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Magnetic circular dichroism of chlorofullerenes: Experimental and computational study

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ABSTRACT

Magnetic circular dichroism (MCD) spectra of $C_{60}Cl_6$, $C_{70}Cl_{10}$ and $C_{60}Cl_{24}$ were measured and interpreted using a sum-over-state (SOS) protocol exploiting time dependent density functional theory (TDDFT). Unlike for plain absorption, the MCD spectra exhibited easily recognizable features specific for each chlorinated molecule and appear as a useful tool for chlorofullerene identification. MCD spectrum of $C_{60}Cl_{24}$ was below 400 nm partially obscured due to scattering and low solubility. In all cases a finer vibrational structure of the electronic bands was observed at longer wavelengths. The TDDFT simulations provided a reasonable basis for interpretation of the most prominent spectral features.

1. Introduction

Chlorination of fullerenes leads to halogenated compounds that can conveniently be used in organic synthesis of more complex fullerene derivatives. Such materials promise many applications in biology and industry [1]. Fullerene derivatization is also important for their metabolic processing, which currently raises many security concerns (http://cordis.europa.eu/project/rcn/89325_en.html). The chlorination is performed with various agents including chlorine gas, PCl_5, VCl_4, $SbCl_5$, ICl, ICl_3, or $KICl_4$ [2,3]. According to the reaction conditions, multiple products may be formed and various addition patterns are possible. In addition, chlorofullerenes of the same stoichiometry sometimes form stable isomers [4]. For example, the Buckminster fullerene (C_{60}) chlorinates to compounds ranging from $C_{60}Cl_2$ up to $C_{60}Cl_{24}$, although not all of them are stable [4]. In the present study, we investigate the spectroscopy of magnetic circular dichroism (MCD) of selected derivatives as a method helpful in separation and identification of these compounds.

In general, determination of the composition of chlorinated fullerene mixture is difficult. Standard methods involve nuclear magnetic resonance (NMR), mass spectroscopy (MS), high-performance liquid chromatography (HPLC), and optical spectroscopy. Even a combination of such techniques, however, may not be sufficient for reliable analysis [3]. Limited solubility of some derivatives is often critical for the NMR measurements. Some species are unstable and may decompose in solution, at elevated temperatures, and due to irradiation by light [3].

The MCD spectroscopy detects a small difference in absorption of the left- and right-circularly polarized light in a presence of static magnetic field. Because the difference can be both positive and negative, the technique can inherently provide more easily decipherable information about the electronic and molecular structure than plain absorption [5–7]. Recently, modern implementations of the quantum-chemical expressions of MCD intensities [8,9], in particular within the density functional theory (DFT) framework, provide a handy tool for interpretation of the spectra and stimulate new applications of MCD spectroscopy [10–17].

For fullerenes, first MCD studies of C_{60} were published in late 80s and early 90s [18,19]. The fact that (unsubstituted) fullerenes provide very rich and characteristic MCD spectra has been confirmed recently [20]. In fact, MCD signal is specific both for fullerenes of different chemical formulae and isomers [20]. Similarly, distinct MCD signals were observed for endohedral fullerenes $La@C_{82}$, $La_2@C_{80}$ and $Sc_3N@C_{80}$ [21].

In the present study three model molecules, $C_{60}Cl_6$, $C_{70}Cl_{10}$ and $C_{60}Cl_{24}$, were synthesized, their absorption and MCD spectra measured, and the results are discussed on the basis of time dependent density functional theory (TDDFT). A computationally efficient sum over states (SOS) methodology [10,22] is used to simulate chlorofullerene MCD spectra. As discussed below, such TDDFT computations provide a reasonable basis for the experiment.

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2. Methods

The $C_{60}Cl_6$, $C_{70}Cl_{10}$ and $C_{60}Cl_{24}$ compounds were synthesized using previously published procedures as specified in the Supporting Information. Absorption and MCD spectra were measured at room temperature (~293 K) on a Jasco J-815 CD spectrometer equipped with a 1.4 T permanent magnet. Samples dissolved in 1,2-dichlorobenzene were placed in a 1 cm fused-silica cell, the scanning speed was 5 nm/min, detector response constant 32 s, and data pitch 0.05 nm. Presented data are averages of two accumulations. $C_{60}Cl_6$ concentrations ranged from 0.4 mg/ml to 0.0267 mg/ml, $C_{60}Cl_{24}$ was measured as a saturated solution (~0.15 μg/ml), and $C_{70}Cl_{10}$ was measured for 0.16 and 0.08 mg/ml.

For the theoretical modeling, $C_{60}Cl_6$, $C_{70}Cl_{10}$ and $C_{60}Cl_{24}$ molecular geometries (Figure 1) were optimized using the BP86 and B3LYP functionals, and standard def-TZVP and 6-311+G* basis sets. The polarizable continuum solvent model (PCM) [23] was used to account for the 1,2-dichlorobenzene environment. The GAUSSIAN 09 revision D.01 program [24] was used for the geometry optimization; some computations were also done in Turbomole 6.3.1 [25].

By default, electronic absorption spectra were calculated at the B3LYP/PCM/6-31G* level for the B3LYP/PCM/6-311+G* geometries using TDDFT [26] as implemented in the Gaussian and Turbomole programs. In a test a larger 6-31+G* basis set (Figure S1) provided within the experimentally accessible region very similar absorption and MCD intensities as 6-31G*; we use the 6-31G* basis set as default as it allows us to compute more excited states covering a larger interval of wavelengths than the larger 6-31+G* basis. A truncated (400 state) SOS expansion is used for the generation of MCD intensities. From the TDDFT expansion coefficients approximate excited states were used in a sum over states (SOS) formula for MCD as implemented in the Guvcde program [10,22] interfaced to Gaussian and Turbomole. Spectral intensities were generated with Gaussian bands 0.1 eV wide (full width at half height). Control MCD computations were also performed with the Dalton 2011 code [27] using the complex polarization propagator (CPP) variant of the response theory [15], which provided very similar intensities as the SOS method, but with much higher demands on the computational resources. The CPP curves were generated with 5 nm increments (i.e. irregular energy intervals), computing five points at once, the gamma width was set to 0.0046 hartree. Typically, the computations were run in parallel at 4–8 processors.

3. Results and discussion

3.1. Experimental spectra

Absorption and MCD spectra of $C_{60}Cl_6$, $C_{60}Cl_{24}$ and $C_{70}Cl_{10}$ are plotted in Figure 2, together with those of C_{60} and C_{70} obtained previously [20]. The 'bare' fullerenes were measured in a relatively transparent *n*-hexane down to ~200 nm. The chlorinated derivatives were not much soluble in it, and their spectra could be measured to ~300 nm only, due to the high absorption of the 1,2-dichlorobenzene solvent. The long-wavelength absorption threshold of $C_{60}Cl_6$ (weak signal starting at ~522 nm, a larger one at ~400 nm) is slightly higher if compared to C_{60} (cf. the first strong peak at 328 nm). In $C_{60}Cl_{24}$ the absorption range is not much changed in comparison with $C_{60}Cl_6$, but the intensity within 400–550 nm is increased and the bands are sharper. The chlorination of C_{70} to $C_{70}Cl_{10}$ brings similar effects for the shift of the strongest absorption (254 nm → 315 nm); however, within 300–650 nm the C_{70} molecule exhibits many weaker bands already, intensity of which is redistributed after the chlorination.

The MCD spectra (right hand side of Figure 2) show a larger variability and reveal presence of more electronic transitions (also with several vibrational components) than the absorption. Note also that the signal might slightly depend on experimental conditions; for C_{60}, for example, the '−−+' bands at 251, 324 and 334 nm found in *n*-hexane (Figure 2) exist in an Argon matrix [28], too, but an additional positive signal around 255 nm was found in the latter environment. For $C_{60}Cl_6$, there are two strong MCD positive bands at 360 and 396 nm, a negative signal going down to the 300 nm limit, and six weaker bands above 400 nm, alternating in MCD sign but approximately of the same magnitude. $C_{60}Cl_{24}$ exhibits strong positive bands at 410 and 469 nm, a negative one at 460 nm with clear vibrational substructure, and a 510 nm positive peak. The $C_{60}Cl_{24}$ MCD spectra below 400 nm might not be reliable because of the limited solubility and a high scattering of the sample.

The MCD pattern of $C_{70}Cl_{10}$ is again quite unique; the signal above 400 nm is much stronger than for $C_{60}Cl_6$, but there are fewer (about three) strong bands resolved. As for $C_{60}Cl_6$, a weak MCD $C_{70}Cl_{10}$ signal is apparent up to about 570 nm. An interesting effect of the $C_{70} \rightarrow C_{70}Cl_{10}$ chlorination is the sign inversion of the strongest MCD band (324 → 343 nm).

3.2. Simulated absorption and MCD spectra

Similarly as previously observed for unsubstituted fullerenes [20] the calculated absorption and MCD spectra (Figure 3) reasonably well reproduce the main experimental features in studied chlorofullerenes. For the $C_{60}Cl_6$ absorption, the computation predicts higher intensity above 320 nm if compared to C_{60}; for $C_{70}Cl_{10}$ the intensity in this region diminishes relative to C_{70}, although the fine vibrational pattern is obviously not reproduced at the static approximation.

The signs of the principal MCD bands are reproduced correctly, although detailed features differ and transition wavelengths are calculated too low. For $C_{60}Cl_6$, the MCD experimental main maxima at 360 and 396 nm are reproduced at 257 and 314 nm; a weaker negative band at 420 nm (exp.) is calculated at 341 nm. Above 450 nm the fine experimental structure is not simulated

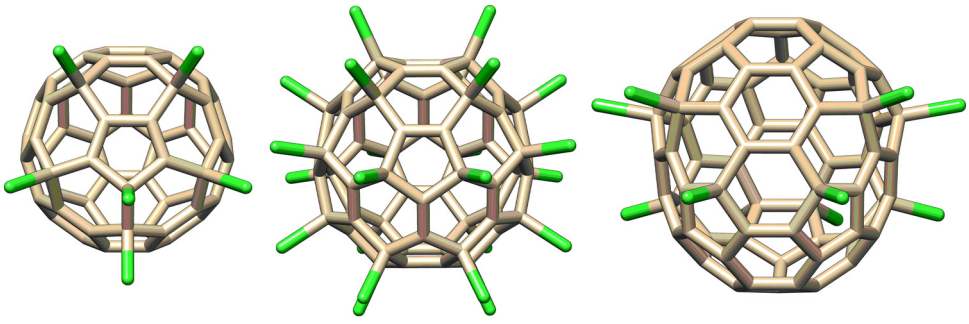

Figure 1. Optimized (B3LYP/CPCM/6-311++G**) $C_{60}Cl_6$, $C_{60}Cl_{24}$ and $C_{70}Cl_{10}$ geometries.