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Seven-Minute Synthesis of Pure C_s-$C_{60}Cl_6$ from [60]Fullerene and Iodine Monochloride: First IR, Raman, and Mass Spectra of 99 mol % $C_{60}Cl_6$

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Abstract: Three previously reported procedures for the synthesis of pure C_s-$C_{60}Cl_6$ from C_{60} and ICl dissolved in benzene or 1,2-dichlorobenzene were shown to actually yield complex mixtures of products that contain, at best, 54–80% C_s-$C_{60}Cl_6$ based on HPLC integrated intensities. MALDI mass spectrometry was used for the first time to identify other components of the reaction mixtures. An improved synthetic procedure was developed for the synthesis of about 150 mg batches of chlorofullerenes containing 90% C_s-$C_{60}Cl_6$ based on HPLC intensities. The optimum reaction time was decreased from several days to seven minutes. Small amounts of the product were purified by HPLC (toluene eluent) to 99% purity. The pure compound C_s-$C_{60}Cl_6$ is stable for at least three months as a solvent-free powder at 25 °C. The Raman, far-IR, and MALDI mass spectra of pure C_s-$C_{60}Cl_6$ are reported for the first time. The Raman and far-IR spectra, the first reported for any $C_{60}Cl_n$ chlorofullerene, were used to carry out a vibrational analysis of C_s-$C_{60}Cl_6$ at the DFT level of theory.

Keywords: fullerenes · iodine · mass spectrometry · Raman spectroscopy

Introduction

Among the simple, σ-bonded derivatives of fullerenes, halogenated compounds have attracted a great deal of attention over the years. Dozens of C_{60} derivatives containing from 2 to 48 fluorine atoms and, in many cases, other substituents as well have been extensively studied.[1,2] In addition, bromination of C_{60} yielded the three single-composition/single-isomer products C_s-$C_{60}Br_6$, C_{2v}-$C_{60}Br_8$, and T_h-$C_{60}Br_{24}$, all of which have been structurally characterized.[3,4] As far as chloro[60]fullerenes are concerned, the situation is paradoxical. Although chlorination was one of the first C_{60} derivatizations reported in the literature, revealing the formation of $C_{60}Cl_6$[5] and putative $C_{60}Cl_n$ compounds with up to 24 chlorine atoms σ-bonded to the C_{60} cage,[6,7] structurally-characterized compounds such as T_h-$C_{60}Cl_{24}$,[8] C_1-$C_{60}Cl_{28}$,[9] C_2-$C_{60}Cl_{30}$,[9] and D_{3d}-$C_{60}Cl_{30}$[10] have only been reported in the past few months (the compound $C_{60}Cl_6$ is believed to have the same structure as C_s-$C_{60}Br_6$ based on its ^{13}C NMR spectrum[5]). Nevertheless, after nearly 15 years the compositional purity of $C_{60}Cl_6$, which has always been assumed to be high,[5,11,12] has never been satisfactorily demonstrated (i.e., none of the three previous reports of its synthesis properly established its purity[5,11,12]). In fact, recent work by us[13] and others[14] suggests that it may be only about 75% pure.

The facile transformation of fullerene C−Cl bonds into C−R or C−Ar bonds by Olah and co-workers in 1991 suggested that chlorofullerenes could be useful synthons.[7] Subsequent papers by others reported the use of $C_{60}Cl_6$ to prepare organic derivatives of C_{60}.[14–16] It is possible that chlorofullerenes could also be used to prepare new inorganic fullerene derivatives under mild conditions (a recent, related example involving a bromofullerene is the transformation of T_h-$C_{60}Br_{24}$ to kinetically-stable T_h-$C_{60}F_{24}$ at 25 °C[17]). However, significant progress in the use of chlorofullerene synthons

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will depend on the availability of 10+ milligram batches of a variety of pure chlorofullerenes with specific compositions and structures. For this reason, we have started a systematic study of fullerene chlorination reactions and have continued to develop Raman and mass spectrometry[18] procedures for the analysis of chlorofullerenes. This paper, the first in a series, describes an improved, rapid method for the preparation of 150+ mg batches of $C_{60}Cl_6$ with 90% yield/purity (HPLC integrated intensity). We also report for the first time the Raman, far-IR, and mass spectra of a sample of $C_{60}Cl_6$ purified by HPLC to 99% and a DFT analysis of its vibrational spectra.

Experimental Section

Reagents and solvents: Benzene (Na), chlorobenzene (CaH_2), and 1,2-dichlorobenzene (CaH_2) were ACS Reagent Grade (Sigma-Aldrich) and were distilled from the indicated drying agent under a purified N_2 atmosphere prior to use. HPLC Grade toluene (Fisher) was used as received. Iodine monochloride (Sigma Aldrich, ACS Reagent Grade), *trans*-2-[3-{4-*tert*-butylphenyl}-2-methyl-2-propenylidene]malononitrile (Fluka), chromium(III) acetyl acetonate (Sigma Aldrich), and KBr (Sigma Aldrich, 99+ % FTIR grade) were used as received. Since ICl is moisture sensitive, all syntheses were carried out under a purified N_2 atmosphere by using standard Schlenk and glovebox techniques unless otherwise noted.[19] The compound C_{60}, with a specified purity of 99.9%, was a gift from Term-USA.

Preparation of $C_{60}Cl_6$ by previously published procedures: The three literature methods for the preparation of C_s-$C_{60}Cl_6$ were repeated in this work, resulting in reaction products hereinafter referred to as samples **1**–**3**. The reaction conditions and analytical techniques used to characterize the samples are listed in Table 1. Sample **1** was obtained by mixing a solution of C_{60} (23 mg, 0.032 mmol) in benzene (30 mL) with a solution of ICl (75 mg, 23 μL, 0.46 mmol) in benzene (5 mL).[5] After 3 d, all volatiles (benzene, excess ICl, I_2) were removed under vacuum at 25 °C and the orange solid product mixture, sample **1**, was collected. Identical conditions but a longer reaction time, 5 d, led to the isolation of sample **2**.[20]

Sample **3** was obtained by mixing a filtered saturated solution of C_{60} (13.5 mg, 0.0188 mmol) in 1,2-dichlorobenzene (0.5 mL) with ICl (20 mg, 6 μL, 0.12 mmol).[12] After 7 d, the red precipitate that had formed was separated from the supernatant by decantation, washed with benzene, and dried under vacuum. All volatiles were removed from the decanted 1,2-dichlorobenzene supernatant under vacuum at 25 °C and the orange solid product, sample **3**, was collected. Since the red precipitate was not mentioned in the published procedure,[12] we also performed this reaction without excluding air. The same red precipitate and the same orange product mixture were obtained.

New seven-minute synthesis of C_s-$C_{60}Cl_6$: Sample **4** was obtained by mixing a filtered solution of C_{60} (0.12 g, 0.17 mmol) in chlorobenzene (20 mL) with ICl (0.81 g, 0.25 mL, 5.0 mmol) at 15 °C in the glass reactor of local design shown in Figure 1. Within seconds of adding ICl, the reaction mixture was placed under vacuum to evaporate all volatiles (chlorobenzene, excess ICl, I_2) as rapidly as possible but without warming the reaction mixture. The time for complete evaporation to dryness under these conditions was seven minutes. (When a standard 50 mL Schlenk flask was used instead of the reactor in Figure 1, the time required to evaporate the chlorobenzene reaction mixture to dryness at 15 °C was two hours.) Approximately 160 mg of solid orange product, sample **4**, was collected from the walls of the evaporation chamber by washing with, and then evaporating, a minimum amount of dichloromethane. Integration of the HPLC peaks (see below) showed that 91% of the integrated intensity was due to C_s-$C_{60}Cl_6$. An HPLC purification of small portions of sample **4** resulted in 99% pure C_s-$C_{60}Cl_6$.

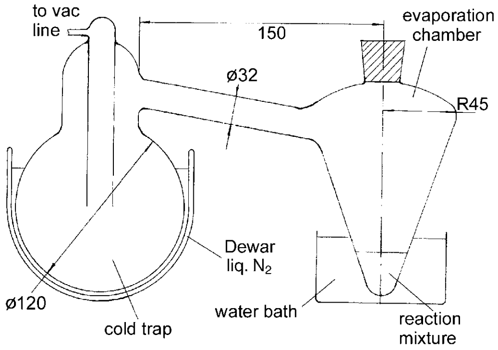


Figure 1. Glass reactor fabricated for the seven-minute synthesis of $C_{60}Cl_6$ (dimensions shown are in mm). The large diameter of the tubing connecting the evaporation chamber and the cold trap and the large surface area of the cold trap result in rapid evaporation of the volatiles from the reaction mixture.

Reaction of C_{60} and ICl in dichloromethane: Sample **5** was obtained by stirring solid C_{60} (10 mg, 0.014 mmol), which is only sparingly soluble in dichloromethane, with a solution of ICl (68 mg, 21 μL, 0.42 mmol) in dichloromethane (5 mL). Small aliquots of the supernatant were removed periodically and analyzed by HPLC until two successive aliquots gave identical HPLC traces. The total reaction time was seven days. All volatiles were removed from the now-homogeneous reaction mixture under vacuum and the solid orange reaction product, sample **5**, was collected.

Table 1. Conditions used for the synthesis of C_s-$C_{60}Cl_6$.[a]

Sample no.	C_{60} conc. mM	ICl/C_{60} mol ratio	Solvent, mL[b]	Reaction time	Methods of analysis[c]	Ref.
1	0.91	14	BN, 35	3 d	HPLC, MS	this work
	0.98	14	BN, 65	3 d	EA, NMR, IR	[5]
2	0.97	14	BN, 35	5 d	HPLC, MS, IR	this work
	0.97	14	BN, 35	5 d	EA	[20]
3	38	6	*o*-DCB, 0.5	7 d	HPLC, MS, IR	this work
	38	6	*o*-DCB, –[d]	7 d	EA, IR	[12],[d]
4	8.3	30	CB, 20	7 min	HPLC, MS, NMR, IR, Raman, TGA	this work
5	10 mg[e]	30	CH_2Cl_2, 5	7 d	HPLC, MS, IR	this work

[a] All reactions were performed at room temperature (23 ± 1 °C) under a purified N_2 atmosphere unless otherwise noted; data for samples **1**–**5** are from this work; literature data that match the conditions for samples **1**–**3** are also shown. [b] The volume in mL of the indicated solvent is listed after the solvent abbreviation; BN = benzene; *o*-DCB = 1,2-dichlorobenzene; CB = chlorobenzene. [c] HPLC = high-performance liquid chromatography; MS = MALDI mass spectrometry; EA = elemental analysis; NMR = ^{13}C NMR; TGA = thermogravimetric analysis. [d] The volume and temperature used and the presence or absence of air were not specified. [e] The reaction mixture was heterogeneous.

Methods of analysis: Portions of samples **1**–**4** were dissolved in toluene and analyzed by HPLC by using an HP Series 1050 chromatograph (250 × 10 mm Cosmosil Buckyprep column; eluent = 5 mL toluene per min; 300 nm UV detection). The dominant $C_{60}Cl_6$ peak eluted at 9.8 min. The minor components that eluted at 7.8, 9.3 and 12 min were subsequently shown by MALDI mass spectrometry to be $C_{60}Cl_{14}$, $C_{60}Cl_{12}$, and a mixture of $C_{60}Cl_8$ and $C_{60}Cl_{10}$, respectively. HPLC peaks due to $C_{60}Cl_nPh_m$ were also observed in samples **1** and **2**. HPLC purification of $C_{60}Cl_6$ from sample **4** was accomplished by collecting a fraction of the 9.8 min toluene-eluent peak. Subsequent HPLC analyses of the purified product by using 60:40 toluene/hexane and 20:80 toluene/hexane revealed virtually no components other than $C_{60}Cl_6$ (see below). On this basis, the purity of sample-**4** derived $C_{60}Cl_6$ was 99 %.

Positive- and negative-ion MALDI mass spectra were recorded by using a Kompact MALDI IV (Kratos Analytical, Manchester, UK) time-of-flight mass spectrometer in the linear mode. A 337 nm N_2 laser was used for target activation. Each mass spectrum was the average of 50–100 laser shots. Chlorofullerene samples and the *trans*-2-[3-{4-*tert*-butylphenyl}-2-methyl-2-propenyl-idene]malononitrile matrix material (DCTB) were dissolved separately in toluene and were mixed in a 1:10 mol/mol sample/DCTB ratio assuming the sample contained only $C_{60}Cl_6$. A drop of each sample/DCTB solution was deposited on a stainless steel slide by using a capillary and dried under a strong stream of cool air from an air-sprayer/brush in order to achieve a uniform sample surface.

The ^{13}C NMR spectrum of 99 % pure $C_{60}Cl_6$ from sample **4** was recorded with a Varian INOVA-unity 400 spectrometer operating at 100 MHz (0.7 mL $CDCl_3$ solution with added $Cr(acac)_3$ (7 mg) as a relaxation agent). The spectrum matched the literature spectrum.[8]

Infrared spectra of 99 % pure $C_{60}Cl_6$ were recorded by using a Bruker Equinox 55 FTIR spectrometer operating at 1 cm^{-1} resolution. Samples were either pressed pellets of pure $C_{60}Cl_6$ or pressed pellets of $C_{60}Cl_6$ diluted with KBr. Raman spectra of $C_{60}Cl_6$ were recorded with a Bruker RFS-100 spectrometer operating at 3 cm^{-1} resolution.

Weighed portions of unpurified sample **4** and the red precipitate from the sample-**3** reaction were analyzed by thermogravimetry with a TA Instruments TGA-2950 apparatus (platinum sample pans, 3–10 mg sample size, 25–500 °C temperature range).

Theoretical calculations: Harmonic vibrational frequencies and IR transition probabilities were calculated at the DFT level of theory with the PRIRODA package[21] by using the GGA functional of Perdew, Burke, and Ernzerhof (PBE).[22] The TZ2P-quality Gaussian basis sets {6,1,1,1,1,1/4,1,1/1,1} and {6,1,1,1,1,1,1,1,1,1/6,1,1,1,1,1/1,1} were used for all carbon and chlorine atoms. The quantum-chemical code employed expansion of the electron density in an auxiliary basis set to accelerate the evaluation of the Coulomb and exchange-correlation terms. Raman intensities were computed numerically at the PBE/6-31G* level of theory by using the PC version[23] of the GAMESS quantum chemical package.[24] Potential energy distribution analysis of the vibrational modes were performed with the DISP suite of programs.[25] The Cartesian DFT force field of $C_{60}Cl_6$ was transferred into a redundant internal coordinate system, which included all chemical bonds and bond angles, with a total of 294 coordinates.

Results and Discussion

The need for a new synthesis: Since 1994, synthetic chemists who have used $C_{60}Cl_6$ as a synthon[11,15,20,26] have assumed that the original procedure for its synthesis[5] provided a quantitative yield of pure material. The fact that this assumption went unchallenged for so long is probably due to the fact that chlorofullerene samples are particularly difficult to analyze. The reported purity and yield of $C_{60}Cl_6$ prepared by using the three reported syntheses that we have repeated were based on elemental analysis and IR and/or ^{13}C NMR spectroscopy.[5,12,20] However, elemental analysis only gives the average composition of a sample, IR spectroscopy is probably not sensitive enough to detect, for example, 10 % $C_{60}Cl_{12}$ in a sample of $C_{60}Cl_6$, and ^{13}C NMR spectra of natural abundance, low-symmetry fullerene derivatives generally have such low signal-to-noise ratios that their value as an analytical tool is severely limited.

In 2002 Al-Matar et al. reported[14] the methylation of $C_{60}Cl_6$ that had been prepared by using the same literature procedure[5] we used to prepare sample **1**. They stated that the sample of $C_{60}Cl_6$ they prepared "was used without further purification in order to avoid degradation" but did not cite any specific evidence for the degradation of $C_{60}Cl_6$ under HPLC conditions. Among the methylation products they isolated and identified were $C_{60}Me_6$, $C_{60}Me_5Cl$, $C_{60}Me_5O_2OH$, $C_{60}Me_5O_3H$, $C_{60}Me_5OOH$, and $C_{60}Me_4PhO_2OH$.[14] The presence of the phenyl group in the last compound was assumed to be due to the presence of $C_{60}Cl_5Ph$ in the $C_{60}Cl_6$ starting material, and they cited unpublished work that "shows that by-products comprise as much as 25 % of the total yield" of $C_{60}Cl_6$.[14]

In 2003 we attempted to use S_8-MALDI mass spectrometry to analyze chloro[60]fullerenes prepared by using entirely different procedures.[13] Although no positive ions containing chlorine atoms were observed by using sulfur as the MALDI matrix, samples of $C_{60}Cl_6$ that had been prepared by using benzene as the solvent gave S_8-MALDI mass spectra with $C_{60}{}^+$, $C_{60}Ph^+$, and $C_{60}Ph_2{}^+$ fragments while samples of $C_{60}Cl_6$ prepared without the use of aromatic hydrocarbon solvents gave spectra with only the $C_{60}{}^+$ fragment ion observed. There was no longer any doubt that $C_{60}Cl_6$ was not as pure as had been assumed and that benzene was not a suitable solvent for its preparation. A new synthesis/purification procedure was clearly needed. However, a new synthesis/purification procedure could not be properly evaluated unless sensitive analytical methods for the detection of by-products were available. We chose analytical HPLC and MALDI mass spectrometry by using *trans*-2-[3-{4-*tert*-butylphenyl}-2-methyl-2-propenylidene]malononitrile (DCTB) as the matrix as the most promising methods.

HPLC as a method of analysis: Figure 2 shows a greatly expanded HPLC trace of 99 % $C_{60}Cl_6$ that was purified from the crude seven-minute reaction product (i.e., sample **4**) by HPLC in toluene (see below).[27] The integrated intensities of the very small features between 5 and 8 min and the shoulder just before the 9.8-minute $C_{60}Cl_6$ peak are less than 1 % of the total intensity. This chromatogram was recorded after the sample had been dissolved in toluene, in the presence of air, for several hours. After nine days under the same conditions, the HPLC trace exhibited a greater number of higher-intensity minor HPLC peaks, as also shown in Figure 2. The integrated intensities of the minor peaks are about 5 % of the total intensity. These data, along with the additional HPLC data discussed below, show conclusively that crude samples of $C_{60}Cl_6$ dissolved in toluene can be rapidly purified by HPLC with negligible degradation. The data also show that $C_{60}Cl_6$ does react, albeit slowly, with toluene and/or oxygen and/or traces of water in air. We have not yet identified the compounds that give rise to the minor peaks in the lower trace in Figure 2.

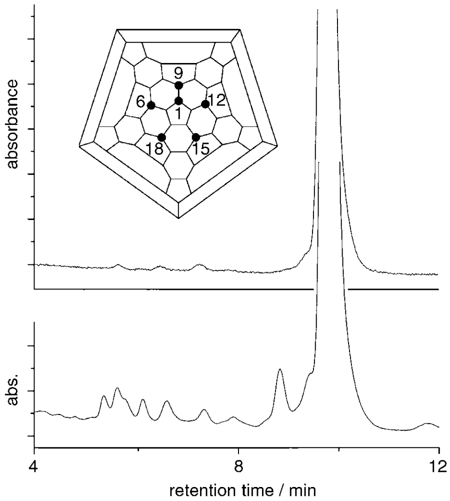


Figure 2. HPLC traces of 99 % $C_{60}Cl_6$ dissolved in toluene after several hours (top trace) and after nine days (bottom trace; Cosmosil Buckyprep column; toluene eluent). The Schlegel diagram shows the C_s-symmetry structure of $C_{60}Cl_6$ (the numbering scheme shown is the one currently accepted by the IUPAC and Chemical Abstracts Service[27]). The establishment of 99 % purity for the purified fraction of sample **4** is based on the top HPLC trace.

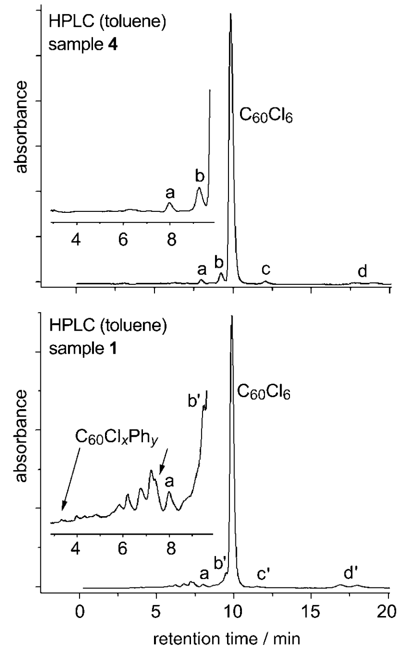


Figure 3. HPLC traces of two samples of crude $C_{60}Cl_6$ prepared in this work (Cosmosil Buckyprep column; toluene eluent). The top trace is sample **4**. The minor peaks, identified by MALDI mass spectrometry, are due to $C_{60}Cl_{14}$ (a), $C_{60}Cl_{12}$ (b), and a mixture of $C_{60}Cl_8$ and $C_{60}Cl_{10}$ (c). The bottom trace is sample **1**. The minor peaks are due to $C_{60}Cl_{14}$ (a), $C_{60}Cl_{12}$ (b′), $C_{60}Cl_{8,10}$ (c′). The small peaks at 16–18 min (d) are not due to any fullerene derivative. The slightly different retention times for the peaks labelled b and b′ and for c and c′ may indicate that different isomers of the same compositions are formed in the two reactions. The insets show vertical expansions of the same chromatogram from 2 to 10 min.

Having established that HPLC conditions do not result in the rapid degradation of $C_{60}Cl_6$, we used analytical HPLC to examine samples **1**–**5**. All five samples showed minor peaks in addition to the main $C_{60}Cl_6$ peak. Representative HPLC traces for samples **1** and **4** are shown in Figure 3. The data for samples **1**–**4** are listed in Table 2. The assignments of the peaks due to $C_{60}Cl_{6,8,10,12,14}$ are based on MALDI mass spectra of fractions of these peaks, as discussed below. The assignments of peaks due to various $C_{60}Cl_xPh_y$ derivatives are based on the fact that the S_8-MALDI mass spectrum of sample **1** exhibited $C_{60}Ph^+$ and $C_{60}Ph_2^+$ fragment ions, as shown in Figure S1 of the Supporting Information. The data in Table 2 clearly show that sample **4**, prepared by using the new seven-minute synthesis, contains the highest percentage of $C_{60}Cl_6$.

Table 2. Relative HPLC peak integrated intensities of crude $C_{60}Cl_6$ samples **1**–**4**.[a]

Component	Relative integrated peak intensity [%][b]			
	sample **1** (C_6H_6, 3 d)	sample **2** (C_6H_6, 5 d)	sample **3** (1,2-$C_6H_4Cl_2$, 7 d)	sample **4** (C_6H_5Cl, 7 min)
$C_{60}Cl_6$	80	75	54[c]	91
$C_{60}Cl_{8,10}$	6	13	6	4
$C_{60}Cl_{12}$	4	2	9	4
$C_{60}Cl_{14}$	0	0	1	1
$C_{60}Cl_xPh_y$	10	10	0	0
insoluble product(s)	0	0	30[d]	0

[a] All data from this work. Samples **1**, **2**, and **3** were prepared under the same conditions reported in refs. [5], [20], and [12], respectively; see Table 1 for more details. [b] The solvent and the reaction time are shown in parentheses. [c] A 98 % yield of $C_{60}Cl_6$ was claimed in ref. [12] but this appears to be a gross overestimation. [d] This percentage is based on the mass of the red precipitate that formed during the reaction.

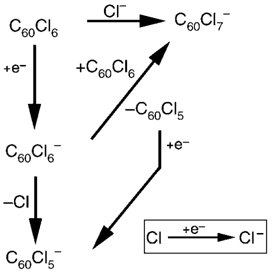
It is not possible to use the HPLC integrated intensities to precisely determine the relative molar amounts of $C_{60}Cl_6$ and the other by-products because the molar extinction coefficients, ε, of chlorofullerenes (and phenylated chlorofullerenes) at 300 nm are not known at this time. Since a sample of 99 % pure $C_{60}Cl_6$ was available for the first time, we determined its ε(300 nm) value in toluene to be $3.44 \times 10^4\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$. If we assume that the ε(300 nm) values for each of the by-products is one-half this value, then the mol % of $C_{60}Cl_6$ in sample **4** is 84 %. Since the HPLC purification allows for the isolation of about ninety percent of the $C_{60}Cl_6$ in sample **4**, the overall yield of 99 % pure $C_{60}Cl_6$ prepared by the new seven-minute synthesis is about 70 % (i.e., this would be the yield of one batch of product if a preparative-scale Buckyprep HPLC column were used instead of our analytical-scale Buckyprep HPLC column). The yield may in fact be higher, because our experience with fluorofullerene visible spectra is that ε values do not change by a factor of two over such a small range of compositions.[28]

MALDI mass spectrometry as a method of analysis: Until this paper, mass spectrometry was not considered to be suitable for the analysis of chlorofullerene compositions. Both

FAB[20] and MALDI[18,29] methods of ionization resulted in substantial fragmentation (i.e., loss of many chlorine atoms) when the substrates were chlorofullerenes with more than 24 chlorine atoms. Chlorofullerenes with low chlorine content, such as $C_{60}Cl_6$, were found to undergo complete C–Cl fragmentation under MALDI conditions to produce only chlorine-free ions such as C_{60}^+.[13,30]

We recently compared *trans*-2-[3-{4-*tert*-butyl-phenyl}-2-methyl-2-propenylidene]malono-nitrile (DCTB), a commonly used matrix for organic fullerene derivatives,[31] with four other MALDI-MS matrix materials for the fluorofullerene substrates $C_{60}F_{18}$, $C_{60}F_{36}$, and $C_{60}F_{48}$.[32] It was found that DCTB gave negative-ion MALDI mass spectra with the highest yield of parent molecular ions for $C_{60}F_{18}$ and $C_{60}F_{36}$ (none of the matrixes gave the parent ion $C_{60}F_{48}^-$ for samples containing $C_{60}F_{48}$). This was due, in part, to the lower laser fluence needed to obtain observable ion currents from $C_{60}F_n^-$ species. We now report that DCTB is a suitable matrix for MALDI-MS analysis of chloro[60]fullerene mixtures.

Figure 4 shows the DCTB-MALDI mass spectrum of 99% $C_{60}Cl_6$. As expected, the predominant peak is $C_{60}Cl_5^-$, a stable closed-shell anion formed via dissociative ionization of $C_{60}Cl_6$ (i.e., electron attachment accompanied by loss of a chlorine atom). The molecular anion $C_{60}Cl_6^-$ was not detected. However, an unexpected, lower intensity signal at *m/z* 969, consistent with the formula $C_{60}Cl_7^-$, was observed. A spectrum recorded on an instrument with higher resolution (not shown) confirmed the proper isotope pattern for $C_{60}Cl_7^-$. Since the HPLC trace for this sample, also shown in Figure 4, proves that $C_{60}Cl_8$ or higher chloro[60]fullerenes were not present in the sample, it appears that $C_{60}Cl_7^-$ ions are formed from $C_{60}Cl_6$ by one or more gas-phase ion-molecule reactions in the MALDI plume. Scheme 1 shows a number of plausible gas-phase reactions that might form the $C_{60}Cl_5^-$ fragment ion and the $C_{60}Cl_7^-$ adduct ion (the Cl^- atomic ion was an abundant species in the low-mass region of the spectrum). We recently observed adduct-ion formation in an LDI/MALDI-MS study of the pure fluorofullerene $C_{60}F_{18}$. In addition to the $C_{60}F_{18}^-$ molecular ion and the $C_{60}F_{17}^-$ fragment ion, the $C_{60}F_{19}^-$ adduct ion was also observed (its intensity was 10% of the intensity of the molecular ion).[32]



Scheme 1. Plausible gas-phase reactions for the formation of the $C_{60}Cl_5^-$ fragment ion and the $C_{60}Cl_7^-$ adduct ion.

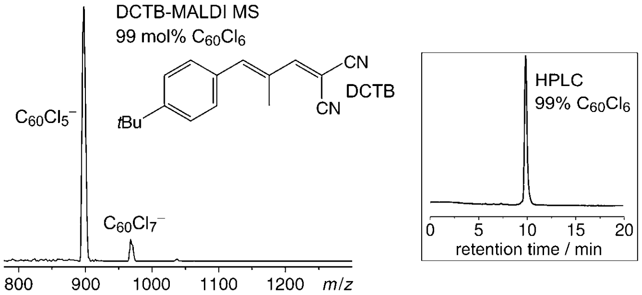


Figure 4. DCTB-MALDI mass spectrum of HPLC-purified 99% $C_{60}Cl_6$ from sample **4**. The inset shows the HPLC trace of the actual sample used to obtain the mass spectrum.

Positive- and negative-ion DCTB-MALDI mass spectra for unpurified (i.e., crude) samples **1**–**4** were recorded under similar laser-fluence conditions, and the relative intensities of the observed ions were reproducible to within 10–15%. Spectra for samples **1**, **3**, and **4** are shown in Figure 5 (the spectra for sample **2** were very similar to those for sample **1**). Comparison with the spectrum of pure $C_{60}Cl_6$ in Figure 4 confirms the presence of varying amounts of $C_{60}Cl_{8,10,12,14}$ in the crude samples (these higher chlorofullerenes had also been detected in HPLC traces of these samples (see Figure 3 and Table 2). In addition to the highest-intensity peak due to $C_{60}Cl_5^-$, the adduct and/or fragment ions $C_{60}Cl_n^-$ (n = 7, 9, 11, 13, 15) were also observed in varying amounts. The relative abundance of $C_{60}Cl_5^-$, most of which is probably derived from $C_{60}Cl_6$, is different for the three

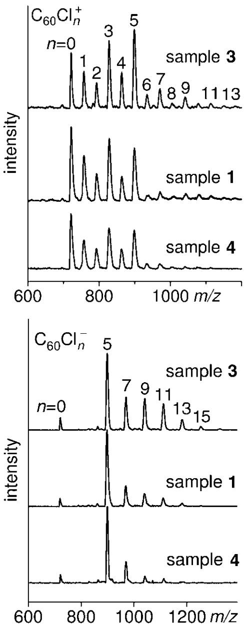


Figure 5. DCTB-MALDI mass spectra of $C_{60}Cl_6$ samples **1**, **3**, and **4**. Top: positive-ion spectra. Note the abundant presence of fragment ions $C_{60}Cl_n^+$ with n = 0–4). Bottom: negative-ion spectra. Note the virtually complete absence of fragment ions $C_{60}Cl_n^-$ with n = 1–4) and the low intensity of the peak due to C_{60}^-.

samples. The maximum content was observed for sample **4** and the minimum content for sample **3**, in harmony with the HPLC results.

The positive-ion spectra exhibit peaks for $C_{60}Cl_n^+$ ions with both odd and even n values and with n values less than 5. The alternation of intensities, with even n-value peaks having lower intensities than the corresponding $n+1$ and $n-1$ peaks, suggests that radical species (i.e., species with even n values) are less stable than closed-shell species with one fewer or one more chlorine atom (the exception is C_{60}^+, which is the highest intensity peak for samples **1** and **4**).

In contrast, only odd n values were observed for the negative ions $C_{60}Cl_n^-$ and, except for C_{60}^-, n values less than 5 were not observed. This could be due to the special stability expected for the C_{5v} isomer of $C_{60}Cl_5^-$ that would result if the chlorine atom at C1 were removed (see Figure 2). Such a structure would possess a stabilizing, six-electron, isolated, aromatic cyclopentadienyl ring such as those observed in Tl-($C_{60}Ph_5$)[33] and related organometallic compounds containing $C_{60}R_5^-$ Cp-like ligands.[34]

The mass spectra clearly demonstrate, for the first time, that samples of $C_{60}Cl_6$ prepared in the past contained one or more of the higher chlorofullerenes $C_{60}Cl_8$, $C_{60}Cl_{10}$, $C_{60}Cl_{12}$, and $C_{60}Cl_{14}$. This is also true for the new seven-minute synthesis, but the amounts of higher chloro-fullerene by-products are clearly smaller. Nevertheless, like the HPLC integrated intensities, the mass spectra cannot be used to precisely determine the relative molar amounts of $C_{60}Cl_6$ and the by-products because of the analyte suppression effect, which can occur if the components of a sample have significantly varying ionization characteristics.[35] For example, compare the positive- and negative-ion spectra for sample **3** in Figure 5. The intensities of the closed-shell cations $C_{60}Cl_7^+$, $C_{60}Cl_9^+$, and $C_{60}Cl_{11}^+$ exhibit a much greater decrease from $n=7$ to $n=9$ than do the intensities of the corresponding closed-shell species $C_{60}Cl_7^-$, $C_{60}Cl_9^-$, and $C_{60}Cl_{11}^-$. This is because the ionization energies *and* the electron affinities of the parent species probably increase in the order $C_{60}Cl_8 < C_{60}Cl_{10} < C_{60}Cl_{12}$. Therefore, the formation of the molecular ion $C_{60}Cl_{12}^+$ in the MALDI plume is less favorable than the formation of the molecular ions $C_{60}Cl_{10}^+$ and $C_{60}Cl_8^+$, but the formation of $C_{60}C_{12}^-$ is more favorable than the formation of $C_{60}C_{10}^-$ and $C_{60}C_8^-$. Although no gas-phase ionization data that would support this hypothesis have been reported for chlorofullerenes, it is reasonable to assume that a gradual increase in both ionization energy and electron affinity will occur as the $C_{60}Cl_n$ n value increases, as is the case for fluorofullerenes $C_{60}F_n$.[1]

Finally, although MALDI mass spectrometry is not yet an analytical tool that can provide precise mol% data for chlorofullerene compositions, we have shown that it can be used to screen a series of reaction products for relative purity as reaction parameters are varied, and eventually optimized, to achieve the selective synthesis of a given chlorofullerene.

The seven-minute synthesis of C_s-$C_{60}Cl_6$: The S_8-MALDI mass spectrum in Figure S1 (Supporting Information) established that the reaction of C_{60} and ICl in benzene produced a variety of phenylated by-products. A by-product with one phenyl group was recently shown to be among the products of the reaction of a sample-**1**-like batch of $C_{60}Cl_6$ with MeLi.[14] The authors of that work stated that "the high electrophilicity of the cage allows [phenylation of $C_{60}Cl_6$] to occur even in the absence of Friedel–Crafts catalysts."[14] However, ICl is a reasonably strong Lewis acid (enthalpies of adduct formation with EtOAc for I_2, ICl, BF_3, and are 12, 26, and 54 kJ mol^{-1}, respectively[36]), and it has been used as a Friedel–Crafts catalyst.[37] Therefore, since the chlorinating agent ICl is also a Lewis acid and a known Friedel–Crafts catalyst, a non-aromatic solvent or a less-reactive aromatic solvent is clearly necessary.

The solubility of C_{60} in non-aromatic solvents such as alkanes and haloalkanes is relatively low.[38] Nevertheless, we explored the heterogeneous reaction of C_{60} and ICl in dichloromethane (sample **5** in Table 1). As expected, the heterogeneity greatly reduced the selectivity of the reaction. HPLC and MALDI-MS analysis showed that a wide range of $C_{60}Cl_n$ derivatives were formed (n = 6–24). Therefore, we next explored the less-reactive aromatic solvents 1,2-dichlorobenzene and chlorobenzene. These solvents were chosen for four reasons: i) C_{60} has a relatively high solubility in various chlorinated benzenes (e.g., one of the highest solubilities reported for C_{60} is 27 mg mL^{-1} in 1,2-dichlorobenzene[38]); ii) unlike benzene, chlorinated benzenes are virtually inert to further chlorination by ICl; iii) chlorinated benzenes should be much less prone to Friedel–Crafts substitution reactions than benzene; and iv) a recent report claimed that a 98% yield of $C_{60}Cl_6$ was possible by using ICl in 1,2-dichlorobenzene.[12]

When we repeated (several times) the procedure of Troshin et al. (sample **3**),[12] we observed the formation of an insoluble red material (ca. 30% by weight) whether the reaction was performed under aerobic or anaerobic conditions. There was no mention of a red precipitate in the reported procedure.[12] Of the many organic solvents tried, only carbon disulfide dissolved the red precipitate, but we were unable to obtain a ^{13}C NMR spectrum with this solvent even after 12 h of signal averaging. The FTIR and Raman bands for the red precipitate were different than those for $C_{60}Cl_6$ (see below) by 3–5 cm^{-1}, and additional bands not present in the spectra of $C_{60}Cl_6$ were observed for the red precipitate, at 536, 603, 753, 793, and 1468 cm^{-1} in the IR spectrum and at 262, 781, 785, and 823 cm^{-1} in the Raman spectrum. Thermogravimetric analysis of the red precipitate showed a mass loss equivalent to 4.6 ± 0.5 chlorine atoms per C_{60} cage at 270 °C. In contrast, thermogravimetric analysis of bonafide $C_{60}Cl_6$ showed a mass loss equivalent to 6.0 ± 0.5 chlorine atoms. Although the composition of the red precipitate is not known at this time, we note that its low solubility may indicate that it is an oligomer or a polymer. The formation of fullerene dimers from two photochemically-generated $C_{60}R_f$ radicals has been reported (R_f is one of several perfluoroalkyl groups).[39] Since the reaction of ICl with C_{60} may involve the intermediacy of $C_{60}Cl_{2n\text{-}1}$ radical species, in-

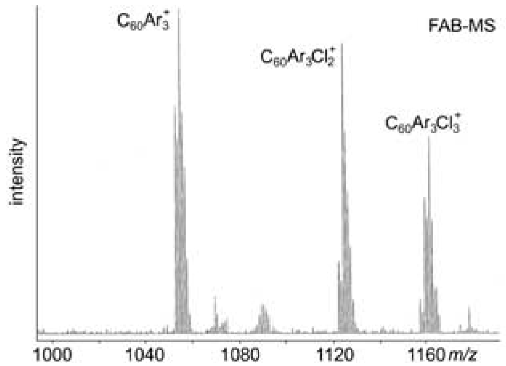


Figure 6. Fast-atom bombardment (FAB) mass spectrum of the 5.3 min fraction of the product mixture prepared by heating C_{60} and ICl in chlorobenzene to 50 °C ($Ar = C_6H_4Cl$).

cluding the presumably relatively stable $C_{60}Cl_5$ cyclopentadienyl-like radical,[2] the red precipitate may contain oligomers or dimers such as $[C_{60}Cl_5]_2$.

Sample **3**, obtained from the supernatant after removal of the red precipitate, contained a variety of higher chlorofullerenes in addition to $C_{60}Cl_6$, as shown in Figures 2 and 6 and in Table 2. For several reasons, therefore, it does not appear to be possible to prepare a high yield of pure $C_{60}Cl_6$ by using 1,2-dichlorobenzene as the solvent if the reported procedure[12] is followed.

The reaction of a saturated chlorobenzene solution of C_{60} ($7\,mg\,mL^{-1}$[38]) with a stoichiometric amount of ICl (i.e., 6 equiv) for 6 h produced the same red precipitate isolated from the 1,2-dichlorobenzene reactions. The red precipitate was also formed when the amount of ICl was increased to 20 equiv. In both cases, the red precipitate was more than 15–20 % by weight of the isolated solid products. However, only a trace amount of the red precipitate was formed when 30 equiv of ICl were used (the reaction time was also 6 h). In this case, the principle product was $C_{60}Cl_6$ along with minor amounts of higher chlorofullerenes. Decreasing the reaction time from several hours to seven minutes and increasing the amount of ICl to 60 equiv led to the isolation of sample **4**, which contained relatively pure $C_{60}Cl_6$ with the smallest amounts of higher chlorofullerene impurities observed to date.

In a series of control experiments, 10–50 µL aliquots of sample-**4** reaction mixtures were removed 10 sec after the reagents were mixed in chlorobenzene, and the volatiles were flash-evaporated under vacuum within another 10 seconds. HPLC and MALDI-MS analysis of the solid residues revealed that $C_{60}Cl_6$ had formed during this brief amount of time. No C_{60} was present. Small amounts of such reaction mixtures can be quenched within seconds by flash evaporation, but this is not possible if the goal is to prepare 100+ mg batches of pure $C_{60}Cl_6$. Heating a sample-**4** reaction mixture to 50 °C during the evaporation of volatiles in order to more rapidly quench the reaction had a deleterious effect on the purity of the product. Several new species with HPLC retention times between 3 and 7 min were formed (eluent = 5 mL toluene per min). Several of these were shown by MALDI-MS and FAB-MS to be $C_{60}Cl_nAr_m$ derivatives ($Ar = C_6H_4Cl$). For example, the FAB mass spectrum of a fraction that eluted at 5.6 min, and that is believed to contain $C_{60}Cl_3Ar_3$, is shown in Figure 6 (the complete characterization of several of these arylated chlorofullerenes will be reported in a future publication). The arylated derivatives were not formed unless the reaction mixture was heated above 25 °C. Therefore, the evaporation of excess ICl, I_2, and chlorobenzene (normal boiling point = 132 °C) can only be carried out at 25 °C or below.

A special reaction vessel, described in the Experimental Section, was made to minimize the time necessary to evaporate all volatiles from sample-**4** reaction mixtures (total volume = 20 mL). As soon as the reagents were mixed, the vessel was evacuated. Complete evaporation of all volatiles required seven minutes, during which time the reaction mixture was kept at 15 °C. This process, referred to in this paper as the seven-minute synthesis of $C_{60}Cl_6$, yielded 100+ mg batches of no less than 84 % pure $C_{60}Cl_6$ with no observable arylated by-products. As discussed elsewhere, this material can be purified to 99 % $C_{60}Cl_6$ by a single-stage HPLC purification. We are continuing to investigate this reaction methodology in order to prepare gram-scale batches of relatively pure $C_{60}Cl_6$.

Vibrational analysis of C_s-$C_{60}Cl_6$: Figure 7 displays the experimental and DFT-predicted infrared and Raman spectra of $C_{60}Cl_6$. In sharp contrast to the simple vibrational spectra of C_{60} (four infrared-active[40] and ten Raman-active bands[41]), at least 90 bands were observed for C_s-$C_{60}Cl_6$. The low symmetry of this molecule renders all 192 normal modes of vibration singly degenerate and both IR and Raman active. The vibrational representation consists of 99 A' modes and 93 A'' modes.

In view of this complexity, an analysis of the vibrational spectra of C_s-$C_{60}Cl_6$ required simulating the spectra at an adequate level of theory. We performed quantum-chemical calculations of the IR and Raman spectra of C_s-$C_{60}Cl_6$ by using the density functional of Perdew, Burke and Ernzerhof (PBE).[22] In previous work, we found that DFT considerably underestimated force constants for q(CX) and α(CCX) internal coordinates (X = halogen atom).[42] Therefore, the PBE force field for $C_{60}Cl_6$ was scaled with scaling factors transferred from $C_{60}Cl_{24}$.[8] This procedure resulted in a virtual peak-to-peak congruence of the experimental and calculated frequencies and in a reasonable correspondence of experimental and calculated band intensities, as shown in Figure 7.

Changes to the structure of the C_{60} framework introduced by the addition of six chlorine atoms should be localized in the portion of the molecule containing the chlorine atoms (this is borne out by comparing the most precise X-ray structures of C_{60}[43] and C_s-$C_{60}Br_6$[4]). Therefore, it is sensible that many vibrations of $C_{60}Cl_6$ would resemble those of the parent C_{60} molecule, and descriptions of the normal modes of $C_{60}Cl_6$ could be presented in terms of correlations be-

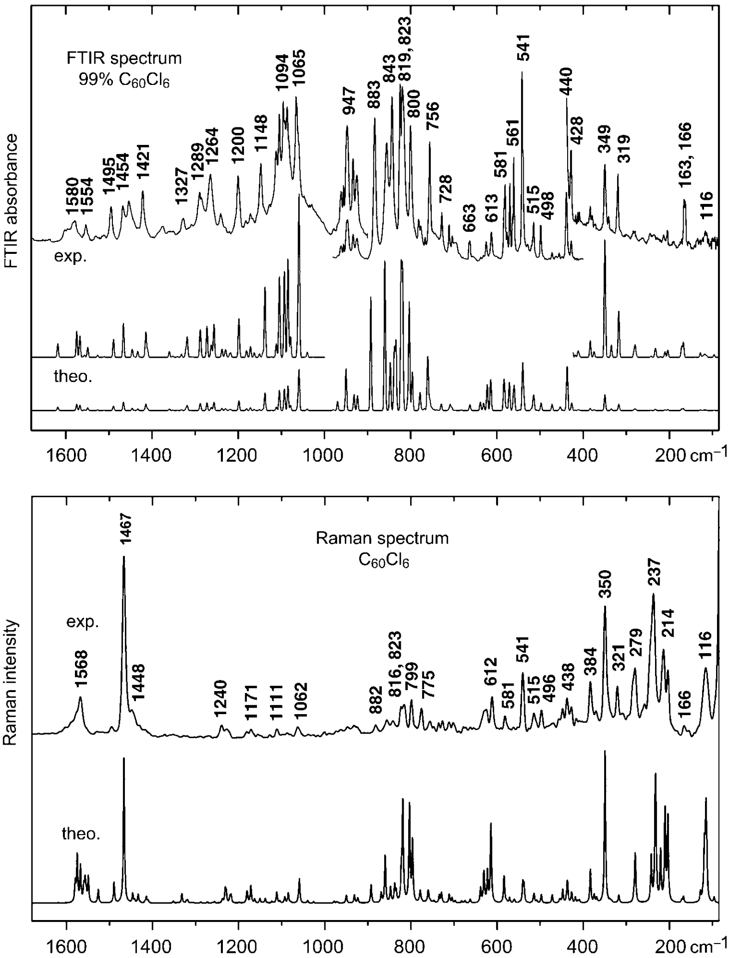


Figure 7. FTIR and Raman spectra of C_s-$C_{60}Cl_6$ (exptl = experimental spectrum, theo. = DFT calculated spectrum).

tween $C_{60}Cl_6$ and C_{60} vibrations rather than in terms of a conventional potential energy distribution (PED) analysis. Such correlations may be established explicitly with the help of the projection technique.[44] On the other hand, this approach would be inadequate for vibrations associated with the functionalized portion of $C_{60}Cl_6$, and PED considerations are preferable in this case. In fact, the description of halofullerene vibrations will be meaningful only if both method of analysis are combined, and this was the strategy adopted in this work. A complete list of experimental and calculated frequencies, relative intensities, and normal-mode descriptions for $C_{60}Cl_6$ in terms of C_{60} vibrations and in terms of a PED among the internal coordinates are available in the Supporting Information. Table 3 contains the corresponding data for the 60 most prominent bands.

Analysis of the normal coordinates of $C_{60}Cl_6$ enabled us to designate four principal regions of its vibrational spectra. First, the eight lowest-frequency modes, in the 100–130 cm^{-1} range, involve predominantly chlorine-atom motion. They are essentially pure C–Cl bending vibrations and appear in the experimental spectra as only one very weak IR band and one medium-strong Raman band at 116 cm^{-1}. Either these vibrations are essentially isoenergetic or some of them must have very small intensities.

In the 140–400 cm^{-1} range, carbon and chlorine atoms equally participate in the vibrations of $C_{60}Cl_6$. Three modes with computed frequencies at 140, 167 and 172 cm^{-1} also represent C–Cl bends if treated with PED considerations, but possess rather specific forms since changes in C-C-Cl angles are accompanied by translational–rotational displacements of the carbon skeleton as a whole. The intensities of these unusual vibrations are low, and two modes of this sort are observed in the experimental spectra as weak features at 163 and 166 cm^{-1}. A group of weak IR bands and strong-to-medium Raman bands in the 200–400 cm^{-1} region correspond to the "breathing" radial deformations of the carbon skeleton of $C_{60}Cl_6$, that can be correlated with the $H_g(1)$, $T_{2u}(1)$, and $G_u(1)$ modes of C_{60} at 272, 342, and 353 cm^{-1}, respectively.

Above 400 cm^{-1}, the vibrations of $C_{60}Cl_6$ are localized on the carbon skeleton of the molecule with negligible chlorine-atom motion. However, it does not mean that internal coordinates associated with chlorine atoms (C–Cl stretches and bends) do not contribute to the vibrations of the chlorofullerene molecule. Radial displacements of the carbon atoms inevitably result in the changes of C–Cl distances and C-C-Cl angles, and a portion of q(C–Cl) and α(CCCl) coordinates in PED remain considerable as long as skeleton vibrations retain their radial character (at least up to ca. 900 cm^{-1}). Although it was possible to distinguish the spectral range where C–Cl bending vibrations dominate, we were not able to find such a domain for C–Cl stretches. Contributions from q(C–Cl) in the PED were scattered in the 200–900 cm^{-1} range and rarely exceeded 20%. In general, the 400–900 cm^{-1} range may be characterized as extremely rich in the IR spectrum, with a large number of strong and medium intensity bands. Half of these bands have counterparts in the Raman spectrum but with much lower relative intensities. All of these bands correspond to radial vibrations of the carbon skeleton and may be correlated with the modes of the parent C_{60} fullerene. For example, absorptions at 539 and 541 cm^{-1} correspond to the C_{60} $T_{1u}(1)$ modes

Table 3. Observed and DFT-calculated IR and Raman frequencies and band intensities for C_s-$C_{60}Cl_6$.

	Calculated[a]			Observed[b]			Assignment[c] [%]	
sym	ν	IR int	R int	IR, int	R, int	d[d]	C_{60} modes	PED[e]
A'	115.1	0.1	30.8	116, vw	116, ms	2		66 α(CCCl)
A'	118.7	0.3	31.9	116, vw,	116, ms	8		57 α(CCCl)
A''	167.0	1.6	4.2	163, w	166, w	52	36 translation rotation	71 α(CCCl)
A'	203.9	0.6	55.2	204, vw	203, m	49	40 H_g(1)	29 γ(C=CC), 15 γ(CC(Cl)C), 15 α(CCCl)
A''	210.2	0.4	59.8	213, vw	214, ms	56	48 H_g(1)	31 γ(C=CC), 15 γ(CC(Cl)C)
A''	231.3	0.5	54.6	n.o.	237, s	74	69 H_g(1)	30 γ(C=CC)
A'	279.5	0.9	31.9	279, vw	279, ms	37	21 T_{2u}(1)	25 q(CCl), 20 γ(CC(Cl)C), 17 α(CCCl), 15 γ(C=CC)
A'	317.7	1.8	3.9	319, w	321, m	87	51 G_u(1), 31 H_g(1)	55 γ(C=CC), 15 q(CC)
A'	349.7	9.8	100.0	349, w	350, s	69	26 T_{2u}(1), 18 H_g(1)	22 q(CCl), 21 γ(C=CC), 15 γ(CCC)
A'	383.4	1.3	21.8	383, vw	384, m	81	40 T_{2u}(1), 15 H_g(2)	31 γ(C=CC), 15 q(CCl)
A'	437.8	13.6	7.1	440, m	438, w	84	24 G_u(1), 20 G_g(1)	38 γ(C=CC), 20 q(CCl)
A'	497.2	5.6	5.6	498, m	497, w	93	37 T_{1u}(1), 23 A_g(1)	46 γ(C=CC)
A'	514.2	7.6	5.9	515, m	515, w	97	42 H_u(2), 19 G_g(1)	42 γ(C=CC), 19 γ(CCC), 16 q(CC)
A'	537.6	7.4	9.8	539, sh	541, ms	98	42 T_{1u}(1), 20 H_u(2)	55 γ(C=CC), 15 q(CC)
A'	540.1	29.1	12.2	541, vs	541, ms	99	38 T_{1u}(1), 29 T_{1u}(2), 17 A_g(1)	43 γ(C=CC), 27 q(CC)
A'	559.7	13.0	1.9	561, s	562, vw	99	38 G_g(2), 23 T_{1g}(1)	47 γ(C=CC), 18 γ(CCC)
A'	571.1	17.9	3.5	570, ms	n.o.	96	45 G_g(2), 18 T_{1u}(1)	37 γ(C=CC), 21 γ(CCC)
A''	576.8	1.3	0.3	576, sh	n.o.	100	79 G_g(2)	45 γ(C=CC), 29 γ(CCC)
A''	582.1	8.1	0.0	581, ms	581, w	100	36 G_g(2), 34 T_{1u}(2)	36 γ(C=CC), 17 q(CC), 15 γ(CCC)
A'	583.8	13.5	17.8	583, sh	581, w	94	31 T_{1u}(2), 19 G_g(2), 18 T_{1u}(1)	32 γ(C=CC), 15 γ(CCC), 15 q(CCl)
A'	614.4	16.2	52.8	613, m	612, m	87	32 T_{1u}(2), 15 H_u(2)	38 q(CCl)
A''	622.3	15.2	20.5	625, w	625, w	95	38 T_{1g}(1), 30 T_{1u}(2)	46 γ(C=CC), 18 q(CCl), 15 q(CC)
A'	662.2	2.6	2.3	663, w	662, vw	100	83 H_u(3)	63 γ(C=CC)
A''	708.5	4.2	0.1	711, w		100	85 H_g(3)	55 γ(C=CC), 39 γ(CCC)
A''	729.1	6.1	6.7	728, m	727, w	100	42 H_g(4), 15 H_u(4), 15 G_u(2)	22 γ(CCC), 18 γ(C=CC), 16 q(C(Cl)C)
A'	760.6	30.3	5.4	756, s	756, w	99	60 H_g(4)	28 q(CC), 19 γ(CCC), 17 γ(C=CC), 15 q(C=C)
A''	778.0	7.8	4.2	777, sh	775, m	100	65 G_u(3), 15 H_g(4)	73 γ(C=CC)
A'	796.4	24.7	40.1	n.o.	799, m	98	20 H_g(3), 16 G_u(3), 16 T_{2u}(2)	29 γ(C=CC), 17 q(CCl), 16 α(CCCl), 15 γ(CC(Cl)C)
A'	803.3	65.8	63.8	800, s	799, m	99	58 T_{2g}(3)	35 γ(C=CC), 20 γ(CCC)
A'	818.8	83.6	65.8	819, vs	816, m	97	18 H_g(3), 18 T_{2g}(3), 15 H_g(4)	22 γ(C=CC), 18 α(CCCl), 16 γ(CC(Cl)C)
A''	822.3	92.7	18.3	825, vs	823, m	99	29 T_{1g}(2), 15 G_g(3)	33 γ(C=CC), 15 γ(CC(Cl)C)
A''	834.0	45.7	7.1	843, vs	842, w	99	56 T_{1g}(2)	41 γ(C=CC)
A'	837.7	40.4	11.6	843, vs	842, w	99	66 T_{1g}(2)	56 γ(C=CC)
A'	860.0	100.0	31.1	856, s	856, w	99	18 T_{1g}(2)	24 α(CCCl), 22 γ(CC(Cl)C), 15 γ(C=CC)
A'	892.5	78.5	12.1	883, vs	882, w	99	16 T_{2g}(2), 15 G_u(3)	26 α(CCCl), 22 γ(CC(Cl)C), 16 q(CCl)
A''	923.3	9.7	3.6	925, w	926, sh	100	67 G_u(4)	29 q(C(Cl)C), 25 q(CC)
A'	931.4	10.3	5.5	934, w	932, w	100	66 G_u(4), 18 T_{2u}(3)	32 q(CC), 22 q(C(Cl)C)
A'	949.9	19.7	2.9	947, m	947, w	100	56 G_u(4), 28 T_{2u}(3)	29 q(CC), 18 q(C(Cl)C)
A'	1059.1	26.5	15.7	1065, m	1062, w	100	70 H_g(5)	29 q(CC), 23 q(C(Cl)C), 19 γ(C=CC)
A''	1084.8	17.2	6.8	1086, m	1087, vw	100	40 G_g(4), 15 H_g(5)	34 q(CC), 31 q(C(Cl)C)
A'	1092.8	14.5	4.1	1094, m	n.o.	100	25 G_g(4), 25 H_g(5)	30 q(CC), 27 q(C(Cl)C)
A''	1104.5	13.8	1.4	1105, w	n.o.	100	32 G_g(4), 23 H_g(5)	37 q(CC), 23 q(C(Cl)C), 15 γ(CCC)
A''	1111.3	1.2	5.1	1112, w	1111, w	100	58 G_g(4), 17 H_g(5)	55 q(CC), 15 q(C(Cl)C), 15 γ(C=CC)
A'	1138.0	12.6	3.2	1148, w	n.o.	100	20 H_u(5), 15 H_g(5)	37 q(C(Cl)C), 21 q(CC)
A'	1171.8	1.1	11.6	1172, vw	1171, w	100	55 T_{1u}(3), 30 T_{2u}(4)	62 q(CC), 16 γ(CCC)
A'	1198.6	7.2	0.6	1200, w	n.o.	100	59 T_{2u}(4), 35 T_{1u}(3)	67 q(CC), 18 γ(CCC)
A'	1229.1	1.3	7.0	1240, vw	1240, w	100	52 H_g(6), 16 H_u(5)	51 q(CC), 29 γ(C=CC)

Table 3. (Continued)

	Calculated[a]			Observed[b]			Assignment[c] [%]	
sym	ν	IR int	R int	IR, int	R, int	d[d]	C_{60} modes	PED[e]
A'	1256.4	4.5	1.0	1264, w	n.o.	100	93 $H_g(6)$	52 q(CC), 28 γ(C=CC)
A''	1288.6	3.3	0.3	1289, w	n.o.	100	30 $G_u(5)$, 27 $G_g(5)$	40 q(CC), 31 γ(C=CC), 17 γ(CCC)
A''	1414.2	4.3	1.6	1421, w	1420, sh	100	53 $H_g(7)$, 33 $G_u(6)$	50 q(C=C), 30 q(CC)
A'	1445.9	2.3	6.1	1454, w	1448, sh	100	75 $T_{1u}(4)$, 20 $G_u(6)$	60 q(C=C), 29 q(CC)
A'	1466.4	8.2	96.1	1468, w	1467, vs	100	71 $A_g(2)$	63 q(C=C), 32 q(CC)
A'	1489.4	1.8	7.4	1495, w	1495, w	100	77 $G_g(6)$	46 q(C=C), 21 q(C–C), 16 γ(CCC), 14 γ(C=C–C)
A'	1567.2	2.3	16.8		1568, m	100	83 $H_g(8)$	50 q(C=C), 16 γ(C=C–C), 16 q(CC), 15 γ(CCC)
A'	1574.9	4.3	30.5	1580, w	1568, m	100	81 $H_g(8)$	49 q(C=C), 15 γ(CCC), 15 γ(C=CC), 15 q(C–C)

[a] Calculated IR and Raman intensities are % of the most intense transitions. [b] vs = very strong, s = strong, m = medium, ms = medium strong, w = weak, vw = very weak, sh = shoulder, n.o. = not observed. [c] Contributions that are less than 15% have been omitted. [d] d = total % contribution of carbon skeleton displacements into the $C_{60}Cl_6$ vibration. [e] Internal coordinates used in the potential energy distribution (PED) analysis were: α(CCCl), C-C-Cl angles; γ(C=C–C), angles between double and ordinary CC bonds; γ(CC(Cl)C), C-C-C angles with a central chlorine-bearing carbon atom; γ(CCC), C-C-C angles with a central sp^2-hybridized carbon atom; q(C–Cl), C–Cl bonds; q(C(Cl)–C), ordinary CC bonds between sp^2- and sp^3-hybridized carbon atoms; q(C–C), ordinary CC bonds between two sp^2-hybridized carbon atoms; q(C=C), C=C double bonds.

(526 cm^{-1}); at 561, 569, and 581 cm^{-1} to the C_{60} $G_g(2)$ modes (567 cm^{-1}); at 728 and 755 cm^{-1} to the C_{60} $H_g(4)$ modes (772 cm^{-1}); at 800 cm^{-1} to the C_{60} $T_{2g}(3)$ modes (796 cm^{-1}); and at 842 cm^{-1} to the C_{60} $T_{1g}(2)$ modes (827 cm^{-1}). At the same time, strong absorptions at 817, 824, 855, and 883 cm^{-1} are due to vibrations with enhanced contributions from γ(CC(Cl)C) and α(CCCl) deformations. Since these modes are considerably localized on the chlorinated fragment of the molecule, their interpretation in terms of C_{60} modes is not meaningful.

In the 900–1600 cm^{-1} range, vibrations of the $C_{60}Cl_6$ carbon skeleton have considerable tangential character and in PED terms they may be described as ν(CC) stretching vibrations. In accordance with the gradual decrease in the bond length, C(Cl)–C vibrations fall in the 900–1200 cm^{-1} interval where they are partially mixed with vibrations of ordinary bonds between sp^2 hybridized carbon atoms; the latter also appear in the 1200–1400 cm^{-1} interval, while C=C stretching modes occur in the 1400–1600 cm^{-1} range. Although the intensities of the C–C bands were rather low, the C=C stretches exhibited significant Raman activity with two principal bands at 1467 and 1568 cm^{-1} corresponding to the $A_g(2)$ and $H_g(8)$ modes of C_{60} at 1468 and 1575 cm^{-1}. Three vibrations in the calculated spectra, at 1549, 1580, and 1619 cm^{-1}, are essentially localized on the cyclopentadienyl ring. However, their frequencies could not be precisely determined from the experimental spectra due to their low intensities and overlap with other bands.

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