Scientific Research Publishing

Measurements for Electric Dipole of Selected Clusters Sc_n-C_{60} in Gaseous Phase

Mohamad Abd El Rahim[1,2*], Rabih Mourad[2], Michel Broyer[3], Iyad Karamé[2]

[1]Department of Physics, Lebanese University, Faculty of Sciences I, Beirut, Lebanon
[2]Laboratory of Catalysis Organometallic and Material LCOM, Department of Chemistry, Lebanese University, Faculty of Sciences I, Beirut, Lebanon
[3]Institut Lumière Matière, UMR 5306, Univ-Lyon, Université Claude Bernard Lyon 1, Villeurbanne, France
Email: *marc-abd80@hotmail.com

Abstract

We have measured the electric dipole moment of several Sc_n-C_{60} molecules (n = 1 - 6) in gaseous phase, by coupling a matrix-assisted laser desorption source to an electric beam deflection setup which is an electric equivalent of the famous Stern Gerlach [1] one. Experimental results are compared to a qualitative charge transfer that occurs between Sc and fullerene.

Keywords

Electric Dipole Moment, Sc_n-C_{60}, Electric Deflection, Charge Transfer

1. Introduction

Measurement of electric dipole moment is an excellent probe of structure and dynamics of molecules since it is directly related to the geometry and charge transfer in compounds [2] [3]. In literature, we find many detailed results and experiments on molecules and their electronic optical proprieties in solution with a solvent [4] [5] [6]. Few results are available on systems in gas phase at their fundamental states. Naturally, experiments in vacuum for isolated molecules lead to a better information about systems and their fundamental proprieties. Moreover, the effect of solvent on molecules should be included in the calculation [7] by considering any model which is relatively a hard task, thus calculation in gas phase is more practical if we are intended to compare experimental results to theoretical ones. The molecular beam deflection technique is a powerful experimental method that is used for many years [8] [9] [10] [11] in order to measure magnetic and electric dipole of molecules in gas phase. This method is inspired from the famous Stern-Gerlach [1] experiment (where an inhomoge-

neous magnetic field ensures the deflection of an atomic silver beam). For many years, improvements are realized on the experiment but still relatively limited to simple molecules. Our Experimental setup [12] developed in Lyon (France) allows the extension of studies on large range of molecules starting from simple atoms to biomolecules and clusters. This extension is due to the high-resolution power in the determination of mass and position of molecules. In this report, we will present a new result on complex system of Sc_n-C_{60}, where we have succeeded to produce a beam with several sizes of such molecule. The number n represents how many atoms of scandium are located on the cage of the fullerene C_{60}. In fact, fullerene metals complexes family are novel and very promising compounds for optical and nano-applications [13] [14] [15] and the particular importance of such system is in the clear origin of the permanent electric dipole which emerges from the charge transfer that occurs between the transition metal of scandium and the fullerene. This charge transfer or interaction between donor and acceptor is similar to push-pull system [16] and any experimental data on it will be very helpful to achieve better understanding of optical and electronic proprieties of several systems used in the area of nano-technological devices. Moreover, experimental data on complex molecules is very interesting for theoretical calculation in order to test and assess their validity. In fact, calculation is used to compute the geometry and the electronic properties of compounds [17] [18] and there appears the importance of experimental results especially for complex system where pure theoretical studies are not sufficient to confirm the molecular proprieties.

2. Experimental Setup

As mentioned above, we used the molecular beam deflection technique to measure electric dipole for compounds at in vacuum. In order to produce the beam molecules, a double-laser vaporization source coupled to a pulsed neon carrier gas is used (Figure 1). Two pure rod of fullerene C_{60} and scandium are inserted in the source, and are distanced about one cm from each other. The third harmonic of a Nd^{3+}: YAG laser (355 nm) ensures the vaporization of rods. The molecules of C_{60} generated by the first desorption go through the metal vapor. The new metal-C_{60} compounds are carried out by a pulsed valve of neon gas which is synchronized with the desorption laser shot. At the exit of the source, the beam molecule is thermalized in a 5 cm-long nozzle (3 mm diameter). As a result, a thermal molecular beam was produced without supersonic expansion and then two skimmers and two slits are used to collimate the beam. A mechanical chopper placed after the first slit allows the selection and the measurement of the beam velocity, molecules pass then through a 15 cm-long electric deflector. The two cylindrical poles of the deflector are about 1.7 mm apart. This specific geometry was designed in order to produce an inhomogeneous "two-wire" electric field. The electric field F and the field gradient $\partial F/\partial z$ are both perpendicular to the axis of the beam and are approximately constant over its width.
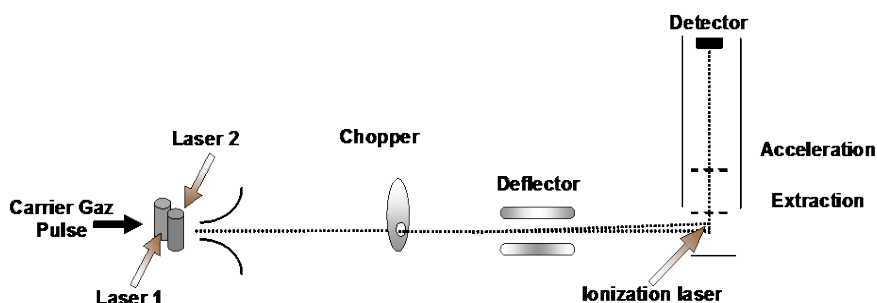
Figure 1. Experiment principle representation.

The molecular electric dipole moment μ interacts with the electric field inside the deflector, thus an instantaneous force *f* along the field direction acts on the molecule:

$$f = \mu \, \partial F / \partial Z$$

Z is the direction of the electric field and of its gradient).

Under this condition the beam trajectory will be deflected with an amount proportional to the time-averaged value ($\langle \mu_z \rangle$), but it also depends on the mass and the speed of the molecules. After the deflector and about 1.025 m, an argon fluoride ArF (193 nm) is used to ionize molecules so they can be detected. A time of flight mass spectrometer ensures the extraction and the measurement of the mass of each compound in the beam. Finally, a position-sensitive detector coupled to the spectrometer allows the determination of the position of the beam.

By comparing and analyzing the beam profiles of respectively deflected and non-deflected molecules for several electric fields, we can determine the dipole of the selected molecule. For a molecule of mass *m* and a velocity *v*, a measured deviation *d* of the beam is given by:

$$d = K \frac{f}{mv^2}$$

K is a geometrical constant, determined by calibration with lithium and sodium that are chosen since we know the polarizability of each with high accuracy from interferometry measurements [19].

3. Results

A molecular beam containing several sizes of $Sc_n\text{-}C_{60}$ was recorded at room temperature (**Figure 2**). The number of scandium atoms n adsorbed on the fullerene varies from 1 to 8. The mass spectrum detected confirms the presence of the compounds in the beam.

The Position sensitive detection PSD allows measuring the position of each selected compound respectively with and without electric field in the deflector. As described previously by measuring the beam shift in position, the average force, thus $\langle \mu_z \rangle$ is determined.
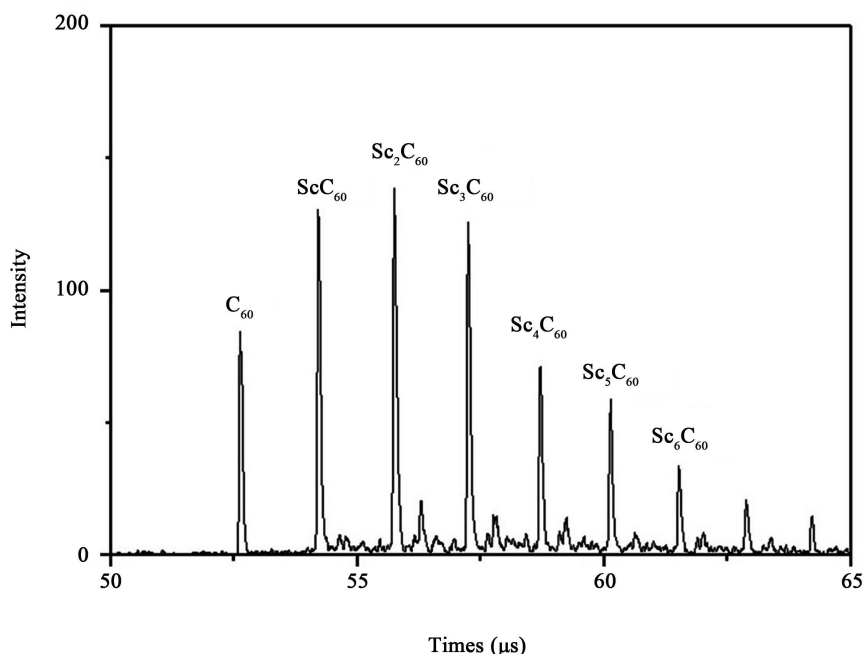
Figure 2. Mass spectrum of Sc_n-C_{60} molecules recorded with ArF ionization laser.

Using the Langevin-Curie model, where the dipole moment is statistically orientated in the electric field: $\langle \mu_z \rangle = \chi \cdot F$ and the electric susceptibility is given by:

$$\chi = \frac{\langle \mu \rangle}{F} = \frac{\mu^2}{3kT} + \alpha$$

In the metal-C_{60} molecule, the polarizability α is close to the C_{60} one ($\alpha \sim 80°A3$). [20] An experimental measurement of $\langle \mu_z \rangle$ leads to the determination of the electric dipole. **Figure 3** shows the evolution of the dipole moment with the size of the compound (n). It was shown that the electric dipole moment increases with the size of the molecule Sc_n-C_{60}.

4. Discussion of Results and Comparison to Theoretical Prediction

Theoretical calculation was done previously on M-C_{60} where M is an alkali metal found generally that the metal has its most stable site at the center of the hexagonal ring of the fullerene [21] [22] and the charge transfer between metal and fullerene is about one electron. For transition metal and especially for several atoms case, the quantum calculation seems to be more difficult and no group yet has developed it. Therefore, we have developed a simple statistical model where the electric dipole moment and charge transfer can be obtained by considering all possible geometric configuration that correspond to repartition of n atoms of scandium on the 20 hexagonal sites of the fullerene C_{60}. This model is based on Boltzmann distribution, where we consider the interaction between metallic ions.

The adjusting between experimental results and the ones obtained from the model above leads to estimate the charger transfer per atom. **Figure 4** shows the evolution of the charge transfer per scandium atom versus to the size of the cluster Sc_n-C_{60} and that is according to adjusting explained above.
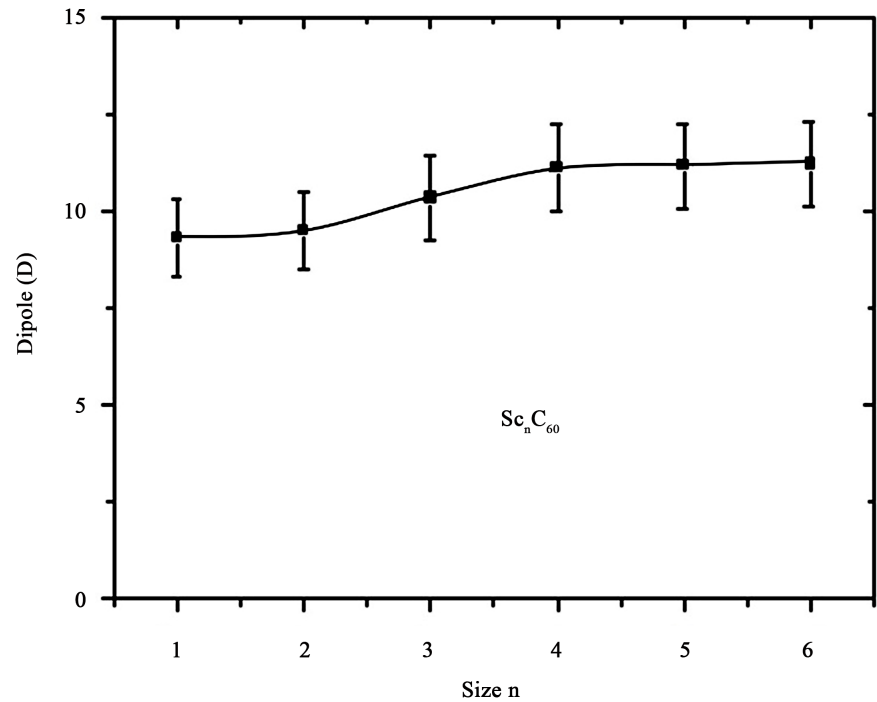

Figure 3. Evolution of electric dipole in Debye units versus the size n for the Sc_n-C_{60}.
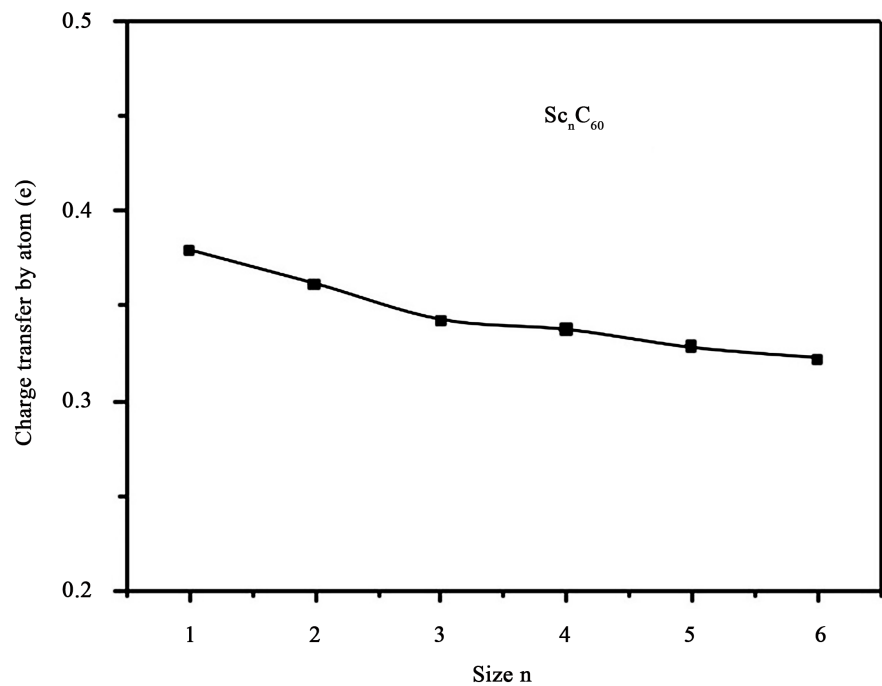

Figure 4. Evolution of the calculated charge transfer per atom versus the size n for the Sc_n-C_{60}.

This qualitative result (based on a simple semi-classical model) shows that the charge transfer per atom decreases with the number of adsorbed scandium atoms that is reflecting simply the fact that a saturation of charge transfer may occur between the fullerene and the metal part when n increases.

The dipole increases slightly, which means the molecules symmetry is changed slightly with the load of Sc, otherwise the dipole will decrease drastically, whereas transfer of charge decreases due to the saturation. From that we can imagine that adsorbed scandium atoms are more located on one side, relatively in close sites. We would like to notice that this preliminary point of view should be completed by full quantum calculation studies to compare with our experimental results.

5. Conclusion

The permanent electric dipole moment of several compounds Sc_n-C_{60} (n = 1 to 6) is measured by using the molecular beam deflection technique. The analysis of results gives an idea about the evolution of the dipole versus the size. In order to understand better our results, we have developed a statistical model that shows qualitatively a decrease in the charge transfer per atom versus the size of the cluster, but still complementary quantum or theoretical calculation is essential to achieve a deep interpretation of results. Even so, our experimental data can be used to test the validity of eventual calculations in the future and may seriously help to provide a better understanding for the studied systems.

Acknowledgements

References

[1] Gerlach, W. and Stern, O. (1924) *Annals of Physics*, **379**, 673-699. https://doi.org/10.1002/andp.19243791602

[2] Bonin, K.D. and Kresin, V.V. (1997) Electric-Dipole Polarizabilities of Atoms, Molecules and Clusters. World Scientific, Singapore. https://doi.org/10.1142/2962

[3] Billas, I.M.L., Châtelain, A. and de Heer, W.A. (1997) *Journal of Magnetism and Magnetic Materials*, **168**, 64-84. https://doi.org/10.1016/S0304-8853(96)00694-4

[4] Runser, C., Fort, A., Barzoukas, M., Combellas, C., Suba, C., Thiébault, A., Graff, R. and Kintzinger, J.P. (1995) *Chemical Physics*, **193**, 309-319. https://doi.org/10.1016/0301-0104(95)00427-P

[5] Oudar, J.L. and Zyss, J. (1982) *Physical Review A*, **26**, 2016-2027. https://doi.org/10.1103/PhysRevA.26.2016

[6] Kanis, D.R., Ratner, M.A. and Marks, T.J. (1994) *Chemical Reviews*, **94**, 195-242. https://doi.org/10.1021/cr00025a007

[7] Painelli, A. and Terenziani, F. (2000) *The Journal of Physical Chemistry A*, **104**, 11041-11048. https://doi.org/10.1021/jp0016075

[8] Scheffers, H. and Stark, J. (1934) *Physikalische Zeitschrift*, **35**, 625-627.

[9] Miller, T.M. and Bederson, B. (1978) *Advances in Atomic and Molecular Physics*, **13**, 1-55. https://doi.org/10.1016/S0065-2199(08)60054-8

[10] Bucher, J.P. and Bloomfield, L.A. (1993) *International Journal of Modern Physics B*, **7**, 1079-1114. https://doi.org/10.1142/S0217979293002249

[11] Abd El Rahim, M., Antoine, R., Broyer, M., Rayane, D. and Dugourd, Ph. (2005) *The Journal of Physical Chemistry A*, **109**, 8507-8514. https://doi.org/10.1021/jp053127p

[12] Abd El Rahim, M., Antoine, R., Arnaud, L., Barbaire, M., Broyer, M., Clavier, Ch., Compagnon, I., Dugourd, Ph., Maurelli, J. and Rayane, D. (2004) *Review of Scientific Instruments*, **75**, 5221-5227. https://doi.org/10.1063/1.1813112

[13] Ge, M., Nagel, U., Hüvonen, D., Rõõm, T., Mamone, S., Levitt, M.H., Carravetta, M., Murata, Y., Komatsu, K., Chen, J.Y.-C. and Turro, N.J. (2011) *The Journal of Chemical Physics*, **134**, Article ID: 054507. https://doi.org/10.1063/1.3535598

[14] Mateo-Alonso, A., Guldi, D.M., Paolucci, F. and Prato, M. (2007) *Angewandte Chemie International Edition in English*, **46**, 8120-8126. https://doi.org/10.1002/anie.200702725

[15] Bai, J., Zeng, X.C., Tanaka, H. and Zeng, J.Y. (2004) *Proceedings of the National Academy of Sciences*, **101**, 2664-2668. https://doi.org/10.1073/pnas.0308467101

[16] Oudar, J.L. (1977) *The Journal of Chemical Physics*, **67**, 446-457. https://doi.org/10.1063/1.434888

[17] Anafcheh, M. and Ghafouri, R. (2012) *Computational and Theoretical Chemistry*, **1000**, 85-91. https://doi.org/10.1016/j.comptc.2012.09.026

[18] Ensing, B., Costanzo, F. and Silvestrelli, P.L. (2012) *The Journal of Physical Chemistry A*, **116**, 12184-12188. https://doi.org/10.1021/jp311161q

[19] Ekstrom, C.R., Schmiedmayer, J., Chapman, M.S., Hammond, T.D. and Pritchard, D.E. (1955) *Physical Review A*, **51**, 3883-3888. https://doi.org/10.1103/PhysRevA.51.3883

[20] Ballard, A., Bonin, K. and Louderback, J. (2000) *The Journal of Chemical Physics*, **113**, 5732-5735. https://doi.org/10.1063/1.1290472

[21] Östling, D. and Rosén (1997) *Chemical Physics Letters*, **281**, 352-359. https://doi.org/10.1016/S0009-2614(97)01252-9

[22] Hamamoto, N., Jitsukawa, J. and Satoko, C. (2002) *The European Physical Journal D*, **19**, 211-221.

Graphical Abstract
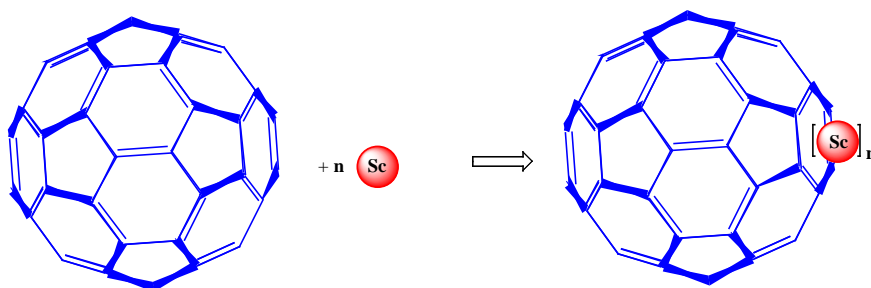
Electric dipole moments of several Scn-C60 (n = 1 - 6) molecules have been measured in gaseous phase using matrix-assisted laser desorption source coupled to an electric beam deflection setup—Stern Gerlach like.