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Research Article

Recent Advances in IR and UV/VIS Spectroscopic Characterization of the C_{76} and C_{84} Isomers of D_2 Symmetry

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The stable isomers of the higher fullerenes C_{76} and C_{84} with D_2 symmetry as well as the basic fullerenes C_{60} and C_{70} were isolated from carbon soot and characterized by the new and advanced methods, techniques, and processes. The validity of several semiempirical, ab initio, and DFT theoretical calculations in predicting the general pattern of IR absorption and the vibrational frequencies, as well as the molecular electronic structure of the C_{76} and C_{84} isomers of D_2 symmetry, is confirmed, based on recent experimental results. An excellent correlation was found between the previously reported theoretical data and the recently obtained experimental results for these molecules over the relevant spectral range for the identification of fullerenes. These results indicate that there are no errors in the calculations in the significant spectral regions, the assumptions that were based on previous comparisons with partial experimental results. Isolated fullerenes are important for their applications in electronic and optical devices, solar cells, optical limiting, sensors, polymers, nanophotonic materials, diagnostic and therapeutic agents, health and environment protection, and so forth.

1. Introduction

There is only one stable isomer of the higher fullerene C_{76}, as well as of the basic fullerenes, characterized by D_2, icosahedral (Ih) and D_{5h} symmetry, isolated pentagons, and an electronic closed shall structure [1]. From the 24 possible isomers of C_{84} obeying the isolated pentagon rule [2, 3], the two most stable, most abundant, and almost isoenergetic structures are those with D_2 and D_{2d} symmetry [4–12], found in a 2 : 1 ratio [13–15].

Some of the numerous possible vibrational modes of the higher fullerenes C_{76} [16, 17], C_{84} [5, 6], and its D_2(IV) [18–20] and D_{2d}(II) isomers [19, 21] were detailed in previous studies.

In this research, a series of unique, new, and dominant IR absorption maxima of the isolated C_{76} and the most abundant, stable C_{84} isomer of D_2 symmetry is registered and confirmed in the spectral region relevant for the identification of fullerenes, from ca. 450 to 1650 cm^{-1}. The general pattern of the obtained spectra and all the observed absorption bands of the chromatographically isolated samples of the stable C_{76} and C_{84} isomers with D_2 symmetry from the several different original, advanced separation processes [22–28] are in excellent agreement with the semiempirical, ab initio, and density functional theory (DFT) theoretical calculations for these molecules [5–12, 29, 30] over the mentioned relevant region. It should be noted that some low frequencies can exist below the observational limit of 400 cm^{-1}.

These results have not been previously reported. Some discrepancies between the previous experimental data [16–19] and the aforementioned theoretical calculations [5–12, 29, 30] appeared in the significant spectral regions.

Quantum chemical force field for π electrons theoretical (QCFF/PI) calculations yielded a set of the vibrational frequencies for the stable C_{76} isomer of D_2 symmetry [29]. The IR vibrational properties of C_{76} were also studied using the high-level ab initio B3LYP DFT with the TZVP basis set [30].

The IR vibrational spectra of the two most abundant and most stable, major C_{84} isomers, the D_2:22 and D_{2d}:23 isomers,

were previously theoretically studied using the semiempirical PM3, AM1, MNDO [5–8], QCFF/PI [9], and tight-binding (TB) potential calculations [10]. Vibrational properties of the D_2, D_{2d}, and C_2 isomers of C_{84} were determined by ab initio Hartree Fock (HF) calculations with the STO-3G, 3-21G, and D95V basis sets [11]. The IR vibrational properties of the two major C_{84} isomers were also studied using the B3LYP DFT with the basis sets as large as 6-31G* [12].

These calculations were already shown to be successful in predicting the overall absorption pattern and the vibrational frequencies, as well as the molecular structures of the basic fullerenes C_{60} and C_{70} [31–35]. Excellent agreement with the experimental data was observed [23, 24, 36–38].

IR spectra of the chromatographically isolated C_{76}-D_2 and C_{84}-D_2:22 isomers were recorded over the entire relevant region from 400 to 2000 cm^{-1}, by the KBr disk technique. Characterization of the obtained C_{76} and C_{84} fractions from the previous separation processes was performed using different IR techniques, in different spectral regions [5, 6, 16–21].

In the previous articles, the UV/VIS absorption of the higher fullerenes C_{76} and C_{84} and its D_2(IV) and D_{2d}(II) isomers was recorded in different spectral regions. Their solutions in different solvents, of different concentrations, were used [14, 39–47].

In this study, the UV/VIS absorption of the chromatographically purified C_{76} and C_{84} isomers of D_2 symmetry is registered over the entire relevant region from 200 to 900 nm. A series of their unique, new, and dominant UV absorption maxima are registered and confirmed in the most significant spectral region from 200 to 400 nm, where fullerenes intensively absorb. Solutions of these fullerenes in hexane of determined concentrations were used. It should be mentioned that the region from 200 to 300 nm has not been previously presented for C_{84} and its isomers under any experimental conditions. Complete appearance of their electronic absorption spectra and all the observed absorption bands [22–28] correlates well with the previous semiempirical QCFF/PI, TB, and DFT theoretical predictions of the molecular electronic structure and the optical absorption of these molecules that behave as electron deficient arenes [48–51]. Their overall absorption also correlates well with the experimentally obtained photoemission spectra (PES) of C_{76} and C_{84} [49–51].

It is important to mention that fullerenes C_{60} and C_{70} were recently found in space around various astrophysical objects [52], such as certain planetary [53] and protoplanetary nebulae [54] and in other space environments ranging from postasymptotic giant branch stars [55], to young stellar objects [56], to reflection nebulae [57], and to certain R-Coronae Borealis stars [58]. It is expected that also higher fullerenes, such as C_{76} and C_{84} and their stable isomers with D_2 symmetry, can be found in space.

The obtained original spectra of the isolated stable C_{76} and C_{84} isomers, measured at room temperature in this study, as well as their comparison with the recent spectra of C_{76} and C_{84} (mixture of isomers) at temperatures between −180°C and +250°C [52], are very significant for better understanding of IR and UV/VIS optical absorption properties of these higher fullerenes and for their identification either in natural resources in space and on Earth or in artificially synthesized carbon soots.

2. Experimental Methods

In the first phase of this research, C_{60}, C_{70}, and the higher fullerenes, mainly C_{76} and C_{84}, 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, AZ, USA). Solvents used were *n*-heptane, toluene, chlorobenzene, *p*-xylene, xylenes, and pyridine, as well as the successive use of toluene and chlorobenzene, and *p*-xylene and pyridine. The extractions were performed until the complete disappearance of color in the Soxhlet extraction thimble. The yields and the compositions of all the extracts were determined by the spectroscopic and chromatographic methods. The procedures for increases of fullerenes yields, as well as for additional selective extraction of higher order fullerenes, were found [22–28, 36–38].

In the second phase, C_{60}, C_{70}, and the higher fullerenes C_{76} and C_{84} from the obtained soot extracts were chromatographically separated on the activated Al_2O_3 columns by the new and improved methods [22–28]. The elution was performed continuously with the several different original, defined gradients of solvents: from pure hexane or 5% toluene in hexane to pure toluene, at ambient conditions. The main advancement, in comparison to previous methods under pressure [13–19, 39–45], is the isolation of the purified stable isomers of the higher fullerenes C_{76} and C_{84} (the only stable C_{76}-D_2 isomer and the most abundant, stable C_{84} isomer of D_2 symmetry, the C_{84}-D_2:22 isomer), 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 milligrams yields. The other advantages of the developed methods are the use of significantly smaller amounts of the initial materials, including fullerene extracts (10 mg), 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, as well as less expensive laboratory equipment. The entire material and energy expense and the time spent on the purification processes were decreased. The environment pollution was also decreased, using smaller amounts of less toxic solvents [22–28].

Before separation, each sample of the extract (ca. 10 mg) was dissolved in hexane and toluene (few mL), dispersed onto silica (1 g), which adsorbed the solvent producing gelatinous mass, and finally put onto top of the new alumina column.

Purification of 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 [14, 39–43].

Characterization of the chromatographically purified fullerene fractions, as well as of the obtained fullerenes soot extracts, was performed using determined techniques of IR and UV/VIS spectroscopy that have not been presented previously for the higher fullerenes [22–28, 36–38].

In this paper, the IR spectra of the chromatographically isolated samples of the C_{76} and C_{84} isomers of D_2 symmetry were measured by a Nicolet FT-IR 6700 spectrometer Thermo Scientific, by the KBr disk technique, at room temperature, 23°C, over the entire relevant region from 400 to 2000 cm^{-1}.

The UV/VIS spectra of the chromatographically purified samples of the C_{76} and C_{84} isomers of D_2 symmetry were recorded on GBC Cintra 40 spectrophotometer, in the region from 200 to 900 nm. Diluted solutions of fullerenes in hexane, concentrations 10^{-3} to 10^{-4} mol/dm^{-3}, were used.

The UV/VIS spectra of the chromatographically purified samples of the C_{76} and C_{84} isomers of D_2 symmetry were also recorded on a Perkin-Elmer Lambda 5 spectrophotometer, from 200 to 900 nm, using both diluted solutions of fullerenes in hexane, concentrations 10^{-3} to 10^{-4} mol/dm^{-3}, and much diluted solutions of fullerenes in hexane to complete discoloring, for comparison.

In the previous articles, the IR and UV/VIS absorption of the obtained samples of the higher fullerenes C_{76}, C_{84}, and its D_2(IV) and D_{2d}(II) isomers were recorded in different spectral regions, using different techniques [5, 6, 14, 16–21, 39–47].

3. Results and Discussion

The main advancement in spectroscopic characterization of the higher fullerenes C_{76} and C_{84} in this research [22–28], in comparison to previously obtained experimental results [5, 6, 16–21], is the observation of the unique, new, and the main, dominant absorption maxima of the isolated stable C_{76} and C_{84} isomers of D_2 symmetry in the spectral regions where they intensively absorb, in excellent agreement with the semiempirical, ab initio, and DFT theoretical calculations for these molecules [5–12, 29, 30].

The achieved agreement between our experimental results [22–27] and the aforementioned theoretical predictions [29, 30] is better in comparison to previous characterizations of C_{76} samples from other separation processes, by other IR techniques [16, 17].

Whereas there is a good correlation between our experimental results [22–27] and the theoretical predictions [29, 30], in the previous experimentally obtained IR spectra of the C_{76} samples [16, 17], some discrepancies of the general pattern and vibrational frequencies with the theoretical predictions [29, 30] appear in the central significant part of the spectrum, from ca. 800 to 1200 cm^{-1}.

In the first, partial IR spectrum of C_{76} [16], some disagreements of absorption bands with the theoretical calculations [29, 30] occur in the mentioned region, as well as from ca. 1500 to 1600 cm^{-1}, of up to 40–60 cm^{-1} [16, 29].

The next IR measurement [17] was not in agreement with the mentioned first published spectrum of C_{76}, suggesting that the previous measurement was carried out with an impure sample [16, 17]. In this study, the absorption bands were not registered from ca. 800 to 1000 cm^{-1}. In the remaining part of the spectrum [17], a larger number of C_{76} features were observed and also some discrepancies with the theoretical calculations [29, 30] in the region around 1020 to 1030 cm^{-1}, as large as 26 cm^{-1} [17, 29]. The observed IR features of the higher fullerene C_{76} from this separation process were tentatively rather assigned to a subset of fundamental vibrations, although there was presumption that some of these features were weaker overtone or combination bands [17], which our results also confirm.

There is a general agreement between the IR absorption bands of C_{76} observed previously and those observed in this work. In several cases, smaller shifts are observed. However, new, characteristic, and the main, dominant absorption bands not reported in previous works [16, 17] were registered in the central significant part of the region relevant for the identification of fullerenes, from ca. 800 to 1200 cm^{-1}, as well as in the region from ca. 1530 to 1740 cm^{-1}.

In Table 1 are reported the IR absorption bands of the chromatographically purified C_{76} samples as measured in this work at 23°C in comparison with the recent data at different temperatures, as well as with the theoretical calculations by the QCFF/PI method [29].

The original experimentally obtained IR spectrum of the chromatographically isolated C_{76}-D_2 sample is presented in Figure 1 (Table 1, first IR).

In this paper, the main, most intense, sharp, well resolved absorption maxima of the higher fullerene C_{76} were observed at 967, 1082, and 1187 cm^{-1}. Weak neighboring features at 1025, 1057, 1122, and 1162 cm^{-1} correspond to C_{76}. In the recent work [52], a group of four close C_{76} intense absorption bands were found at 1175, 1102, and 1086 and the most intense at 1030 cm^{-1}, with the neighboring feature at 961 cm^{-1}, appearing in the form of one strong, broad absorption band. Some of these bands were reported with weak intensity in previous works [16, 17], such as features at 1031 and 1175 cm^{-1} [17].

Characteristic, sharp bands unique to the higher fullerenes C_{76} were observed in the first relevant part of our spectrum at 892 and 823 cm^{-1}, with the neighboring absorption at 789 cm^{-1}. Pronounced C_{76} absorption bands also appear at 705 cm^{-1}, with the shoulders at 729 and 743 cm^{-1}, at 603 cm^{-1} next to absorption at 646 cm^{-1}, and at 533 cm^{-1}. The three most intense absorption bands in the first relevant part of the recent spectrum [52] were observed at 709 and 654 and the main band at 526 cm^{-1}. Their neighboring features appear at 743, 608, and 550 cm^{-1}. Several other neighboring bands are listed in Table 1. Corresponding bands from the previous report were found with some shifts at 693, 628, and 538 cm^{-1} [17].

In the second relevant part of our spectrum, the most intense, strong absorption band appears at 1461 cm^{-1} and the next pronounced intense band at 1386 cm^{-1}, with the neighboring feature at 1398 cm^{-1}. Intense band was found at 1438 cm^{-1} in the recent spectrum, followed by the features at 1393 and 1383 cm^{-1} [52]. It appears at 1438 cm^{-1}, with the neighboring bands at 1461 and 1466 cm^{-1} in the previous report [17]. Sharp C_{76} feature observed at 1312 cm^{-1} in our spectrum, with the next bands at 1276 and 1248 cm^{-1}, was found at 1315 cm^{-1} recently at 45°C. The neighboring band was observed at 1288 cm^{-1} at –178°C [52]. Band at 1493 cm^{-1} was found at 1498 cm^{-1} in the recent spectrum [52] and at 1513 cm^{-1} in the previous work [17]. Pronounced bands were

Table 1: Experimental and theoretically calculated absorption bands of C_{76} between 400 and 1770 cm^{-1}.

Calculated	Experimental					
Orlandi et al.[a]	This work			Cataldo et al.[b]		
Absorption bands (cm^{-1})	IR1 (cm^{-1})	IR2 (cm^{-1})	IR3 (cm^{-1})	−178°C (cm^{-1})	+45°C (cm^{-1})	+250°C (cm^{-1})
	405			409	409	
		426	429	420	420	420
	436			444		440
457		456				
460	460	462	462			461
477			476	477	477	476
488	487	484				
			494	491	491	494
513	507					505
534	533	538				
543	539		539			
547				549	550	550
555	555					
				571	572	571
581			581		588	
596	603	605	605		608	607
632						629
652	646	647	648	650	654	652
662	661	665	664		668	669
684	682					
707	705	703	704			
710				710	709	710
730	729					
746	743	742	740	744	743	742
760				763		763
770			767		765	
787	789	792	796	790	791	791
810				805	806	804
823	823	823	821			
825				824	825	825
841				848	847	847
895	892	893	892			
971	967	967	968	963	971	963
	1024				1024	1017
1043	1033	1029	1030	1032		
1046		1046				
1058	1056		1057			1061
	1067			1065	1066	
1079	1082	1082	1082			1086
1100	1098		1101	1102	1102	
1124	1122	1122	1122	1124		
1165	1162	1160			1168	
1171				1171	1175	
1189	1187	1187	1185			
1204	1209	1206	1211			
1243	1248	1248	1248			

Table 1: Continued.

Calculated	Experimental					
Orlandi et al.[a]	This work			Cataldo et al.[b]		
Absorption bands (cm^{-1})	IR1 (cm^{-1})	IR2 (cm^{-1})	IR3 (cm^{-1})	−178°C (cm^{-1})	+45°C (cm^{-1})	+250°C (cm^{-1})
1256			1263			1260
1270	1276	1273			1270	
1294	1291			1288		
1312	1312	1312	1311	1317	1315	1312
1327	1339					1339
1369	1364	1364	1363			1373
1388	1386	1386	1385	1386	1383	1386
1402	1398	1397	1400	1395	1393	1394
1434				1438	1438	1435
1464	1461	1462	1460			
1489	1493	1494	1493	1491	1498	1488
1529	1533					
1549		1541	1542			
1552	1552					
1556			1558			
1580	1580	1582	1576	1580	1580	1577
1607		1605		1601	1598	1597
1635	1633	1635	1631			
1650		1654	1653			
	1681	1684		1684	1688	1698
	1713		1711			
	1734	1735	1735	1718	1721	1730
		1773	1774			

[a]Reference [29].
[b]Reference [52].

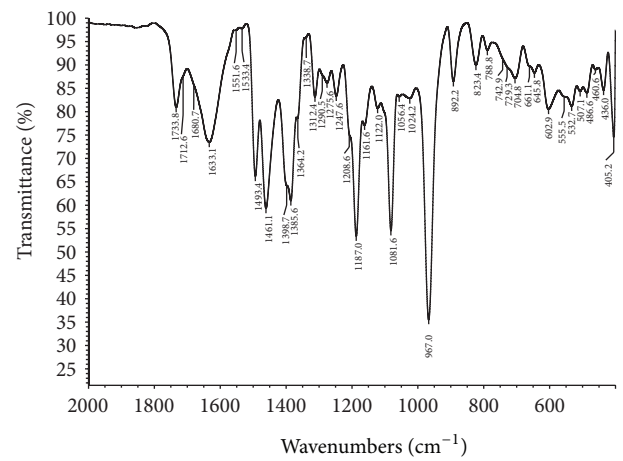

Figure 1: The IR spectrum of the chromatographically purified C_{76}-D_2 sample.

also observed in this work at 1735 and 1631 cm^{-1}, with the shoulders at 1580 and 1681 cm^{-1}. The most intense maximum in the recent spectrum was registered at 1688 cm^{-1}, with the next intense band at 1721 cm^{-1} and the neighboring band at 1598 cm^{-1}, in addition to the band at 1580 cm^{-1} [52] which

was detected only with Raman spectroscopy in the previous work [17].

Concerning the dependence of the C_{76} infrared bands with temperature, some smaller band shifts were observed in our spectrum at 23°C in comparison to recent spectra at various temperatures [52]. There is observed a remarkable change of the intensity of certain characteristic infrared bands, depending on temperature.

No important and evident band shifts as a function of temperatures were observed in the mentioned recent spectra as a function of temperature. Their main characteristics and the overall absorptions are similar. However, the intensity of certain infrared bands of C_{76} is remarkably sensitive to temperature. For example, the band at 1317 cm^{-1} is sharp at −178°C [52], and still in our spectrum at room temperature, registered at 1312 cm^{-1}, and becomes less intense at +45°C and weak at +250°C. Another example is the group of bands comprised between 1288 and 1032 cm^{-1} which are well defined and separated at −178°C [52] and also in our spectrum seen at 1276 and 1248 cm^{-1}, but appear much less intense at +250°C. The IR spectrum of C_{78} that was also presented in the recent work has different properties [52].

It is important to mention that the general pattern of our C_{76}-D_2 spectrum and all of the experimentally observed IR absorption bands over the spectral region relevant for the identification of fullerenes are in excellent agreement with the theoretical calculations for the only stable C_{76} isomer of D_2 symmetry, by the semiempirical QCFF/PI method [29], as well as by the most recent ab initio DFT [30].

The overall configuration of absorption of our experimentally obtained FT-IR(KBr) spectra of the chromatographically isolated samples of the neutral solid C_{76} [22–28] correlates well with the next obtained, most recent infrared multiphoton electron detachment (IR-MPED) spectrum of the unsolvated gas-phase dianion C_{76}^{2-}, as well as with the adequate most recent B3LYP/TZVP DFT calculations [30].

The obtained generally good correlation between our recent results for the neutral C_{76} [22–28] and the most recent IR spectrum of C_{76}^{2-} [30] provides the significant experimental evidence 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. This statement was previously based on comparison of the experimental C_{76}^{2-} IR spectrum with the DFT calculations [30]. Spectral shifts of characteristic C_{76}^{2-} tangential modes, as well as some changes of their intensity [30], observed relative to the neutral C_{76} cage [22–28, 30], were shown to originate from the excess charge density on the fullerene cage that leads to some specific changes of bond lengths [30].

The presented results in this study indicate that the previous semiempirical QCFF/PI [29], as well as the recent ab initio DFT theoretical calculations [30], provides an overall excellent prediction of the IR spectrum and vibrational frequencies of the higher fullerene C_{76}. A one to one assignment is achieved over the entire relevant spectral region for fullerenes. Only in a few cases is the accuracy not enough to permit a one to one assignment, as when two IR bands are separated by a small frequency interval. Their assignment can be supported by considering the calculated frequencies by DFT [30] in addition to the QCFF/PI frequencies [29] and conversely.

On the basis of the previous theoretical calculations for the higher fullerene C_{84}, two most abundant stable D_2:22 and D_{2d}:23 isomers [5–12], a series of characteristic absorption bands is predicted to occur around 780 cm^{-1} (from ca. 700 to 840 cm^{-1}), followed by the bands around 630 and 475 cm^{-1}. Some minor bands should also appear between ca. 585 and 520 cm^{-1}, in the first relevant part of the spectrum (ca. 450 to 850 cm^{-1}). Pronounced and dominant, most intense absorption bands are predicted to occur in the second relevant part (ca. 1050 to 1650 cm^{-1}), around 1600 cm^{-1} and a group between ca. 1125 and 1390 cm^{-1}, including the main band. A cluster of minor bands should appear at higher wave numbers than the main band.

The two calculated D_2-C_{84} and D_{2d}-C_{84} spectra resemble each other, the difference being that the D_2 isomer shows more IR active lines due to splitting of the lines from the higher symmetry D_{2d} isomer. However, these splitting are much too small and they could not be resolved in the first published IR spectrum of C_{84}, between 500 and 2000 cm^{-1} [5], or in the previous infrared resonance enhanced multiphoton ionization (IR-REMPI) spectrum of C_{84}, presented between 450 and 1600 cm^{-1} [6]. This spectrum consisted of only three absorption bands at 748, 632, and 475 cm^{-1} in the first part, followed by a series of partially unresolved peaks, ranging from ca. 1050 to 1600 cm^{-1}.

Our experimentally obtained IR spectra of the chromatographically purified samples of the most abundant, stable C_{84} isomer of D_2 symmetry, C_{84}-D_2:22 [23–28], have much better resolution of absorption bands, in comparison to the first published IR absorption spectrum of C_{84} [5] and to the previous IR-REMPI spectrum [6], as well as to the IR spectra of the C_{84}-D_{2d} samples, presented in the regions from 484 to 1631 cm^{-1} [19], as well as from 50 to 500 cm^{-1} and 500 to 800 cm^{-1} [21]. They agree and look more similar to the theoretically calculated spectrum of the D_2:22 isomer [5–12], which shows more IR active lines.

The achieved agreement between our experimental results [23–28] and the aforementioned theoretical predictions [5–12] is better in comparison to previous characterizations of C_{84} samples (partially separated isomers), from other separation processes, by other IR techniques [18, 19].

Whereas there is a good correlation between our experimental results [23–28] and the theoretical calculations [5–12], in the previous experimental IR spectrum of the main chromatographically purified fraction of the higher fullerene C_{84} (partially separated isomers, presented from 400 to 1650 cm^{-1}) [18], as well as in the next IR spectrum of the obtained C_{84}-D_2 fraction from another separation process (presented from 484 to 1631 cm^{-1}) [19], some discrepancies of the general pattern and vibrational frequencies with the theoretical predictions for the most abundant, stable C_{84} isomer of D_2 symmetry (the C_{84}-D_2:22 isomer) [5–12] appeared in the significant spectral regions from ca. 450 to 850 cm^{-1}, as well as from ca. 1050 cm^{-1} to 1650 cm^{-1}. The main disagreement [5–12] is the appearance of the three

strong, dominant absorption bands in the first relevant part of the spectrum at 792 and 794 and the most intense 648 cm^{-1} [18, 19], unlike our results.

There is a general agreement between most of the vibration modes reported in the previous spectrum of the C_{84}-D_2 fraction [19], as well as in another study [18] and those observed in this work. However, significant changes of relative intensities of certain absorption bands were observed. Characteristic and the main, dominant absorption bands were registered in the second relevant part of the spectrum.

In Table 2, the IR absorption bands of the chromatographically purified C_{84}-D_2:22 samples are reported as measured in this work at 23°C in comparison with the recent data for the C_{84} sample (mixture of isomers) at different temperatures [52], as well as with the theoretical calculations by the QCFF/PI method [9].

The original experimentally obtained IR spectrum of the chromatographically isolated C_{84}-D_2:22 sample in this research is presented in Figure 2 (Table 2, first IR).

There is a considerable change of intensity of IR bands in our spectrum of C_{84}-D_2:22, in comparison to IR spectra of the C_{84} sample (mixture of isomers) at different temperatures. The main characteristics of the reported spectra [52] are similar. However, the intensity of certain infrared bands of C_{84} is changing significantly with temperature.

The most intense, dominant absorption bands in our spectrum appear in the second relevant part. The first group is present between absorption band at 1122 cm^{-1}, with the neighboring features at 1107 and 1095 cm^{-1}, and the most intense maximum in the spectrum at 1385 cm^{-1}, with a neighboring absorption at 1398 cm^{-1}. Pronounced bands also appear around 1600 cm^{-1}, between the next intense maxima at 1456 cm^{-1}, with a neighbor very weak absorption at 1433 cm^{-1}, and at 1731 cm^{-1}. A cluster of minor bands appears from 1494 to 1558 cm^{-1} at the wave numbers higher than the main band.

The group of bands with the main maximum at 1433 cm^{-1} in the second relevant part of the recent spectra of C_{84} is more intense than the following band at 1384 cm^{-1} at −170°C. However, at +50°C and +250°C, the two groups of bands, although less defined, have approximately the same intensity. Similarly, in the mentioned previous spectrum of C_{84} (partially separated isomers) [18], as well as in the IR spectrum of the obtained C_{84}-D_2 fraction at room temperature [19], the two main, most intense bands in the second part of approximately the same intensity appear at 1432 and 1383 cm^{-1}. Relatively broad feature at 1730 cm^{-1} was recorded in the IR spectrum of C_{84} at −170°C and +250°C, but not so evident at 50°C [52].

In the first relevant part of our spectrum, a series of characteristic sharp absorption maxima are observed around 780 cm^{-1}, at 699, 711, 746, 779, 826, and 843 cm^{-1}, with the neighbor very weak absorption at 884 cm^{-1}. The absorption bands around 635 cm^{-1} (from 574 to 657 cm^{-1}) and 473 cm^{-1} (from 402 to 540 cm^{-1}) follow them. Weak feature at 647 cm^{-1} is hardly observable. A group of minor bands is registered from 516 to 574 cm^{-1}.

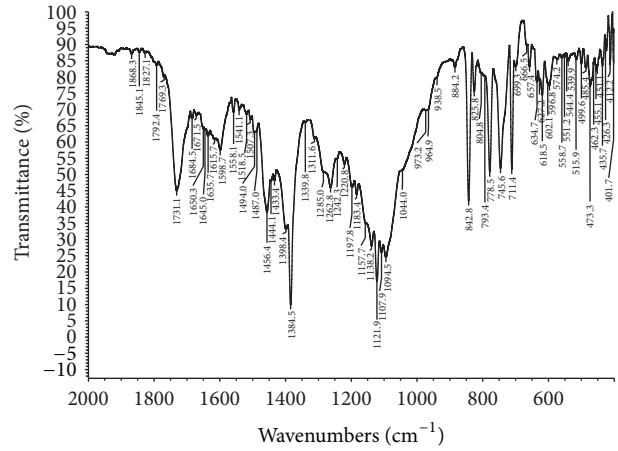

Figure 2: The IR spectrum of the chromatographically purified C_{84}-D_2:22 sample.

The main bands in the first part of the recent spectra of C_{84} at different temperatures [52] appear at 470 and 647 and the most intense at 797 cm^{-1}. The two distinct bands at 670 and 648 cm^{-1} observed at −170°C appear much less intense at +50°C and +250°C with the band at 670 cm^{-1} reduced to a weak feature. The most intense bands in the previous spectrum of C_{84} (partially separated isomers [18]), as well as in the IR spectrum of the obtained C_{84}-D_2 fraction, appear at 648, 792, and 797 cm^{-1} [19].

There are no pronounced absorption bands in our spectrum of C_{84}-D_2:22 between ca. 850 and 1050 cm^{-1}. Several weak features were observed. In the case of C_{84} sample, the FT-IR spectra [52] show a dominant, broad band centered at 1077 cm^{-1} and 1031 cm^{-1}, which were already reported in the literature [5–12, 18, 19], but not as intense as detected recently [52].

The general pattern of our spectrum, its fine structure with more splitter lines, and all of the experimentally observed IR absorption bands, in the entire spectral region relevant for the identification of fullerenes, are in excellent agreement with the aforementioned semiempirical [5–10], as well as with the ab initio HF [11], and DFT theoretical calculations [12] for the most abundant, stable C_{84} isomer of D_2 symmetry.

The presented results in this study indicate that the aforementioned semiempirical [5–10], ab initio, and DFT calculations [11, 12] provide an overall excellent prediction of the IR spectrum and vibrational frequencies of the most abundant stable isomer of the higher fullerenes C_{84} with D_2 symmetry. A one to one assignment is achieved over the entire relevant spectral region for fullerenes. Only in a few cases is the accuracy not enough to permit a one to one assignment, as when two IR bands are separated by a small frequency interval. Their assignment can be supported by considering the frequencies obtained by the ab initio and DFT calculations [11, 12] in addition to the frequencies obtained by the semiempirical PM3, AM1, MNDO, and QCFF/PI, as well as by the TB potential calculations [5–10], and conversely.

Table 2: Experimental and theoretically calculated absorption bands of C_{84} fullerene between 400 and 1770 cm^{-1}.

Calculated	Experimental					
Negri et al.[a]	This work			Cataldo et al.[b]		
Absorption bands (cm^{-1})	IR1 (cm^{-1})	IR2[c] (cm^{-1})	IR3 (cm^{-1})	−170°C (cm^{-1})	+50°C (cm^{-1})	+250°C (cm^{-1})
	402		402			
	412		409			
	427	419		423	427	428
437	436	434	434			
440		440		446	444	442
449			447			
451	451	451				
452	455	456				
461	462	464	464			
472	473			473	470	470
479		476	479			
483	485					
499	497		494	493	493	491
513	516	515	517			
533		532	533			
539	540					
552	551	548	546			
558	559		560	560	559	
572		570				
575	573		575			
578		582		582	582	579
589			588			
593	597	593				
610	602	605				
618	618	616	616			
633	635	632	631			
652		647	647	648	647	648
659	657		656			
669		669		670	669	670
699	699	700				
703			703		703	703
713	711	711				
720			722			
740	746	743	741	763	763	737
753			752			
777	778	777	777			
791	793			794	797	795
806	805	801				
822			820			
827	826					
843	843	842	844		845	845
856			857			
883	885					
909			908			
941	939					
	965	967				

Table 2: Continued.

Calculated	Experimental					
Negri et al.[a]	This work			Cataldo et al.[b]		
Absorption bands (cm^{-1})	IR1 (cm^{-1})	IR2[c] (cm^{-1})	IR3 (cm^{-1})	−170°C (cm^{-1})	+50°C (cm^{-1})	+250°C (cm^{-1})
973	973		974			
1029		1030	1028	1031	1031	1029
1041	1044					
1077		1080	1078	1077		1078
1093	1094			1092		
1113	1107					
1129	1122	1122	1123			
1132	1138			1142		
1164			1169			
1187	1183	1187				
1190	1198					
1208			1208			
1211			1211			
1219	1219					
1241	1242					
1247			1247			
1266	1263	1264	1263	1258	1257	1261
1290	1285					
1299		1304	1304			
1317	1312					1319
1327				1324		
1340	1340			1339		
1358						1360
1383	1384	1385	1377	1384	1378	1377
1398	1398	1400				
1416				1418		
1433	1433			1433	1432	1428
1452	1456			1456	1454	1455
1466		1465	1463			
1494	1494					
1501	1507		1509	1505	1504	1504
1522	1518			1520		
1545	1540	1541	1542	1540	1535	
1564	1558	1558	1558	1558	1557	1556
1596	1599		1602			
1612	1616	1616		1616	1610	1622
1646	1635			1633	1631	
1647	1645	1650	1656	1654		1647
1672	1671					
1683	1684	1686		1683		
				1697		
1711				1715	1708	1714
	1731	1732	1735	1733	1729	1729
	1769			1772	1788	1766

[a]Reference [9].
[b]Reference [52].
[c]Reference [28].

These results remove the need for the assumptions of possible errors of the theoretical calculations for the C_{76} and C_{84} isomers with D_2 symmetry [5–12, 29, 30] in the significant spectral regions, based on the previous comparisons with partial experimental results [16–19]. They provide the evidence of their validity over the entire relevant region.

In this study also, the unique UV/VIS absorption maxima of the chromatographically purified C_{76} and C_{84} isomers of D_2 symmetry are registered over the entire region from 200 to 900 nm, including the most significant region from 200 to 400 nm where fullerenes have allowed transitions and intensively absorb.

The experimentally obtained UV/VIS spectrum of the chromatographically isolated C_{76}-D_2 sample is presented in Figure 3. Dominant UV absorption maxima are present at 256 and 329 nm. Their relative intensities are decreased in comparison to the spectra of the previous chromatographically purified C_{60} and C_{70} fractions [23, 24, 36–38]. The third dominant, most intense band appears as a shoulder at ca. 210 nm. The absorption is prolonged to the region below 200 nm, which is characteristic for C_{76}. Pronounced C_{76} shoulder is registered at 275 nm, as well as its shoulders at ca. 230, 285, 350, and 378 nm. In the visible part, a weaker C_{76} band appears at 405 nm. Absorption is prolonged to 900 nm.

In the UV/VIS spectrum of the purified C_{76} sample from much diluted hexane solution to complete discoloring, we also recorded for comparison a series of more splitter absorption maxima which are registered at 229 and 285 nm, with the neighbors at ca. 256 and 275 nm, as well as at 328, 350, 378, and 405 nm. This spectrum has shown some differences and some similarities compared to the mentioned spectrum of C_{76} measured from more concentrated solution in hexane. With the change of solution concentration, such as significant dilution, the appearance of several new close absorption maxima or the fine structure may occur.

The experimentally obtained UV/VIS absorption spectrum of the chromatographically isolated sample of the most abundant, stable isomer of the higher fullerene C_{84} is presented in Figure 4. The most intense maximum is present at 239 nm, with a shoulder at 230 nm. The next intense absorption maximum appears at 272, with the neighboring bands at 251, 261, and 287 nm. They are followed by the bands at 333, 305, 318, 357, and 381 nm.

Complete configuration of absorption and all the observed absorption bands in the spectra of the purified C_{76}-D_2 and C_{84}-D_2:22 samples is in good correlation with the semiempirical QCFF/PI, TB, and DFT theoretical predictions for these molecules [48–51], which behave as electron-deficient arenes. It also correlates well with the previously obtained PES of C_{76} and C_{84} [49–51].

In the previous work of Jinno et al. [39, 40], the UV/VIS spectra of the chromatographically purified C_{76} and C_{84} fractions were recorded from the mixture of acetonitrile and toluene (55 : 45 or 50 : 50, v/v) in the region from 300 to 600 nm. Kikuchi et al. [41, 42] presented the optical absorption of the purified higher fullerenes C_{76} and C_{84} dissolved in benzene, in the range of 500 to 1100 nm. Ettl et al. [16] and Diederich and Whetten [43] reported the UV/VIS spectra of the molecule C_{76}, as well as that of

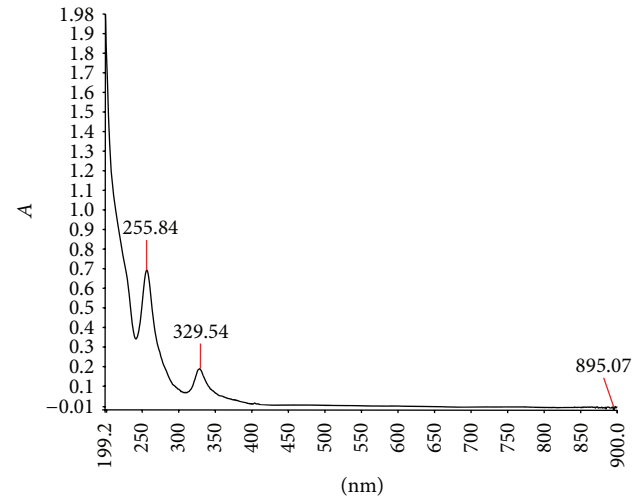

Figure 3: The UV/VIS spectrum of the chromatographically purified C_{76}-D_2 sample.

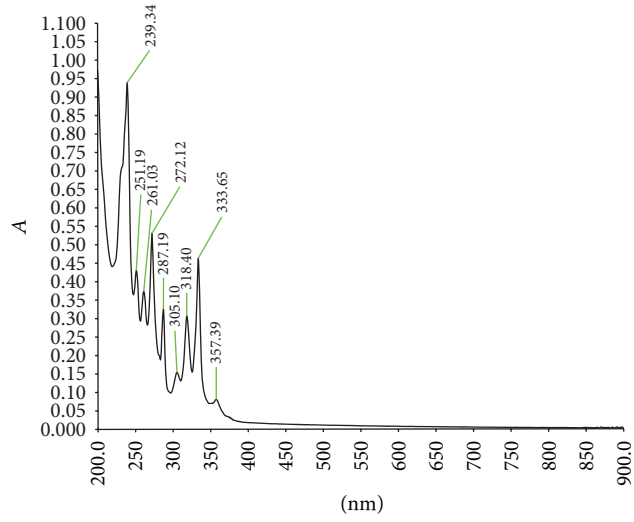

Figure 4: The UV/VIS spectrum of the chromatographically purified C_{84}-D_2:22 sample.

other higher fullerenes from dichloromethane solutions, in different regions. In the previous paper by Diederich et al. [14], the UV/VIS spectrum of C_{76} recorded from very diluted solution in hexane was presented in the region from 200 to 800 nm. Locations of C_{84} absorption bands, measured from 280 to 912 nm, from dichloromethane solution were only mentioned in this paper. Dennis et al. reported the UV/VIS/NIR absorption spectra of the isolated fractions of the D_2(IV) and D_{2d}(II) isomers, as well as of other six minor isomers of the higher fullerene C_{84}, from 400 to 2000 nm [44, 45]. Xenogiannopoulou et al. presented the absorption spectra of C_{84} and its D_2(IV) and D_{2d}(II) isomers dissolved in toluene in the range of ca. 300–350 nm to 1100 nm [46, 47].

All the presented results indicate the achieved progress in the spectroscopic characterization and chromatographic separation of the C_{76} and C_{84} isomers of D_2 symmetry, as well

as of the basic fullerenes, due to the application of the new and advanced experimental methods and processes.

Identification of fullerenes in the chromatographically purified fractions, as well as in the obtained extracts, was performed using determined IR and UV/VIS techniques that have not been presented for the higher fullerenes before.

The results of UV/VIS analysis are in agreement with the results of IR analysis. Characteristic properties, the unique and new absorption bands, and changes of relative intensities and locations of absorption maxima are observed, showing isolation and separation of the basic and the higher fullerenes in the similar, regular way within the several different original, advanced separation processes [22–28].

The obtained original IR and electronic absorption spectra of the isolated C_{76}-D_2 and C_{84}-D_2:22 isomers, in the spectral regions relevant for the identification of fullerenes, where they intensively absorb, are in excellent agreement with the several theoretical predictions for these molecules, which has not been previously presented.

For the first time, the validity of semiempirical, ab initio, and DFT calculations in predicting the general pattern of IR absorption and the vibrational frequencies, as well as the molecular electronic structure of the stable C_{76} and C_{84} isomers of D_2 symmetry, is confirmed over the entire relevant spectral range, based on comparison with our recent experimental results.

4. Conclusion

The obtained excellent correlation between the experimentally observed general pattern of IR absorption and vibrational frequencies of the isolated stable isomers of the higher fullerenes C_{76} and C_{84} isomers with D_2 symmetry [22–28] and the theoretical predictions [5–12, 29, 30] for these molecules is presented in this paper. These results provide the first significant experimental evidence of validity of the aforementioned semiempirical, ab initio, and DFT calculations for the C_{76}-D_2 [29, 30] and the C_{84}-D_2:22 [5–12] isomers over the entire relevant spectral region, from ca. 450 to 1650 cm^{-1}.

The experimentally obtained electronic absorption of the isolated C_{76} and C_{84} isomers of D_2 symmetry over the relevant region from 200 to 900 nm, including the most significant region from 200 to 400 nm [22–28], is also in very good correlation with the previous semiempirical QCFF/PI, TB, and DFT theoretical predictions for these molecules [48–51].

It is important to mention also that the obtained generally good correlation between the overall configuration of absorption in our recent experimental IR spectra of the neutral solid C_{76} [22–28] and the next obtained, most recent IR-MPED spectrum of the unsolvated gas phase C_{76}^{2-} [30], as well as with the adequate most recent B3LYP/TZVP DFT calculations [30], provides the significant experimental evidence that the dianionic molecule retains its symmetry (i.e., D_2 point group) with $^1A_1$ ground state with respect to the neutral cage.

These results are of great importance for further possible and even more sophisticated calculations of vibrational properties and molecular electronic structure of fullerenes and other molecules.

The presented original spectra in this study, as well as their comparison with the recent spectra of C_{76} and C_{84} (mixture of isomers) at different temperatures [52], will significantly contribute to better understanding of the IR and UV/VIS optical absorption properties of the higher fullerenes C_{76} and C_{84}, and their stable isomers with D_2 symmetry, as well as of fullerenes generally. They will enable easier identification of C_{76}, C_{84}, and its most abundant isomer, as well as of C_{60} and C_{70}, either in artificially synthesized carbon soot or in natural resources in space and on Earth.

Isolated fullerenes and their derivatives are important for the applications in electronic and optical devices, superconductors, semiconductors, solar cells, optical limiting, sensors, polymers, nanophotonic materials, lenses with optical absorption properties closer to human eye light sensitivity, diagnostic and therapeutic agents, encapsulation of metal atoms and radio isotopes, targeted drug and gene delivery, free radicals scavengers, health and environment protection, DNA cleavage, antibacterial and antiviral agents, water purification, storage of hydrogen, high energetic batteries, lubricants, synthesis of diamond, catalysts, and so forth.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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