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Isotopic and isomeric effects in high-pressure hydrogenated fullerenes studied by Raman spectroscopy

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Abstract

Raman spectra of hydro- and deuterofullerenes, $C_{60}H_{36}$ and $C_{60}D_{36}$, prepared under hydrogen or deuterium pressure of 3.0 GPa at different conditions of temperature and hydrogenation time, have been measured at room temperature and normal pressure. Spatially resolved micro-Raman study shows that the homogeneity and optical properties of the samples depend primarily on the synthesis temperature. The Raman spectrum of hydrofullerene contains a large number of prominent peaks originating from the various isomers. The comparison of the experimental data with results of molecular dynamics calculations shows that various isomers are present in the samples, with the most abundant of them being the ones with symmetries S_6, T and D_{3d}. The Raman spectrum of the deuterofullerene is similar in structure to that of the hydrofullerene, however, significant differences occur in the frequency positions of the C–H and C–D stretching and bending modes which are expected from the isotopic effect. In particular, the isotopic shift ratio for the stretching mode, $\Omega_H/\Omega_D \approx 1.32$, is smaller than the expected one from the mass ratio for pure C–H and C–D stretching modes. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Fullerenes; High-pressure hydrogenation; Isomers; Isotopic effect; Raman spectrum

1. Introduction

Hydrofullerene $C_{60}H_{36}$ is a hydrogenated derivative of the pristine C_{60} molecule, which can be prepared using either high-pressure hydrogenation [1] or hydrogen atom transfer to C_{60} from other reagents in solution [2]. Although various compounds of $C_{60}H_x$ with x varying between 2 and 44 have been synthesized [3], the most stable of them have been found to be the hydrofullerenes, $C_{60}H_{18}$ and $C_{60}H_{36}$ [1,3]. Usually the hydrofullerene samples, prepared by the use of both methods, are rather non-uniform and may contain additional hydrides with various mass weights, as well as a small amount of reagents. Thus the characterization of the hydrogenation reaction products is of great importance and various methods like electron, X-ray and neutron diffraction, nuclear magnetic resonance, infrared spectroscopy and laser desorption mass spectrometry have been used for this purpose [1,4–8].

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Recently, Raman scattering was successfully used for the study of the vibrational spectrum of the $C_{60}H_{36}$ prepared by the transfer hydrogenation method [9]. The incorporation of 36 hydrogen atoms in the C_{60} cage lowers the molecular symmetry and therefore activates Raman scattering from a variety of initially forbidden phonon modes. In addition, the presence in the final product of a number of isomers with different symmetry, as well as the appearance of new C–H stretching and bending modes, makes the Raman spectrum of hydrofullerene very rich [9]. The comparison of the calculated phonon frequencies for five principal isomers of $C_{60}H_{36}$ obtained by molecular dynamics calculations [9], with the experimentally observed phonon frequencies has led to the conclusion that the material prepared by the transfer hydrogenation method contains mainly two isomers, those with symmetries D_{3d} and S_6. Therefore, the comparison of the calculated and experimental Raman frequencies, measured by micro-Raman sampling with high spatial resolution, can provide a wealth of information on the phonon spectrum itself, isomer composition and homogeneity of the samples synthesized under various parameters of hydrogenation.

In this paper we present the results of a micro-Raman study of the hydro- and deuterofullerenes, $C_{60}H_{36}$ and $C_{60}D_{36}$, prepared by high-pressure hydrogenation. The aim of this research is to study the Raman spectra of high-pressure hydrogenated fullerenes, the influence of the hydrogenation parameters, namely pressure, temperature and reaction time, on the isomer composition and homogeneity of the samples, as well as the isotopic effects in the vibrational spectra of hydro- and deuterofullerenes. The Raman spectra of the high-pressure hydrogenated and deuterated samples, measured for the first time, are compared with the results of Raman measurements on samples synthesized by transfer hydrogenation, as well as with the results of molecular dynamics calculations [9]. The data obtained show the presence of all principal isomers in the high-pressure hydrogenated fullerenes, large isotopic shifts for the C–H stretching and bending modes, whereas the shifts for the vibrational modes related to the fullerene molecular cage are very small.

2. Experimental

The starting commercial material, C_{60} of 99.99% purity, was sublimed twice in vacuum better than 10^{-5} Torr at 800 K, and then it was compacted into pellets of 12 mm diameter and 1 mm in thickness. Each pellet was placed into a copper capsule, covered with a disc of 0.01 mm thick Pd foil, and then annealed in vacuum at 620 K for 2 h to expel any desorbed gases, which may have been dissolved during compactification. The remaining volume in the capsule was filled with AlH_3 or AlD_3 for hydrogenation or deuteration respectively, and then was tightly plugged with a copper lid using gallium as solder. This encapsulation procedure prevents effectively hydrogen or deuterium losses during subsequent treatment, since both Cu and Ga are largely impermeable by hydrogen.

The assembled capsules were pressurized to 3.0 GPa in a toroid-type high-pressure chamber and maintained at 650 ± 10 or 700 ± 10 K for a time of 24 or 48 h. The AlH_3 decomposes above 400 K [10], producing hydrogen. Hydrogen is reacting with the fullerite after permeating the Pd foil, which isolates the fullerite from the chemically active Al. The amount of hydrogen gas, produced inside the capsule corresponds to a particle ratio $H/C_{60} \approx 90$. Therefore, the available hydrogen quantity is always in excess of the C_{60} particle number during the hydrogenation procedure. The hydrogenation procedure was repeated for a second run, taking the product of the first run as a starting material for the second run. Preliminary mass-spectrometry data show that at least 95% of the material in the capsule is hydrofullerene $C_{60}H_{36}$. The remaining 5% of the material contains partially hydrogenated fullerenes with different content of hydrogen. The X-ray analysis, of the obtained material, shows that it has the bcc structure, typical for $C_{60}H_{36}$ [7], with lattice parameter 11.83 Å. For the optical measurements, visually uniform colorless or slightly yellow-colored transparent specimens were selected.

Raman spectra were recorded using a triple monochromator DILOR XY-500 equipped with a CCD liquid-nitrogen cooled detector system. The spectra were taken in the back-scattering geometry by the use of the micro-Raman system comprising by an OLYMPUS microscope equipped with MSPlan100 objective with magnification 100× and spatial resolution of ~1.7 μm. The spectral width of the system was ~2.0 cm^{-1}. The Raman frequency was calibrated by the use of low pressure Ne lamp providing accuracy better than 0.2 cm^{-1}. To avoid interference to the Raman scattering from the luminescence of hydrofullerene, the sample was excited by the 676.4 nm line of the Kr^+ laser, whose energy is below the fundamental absorption gap of the material. The laser power was varied from 5 to 10 mW, measured directly before the sample. At this laser power the samples were stable under laser irradiation in air for many days. The increase of the laser power to higher levels led sometimes to the destruction of the samples by laser heating. The phonon frequencies were obtained by fitting Gaussian line shapes to the experimental Raman spectra.

3. Results and discussion

The Raman spectra of four $C_{60}H_{36}$ samples taken in the frequency region 140–540 cm^{-1} at room temperature and ambient pressure are shown in Fig. 1. The spectra in (a) and (b) show the Raman spectra of two different samples synthesized in the first ampoule at $P = 3$ GPa, $T = 700$ K and reaction time ~24 h. Spectra in (c) and (d) are from two samples of the second ampoule, which were synthesized at $P = 3$ GPa, $T = 650$ K and reaction time 48 h. The spectrum in Fig. 1(a) consists of about 40 sharp peaks and is the most intense and well-resolved spectrum. The Raman spectrum of pristine C_{60} in the corresponding region contains only three active modes, $H_g(1)$, $H_g(2)$ and $A_g(1)$, with frequencies 272, 433 and 496 cm^{-1} respectively. The spectrum in Fig. 1(a) was taken at the best site of the best sample, selected from the contents of the first ampoule by micro-Raman probing as having the richest Raman spectrum. The spectrum in Fig. 1(b) is typical for a number of other, rather good samples, from the first ampoule and has almost the same structure but its peaks appear less intense with respect to (a), due to the relatively larger background. The higher background observed in (b) is not related to the fluorescence of $C_{60}H_{36}$, it is probably a result of higher concentration of structural defects and impurities in the sample under study. These impurities most likely may be microscopic amounts of partially hydrogenated fullerenes, which are fluorescing under the 676.4 nm Kr laser excitation in this spectral region. The spectrum in Fig. 1(c) is taken from the best sample in the second ampoule and has well-resolved structure with sharp peaks but their positions and intensity distribution are somehow different from the first two spectra. Finally, the spectrum in Fig. 1(d) belongs to

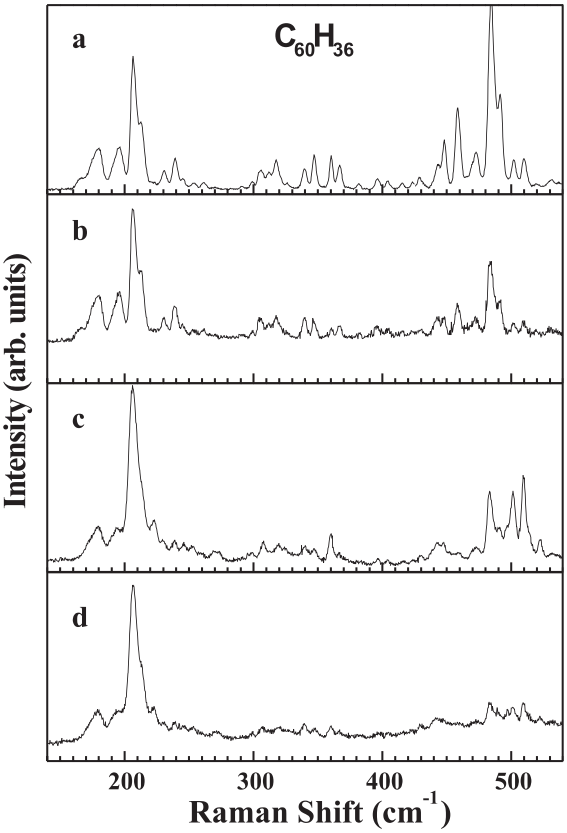

Fig. 1. Raman spectra of high-pressure hydrogenated $C_{60}H_{36}$ at room temperature and ambient pressure. Spectra (a) and (b) are taken from two different samples, synthesized at $P = 3$ GPa, $T = 700$ K and reaction time ~24 h. Spectra (c) and (d) are from two different samples, synthesized at $P = 3$ GPa, $T = 650$ K and reaction time ~48 h.

another typical sample from the second ampoule, its structure is not well resolved compared to the previous spectra and has the largest background.

It should be noted that samples (a) and (c) were selected from the contents of the first and second ampoules as the best ones, whereas the samples (b) and (d) were selected as typical ones. The majority of the samples, in both ampoules, are similar to (b) and (d), but there are also many samples, which give a very large background that obscures the structure of the Raman spectrum. These measurements show that the samples obtained by high-pressure hydrogenation are highly non-uniform and great care should be exercised in the sample selection. Taking advantage of the micro-Raman probe, we have checked several samples from the ampoules in order to examine their quality and relation to the hydrogenation parameters, namely, temperature and reaction time. The Raman spectra indicate that the sample quality does not differ significantly for both used reaction times, whereas temperature is affecting drastically their optical quality. Samples hydrogenated at 700 K show a better optical quality than those at 650 K. The Raman spectra of both hydro- and deuterofullerenes synthesized at 700 K show very rich structure with well-resolved and intense peaks.

Fig. 2 shows the Raman spectrum of the hydrofullerene $C_{60}H_{36}$ in the energy region from 50 to 3100 cm^{-1}. The sample used for these measurements was synthesized under conditions similar to those used for the first ampoule. The observed spectrum contains 126 sharp peaks with the lowest frequency mode located at 86 cm^{-1} and the highest at 2912 cm^{-1}. The most important differences in the Raman spectrum of hydrofullerene with respect to that of the pristine C_{60} are the following:

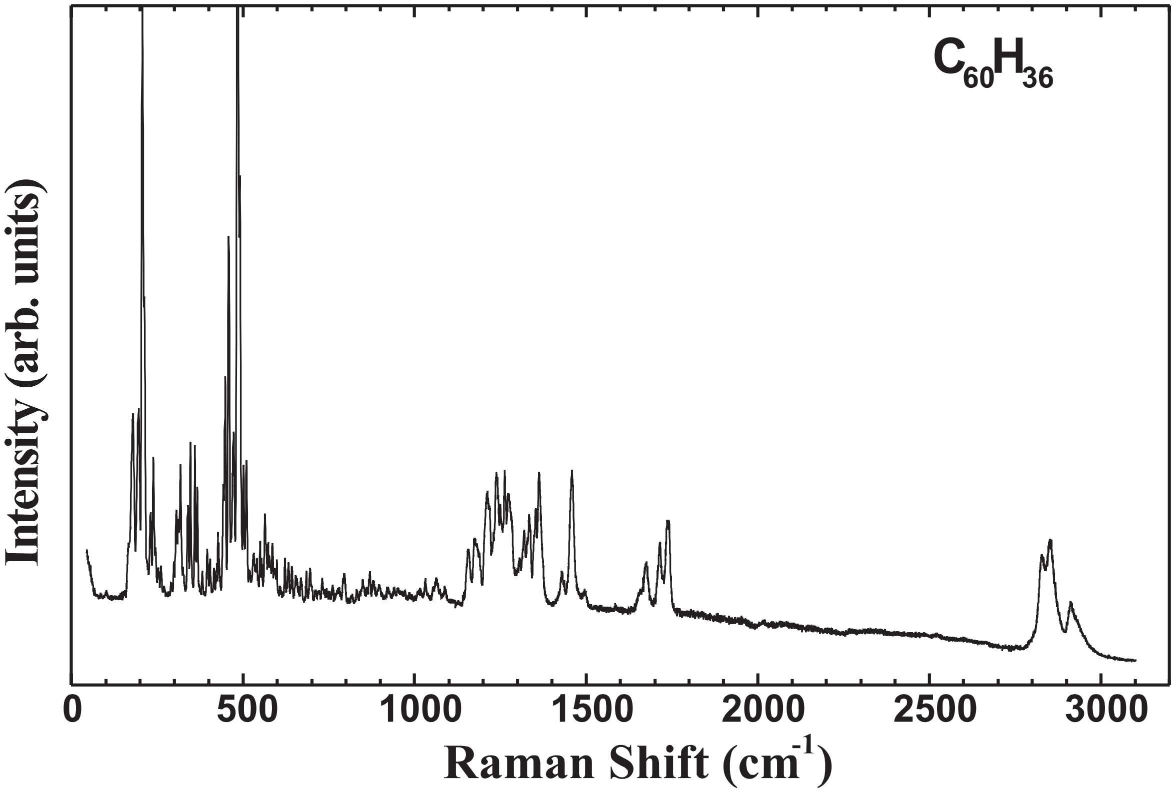

Fig. 2. Raman spectrum of high-pressure hydrogenated $C_{60}H_{36}$ taken at ambient conditions in the energy region 50–3100 cm^{-1}. The sample was prepared at $P = 3$ GPa, $T = 700$ K and reaction time ~24 h.

(i) the number of the Raman active modes has been increased dramatically;
(ii) the low energy radial modes (200–600 cm^{-1}) exhibit a considerable intensity enhancement with respect to high energy tangential modes (1400–1700 cm^{-1});
(iii) new modes appear which are related to the C–H bending (1150–1350 cm^{-1}) and stretching (2800–3000 cm^{-1}) vibrations.

The vibrational data, obtained from the Raman spectrum of $C_{60}H_{36}$, are summarized in Table 1. The first three columns of Table 1 contain the experimental results for the number, position and intensity of the Raman peaks obtained in the present work. The next two columns contain experimental results for the positions and intensities of the Raman peaks of $C_{60}H_{36}$ reported in previous studies [9,11]. The last three columns of Table 1 contain data concerning the frequency, Raman cross-section and symmetry of the various isomers of the $C_{60}H_{36}$ molecule calculated using the modified MNDO method [9]. The comparison of the present experimental data with those reported in the previous studies [9,11] shows that the Raman spectrum of the high-pressure hydrogenated $C_{60}H_{36}$ is richer than that of $C_{60}H_{36}$ prepared by the transfer hydrogenation method. Raman spectra of the samples prepared by the later method contain about one-fifth of the peaks observed in the samples prepared by high-pressure hydrogenation. The majority of the experimentally observed Raman peaks (86 peaks out of a total number of 126) coincide, within ±5 cm^{-1}, with the calculated frequencies of the Raman active modes, while their intensities are compatible with the calculated cross-sections. Their total number for the five principal isomers, studied theoretically, is equal to ~400 [9]. The experimentally observed peaks, which coincide with the calculated ones, are assigned to all principal isomers, but the majority of them belong to the isomers with symmetry S_6, T and D_{3d}. The experimental peaks, which do not coincide with any of the calculated Raman frequencies, belong mainly to the low energy radial vibrations of the fullerene molecule. They may be associated either with other isomers of $C_{60}H_{36}$ or with partially hydrogenated fullerenes. It should be emphasized that the complexity of the calculated vibrational spectrum, the large number of isomers and the accuracy of the molecular dynamics calculations might result sometimes in an accidental agreement of the experimental and calculated results.

The Raman spectrum of deuterofullerene $C_{60}D_{36}$, taken at room temperature and normal pressure, is shown in Fig. 3. The sample used for these measurements was prepared under conditions similar to those of $C_{60}H_{36}$ used for ampoule 1. The spectrum contains about 80 peaks and therefore is not as rich, in structure, as that of $C_{60}H_{36}$. This may be due to a different isomer composition in $C_{60}D_{36}$. A first glance at the Raman spectra of hydro- and deuterofullerene indicates that they have several similarities, but an important difference exists between them. The positions of the C–D stretching modes are shifted towards lower energies. Similar shift is also observed for the C–D bending modes, which are located in the frequency regions 800–1200 and 1150–1350 cm^{-1} for $C_{60}D_{36}$ and $C_{60}H_{36}$, respectively. Note that the Raman spectrum of $C_{60}D_{36}$ contains also several very weak peaks near 2900 cm^{-1}, which are coincident with C–H stretching modes of $C_{60}H_{36}$. This is related to the isotopic purity of the $C_{60}D_{36}$ sample, which contains a small amount of hydrofullerene reflecting the initial isotopic purity of deuterium in the provider, AlD_3, used for the high-pressure deuteration.

The shift of the C–H stretching and bending modes is caused by the isotopic effect on the vibrational frequencies by the substitution of hydrogen by deuterium. The isotopic shift of the frequencies of the pure C–H/C–D stretching vibrational modes can be estimated from the formula

$$\frac{\Omega_{\mathrm{H}}}{\Omega_{\mathrm{D}}} \sim \left(\frac{M_{\Omega_{\mathrm{H}}}}{M_{\Omega_{\mathrm{D}}}}\right)^{1/2}, \qquad (1)$$

where Ω_H and Ω_D are vibrational frequencies of the hydrogenated and deuterated molecules respectively, and M_{Ω_H} and M_{Ω_D} the reduced masses involved in the respective vibrations. The large difference between the masses of the hydrogen atom and the C_{60} molecule indicates that the C–H

Table 1
Frequencies and intensities of the observed Raman peaks in $C_{60}H_{36}$[a]

No.	Experiment				Theory [9]		
	Present work		Frequency (cm^{-1})				
	Frequency (cm^{-1})	Intensity[b]	Ref. [9]	Ref. [11]	Frequency (cm^{-1})	σ[c]	Isomer
1	86.0	vw	85				
2	101.1	w		128			
3	165.7	m	136				
4	176.6	vs	175	180	176	7	T
5	192.3	s			194	7	D_{3d}(c-k)[d]
6	196.9	vs			198	14	T_h
7	206.6	vs		207	206	21	T
8	212.4	vs	211		214	22	T_h
9	230.6	s			229	18	D_{3d}
10	239.3	s		239			
11	245.3	m					
12	253.6	m					
13	261.3	m	264				
14	291.0	m					
15	298.7	s			294	11	T
16	305.5	s					
17	311.8	m	313				
18	317.8	s					
19	326.4	m			325	3	D_{3d}
20	339.6	s			341	14	D_{3d}
21	347.2	s			346	8	S_6
22	360.3	s			363	2	T_h
23	366.9	s			367	10	D_{3d}(c-k)
24	381.8	m			379	1	T
25	396.3	s	395	395	396	2	D_{3d}
26	404.3	m			404	1	D_{3d}(c-k)
27	415.3	m			415	7	D_{3d}(c-k)
28	423.0	m			422	9	S_6
29	429.4	m			427	4	D_{3d}
30	443.0	s		444	443	1	D_{3d}
31	448.4	vs	448				
32	458.6	vs		458	460	17	S_6
33	465.6	s			465	1	D_{3d}
34	473.2	s			473	1	T
35	484.4	vs	484	484	488	44	T
36	491.3	vs			491	4	D_{3d}(c-k)
37	501.9	s					
38	509.9	s			509	31	S_6
39	522.0	m			522	1	T
40	531.0	m					
41	537.0	m					
42	541.4	m			545	1	T
43	549.9	s					
44	554.9	m					
45	565.0	s			569	14	T
46	573.1	m			570	11	D_{3d}(c-k)
47	577.6	m			579	30	S_6
48	580.6	m			581	7	S_6
49	585.7	s			586	6	D_{3d}
50	590.7	m					
51	596.3	m			597	52	D_{3d}(c-k)

Table 1 (*continued*)

No.	Experiment				Theory [9]		
	Present work		Frequency (cm^{-1})				
	Frequency (cm^{-1})	Intensity[b]	Ref. [9]	Ref. [11]	Frequency (cm^{-1})	σ[c]	Isomer
52	622.6	w					
53	632.4	w			634	1	D_{3d}(c-k)
54	642.5	w			644	20	D_{3d}
55	653.3	w			653	3	T
56	657.7	w					
57	662.0	w			663	1	D_{3d}
58	669.5	w			670	6	T_h
59	685.0	m					
60	696.3	w			695	54	D_{3d}(c-k)
61	711.6	m					
62	720.6	m			720	32	S_6
63	731.6	m			731	36	D_{3d}
64	744.5	w			747	42	T
65	752.3	w		753	754	26	D_{3d}(c-k)
66	761.1	w			761	35	S_6
67	774.2	w					
68	781.3	w					
69	791.3	m			791	92	T_h
70	795.9	m			796	74	D_{3d}
71	817.2	w					
72	832.4	w			828	1	T
73	849.5	m			852	7	S_6
74	861.7	w			860	2	T
75	869.2	m			866	40	S_6
76	880.4	m			877	138	T_h
77	922.2	w			921	3	T_h
78	940.2	w			939	1	T
79	951.1	w			948	1	S_6
80	960.8	w			959	5	T_h
81	972.3	w			973	4	D_{3d}
82	985.6	vw			983	11	T
83	991.4	w			988	5	T_h
84	1015.1	w	1015	1008	1018	2	S_6
85	1032.4	m	1039	1039			
86	1054.1	w			1053	4	S_6
87	1064.0	m					
88	1073.2	w			1073	2	T_h
89	1088.6	w			1088	14	D_{3d}(c-k)
90	1125.2	w			1126	10	T
91	1154.0	m	1154		1154	16	D_{3d}(c-k)
92	1173.9	m			1173	83	D_{3d}
93	1181.3				1183	101	D_{3d}
94	1189.7	m		1186	1188	18	D_{3d}(c-k)
95	1207.7	m			1208	20	D_{3d}(c-k)
96	1212.6	s	1212	1213	1213	44	T_h
97	1218.7	s			1217	23	S_6
98	1227.2	m			1229	67	S_6
99	1231.8	m			1232	1	S_6
100	1240.3	s			1238	36	T
101	1250.3	s			1251	6	D_{3d}
102	1256.9	m			1258	19	S_6
103	1263.2	s		1262	1263	42	D_{3d}

(*continued on next page*)

Table 1 (*continued*)

No.	Experiment				Theory [9]		
	Present work		Frequency (cm^{-1})				
	Frequency (cm^{-1})	Intensity[b]	Ref. [9]	Ref. [11]	Frequency (cm^{-1})	σ[c]	Isomer
104	1274	s	1276		1274	74	D_{3d}
105	1283.8	m			1283	32	S_6
106	1306.1	w			1304	31	D_{3d}(c-k)
107	1314.4	m			1313	29	T_h
108	1319.6	s			1318	22	D_{3d}(c-k)
109	1328.3	m			1330	27	S_6
110	1334.9	s			1334	1	D_{3d}(c-k)
111	1348.3	m					
112	1353.2	s					
113	1362.9	s			1363	9	D_{3d}
114	1369.4	m	1386		1370	11	S_6
115	1430.6	m		1402	1430	12	S_6
116	1457.0	s	1462	1462			
117	1496.6	w	1508	1497			
118	1653.8	w					
119	1674.8	m			1671	401	S_6
120	1714.0	s	1714		1712	211	D_{3d}(c-k)
121	1724.5	w					
122	1739.4	s	1736		1739	333	D_{3d}(c-k)
123	2826.8	s	2830	2829			
124	2852.5	s	2853	2852	2856	55	D_{3d}
125	2911.9	s	2913	2911	2911	1808	D_{3d}
126	2931.2	m					

[a] For comparison data from other experimental studies are included along with results of theoretical calculations on frequencies and cross sections.

[b] Intensity characterization: very weak (vw), weak (w), medium (m), strong (s), and very strong (vs).

[c] Raman cross section ($Å^4$/amu) [9].

[d] D_{3d}(c-k) – the lowest energy isomer with D_{3d} symmetry [13].

stretching mode in hydrofullerene $C_{60}H_{36}$ is associated with the displacements of the hydrogen atom along the bond direction, whereas the C_{60} molecule remains practically stationary. The isotopic shift of the C–H stretching mode, in this case, is expected to be close to the square root of the mass ratio of the deuterium to hydrogen. The same is expected also for the isotopic shift of the C–H bending mode.

In Table 2 we have tabulated the frequencies of the most intense intramolecular vibrations, related to the fullerene molecular cage, the C–H stretching modes and the isotopic shifts for these modes. The less intense Raman modes are not included in Table 2 because it is rather difficult to identify the corresponding vibrations of hydro- and deuterofullerene among numerous closely located weak peaks. The C–H bending modes are also not included in Table 2 due to uncertainties in their assignment. The largest values of isotopic shifts, $[\Omega_H/\Omega_D]^2$, were observed for the C–H stretching modes which vary in the region 1.73–1.79. These values are close to the mass ratio of deuterium and hydrogen, $M_D/M_H = 2$. The isotopic shifts for the modes related to the fullerene molecular cage vibrations, vary from 1 to 1.032, which is quite different from that of the stretching modes. This is due to the fact the hydrogen or deuteron masses do not contribute essentially in these vibrations. It is interesting to note that our results on the stretching mode frequencies and isotopic shifts for hydro- and deuterofullerene are very close to those obtained recently by means of surface-enhanced Raman scattering of hydrogen and deuterium chemisorbed on diamond (1 0 0) surface [12]. The frequencies of the C–H and C–D stretching modes

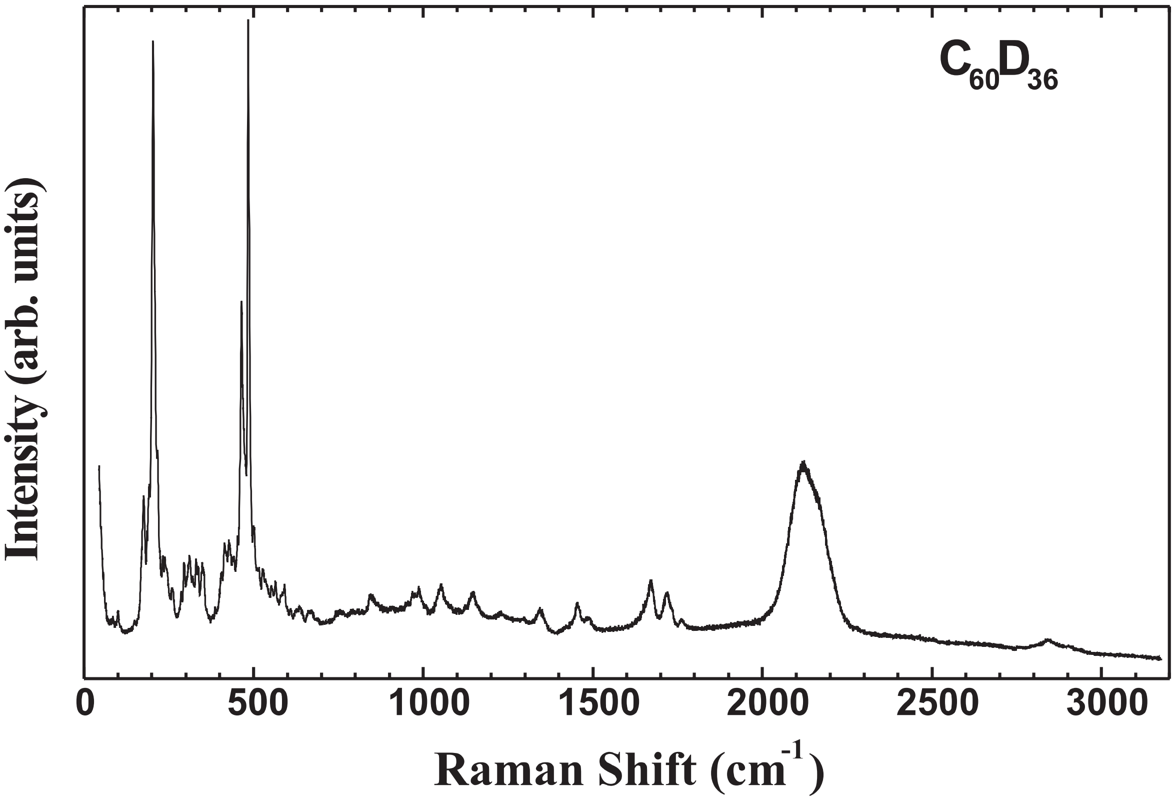

Fig. 3. Raman spectrum of high-pressure deuterated $C_{60}D_{36}$ taken at ambient conditions in the energy region 50–3100 cm^{-1}. The sample was prepared at $P = 3$ GPa, $T = 700$ K and reaction time ~24 h.

in Ref. [12] are equal to 2830, 2865, 2928 and 2102, 2165, 2195 cm^{-1}, respectively, and the isotopic shifts vary within the range 1.75–1.81. The characteristics of the C–H stretching modes of hydrofullerene could be similar to those of hydrogen, bonded with carbon atoms on the diamond surface. This similarity is related, in our opinion, to the large difference between the masses of hydrogen atom and the fullerene molecule or the carbon network in diamond. In addition, the C–H bonding in both cases takes place with sp^3 coordinated carbon atoms.

Table 2
Molecular cage vibrations and C–H stretching modes with their isotopic shift ratios

$C_{60}H_{36}$		$C_{60}D_{36}$		Ω_H/Ω_D	$[\Omega_H/\Omega_D]^2$
Ω (cm^{-1})	Intensity[a]	Ω (cm^{-1})	Intensity[a]		
206.6	vs	203.4	vs	1.016	1.032
212.4	vs	209.7	vs	1.013	1.026
464.2	vs	464.2	vs	1	1
484.4	vs	484.4	vs	1	1
2826.8	s	2113.6	s	1.337	1.789
2852.5	s	2169.7	s	1.315	1.728
2911.9	s	2209.3	s	1.318	1.737

[a] Intensity characterization: strong (s), and very strong (vs).

4. Conclusions

The Raman spectrum of hydrofullerene $C_{60}H_{36}$ prepared by high-pressure hydrogenation has very rich structure and contains about five times more peaks than that of $C_{60}H_{36}$ prepared by the transfer hydrogenation method. The comparison of the experimental Raman peaks with recent data of molecular dynamics calculation [9] shows the presence of all five principal isomers in the samples investigated. The majority of the experimentally observed Raman peaks belong to the S_6, T and D_{3d} isomers. The micro-Raman probing of several samples prepared by high-pressure hydrogenation under different reaction parameters shows that the homogeneity of the samples depends strongly on the reaction temperature. The Raman spectrum of deuterofullerene $C_{60}D_{36}$, prepared by the same method, is similar in its main features to that of the $C_{60}H_{36}$. The important difference between the two spectra is the large isotopic shift of the C–D stretching modes with respect to the corresponding C–H ones. The observed isotopic shift in the modes, associated with the fullerene molecular cage, is very small. This is a strong indication that the hydrogen atoms do not play any important role in the frequencies of the $C_{60}H_{36}$ molecular cage vibrations.

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