15 March 1996

ELSEVIER

Chemical Physics Letters 251 (1996) 111-114

CHEMICAL PHYSICS LETTERS

Long wavelength optical response of incipient fullerene nanotubes

H.E. Roman [a,b], G. Colò [b], F. Alasia [b], R.A. Broglia [b,c]

[a] *Institut für Theoretische Physik, Universität Giessen, Heinrich-Buff-Ring 16, D-35392 Giessen, Germany*
[b] *Dipartimento di Fisica, Università di Milano and INFN, Sezione di Milano, Via Celoria 16, 20133 Milan, Italy*
[c] *The Niels Bohr Institute, University of Copenhagen, DK-2100 Copenhagen, Denmark*

Received 2 January 1996

Abstract

The electromagnetic response of elongated fullerenes is calculated in the time-dependent local density approximation. The long wavelength optical behaviour of these systems is found to be very similar to that expected for the case of elongated metallic particles.

Carbon nanotubes can now be produced in large quantities, either as multishells [1,2] or as single-layer tubes [3–5]. The small diameter of nanotubes indicate they can be thought as quantum wires [6]. Recently, Smalley and co-workers have observed field emission from fullerene nanotubes finding results which seem to be similar to those expected from metallic wires [7,8]. However, trying to measure electronic properties of such small material has been proven to be a challenging task. A complementary way for characterizing the electronic response of fullerene nanotubes other than to subject them to a bias voltage, is to study their optical/UV response.

In the present Letter, we present results of a study of the electromagnetic response of the elongated C_{90} and C_{110}, fullerenes which can be viewed as incipient nanotubes. It will be concluded that the long wavelength electromagnetic response behaviour of these systems parallel to the long axis of the molecule (parallel response), is similar to that of elongated metallic particles (cf. e.g. Ref. [9]).

The structure of the elongated fullerenes can be best understood starting from C_{70}. This molecule can be viewed as two halves of C_{60} cluster joined by a belt of five benzenoid rings. This belt adds ten carbon atoms to the molecule. Fullerene C_{90} and C_{110} are obtained by joining with three and five belts, respectively, the two halves of C_{60} as shown in Fig. 1. Aside from C_{70}, which is the second most abundant extractable carbon cluster in the soot produced by the vaporization of grafite [10], C_{90} has been isolated from the CS_2 extracts [11]. In keeping with structural studies carried out on C_{70} (cf. e.g. Ref. [12]) the elongated fullerene discussed in the present paper has three different bond lengths with values 1.40 Å, 1.42 Å and 1.46 Å (cf. Fig. 1). The Kohn–Sham equations (cf. e.g. Ref. [13]) have been solved in a basis composed of spherical states $|nlm\rangle$, characterized by the radial quantum number n, the orbital quantum number l and the magnetic quantum number m. The exchange–correlation energies as calculated by Ceperley and Alder and parametrized

PII S0009-2614(96)00064-4

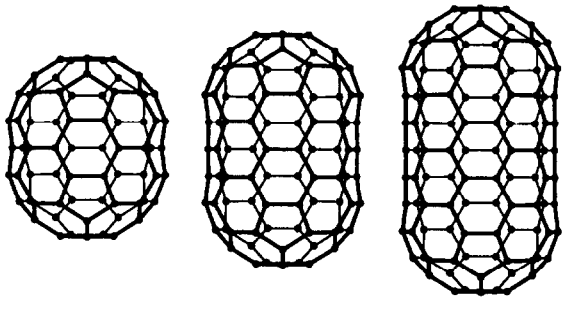

Fig. 1. Molecular models of C_{70}, C_{90} and C_{110}. The ratios of the shortest to the longest radii $R_\perp : R_\parallel$ are also shown.

by Perdew and Zunger [14] were used in the LDA calculation. The role of carbon atoms were taken into account in terms of norm conserving pseudopotentials [15]. For details of the calculation we refer to Ref. [16].

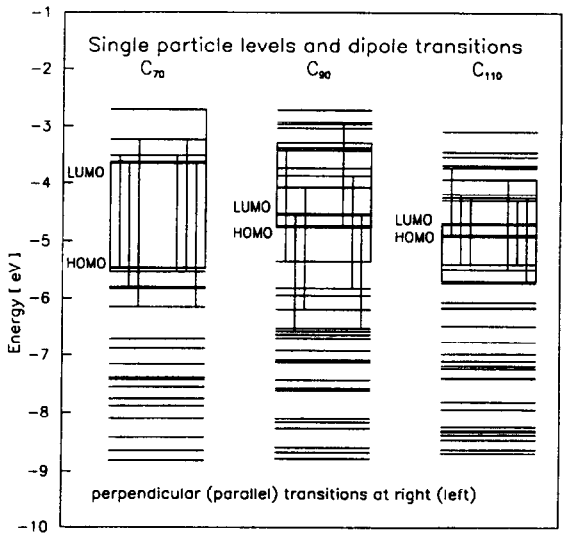

Fig. 2. Single-particle levels of C_{70}, C_{90} and C_{110}. The lowest dipole transitions between orbits mainly concentrated along the shortest (perpendicular) and longest (parallel) axis of the fullerenes are shown.

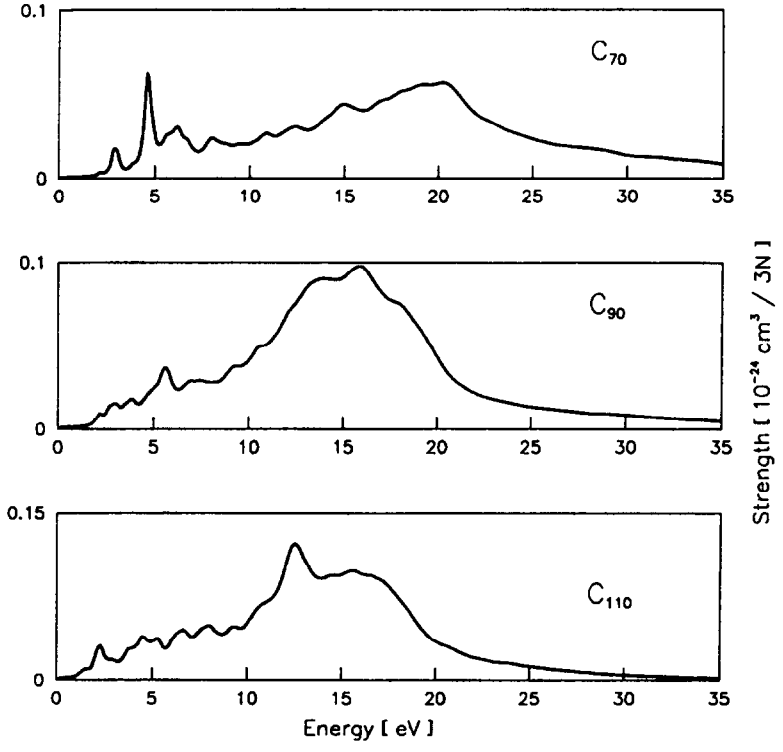

Fig. 3. Electromagnetic response associated with the oscillations of electrons along the largest axis of the fullerenes C_n ($n = 70, 90, 110$) in Å^3, normalized by dividing the response function by 3 times the number of electron in the system.

The single-particle spectra of C_{90} and C_{110} resulting from the calculations are shown in Fig. 2. For comparison the corresponding spectrum of C_{70} is also displayed [17]. Indicated in these figures are also the lowest-lying allowed dipole particle–hole transitions. Excitations between states which are mainly concentrated along the short axis of the molecule (perpendicular excitations) have energies which are rather independent from the elongation of the system and are similar to the corresponding energies associated within dipole particle–hole excitations in C_{60}. On the other hand, the energy associated with particle–hole excitations between electronic states whose wavefunctions are mainly concentrated along the longer axis of the molecule (parallel excitations) is considerably smaller than typical energies associated with perpendicular excitations. Furthermore, the energy of the parallel excitations decreases with the elongation of the system.

These arguments become more transparent by looking at the screened response functions calculated in the time-dependent local density approximation (cf. e.g. Refs. [16,18]) as shown in Fig. 3. Also, by comparing them to the associated results for the spheroidal fullerene C_{60} [16]. While the lowest peak of the calculated optical spectrum of C_{60} is at 3.5 eV, that associated with the parallel electromagnetic response of C_{110} lies in the infrared at 1.5 eV, and the one associated with C_{70} and C_{90} are found at 2.2 and 2.1 eV, respectively. The second lowest peak of C_{60} is calculated at 5 eV, the corresponding excitation in the elongated fullerenes calculated along the longest axis are found at ≈ 3 eV (C_{70}), 2.5 eV (C_{90}) and 2.2 eV (C_{110}).

The energy variations of the lowest peaks ($i = 1$ lowest, $i = 2$ second lowest, etc.) of the electromagnetic response of the elongated fullerenes, C_n, can be parametrized by

$$\omega_i^2(C_n) = L(C_n)\,\omega_0^2(i), \tag{1}$$

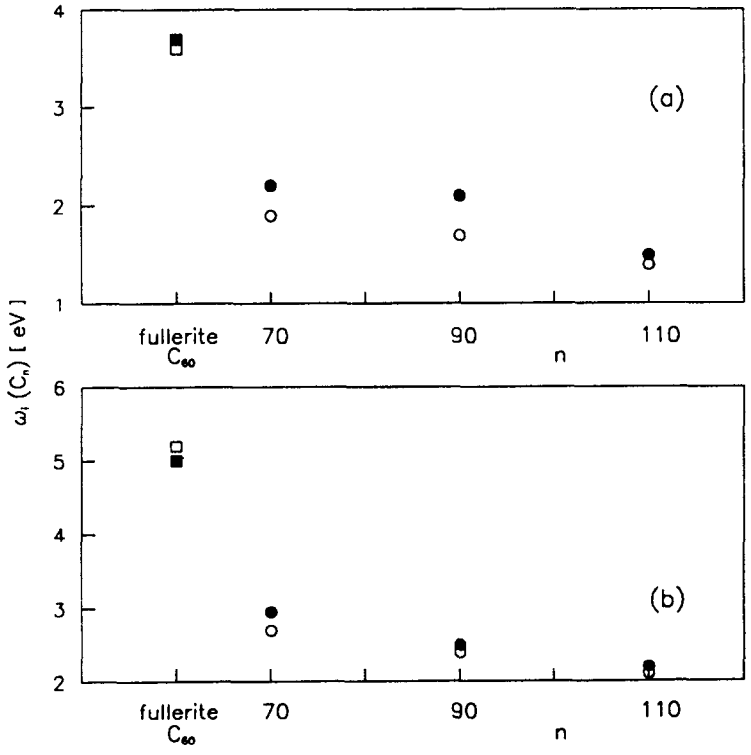

Fig. 4. Energy of the (a) first and (b) second peak of the electromagnetic response function of C_{70}, C_{90} and C_{110}, calculated in TDLDA (solid circles), and according to the relation given in Eqs. (1)–(3) (open circles) as described in the text. Also displayed are the values of $\omega_0(i)$ ($i = 1, 2$) (solid squares) in comparison with the energies of the first and second peaks (open squares) of the C_{60} fullerite [19].

where

$$L(C_n) = \frac{1-e^2}{e^2}\left[-1+\frac{1}{2e}\ln\left(\frac{1+e}{1-e}\right)\right], \qquad (2)$$

is the depolarization of the system along the longest axis of the fullerene, while

$$e^2 = 1 - \left(\frac{R_\perp(C_n)}{R_\parallel(C_n)}\right)^2, \qquad (3)$$

the quantities $R_\perp$ and $R_\parallel$ being the shortest and longest radii of the molecule. This expression is derived in standard textbooks [9] to describe the surface modes of elongated metallic particles, making use of electrostatics and the Drude theory of metals. In that case ω_0 is the bulk plasmon frequency. In the present case it is a parameter which we shall determine from the calculated value of the lowest peaks of the electromagnetic response of C_{110} (cf. Fig. 3), and from the ratio $R_\perp(C_{110})/R_\parallel(C_{110})$ (cf. Fig. 1). The values associated with the first and second excited peaks of the electromagnetic response of C_{110} are $\omega_0(1) = 3.6$ eV and $\omega_0(2) = 5.2$ eV. As seen from Fig. 4, these values of ω_0 lead, through the relation given in Eq. (1), to a rather accurate parametrization of the values which TDLDA theory predicts for the lowest energy peaks of C_{70} and C_{90}. Furthermore, these values of ω_0 are very close to the energy of the two lowest peaks of the energy loss function of C_{60} fullerite calculated in the TDLDA [19] (cf. also Ref. [20]).

Extrapolating the results of Eqs. (1)–(3) to the case of nanotubes of dimension ≈ 3 nm (C_{250}) and 10 nm (C_{850}) one obtains ≈ 1 eV and 0.4 eV, respectively, for the energy of the lowest peak of the electromagnetic response [1]. Further evidence for the concentration of the strength observed at low energies as a function of the elongation of the system is provided by the percentage of the energy weighted sum rule (oscillator strength) predicted by the calculations for the elongated fullerenes. Below 3 eV one expects 0.14%, 0.18% and 0.38% of the energy weighted sum rule for C_{70}, C_{90} and C_{110}, respectively.

We conclude that the long wavelength electromagnetic response of elongated fullerenes displays a behaviour similar to that of an elongated metallic particle. The spectrum shows peaks generated by strongly screened electronic transitions which already for the elongated C_{250} fullerene are expected to have an energy lower than 1 eV.

Financial support by NATO under grant CRG 940231 is gratefully acknowledged. FA gratefully acknowledges financial support from Consorzio Milano Ricerche.

[1] Because the calculated energies of the peaks associated with the dielectric function of C_{60} fullerite are typically 0.5 eV higher in energy than the experimentally observed values, we expect the accumulation of strength for $\omega \to 0$ (long wavelength limit), to be even more conspicuous than here predicted.

References

[1] T.W. Ebbesen and P.M. Ajayan, Nature 358 (1992) 220.
[2] T.W. Ebbesen, H. Hiura, J. Fujita, Y. Ochiai, S. Matsui and K. Tanigaki, Chem. Phys. Lett. 209 (1993) 83.
[3] S. Jijima and T. Ichihashi, Nature 363 (1993) 603.
[4] D.S. Bethune et al., Nature 363 (1993) 605.
[5] T.W. Ebbesen et al., Nature 367 (1994) 519.
[6] T.W. Ebbesen, Ann. Rev. Mat. Sci. 29 (1994) 235.
[7] A.G. Rinzler, J.H. Hafner, D.T. Colbert and R.E. Smalley, Mat. Res. Soc. Symp. Proc. 359 (1995) 61.
[8] A.G. Rinzler et al., Science 269 (1995) 1550.
[9] C.F. Bohren and D.R. Huffman, Absorption and scattering of light by small particles, (Wiley, New York, 1983).
[10] W. Krätschmer et al., Nature 347 (1990) 35.
[11] M. Kikuchi, N. Nakahara, T. Wakabayashi, M. Honda, H. Matsumiya, T. Moriwaki, S. Suzuki, H. Shiromaru, K. Saito, K. Yamauchi, I. Ikemoto and Y. Achiba, Chem. Phys. Letters 188 (1992) 177.
[12] J. Cioslowski, Electronic structure calculations on fullerenes and their derivatives (Oxford Univ. Press, Oxford, 1995).
[13] R.G. Parr and W. Yang, Density-functional theory of atoms and molecules (Oxford Univ. Press, Oxford, 1989).
[14] J.P. Perdew and A. Zunger, Phys. Rev. B 23 (1981) 5048.
[15] G.B. Bachelet et al., Phys. Rev. B 26 (1982) 4199.
[16] F. Alasia, R.A. Broglia, H.E. Roman, Ll. Serra, G. Colò and J.M. Pacheco, J. Phys. B 27 (1994) L643.
[17] F. Alasia, R.A. Broglia, G. Colò and H.E. Roman, Chem. Phys. Letters 247 (1995) 502.
[18] G.F. Bertsch and R.A. Broglia, Oscillations in Finite Quantum Systems, Cambridge University Press (1994).
[19] F. Alasia, R.A. Broglia, G. Colò, H.E. Roman and Ll. Serra, to be published.
[20] Y.N. Xu, M.Z. Huang and W.Y. Ching, Phys. Rev. B 44 (1991) 13171.