

See discussions, stats, and author profiles for this publication at:  
<https://www.researchgate.net/publication/244285820>

# Ab initio calculation of X-ray emission and IR spectra of the hydrofullerene C<sub>60</sub>H<sub>36</sub>

ARTICLE *in* JOURNAL OF MOLECULAR STRUCTURE · MAY 2001

Impact Factor: 1.6 · DOI: 10.1016/S0022-2860(00)00862-0

---

CITATIONS

8

---

READS

13

4 AUTHORS, INCLUDING:



Alexander Okotrub

Russian Academy of Sciences

275 PUBLICATIONS 2,613 CITATIONS

SEE PROFILE



Anatoly Lobach

Russian Academy of Sciences

124 PUBLICATIONS 1,239 CITATIONS

SEE PROFILE

## Ab initio calculation of X-ray emission and IR spectra of the hydrofullerene C<sub>60</sub>H<sub>36</sub>

L.G. Bulusheva<sup>a,\*</sup>, A.V. Okotrub<sup>a</sup>, A.V. Antich<sup>a,b</sup>, A.S. Lobach<sup>c</sup>

<sup>a</sup>*Institute of Inorganic Chemistry, Russian Academy of Sciences, 3, Ac. Lavrentyeva Avenue, 630090 Novosibirsk, Russian Federation*

<sup>b</sup>*Novosibirsk State University, ul. Pirogova 2, 630090 Novosibirsk, Russian Federation*

<sup>c</sup>*The Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Moscow, Russian Federation*

Received 14 August 2000; revised 23 October 2000; accepted 23 October 2000

### Abstract

Two isomers of the hydrofullerene C<sub>60</sub>H<sub>36</sub> with *T* and *D*<sub>3d</sub> symmetry were calculated using ab initio Hartree–Fock self-consistent field (HF-SCF). The *T* symmetry isomer in which the benzenoid rings occupy tetrahedral positions is predicted to be lower in energy than the other considered isomer. Simulated CK<sub>α</sub> spectra of the isomers were compared with the X-ray fluorescence spectrum of the hydrofullerene C<sub>60</sub>H<sub>36</sub> prepared by the transfer hydrogenation method. The short-wave maximum intensity of the CK<sub>α</sub> spectrum of C<sub>60</sub>H<sub>36</sub> was shown to be sensitive to the number of  $\pi$  electrons in the high-occupied levels of the molecule. Although the theoretical spectra are similar in appearance, the *T* isomer seems to be in better accordance with the experiment. Furthermore, the computed infrared frequencies and intensities for this isomer were found to correlate well with features in the measured spectrum of C<sub>60</sub>H<sub>36</sub>. The most intense peak in the low-frequency spectral region was shown to correspond to the skeletal vibrations of the benzenoid rings. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Hydrofullerene; X-ray fluorescence spectra; Infrared spectra; Ab initio method

### 1. Introduction

Although C<sub>60</sub>H<sub>36</sub> was among the first synthesized derivatives of fullerene C<sub>60</sub>, its structure still has not been determined. Identified as the major product of the Birch reduction of C<sub>60</sub>, the hydrofullerene C<sub>60</sub>H<sub>36</sub> was proposed to possess unconjugated double bonds [1]. However, spectroscopic measurements showed that the molecular symmetry of C<sub>60</sub>H<sub>36</sub> is lower than *T<sub>h</sub>*, which is a result of complete isolation of the double bonds [2–4]. Then, C<sub>60</sub>H<sub>36</sub> was prepared by other means [5–7]. It was suggested that various

synthetic techniques might result in the synthesis of different isomers of C<sub>60</sub>H<sub>36</sub> [8]. Furthermore, the change in the synthetic conditions of a particular method leads to the production of samples with somewhat different spectral characteristics [9].

There are roughly 10<sup>14</sup> possible isomers for C<sub>60</sub>H<sub>36</sub> [10], but only five molecules that belong to the *T<sub>h</sub>*, *T*, *D*<sub>3d</sub> (two isomers) and *S*<sub>6</sub> symmetry are predicted to have low energy and are considered as probable synthesis product structures. The *T* isomer has four benzenoid rings that occupy tetrahedral positions. The *D*<sub>3d</sub> and *S*<sub>6</sub> symmetric structures contain two benzenoid rings at the poles along the three-fold axis and six isolated double bonds. Various quantum chemical

\* Corresponding author. Fax: +7-3832-344489.

E-mail address: bul@che.nsk.su (L.G. Bulusheva).

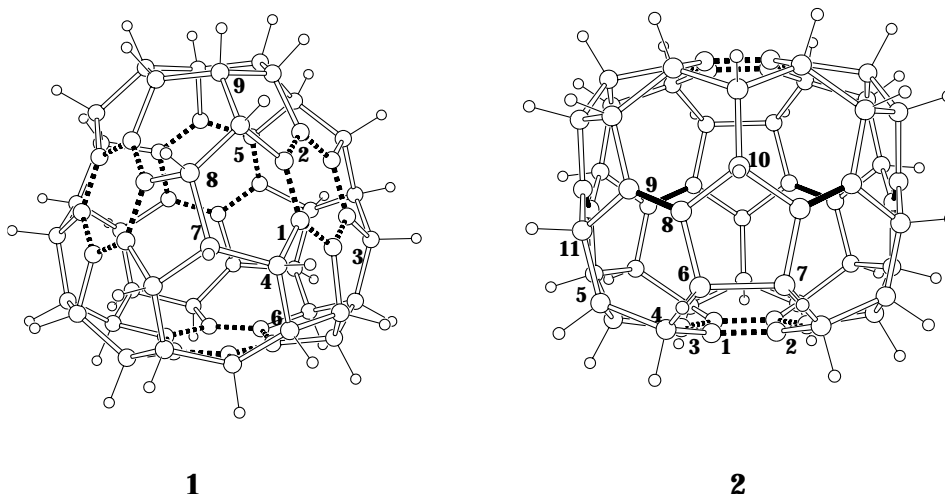


Fig. 1. Optimized structures of the: (1) *T* and (2) *D*<sub>3d'</sub> isomers of C<sub>60</sub>H<sub>36</sub>. The conjugated bonds in the benzenoid rings are dashed; the double bond is shown by a solid line.

calculations showed that the *T* isomer is the most stable in the considered series [11–13].

The probable structure of the hydrofullerene C<sub>60</sub>H<sub>36</sub> is usually chosen from the comparison between experimental spectroscopic measurements and theoretical calculations. For example, electron diffraction data for C<sub>60</sub>H<sub>36</sub> prepared by using high-pressure hydrogenation of fullerite are best described by the *D*<sub>3d</sub> symmetric structure [14], six isolated double bonds which are located along the parallels of the C<sub>60</sub> cage, while the X-ray emission and absorption spectral features of this hydrofullerene agreed with the DV-X $\alpha$  molecular orbital (MO) calculation of the *T* isomer [15]. <sup>3</sup>He chemical shift values of He@C<sub>60</sub>H<sub>36</sub> samples prepared by two different synthetic methods are practically not distinguished [16] and correspond to the computed shifts for the *D*<sub>3d'</sub> isomer possessing double bonds located along the molecule equator [13]. Infrared (IR) and Raman data for the hydrofullerene C<sub>60</sub>H<sub>36</sub> synthesized by transfer hydrogenation using 9,10-dihydroanthracene as the hydrogen source are claimed to be satisfactorily interpreted assuming that the reaction product contains a mixture of *D*<sub>3d'</sub> and *S*<sub>6</sub> isomers, the former being the major component [9]. Comparison of the X-ray photoelectron and X-ray fluorescence spectra of C<sub>60</sub>H<sub>36</sub> prepared by the same synthetic method with the theoretical spectra indicated the *T* symmetric structure as the most probable isomer [17].

The purpose of the present work is the comparison of the X-ray fluorescence and IR spectra of the hydrofullerene C<sub>60</sub>H<sub>36</sub> prepared by the transfer hydrogenation method with high-level ab initio calculations of the *T* symmetric structure to clarify whether this isomer is the major component of the reaction product or not.

## 2. Experimental details

The fullerene C<sub>60</sub> (99.5%) was produced by the Kratschmer–Huffman method as described in Ref. [18]. Dihydroanthracene (99%) was supplied by Lancaster Synthesis Ltd, and purified by double sublimation. The sample of C<sub>60</sub>H<sub>36</sub> was prepared by transfer hydrogenation of C<sub>60</sub> in the following way [19]: 100 mg (139  $\mu$ mol) of C<sub>60</sub> was heated with 2.5 g (13.9 mmol) of 9,10-dihydroanthracene in a glass ampoule (sealed under Ar) for 25 min at 350°C. Anthracene and its derivatives were sublimated at 110°C for 9 h. The final product of C<sub>60</sub>H<sub>36</sub> composition had a light yellow color. Hydrofullerene was characterized by mass-spectrometric, IR, UV and NMR spectroscopic methods [20]. The IR spectrum of C<sub>60</sub>H<sub>36</sub> in a KBr disk was measured at room temperature between 400 and 3200 cm<sup>−1</sup> with a Perkin–Elmer-1600 spectrometer.

X-ray fluorescence spectra of C<sub>60</sub> and C<sub>60</sub>H<sub>36</sub> were

Table 1  
Energetics of the C<sub>60</sub>H<sub>36</sub> isomers

Isomer	<i>T</i>	<i>D</i> <sub>3d'</sub>
Total energy ( <i>E</i> <sub>h</sub> )	−2290.5966	−2290.5546
HOMO symmetry	e	e <sub>u</sub>
HOMO energy (eV)	−7.70	−7.88
LUMO symmetry	t	a <sub>2u</sub>
LUMO energy (eV)	4.18	4.31

recorded with a ‘Stearat’ spectrometer using an ammonium biphtalate (NAP) single crystal as a crystal-analyzer. This crystal has nonlinear reflection efficiency, which is corrected by the procedure described elsewhere (Ref. [21]). The samples were deposited on copper supports and cooled down to liquid nitrogen temperature in the vacuum chamber of the X-ray tube with copper anode (*U* = 6 kV, *I* = 0.5 A). Determination accuracy of X-ray band energy was ±0.15 eV with a spectral resolution of 0.4 eV.

### 3. Calculation

Two isomers of C<sub>60</sub>H<sub>36</sub> (Fig. 1) were calculated in the framework of the Hartree–Fock self-consistent field (HF-SCF) using the 6-21G basis set within the GAMESS package [22]. The geometry of the molecules was optimized to the gradient value of 10<sup>−4</sup> Ha/Bohr in the *T* and *D*<sub>3d</sub> point group symmetry. The calculated total energy of the isomers, their symmetry and one-electron energies of the frontier orbitals are presented

Table 2  
Bond lengths and bond orders for the *T* isomer

Bond	Bond length (Å)	Bond order
C1–C2	1.359	1.464
C1–C3	1.373	1.354
C1–C4	1.492	0.897
C2–C5	1.486	0.894
C4–C6	1.595	0.897
C4–C7	1.564	0.908
C5–C8	1.571	0.925
C5–C9	1.648	0.899
C4–H	1.087	0.908
C5–H	1.085	0.916
C9–H	1.081	0.929

Table 3  
Bond lengths and bond orders for the *D*<sub>3d'</sub> isomer

Bond	Bond length (Å)	Bond order
C1–C2	1.358	1.464
C1–C3	1.372	1.356
C1–C4	1.488	0.896
C4–C5	1.611	0.900
C4–C6	1.559	0.920
C5–C11	1.548	0.906
C6–C7	1.631	0.881
C6–C8	1.513	0.908
C8–C9	1.304	1.943
C8–C10	1.515	0.888
C4–H	1.086	0.914
C5–H	1.081	0.930
C6–H	1.085	0.915
C11–H	1.090	0.908

in Table 1. The *T* symmetric structure is lower in energy than the *D*<sub>3d'</sub> isomer by 1.14 eV. Tables 2 and 3 contain the values of optimized bond lengths and their orders for considered molecules. Significant delocalization of  $\pi$  electrons is observed in the rings of carbon atoms lacking hydrogen atoms. The orders of nonhydrogenated carbon–carbon bonds (for example, between the C8 and C9 atoms) in the *D*<sub>3d'</sub> isomer are characteristic for the double bonds. The C–C bonds in completely hydrogenated hexagons are elongated up to 1.648 and 1.631 Å in the *T* and *D*<sub>3d'</sub> isomers, respectively.

Energies of X-ray transitions were calculated based on Koopmans’ theorem, neglecting any changes which may occur in the orbitals of the ionized state compared to the ground state of a compound. In this approximation, the transition energy from the *j*th to the *i*th orbital is equal to the difference of ab initio one-electron energies for corresponding levels:

$$E_{ji} = \varepsilon_i - \varepsilon_j. \quad (1)$$

Intensities of the CK <sub>$\alpha$</sub>  spectrum were calculated in the one-center model [23] assuming that the initial vacancy is located on one atomic site A and significant contribution to the transition intensity is made by orbitals of this atom only:

$$I_{ji} = \sum_A \sum_m \sum_n |C_{im}^A C_{jn}^A|^2, \quad (2)$$

where A denotes a carbon atom, *C*<sub>*im*</sub> and *C*<sub>*jn*</sub> are the

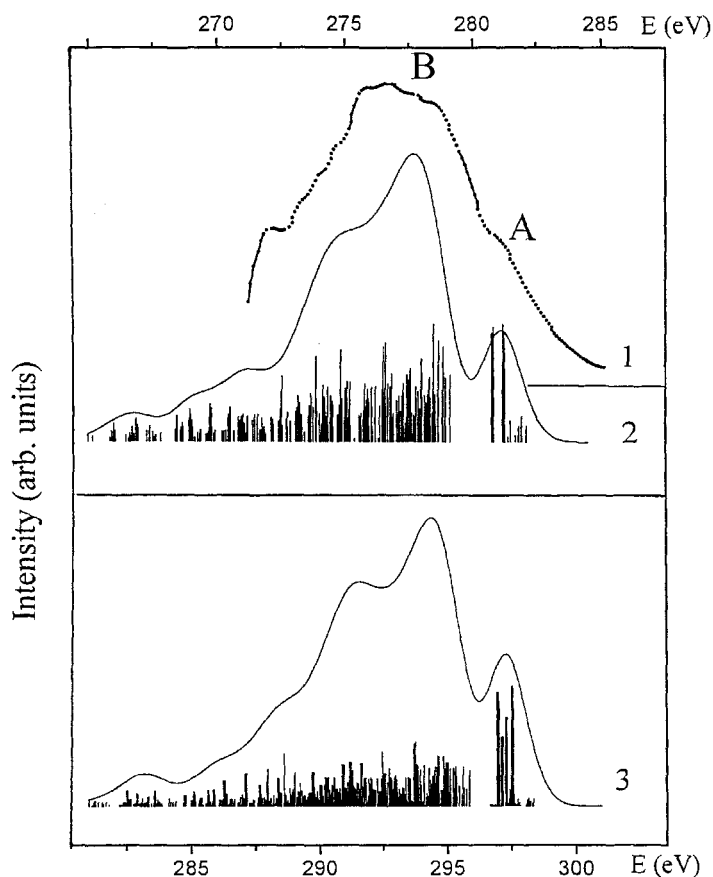


Fig. 2. (1) X-ray fluorescence spectrum of  $C_{60}H_{36}$ . Theoretical  $CK_{\alpha}$  spectra of the (2)  $T$  and (3)  $D_{3d'}$  isomers. The upper and the lower scales correspond to the measured and the calculated X-ray transition energies, respectively.

coefficients with which  $1s$  atomic orbitals (AO) and  $2p$ -AOs participate in the construction of the  $i$ th inner or the  $j$ th valence MO. As was previously shown, the theoretical spectra plotted from the results of ground state calculation of  $C_{60}$  and  $C_{70}$  molecules are in satisfactory agreement with the experimental  $CK_{\alpha}$  spectra [24–26]. The calculated intensities were normalized by maximal value and broadened by convolution of the Gaussian functions with half width at half maximum (HWHM) of 0.9 eV.

Harmonic vibration frequencies were determined by numerical calculation of the force constant matrix near the equilibrium geometry of the  $T$  isomer. IR active frequencies were scaled by a factor of 0.908 to provide correction of anharmonicity [27].

## 4. Results and discussion

### 4.1. X-ray fluorescence spectrum of $C_{60}H_{36}$

The X-ray fluorescence spectrum of the  $C_{60}H_{36}$  hydrofullerene (Fig. 2) exhibits a main broad maximum B (275–280 eV) and a short-wave shoulder at 282 eV. Our spectrum reproduces the basic peculiarities from the  $CK_{\alpha}$  spectrum of  $C_{60}H_{36}$  recorded by using synchrotron radiation [15]; some deviations in the structure of the main maximum may be connected with the measurements on the samples produced by the different synthetic techniques. Actually, the hydrofullerene studied in the present work had a light yellow color while another sample of hydrofullerene was orange yellow colored [15]. Fig. 2 shows also the calculated  $CK_{\alpha}$  spectra of the  $T$  and  $D_{3d'}$

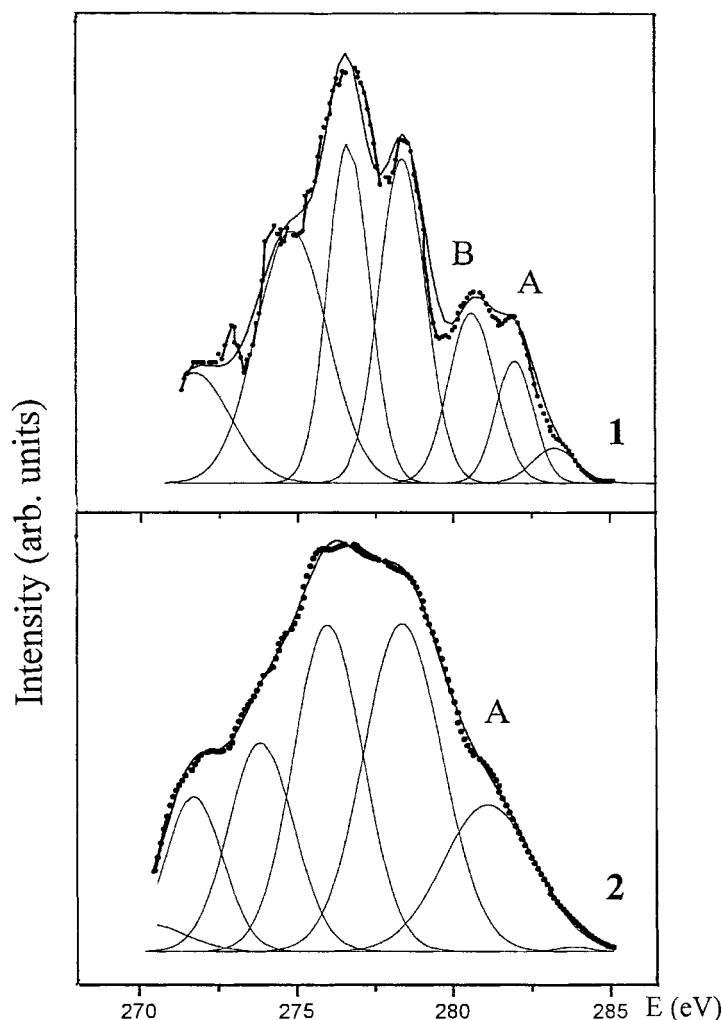


Fig. 3. Deconvolution of X-ray fluorescence spectra of the: (1) fullerene  $C_{60}$  and (2) hydrofullerene  $C_{60}H_{36}$ . Points are experimental observations; thin solid lines designate the Gaussian curves and the summing over these curves.

isomers. The difference between the measured and calculated X-ray transition energies is a result of omitting electron level relaxation for the ionized states [28]. Theoretical spectral profiles being quite similar in appearance are characterized by the short-wave feature A, which is more clearly defined than that in the experiment, and the splitting maximum B. The calculated spectra agreed quite well with the experimental one, the more unresolved structure of which may be explained by solid effects or the presence of some portion of another isomer of  $C_{60}H_{36}$  in the sample. Some deviation of the long-wave part of the

maximum B relative intensity from the experimental value is probably due to the neglect of interatomic contribution [29] in the one-center model used. As the X-ray transition probability between two different atomic sites is close to zero, when the electron is emitted from  $\pi$ -like levels, the short-wave spectral region namely should be used to determine the more probable isomer of  $C_{60}H_{36}$ .

The most noticeable difference between the spectra of the two isomers is in the intensities of the short-wave maximum A. The same difference was observed in the theoretical spectra of the  $T$  and  $D_{3d}$  isomers

calculated by the DV-X $\alpha$  method [15]. Maximum A in the *T* isomer spectrum is formed by electron transitions from eight high-occupied levels, the electron density of which is mainly localized on the four benzenoid fragments. These MOs may be regarded as an analog of the highest occupied  $\pi$ -type MO of benzene of  $e_{1g}$  symmetry. Maximum A in the  $D_{3d'}$  isomer spectrum corresponds to 10 levels; the electron density from four of them is localized on two benzenoid fragments while the rest of the levels are occupied by  $\pi$  electrons of the double bonds. The fact that the X-ray transition energies of electrons from the double bonds and the conjugated  $\pi$  bonds in the benzenoid fragments are close is principal for the determination of the number of electrons in the levels corresponding to the short-wave maximum of CK $_{\alpha}$  fluorescence spectrum of C<sub>60</sub>H<sub>36</sub>.

The integral intensity of the measured CK $_{\alpha}$  spectrum ( $I^{\text{tot}}$ ) is proportional to the population of 2p-AOs of carbon atoms composing a molecule. In the case of the C<sub>60</sub> fullerene,  $I_{C_{60}}^{\text{tot}}$  is determined by 120 C2p-electrons. The short-wave maxima A and B in the spectrum (Fig. 3) correspond to 6g<sub>g</sub>, 10h<sub>g</sub> and 6h<sub>u</sub> MOs of the icosahedral C<sub>60</sub> molecule. These MOs are  $\pi$ -type orbitals with small contributions of carbon 2s-electrons [30] and, therefore, roughly 28 electrons will determine the total intensity of maxima A and B. To compute the integral intensity of a separate maximum, the CK $_{\alpha}$  spectrum of fullerene was resolved into Gaussian shape lines. In this process we have also taken into account the nondiagrammatic line (shortest-wave shoulder) caused by re-emission of the C1s electron excited on to the lowest unoccupied molecular orbital (LUMO) of C<sub>60</sub> [25]. The resulting ratio of the integral intensities of maxima A and B,  $I_A/I_B$ , is equal to 0.54. This value correlates excellently with the value of 0.56 estimated from the population of 6h<sub>u</sub> MO corresponding to the maximum A, and the total population of 10h<sub>g</sub> and 6g<sub>g</sub> MOs corresponding to the maximum B.

Using this strategy, the number of  $\pi$  electrons occupying the high levels of the hydrofullerene C<sub>60</sub>H<sub>36</sub> can be estimated from the ratio of the integral intensities of the CK $_{\alpha}$  spectrum,  $I_{C_{60}H_{36}}^{\text{tot}}$ , and of the short-wave maximum A,  $I_{C_{60}H_{36}}^A$ . Unfortunately, our technique of carbon X-ray fluorescence spectrum measurement does not allow recording of its longer-wave part (Fig. 3). The CK $_{\alpha}$  spectrum integral intensity

measured in our experiment ( $I^{\text{meas}}$ ) will be different from  $I^{\text{tot}}$  by the value of the longer-wave part intensity. Assuming that the relative intensity of this part  $\eta = (I^{\text{tot}} - I^{\text{meas}})/I^{\text{tot}}$  in the spectrum of C<sub>60</sub>H<sub>36</sub> is the same as that in the spectrum of C<sub>60</sub>, its value may be determined from the expression:

$$I_{C_{60}}^{\text{meas}}/I_{C_{60}}^{A+B} = (1 - \eta)(N^{\text{tot}}/N^{A+B}), \quad (3)$$

where  $I_{C_{60}}^{A+B}$  is the total intensity of the maxima A and B, and  $N^{\text{tot}}$  and  $N^{A+B}$  denote the number of C2p electrons in the C<sub>60</sub> molecule and the number of electrons occupying the levels corresponding to the maxima A and B, respectively.

As a result of hydrogenation of the fullerene C<sub>60</sub> to the composition of C<sub>60</sub>H<sub>36</sub>, the total population of C2p-AOs is increased up to 124.7e; this follows from Mulliken population analysis of the orbitals in the C<sub>60</sub> and C<sub>60</sub>H<sub>36</sub> molecules. Therefore, the number of electrons occupying the C<sub>60</sub>H<sub>36</sub> high levels that correspond to the maximum A of the spectrum may be estimated as:

$$N_A = (124.7e \times 28e/120e)(I_{C_{60}}^{\text{meas}}/I_{C_{60}}^{A+B})(I_{C_{60}H_{36}}^A/I_{C_{60}H_{36}}^{\text{meas}}). \quad (4)$$

The calculated value of  $N_A$  is equal to 15.7e with an accuracy of about 1–1.5e. From the theoretical viewpoint, such a number of electrons in the high-occupied levels of C<sub>60</sub>H<sub>36</sub> can be realized only in the case of the *T* isomer.

#### 4.2. Electronic structure of the *T* isomer

The analysis of partial electron density distribution for the symmetry nonequivalent atoms of the *T* isomer points to considerable delocalization of the electrons. Hydrogen AOs participate in the formation of virtually all the valence orbitals, even by 1–2% in the highest occupied molecular orbital (HOMO). Electron density from eight high-occupied levels is mainly localized on the benzenoid fragments of the molecule. Radial directed carbon AOs form  $\rho$ -type orbitals, being analogous to the  $\pi$  orbitals of an aromatic molecule.

Energy deeper MOs corresponding to the maximum B of the X-ray spectrum are  $\tau$ - and  $\rho$ -type orbitals. The former orbitals are tangentially directed to the C<sub>60</sub> cage and provide  $\sigma$  interaction between the carbon atoms. The latter orbitals are

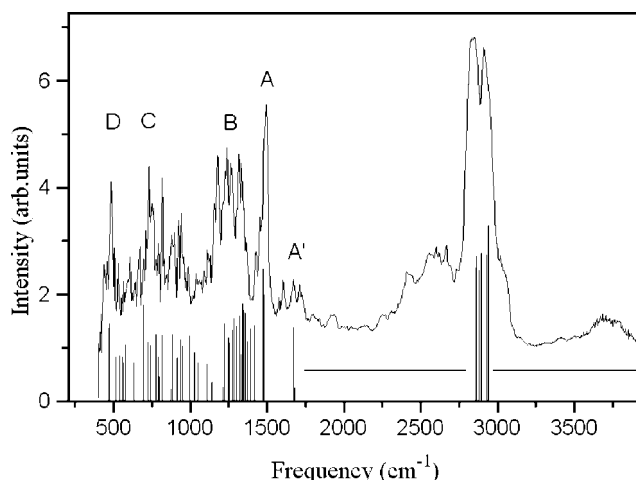


Fig. 4. IR absorption spectrum of  $C_{60}H_{36}$ , calculated IR-active frequencies and their intensities for the *T* isomer.

suited to the  $\sigma$ -bonding of carbon and hydrogen atoms in CH-groups. The  $C_{60}$  cage curvature causes the radial AOs of neighboring carbon atoms to overlap inside of the cage. The electron density from the low energetic levels of  $C_{60}H_{36}$  distributes uniformly within all atoms of the molecule. This does not allow dividing of the MOs, which are mainly formed by 2p-AOs of carbon atoms from the benzenoid rings and which could be similar to the  $b_1$  symmetry  $\pi$ -bonding orbital of the  $C_6H_6$  molecule.

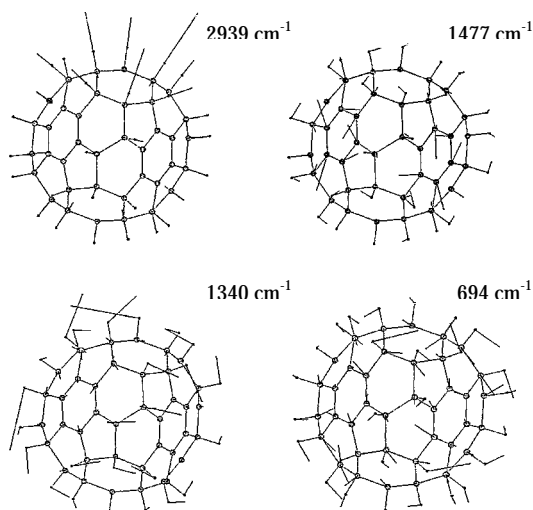


Fig. 5. Calculated modes of the most intense vibrations and their frequencies for the *T* isomer of  $C_{60}H_{36}$ .

#### 4.3. Vibrational properties of $C_{60}H_{36}$

The IR absorption spectrum of the hydrofullerene  $C_{60}H_{36}$  is shown in Fig. 4. Our IR spectrum has the same principal features as the spectra of  $C_{60}H_{36}$  produced by high-pressure hydrogenation of fullerite [6] and by the transfer hydrogenation technique, but under somewhat different synthetic conditions [9]. Three C–H stretch bands are observed in these spectra whereas only two absorption bands are resolved in this spectral region for  $C_{60}H_{36}$  prepared by Zn reduction [7] and Birch reduction [1] of  $C_{60}$ . A vertical line in Fig. 4 corresponds to the frequency of IR active vibration for the *T* isomer; its height is equal to the logarithm of the relative calculated intensity. Quite a good agreement between the experimentally observed peaks in the IR spectrum of  $C_{60}H_{36}$  and the calculated frequencies is observed. Weak features in the range of 2300–2700  $cm^{-1}$  probably are not associated with the vibrations of the  $C_{60}H_{36}$  molecule.

Calculated high-frequency modes are grouped in three bands, which correspond well to the experimental peaks at 2912, 2850 and 2831  $cm^{-1}$ . One of the modes of *t* symmetry vibration with frequency of 2939  $cm^{-1}$  is shown in Fig. 5. It represents stretching of the C–H bonds. The calculated interval ( $\approx 82\text{ }cm^{-1}$ ) of CH stretching is in excellent agreement with the measured interval of 81  $cm^{-1}$ . Semi-empirical MNDO calculations of IR spectra for the *T* isomer yield the interval of 49  $cm^{-1}$  for these valent



vibrations (nonscaling frequencies) [2] and the interval of  $44\text{ cm}^{-1}$  when the frequencies are scaled by a factor of 0.9 [9]. From this comparison it can be concluded that semiempirical quantum chemical methods cannot accurately describe the vibrational structure of the hydrofullerene  $\text{C}_{60}\text{H}_{36}$ , and the results of such calculations should be used with caution.

The low-frequency region of the IR spectrum of the hydrofullerene  $\text{C}_{60}\text{H}_{36}$  is very complicated because of the appearance of a bunch of weak lines. We divide this region into three bands A, B and C (Fig. 4). The modes for the most intense calculated vibrations for each band with the frequencies of  $1477$ ,  $1340$  and  $694\text{ cm}^{-1}$  are shown in Fig. 5. The vibrations near  $1477\text{ cm}^{-1}$  are attributed to the displacements of the carbon atoms in the benzenoid fragments and correspond to the experimental vibration at  $1492\text{ cm}^{-1}$ , being the most intense in the low-frequency spectral region. The calculated mode at  $1676\text{ cm}^{-1}$  is also associated with the skeletal vibrations of the benzenoid rings while the features in the  $1750\text{--}1540\text{ cm}^{-1}$  region (the shoulder A' in Fig. 4) are usually depicted as very weak. These characteristic frequencies are of basic importance for the structural characterization of the hydrofullerene  $\text{C}_{60}\text{H}_{36}$  with IR spectra. Strong features at the frequencies of  $1489$  and  $1490\text{ cm}^{-1}$  in the IR spectra of  $\text{C}_{60}\text{H}_{36}$  samples, prepared by transfer hydrogenation [9] and high-pressure hydrogenation techniques [6], correspond to the frequency of  $1492\text{ cm}^{-1}$  in our spectrum within experimental error. The modes corresponding to the vibrations of carbon atoms in the benzenoid rings also exist in the IR spectra, plotted on the basis of MNDO calculations of the  $D_{3d}$ ,  $D_{3d'}$ , and  $S_6$  isomers [9]. Because these isomers have only two benzenoid fragments, the intensities of the vibrations are much smaller compared to those for the  $T$  isomer.

From the analysis of the calculated modes, the B band in the low-frequency spectral region may be associated with the deformational vibrations of the C–H bonds, during which a carbon atom and the attached hydrogen atom are displaced in opposite directions (Fig. 5). Vibrations with lower frequencies (the band C) are skeletal. All atoms of the molecule have approximately equal vibrational amplitudes and the atoms of the C–H bonds are displaced in the same direction.

## 5. Conclusions

Hydrogenation of the fullerene  $\text{C}_{60}$  to the  $\text{C}_{60}\text{H}_{36}$  results in the conservation of the  $\text{C}_{60}$  cage areas, which are free from hydrogen atoms. Their existence as the benzenoid fragments or the isolated double bonds is the most energetically preferred. We have performed ab initio calculation of two  $\text{C}_{60}\text{H}_{36}$  isomers,  $T$  and  $D_{3d'}$ . If the former isomer possesses only four benzenoid rings, the latter has two benzenoid rings and six double bonds. Electronic density from eight and four high-occupied levels of the  $T$  and  $D_{3d'}$  isomers, respectively, is considerably localized on the benzenoid fragments present in the molecular structures. MOs that correspond to these electron levels are analogous to the doubly degenerated HOMO of the benzene molecule. Ab initio calculation of  $\text{C}_{60}\text{H}_{36}$  isomers showed that the energies of the X-ray transitions involving  $\pi$  electrons from MOs of this type and  $\pi$  electrons from the double bonds are very close, that is, these transitions form the short-wave maximum in the  $\text{CK}_\alpha$  spectrum of hydrofullerene. The experimentally estimated number of electron levels corresponding to this maximum is roughly equal to 16, which is more closely suited to the  $T$  isomer.

Furthermore, we obtained satisfactory agreement of the IR absorption spectrum of  $\text{C}_{60}\text{H}_{36}$  with the calculated frequencies and intensities of IR active vibrations for the  $T$  isomer. The calculated frequencies for the CH stretch form three groups, which is also observed in the experimental IR spectrum. The values of the calculated and the measured intervals that include these frequencies agree quite well. The most intense low-frequency vibration corresponds to the skeletal vibrations of the benzenoid rings, as was shown by the calculation results.

The present study demonstrates that the results of ab initio calculation of the  $T$  isomer describe reasonably well the experimentally measured electron and vibration density distribution for  $\text{C}_{60}\text{H}_{36}$  synthesized by transfer hydrogenation of  $\text{C}_{60}$  using 9,10-dihydroanthracene as the hydrogen source. From the comparison between the calculations and the experimental X-ray fluorescence and IR-spectra, the  $T$  isomer may be selected as preferable to the  $D_{3d'}$  isomer. Precise determination of the spatial structure of the hydrofullerene  $\text{C}_{60}\text{H}_{36}$  needs further investigation.

## Acknowledgements

The authors are grateful to the Russian scientific and technical program ‘Fullerenes and atomic clusters’ (Projects No. 98055 and No. 99028) and the Russian Education Ministry for the grant in the fundamental natural science field.

## References

- [1] R.E. Haufler, J. Conceicao, L.P.F. Chibante, Y. Chai, N.E. Byrne, S. Flanagan, M.M. Haley, S.C. O'Brien, C. Pan, Z. Xiao, W.E. Billups, M.A. Ciufolini, R.H. Hauge, J.L. Margrave, L.J. Wilson, R.F. Curl, R.E. Smalley, *J. Phys. Chem.* 94 (1990) 8634.
- [2] A. Rathna, J. Chandrasekhar, *Chem. Phys. Lett.* 206 (1993) 217.
- [3] A. Govindaraj, *Curr. Sci.* 65 (1993) 868.
- [4] S.J. Austin, R.C. Batten, P.W. Fowler, D.B. Redmond, R. Taylor, *J. Chem. Soc., Perkin Trans. 2* (1993) 1383.
- [5] C. Ruchardt, M. Gerst, J. Ebenhoch, H.D. Beckhaus, E.E.B. Campbell, R. Tellgmann, H. Schwarz, T. Weiske, S. Pitter, *Angew. Chem., Int. Ed. Engl.* 32 (1993) 584.
- [6] M.I. Attalla, A.M. Vassallo, B.N. Tattam, J.V. Hanna, *J. Phys. Chem.* 97 (1993) 6329.
- [7] A.D. Darwish, A.K. Abdul-Sada, G.J. Langley, H.W. Kroto, R. Taylor, D.R.M. Walton, *J. Chem. Soc., Perkin Trans. 2* (1995) 2359.
- [8] R.V. Bensasson, T.J. Hill, E.J. Land, S. Leach, D.J. McGarvey, T.G. Truscott, J. Ebenhoch, M. Gerst, C. Ruchardt, *Chem. Phys.* 215 (1997) 111.
- [9] R. Bini, J. Ebenhoch, M. Fanti, P.W. Folwer, S. Leach, G. Orlandi, Ch. Ruchardt, J.P.B. Sandall, F. Zerbetto, *Chem. Phys.* 232 (1998) 75.
- [10] B.W. Clare, D.L. Kepert, *J. Mol. Struct.* 315 (1994) 71.
- [11] L.D. Book, G.E. Scuseria, *J. Phys. Chem.* 98 (1994) 4283.
- [12] B.I. Dunlap, D.W. Brenner, G.W. Schriver, *J. Phys. Chem.* 98 (1994) 1756.
- [13] M. Buhl, W. Thiel, U. Schneider, *J. Am. Chem. Soc.* 117 (1995) 4623.
- [14] L.E. Hall, D.R. McKenzie, M.I. Attalla, A.M. Vassallo, R.L. Davis, J.B. Dunlop, D.J.H. Cockayne, *J. Phys. Chem.* 97 (1993) 5741.
- [15] Y. Muramatsu, Y. Ueno, T. Hayashi, M.M. Grush, E.M. Gullikson, R.C.C. Perera, *J. Electron Spectrosc. Relat. Phenom.* 107 (2000) 177.
- [16] W.E. Billups, A. Gonzalez, C. Gesenberg, W. Luo, T. Marriott, L.B. Alemany, M. Saunders, H.A. Jimenez-Vazquez, A. Khong, *Tetrahedron Lett.* 38 (1997) 175.
- [17] A.V. Okotrub, L.G. Bulusheva, I.P. Asanov, A.S. Lobach, Yu.M. Shulga, *J. Phys. Chem. A* 103 (1999) 716.
- [18] N.G. Spitsyna, L.I. Buravov, A.S. Lobach, *Russ. J. Anal. Chem.* 50 (1995) 613 (English translation).
- [19] A.S. Lobach, A.A. Perov, A.I. Rebrov, O.S. Roshupkina, V.A. Tkacheva, A.N. Stepanov, *Russ. Chem. Bull.* 46 (1997) 641 (English translation).
- [20] A.S. Lobach, Yu.M. Shul'ga, A.I. Rebrov, A.A. Perov, Yu.G. Morozov, *Rec. Adv. Chem. Phys. Fullerenes Relat. Mater.* 4 (1997) 246.
- [21] V.D. Yumatov, A.V. Okotrub, L.N. Mazalov, *Zh. Strukt. Khim. (Russ.)* 26 (1985) 59.
- [22] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Kosaki, N. Matsunaga, K.A. Nguyen, S.J. Su, T.L. Windus, M. Dupluis, J.A. Montgomery, *J. Comput. Chem.* 14 (1993) 1347.
- [23] H. Agren, J. Nordgren, *Theor. Chim. Acta (Berl.)* 58 (1981) 111.
- [24] J. Kawai, M. Motoyama, *Phys. Rev. B* 47 (1993) 12,988.
- [25] J.-H. Guo, P. Glans, P. Skytt, N. Wassdahl, J. Nordgren, Y. Luo, H. Agren, Y. Ma, T. Warwick, P. Heimann, E. Rotenberg, J.D. Denlinger, *Phys. Rev. B* 52 (1995) 10,681.
- [26] A.V. Okotrub, L.G. Bulusheva, V.N. Ivanova, N.F. Goldshleger, *Rec. Adv. Chem. Phys. Fullerenes Relat. Mater.* 6 (1998) 749.
- [27] J.A. Pople, H.B. Schlegel, R. Krishnan, D.J. Defrees, J.S. Binkley, M.J. Frisch, R.A. Whiteside, R.F. Hout, W.J. Hehre, *Int. J. Quantum Chem. Quantum Chem. Symp.* 15 (1981) 269.
- [28] L.N. Mazalov, V.D. Yumatov, V.V. Murakhtanov, F.H. Gelmukhanov, G.N. Dolenko, E.S. Gluskin, A.V. Kondratenko, *X-ray Spectra of Molecules*, Nauka, Novosibirsk, 1977.
- [29] F.P. Larkins, T.W. Rowlands, *J. Phys. B: At. Mol. Phys.* 19 (1986) 591.
- [30] A.V. Okotrub, V.V. Murakhtanov, L.N. Mazalov, N.V. Terpugov, A.A. Nikiforov, S.N. Lunegov, Yu.V. Shevtsov, G.S. Belikova, T.N. Turskaya, *Dokl. Akad. Nauk (Russ.)* 329 (1993) 752.