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Electric polarizability of isolated C_{70} molecules

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We present the gas phase measurement of the static electric dipole polarizability of C_{70} fullerenes. The value is $102\pm14\ \text{Å}^3$. The increase in polarizability from C_{60} to C_{70} is discussed and compared to different theoretical predictions.

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The electric dipole polarizability is of primary importance in understanding electronic properties of molecules and clusters [1–3]. In this respect, precise experimental measurements are crucial to test theoretical methods and calculations. For fullerenes, two main experimental approaches are possible. First, the measurements may be performed on molecular solids or fullerites. The molecular polarizability is obtained from the dielectric constant provided that local field corrections can be reliably estimated. In practice, people use the Clausius-Mossotti relation. Second, direct measurements on isolated molecules are possible, for example, by molecular beam deviation experiments [4,5]. Both methods lead to valuable results, but clearly the indirect approach is dependent on the bulk structure that must be perfectly known for each measurement. Moreover, approximations must be done in the extraction process, in particular, deviations from the Clausius-Mossotti relation may occur. Measurements on isolated molecules do not suffer from these restrictions.

For C_{60}, recent molecular beam experiments have led to precise values for the dc and ac electric polarizability [4,5]. For C_{70}, the only available values have been deduced from bulk samples [6,7]. As outlined in a recent review [3], the size evolution of fullerenes polarizability is of great importance because fullerenes are cage molecules with electrons delocalized in a thin shell. The investigation of electric polarizability of hollow objects is a new and interesting problem both on theoretical and experimental sides. We report in this paper the direct measurement of the electric polarizability of C_{70}. The results are discussed and compared to different theoretical predictions.

The fullerene beam is produced with a pulsed laser vaporization source. A commercial powder of fullerenes (90% C_{60}, 10% C_{70} purchased by MER corporation) is pressed into a rod. We use the third harmonic of a Nd 3+:YAG (yttrium aluminum garnet) to vaporize the rod and neon or helium as carrier gas (the velocity of the beam depends on the carrier gas). A low laser power is used in order to avoid any fragmentation of the fullerenes. The clusters leave the source through a 5-cm long nozzle and the beam is collimated by two slits. It is deflected after the slits by an inhomogeneous electric field E. The value of the electric field in the deflector is 1.5×10^7 V/m for a voltage of 25 kV across the two cylindrical poles. The clusters are ionized 1 m after the deflector in the extraction region of a time-of-flight mass spectrometer. Two different wavelengths were used for the ionization (193 and 213 nm). The electric fields in the extraction and acceleration regions of the time-of-flight mass spectrometer are adjusted so that the arrival time at the detector is sensitive to the initial position of the molecule in the extraction region (position-sensitive time of flight [3]). The profile of the beam is directly obtained from the arrival time distribution at the detector.

When the fullerene rod is vaporized, the only peaks observed in the mass spectra correspond to C_{60} and C_{70}. Figure 1 shows beam profiles of C_{60} and C_{70} molecules measured with and without an electric field in the deflector using neon as the carrier gas. The profiles measured with the electric field are slightly shifted toward the high electric field region in the deflector. In Fig. 1, the deviation of the beam is d

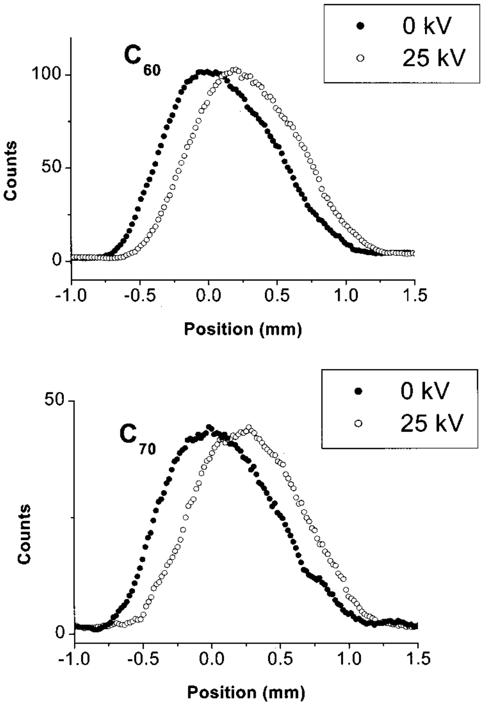

FIG. 1. Beam profiles of C_{60} and C_{70} molecules measured without electric field in the deviator (0 kV) and with $E=1.5\times10^7$ V/m in the deviator (25 kV). The measurement was performed at room temperature with neon as the carrier gas. The velocity of the beam was 593 m/s.

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TABLE I. Experimental and theoretical results for the averaged static polarizability of C_{60} and C_{70}. For C_{60} and C_{70} films, the polarizability value is extracted from the experimental dielectric function by using the Clausius-Mossotti relation.

Method	$\alpha(C_{60})$ (Å^2)	$\alpha(C_{70})$ (Å^3)	$\alpha(C_{70})/\alpha(C_{60})$
Experiment			
Gas phase			
Molecular beam deviation[a]	76.5 ± 8	102 ± 14	1.33 ± 0.03
C_{60} and C_{70} films			
Optical measurements: ellipsometry and reflection/transmission[b]	79.0	97.0	1.23
Electron energy-loss spectroscopy[c]	83.0	103.5	1.25
Theory			
Iterative coupled Hartree-Fock (STO-3G basis set)[d]	45.6	57.0	1.25
Pariser-Parr-Pople Hamiltonian[e]	49.4	63.8	1.29
Atom monopole-dipole interaction[f]	60.8	73.8	1.21
Semiempirical calculation (MNDO/PM3)[g]	63.9	79.0	1.24
Ab initio SCF 6-31++*G* basis set)[h]	75.1	89.8	1.20
Tight binding linear response[i]	77.0	91.6	1.19
Bond polarizability model[j]	89.2	109.2	1.22
Valence effective Hamiltonian[k]	154.0	214.3	1.39
Model			
Additivity model			1.17
Conducting shell model			1.22

[a] This work.

[b] From Ref. [6]. In the Clausius-Mossotti relation, we used a lattice constant $a=14.17$ Å for C_{60} and $a=15.01$ for C_{70}.

[c] From Ref. [7].

[d] From Ref. [11].

[e] From Ref. [12].

[f] From Ref. [10].

[g] From Ref. [13].

[h] From Ref. [16].

[i] This work. The static polarizability is obtained by applying the linear response theory within a sp^3s* tight-binding model that reproduces accurately the valence bands and the lowest conduction bands of diamond carbon [P. Vogel, H.P. Hjalmarson, and J.W. Dow, J. Phys. Chem. Solids 44, 365 (1983)]. This last feature is essential since the static polarizability depends implicitly on the electronic excitation spectrum. The dipole transition matrix element $d=\langle 2s|r|2p\rangle\approx 0.91$ bohr has been calculated from the carbon Slater orbitals tabulated in the literature. Screening effects are taken into account by self-consistently evaluating the local field and the induced charge and dipole modifications at each carbon site.

[j] From Ref. [14].

[k] From Ref. [15].

$=0.19$ mm for C_{60} and $d=0.215$ mm for C_{70}. The deviation d is proportional to the averaged polarizability α of the molecule,

$$d=K\frac{\alpha}{mv^2}E\nabla E, \tag{1}$$

where E and ∇E are the values of the electric field and its gradient in the deviator, m and v are the mass and the velocity of the cluster, and K is a geometrical factor. The velocity v is selected and measured with a mechanical chopper that is directly located in front of the first slit. The polarizability of C_{70} was determined relative to the polarizability of C_{60}, $\alpha_{C_{70}}/\alpha_{C_{60}}=[d(C_{70})/d(C_{60})](70/60)$. Simultaneous measurements were performed at different beam velocities. The data analysis gives $\alpha_{C_{70}}/\alpha_{C_{60}}=1.33$. The precision on the ratio is 3%. The uncertainty is mainly due to the uncertainty of the deviation values. Using the value of the static polarizability that was previously measured for C_{60} (76.5 ± 8 Å^3 [4]), the value of the polarizability of C_{70} is 102 ± 14 Å^3.

As discussed at the beginning of this paper, the size evolution of the polarizability of fullerenes is of particular interest. Different behaviors have been suggested in the literature. Simple additivity of atomic contributions would lead to a polarizability proportional to the number of atoms n and to a ratio of $\alpha(C_{70})$ to $\alpha(C_{60})$ of 1.17. An opposite approach is to consider that the fullerene behaves as a conducting shell. The polarizability would then, in first approximation, increase as the volume of the cluster that for a cage scales as $n^{3/2}$. For C_{60}, the outer radius of the conducting shell can be obtained by adding the radius of the ionic frame (3.51 Å) and half the thickness of the electron cloud (1.5 Å) [3]. This corresponds to a shell with an outer radius of 4.26 Å and a polarizability equal to 77 $Å^3$. This value is very close to the experimental value. For larger fullerenes, it is reasonable to scale the surface of the ionic frame as a function of the number of atoms (the radius of the cage scales as $n^{1/2}$) and to use the same thickness for the electron cloud. For C_{70}, these crude approximations lead to a radius equal to 4.54 Å and a polarizability of 94 $Å^3$. The calculated ratio of $\alpha(C_{70})$ to $\alpha(C_{60})$ is 1.22. The same behavior is obtained when fullerenes are modeled as classical dielectric shells [8].

Beyond these two extreme approaches, a discussion of the size evolution of fullerene polarizability based on semiempirical models can be found in Refs. [9,10]. For C_{60} and C_{70}, several calculated values are available in the literature. Results of calculations that were performed on both sizes are given in Table I (a more extended set of calculations for C_{60} can be found in Ref. [3]). The *ab initio* values of Jonsson *et al.* [16] are in agreement with our experimental values, at least for C_{60}. Among semiempirical approaches, only the bond polarizability and the tight-binding approaches lead to absolute values in agreement with experiment. Other models lead to values that clearly differ from experimental values. Concerning the size evolution, most of the calculations predict a ratio of $\alpha(C_{70})$ to $\alpha(C_{60})$ greater than 7/6 and close to the ratio expected for a conducting shell.

The calculations slightly underestimate the experimental behavior. We have no clear explanation for this difference, but a few leads might be developed. First, C_{70} has a lower symmetry than C_{60} and its polarizability is not isotropic. In beam deviation experiments, the main effect of anisotropy is to induce a broadening of the profile [17]. For C_{70}, this effect can be fully neglected at room temperature. It is clear that the shape of the cage has also an influence on the value of the averaged polarizability. This effect is not taken into account in the crude conducting spherical shell model but it is in *ab initio* or semiempirical calculations. From the experimental point of view, one cannot exclude the fact that the desorption laser induces some isomerization of fullerene molecules into different structures [18]. Preliminary results show that the polarizability of carbon clusters obtained from graphite vaporization (C_n clusters with only even sizes and $n \geqslant 58$ in the mass spectrum) are significantly larger than those obtained from C_{60} and C_{70} fullerenes desorption [19]. The isomerization of a small amount of C_{70} molecules into structures having a polarizability higher than that of the D_{5h} isomer would affect the experimental result. However, as previously outlined, low laser power is used for the desorption, in particular no fragmentation is observed in the mass spectrum. Finally, the finite temperature of the experiment is not taken into account in the calculations. While temperature effects are expected to be smaller than those for sodium clusters [20], a temperature dependence different between C_{60} and C_{70} may account for part of the discrepancy observed between calculations and experiments. Further experimental and theoretical investigations of the polarizability of fullerenes, in particular, measurements for fullerenes with sizes larger than C_{70} or smaller than C_{60} [21], are necessary to conclude.

In summary, we have reported the gas phase measurement of the static polarizability of C_{70}. The measured value is $102 \pm 14\,Å^3$. The increase in polarizability from C_{60} to C_{70} is slightly larger than the increase that is expected for a conducting shell or predicted by more refined models.

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[1] T. M. Miller and B. Bederson Adv. At. Mol. Phys. **13**, 1 (1977).

[2] W. A. de Heer, Rev. Mod. Phys. **65**, 611 (1993).

[3] K. D. Bonin and V. V. Kresin, *Electric-dipole Polarizabilities of Atoms, Molecules and Clusters* (World Scientific, Singapore, 1997).

[4] R. Antoine, P. Dugourd, D. Rayane, E. Benichou, M. Broyer, F. Chandezon, and C. Guet, J. Chem. Phys. **110**, 9771 (1999).

[5] A. Ballard, K. Bonin, and J. Louderback, J. Chem. Phys. **113**, 5732 (2000).

[6] S.-L. Ren, K.-A. Wang, P. Zhou, Y. Wang, A. M. Rao, M. S. Meier, J. P. Selegue, and P. C. Eklund, Appl. Phys. Lett. **61**, 124 (1992).

[7] E. Sohmen, J. Fink, and W. Krätschmer, Z. Phys. B: Condens. Matter **86**, 87 (1992).

[8] J. U. Andersen and E. Bonderup, Eur. Phys. J. D **11**, 413 (2000).

[9] A. Ruiz, J. Breton, and J. M. Gomez-Llorente, J. Chem. Phys. **114**, 1272 (2001).

[10] B. Shanker and J. Applequist, J. Phys. Chem. **98**, 6486 (1994).

[11] J. Baker, P. W. Fowler, P. Lazzeretti, M. Malagoli, and R. Zanasi, Chem. Phys. Lett. **184**, 182 (1991).

[12] F. Willaime and L. M. Falicov, J. Chem. Phys. **98**, 6369 (1993).

[13] N. Matsuzawa and D. A. Dixon, J. Phys. Chem. **96**, 6241 (1992).

[14] S. Guha, J. Menéndez, J. B. Page, and G. B. Adams, Phys. Rev. B **53**, 13 106 (1996).

[15] Z. Shuai and J. L. Brédas, Phys. Rev. B **46**, 16 135 (1992).

[16] D. Jonsson, P. Norman, K. Ruud, H. Agren, and T. Helgaker, J. Chem. Phys. **109**, 572 (1998); K. Ruud, D. Jonsson, and P. R. Taylor, *ibid.* **114**, 4331 (2001).

[17] R. Antoine, D. Rayane, A. R. Allouche, M. Aubert-Frécon, E. Benichou, F. W. Dalby, P. Dugourd, M. Broyer, and C. Guet, J. Chem. Phys. **110**, 5568 (1999).

[18] G. von Helden, M.-T. Hsu, P. R. Kemper, and M. T. Bowers, J

. Chem. Phys. **95**, 3835 (1991).
[19] R. Antoine, M. Broyer, P. Dugourd, and D. Rayane (unpublished).
[20] L. Kronik, I. Vasiliev, and J. R . Chelikowski, Phys. Rev. B **62**, 9992 (2000).
[21] H. Prinzbach, A. Weiler, P. Landenberger, F. Wahl, J. Wörth, L. T. Scott, M. Gelmont, D. Olevano, and B. V. Issendorff, Nature (London) **407**, 60 (2000).