[1] a) J. Roncali, *Chem. Rev.* **1997**, *97*, 173; b) W. J. Feast, J. Tsibouklis, K. L. Pouwer, L. Groenendaal, E. W. Meijer, *Polymer* **1996**, *37*, 5017; c) *An Introduction to Molecular Electronics* (Eds: M. C. Petty, M. R. Bryce, D. Bloor), Edward Arnold, London, **1995**; d) J. M. Tour, *Adv. Mater.* **1994**, *6*, 190; e) U. Scherf, K. Müllen, *Synthesis* **1992**, 23; f) F. Effenberger, H. Schlosser, P. Bäuerle, S. Maier, H. Port, H. Wolf, *Angew. Chem. Int. Ed. Engl.* **1998**, *27*, 281; g) J. M. Lehn, *Proc. Nat. Acad. Sci.* **1986**, *83*, 5355; h) *Handbook of Conducting Polymers*, (Ed. T. A. Skotheim), Marcel Dekker, New York, **1986**.
[2] T. Förster, *Discuss. Faraday Soc.* **1959**, *27*, 7.
[3] D. L. Dexter, *J. Chem. Phys.* **1953**, *21*, 836.
[4] a) A. G. Martínez, J. O. Barcina, A. F. Cerezo, R. G. Rivas, *J. Am. Chem. Soc.* **1998**, *120*, 673; b) A. G. Martínez, J. O. Barcina, A. Albert, F. H. Cano, L. R. Subramanian, *Tetrahedron Lett.* **1993**, *34*, 6753.
[5] a) T. Strassner, *Can. J. Chem.* **1997**, *75*, 1011; b) M. Feigel, *J. Mol. Struct. (Theochem)* **1996**, *366*, 83; c) W. Weissensteiner, *Monatsh. Chem.* **1992**, *123*, 1135; d) J. C. Barnes, J. D. Paton, J. R. Damewood, K. Mislow, *J. Org. Chem.* **1981**, *46*, 4975; e) D. Gust, K. Mislow, *J. Am. Chem. Soc.* **1973**, *95*, 1535; f) G. Montaudo, P. Finocchiaro, *J. Am. Chem. Soc.* **1972**, *94,* 6745.
[6] a) M. Rehahn, A.-D. Schlüter, G. Wegner, *Makromol. Chem.* **1990**, *191*, 1991; b) A.-D. Schlüter, G. Wegner, *Acta Polym.* **1993**, *44*, 59.
[7] Y. Kobayashi, I. Kumadaki, T. Yoshida, *J. Chem. Res.* **1977**, 215.
[8] N. Miyaura, T. Yanagi, A. Suzuki, *Synth. Commun.* **1981**, *11*, 513.
[9] M. Rehahn, A.-D. Schlüter, W. J. Feast, *Synthesis* **1988**, 386.
[10] P. Galda, M. Rehahn, *Synthesis* **1996**, 614.
[11] Heinz-Helmut Perkampus, *UV-Vis. Atlas of Organic Compounds, 2nd* ed., VCH, Weinheim, **1992**.
[12] Oligomers with stacked aromatic rings, both homoconjugated and non-homoconjugated, are described in: a) S. Mataka, Y. Mitoma, T. Thiemann, T. Sawada, M. Taniguchi, M. Kobuchi, M. Tashiro, *Tetrahedron* **1997**, *53*, 3015; b) S. Breidenbach, S. Ohren, F. Vögtle, *Chem. Eur. J.* **1996**, *2*, 832; c) M. Kuroda, J. Nakayama, M. Hoshino, N. Furusho, T. Kawata, S. Ohba, *Tetrahedron* **1993**, *49*, 3735; d) W. Grimme, H. T. Kämmerling, J. Lex, R. Gleiter, J. Heinze, M. Dietrich, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 205; e) K. Yamaguchi, G. Matsumura, H. Kagechika, I. Azumaya, Y. Ito, A. Itai, K. Shudo, *J. Am. Chem. Soc.* **1991**, *113*, 5474; f) T. Otsubo, T. Kohda, S. Misumi, *Bull. Chem. Soc. Jp* **1980**, *53*, 512; g) M. Nakazaki, K. Yamamoto, S. Tanaka, H. Kametani, *J. Org. Chem.* **1977**, *42*, 287.
[13] a) P. G. Gassman, P. G. Pape, *J. Org. Chem.* **1964**, *29*, 160. b) P. G. Gassman, J. L. Marshall, *Org. Synth.* **1968**, *48*, 68.
[14] H. Tanida, T. Tsushima, *J. Am. Chem. Soc.* **1970**, *92*, 3397.

Clusters of C_{60} Molecules**

By *Doroteo Mendoza,* Gonzalo Gonzalez,* and
Roberto Escudero

After the discovery of the method for production of large quantities of C_{60},[1] the structural and optical properties of this material have been studied in the form of single crystals, thin films, or in solution in a variety of liquid solvents.[2] The commonly accepted crystalline structure of solid C_{60} consists of a fcc lattice at room temperature that undergoes a structural transition to a sc phase at $\simeq$249 K.[3] Nevertheless, other studies indicate that, depending on the experimental conditions in which solid C_{60} has been obtained, a mixture of fcc and hcp phases may coexist at room temperature.[4–6] The optical absorption spectra in the UV–vis range are very similar among the different forms in which C_{60} has been studied, namely in solid form and in solution.[7] This implies that the intermolecular interactions are weak, of the van der Waals type, and that solid C_{60} is considered as a molecular crystal.[8] Generally speaking, the four main peaks in the absorption spectra, located in the range of 2–6 eV, remain the same with small red shifts in energy and broadening in the peaks of solid C_{60} compared with those in the molecules.[7] On the other hand, C_{60} has also been studied in the form of clusters in the range of 13–55 molecules, being the intermediate clusters in a set of "magic" numbers.[9] One of the main conclusions of that work is that, in these small clusters, icosahedral symmetry is preferred. Greater aggregates of C_{60} molecules, in the range of 100–140 nm, have also been synthesized via aerosol routes.[10] In this case, the clusters of C_{60} molecules are spheroidal and polycrystalline. To our knowledge, no optical properties have been reported for these kinds of systems.

In the present work we report on the synthesis and characterization of clusters of C_{60} molecules. The most intriguing finding is that the optical absorption spectrum in the UV–vis range of the material obtained is different to that usually observed in C_{60} thin films. The results presented here might be useful in future optical applications or for catalytic purposes, such as have been proposed for similar nanophase fullerene particles obtained by a different method than that reported here.[10]

Figure 1a shows a TEM micrograph of one of the samples. It can be observed that the sample consists of isolated spheroidal clusters which, based on statistical analysis of the size distribution, have a mean diameter of 180 nm. Figure 1b shows the electron diffraction pattern associated with the cluster system, which indicates its nanocrystalline nature. Simple analysis of the diameter of some of the most prominent diffraction rings gives the following interplanar spacing: 8.19, 5.01, 4.29, 3.21, and 2.9 Å. These interplanar spacings can be attributed to either a fcc (with a lattice parameter of a $\simeq$14.1 Å) or a hcp (with lattice parameters a $\simeq$10 Å, and c $\simeq$16.4 Å) crystalline structures.[4–6] With the present data we are not able to determine which of the crystalline structures might correspond to the clusters of C_{60} molecules, and further analysis will be necessary in this respect. Nevertheless, it is certain that these interplanar distances do not belong to graphite or any other possible residual phases resulting during the preparation process.

In Figure 2 the optical absorption spectrum in the UV–vis range of the cluster system is shown (solid line). For comparison the spectrum corresponding to a film obtained under high vacuum conditions is also presented (dashed line). Note the typical absorption spectrum for this film, and note for the cluster system a red shift of the main absorption bands. It is worth mentioning the large enhancement of the ratio of the absorbance at low energies (2 eV)

---

[*] Dr. D. Mendoza, Dr. G. Gonzalez, Dr. R. Escudero
Instituto de Investigaciones en Materiales
Universidad Nacional Autónoma de México
Apdo. Postal 70-360, México, D.F. 04510 (Mexico)

[**] We thank M.A Canseco for the UV–Vis and IR measurements. This work was partially supported by grants CONACYT-G0017E and DGAPA-IN105597

0935-9648/99/0101-0031 $ 17.50+.50/0

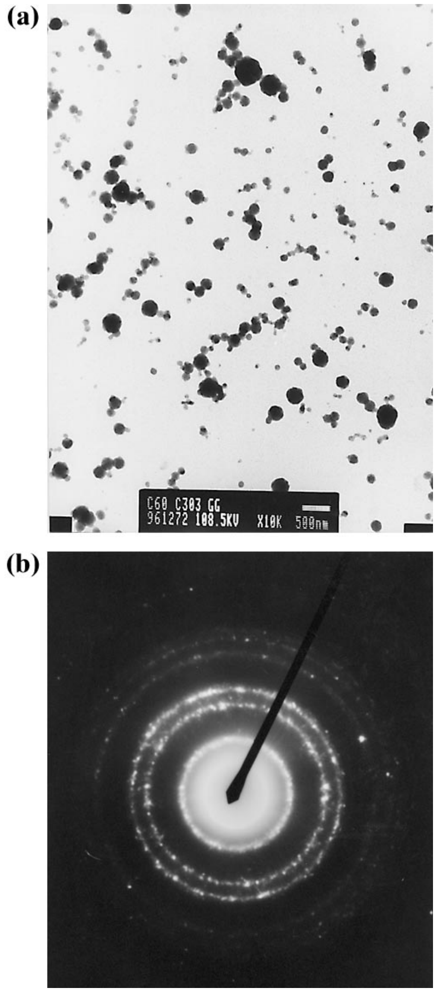

Fig. 1. a) Electron transmission micrograph of clusters of C_{60} deposited on an amorphous carbon-coated copper grid, the mean diameter of the clusters is about 180 nm. b) Electron diffraction pattern associated with the clusters. The most prominent rings beginning from the center of the pattern give the following interplanar spacing: 8.19, 4.29, 3.2, 2.9, and 2.76 Å.

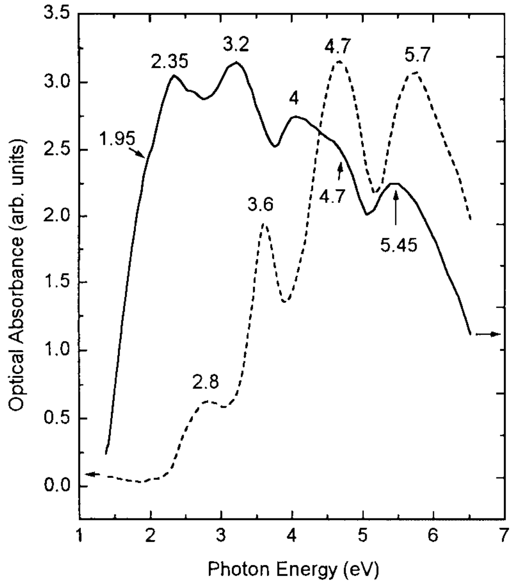

Fig. 2. Optical absorbance of the cluster system obtained by thermal evaporation under an argon atmosphere (solid line), and for a continuous film deposited under high vacuum conditions (dashed line). The numbers indicate the position in energy (eV) for the main peaks.

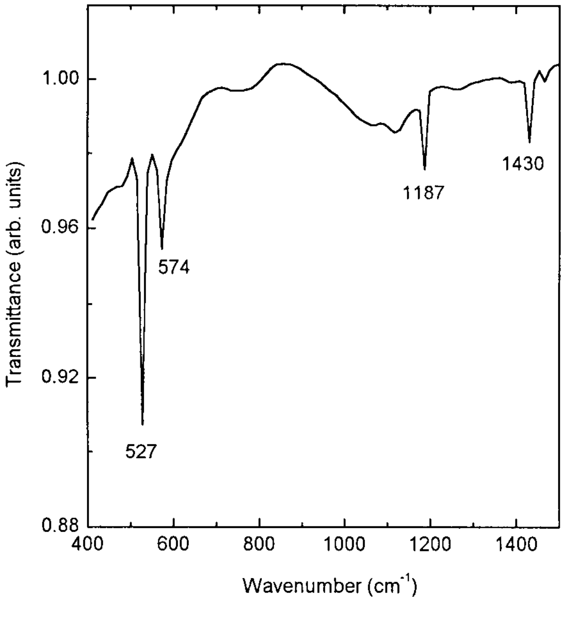

Fig. 3. Infrared spectrum of the C_{60} clusters mixed with KBr (the KBr background has already been subtracted). Note that the main four peaks associated with the pristine C_{60} are present in this spectrum.

with respect to the high energy region (6 eV, for example) compared with that of the film obtained under high vacuum conditions. This is a surprising finding since we should not expect any chemical modification of the C_{60} molecules due to the method used to obtain the samples.

To obtain more information about the chemical nature of the clusters, we scraped some material from the fused quartz substrate and mixed it with KBr powder to form a pellet for IR characterization. Figure 3 shows the IR spectrum where the four most prominent peaks associated with C_{60} are observed,[1,11] confirming that the clusters mainly consist of C_{60} molecules without any chemical modification suffered during the thermal evaporation in the argon atmosphere. Additional evidence of the integrity of the C_{60} molecules was obtained by scraping material from the fused quartz substrate and dissolving it in toluene. The UV–vis spectrum gives the characteristic band of C_{60} at about 3.7 eV in toluene solution, as reported by Hora et al.[7] (see inset in Fig. 4 of that reference). Clearly this further evidence confirms that the C_{60} molecules remain after the evaporating process in the argon atmosphere.

The question remains whether some kind of polymerized C_{60} was formed. Polymerization by thermal evaporation of C_{60} under an argon plasma has been reported,[12] but the IR spectra of the material obtained show broader bands located at different wavenumbers instead of the four main peaks associated with the C_{60} molecules. Also, the UV–vis spectrum of that material is different to that shown in our

0935-9648/99/0101-0032 $ 17.50+.50/0

Figure 2 for the cluster system (solid line). In addition, the optical absorption spectrum in the UV–vis of polymerized C_{60} films obtained by another method (i.e., photopolymerization) is similar to that of a continuous film,[13] but different to that obtained in the present work (Fig. 2, solid line). One partial conclusion is that our cluster system presents different optical properties than the polymerized C_{60} reported so far, and an alternative explanation of our results is needed.

As an attempt to explain the optical absorption spectrum of our cluster system, we considered the following system: assume spherical C_{60} clusters embedded into a dielectric matrix (vacuum for instance). Then we can proceed to calculate the optical absorption following the Maxwell–Garnett approximation, using for this purpose the real and imaginary parts of the energy-dependent dielectric function of pristine C_{60} reported in the literature.[14] As a free parameter we used the volume fraction (f) occupied by the C_{60} clusters with respect to the vacuum. The result gives an optical spectrum similar to that of a typical continuous film but with an overall decrease in the absorption intensity and small shifts of the absorption bands to the ultraviolet region as f is decreased. Therefore we can discard an effective medium effect to explain our results for the cluster system.

Nevertheless, it is worth mentioning that an optical absorption spectra with close resemblance to that presented in our Figure 2 (solid line) has been reported,[6,15] but the experimental conditions in which those samples were obtained are different to those used in the present work. These authors found that after prolonged periods of annealing, the absorption spectrum in the UV–vis range changes from the typical spectrum for the continuous film to that similar to the spectrum shown in our Figure 1 for the cluster system. The authors claim that after the prolonged thermal treatment, the structure of the pristine C_{60} film changes to a closer packed lattice (hcp lattice), which is accompanied by the change in the optical absorption spectrum.[6,15] This could explain our results for the cluster system, as we pointed out at the beginning of this work; however, with the results of the analysis of our electron diffraction patterns we are not able to decide the crystalline structure of the clusters, and a hcp lattice might be the case. It is important to mention that a red shift of the absorption bands is consistent with a closer packing of the C_{60} molecules observed in going from the free molecules in solution to the solid phase, and to those experiments where an increase of the optical absorption of solid C_{60} subjected to external pressure for photon energies less than $\simeq 2\,\mathrm{eV}$ is observed.[16,17] In any case, the strong change in the optical absorption spectrum for our cluster system remains to date an open question, mainly because in principle, one should not expect such a noticeable change due to the fact that the interaction between C_{60} molecules is weak.

In conclusion, we have synthesized clusters of C_{60} molecules which show an optical absorption spectrum different to that usually observed in thin films obtained in high vacuum conditions. IR spectroscopy shows that no chemical modification of the C_{60} molecules exists, and we also discard the existence of some kind of known polymerized phase. Besides, no explanation for the optical absorption spectrum from an effective medium effect based on a Maxwell–Garnett analysis is compatible with our experimental results. Instead, it might be possible that the clusters consist of a hcp majority phase, and that this closer packed lattice is the origin of the observed optical absorption spectrum. More careful structural analysis of the clusters is necessary in order to establish this point.

Experimental

The samples reported in this work were prepared by thermal evaporation of C_{60} powder (99.5 % purity from MER Corporation), under two conditions: high purity (99.9 %) argon atmosphere at 30 Torr, and high vacuum conditions ($\simeq 4 \times 10^{-6}$ Torr). Fused quartz substrates for optical characterization and copper grids (amorphous carbon coated) for transmission electron microscopy observations were loaded at 8.5 cm above the tungsten boat in the same run. The substrates were held at room temperature, and the role of the substrate temperature was not studied. The optical density of the cluster system deposited on the fused quartz substrate was controlled only by the time of evaporation, keeping a constant rate. In spite of this, we never obtained a continuous film under the 30 Torr conditions, although this was obtained under high vacuum conditions.

Currently we are carrying out experiments in order to test different conditions to form clusters of C_{60} molecules to obtain more insight about the physical nature of this interesting system.

Received: April 8, 1998
Final version: July 3, 1998

---

[1] W. Krätschmer, L. D. Lamb, K. Fostiropoulos, D. R. Huffman, *Nature* **1990**, *347*, 354.

[2] See for example: *Science of Fullerenes and Carbon Nanotubes* (Eds: M. S. Dresselhaus, G. Dresselhaus P. C. Eklund), Academic Press, San Diego, CA **1996**.

[3] P. A. Heiney, J. E. Fischer, A. R. McGhie, W. J. Romanov, A. M. Denestein, J. McCauley, Jr., A B. Smith, III, *Phys. Rev. Lett.* **1991**, *66*, 2911.

[4] G. Zhennan, Q. Jiuxin, Z. Xihuang, W. Yongqing, Z. Xing, F. Sunqi, G. Zizhao, *J. Phys. Chem.* **1991**, *95*, 9615.

[5] Z. G. Li, P. J. Fagan, *Chem. Phys. Lett.* **1992**, *194*, 461.

[6] L. Akselrod, H. J. Byrne, T. E. Sutto, S. Roth, *Chem. Phys. Lett.* **1995**, *233*, 436.

[7] J. Hora, P. Pánek, K. Navrátil, B. Handlívřová, J. Humlívček, H. Sitter, D. Stifter, *Phys. Rev. B* **1996**, 54, 5106.

[8] M. Muccini, *Synth. Met.* **1996**, *83*, 213.

[9] T. P. Martin, U. Schaber, U. Zimmermann, *Phys. Rev. Lett.* **1993**, *70*, 3079.

[10] J. Joutsensaari, P. Ahonen, U. Tapper, E. I. Kauppinen, J. Laurila, V.-T. Kuokkala, *Synth. Met.* **1996**, *77*, 85.

[11] R. Meilunas, R. P. H. Chang, S. Liu, M. Jensen, M. M. Kappes, *J. Appl. Phys***.** **1991**, *70*, 5128.

[12] N. Takahashi, H. Dock, N. Matsuzawa, M. Ata, *J. Appl. Phys.* **1993**, *74*, 5790.

[13] M. S. Dresselhaus, G. Dresselhaus, A. M. Rao, P. C. Eklund, *Synth. Met.* **1996**, *78*, 313.

[14] E. Sohmen, J. Fink, W. Krätschmer, *Z. Phys.* **1992**, *B 86*, 87.

[15] L. Akselrod, H. J. Byrne, M. Kaiser, S. Roth, *Synth. Met.* **1995**, *70*, 1427.

[16] D. W. Snoke, K. Syassen, A. Mittelbach, *Phys. Rev. B* **1993**, *47*, 4146.

[17] C. Hartmann, M. Zigone, G. Martinez, E. L. Shirley, L. X. Benedict, S. G. Louie, M. S. Fuhrer, A. Zettl, *Phys. Rev. B* **1995**, 52, R5550.

0935-9648/99/0101-0033 $ 17.50+.50/0