

# Susceptibility and electric dipole in metal C<sub>60</sub> compounds

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**Abstract.** The permanent electric dipole moment of metal atom-C<sub>60</sub> compounds is measured. A column (alkali) and a row (transition metals) of the periodic table are systematically investigated. Most of the experimental results are obtained at high temperature when the atom is mobile on the C<sub>60</sub> cage. For a given example (NaC<sub>60</sub>), the dipole moment is also measured by a different method at low temperature and both results are consistent. For alkali, the results are compared to *ab initio* calculations. A good agreement is obtained, both for absolute values and for the evolution of the bonding in the alkali column. For transition metals, the relative values of the dipole moments are in qualitative agreement with the ionic character of the compounds.

**PACS.** 33.15.Kr Electric and magnetic moments (and derivatives), polarizability, and magnetic susceptibility – 61.48.+c Fullerenes and fullerene-related materials – 31.15.Ew Density-functional theory

## 1 Introduction

The electric polarizability of atoms and small molecules are studied for a long time by various methods [1]. Only recently, complex systems started to be measured [2]. For such systems, which have very complicated excited states, the ground state properties are the most important for applications or to test theoretical methods and calculations. Among complex systems, the metal-fullerene molecule is of particular interest. It is a very simple system where the electric dipole clearly emerges from the charge transfer between the metal and C<sub>60</sub>. The dynamics of the molecule can be easily simplified by considering the jumps of the metal atom from one site to another. Moreover, a better understanding of the metal-fullerene interaction is very important for electric and optical devices in the nanotechnology area, including superconductivity [3,4]. On the experimental side, the metal coated fullerenes were studied by mass spectrometry [5] and photoelectron spectroscopy [6,7]. The theoretical calculations of MC<sub>60</sub> (where M is a metal atom) concern mainly alkali metals [8–13]. They generally found that the most stable site for the metal atom is the center of a hexagonal ring and that the charge transfer is close to 1 electron. In the present paper, we focus on the dipole moment of MC<sub>60</sub> where M is an alkali or a transition metal. For these systems, the dynamics of the atomic motion on the C<sub>60</sub> surface is important. For alkali atoms, the measurements are performed as a function of the temperature and we show that we are able to measure the electric dipole mo-

ment both at low temperature when the molecule is rigid and at high temperature when the atom is mobile on the C<sub>60</sub> surface [14]. The results are compared to *ab initio* calculations. For transition metals, the measurements are performed mainly at high temperature and the electric dipole value is obtained for a series of metals and compared to the ionic character of the C<sub>60</sub>-metal bond.

## 2 Experimental

The electric dipole susceptibility of metal C<sub>60</sub> compounds is measured by molecular beam deflection in an inhomogeneous electric field [14]. MC<sub>60</sub> molecules are produced in a double rod laser vaporization source. A first laser desorbs C<sub>60</sub> molecules from a pure C<sub>60</sub> rod. The molecules are carried out by a helium pulse. One centimeter after the first rod, C<sub>60</sub> molecules go through a metal vapor produced by laser ablation of a pure metal rod. Metals used in the experiments are alkali metals and transition metals. Clusters are then thermalized in a 5 cm long nozzle. The temperature of the nozzle can be adjusted from 77 K to 500 K. The molecular beam is skimmed, collimated by two rectangular slits and goes through the electric deflector. The deflector produces a two wire electric field [1]. The molecules are ionized with an ArF laser (193 nm), 1 m after the deflector, in the extraction region of a position-sensitive time of flight mass spectrometer. The deviation  $d$  of a molecule is given by:

$$d = K \frac{\langle \mu_z \rangle}{mv^2} \nabla F_z \quad (1)$$

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where  $v$  and  $m$  are the velocity and the mass of the molecule,  $K$  is a geometrical factor and  $\nabla F_Z$  is the gradient of the electric field in the deflector.  $Z$  is the direction of the field which is perpendicular to the molecular beam axis.  $\langle \mu_Z \rangle$  is the time-averaged value of the dipole of the molecule in the electric field. The velocity is selected and measured with a mechanical chopper. The arrival time at the detector is a function of the mass  $m$  of the particle and of the deviation  $d$ .

### 3 Results for alkali C<sub>60</sub>

The beam profile measured for MC<sub>60</sub> depends strongly on the cluster temperature. Therefore, we will discuss two main situations: the first one occurs at low temperature when the cluster is rigid, the second one occurs at high temperature when the cluster is no more rigid and the dipole may be statistically oriented in the electric field.

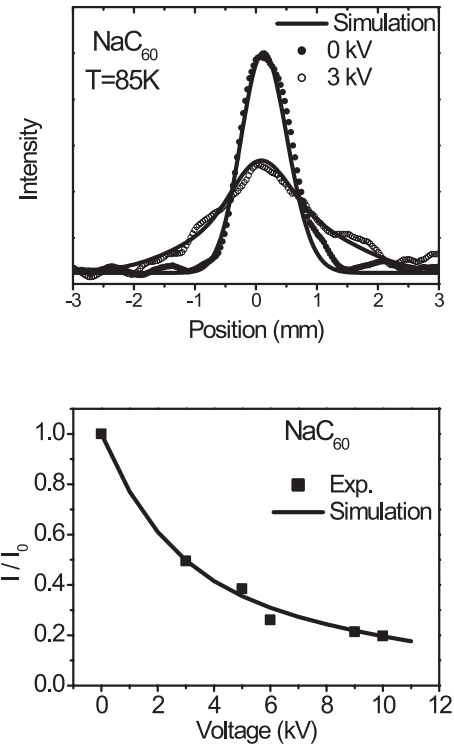
#### 3.1 Rigid clusters

In this case  $\langle \mu_Z \rangle$  may be written:

$$\langle \mu_Z \rangle = \mu_0 \langle \cos \theta \rangle \quad (2)$$

where  $\theta$  is the angle between the direction  $Z$  of the electric field and the direction  $z$  of the electric dipole. As a consequence of equations (1, 2), the deviation of the molecules in the beam depends on their average orientation with respect to the electric field. The result is a broadening of the beam when the electric field increases. This situation is illustrated for NaC<sub>60</sub> at 85 K in Figure 1. The motion of NaC<sub>60</sub> in the electric field is similar to that of a symmetric top body in the gravitational field. It may be classically calculated as it was recently demonstrated [15]. The permanent electric dipole may be deduced from the comparison between experiment and simulation. Profiles of deviation were systematically recorded as a function of the voltage across the deflector. In the low part of Figure 1, we have plotted the variation of the intensity at the peak maximum as a function of the voltage across the deflector. The relative intensity decreases as the voltage increases. It is a measure of the broadening of the beam. This curve is fitted in order to determine the experimental permanent dipole value. The inertia moments and the rotational temperature are needed for the simulation. In our experiment, the molecules are thermalized at the nozzle temperature.

To determine the lowest energy structure of NaC<sub>60</sub>, we performed DFT calculations using the hybrid functional B3LYP and the LANL2DZ and SDD basis sets (see below). The lowest energy structure is obtained with the sodium atom located above the center of an hexagon in agreement with previous authors [8–13]. The distance between the sodium atom and the center of the hexagon is equal to 2.28 Å. This allows to calculate the inertia moments of the molecule and to simulate its rotational motion in the electric field. The fit of the experimental curve shown in Figure 1 leads to  $\mu = 14.8 \pm 1.5$  Debye for NaC<sub>60</sub> at 85 K.



**Fig. 1.** Upper part, experimental (symbols) and calculated (full line) beam profiles of NaC<sub>60</sub> for two values of the voltage in the deflector (0 kV and 3 kV). Lower part: variation in the intensity at the maximum of the beam profile as a function of the voltage across the deflector. In both parts, the full lines corresponds to calculated profiles for  $\mu = 14.8$  D. The temperature was 85 K.

#### 3.2 Non rigid clusters

By increasing the temperature, the alkali atom becomes mobile and can skate from one site to another one on the surface of the fullerene. The permanent electric dipole becomes statistically oriented in the electric field and a global deviation of the beam is observed [14]. In that case:

$$\langle \mu_Z \rangle = \chi F_Z \quad (3)$$

and the electric susceptibility  $\chi$  is given by:

$$\chi = \frac{\langle \mu^2 \rangle_T}{3kT} + \alpha. \quad (4)$$

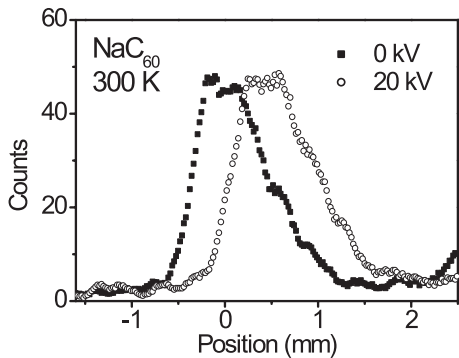
In the metal-C<sub>60</sub> molecule, the polarizability  $\alpha$  is close to the C<sub>60</sub> polarizability ( $\alpha \sim 80$  Å<sup>3</sup> [16, 17]).  $\langle \mu^2 \rangle_T$  is close to  $\mu^2$  at  $T = 0$  K.  $\mu$  probably tends to slightly increase with the temperature, mainly because the average distance between the metal atom and C<sub>60</sub> increases when the metal atom leaves its hexagonal site [12]. As illustrated in previous measurements performed at high temperature,  $\alpha$  is small as compared to  $\mu^2/3kT$  [14, 18].

Figure 2 shows the beam profile observed for NaC<sub>60</sub> at a voltage of 20 kV compared to 0 kV. A clear deviation is observed in agreement with equations (1, 3, 4). Formula (4) is valid when the hopping frequency of the alkali

**Table 1.** Relative energy of the pentagonal site as compared to the hexagonal site. Distance between the atom and the center of the ring, Mulliken charge on the alkali atom and permanent electric dipole for AC<sub>60</sub> for the metal atom on the hexagonal and pentagonal sites.

	Calculation	Hexagonal site			$\Delta E$ (eV)	Pentagonal site		
		Distance (Å)	Charge (e)	Dipole (D)		Distance (Å)	Charge (e)	Dipole (D)
LiC <sub>60</sub>	a	1.87	0.71	9.89	-0.017	1.92	0.74	10.23
	b	1.86	0.67	9.77	-0.013	1.92	0.72	9.93
	c		0.78	9.57			0.81	10.70
NaC <sub>60</sub>	a	2.35	0.86	14.35	0.040	2.39	0.86	15.08
	b	2.28	0.90	13.63	0.033	2.32	0.93	14.26
	c		0.90	13.93			0.90	14.98
KC <sub>60</sub>	a	2.79	0.97	18.02	0.039	2.82	0.96	18.70
	b	2.78	0.96	17.93	0.039	2.81	0.96	18.58
	c		0.99	17.71			0.99	18.53
RbC <sub>60</sub>	a	3.01	0.96	19.66	0.039	3.04	0.96	20.38
	b	2.97	0.96	19.38	0.039	2.99	0.96	20.05
	c		0.99	19.40			0.99	20.28
CsC <sub>60</sub>	a	3.25	0.97	21.53	0.035	3.27	0.97	22.1
	b	3.19	0.98	20.98	0.035	3.19	0.97	20.9
	c		0.99	20.90			0.99	21.9

<sup>a</sup> B3LYP/LANL2DZ calculation. <sup>b</sup> B3LYP/SDD calculation. <sup>c</sup> HF/LANL2DZ//B3LYP/LANL2DZ calculation.

**Fig. 2.** Beam profiles of NaC<sub>60</sub> at 300 K for two different voltages in the deflector (0 kV and 20 kV).

atom is large as compared to the rotational frequency of the molecule. When the temperature decreases, a broadening of the beam profile occurs and formula (4) is no longer valid [14,18,19]. This evolution is perfectly reproduced by a simple statistical model of relaxation which takes into account the rotational motion of the molecule. Formula (4) may be generalized to (see Ref. [19]):

$$\chi = \alpha + \frac{\langle \mu^2 \rangle_T}{3kT} \frac{1 + \cos^2(\gamma)\Omega^2\tau^2}{1 + \Omega^2\tau^2} \quad (5)$$

where  $\Omega$  is the angular velocity of the molecule and  $\gamma$  the angle between the molecular angular momentum axis and the axis of the electric field.  $\tau$  is the characteristic relaxation time due to the hopping of the metal atom on the C<sub>60</sub> cage. This model allows a precise determination of the permanent dipole of the molecule.

It is interesting to compare the dipole moment of NaC<sub>60</sub> obtained by the two independent methods at low and high temperatures. At high temperature, we find  $\mu = 16.3 \pm 1.6$  Debye [18] as compared to  $\mu = 14.8 \pm 1.5$  Debye at 85 K. The two values are in agreement within the experimental errors. Moreover,  $\mu$  is expected to slightly increase with the temperature, because as already noted the averaged distance between the C<sub>60</sub> cage and the metal atom slightly increases. This is in agreement with experimental results.

### 3.3 Calculations

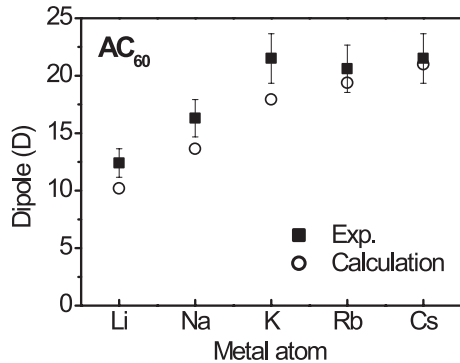
Equilibrium structures and permanent electric dipoles were calculated for AC<sub>60</sub> molecules (with A = Li, Na, K, Rb and Cs). Experimental results for Li, K, Rb and Cs were reported in a previous paper [18]. As mentioned above, we performed DFT calculations using the hybrid functional B3LYP and the LANL2DZ [20] and SDD [21] basis sets. Geometries with the metal atom above the center of a pentagon or a hexagon were optimized. The C<sub>60</sub> is frozen and only the distance between the metal atom and the center of the ring is optimized. HF single point calculation was also performed with the LANL2DZ basis set using the B3LYP-DFT/LANL2DZ optimized geometry. All the calculations were performed with the Gaussian 98 package [22].

Results are summarized in Table 1. First, in agreement with the recent results of Hamamoto *et al.* [12], we found that for lithium the lowest energy structure is obtained with the lithium located above a pentagonal ring. For all the other alkali atoms, the metal atom is located

**Table 2.** Comparison between experimental results and theoretical calculations. The calculated dipole value is given for the lowest energy structure.

	LiC <sub>60</sub>	NaC <sub>60</sub>	KC <sub>60</sub>	RbC <sub>60</sub>	CsC <sub>60</sub>
Exp. <sup>a</sup>	12.4 ± 2.0 <sup>d</sup>	16.3 ± 1.6 <sup>d</sup> 14.8 ± 1.5 <sup>e</sup>	21.5 ± 2.2 <sup>d</sup>	20.6 ± 2.1 <sup>d</sup>	21.5 ± 2.2 <sup>d</sup>
Theory <sup>b</sup>	9.93	13.63	17.93	19.38	20.98
Theory <sup>c</sup>	11.62	14.63	18.49		

<sup>a</sup> From reference [18]. <sup>b</sup> This work, B3LYP/SDD calculation. <sup>c</sup> Reference [12]. <sup>d</sup> High temperature value (see text). <sup>e</sup> 85 K value.



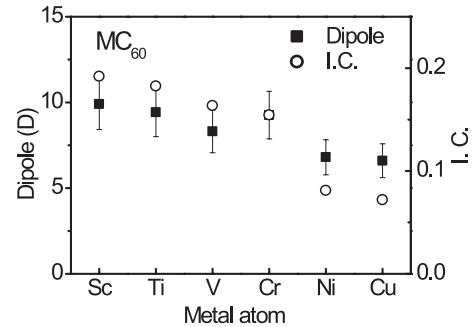
**Fig. 3.** Electric dipole moments of AC<sub>60</sub> where A is an alkali atom. Experimental results are compared to B3LYP/SDD calculations with the structure of lowest energy.

above a hexagonal ring. The different values obtained for the dipole are in agreement. In particular HF and DFT values are very close. One can notice that the increase in the basis set induces a slight decrease in the value of the electric dipole. This is observed for every compound. The value obtained with the largest basis set for NaC<sub>60</sub> is in very good agreement with the experimental value obtained at low temperature. The dipoles calculated for the sodium atom above a pentagonal ring or a C–C bond (see Ref. [12]) are higher and get closer to the experimental value obtained at high temperature where the metal atom skates on the fullerene surface and explores various sites.

For other alkali atoms, experimental values are available only with metal atoms mobile on the fullerene surface. They are given in Table 2 and plotted in Figure 3. The dipole increases as the size of the alkali atoms increases. A good agreement is observed between experiment and calculation even if calculations slightly underestimate the experimental value which can be attributed to the effect of temperature. The increase in dipole moment is due to an increase both in the charge transfer and in the equilibrium distance (see Tab. 1).

## 4 Results for transition metal-C<sub>60</sub>

The system M–C<sub>60</sub> where M is a transition metal may also be investigated by the same methods. Figure 4 shows results obtained for a group of transition metals belonging to the same row of the periodic table. The measurements are performed at room temperature. Electric dipoles are



**Fig. 4.** Electric dipole moments of MC<sub>60</sub> where M is a transition metal atom. Experimental results are compared to the ionic character (see text). The IC scale has been adjusted so that  $\mu$  and IC are on the same position for chromium.

in the range of 6 to 10 Debye which is slightly lower than the value measured for potassium which belongs to the same row in the periodic table. For transition metals, the dipole tends to decrease as the number of electron increases but no dramatic change is observed in Figure 4. For these molecules, *ab initio* calculations are much more difficult. Therefore, we compare the experimental results to the empirical ionic character (IC) defined by [23]:

$$IC = (IP_{C_{60}} + EA_{C_{60}} - IP_{\text{metal}} - EA_{\text{metal}}) / 18.48 \quad (6)$$

where  $IP$  and  $EA$  are in eV. Only relative values of  $IC$  may be compared to the relative values of the permanent dipole  $\mu$  and we expect to obtain a larger permanent dipole for a stronger ionic character. This comparison is shown in Figure 4. The agreement is qualitatively good in view of this crude model. In particular, the comparison outlines that, as this is observed for alkali-C<sub>60</sub> compounds, the evolution of the dipole value is mainly due to the evolution of the ionization potential of the metal atom.

## 5 Conclusion

We have measured the electric dipole moments of the system metal atom-C<sub>60</sub> for alkali and transition metals. We have checked for sodium, that the measurements performed at low and high temperatures are consistent. This demonstrates that the simple models used in both cases to interpret experimental signals are valid. A column and a row of the periodic table have been investigated. This allows to have a complete description of the metal C<sub>60</sub>

bonding and of the evolution of the charge transfer in these nanosystems as a function of the valence or of the size of the electronic core of the metal atom. *Ab initio* calculations for alkali metals are in good agreement with experiment, both for absolute values and for the evolution of the charge transfer in the column. For transition metal clusters, our experimental results will be important to test future *ab initio* calculations.

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