mixed modes with nearly equal contributions of these torsional, rocking, and linear bending vibrations (see Table 6).

The assignment of bending vibrations of the Sn—C≡C—Sn linear fragment has not been discussed in the original study[21]; at the same time, it can substantially affect the adequacy of vibrational characteristics u_{ij} and δ_{ij} calculated from spectral data. Based on the above-mentioned similarity of quantum-chemical force fields and on transferability of the scale factors for molecules **1** and **2**, one can expect that the experimental spectra will also be similar. According to our data, the IR bands corresponding to the pure E_u linear bending mode (ν_{52}, see Tables 5 and 6) should be observed at 30—35 cm^{-1}, which is beyond the spectral region investigated in the original study.[21] Therefore, as in the case ~~of compound **1**,[15] we would have to restrict ourselves to~~ consideration of the E_g Raman modes in the spectral region below 400 cm^{-1}, which include the contributions of linear bending vibrations.

As was mentioned above, intense depolarized bands at 100 and 90 cm^{-1} recorded in the Raman spectra of the light and perdeuterated isotopomers of compound **2**, respectively, were assigned to the E_g mixed modes, which include contributions of the vibrations under consideration (ν_{39}, see Table 5, and ν_{38}, ν_{39}, see Table 6 and Fig. 2). However, attempts at detecting any signals in the region near 300 cm^{-1} in both spectra failed. According to our calculations, this is another spectral region in which high-frequency bands corresponding to the E_g linear bending modes (ν_{36}, see Tables 5 and 6) should be observed. Depolarized bands at 405 and 390 cm^{-1} correspond to these modes in the Raman spectra of the light and perdeuterated isotopomers of compound **1**, respectively.[15] On the whole, the problem requires a more detailed experimental study. Indirectly, this was done by comparing the RMS amplitudes obtained from spectroscopic calculations and electron diffraction experiment in the study of compound **2**.[46]

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