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# Direct measurement of the electric polarizability of isolated C<sub>60</sub> molecules

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Since the discovery of the C<sub>60</sub> molecule,<sup>1,2</sup> fullerenes have been extensively studied, mainly in the condensed matter phase. A wide variety of interesting chemical and physical properties have been measured. Electric dipole polarizability is an important physical property to determine the electronic structure of clusters.<sup>3</sup> The electric polarizability of C<sub>60</sub> in bulk samples has been obtained from optical and conductivity measurements. The values which are extracted from the dielectric constant of fullerites crystals through the Clausius–Mossotti relation, are in the range  $\alpha(\text{C}_{60}) \cong 80\text{--}90 \text{ \AA}^3$ .<sup>4</sup> Surprisingly, up to date, no reliable measurement of the electric polarizability of isolated C<sub>60</sub> molecules has been reported. The only reported experiment in gas phase<sup>5</sup> gives a values of order of  $1000 \text{ \AA}^3$  which is inconsistent with bulk value informations. On the theoretical point of view, a large number of quantum mechanical or empirical calculations of the polarizability of isolated C<sub>60</sub> molecules have been reported in the literature. The calculated values form a broad distribution centered around  $80\text{--}85 \text{ \AA}^3$  extending up and down by a factor of 2 (for a review see, for example, Ref. 4). Thus, it is of fundamental interest to have a direct and accurate value of the polarizability of isolated C<sub>60</sub> molecules, both to test the ability of calculations to determine the electronic properties of this molecule and to understand the possible changes in the electronic polarizability of C<sub>60</sub> in fullerite crystals due to intermolecular interactions.

In this paper, we present the first direct measurement of the electric polarizability of isolated C<sub>60</sub> molecules by molecular beam deflection technique. The polarizability of C<sub>60</sub> molecules has been calibrated using the value of the literature for the polarizability of the lithium atom.<sup>6</sup>

The C<sub>60</sub> molecular beam is generated with a laser vaporization source. The experimental setup is similar to the one described in Ref. 7. A laser vaporization source for the C<sub>60</sub> production and a chopper for the velocity measurements, have been added. Briefly, a fullerene thin film is grown on a pure copper rod. We use a mixed fullerene refined powder (purchased by MER Corporation) which essentially consists of a C<sub>60</sub> and C<sub>70</sub> mixture (about 90% C<sub>60</sub>, 10% C<sub>70</sub>). Fullerene molecules are laser desorbed from the film into the middle of a krypton pulse generated with a piezoelectric pulse valve. For the laser desorption, we use the third harmonic of a Nd<sup>3+</sup>:YAG laser. A very low laser power is used to avoid fragmentation of C<sub>60</sub> and C<sub>70</sub> fullerenes and nucleation of larger sizes. The vapor is expanded through a nozzle and skimmed into a molecular beam. The molecular beam is

collimated by two slits and it passes between the two poles of the deflector. The poles are two 15 cm long cylinders which are 1.7 mm apart. This geometry provides an inhomogeneous electric field which is equivalent to an “electrical two-wire field.”<sup>8</sup> For a voltage of 27 kV, the values of the electric field  $E$  and of the gradient of the electric field ( $dE/dz$ ) are, respectively,  $1.62 \times 10^7 \text{ V/m}$  and  $2.88 \times 10^9 \text{ V/m}^2$  in the center of the deflector. The deflection of C<sub>60</sub> is measured 1 m after the deflector in the extraction region of the first time of flight. The deviation  $d$  is proportional to the averaged polarizability  $\alpha$  of the molecules,

$$d = K \frac{\alpha E}{mv^2} \frac{dE}{dz}, \quad (1)$$

where  $K$  is a constant depending on the geometry of the apparatus,  $m$  the mass, and  $v$  the velocity of the molecules. The neutral C<sub>60</sub> molecules are ionized by the fifth harmonic of a Nd<sup>3+</sup>:YAG laser ( $\lambda = 212.8 \text{ nm}$ ). C<sub>60</sub> ions are then accelerated perpendicularly to the neutral beam in the time of flight mass spectrometer. The electric field in the extraction and acceleration region of the time of flight are adjusted so that the arrival time of a C<sub>60</sub> molecule at the detector is sensitive to the initial position of the molecule in the extraction region (position sensitive time-of-flight technique). The deflection  $d$  of C<sub>60</sub> is determined by the comparison of its arrival time at the detector with electric field in the deflector to the arrival time measured without electric field in the deflector.<sup>7</sup> C<sub>60</sub> ions are detected on microchannel plates. The

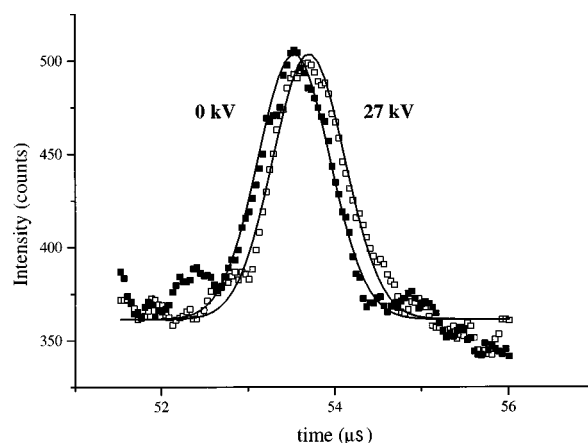


FIG. 1. Arrival time distribution profiles of C<sub>60</sub> molecules, with and without electric field in the deflector (0 kV and 27 kV). The solid lines represent the fits obtained with a Gaussian profile. The time shift between the two profiles is 160 ns.

arrival time distribution (ATD) profiles of  $C_{60}$  molecules are then recorded with a multichannel scaler (turbo-MCS EG&G-Ortec). The velocity of  $C_{60}$  in the beam is selected and measured by means of a chopper that is located directly in front of the first slit.

Figure 1 shows ATD profiles of  $C_{60}$  molecules, with and without electric field in the deflector (0 kV and 27 kV). A large amount of ATD profiles with and without electric field were recorded. First of all, we see that the photoionization of  $C_{60}$  with 212.8 nm laser radiation leads to a sharp and symmetric peak. Only a very few fragmentation and no tail due to delayed ionization are observed. With wavelength inferior or close to 212.8 nm, direct two-photon ionization is the dominant process.<sup>9</sup> The ATDs have been fitted with a Gaussian profile (see solid lines in Fig. 1). The difference in arrival time for  $C_{60}$  molecule, with and without electric field, deduced from all the profiles that we have recorded is 160 ns. This difference corresponds to a deviation of  $d=0.205$  mm. In order to have an accurate absolute value of the polarizability of  $C_{60}$ , we calibrate the one obtained for lithium atoms. Lithium atomic beam was obtained by vaporizing a pure isotopically lithium rod ( $^7\text{Li}$ ) into a helium pulse. Using the same electric field in the deflector, the polarizability of  $C_{60}$  is given by

$$\frac{\alpha_{C_{60}}}{\alpha_{\text{Li}}} = \frac{d_{C_{60}}}{d_{\text{Li}}} \frac{m_{C_{60}}}{m_{\text{Li}}} \left( \frac{v_{C_{60}}}{v_{\text{Li}}} \right)^2. \quad (2)$$

The deflections with 27 kV, are 0.205 mm and 0.550 mm for  $C_{60}$  molecules and lithium atoms, respectively. Velocities are 550 m/s for  $C_{60}$  and 1920 m/s for Li. This leads, with the literature value of Li atom polarizability [ $24.3 \text{ \AA}^3$  (Ref. 6)], using Eq. (2), to a polarizability of  $76.5 \text{ \AA}^3$  for  $C_{60}$  molecules.

The precision on the value of the polarizability depends on several factors. For  $C_{60}$  molecules, for a given set of data (ATDs profiles with and without electric field), the fit of the profiles with a Gaussian allows to determine the time shift of the two distributions with a precision better than  $\pm 10$  ns. By measuring about ten distributions with and without electric field (similar to Fig. 1), we have statistically reduced this incertitude to  $\approx 3$  ns which leads to a precision on the value of the deflection inferior to  $\pm 2\%$ . The precision on the value of the deflection for lithium atoms is similar. The precision on the velocities using a chopped beam method is 1.5%. Finally, the estimated precision on the literature value of the lithium atom polarizability is 2%.<sup>6</sup> This leads to an overall precision of  $\approx 10\%$ , and to an absolute polarizability for isolated  $C_{60}$  molecules of  $76.5 \pm 8.0 \text{ \AA}^3$ .

The polarizability of isolated  $C_{60}$  molecules is in reasonable agreement with the experimental polarizabilities deduced from dielectric constants of fullerite crystals which range from 84 to  $93 \text{ \AA}^3$ .<sup>10–14</sup> However, our value is slightly lower. Several reasons may explain this difference. First, in bulk samples the measured polarizability is the sum of an electronic and a lattice contribution. The contribution from the lattice is close to  $2 \text{ \AA}^3$ .<sup>10</sup> This additional contribution is however too small to account for the difference between the polarizability measurement for isolated molecules and assembled molecules. Secondly, the polarizability values for

fullerites crystals are extracted from the static dielectric constant  $\epsilon_0$ , with the Clausius–Mossotti relation. This relation is based on the assumption that the electronic polarizability of a molecule is not modified by neighboring molecules. Intermolecular interactions may introduce corrections to the Clausius–Mossotti relation. While the  $C_{60}$  molecules are weakly bound, the density of molecules in fullerites crystals is high and it seems necessary to go beyond the Clausius–Mossotti relation to connect the bulk dielectric constant to the molecular polarizability.

As mentioned in the Introduction, a large number of theoretical approaches have been used for the calculation of the polarizability of  $C_{60}$  molecules. The predicted values range from  $36 \text{ \AA}^3$  to  $154 \text{ \AA}^3$ .<sup>4</sup> The value obtained with a conducting sphere model ( $\alpha=R^3$ ) is  $80 \text{ \AA}^3$ .<sup>4</sup> In this simple model, valence electrons are delocalized and the polarizability depends on the volume of the fullerene. A very different approach consist in supposing that the fullerene is built of 60 discrete atomic dipoles. This model leads to  $77 \text{ \AA}^3$ .<sup>15</sup> Our precision is presently not sufficient to decide between these two crude models. However, these models predict different evolution of the polarizability with the size of the fullerenes.<sup>4,16</sup> The measurement of the polarizability of higher fullerenes would be very interesting to determine the best approach to compute electronic properties of fullerenes.

In conclusion, we have measured the electric polarizability of  $C_{60}$  molecules by molecular beam deflection technique. We have obtained a value of  $76.5 \pm 8.0 \text{ \AA}^3$  which is consistent with most of the recent calculated values and slightly lower than the polarizability of  $C_{60}$  in fullerite crystals.

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