

## Research Article

# The IR Spectra, Molar Absorptivity, and Integrated Molar Absorptivity of the $C_{76}-D_2$ and $C_{84}-D_2:22$ Isomers

Tamara Jovanović,<sup>1</sup> Đuro Koruga,<sup>1</sup> and Branimir Jovančević<sup>2</sup>

<sup>1</sup>Department of Biomedical Engineering, Faculty of Mechanical Engineering, University of Belgrade, Kraljice Marije 16, 11120 Belgrade, Serbia

<sup>2</sup>Department of Applied Chemistry, Faculty of Chemistry, University of Belgrade, Studentski trg 12-16, 11000 Belgrade, Serbia

Correspondence should be addressed to Tamara Jovanović; tamara.jovanovic@sbb.rs

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The FT-IR spectra of the stable  $C_{76}$  and  $C_{84}$  isomers of  $D_2$  symmetry, isolated by the new, advanced extraction and chromatographic methods and processes, were recorded by the KBr technique, over the relevant region from 400 to 2000  $\text{cm}^{-1}$ , at room temperature. All the observed infrared bands are in excellent agreement with the semiempirical QCFF/PI, DFT, and TB potential calculations for these fullerenes, which is presented in this article, as the evidence of their validity. The molar absorptivity  $\epsilon$  and the integrated molar absorptivity  $\psi$  of their IR absorption bands were determined and reported together with the relative intensities. Excellent agreement is found between the relative intensities of the main and characteristic absorption maxima calculated from  $\epsilon_\lambda$  and from the  $\psi_\lambda$  values in adequate integration ranges. These results are significant for the identification and quantitative determination of the  $C_{76}-D_2$  and  $C_{84}-D_2:22$  fullerenes, either in natural resources on Earth and in space or in artificially synthesized and biomaterials, electronic, optical, and biomedical devices, sensors, polymers, optical limiters, solar cells, organic field effect transistors, special lenses, diagnostic and therapeutic agents, pharmaceutical substances in biomedical engineering, and so forth.

## 1. Introduction

Fullerenes  $C_{60}$  and  $C_{70}$  were detected in a series of astrophysical objects and space environments [1–6], such as certain planetary [7, 8] and protoplanetary [9] nebulae, postasymptotic giant branch stars, young stellar objects [10], reflection nebulae [11], certain R-Coronae Borealis stars, and carbon rich stars [12–16], as well as in some resources on Earth [17, 18]. The identification and quantitative assessment of these molecules, both in natural and in artificially synthesized materials, were made possible by the measurement of their IR spectra, the dependence of these spectra on temperature, the molar absorptivity, and integrated molar absorptivity of their absorption bands [2–26].

It is expected that also higher fullerenes can be found in space, besides  $C_{60}$  and  $C_{70}$ . Calculations [27] suggest that, on a per carbon atom basis [1], higher fullerenes are thermodynamically even more stable than  $C_{60}$ ,  $C_{70}$  [28], and from the hydrogenated derivatives fullerenes [17, 18, 29–31]. Their formation through coalescence of smaller fullerenes [32]

and by laser ablation of carbon [17–19, 33, 34] also leads to the conclusion about their possible presence in nature.

For the qualitative detection of  $C_{76}$  and  $C_{84}$  fullerenes, the knowledge of the infrared band position and band widths, as well as the evolution of these parameters with temperature, is necessary. This need was fulfilled, for instance, by the previous works [1, 35–42] in the infrared spectroscopy of  $C_{76}$  and  $C_{84}$ , whereas quantitative assessment of these fullerenes requires knowledge about intensities of their IR absorption bands, which is provided in the current work.

In the first phase of this research, the only stable  $C_{76}-D_2$  isomer [43–45] and the most abundant, stable isomer of the higher fullerene  $C_{84}$  with  $D_2$  symmetry,  $C_{84}-D_2:22$  [46–54], were isolated from carbon soot, by new and advanced chromatographic methods and processes [35–42], in comparison to previous methods for the separation of higher fullerenes under pressure [55–63]. Their IR (KBr) spectra were recorded over the entire relevant region, from 400 to 2000  $\text{cm}^{-1}$  in transparence mode [35–42], and in the absorption mode in this article.

A comparison of the experimentally observed vibrational frequencies in the IR absorption spectra of the isolated  $C_{76}\text{-D}_2$  and  $C_{84}\text{-D}_2:22$  samples [35, 38] with the semiempirical QCFF/PI, DFT, as well as TB potential theoretical calculations for these fullerenes [44, 45, 48–50], is presented in this article, indicating their validity.

In this work also, the molar extinction coefficients and the integrated molar extinction coefficients of their main and characteristic IR absorption bands were determined.

These data are important for the qualitative and quantitative determination of the  $C_{76}\text{-D}_2$  and  $C_{84}\text{-D}_2:22$  isomers, either in natural resources on Earth and in space or in artificially synthesized materials, electronic and optical devices, diagnostic and therapeutic agents for the applications in biomedical engineering, and so forth.

## 2. Experimental Methods

In the first phase of this research,  $C_{60}$ ,  $C_{70}$  [24–26], and the higher fullerenes, mainly  $C_{76}$  and  $C_{84}$  [35–42], were Soxhlet-extracted with a series of different and previously unapplied solvents or combinations of solvents from the samples of carbon soot, produced by electric arc (MER Corporation, Tucson, USA). The extraction procedures were performed until the complete disappearance of color in a Soxhlet extraction thimble. Solvents used were *n*-heptane, toluene, chlorobenzene, *p*-xylene, a mixture of *o/m/p*-xylene, and pyridine, as well as the successive use of toluene and chlorobenzene and *p*-xylene and pyridine. The yields, as well as the compositions of all the extracts, were determined by spectroscopic and chromatographic methods. The procedures for increases of fullerenes yields, as well as for additional selective extraction of higher order fullerenes, were found [24–26, 35–42].

In the second phase,  $C_{60}$ ,  $C_{70}$ , and the higher fullerenes  $C_{76}$  and  $C_{84}$  (the only stable  $C_{60}\text{-Ih}$ ,  $C_{70}\text{-D}_{5h}$ , and  $C_{76}\text{-D}_2$  isomers of the first three mentioned fullerenes and the most abundant, stable  $C_{84}$  isomer of  $D_2$  symmetry) were chromatographically separated from the obtained soot extracts on the activated  $Al_2O_3$  columns, by new and advanced methods [35–42].

The main difference and advancement of these methods [35–42], in comparison to previous methods under pressure [55–63], is the isolation of the purified stable isomers of the higher fullerenes  $C_{76}$  and  $C_{84}$  (the  $C_{76}\text{-D}_2$  and  $C_{84}\text{-D}_2:22$  isomers), successively after the basic fullerenes, in one phase of each of the processes, under atmospheric pressure and smaller flow of 1.5 mL/min, in increased milligram yields. The other advantages of the developed methods [35, 42] are the use of significantly smaller amounts of the initial materials, as well as less expensive laboratory equipment. In these methods [35, 42], the entire materials and energy expense, the time spent on the purification processes, and environmental pollution were decreased, using smaller amounts of less toxic solvents. The yields and the purities of the isolated fullerenes were increased or maximized [35, 36, 39].

Purification of the higher fullerenes under pressure, on a preparative scale, either by flash chromatography or by HPLC, generally required larger amounts of the initial materials and repeated chromatographies, and the fullerenes were obtained in smaller yields [55–63].

In our new methods [35–42], the elution was performed continuously with several different original, defined gradients of solvents: from pure hexane or 5% toluene in hexane to pure toluene. The amounts of the initial materials used were as follows: fullerenes extracts, 10 mg, and finely granulated  $Al_2O_3$ , 50 g, activated for 2 h at 105°C, and eluent (1.5 to 1.75 L) per chromatographic separation [35–42]. Starting from 10 mg of the soluble soot extract, in average ca. 1 mg of  $C_{76}$  and ca. 1 mg of  $C_{84}$  were isolated in purified form per one chromatographic process, or up to few milligrams in some cases. The time spent on the purification processes was from 16.7 to 19.4 h [36, 39].

For comparison, using flash chromatography to separate fullerenes [55], on alumina, with hexane or 5% toluene in hexane as eluent, required about 50 times larger quantities of the initial materials, such as 500 mg of crude fullerenes extract, 2500 mg of alumina, and about 12.5 L of solvent for one chromatographic fraction,  $C_{60}$ , or 75 L for six chromatographic fullerene fractions, per one chromatography and the large size of columns. The entire time of this purification process, including repeated chromatographies, was 66 hours and purified higher fullerenes were obtained in lower yields. From the total amount of 2500 mg of toluene soluble soot extract, 12 mg of  $C_{76}$  and 2 mg of  $C_{84}$  were isolated.

From these data, it follows [36, 39] that 21 times larger amounts of the initial materials (extract, stationary phase, and solvent) and 2 times longer time are needed for obtaining 1 g of purified  $C_{76}$ , and 125 times larger amounts of the initial materials and 10 times longer time are required for obtaining 1 g of purified  $C_{84}$  by the mentioned flash chromatography process [54], in comparison to our protocols [35–42].

In the previous method under pressure [57, 58], the purified basic and higher fullerenes were eluted according to their molecular weights on the monomeric ODS column, using large volumes of solvents, in comparison to our new methods [35–42]. Several tens of liters of a mixture of toluene and methanol (55:45, v/v) per chromatography were used, at a flow rate of 40 mL/min [57, 58]. In the new methods [35–42], under atmospheric pressure and smaller flow rate of 1.5 mL/min, significantly smaller volumes of solvents were used for the elution of the purified basic and higher fullerenes in one phase, 1.5 to 1.75 L per chromatography.

The IR spectra of all the chromatographically purified fractions of the basic and the higher fullerenes from this research, as well as of the obtained soot extracts, were previously recorded on a Perkin Elmer FT-IR 1725 X spectrometer by the KBr pellet technique, from 400 to 4000  $cm^{-1}$ , at a resolution of 1  $cm^{-1}$ , in the transperance mode [24–26, 36, 37, 39–42].

The IR spectra of the  $C_{76}\text{-D}_2$  and  $C_{84}\text{-D}_2:22$  samples, isolated by the new and advanced chromatographic methods [35–42], were also recorded on a Thermo Scientific FT-IR spectrometer Nicolet IR-6700, by the KB disk technique, in

the range of 400–2000  $\text{cm}^{-1}$ , at a resolution of 1  $\text{cm}^{-1}$ , in the transpance mode [35, 38], as well as in the absorption mode in this article.

**2.1. Measurement of the Molar Absorptivity and Integrated Molar Absorptivity of  $C_{76}\text{-D}_2$  and  $C_{84}\text{-D}_2$ :** Chromatographically isolated  $C_{76}\text{-D}_2$  (0.249 mg) and  $C_{84}\text{-D}_2$ :22 (0.270 mg) were mixed with 70.8 mg and with 77.8 mg of KBr, respectively. The obtained powder was compressed at the 4 tons/ $\text{cm}^2$  with the Perkin Elmer press.

The resulting pellets were placed in the FT-IR spectrometer. Measurements of the intensities (heights) of the absorption bands, as well as of the integrated band intensities of  $C_{76}\text{-D}_2$  and  $C_{84}\text{-D}_2$ :22, with automatic subtraction of the baseline, were made possible through the OMNIC software from Thermo Scientific, dedicated to the FT-IR spectrometer. This software has also been recently used for the measurement of relative intensities of IR absorption bands of  $C_{60}$  and  $C_{70}$  [4].

The masses of the resulting pellets were 71.0 mg and 78.1 mg, and the percentages of carbon determined by the elemental analysis were 0.351 and 0.346. Their measured thicknesses ( $b$ ) were 0.67 mm~0.07 cm and 0.74 mm~0.07 cm, the diameters ( $R$ ) were 0.7 cm, and the half diameters ( $r$ ) were 0.35 cm.

The volumes of the pellets ( $V$ ) were determined from the abovementioned  $r$  and  $b$  parameters, by the equation  $V = r^2\pi b$ . The obtained values of the volumes, as well as the thicknesses of pellets, were also confirmed using KBr density (2.753  $\text{g}/\text{cm}^3$ ) [4] and the masses of pellets.

Concentrations ( $c$ ) of fullerenes  $C_{76}$  and  $C_{84}$  in the pellets, as the number of moles per unit of volume, were calculated using the masses of  $C_{76}$  and  $C_{84}$  in the pellets, their molar masses of 912.76  $\text{g}/\text{mol}$  and 1008.84  $\text{g}/\text{mol}$ , and the volumes of pellets.

The  $(bc)^{-1}$  values were determined for the  $C_{76}\text{-D}_2$  and the  $C_{84}\text{-D}_2$ :22 samples in KBr pellets from the abovementioned experimental parameters. The  $(bc)^{-1}$  value found for  $C_{76}\text{-D}_2$  was 1409.7  $\text{L}\cdot\text{cm}^{-1}\cdot\text{mol}^{-1}$  and the  $(bc)^{-1}$  value found for  $C_{84}\text{-D}_2$ :22 was 1436.0  $\text{L}\cdot\text{cm}^{-1}\cdot\text{mol}^{-1}$ .

### 3. Results and Discussion

In the recent works [1, 35–42], the IR spectra of the higher fullerenes  $C_{76}$  and  $C_{84}$  and their stable isomers of  $D_2$  symmetry have been studied. The dependence on temperature of the position and width of their infrared absorption bands has been determined [1, 35]. The molar extinction coefficients and integrated molar absorptivity of the infrared absorption spectra of  $C_{60}$  and  $C_{70}$ , as well as of related hydrogenated derivatives, fullerenes, have also been recently determined [2–5]. However, neither the molar absorptivity nor the integrated band intensity of  $C_{76}\text{-D}_2$  and  $C_{84}\text{-D}_2$ :22 has been reported.

Determination of molar absorptivity of the isolated higher fullerenes, in  $\text{L}\cdot\text{cm}^{-1}\cdot\text{mol}^{-1}$ , at a given wavenumber,  $\epsilon_\lambda$ , was achieved through (1), previously applied for  $C_{60}$  and  $C_{70}$ , as well as for hydrogenated fullerenes [2–6, 64],

according to Lambert and Beer law, using the absorbance  $A_\lambda$  read at a given wavenumber:

$$\epsilon_\lambda = A_\lambda (bc)^{-1}. \quad (1)$$

The determined values of  $(bc)^{-1}$  for both the  $C_{76}\text{-D}_2$  and the  $C_{84}\text{-D}_2$ :22 samples are reported in the Experimental Methods.

It was found that the peak height measurements that correspond to the absorbance  $A$  are sensitive to changes in the resolution of the spectrometers used [2–6, 64]. The measurement of the integrated intensity that corresponds to the total area below a given absorption band is much less sensitive to instrumental resolution than the peak height measurement [2–6, 64].

Thus, the absorbance and the integrated band intensities in the obtained original IR spectra of the isolated  $C_{76}\text{-D}_2$  and  $C_{84}\text{-D}_2$ :22 samples were determined using the OMNIC software of our spectrometer, in both cases subtracting automatically the baseline.

The integrated molar absorptivity of the  $C_{76}\text{-D}_2$  and  $C_{84}\text{-D}_2$ :22 fullerenes, expressed in  $\text{cm}\cdot\text{mol}^{-1}$  or  $10^{-5}\text{ km}\cdot\text{mol}^{-1}$ , was determined by (2), previously applied for the basic fullerenes, as well as for fullerenes [2–6, 64]:

$$\Psi = \int \epsilon_\lambda d\lambda. \quad (2)$$

In this equation,  $\lambda$  is the wavelength and  $\epsilon_\lambda$  is the molar absorptivity measured with a spectrometer with unlimited resolution, integrated over the whole band. In practice, by substituting (1) into (2), we get [2–6, 64]

$$\Psi = (bc)^{-1} \int A_\lambda d\lambda. \quad (3)$$

The original, characteristic, representative IR spectrum of the isolated sample of the  $C_{76}\text{-D}_2$  isomer is obtained in this article in the absorption mode, Figure 1, for determination of the molar absorptivity and integrated molar absorptivity of its absorption bands, which is important for the quantitative assessment of this fullerene and represents the main work of this article. It was previously provided in transpance mode, in supplemental material of our article [35], for the qualitative determination.

The main three, most intense, dominant  $C_{76}$  maxima, registered in this research [35–42], appear at 967, 1082, and 1187  $\text{cm}^{-1}$ , with some weak, distinct shoulders. Characteristic, sharp absorption bands unique to  $C_{76}$  occur in the first relevant part at 893 and 823  $\text{cm}^{-1}$ , with a neighboring shoulder at 792  $\text{cm}^{-1}$ . Several other bands are present at 703  $\text{cm}^{-1}$  with a shoulder at 742  $\text{cm}^{-1}$ , at 605  $\text{cm}^{-1}$  with the shoulders at 647 and 665  $\text{cm}^{-1}$ , and at 484  $\text{cm}^{-1}$  with the shoulders at 538, 462, 456, and 426  $\text{cm}^{-1}$ . Pronounced and intense bands are present in the higher frequency region at 1386  $\text{cm}^{-1}$  with the shoulders at 1397 and 1364  $\text{cm}^{-1}$ , at 1493  $\text{cm}^{-1}$  with a neighboring shoulder band at 1462  $\text{cm}^{-1}$ , as a doublet, and at 1735  $\text{cm}^{-1}$ . Maximum at 1312  $\text{cm}^{-1}$  appears with the neighboring shoulders at 1273 and 1248  $\text{cm}^{-1}$ , as a triplet. Complete absorption in this spectrum [35] is in

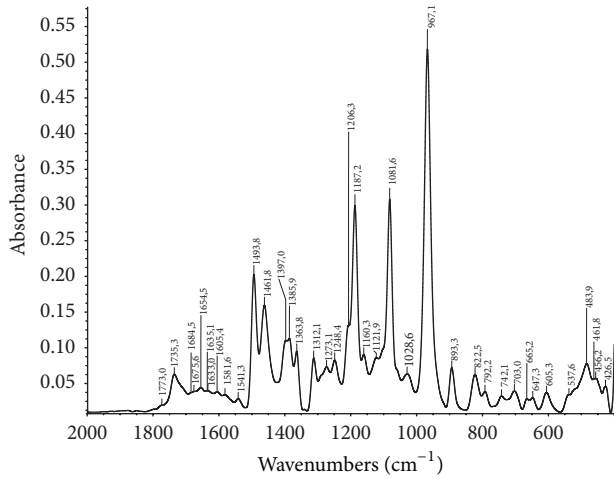


FIGURE 1: The IR spectrum of C<sub>76</sub>-D<sub>2</sub> in a mode.

agreement with the theoretical calculations for C<sub>76</sub>-D<sub>2</sub>, as well as for its dianion [44, 45].

In the previous articles [35, 37], a comparison of the experimentally observed absorption frequencies in the IR spectra of the chromatographically isolated C<sub>76</sub>-D<sub>2</sub> samples, recorded on Perkin Elmer [37, 40–42] and on Thermo Scientific FT-IR spectrometer Nicolet IR-6700 at room temperature [35], with the semiempirical QCFF/PI theoretical calculations for this fullerene [35, 37, 40–42, 44], as well as with the IR spectra of C<sub>76</sub>, recorded on three different temperatures between –180°C and +250°C [1, 35], was presented. On the basis of the obtained excellent agreement [35, 37, 40–42, 44], the validity of both the experimental results [35, 37, 40–42] and the mentioned theoretical calculations for C<sub>76</sub>-D<sub>2</sub> [44] was indicated [35, 37, 44]. In the more recent article [35], a larger number of experimentally registered vibrational frequencies of C<sub>76</sub> were presented and theoretically confirmed [35, 44].

There is also a good agreement between the absorption bands in our infrared spectra at room temperature [35–42] and the recent spectra of C<sub>76</sub>-D<sub>2</sub> at three different temperatures [1]. Only some smaller shifts, as well as some changes of their relative intensities with the temperature, were observed [1, 35].

In this article, a comparison of the experimentally obtained vibrational frequencies (cm<sup>-1</sup>) in the IR absorption spectra of the chromatographically isolated C<sub>76</sub>-D<sub>2</sub> samples (IR1-IR3), recorded from 400 to 2000 cm<sup>-1</sup>, on a Thermo Scientific FT-IR spectrometer Nicolet IR-6700 [35], with the different theoretical calculations, by the QCFF/PI method (Calc. 1, from 286 to 1668 cm<sup>-1</sup>) [44] and DFT method for C<sub>76</sub> (Calc. 2, from 206.7 to 1602.7 cm<sup>-1</sup>) [45], as well as for C<sub>76</sub><sup>2-</sup> (Calc. 3, from 195.7 to 1556.0 cm<sup>-1</sup>) [45], is presented in Table 1. Excellent agreement is obtained between the experimental results [35] and all the aforementioned theoretical calculations for this fullerene [44, 45], as the evidence of their validity.

TABLE 1: Experimentally obtained vibrational frequencies (cm<sup>-1</sup>) of C<sub>76</sub>-D<sub>2</sub> [35] and theoretically calculated values between 400 and 2000 cm<sup>-1</sup> [44, 45].

IR1 <sup>a</sup>	IR2 <sup>a</sup>	IR3 <sup>a</sup>	Calc. 1 <sup>b</sup>	Calc. 2 <sup>c</sup>	Calc. 3 <sup>c</sup>
1635.1	1631.4	1633.1	1635		
1605.4			1607	1602.7	
1581.6			1582	1581.4	
	1557.9		1556		1556.0
		1551.5	1549		1555.7
1541.3	1541.6			1541.4	
1493.8	1492.7	1493.4	1494	1489.7	1494.9
1461.8	1460.2	1461.1	1464	1463.9	1463.4
1397.0	1399.8	1398.7	1401		1400.5
1385.9	1385.4	1385.6	1388	1386.5	1390.7
1363.8	1363.1	1364.2	1369	1365.1	1366.0
1312.1	1311.4	1312.4	1312	1310.9	1309.4
		1275.6		1275.7	1275.9
1273.1			1270	1274.0	
	1263.1		1259		1262.5
1248.4	1247.5	1247.6	1253	1249.4	1246.4
	1210.5	1208.6			1208.7
1206.3			1204		
1187.2	1185.0	1187.0	1189	1180.4	1189.2
1160.3		1161.6	1165	1157.7	1162.2
1121.9	1121.8	1122.0	1124	1126.1	1125.7
	1100.9		1100		1101.5
1081.6	1081.8	1081.6	1079	1072.3	1090.3
	1057.2	1056.4	1058	1054.7	1065.4
1028.6	1030.4		1027		1026.5
		1024.2		1024.9	
967.1	968.4	967.0	971	942.1	991.5
893.3	891.8	892.2	895	897.7	894.1
822.5	821.1	823.4	823	821.0	827.1
792.2	796.4		799	808.7	795.0
		788.8	787	781.7	787.0
742.1		742.9	746	742.0	741.3
	739.9		735	739.6	740.2
	704.0	704.8	707	704.9	704.5
703.0				702.4	703.5
665.2	663.6		667	665.4	665.2
		661.1	662		660.6
647.3	648.3	645.8	652	642.7	650.3
605.3	604.6	602.9	596		596.8
537.6	538.8		543	538.5	536.9
		532.7	534	531.3	535.6
	494.1		494	493.8	494.5
483.9		486.6	485	485.8	486.5
	476.4		477	476.7	479.2
461.8		460.6	460		459.2
456.2			457	456.3	456.9
	451.8		454	452.2	454.0
		436.0		434.8	436.0

TABLE 1: Continued.

IR1 <sup>a</sup>	IR2 <sup>a</sup>	IR3 <sup>a</sup>	Calc. 1 <sup>b</sup>	Calc. 2 <sup>c</sup>	Calc. 3 <sup>c</sup>
426.5	429.3				425.3
		405.2	406	405.0	399.3

<sup>a</sup>Reference [35].

<sup>b</sup>Reference [44].

<sup>c</sup>Reference [45].

The IR spectra of all the chromatographically isolated samples of the  $C_{76}$ - $D_2$  isomer from this research, recorded on the two mentioned spectrometers, have similar properties. All the observed vibrational frequencies and the general pattern of these spectra [35–42] are in agreement with the semiempirical QCFF/PI [44] and DFT theoretical calculations for  $C_{76}$ - $D_2$  [45], as well as for its dianion  $C_{76}$ - $D_2^{2-}$  [45].

The achieved agreement between our experimental results [35–42] and all the aforementioned theoretical predictions of the IR absorption frequencies of  $C_{76}$ - $D_2$  [44, 45], which is presented in this article in Table 1 and Figure 1 [35, 44, 45], is better in comparison to previous, partial experimental results for the obtained  $C_{76}$  samples, from other separation processes, by other IR techniques [59–62].

It is important to mention that the obtained generally good correlation between the overall configuration of absorption and all the observed vibrational frequencies in our recent experimental IR spectra for the neutral  $C_{76}$ - $D_2$  [35–42] and the next obtained infrared multiphoton electron detachment (IR-MPED) spectrum of the unsolved gas phase dianion  $C_{76}$ - $D_2^{2-}$  [45], as well as with the adequate most recent B3LYP/TZVP DFT calculations, presented in this article in Table 1, Figure 1 [35, 45], provides significant experimental evidence [35–42] that the dianionic molecule retains its overall symmetry (i.e.,  $D_2$  point group) with  $^1A_1$  ground state with respect to the neutral cage [45].

From the IR spectrum of  $C_{76}$ - $D_2$  in a mode, presented in Figure 1, the absorbance values  $A_\lambda$ , as well as the integrated absorbance values of the absorption bands, were determined using the OMNIC software.

The molar absorptivity  $\epsilon_\lambda$ , calculated according to (1), the integrated molar absorptivity  $\Psi_\lambda$ , calculated according to (3), and the integration ranges of absorption bands of this fullerene are reported in Table 2.

It can also be seen from Table 2 that excellent agreement is found between the relative intensities of the main and characteristic absorption maxima of  $C_{76}$ - $D_2$  computed from  $\epsilon_\lambda$  and from the  $\Psi$  values, in adequate integration ranges, taking as 100 the most intense vibration mode of  $C_{76}$ - $D_2$  at the frequency of  $967\text{ cm}^{-1}$ .

The original, characteristic, representative IR absorption spectrum of the isolated sample of the isomer  $C_{84}$ - $D_2$ :22 in the absorption mode, Figure 2, for determination of the molar absorptivity and integrated molar absorptivity of its absorption bands, which is important for its quantitative determination, as the main work of this article. It was previously provided in transparenance mode [35], for qualitative determination.

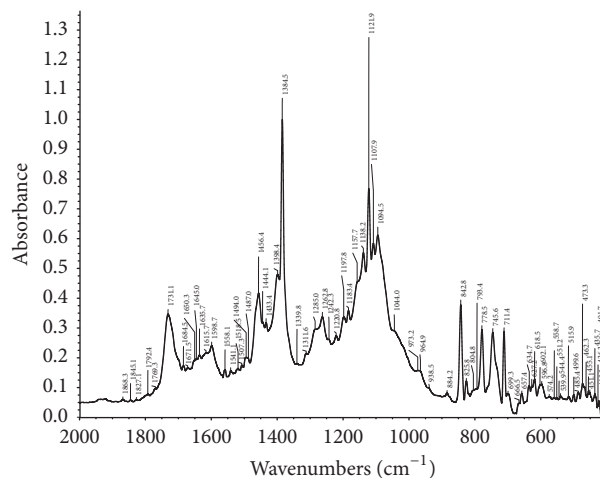


FIGURE 2: The IR spectrum of  $C_{84}$ - $D_2$ :22 in a mode.

A group of sharp, characteristic absorption bands is present between ca.  $700$  and  $840\text{ cm}^{-1}$  [35–42], at  $711$ ,  $746$ ,  $779$ , and  $843\text{ cm}^{-1}$ , followed by the bands at  $635$  and  $473\text{ cm}^{-1}$  in the first relevant part. Dominant and pronounced  $C_{84}$ - $D_2$ :22 maxima appear in the higher frequency region, between ca.  $1390$  and  $1120\text{ cm}^{-1}$ , as well as a group around  $1600\text{ cm}^{-1}$ . The main, most intense band is present at  $1385\text{ cm}^{-1}$ , followed by the bands at  $1263\text{ cm}^{-1}$  and  $1122\text{ cm}^{-1}$ . Intense bands also appear at  $1456$ – $1465\text{ cm}^{-1}$ ,  $1599$ – $1616\text{ cm}^{-1}$ , and  $1731\text{ cm}^{-1}$ . The entire absorption in this spectrum [35] corresponds to the theoretical predictions for  $C_{84}$ - $D_2$ :22 [48–50].

In the previous article [35], a comparison of the experimentally observed absorption frequencies in the IR spectra of the chromatographically isolated  $C_{84}$ - $D_2$ :22 samples, recorded on a Thermo Scientific FT-IR spectrometer Nicolet IR-6700 at room temperature [35, 38], with the semiempirical QCFF/PI theoretical calculations for this fullerene [48], as well as with the IR spectra of  $C_{84}$  (mixture of isomers), recorded on three different temperatures between  $-180^\circ\text{C}$  and  $+250^\circ\text{C}$  [1, 35], was presented. On the basis of the obtained excellent agreement [35, 38, 48], the validity of both the experimental results [35, 38] and the mentioned theoretical calculations [48] was indicated [35].

Most of the absorption maxima in our IR spectra of  $C_{84}$ - $D_2$ :22 at room temperature [35–42] are also in good agreement with the recent IR spectra of  $C_{84}$  (mixture of isomers) at different temperatures between  $-180^\circ\text{C}$  and  $+250^\circ\text{C}$  [1], as presented in the previous article [1, 35, 38]. However, significant changes of relative intensities of the main bands, as well as some shifts, were observed [1, 35].

In this article, a comparison of the experimentally obtained vibrational frequencies ( $\text{cm}^{-1}$ ) in the IR absorption spectra, of the chromatographically isolated  $C_{84}$ - $D_2$ :22 samples (IR1-IR3), recorded from  $400$  to  $2000\text{ cm}^{-1}$ , on a Thermo Scientific FT-IR spectrometer Nicolet IR-6700

TABLE 2: The relative intensities of the absorption bands of  $C_{76}$ - $D_2$  computed from  $\epsilon_\lambda$  and from the  $\Psi$  values in adequate integration ranges.

$\nu$ ( $\text{cm}^{-1}$ )	$\epsilon_\lambda$ ( $\text{L cm}^{-1} \text{mol}^{-1}$ )	Rel. int. [ $\epsilon_\lambda$ ]	Int. range ( $\text{cm}^{-1}$ )	$\Psi$ ( $\text{Km mol}^{-1}$ )	Rel. int. [ $\Psi$ ]
1735.3	88.810	12.1	1770–1699	1.841	12.1
1493.8	286.167	39.1	1505–1451	5.947	39.1
1385.9	159.295	21.8	1397–1348	3.320	21.8
1312.1	119.824	16.4	1319–1242	2.504	16.5
1187.2	420.087	57.4	1227–1144	8.710	57.3
1081.6	434.184	59.3	1140–1005	9.029	59.3
967.1	731.629	100	997–925	15.212	100
893.3	101.498	13.9	912–850	2.136	14.0
822.5	87.401	11.9	850–772	1.818	11.9
703.0	54.978	7.5	763–680	1.135	7.5
605.3	54.273	7.4	674–596	1.147	7.5
483.9	109.956	15.0	550–418	2.285	15.0

[35, 38], with the different theoretical calculations for this fullerene, by the QCFF/PI method (Calc. 1, from 179 to  $1711 \text{ cm}^{-1}$ ) [48], DFT (Calc. 2, from 211 to  $1674 \text{ cm}^{-1}$ ) [49], and TB potential method (Calc. 3, from 190 to  $1726 \text{ cm}^{-1}$ ) [50], is presented in Table 3. Excellent agreement between the experimental results [35, 38] and the aforementioned theoretical calculations for this fullerene [48–50] provides the evidence of their validity.

The IR spectra of all the chromatographically isolated samples of the isomer  $C_{84}$ - $D_2$ :22 from this research, recorded on the mentioned spectrometers, have similar properties. All the observed vibrational frequencies and the overall appearance of these spectra [35–42] are in excellent agreement with the semiempirical QCFF/PI, DFT, and TB potential calculations for this fullerene [48–50].

The achieved agreement between our experimental results [35–42] and the aforementioned theoretical predictions for this molecule [48–50], which is presented in this article in Table 3 and Figure 2 [35, 38, 48–50], is better in comparison to previous experimental results for the obtained  $C_{84}$  samples (partially separated isomers) from other separation processes, by other IR techniques [60–63]. This was also mentioned in the previous article [38].

From the IR spectrum of  $C_{84}$ - $D_2$ :22 in a mode, presented in Figure 2, the absorbance values  $A_\lambda$ , as well as the integrated absorbance values of the absorption bands, were determined using the OMNIC software.

The molar absorptivity  $\epsilon_\lambda$ , as well as the integrated molar absorptivity  $\Psi_\lambda$ , calculated according to (1) and (3), and the integration ranges of the absorption bands of this fullerene are presented in Table 4.

Also in this case, as can be seen from Table 4, excellent agreement is found between the relative intensities of the main and characteristic absorption maxima of  $C_{84}$ - $D_2$ :22 calculated from  $\epsilon_\lambda$  and from the  $\Psi$  values, in adequate integration ranges, taking as 100 the most intense vibration mode of  $C_{84}$ - $D_2$ :22 at the frequency of  $1385 \text{ cm}^{-1}$ .

## 4. Conclusion

In this research, the stable  $C_{76}$  and  $C_{84}$  isomers of  $D_2$  symmetry were isolated from carbon soot, by new and advanced chromatographic methods and processes [35–42]. The IR-KBr spectra of the isolated fullerenes were obtained over the entire fullerenes fingerprint region,  $400$ – $2000 \text{ cm}^{-1}$ , on a Thermo Scientific FT-IR spectrometer, in transparenance mode [35, 38], as well as in the absorption mode in this article.

Based on comparison of the experimentally observed infrared absorption frequencies of the isolated  $C_{76}$ - $D_2$  and  $C_{84}$ - $D_2$ :22 samples [35, 38] with the semiempirical QCFF/PI, DFT, and TB potential calculations for these fullerenes [44, 45, 48–50] and the obtained excellent agreement [35, 38, 44, 45, 48–50], presented in this article, the validity of both the experimental results [35, 38] and all the mentioned theoretical calculations [44, 45, 48–50] is confirmed. These research results can be used for their qualitative determination.

The molar extinction coefficients and the integrated molar extinction coefficients of the IR absorption bands of the  $C_{76}$ - $D_2$  and  $C_{84}$ - $D_2$ :22 isomers were determined at room temperature in KBr matrix. Excellent agreement is found between the relative intensities of the main and characteristic absorption maxima of these fullerenes calculated from the  $\epsilon_\lambda$  values and from the  $\Psi_\lambda$  values in adequate integration ranges. These results can be used for their quantitative determination.

All the obtained data are important for the identification and quantitative assessment of the  $C_{76}$ - $D_2$  and  $C_{84}$ - $D_2$ :22 isomers, either in natural resources on Earth and in space or in artificially synthesized materials, electronic and optical devices, such as polymers, composites, nanophotonic and biocompatible materials, optical limiters, sensors, special lenses with optical absorption properties closer to human eye light sensitivity, diagnostic and therapeutic agents, pharmaceutical substances, and biomaterials.

TABLE 3: Experimentally obtained vibrational frequencies ( $\text{cm}^{-1}$ ) of  $\text{C}_{84}\text{-D}_{2,22}$  [35, 38] and theoretically calculated values between 400 and  $2000 \text{ cm}^{-1}$  [48–50].

IR1 <sup>a</sup>	IR2 <sup>a,b</sup>	IR3 <sup>a</sup>	Calc. 1 <sup>c</sup>	Calc. 2 <sup>d</sup>	Calc. 3 <sup>e</sup>
1731.1	1731.6	1734.9			1726
1684.5	1686.1	1688.8	1685		
1671.5	1671.8		1667	1672	1671
1650.3	1650.9		1647	1652	
1645.0			1646		
1635.7			1638		1636
	1634.3	1633.0		1628	1635
1615.7	1615.8		1613	1616	1612
	1601.6	1602.3			1603
1598.7			1596		1600
1558.1	1558.5	1559.8	1564	1558	1561
1541.1	1541.0	1541.6	1544	1539	1541
1518.5			1522	1520	1518
		1512.9			1512
1507.3	1506.0	1509.2	1501	1509	1500
1494.0	1491.5	1493.2	1492	1495	1490
1487.0			1486		
	1464.9	1463.7	1466	1465	1464
1456.4	1454.2		1461	1453	1448
1444.1			1446		1445
1433.4			1433	1439	1438
		1403.3	1406	1403	
1398.4	1399.8		1398	1395	
1384.5	1384.6		1383	1384	1384
		1377.1		1376	
1339.8		1342.8	1340	1340	1339
1311.6		1311.2	1308		1313
	1304.2	1303.3	1302	1307	1306
		1289.8	1290		1290
1285.0	1284.1		1287	1283	
1262.8	1263.8	1262.3	1272	1265	1265
1242.3			1241	1240	1244
1220.8			1219	1221	1222
		1201.1	1207	1203	1201
1197.8			1195	1194	1196
	1186.6		1187		1185
1157.7			1158	1161	1158
		1169.7	1165	1170	1166
1138.2	1137.7		1146	1139	1141
1121.9	1122.0	1122.7	1129	1130	1133
1107.9		1104.9	1113		
1094.5	1098.2		1099		
1044.0			1041	1044	1038
973.2		975.5	973		
938.5		937.1	941		
		889.6	896	896	895
884.2			884	880	882
		1035.9			1036
	1030.5	1029.4	1029	1030	1030

TABLE 3: Continued.

IR1 <sup>a</sup>	IR2 <sup>a,b</sup>	IR3 <sup>a</sup>	Calc. 1 <sup>c</sup>	Calc. 2 <sup>d</sup>	Calc. 3 <sup>e</sup>
842.8	842.1	843.1	843	840	846
825.8			827	826	825
	823.1		823		823
		819.9	822		822
		808.5		809	810
804.8	800.9		806		804
778.5	777.5	776.7	777	771	777
		756.1	755	756	756
745.6	743.1			744	746
		742.1	740	740	
		721.9	720	721	728
711.4	711.3		713	711	709
699.3	700.0	700.0	699	698	698
634.7	632.4	633.0	633	636	631
618.5	616.3	616.8	618	619	621
	605.4				604
602.1					601
596.8		597.3		598	599
	593.5		593		
574.2		575.5	575		
	569.8		568	570	569
558.7		559.8	558		557
	548.2	546.6		548	
544.4					545
539.9		538.5	539		537
	535.2	535.4	535	533	536
515.9	515.3	517.2	518	514	515
	501.7	503.0	507	504	
499.6			501	499	499
	490.6	492.8		491	493
485.4	486.6	485.6	483	484	489
	476.0	476.8	479		476
473.3			472	474	473
462.3	463.6	461.7	461	461	459
455.1	455.7	455.3	454	454	453
451.1	451.2	450.0	451	449	449
	433.9	433.3		434	
	439.8		440	439	
435.7		435.5	437	438	437
412.2		412.5			413
401.7	401.0	401.9	398		400

<sup>a</sup>Reference [35].

<sup>b</sup>Reference [38].

<sup>c</sup>Reference [48].

<sup>d</sup>Reference [49].

<sup>e</sup>Reference [50].

## Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

TABLE 4: The relative intensities of the absorption bands of  $C_{84}$ -D<sub>2</sub>:22 calculated from  $\epsilon_\lambda$  and from the  $\Psi$  values in adequate integration ranges.

$\nu$ (cm <sup>-1</sup> )	$\epsilon_\lambda$ (L cm <sup>-1</sup> mol <sup>-1</sup> )	Rel. int. [ $\epsilon_\lambda$ ]	Int. range (cm <sup>-1</sup> )	$\Psi$ (Km mol <sup>-1</sup> )	Rel. int. [ $\Psi$ ]
1731.1	498.288	34.7	1753–1719	2.389	34.7
1598.7	344.637	24.0	1626–1572	1.657	24.1
1456.4	598.807	41.7	1475–1447	2.872	41.7
1384.5	1435.989	100	1392–1370	6.886	100
1262.8	483.928	33.7	1299–1232	2.328	33.8
1121.9	1102.810	76.8	1131–1102	5.277	76.7
842.8	542.804	37.8	850–836	2.628	38.2
825.8	173.755	12.1	833–813	0.788	11.5
778.5	422.181	29.4	784–768	1.966	28.6
745.6	409.257	28.5	751–722	1.913	27.8
711.4	413.565	28.8	717–705	2.032	29.5
699.3	113.443	7.9	705–682	0.541	7.9
634.7	150.779	10.5	642–613	0.722	10.5
473.3	163.703	11.4	479–459	0.758	11.0

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