Polarizability of fullerene derivatives

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At the moment there are diverse methods of synthesis of fullerene derivatives (**FD**) with various numbers of addends controlled via reaction conditions, use of catalysts *etc*. **FD** (especially, polar derivatives, such as epoxides or fluorides) are promising compounds for nanomaterials, nanodevices, and medicine. Intermolecular interactions underlie the functioning of the mentioned applications of fullerene containing systems and, while the polarizability determines the intermolecular interactions, its investigations are the base for understanding the mechanisms of processes which fullerenes and its derivatives take part in.

In the present study the diagonalized tensors of polarizability, average polarizability and anisotropy of polarizability (a^2) for series of **FD** ($C_{60}O_n$ and $C_{70}O$ epoxides, $C_{60}(CH_2)_n$ fullerenocyclopropanes, $C_{60}(NH)_n$ fullerenoazyridines, $C_{60}F_m$ and $C_{70}F_k$ fluorofullerenes, and others) have been calculated by PBE/3z density functional method.

This method has been tested on several model molecular systems (including fullerenes C_{60} and C_{70}) and showed a good agreement of calculated results with experimental data. Polarizabilities of fullerene polyadducts have been calculated both quantum-chemically (α_{qc}) and by additive scheme (α_{add}) *via* expressions:

$$\alpha_{add}(C_{60/70}X_n) = \alpha_{qc}(C_{60/70}) + n\alpha_{qc}(X), \text{ where } \alpha_{qc}(X) = \alpha_{qc}(C_{60/70}X) - \alpha_{qc}(C_{60/70}).$$

The difference $\Delta\alpha = \alpha_{add} - \alpha_{qc}$ shows the inadditivity of polarizability and increases with the increase of number of X added to fullerene.

Analyzed the average α values, we can formulate the following regularities:

1) Polarizabilities of exohedral **FD** are higher than those of respective pristine fullerenes.
2) Polarizabilities of 5.6 open isomers of **FD** are higher than those of respective 6.6 closed isomers.
3) The functionalization of C_{60} is accompanying with the increase of anisotropy of polarizability and in the case of C_{70} either increasing or decreasing of a^2 value are possible (e.g., a^2 increases upon C_{70} epoxides formation but become smaller if oxahomo[70]fullerenes are formed).
4) Regio-isomers of $C_{60/70}X_n$ are characterized with the approximately equal average polarizabilities and differ with the anisotropy values.
5) The inadditivity of polarizability of polyadducts $C_{60/70}X_n$ with $n = 3$ appears ($\Delta\alpha > 0$) and increases with the increase of n values (*e.g.*, the polarizability of $C_{60}O_n$ epoxides achieves maximal value 87.4 E^3 at $n = 15$ and then diminishes to 85.3 E^3 for $n = 30$).

A theoretical model of the **FD** polarizability has been proposed. It should be taken into account in the design of fullerene derivatives with high polarizability.