On the state of CH_4 molecule in the octahedral void of C_{60} fullerite

Yu. M. Shul´ga,[a] A. F. Shestakov,[a] V. M. Martynenko,[a] S. A. Baskakov,[a] N. Yu. Trifonov,[a] E. M. Anokhin,[b] and A. V. Maksimychev[b]*

[a] *Institute of Problems of Chemical Physics, Russian Academy of Sciences, 1 prosp. Akad. Semenova, 142432 Chernogolovka, Moscow Region, Russian Federation. E-mail: shulga@icp.ac.ru*

[b] *Moscow Institute of Physics and Technology, 9 Institutskiy per., 141700 Dolgoprudny, Moscow Region, Russian Federation.*

Methane-intercalated fullerite $(CH_4)_{0.56}C_{60}$ was obtained by low-temperature precipitation from solution. Methane transition from the gas phase to the octahedral void of fullerite is accompanied by a bathochromic shift of normal vibrational frequencies (by 19 and 8 cm^{-1} for ν_3 and ν_4, respectively). The methane ^{13}C signal in the proton decoupling ^{13}C NMR spectrum is observed as a singlet at δ −0.42. According to quantum chemical calculations using density functional theory, location of methane in the octahedral void of fullerite $(C_{60})_6$ leads to a decrease in the total energy of fullerite by 4 kcal mol^{-1}.

Key words: methane-intercalated fullerite C_{60}, IR spectroscopy, Raman spectroscopy, NMR spectroscopy, quantum chemical calculations.

The properties of fullerites can be changed by, *e.g.*, doping. For instance, doping of fullerite C_{60} with alkali metal atoms A led to superconductors A_3C_{60} (see, *e.g.*, Ref. 1). Inert gases can also be intercalated into the C_{60} fullerite lattice. The systems thus obtained retain the face-centered cubic (fcc) lattice, the lattice constant increases, and the orientational phase transition (OPT) temperature decreases.[2,3] Recently, intercalation of fullerites has been considered as a promising method for storage of rare gases.[4,5]

A methane-intercalated fullerite C_{60} was described quite recently.[6—10] It was established[6] that at $T = 296$ K, the CH_4 and C_{60} molecules execute uncorrelated free rotation. The OPT temperature decreases from 260 K for pure fullerite to 241 K for $(CH_4)_xC_{60}$ and to 235 K for $(CD_4)_xC_{60}$. At 200 K, the C_{60} molecules in the fulerrite (including methane-intercalated fullerite) lattice are ordered, whereas the CD_4 molecules are completely disordered and continue to execute a free rotation.[6] However, an inelastic neutron scattering study[7] revealed hindered rotation of the CH_4 molecule surrounded by C_{60} molecules at low temperatures ($T < 40$ K). Thermal expansion of $(CH_4)_xC_{60}$ (see Ref. 9) and $(CD_4)_xC_{60}$ (see Ref. 10) at helium temperatures was studied.

Earlier,[8] we have shown that methane from $(CH_4)_xC_{60}$ samples is released in the temperature range from room temperature to 500 °C and that the highest methane pressure over fullerite is achieved at temperatures above 400 °C, which also corresponds to rather fast sublimation of fullerene molecules.

In the present work, we report on the results of an experimental and theoretical study of the state of methane molecule in the octahedral void of fullerite C_{60}. In particular, we for the first time carried out quantum chemical calculation of the CH_4*$(C_{60})_6$ cluster which simulates the methane molecule trapped in the octahedral void of fullerite C_{60}.

Experimental

Methane-intercalated fullerites were obtained by salting-out precipitation.[11] The compounds used were as follows: fullerene C_{60} (purity 99.5%); 1,2-dichlorobenzene as solvent; and high-purity Pr^iOH as the precipitating agent. The solvent and the precipitating agent were additionally distilled immediately prior to use.

The experiment on precipitation of fullerite from a solution in 1,2-dichlorobenzene involved the following steps. The solution (fullerite concentration was 10 mg mL^{-1}) was saturated with methane by bubbling methane over a period of a few hours. Then, Pr^iOH presaturated with methane was added to the solution. Isopropyl alcohol was taken in nearly fivefold excess (v/v) relative to the fullerite solution. Precipitation continued until the solution turned clear. The precipitate was filtered off. Methane-intercalated fullerite powder collected on the filter was dried in air for 5—10 h.

X-ray phase analysis (XPA) of the precipitate was carried out with a DRON ADP-1 diffractometer (monochromatic CuKα radiation). IR spectra were recorded with a Perkin—Elmer Spectrum 100 spectrometer equipped with an UATR accessory. Raman spectra were acquired with an NXT FT-Raman 9650 instrument at a fixed spectral resolution of 4 cm^{-1} using a laser operating at λ = 976 nm as the excitation source. Posi-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1087—1092, June, 2011.

1066-5285/11/6006-1112 © 2011 Springer Science+Business Media, Inc.

tions of spectral maxima were determined using the OMNIC program.

^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity Inova 500M WB spectrometer operating at 500 MHz (for protons) at room temperature. High-resolution NMR spectra were obtained under magic-angle spinning of samples at 5 kHz.

The octahedral void in the C_{60} lattice was simulated within the framework of the density functional theory using the PBE functional[12] and the extended basis set {3,1,1/3,1,1/1,1} for the C atoms, the {3,1,1/1} basis set for the H atoms, and the SBK pseudopotential[13] using the PRIRODA program.[14] This approach gives a correct description of the geometry and properties of C_{60}. For instance, the calculated C—C distances (1.402 and 1.454 Å) coincide, within the limits of experimental error, with the published data 1.401(10) and 1.458(6) Å, respectively.[15] Also, the calculated ionization potential (7.34 eV), electron affinity (3.06 eV), and polarizability of fullerene C_{60} (82.9 Å^3) are in good agreement with the corresponding experimental values, *viz.*, 7.58 eV, 2.69 eV, and (76.5±8) Å^3.[16—18] The CCSD coupled cluster calculations[19] using a specific ZPolX basis set augmented with contracted polarization functions give a very close polarizability value of 82.2 Å^3.

The calculated and experimental[11,20] vibrational frequencies of the fullerene carbon cage and the results of previous calculations[21] are shown in Table 1. The magnetic shielding constants were obtained from full-electron calculations using the {3,1,1/3,1,1/1,1} extended basis set for the C atoms, the {3,1,1/1} basis set for the H atoms, and the geometric parameters found from the PBE/SBK calculations.

Results and Discussion

Methane-intercalated fullerite samples were obtained as shiny black powders. Microscopy studies showed that they are composed of fairly large particles (particle size to a few millimeters) with irregular edges, layered surface, and, in some cases, mirror planes characteristic of single crystals. There was also some amount of small micrometer- and submicrometer-size particles. According to XPA data, the fcc lattice constant (a_o) of the samples studied was in the range from 14.21 to 14.23 Å (*cf.* 14.16±0.01 Å for pure fullerite C_{60} obtained by sublimation). Thus, intercalation of methane into the octahedral void causes the distance between the centers of C_{60} molecules to increase from 10.014±0.007 to 10.050±0.007 Å. Assuming that the methane molecule is located at the center of the octahedral void, the average distance between the centers of the C_{60} and CH_4 molecules is 7.106 Å.

Two most intense absorption bands at 1182.7 and 1429.7 cm^{-1} in the IR spectra of methane-intercalated fullerite (Fig. 1) correspond to the IR active modes (F_{1u}) of highly symmetrical (I_h) C_{60} molecule (see Ref. 15). The IR spectra of fullerite samples containing 1,2-dichlorobenzene exhibited a number of absorption bands, the strongest lying at 746.2 and 1034.4 cm^{-1}. The appearance of these bands in the IR spectrum indicates that the synthesis has failed. The samples containing 1,2-dichlorobenzene were then left out of consideration. The methane molecule is characterized by two IR bands at 3001 and 1297 cm^{-1}. The IR spectrum of gaseous methane is well known (see, *e.g.*, Ref. 22). Owing to high symmetry of the methane molecule, the normal vibrational frequencies coincide with positions of maxima in the Q-branch in the IR spectrum of gas (ν_3 = 3020, ν_4 = 1305 cm^{-1}).[23] Thus, transition of methane molecule from the gas phase to the octahedral void of fullerite is accompanied by a bathochromic shift of asymmetrical C—H stretching and deformation vibrations (by 19 cm^{-1} for ν_3 and by 8 cm^{-1} for ν_4).

The CH_4 molecule has four Raman active modes, of which only the mode corresponding to the symmetrical C—H stretching vibrations (2900 cm^{-1}) is strong enough to allow the corresponding peak to be considered as

Table 1. Vibrational frequencies of the fullerene C_{60} carbon cage (ν/cm^{-1})

Type	Experiment[20]	Calculations	
		Ref. 21	This work
	Raman spectra		
A_g	1470	1525	1491
A_g	498	499	487
H_g	1578	1618	1580
H_g	1426	1475	1437
H_g	1251	1297	1241
H_g	1101	1128	1098
H_g	775	788	772
H_g	711	727	711
H_g	432	431	426
H_g	273	261	260
	IR spectra		
T_{1u}	1429 [1429.7]	1860	1430
T_{1u}	1183 [1182.7]	1224	1183
T_{1u}	576 [576.2]	591	576
T_{1u}	526 [526.7]	535	525

Note. Numbers in brackets represent the data taken from Ref. 11.

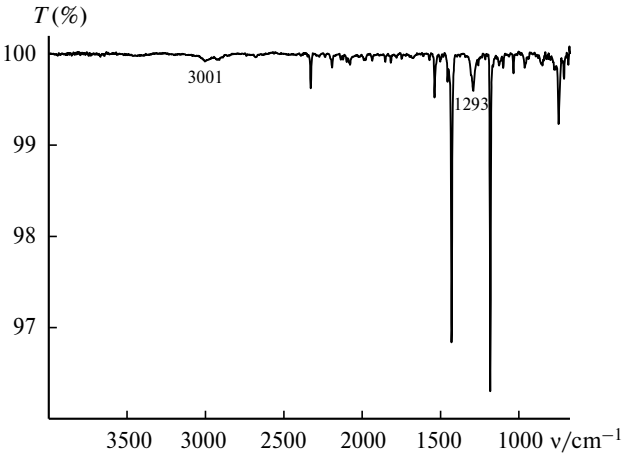

Fig. 1. IR spectrum of fullerite $(CH_4)_xC_{60}$.

a "fingerprint". In the Raman spectrum of the sample under study (Fig. 2), the methane molecule is characterized by a weak peak at 2893 cm^{-1} against the background of intense fullerene peaks at 271, 431, 495, 567, 708, 772, 1099, 1248, 1467, and 1573 cm^{-1}. This peak is absent in the fullerite spectrum obtained with no methane added. For the spectrum shown, the ratio of the peak intensities, I_{2894}/I_{1467}, is approximately 0.0044. Thus, we deal with a bathochromic shift of the band of symmetrical C—H stretching vibration by 7 cm^{-1}.

Interestingly, in the Raman spectra of methane hydrates, the methane ν_{C-H} peak is split into two components lying in the region 2905—2915 cm^{-1}.[23,24] This hypsochromic shift corresponds to the observed increase in the vibrational frequency with an increase in the methane vapor pressure.[24] At a methane vapor pressure of 3.36 MPa, the frequency is 2917.6 cm^{-1}.[25] Thus, the effects of methane environment in the octahedral void of fullerite and in methane hydrates on the methane vibrations are qualitatively different.

The strongest signal in the ^{13}C NMR spectrum of methane-intercalated fullerite is at δ 143.6 relative to Me_4Si, which is in good agreement with the published data (δ 143.6 for fullerite C_{60} intercalated with inert gases[25] and δ 143.7 for pure fullerite C_{60}, see Ref. 26). This signal is due to the resonance of highly symmetrical C_{60} molecule which undergoes fast rotation in the solid state (rotational diffusion coefficient is about $2 \cdot 10^{10}$ s^{-1}, see Ref. 27). The half-width of this peak in the MAS NMR spectrum of $(CH_4)_xC_{60}$ is only 0.11 ppm or 13.75 Hz.

Five well-resolved signals of a quintet in the ^{13}C NMR spectrum (Fig. 3) correspond to methane carbon atom. Positions of maxima of individual components of the quintet, as well as their half-widths and intensities are listed in Table 2. They were obtained by fitting the experimental

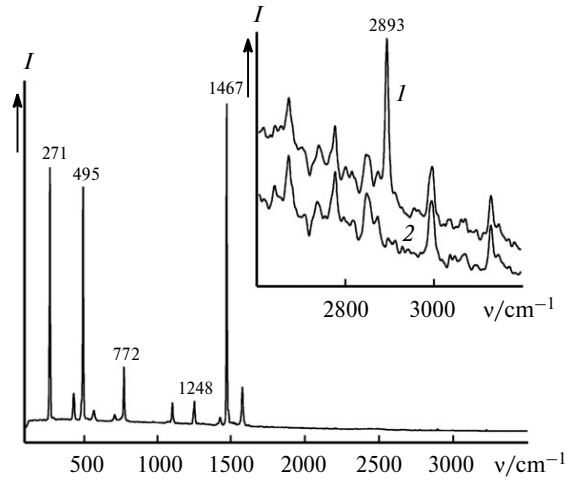

Fig. 2. Raman spectrum of fullerite $(CH_4)_xC_{60}$. Inset: fragments of the spectra of the sample under study (*1*) and pure fullerite (*2*) in the region of methane stretching vibrations.

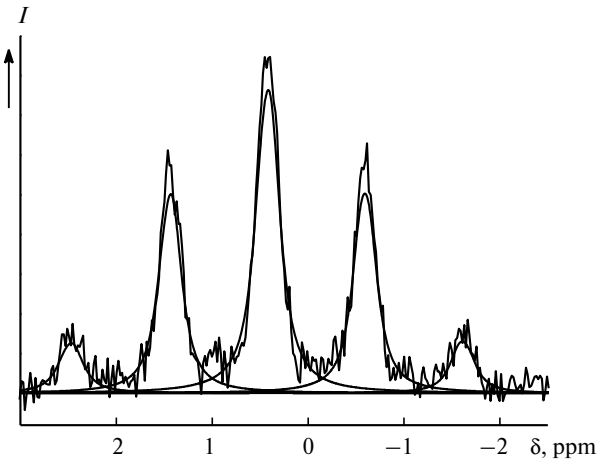

Fig. 3. Signal of methane carbon atom in the ^{13}C NMR spectrum of fullerite $(CH_4)_{0.56}C_{60}$. Smooth lines denote the approximation by Gaussian curves with the parameters listed in Table 2.

spectrum with Gaussian curves. The integrated intensity ratio of the Gaussian peaks is in reasonable agreement with the theoretical intensity ratio 1 : 4 : 6 : 4 : 1 for a ^{13}C nucleus interacting with four equivalent protons oriented in the magnetic field. From the spectral positions of quintet components it follows that the spin-spin coupling constant $^1J_{^{13}C-^1H}$ is 125±1 Hz, thus being equal, within the limits of experimental error, to the spin-spin coupling constant determined for free methane molecule, namely, 125.31 Hz.[28] Taking into account the fact that the vibrational contribution to the spin-spin coupling constant $^1J_{^{13}C-^1H}$ is 4%,[29] one can conclude that the C—H distance in the intercalated methane molecules remains unchanged within the limits of experimental error. The observation of splitting of the carbon signal in the ^{13}C NMR spectrum indicates that the methane molecule in the octahedral void undergoes rotation with a characteristic time longer than 1 ms. This is consistent with the conclusion[7] about hindered rotation of methane molecule in the fullerite.

In the proton decoupling ^{13}C NMR spectrum, the signal of methane ^{13}C atom is observed as a singlet at δ −0.42.

Table 2. Chemical shifts (δ), half-widths ($\Delta\nu_{1/2}$), and relative integrated intensities (I_r) of the methane ^{13}C signals in the ^{13}C NMR spectrum of fullerite $(CH_4)_xC_{60}$

δ, ppm	$\Delta\nu_{1/2}$, ppm	I_r (rel.units)*
−2.46	0.33	1.01 (1)
−1.44	0.25	3.08 (4)
−0.43	0.26	4.80 (6)
0.60	0.25	3.15 (4)
1.60	0.30	0.97 (1)

* Theoretical intensities assuming splitting on four equivalent protons are given in parentheses.

The chemical shift of the ^{13}C NMR signal of gaseous methane extrapolated to zero density is –8.64 ppm.[30] Thus, the signal of methane carbon atom in the ^{13}C NMR spectrum of methane molecule in the octahedral void of fullerite undergoes a large down-field shift by 8.23 ppm. This shift is larger than the shifts observed for methane clathrates[31–34] and for a solution of methane in $CDCl_3$ (–2.3 ppm, see Ref. 35). For a methane molecule in the (5^{12}) methane hydrate cage, the measured chemical shift of the C atom varies from –3.6 to –4.3 ppm (*cf.* –5.9—–6.9 ppm for methane molecule in a larger ($5^{12}6^2$) methane hydrate cage); the latter value is closer to the chemical shift of gaseous methane. The maximum effect of the fullerene environment on the magnetic shielding constant of the ^{13}C nucleus in methane is likely due to the large size of the system of conjugated π-bonds of the C_{60} molecule, which leads to an increase in the eddy currents induced by the external magnetic field.

The ratio of methane-to-fullerene carbon atoms determined from the ratio of integrated peak intensities of methane (δ –0.42) and fullerene (δ 143.6) is 1 : 107. Therefore, the chemical composition of the sample under study can be written as $(CH_4)_{0.56}C_{60}$.

Quantum chemical modeling. The octahedral void of fullerite was simulated by six C_{60} molecules located at the vertices of an octahedron. First, the method used was tested using the C_{60} dimer as an example. There are a total of ten possible orientation types of the C_{60} molecules which are obtained by combining a formally double (D) and single (S) C—C bond and a pentagonal (P) and hexagonal (H) faces. According to published data,[36] the most favorable is the D—H orientation. The calculated distance between the centers of the C_{60} molecules in this van der Waals complex (10.54 Å) and the depth of the potential well (0.21 eV) corresponds to parameters of the effective pair potential equal to 10.05 Å and 0.27 eV (see Ref. 37), which correctly describes the properties of C_{60} in the solid state and is also used for simulation of the structure of large C_{60} clusters.[38] The differences are due to a known drawback of the density functional method, namely that it can not provide a correct description of the van der Waals asymptotics of the pair interaction potential. These drawbacks also become apparent in the calculations of the $(C_{60})_6$ cluster. For instance, at an average distance of 10.81 Å between the centers of C_{60} molecules, the total binding energy is 34.7 kcal mol^{-1}. Accordingly, the effective energy of pair interaction in this cluster (5.78 kcal mol^{-1}) is lower than the value 6.68 kcal mol^{-1} determined from the sublimation energy of C_{60} fullerite (40.1 kcal mol^{-1}, see Ref. 39).

For this reason, the use of the PBE/SBK method gives a negligibly small value of the binding energy of CH_4 to C_{60} at the equilibrium center-to-center distances that are much longer than the sum of the corresponding van der Waals radii. On the other hand, neutral molecules attract one another due to dispersion forces. A simple theoretical estimate of the energy of van der Waals interaction between CH_4 and C_{60} molecules separated by the distance z averaged over the orientations of C_{60}, gives

$$E = -C_6 \frac{R^2 + z^2}{(z^2 - R^2)^4},$$

where R is the radius of the C_{60} molecule and C_6 is the constant of dispersion dipole-dipole interaction of CH_4 with C_{60}. This estimate was obtained assuming that the van der Waals interaction between CH_4 and C_{60} is the sum of the effective van der Waals interactions between CH_4 and all fullerene carbon atoms with the constant C_6 divided by N, where $N = 60$ (number of carbon atoms in fullerene). Taking into account that $C_6(C_{60},C_{60}) = 21N^2$ eV·Å^6 (see Ref. 40), $C_6(CH_4,CH_4) = 77.3$ eV·Å^6 (see Ref. 41), and the combinatorial rule[42]

$$C_6^{AB} = \frac{2\alpha_A\alpha_B C_6^{AA} C_6^{BB}}{(\alpha_B)^2 C_6^{AA} + (\alpha_A)^2 C_6^{BB}}$$

one gets $C_6(C_{60},CH_4) \approx 40N$ eV·Å^6, which gives for the interaction energy of the van der Waals complex (C_{60},CH_4) a value of 1.7 kcal mol^{-1} at the experimental z value equal to 7.106 Å.

The experimental value of the energy of the interaction between methane and fullerene molecules is unknown. However, it can be estimated from the energy of physical adorption of methane on graphite (3.56 kcal mol^{-1}, see Ref. 43) and on the surface of a single-walled (9,0)-nanotube (2.7 kcal mol^{-1}, see Ref. 44). From these data it follows that transition from planar graphite sheet to cylindrical nanotube surface causes the methane interaction energy to decrease by 0.86 kcal mol^{-1}. Assuming that transition from the cylindrical nanotube surface to spherical fullerene surface is also characterized by the same decrease in the interaction energy, this energy can be estimated as 1.84 kcal mol^{-1}. Based on the theoretically estimated energies[45] of the interaction between CH_4 and C_{60} molecules, *viz.*, 3.5 for planar and 2.9 kcal mol^{-1} for cylindrical surface, a close estimate of 2.3 kcal mol^{-1} can be obtained. Correspondingly, we can admit a value of 2.1±0.2 kcal mol^{-1} as the interaction energy of CH_4 with C_{60}.

The introduction of methane molecule into the center of the octahedral cluster $(C_{60})_6$ (Fig. 4) has almost no effect on the cluster geometry. The average distance between the centers of fullerene molecules increases from 10.81 to 10.87 Å. This enhancement qualitatively agrees with the experimentally observed increase by 0.036 Å. A possible reason for quantitative differences is that deformation of isolated cluster $(C_{60})_6$ should clearly be larger than the deformation of the cluster in the crystalline environment. The energy equivalent of this deformation (energy difference between the equilibrium state of the cluster and its state in the presence of methane) is also small, *viz.*, 0.4 kcal mol^{-1}.

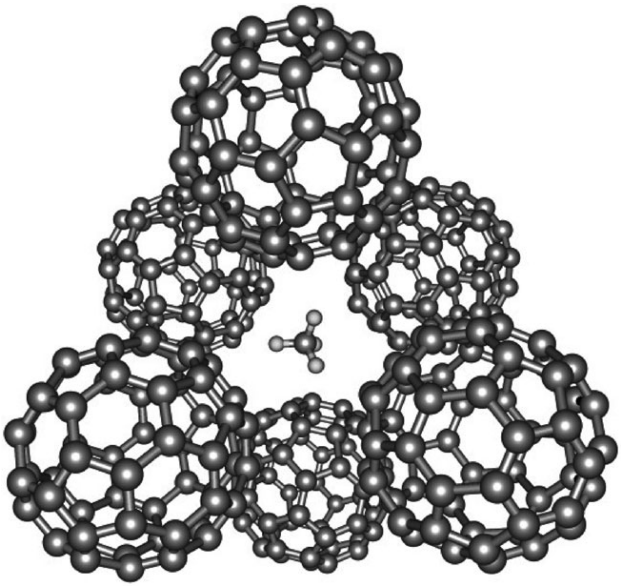

Fig. 4. Octahedral void in the C_{60} fullerite lattice containing a methane molecule. View along the threefold axis.

Expansion of the fullerite lattice due to intercalation of methane, as well as the increase in the volume of the model cluster $(C_{60})_6$ suggest that the distance between the methane and fullerene molecules corresponds to the repulsive branch of the pair interaction potential. PBE/SBK calculations predict an increase in the energy of the system CH_4—$(C_{60})_6$ by 4.0 kcal mol^{-1} upon the introduction of methane molecule into the octahedral void. Since the density functional method ignores the dispersion interaction between CH_4 and C_{60}, the value listed above should be corrected. Taking into account the additive contribution of the pair van der Waals interaction of CH_4 with C_{60} (2.1 kcal mol^{-1}, see above), the energy gain due to the interaction of methane with the octahedral void of fullerene is estimated as 8.6 kcal mol^{-1}.

Since vibrational frequency and entropy calculations for the system $CH_4(C_{60})_6$ are impossible owing to computational problems, we will restrict ourselves to calculations of the changes in the entropy related to restriction of translational motion in the octahedral void. Translational motion of a confined molecule becomes localized (such a localized motion in a box was observed for, *e.g.*, H_2 in fullerite[46]); as a consequence, its entropy considerably decreases. Based on a simple model of a box with infinitely high walls to simulate the octahedral void with an effective diameter of 4.1 Å, the standard entropy of translational motion of methane makes a contribution of 4.7 kcal mol^{-1} to the free energy. Taking into account the standard translational entropy of methane (8.7 kcal mol^{-1})/RT, the equilibrium pressure of methane above the fullerite with filled octahedral voids is 0.01 atm. This estimate agrees with experimental observations, *viz.*, at room temperature, methane is trapped within the fullerite lattice for a long time almost without weight loss[6] and it liberates from $(CH_4)_xC_{60}$ on heating up to the beginning of fullerene sublimation.[8]

Calculations of the ^{13}C magnetic shielding constants for methane molecule give a value of 191.95 ppm, which is in reasonable agreement with the experimental value 195.02 ppm.[31] Similar calculations for methane in the cluster $CH_4(C_{60})_6$ give a value of 189.16 ppm (which is 2.8 ppm smaller), which is in qualitative agreement with the direction of the observed shift. As the number, n, of fullerene molecules in the cluster $CH_4(C_{60})_n$ decreases from 6 to 0, the calculated magnetic shielding constant undergoes a uniform shift to the value characteristic of a free methane molecule. Since the distances between the methane and fullerene molecules in the model cluster and in the crystalline environment are different, we calculated the magnetic shielding constant of the system $CH_4(C_{60})_n$ using the experimental value of 7.106 Å for the distance between the centers of the CH_4 and C_{60} molecules. We found that the decrease in the calculated magnetic shielding constant is 2 ppm. This allows one to estimate the low field shift of the methane ^{13}C signal as about 12 ppm, which is in semiquantitative agreement with the experimental value of 8.2 ppm. Note that B3LYP/HuzIII-su3 calculations also predict a low field shift of 6.0 and 4.7 ppm for the ^{13}C signal of methane in the methane hydrates (5^{12}) and ($5^{12}6^2$), respectively.[47]

The fullerene ^{13}C atoms (both free and in the $CH_4(C_{60})_6$ cluster) are characterized by the same value of the calculated magnetic shielding constant equal to 38.6 ppm. The corresponding theoretical chemical shift of the signal of ^{13}C atoms relative to Me_4Si (δ 145.8) is in reasonable agreement with the experimental value (δ 143.6).

Since vibrational frequency calculations for cluster $CH_4(C_{60})_6$ were impossible, we determined the harmonic vibrational frequencies of the complex $CH_4(C_{60})$ with the same distance between the centers of the molecules as in the octahedral void. It was found that both symmetrical and asymmetrical C—H stretching vibrations undergo a hypsochromic shift of 3.6 and 2.6—4.6 cm^{-1}, respectively. In spite of the approximate character of this estimate, we obtained the correct sign of the vibrational frequency shift. Its numerical value is smaller than the experimentally observed shift equal to 7 and 19 cm^{-1}, respectively. Apparently, due to summation of the pair interaction effects in the case of methane molecule in the octahedral void, an n-fold increase in the shift magnitude becomes possible.

Methane-intercalated fullerite $(CH_4)_{0.56}C_{60}$ was obtained by low-temperature precipitation from solution. Transition of methane molecule from the gas phase to the octahedral void of fullerite is accompanied by a bathochromic shift of normal vibrations. The proton decoupling ^{13}C NMR spectrum of methane exhibits a singlet at δ –0.42. Quantum chemical calculations revealed that the

introduction of methane molecule into the octahedral void of fullerite $(C_{60})_6$ leads to a decrease in the methane free energy by 4.6 kcal mol^{-1}.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 09-03-00597-a).

References

1. J. S. Miller, *Adv. Mater.*, 1991, **3**, 262.
2. G. E. Gadd, S. Moricca, S. J. Kennedy, M. M. Elcombe, P. J. Evans, M. Blackford, D. Cassidy, C. J. Howard, P. Prasad, J. V. Hanna, A. Burchwood, D. Levy, *J. Phys. Chem. Solids*, 1997, **58**, 1823.
3. Yu. M. Shul´ga, V. M. Martynenko, S. N. Polyakov, N. V. Chelovskaya, V. V. Open´ko, E. V. Skokan, L. N. Blinova, Yu. A. Dobrovol´skii, Yu. G. Morozov, V. F. Razumov, D. V. Shchur, *Zh. Neorg. Khim.*, 2009, **54**, 387 [*Russ. J. Inorg. Chem.* (*Engl. Transl.*), 2009, **54**, 341].
4. G. E. Gadd, M. Blackford, S. Moricca, N. Webb, P. J. Evans, A. M. Smith, G. Jacobsen, S. Leung, A. Day, Q. Hua, *Science*, 1997, **277**, 933.
5. G. E. Gadd, P. J. Evans, S. Kennedy, M. James, M. Elcombe, D. Cassidy, S. Moricca, J. Holmes, N. Webb, A. Dixon, P. Prasad, *Fullerene Sci. Technol.*, 1999, **7**, 1043.
6. B. Morosin, R. A. Assink, R. G. Dunn, T. M. Massis, E. J. Schirber, G. H. Kwei, *Phys. Rev. B: Condens. Matter*, 1997, **56**, 13611.
7. G. H. Kwei, F. Trouw, B. Morosin, H. F. King, *J. Chem. Phys.*, 2000, **113**, 320.
8. Yu. M. Shul´ga, V. E. Muradyan, V. M. Martynenko, B. P. Tarasov, N. V. Polyakova, *Mass-Spektrometriya* [*Mass Spectrometry*], 2005, **2**, 41 (in Russian).
9. A. V. Dolbin, V. B. Esel´son, V. G. Gavrilko, V. G. Manzhelii, N. A. Vinnikov, G. E. Gadd, S. Moricca, D. Cassidy, B. Sundqvist, *J. Low Temp. Phys.*, 2007, **33**, 1068.
10. A. V. Dolbin, N. A. Vinnikov, V. G. Gavrilko, V. B. Esel´son, V. G. Manzhelii, G. E. Gadd, S. Moricca, D. Cassidy, B. Sundqvist, *J. Low Temp. Phys.*, 2009, **35**, 226.
11. Yu. M. Shul´ga, V. M. Martynenko, A. F. Shestakov, S. A. Baskakov, V. N. Vasilets, Yu. G. Morozov, *Izv. Akad. Nauk. Ser. Khim.*, 2006, 662 [*Russ. Chem. Bull., Int. Ed.*, 2006, **55**, 687].
12. J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
13. H. Basch, P. G. Jasien, *Can. J. Chem.*, 1992, **70**, 612.
14. D. N. Laikov, *Chem. Phys. Lett.*, 1997, **281**, 151.
15. D. S. Bethune, G. Meijer, W. C. Tang, H. J. Rosen, W. G. Golden, H. Seki, C. A. Brown, M. S. de Vries, *Chem. Phys. Lett.*, 1991, **179**, 181.
16. J. de Vries, H. Steger, B. Kamke, C. Menzel, B. Weisser, W. Kamke, I. V. Hertel, *Chem. Phys. Lett.*, 1992, **188**, 159.
17. X. B. Wang, C. F. Ding, L. S. Wang, *J. Chem. Phys.*, 1999, **110**, 8217.
18. R. Antoine, Ph. Dugourd, D. Rayane, E. Benichou, M. Broyer, F. Chandezon, C. Guet, *J. Chem. Phys.*, 1999, **110**, 9771.
19. K. Kowalski, J. R. Hammond, W. A. de Jong, A. J. Sadlej, *J. Chem. Phys.*, 2008, **129**, 226101.
20. P. Bowmar, W. Hayes, M. Kurmoo, P. A. Pattenden, M. A. Green, P. Day, K. Kikuchi, *J. Phys. Condens. Matter*, 1994, **6**, 3161.
21. D. A. Dixon, B. E. Chase, G. Fitzgerald, N. Matsuzawa, *J. Phys. Chem.*, 1995, **99**, 4486.
22. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1963.
23. A. K. Sum, R. C. Burruss, E. Dendy Sloan, Jr., *J. Phys. Chem. B*, 1997, **101**, 7371.
24. S. Nakano, M. Moritoki, K. Ohgaki, *J. Chem. Eng. Data*, 1999, **44**, 254.
25. G. E. Gadd, S. Moricca, S. J. Kennedy, M. M. Elcombe, P. J. Evans, M. Blackford, D. Cassidy, C. J. Howard, P. Prasad, J. V. Hanna, A. Burchwood, D. Levy, *J. Phys. Chem. Solids*, 1997, **58**, 1823.
26. R. A. Assink, J. E. Shirber, D. A. Loy, B. Morosin, G. Carlson, *J. Mater. Res.*, 1992, **7**, 2136.
27. C. S. Yannoni, R. D. Johnson, G. Meijer, D. S. Bethune, J. R. Salem, *J. Phys. Chem.*, 1991, **95**, 9.
28. A. Antušek, D. Kedziera, K. Jackowski, M. Jaszunski, W. Makulski, *Chem. Phys.*, 2008, **352**, 320.
29. T. A. Ruden, O. B. Lutnæs, T. Helgaker, K. Ruud, *J. Chem. Phys.*, 2003, **118**, 9572.
30. A. Antušek, K. Jackowski, M. Jaszunski, W. Makulski, M. Wilczek, *Chem. Phys. Lett.*, 2005, **411**, 111.
31. S. F. Dec, K. E. Bowler, L. L. Stadterman, C. A. Koh, E. D. Sloan, *J. Phys. Chem. A*, 2007, **111**, 4297.
32. Y.-T. Seo, H. Lee, *Korean J. Chem. Eng.*, 2003, **20**, 1085.
33. S. F. Dec, K. E. Bowler, L. L. Stadterman, C. A. Koh, E. D. Sloan, Jr., *J. Am. Chem. Soc.*, 2006, **128**, 415.
34. A. Gupta, S. F. Dec, C. A. Koh, E. D. Sloan, Jr., *J. Phys. Chem. C*, 2007, **111**, 2341.
35. N. J. R. van E. Hommes, T. Clark, *J. Mol. Model.*, 2005, **11**, 175.
36. F. Tournus, J.-C. Charlier, P. Mélinon, *J. Chem. Phys.*, 2005, **122**, 094315.
37. J. M. Pacheco, J. P. P. Ramalho, *Phys. Rev. Lett.*, 1979, **79**, 3873.
38. J. P. K. Doye, D. J. Wales, W. Branz, F. Calvo, *Phys. Rev. B: Condens. Matter*, 2001, **64**, 235409.
39. C. Pan, M. P. Sampson, Y. Chai, R. H. Hauge, J. L. Margrave, *J. Phys. Chem.*, 1991, **95**, 2944.
40. M. Hasegawa, K. Nishidate, M. Katayama, T. Inaoka, *J. Chem. Phys.*, 2003, **119**, 1386.
41. Q. Wuand, W. Yang, *J. Chem. Phys.*, 2002, **116**, 515.
42. K. T. Tang, *Phys. Rev.*, 1969, **177**, 108.
43. A. Ricca, C. W. Bauschlicher, *Chem. Phys.*, 2006, **324**, 455.
44. A. J. Thomy, *Chim. Physique*, 1970, **67**, 1101.
45. M. Muris, N. Dufau, M. Bienfait, N. Dupont-Pavlovsky, Y. Grillet, J. P. Palmari, *Langmuir*, 2000, **16**, 7019.
46. M. Tomaselli, *Mol. Phys.*, 2003, **101**, 3029.
47. P. Siuda, J. Sadlej, *J. Phys. Chem. A*, 2011, **115**, 612.

Received March 4, 2011