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Calculation of vibrational infrared spectra of bis-adduct $C_{60}(C_6H_{14}N_2O_2)_2$

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Adduct C_{60} with lysine is synthesized using a heterogeneous liquid-phase non-catalytic reaction. Identification was carried out using the methods of high performance liquid chromatography, electron and infrared spectroscopy and complex thermal analysis. The formula of the synthesized crystalline hydrate is defined: $C_{60}(C_6H_{14}N_2O_2)_2 \cdot 5H_2O$. Good compliance of experimental and estimated data by wave numbers of valence vibrations in OH-groups (3460 and 3446 cm^{-1}) and deformation vibrations of COH (1446 and 1441 cm^{-1}) made it possible to conclude on the preferable binding of lysine–fullerene in ε-NH_2 position.

Keywords: $C_{60}(C_6H_{14}N_2O_2)_2$, vibrational spectrum, liquid chromatography, density functional theory.

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1. Introduction

One of the important compounds of C_{60} with amino acids is adducts of C_{60} and lysine, which were synthesized previously using various methods [1–4]. Study of the nature of the bond between the molecules of C_{60} and lysine is of both theoretical interest and enables to determine the nature of biological and molecular-specific interactions. One of the methods to solve such problem is using methods of quantum chemistry [5–8], in particular, quantum-chemical estimate of infrared (IR) spectra of adducts and subsequent comparison with experimental IR-characteristics.

2. Experimental part

Synthesis method. Lysine ($C_6H_{14}N_2O_2 \cdot HCl$) (3,9 g) and sodium hydroxide (15.8 g) were dissolved in 54 ml of water, 267 ml ethanol were added to the produced solution. Then C_{60} (7.6 g) fullerene solution was prepared on o-xylene (130 ml). The produced solutions were combined and mixed for 7 days at room temperature. Further „o-xylene“ phase was separated from „water-alcohol“ phase. To isolate C_{60} fullerene adduct with lysine, methanol was added to „water-alcohol phase“ the recrystallization procedure was repeated 3 times. The produced mix was dried at 60°C for 8 h.

The mixture composition was identified using a complex of physical and chemical methods: elemental analysis (analyzer CHN-628C (LECO)]; HPLC (chromatograph Hitachi Chromaster, eluent — mixture of acetonitrile/o-xylene, column — C8-18, spectrophotometric detection at wavelength of 330 nm, chromatographic purity of adduct $P \approx 98.2 \pm 0.3$ mass.%); electron spectroscopy (spectrophotometer SPECORD M-32, wavelength $\lambda = 200-1100$ nm); thermal analysis (analyzer NETZSCH STA 449 F3, open volume, atmosphere — air, heating speed — 10 K/min, temperature interval 25–1100°C); IR-Fourier-spectroscopy (spectrophotometer Shimadzu IRTracer-100 FTIR, wave number $\tilde{\nu} = 400-4000$ cm^{-1}, KBr pellets). Therefore, the adduct composition was confirmed experimentally: $C_{60}(C_6H_{14}N_2O_2)_2 \cdot 5H_2O$.

3. Calculation part

Quantum-chemical calculations of geometric optimization and vibrational spectra are made in software complex Gaussian 09 [9] using the method of density functional theory (DFT) and hybrid (exchange-correlation) functional B3LYP. For basic ones, the Pople kit was used: 6-31G (d, p), since it may well reproduce the experimental structures of complex organic molecules [10,11]. Generation of input data and analysis of output files were carried out using visualization software GaussView 5.0 [12]. The values of wave numbers of vibrations were adjusted using the corresponding correlation coefficients [13].

First we modelled a structure of monoadduct comprising one molecule of fullerene and one molecule of lysine. We assumed that hydrogen split from the functional group is attached to the adjacent carbon atom of the fullerene core. Geometrically optimized structures capable of binding

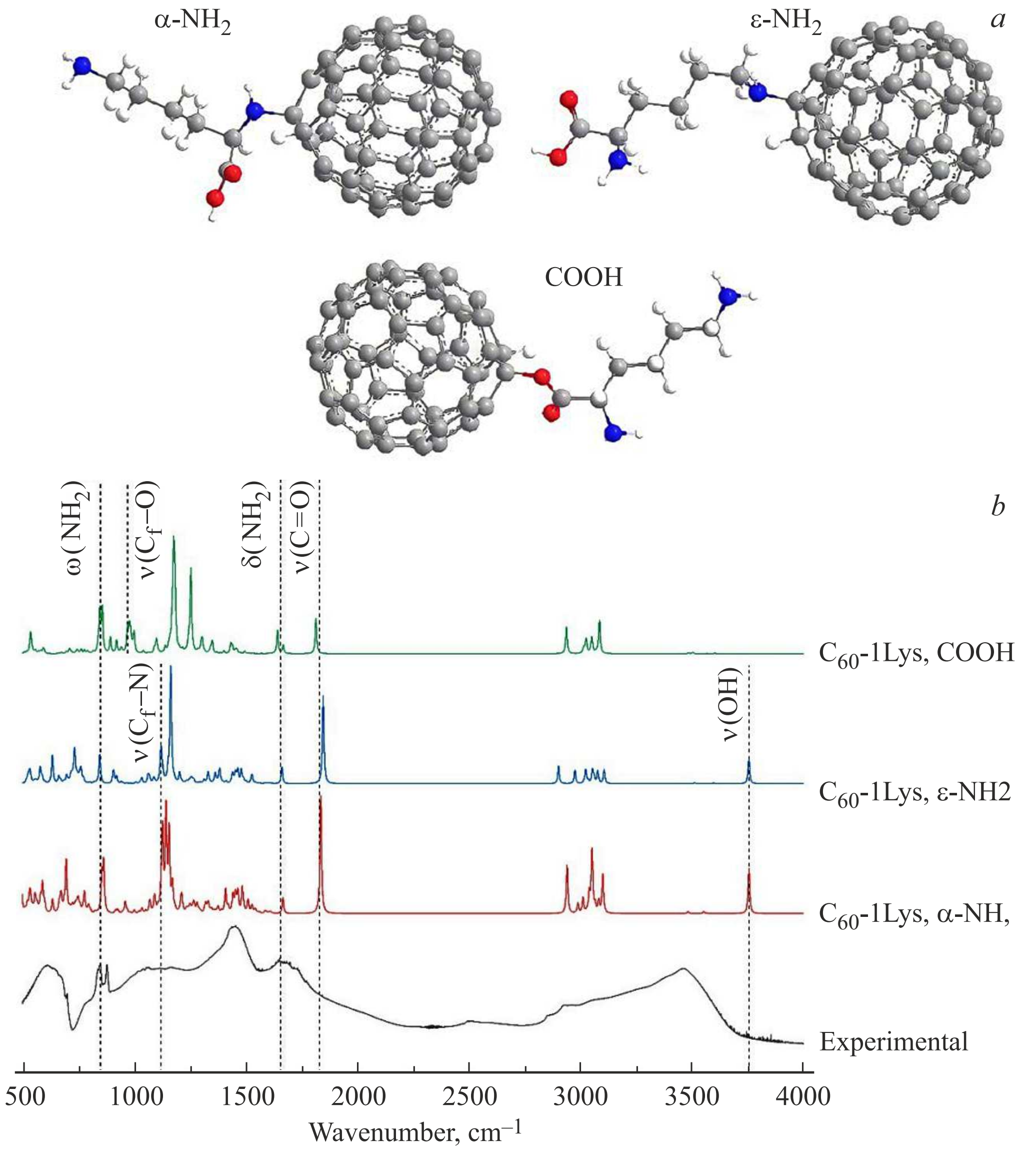

Figure 1. *a*) Geometric optimization depending on the binding variant by means of α-NH$_2$-, ε-NH$_2$-, COOH-groups and *b*) comparison of theoretical estimate with experimental data according to IR-spectra of mono-adduct fullerene — one molecule of lysine.

via α-NH$_2$-, ε-NH$_2$- and COOH-groups are presented in Figure 1. Among the main differences in IR-spectra of adducts with the composition of „fullerene — one molecule of lysine" (Figure 1) — absence of valence vibration of hydroxyl group when coordinated via COOH group and its presence when coordinated via amino group ($\sim 3750\,\mathrm{cm}^{-1}$). A different number of amino group vibrations is observed: two asymmetric valence and two symmetric valence vibrations in case of COOH-group binding, and three vibrations as lysine binds with fullerene via amino group: symmetric valence vibrations NH$_2$, asymmetric NH$_2$ and NH. Intensity of these vibrations is low, and therefore they may not be used to confirm the type of coordination when analyzing the experimental IR-spectrum. The wave numbers of valence vibrations we estimated as compliant with the formation of bonds in monoadducts were as follows: $1129\,\mathrm{cm}^{-1}$ (C–N) when forming a bond via α-NH$_2$-group, $1122\,\mathrm{cm}^{-1}$ (C–N) — via ε-NH$_2$-group, $972\,\mathrm{cm}^{-1}$ (C–O) — via COOH-group.

The composition model of bis-adduct (Figure 2 and 3, table) is based on the assumption on attachment of two lysine molecules on the opposite sides of fullerene core at the angle of 180° between them (provisionally in „para position").

The variants were proposed to form bonds between molecules of fullerene and lysine using α-NH$_2$-, ε-NH$_2$-groups or COOH in *cis*- and *trans*-positions. Hydrogen split from amino acid when forming a bond with fullerene was attached to the adjacent atom of the fullerene core or between pentagon (5) and hexagon (6) (5-6, blue balls), or between two hexagons (6-6, green ball). Variants of *cis*- and *trans*-attachment of lysine and hydrogen to

Energies and distribution of the main bands in theoretical IR-spectra of the proposed $C_{60}(C_6H_{14}N_2O_2)_2$ adduct structures in addition to experimental IR-spectrum of synthesized adduct

Type of coordination		Energy, kJ/mole	Correlation, cm^{-1}					
			$\tilde{\omega}(NH_2)$	$\tilde{\nu}(C_f{-}N)$	$\tilde{\nu}(C_f{-}N)$	$\tilde{\delta}(COH)$	$\tilde{\nu}(OH)$	$\tilde{\nu}(C_f{-}H)$
ε-NH_2	*cis*, 5-6	−8612140	869, 847 m	–	1133, 1116 w	1442, 1441 s	3446, 3444 br s	3055, 3053 vw
	trans, 5-6	−8612144	849, 847 m	–	1129, 1120 w	1441, 1440 s	3449, 3446 br s	3033, 3029 vw
	cis, 6-6	−8612307	850, 849 m	–	1135, 1134 w	1442, 1441 s	3446, 3445 br s	3061, 3059 vw
	trans, 6-6	−8612297	849, 848 m	–	1138, 1123 w	1442, 1441 s	3446, 3445 br s	3033, 3032 vw
α-NH_2	*cis*, 5-6	−8612216	888, 870 m	–	1130, 1122 w	1291, 1288 s	3793, 3789 br s	3036, 3025 vw
	trans, 5-6	−8612216	858, 849 m	–	1124, 1116 w	1292, 1291 s	3796, 3795 br s	3036, 3026 vw
	cis, 6-6	−8612346	869, 859 m	–	1127, 1122 w	1292, 1291 s	3788, 3741 br s	3062, 3061 vw
	trans, 6-6	−8612361	859, 851 m	–	1128, 1123 w	1291, 1290 s	3796, 3795 br s	3050, 3039 vw
COOH	*cis*, 5-6	−8612153	858, 857 m	983, 978 w	–	–	–	3066, 3038 vw
	trans, 5-6	−8612155	863, 859 m	985, 984 w	–	–	–	3064, 3063 vw
	cis, 6-6	−8612308	861, 860 m	989, 988 w	–	–	–	3069, 3068 vw
	trans, 6-6	−8612291	862, 857 m	995, 975 w	–	–	–	3051, 3050 vw
experiment		–	847	–	–	1446	3460	–

Designations: $C_f{-}X$ — bond of fullerene core C_{60} with atom X of lysine; s — strong, m — medium force, wv — weak, vwv — very weak, br — wide peaks; $\tilde{\nu}$ — valence, $\tilde{\delta}$ — deformation; $\tilde{\omega}$ —- wagging vibrations.

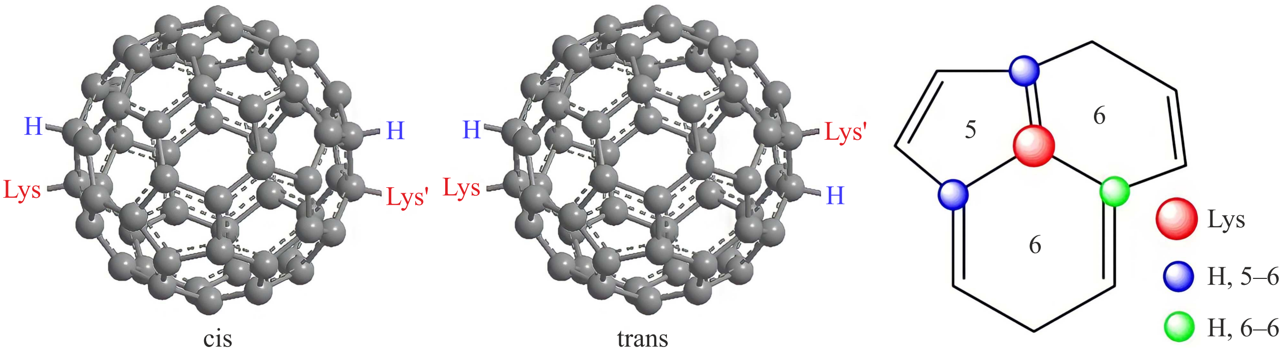

Figure 2. Variants of *cis* — and *trans*-attachment of two lysine groups (Lys, Lys') and hydrogen to fullerene core.

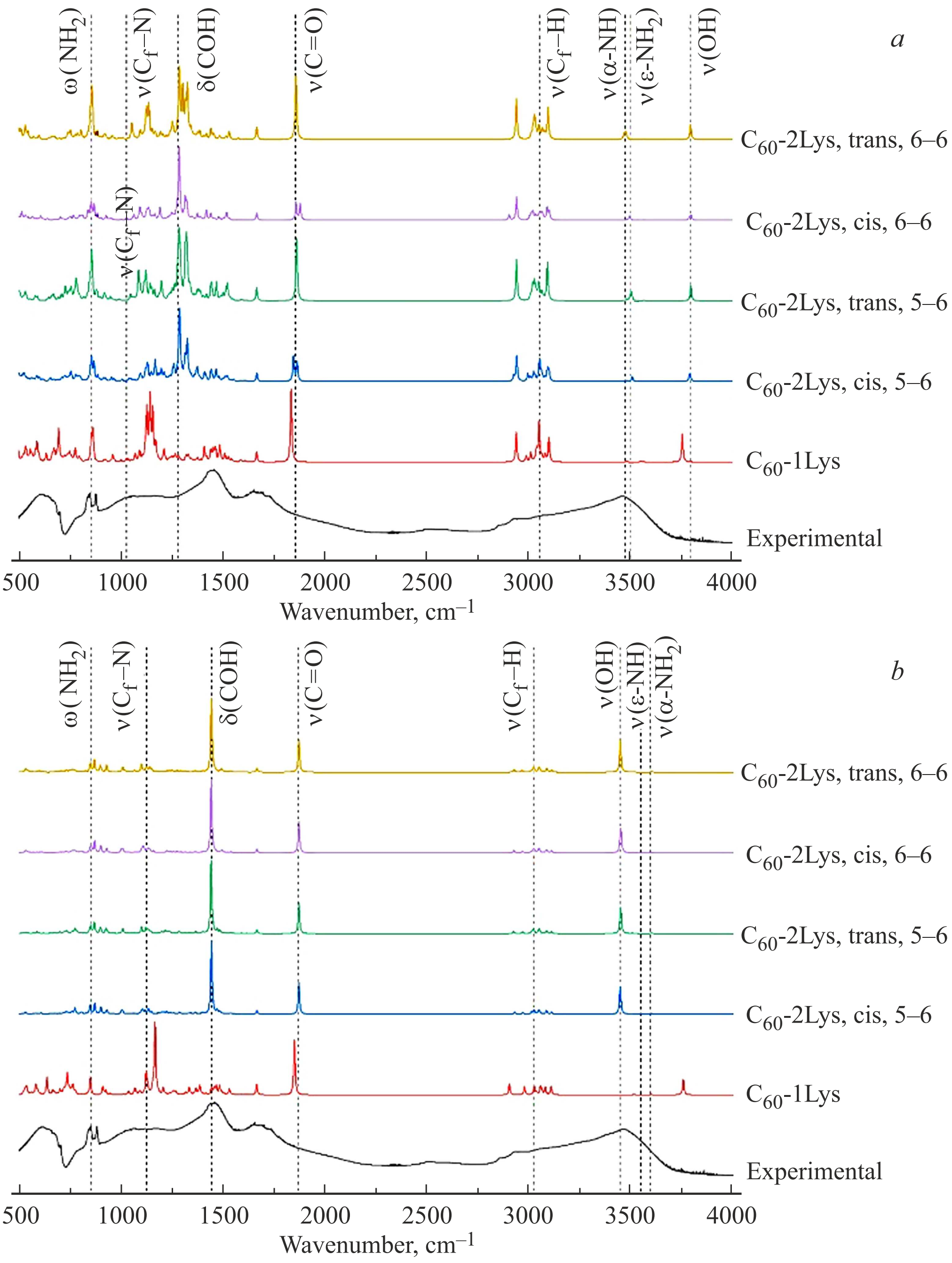

Figure 3. Estimated and experimental data according to IR-spectra of bis-adduct C_{60} with two molecules of lysine when a bond is formed by *a*) α-NH$_2$-group, *b*) ε-NH$_2$-group, *c*) OH-group.

fullerene are shown in Figure 2. When the bond is formed via group α-NH$_2$ in vibrational spectra, we considered vibrations corresponding to the main characteristic groups. Characteristics of these vibrations are presented in the table and in Figure 3. Symmetric and asymmetric valence vibrations of ε-NH$_2$-group are in the range of $3460-3570\,\mathrm{cm}^{-1}$, valence vibration of OH-group meets the values $\sim 3795\,\mathrm{cm}^{-1}$, while in the experimental spectrum there is a wide intense peak, which is most probably the result of imposition of symmetric and asymmetric valence vibrations of water and valence vibrations of OH-group at lower values ($\sim 3460\,\mathrm{cm}^{-1}$). In the region $\tilde{\nu} < 2000\,\mathrm{cm}^{-1}$ the estimated IR-spectrum shows intense valence vibration C=O at $\tilde{\nu} \approx 1860\,\mathrm{cm}^{-1}$ or its splitting with reduction of intensity, specific for *cis*-coordination. Vibration of the bond of the fullerene core with nitrogen atom C_f–N ($\sim 1130\,\mathrm{cm}^{-1}$) has low intensity and is located among other vibrations of lysine and fullerene core and is not identified in the experimental spectrum. Wave numbers of wagging vibrations ε, ε'-NH$_2$ ($\sim 860\,\mathrm{cm}^{-1}$) are close to the

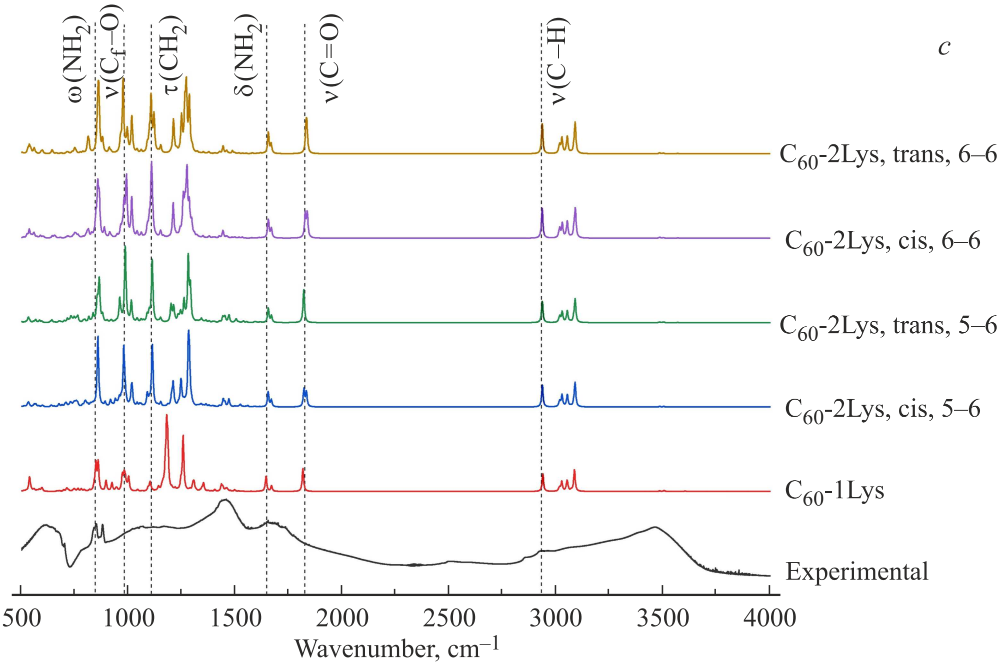

Figure 3 (*continued*).

experimentally produced values ($\sim 847\,\mathrm{cm}^{-1}$). According to the estimates, the coordinates of deformation vibrations of COH group ($\sim 1291\,\mathrm{cm}^{-1}$) are strongly displaced relative to the experimentally observed wide peak meeting the wave numbers of around $1446\,\mathrm{cm}^{-1}$. When a bond is implemented in bis-adduct via COOH group, the estimated spectra lack valence OH vibrations and deformation vibrations of COH groups. The absence of these vibrations in theoretical spectra and on the contrary the presence of the latter in the experimental ones prevents the possibility of such binding variant. The estimate found that the valence vibration C_f–H meets $\tilde{\nu} \approx 3050\,\mathrm{cm}^{-1}$, and its intensity is low. In the range of $750-1300\,\mathrm{cm}^{-1}$ there is a series of highly intensive peaks of specific vibrations $\{\nu(C_{Lys}–O)$, $\delta(C_f–H)$, $\tau(CH_2)$, $\omega(NH_2)\}$, which, however, are absent in the experimental spectrum. One may differentiate strong valence vibration C=O ($\sim 1825\,\mathrm{cm}^{-1}$) and wagging vibrations of α, α-NH$_2$ and ε, ε-NH$_2$-groups ($\sim 860\,\mathrm{cm}^{-1}$). The considered type of binding provides no substantial effect at the wave number of wagging vibrations of NH$_2$ groups. The best compliance with the experimental spectra is demonstrated by theoretically calculated spectra for the variant of fullerene–lysine bond coordination via ε-NH$_2$-group (table and Figure 3). The positions of very close peaks of very low intensity: of valence vibrations ε-NH ($\sim 3506\,\mathrm{cm}^{-1}$), valence symmetric and asymmetric vibrations of α-NH$_2$-group ($\sim 3601\,\mathrm{cm}^{-1}$) and valence vibrations of high intensity of OH-groups ($\sim 3447\,\mathrm{cm}^{-1}$) are well-matched with the experimental value ($\sim 3460\,\mathrm{cm}^{-1}$). Note that estimated and experimental wave numbers are close and make ~ 1441 and $\sim 1446\,\mathrm{cm}^{-1}$ accordingly, which we referred to deformation vibrations of COH group. Certain non-conformity between the experiment and the estimate in the position of valence vibrations C=O is most probably caused by the presence of potential weak particle-to-particle interactions between the end COOH groups with other molecules of adducts (according to the type of hydrogen bonds). In the region of wagging vibrations of α, α-NH$_2$-groups the values $\tilde{\nu}$ — are close to wagging vibrations of ε, ε-NH$_2$ (when α-binding is implemented). Both vibrations are characterized by highest intensity: simultaneous wagging vibration of both α-NH$_2$ groups at $849\,\mathrm{cm}^{-1}$ and joint vibration of groups α-NH$_2$ and torsion vibrations of COH-group at $867\,\mathrm{cm}^{-1}$. Valence vibrations C_f–N in the region $1123-1138\,\mathrm{cm}^{-1}$ are characterized by low intensity. Attachment of hydrogen split from lysine in *trans*-position is somewhat more energetically preferable. The comparison of experimental and estimated spectra may lead to the conclusion for the benefit of forming the fullerene–lysine bond specifically via ε-NH$_2$-group in the area of content of both hexagons.

Conclusion

The results of the completed quantum-mechanical modeling of the vibrational spectrum of bis-adduct of fullerene C$_{60}$ and lysine are in general confirmed by the experimentally obtained infrared spectrum.

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Conflict of interest

The authors declare the absence of the conflict of interest.

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