Vibrational spectra and structure of cesium salts of icosahedral monocarba-*closo*-dodecarborate anion, $[CB_{11}H_{12}]^-$, and its *nido*-derivative, $[CB_{10}H_{13}]^-$

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The Raman and IR spectra of the cesium salts of monocarbon carboranes, [*closo*-$CB_{11}H_{12}]^-$ and [*nido*-$CB_{10}H_{13}]^-$, are reported and the assignment of the normal modes is given. Quantum-chemical calculations of the geometry of undistorted *closo*-anions $B_{12}H_{12}^{2-}$ and $CB_{11}H_{12}^-$ were carried out and normal coordinate analysis for the latter was performed. Structural parameters and spectral characteristics of isoelectronic *closo*-polyhedra $[B_{12}H_{12}]^{2-}$, $[CB_{11}H_{12}]^-$, and *p*-$C_2B_{10}H_{12}$ and those of the *closo*- and *nido*-structures were compared.

Key words: carboranes, Raman spectroscopy, IR spectroscopy, quantum-chemical calculations.

Earlier,[1] we reported a detailed study and comprehensive analysis of the vibrational spectra of dicarba-*closo*-dodecaboranes ($C_2B_{10}H_{12}$) containing two C atoms in the icosahedral cage and of their precursor, a *closo*-borate anion $[B_{12}H_{12}]^{2-}$ (**1**) containing no C atoms. However, the lack of experimental data for icosahedral monocarbon carboranes gave no possibility to follow general trends of the changes in the spectral pattern upon successive introduction of C atoms into the icosahedral boron cage. To bridge the gap, in this work we report the vibrational spectra of monocarba-*closo*-dodecaborate anion $[CB_{11}H_{12}]^-$ (**2**, Fig. 1), which allow a comparative group theory analysis of normal modes of the isoelectronic polyhedra $[B_{12}H_{12}]^{2-}$ (**1**), $[CB_{11}H_{12}]^-$ (**2**), *p*-$C_2B_{10}H_{12}$ (**3**) and a comparison of the results obtained with the experimental data. The results obtained for the unsubstituted molecules can serve as a basis for reliable interpretation of the vibrational spectra of various derivatives of these compounds.

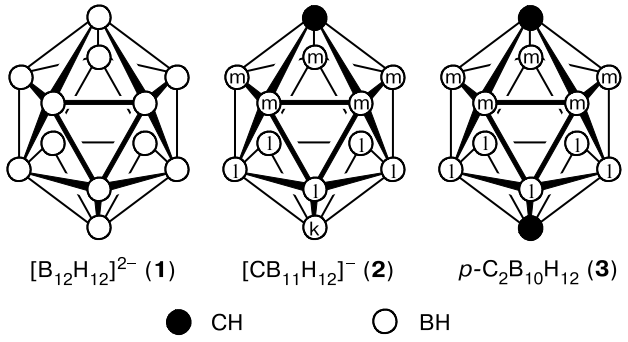

Fig. 1. Structure of icosahedral polyhedra **1**, **2**, and **3**.

The undistorted anion **2** belongs to the C_{5v} point symmetry group. A total of 66 fundamentals of **2** are distributed among symmetry species as follows:

$$\Gamma = 11\ A_1 + 3\ A_2 + 14\ E_1 + 12\ E_2.$$

The A_1 totally symmetric modes and the E_1 degenerate modes are both IR and Raman active. The E_2 modes are Raman active only, whereas the A_2 modes are silent. The A_1 modes must correspond to polarized, while the E_1

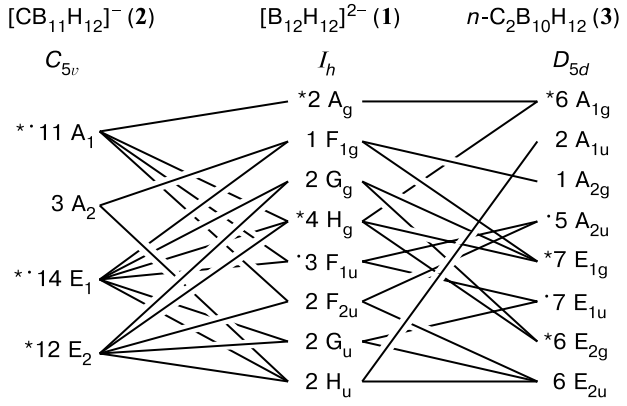

Fig. 2. Correlation between the symmetry species of the C_{5v}, I_h, and D_{5d} point symmetry groups; shown are the Raman active modes (asterisked) and the IR active modes (indicated by points).

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Table 1. Sets of equivalent internal coordinates of $[CB_{11}H_{12}]^-$ anion, which can be involved in vibrations of a given symmetry species

Symmetry species	Number of modes	ν(CH)	δ(CH)	ν(B_kH)	δ(B_kH)	ν(B_lH)	δ(B_lH)		ν(B_mH)	δ(B_mH)		Skeletal vibrations
							I [b]	II [c]		I [b]	II [c]	ν(B_mC), ν(B_mB_m), ν(B_lB_m), ν(B_lB_l) and ν(B_kB_l)
A_1	11	1	—	1	—	1	—	1	1	—	1	5
A_2	3	—	—	—	—	—	1	—	—	1	—	1
E_1	14	—	1	—	1	1	1	1	1	1	1	6
E_2	12	—	—	—	—	1	1	1	1	1	1	6

[a] For notations of the boron atoms (k, l, and m), see Fig. 1; ν and δ are the stretching and deformation vibration, respectively.
[b] In-plane vibrations.
[c] Out-of-plane vibrations.

and E_2 modes must correspond to depolarized Raman lines. The results of group theory analysis, showing which sets of equivalent internal coordinates can be involved in the vibrations of a given symmetry species, can be found in Table 1. A correlation between the symmetry species of the vibrational modes of icosahedral entities **1** (point symmetry group I_h), **2** (point symmetry group C_{5v}), and **3** (point symmetry group D_{5d}) is presented in Fig. 2.

Based on the results of spectral studies of all isomers of the $C_2B_{10}H_{12}$ molecule, one can expect that some vibrational modes of anion **2**, which do not involve the CH "hetero-fragment," will be "insensitive" to symmetry lowering (due to close atomic masses of B and C, small difference between the B—B and B—C interatomic distances, and similarity of the electronic structure of *closo*-borates and *closo*-carboranes) and will still obey the effective icosahedral symmetry. This should lead to coincidence of the frequencies of vibrational modes belonging to different symmetry species but having similar eigenvectors and to low intensities of the vibrations originated from the inactive modes of icosahedron **1**.

The *nido*-anion $[CB_{10}H_{13}]^-$ (**4**) is of low symmetry (C_s); therefore, all vibrational modes of **4** should be both IR and Raman active.

Experimental

The samples of [*closo*-$CB_{11}H_{12}$]Cs and [*nido*-$CB_{10}H_{13}$]Cs were synthesized following the known procedures.[2,3]

The Raman spectra of both solid samples and their saturated aqueous solutions were recorded using T64000 and U-1000 Raman laser spectrometers (Jobin—Yvon, France) with excitation by the line λ = 514.5 nm of an SP-2020 Ar^+ laser. The depolarization ratios of the Raman lines in the spectrum of the aqueous solution of **2** were estimated qualitatively. The IR spectra of KBr pellets, hexachlorobutadiene mulls, and solutions in D_2O were recorded on a Carl Zeiss M-82 spectrophotometer.

Geometry optimization and calculations of the Mulliken atomic charges, vibrational frequencies, and atomic displacements for anions **1** and **2** were carried out using the density functional approach with the three-parameter B3LYP functional, the 6-311++G(d,p) basis set, and the G94W program suite.[4]

Results and Discussion

Calculated geometries of $[B_{12}H_{12}]^{2-}$ and $[CB_{11}H_{12}]^-$ anions. The geometry of undistorted anion **2** has not been experimentally determined with certainty. Most structures containing unsubstituted anions **1** and **2** (retrieved from the Cambridge Structural Database) exhibit disordered polyhedra. That is why an unambiguous location of

Table 2. Bond lengths (d) in $[B_{12}H_{12}]^{2-}$ and $[CB_{11}H_{12}]^-$ anions and in *p*-$C_2B_{10}H_{12}$ molecule

Compound	Bond	d[a]/Å
$[B_{12}H_{12}]^{2-}$	B—B	1.787
	B—H	1.201
$[CB_{11}H_{12}]^-$	B—C	1.707
	B_l—B_m	1.774
	B_m—B_m	1.780
	B_l—B_l	1.790
	B_k—B_l	1.786
	B_m—H	1.187
	B_l—H	1.189
	B_k—H	1.190
	C—H	1.081
p-$C_2B_{10}H_{12}$	B—C	1.707 (1.710)
	B_l—B_m	1.774 (1.772)
	B_m—B_m [b]	1.792 (1.792)
	B—H	1.178
	C—H	1.073

[a] Given are the results of B3LYP/6-311++G(d,p) calculations[6] and the experimental gas-phase electron diffraction data[5] (figures in brackets).
[b] For *p*-$C_2B_{10}H_{12}$ molecule, the B_m—B_m and B_l—B_l distances are equal (see Fig. 1).

the C atom in anion **2** was not possible. For some salts of anion **1** the structures with ordered unsubstituted dianions are available. However, numerous shortened contacts with cations present in these structures lead to substantial distortion of the icosahedron geometry, thus making a correct comparison of the bond lengths for the dianion in the crystal and in the gas phase impossible.

The bond lengths for anions **1** and **2** calculated in this work are listed in Table 2. For comparison, we also present here the published data[5,6] for molecule **3**. Analysis of the bond lengths in the series **1**, **2**, **3** has shown that the geometry of anion **2** is intermediate between those of **1** and **3**. As in the case of molecule **3**, replacement of a B atom by the C atom results in two inequivalent types of B—B bonds. The first type includes somewhat longer (or "latitudinal") $B_m—B_m$ bonds (for designations, see Fig. 1) while the second type includes somewhat shorter (or "meridional") $B_l—B_m$ bonds. As the B—B bonds in anion **2** recede from the C atom, their lengths become virtually indistinguishable from those in anion **1**. Close values of the C—B bond lengths and the $B_l—B_m$ "meridional" bond lengths in anion **2** and molecule **3** are notable, whereas

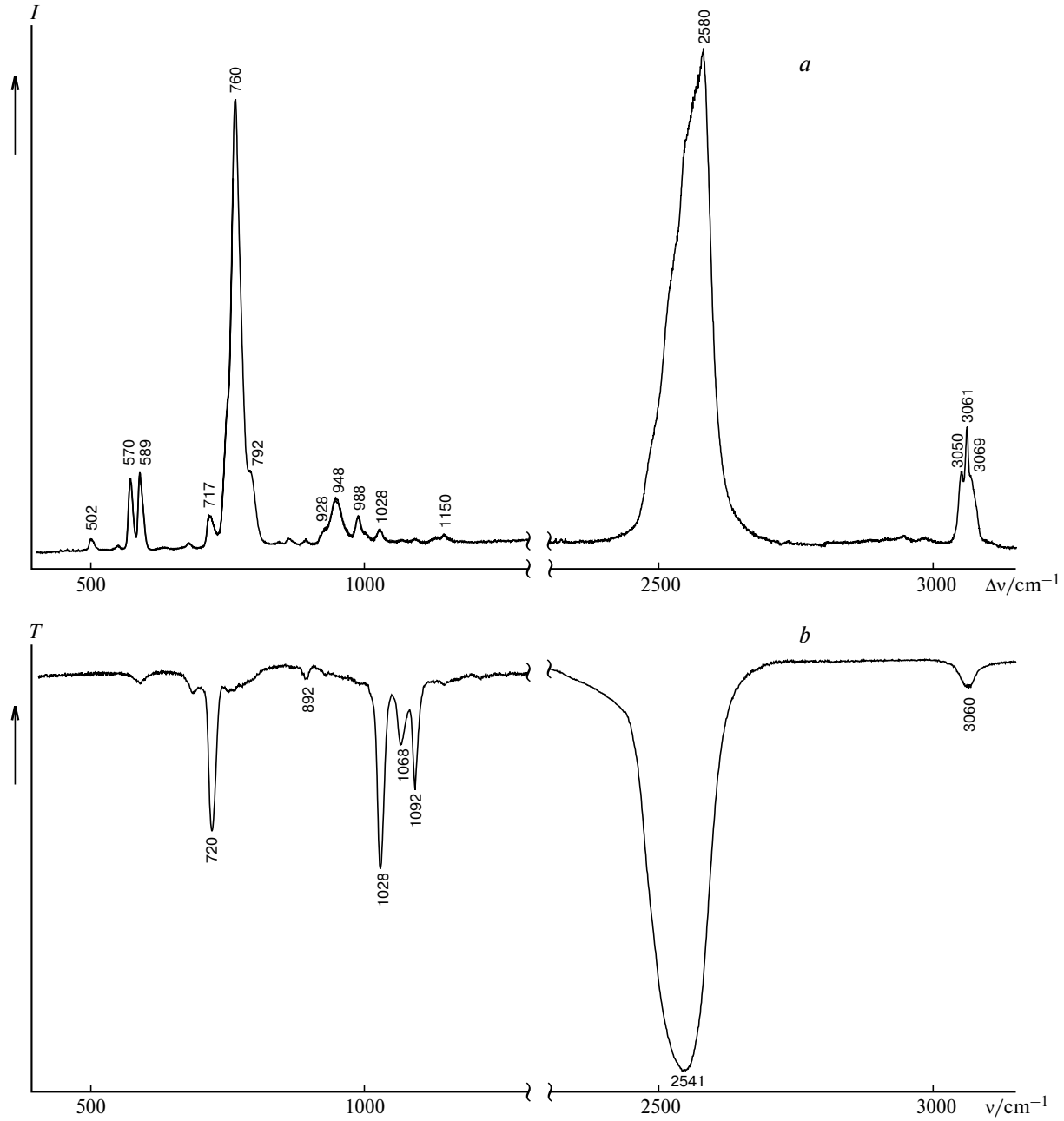

Fig. 3. Raman spectrum (*a*) and IR spectrum (*b*) of a solid salt $[CB_{11}H_{12}]Cs$.

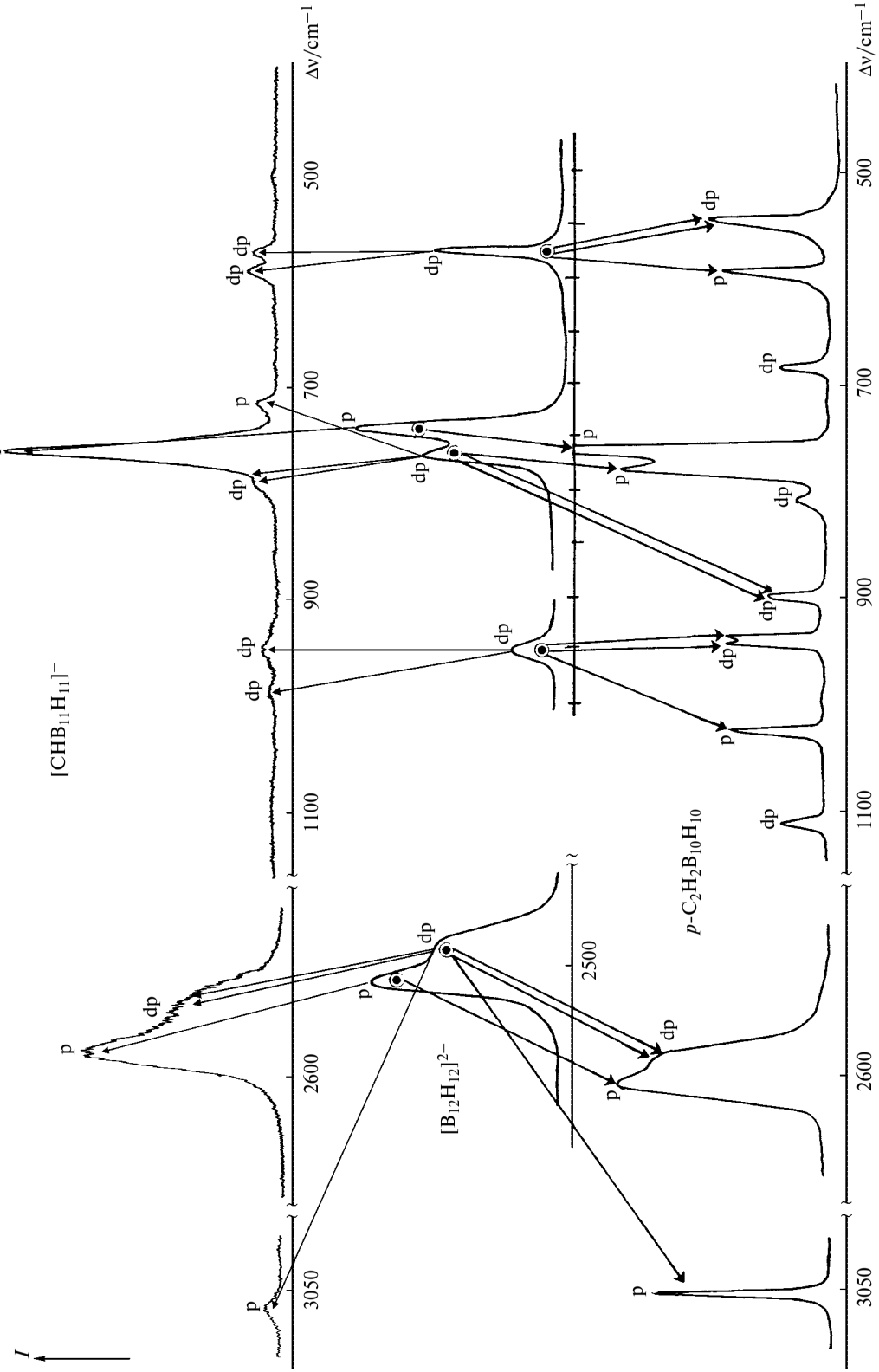

Fig. 4. Raman spectra of $[B_{12}H_{12}]^{2-}$, $[CHB_{11}H_{11}]^{-}$, and *p*-$C_2H_2B_{10}H_{10}$ in solutions; a correlation between the Raman active modes is shown (see text).

Table 3. Results of normal coordinate analysis for [*closo*-$CB_{11}H_{12}]^-$ anion: frequencies (ν) and vibrational mode eigenvectors[a]

ν/cm^{-1}				Symmetry species	Vibrational mode eigenvector
Calculations	IR spectrum[b]	Raman spectrum[c]			
		I	II		
3188	3060 w	3060 m	3068 m, p	A_1	ν(CH)
2641	—	2580 v.s	2578 v.s, p	A_1	$\nu(B_kH) + \nu(B_lH) + \nu(B_mH)$
2624	—	—	—	E_1	$\nu(B_mH)$
2613	2541 v.s.br	2530 v.s, sh	2534 v.s, sh, dp	E_2	$\nu(B_mH)$
2609	—	—	—	A_1	$\nu(B_mH) - \nu(B_lH) + \nu(B_kH)$
2597	—	—	—	E_1	$\nu(B_lH)$
2590	—	—	—	E_2	$\nu(B_lH)$
2584	—	—	—	A_1	$\nu(B_lH) - \nu(B_kH)$
1162	1147 w	1150 w	1150 w, dp	E_1	$\delta(CH) + \delta(B_mH)_o$
1096 (A_1)	1092 m	—	—	$A_1 + E_1 = F_{1u}$	$\delta(B_mH) + \delta(B_lH)_o$
1033 (E_1)	1068 w	—	—	$A_1 + E_1 = F_{1u}$	$\delta(B_mH) + \delta(B_lH)_o + \delta(CH) + \delta(B_kH)$
	1028 m	1028 w	1028w, dp	E_1	$\delta(B_mH) + \delta(B_lH)_o$
959	990 v.w	988 w	986 w, dp	E_1	$\delta(B_mH) + \delta(B_lH)_o$
952	953 v.w	948 m	948 m, dp	E_1	$\delta(B_mH) + \delta(B_lH)_o$
897	892 w	891 v.w	—	E_1	$\delta(B_lH)_o + \nu(B_kB_l) + \delta(CH)$
872	—	864 v.w	—	E_2	$\delta(B_lH) + \delta(B_mH)_i$
785	791 w	792 m, sh	792 m, sh, dp	E_1	$\nu(BC) + \delta(B_lH) + \delta(B_mH)_o + \delta(CH)$
756	760 w	760 v.s	760 v.s, p	A_1	ν(BB) + ν(BC)
711	720 s	717 w	718 w, p	A_1	$\nu(B_kB_l) - \nu(BC)$
670	679 w	680 w	—	E_1	$\nu(B_lB_m) + \delta(B_lB_m)$
587	—	589 m	589 m, dp	E_2	$\nu(B_lB_m) + \delta(B_lB_m)$
565	—	570 m	570 m, dp	E_2	$\nu(B_kB_l) + \delta(B_kB_l)$

[a] Abbreviations are as follows: p is polarized and dp is depolarized; v.s is very strong, s is strong, m is medium, and w is weak; br is broad; sh is shoulder; and i and o is the in-plane and out-of-plane vibration, respectively.
[b] IR spectra were recorded for solid samples as KBr pellet and as hexachlorobutadiene mull (in the region 2400—3600 cm^{-1}).
[c] Obtained for a solid sample (I) and for aqueous solution (II).

the B_m—B_m "latitudinal" bonds in **2** are somewhat shortened and the C—H bond is, in contrast, elongated in **2** compared to **3**. The differences observed seem to be due to significant changes in the atomic charges and first of all to an increase in the positive charge of the C atom in anion **2** to 0.34 e and to an increase in the negative charge on the neighboring B atoms to −0.17 e (*cf.* 0.15 and −0.12 e for **3**, respectively). It should be noted that the charge on the H atom involved in the bonding with the C atom remains virtually unchanged (0.32 e for **2** and 0.30 e for **3**). Taking into account the above-mentioned increase in the atomic charge of C, this should decrease the polarity of the C—H bond in anion **2**.

Vibrational spectrum of $[CB_{11}H_{12}]^-$ anion. The experimental IR and Raman spectra of anion **2** are shown in Fig. 3. The normal mode assignment to symmetry species and to particular molecular vibrations (Table 3) was based on (i) the experimental data on the vibrational mode activity and the degrees of polarization of the Raman lines and (ii) comparison with the spectra of anion **1** and molecule **3**. The assignment proposed was confirmed by the results of our quantum-chemical calculations. Noteworthy is a good agreement between the experimental and calculated frequencies of the vibrations involving the atoms of the icosahedral skeleton, whereas those of the ν(CH) and ν(BH) stretching modes differ appreciably, as was expected, because of the harmonic approximation used. Thus, the computational method employed in this work seems to be suitable for an adequate description of rigid molecular systems.

Analysis of the experimental spectra shows that, similarly to the $C_2B_{10}H_{12}$ molecule,[1] the number of experimentally observed IR bands and Raman lines for anion **2**

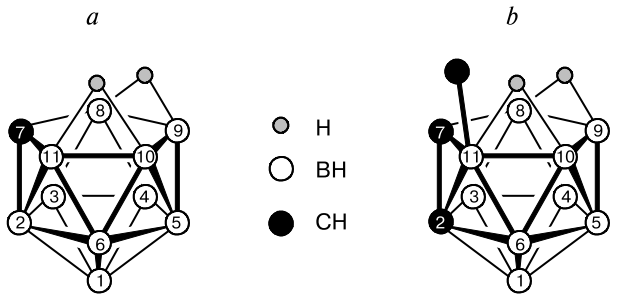

Fig. 5. Structure of *nido*-carboranes $[CB_{10}H_{13}]^-$ (*a*) and 11-Me-2,7-$C_2B_9H_{12}$ (*b*).

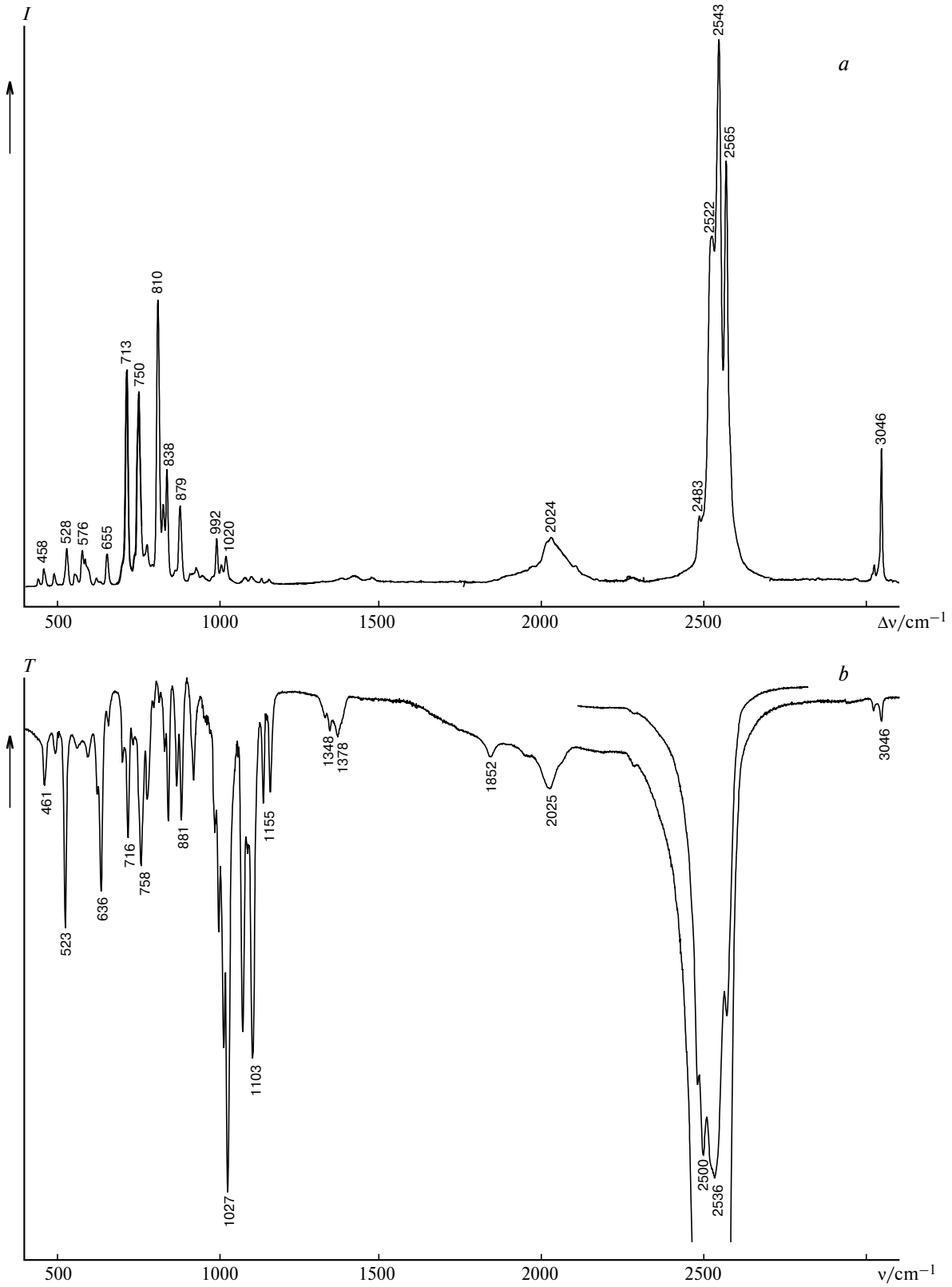

Fig. 6. Raman spectrum (*a*) and IR spectrum (*b*) of a solid salt [*nido*-$CB_{10}H_{13}$]Cs.

is much less than the theoretically predicted number (see Fig. 3). This is also illustrated in Fig. 4, where we compare the Raman spectra of aqueous solutions of isoelectronic polyhedra **1**, **2**, and **3** [1] and follow the evolution of the Raman active normal modes upon symmetry lowering of the icosahedral entity, in accord with the correlation shown in Fig. 2. In particular, the Raman spectrum of anion **2** exhibits no totally symmetric components in the region 600—1050 cm^{-1}, corresponding to the splitting of the H_g bands of the icosahedron. This seems to be due to the low intensities of these lines.

The results obtained allow one to compare the Raman spectra (see Fig. 4) and the IR spectra in the series of compounds **1**, **2**, **3** and to correlate the spectral patterns with the structure of the polyhedra. Successive replacement of B atoms in the icosahedral cage by C atoms causes an increase in the ν(BH) stretching frequencies, which is consistent with the shortening of the B—H bonds (see Table 2). The ν(CH) stretching frequency of anion **2** is slightly higher than that of molecule **3**; however, the corresponding band intensities differ substantially. The ν(CH) band in the IR spectrum of monocarbon carborane is of lower intensity, which is in accord with a decrease in the polarity of the C—H bond (see above). Noteworthy is that the "fingerprints" of icosahedral carboranes, namely,

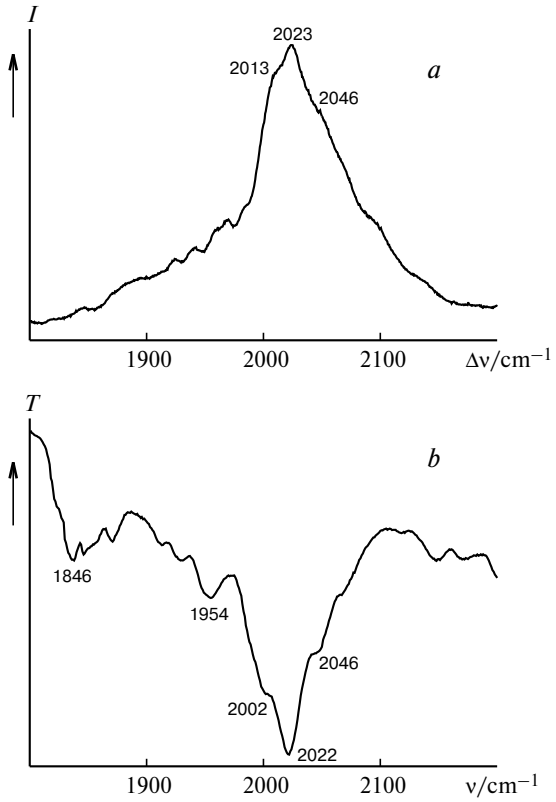

Fig. 7. Spectral regions corresponding to the stretching vibrations of "extra" hydrogen atoms in the Raman spectrum (*a*) and in the IR spectrum (*b*) of [*nido*-$CB_{10}H_{13}]^-$.

the most intense Raman line corresponding to the cage breathing vibration (~760 cm^{-1}) and the intense IR band corresponding to the out-of-phase stretching vibration of two "hemispheres' of the icosahedron (720 cm^{-1}) conserve close frequencies for **2** and **3**. These spectral features can be used for analytical purposes.

Vibrational spectrum of *nido*-anion $[CB_{10}H_{13}]^-$. To characterize the changes in the spectral pattern upon *closo*-carborane degradation with elimination of a B atom to give a *nido*-structure, we studied the IR and Raman spectra of a *nido*-anion **4** (Fig. 5, *a*). The spectra obtained are shown in Fig. 6. Comparison with the spectrum of anion **2** first of all demonstrates a complication of the spectral pattern due to a symmetry lowering and a characteristic low-frequency shift of the "center of gravity" of the complex band corresponding to the ν(BH) modes belonging to different symmetry species.[1] A decrease in the ν(CH) frequency by about 20 cm^{-1} should also be pointed out. This reflects a decrease in the corresponding force constant, since the ν(CH) mode is well-localized. The weak, broad complex-shaped band observed in both the IR and Raman spectra of anion **4** in the region 1800—2200 cm^{-1} (Fig. 7) can be assigned to the stretching vibrations of the "extra" hydrogen atoms located on the open face of the polyhedron (see Fig. 5, *a*). A similar spectral pattern in this region was observed earlier[7] for the 11-Me-2,7-$C_2B_9H_{12}$ molecule (Fig. 5, *b*) characterized by the same open face structure as anion **4**. A complicated contour of the band corresponding to the "extra" hydrogen atoms is due to the Fermi resonance.[1,7]

The experimental spectra of monocarbon carborane anions (see above) and the calculated bond lengths in isoelectronic icosahedral *closo*-entities have allowed one to compare their spectral and structural changes and to follow the evolution of the spectral pattern in the series of *closo*-polyhedra $[B_{12}H_{12}]^{2-}$, $[CB_{11}H_{12}]^-$, and *p*-$C_2B_{10}H_{12}$ upon successive introduction of C atoms in the boron cage and on going from the *closo*-structure to the *nido*-structure.

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