

**Figure 1.** Part of the NH- $C_{\alpha}H$  region of the 300-MHz NOESY spectrum ( $2K \times 2K$  data matrix) of the decapeptide LHRH. The two framed regions 1 and 2 showing severe overlaps are also plotted on expanded scales. The corresponding regions from the NOESY TR spectrum ( $700 \tau$ , samples zero filled to  $2K \times 2K$ ) exhibiting homonuclear decoupling in the  $\omega_1$  dimension are shown in the frames 1' and 2'. No undesired cross peaks (see text) appeared in the NH- $C_{\alpha}H$  region so suppression<sup>10</sup> was unnecessary.  $N = 4$  (see text) was sufficient in this experiment since the  $C_{\alpha}$  protons can have at maximum three coupling partners, leading to the seven-step cycle  $\{\beta_j; W_j\}$ :  $[0^\circ; 0.500]$ ,  $[45^\circ; -0.586]$ ,  $[90^\circ; 1.000]$ ,  $[135^\circ; -3.414]$ ,  $[225^\circ; -3.414]$ ,  $[270^\circ; 1.000]$ ,  $[315^\circ; -0.586]$ .

multiplet structure in  $\omega_1$ . If necessary, the undesired peaks can also be suppressed<sup>10</sup> in a way similar to the suppression of zero-quantum coherence in NOESY.<sup>15</sup>

An application of NOESY to the decapeptide LHRH (p-Glu-His-Trp-Ser-Tyr-Gly<sup>6</sup>-Leu-Arg-Pro-Gly<sup>10</sup>-NH<sub>2</sub>) is demonstrated in Figure 1. Severe overlaps of the cross peaks in the two framed regions 1 and 2 impede assignments and render impossible quantitative NOE measurements. The problems can be resolved by decoupling in the  $\omega_1$  dimension by the application of NOESY TR. A comparison of the blowups 1, 2 and 1', 2' obtained with conventional NOESY and NOESY TR, respectively, clearly demonstrates the advantages of  $\omega_1$ -decoupling obtained with the proposed technique.

In conclusion, we have shown that it is indeed possible to reverse the  $J$  coupling evolution and demonstrated the utility in combination with 2D NOE spectroscopy. The technique is easy to implement on modern spectrometers, and the resulting spectra can enjoy considerable simplification compared to conventional spectra. The TR element can be inserted to achieve  $\omega_1$  decoupling in all homo- or heteronuclear 2D experiments where the components in phase with respect to the homonuclear couplings are

selected at the end of the evolution period.

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### Lanthanum Complexes of Spheroidal Carbon Shells

J. R. Heath,<sup>†</sup> S. C. O'Brien,<sup>†</sup> Q. Zhang, Y. Liu, R. F. Curl, H. W. Kroto,<sup>‡</sup> F. K. Tittel, and R. E. Smalley\*

Rice Quantum Institute and Departments of Chemistry and Electrical Engineering, Rice University  
Houston, Texas 77251

School of Chemistry and Molecular Sciences  
University of Sussex  
Brighton, U.K. BN1 9QJ

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In a recent letter<sup>1</sup> laser vaporization of graphite in a high-pressure supersonic nozzle was demonstrated to produce a remarkably stable  $C_{60}$  molecule in high yield. It was suggested that the stability of this new species arises from its unique ability to close into a highly aromatic, spheroidal shell: a truncated icosahedron where all carbons occupy equivalent sites at the juncture of (two) six-membered and (one) five-membered rings. This "soccerball" structure contains a central cavity which should be an exceptionally strong binding site for a wide range of even quite large atoms. In accord with this notion, we now present evidence for the formation of a stable  $C_{60}La$  complex. Also formed are a variety of less symmetrical  $C_nLa$  complexes, all of which are much more stable than the corresponding bare  $C_n$  cluster. None of the complexes shows any tendency to pick up an additional La atom. In all cases the complexes are thought to have the single La atom either wholly or partially surrounded by an aromatic shell of carbons arranged in networks of five- and six-membered rings.

The carbon source for this experiment was a low-density graphite disk<sup>2</sup> impregnated with lanthanum by exposure to a boiling, saturated solution of  $LaCl_3$  in water. After rinsing and drying, this disk was mounted in a rotation/translation device on the side of a pulsed supersonic nozzle.<sup>3</sup> Vaporization was performed by 5 ns, 35-mJ pulses of a Nd:YAG laser at 532 nm, focused to a 1-mm diameter spot on the graphite disk. The helium carrier (roughly 1 atm pressure) present in the pulsed nozzle at the time of laser vaporization thermalized the carbon fragments ejected from the graphite surface and provided a buffer gas to stabilize the La- $C_n$  reaction products. Expansion of this cluster-laden gas then produced a supersonic beam which was probed 1.2-m downstream by a time-of-flight (TOF) mass spectrometer. Ionization of the carbon clusters and reaction products was produced by ArF excimer laser radiation at 6.4 eV. Details of this apparatus have appeared elsewhere.<sup>4</sup>

Figure 1 displays the TOF mass spectrum of this carbon + lanthanum cluster beam at two widely differing fluences for the ionizing laser pulse. The vertical scale has been deliberately expanded as the dominant peak remains  $C_{60}$  as in our previous results<sup>1</sup> with pure graphite disks. The expanded scale shows many carbon clusters<sup>5</sup> in the form  $C_nLa$  where  $n$  is an even number

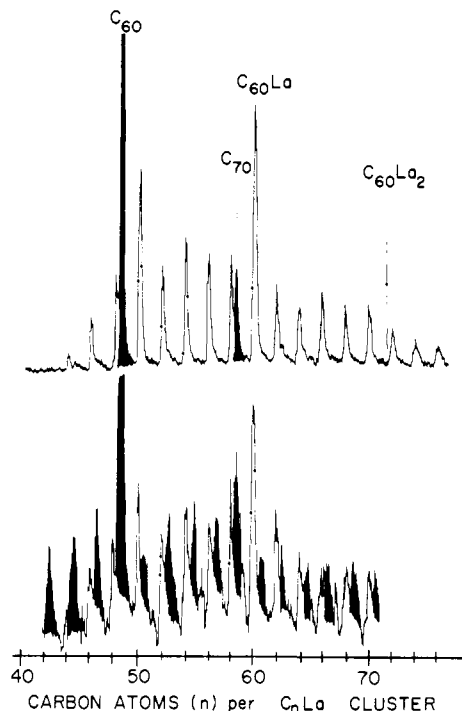
<sup>†</sup> Robert A. Welch Predoctoral Fellows.

<sup>‡</sup> University of Sussex.

(1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature (London)*, accepted for publication.

(2) Poco Graphite Inc., CZR-1 grade low density graphite, 1.54 gm cm<sup>-3</sup>.  
(3) O'Brien, S. C.; Liu, Y.; Zhang, Q.; Heath, J. R.; Tittel, F. K.; Curl, R. F.; Smalley, R. E. *J. Chem. Phys.*, submitted for publication.

(4) (a) Dietz, T. G.; Duncan, M. A.; Powers, D. E.; Smalley, R. E. *J. Chem. Phys.* **74**, 1981, 6511. (b) Powers, D. E.; Hansen, S. G.; Geusic, M. E.; Puiu, A. C.; Hopkins, J. B.; Dietz, T. G.; Duncan, M. A.; Langridge-Smith, P. R. R.; Smalley, R. E. *J. Phys. Chem.* **1982**, *86*, 2566. (c) Hopkins, J. B.; Langridge-Smith, P. R. R.; Morse, M. D.; Smalley, R. E. *J. Chem. Phys.* **1983**, *78*, 1627.



**Figure 1.** Time-of-flight mass spectrum of  $C_nLa$  cluster complexes (open peaks) and bare  $C_n$  clusters (blackened peaks) produced by laser vaporization of a lanthanum-impregnated graphite disk in a pulsed supersonic nozzle. The bottom trace was taken at low ( $<0.01 \text{ mJ cm}^{-2}$ ) ionizing fluence from an ArF excimer laser (6.4 eV, 10 ns). The top trace was taken with much higher ArF laser fluence ( $1\text{--}2 \text{ mJ cm}^{-2}$ ). Here multiphoton-induced fragmentation has reduced the mass spectrum to only the most stable photoions. Except for the particularly stable  $C_{60}$  and  $C_{70}$  species corresponding to the blackened peaks in this figure, the most stable photoions are found to contain a single lanthanum atom.

ranging from 44 to more than 76. At the much higher ArF ionizing laser fluence used to produce the top mass spectrum in Figure 1, fragmentation induced by multiphoton processes reveals the  $C_nLa^+$  species (and particularly  $C_{60}La^+$ ) to be the most stable possible photoions other than  $C_{60}^+$ . In fact,  $C_{60}^+$  and  $C_{70}^+$  are virtually the only bare carbon cluster ions detected. Note further that there is no evidence of any cluster picking up more than one La atom, suggesting that there is only one highly stable binding site in the  $C_n$  ligand.<sup>6</sup>

In accord with earlier workers,<sup>7</sup> our experiments on graphite indicate that large even-numbered clusters of carbon are ejected intact in the laser vaporization process.<sup>8</sup> This behavior is unique to graphite and probably results from the high stability of the graphite hexagonal sheets and the weak intersheet forces. Once in the gas phase, the even-numbered  $C_n$  clusters thus produced would not be expected to prefer the planar hexagonal structure of the bulk, since this leaves too many unsatisfied valences at the edges. Instead, these experiments suggest that these graphite fragments rearrange to a network of five- and six-membered rings, a process that bends the sheet back on itself with a curvature that ultimately produces a sphere of roughly 7-Å diameter.

As discussed elsewhere,<sup>1</sup> the most stable ultimate form,  $C_{60}$ , is thought to be a truncated icosahedron. Addition of an extra band of hexagons around the middle produces a reasonable candidate for the next most stable form: an egg-shaped  $C_{70}$ . Both these structures are closed, with all valences satisfied in a highly resonance-stabilized, rigid structure. Experiments such as those

(5) We assume species of the form  $C_nCl_x$  and  $C_nLaCl_x$  are also present in the beam but are not ionized to produce chlorine-containing photoions under these conditions.

(6) Similar results have now been obtained for  $C_nM$  clusters where  $M = Ca, Ba, \text{ and } Sr$ .

(7) Rohlffing, E. A.; Cox, D. M.; Kaldor, A. *J. Chem. Phys.* **1984**, *81*, 3322.

(8) Heath, J. R.; O'Brien, S. C.; Liu, Y.; Zhang, Q.; Curl, R. F.; Tittel, F. K.; Kroto, H. W.; Smalley, R. E., unpublished results.

of Figure 1 reveal that  $C_nLa$  complexes are also highly stable—particularly  $C_{60}La$ —just as would be expected if these  $C_n$  species surround the metal atom much as an egg (shell) surrounds its yoke.

Such aromatic “egg shell” complexes of metal atoms may be stable enough to survive in normal condensed-phase chemical environments. If so, they would provide interesting starting materials for new classes of compounds, reagents, and catalysts.

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### Separation of Oxygen Isotopic Compounds by Reversed-Phase Liquid Chromatography on the Basis of Oxygen Isotope Effects on the Dissociation of Carboxylic Acids

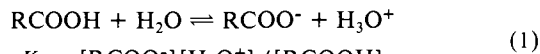
Nobuo Tanaka\* and Mikio Araki

Faculty of Textile Science  
Kyoto Institute of Technology  
Matsugasaki, Sakyo-ku, Kyoto 606, Japan  
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Separation of isotopic compounds is of much interest in modern liquid chromatography. Reversed-phase liquid chromatography (RPLC) using a hydrophobic stationary phase and an aqueous mobile phase has enabled the separation of hydrogen isotopic compounds,<sup>1</sup> including the separation between  $C_6H_6$  and  $C_6H_5D$ .<sup>1c</sup> We wish to report here the first example of the separation of oxygen isotopic compounds by RPLC. The three isotopic benzoic acids,<sup>2</sup>  $C_6H_5C^{16}O^{16}OH$  ( $1\text{-}^{16}O_2$ ),  $C_6H_5C^{16}O^{18}OH$  ( $1\text{-}^{16}O\text{-}^{18}O$ ), and  $C_6H_5C^{18}O^{18}OH$  ( $1\text{-}^{18}O_2$ ), were completely separated by the ionization control technique in RPLC<sup>3</sup> in about 20 h on the basis of the very slight difference in their acid dissociation constants.

The retention of solutes in RPLC is primarily determined by the hydrophobic property of the solutes.<sup>4</sup> Thus, carboxylic acids in the undissociated form show much larger retention than the corresponding carboxylate ions.<sup>3,5c</sup>

The retention ( $k'$ , or capacity factor) of a carboxylic acid in RPLC can be described by eq 2,<sup>3</sup> where  $k'_{AH}$ ,  $k'_{A^-}$ , and  $K_a$  stand



$$K_a = \frac{[RCOO^-][H_3O^+]}{[RCOOH]} \quad (1)$$

$$k' = \frac{k'_{AH}[RCOOH]}{[RCOOH] + [RCOO^-]} + \frac{k'_{A^-}[RCOO^-]}{[RCOOH] + [RCOO^-]} = \frac{k'_{AH}}{1 + K_a/[H_3O^+]} + \frac{k'_{A^-}K_a/[H_3O^+]}{1 + K_a/[H_3O^+]} \quad (2)$$

for the  $k'$  of the undissociated acid, the  $k'$  of the carboxylate ion, and the acid dissociation constant, respectively.

(1) (a) Tanaka, N.; Thornton, E. R. *J. Am. Chem. Soc.* **1976**, *98*, 1617-1619. (b) Cartoni, G. P.; Ferretti, I. *J. Chromatogr.* **1976**, *122*, 287-291. (c) Yamazaki, S.; Tanimura, T. Eighth International Symposium on Column Liquid Chromatography, Abstract 1a-44, New York, May, 1984.

(2)  $1\text{-}^{18}O_2$  stands for ordinary benzoic acid without any isotopic enrichment, unless its separation from other isotopic benzoic acids is specifically indicated.  $1\text{-}^{18}O_2$  and  $1\text{-}^{16}O\text{-}^{18}O$  were prepared from  $\alpha,\alpha,\alpha$ -trichlorotoluene and benzoyl chloride, respectively, by hydrolysis with  $H_2^{18}O$  of 97% enrichment. No exchange reaction seemed to take place during the separation.

(3) Karger, B. L.; LePage, J. N.; Tanaka, N. "High Performance Liquid Chromatography"; Horváth, C., Ed.; Academic Press: New York, 1980; pp 113-206.

(4) (a) Horváth, C.; Melander, W.; Molnár, I. *J. Chromatogr.* **1976**, *125*, 129-156. (b) Karger, B. L.; Gant, J. R.; Hartkopf, A.; Weiner, P. H. *Ibid.* **1976**, *128*, 65-78. (c) Tanaka, N.; Thornton, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 7300-7307.

(5) (a) Ellison, S. L. R.; Robinson, M. J. T. *J. Chem. Soc., Chem. Commun.* **1983**, 745-746. (b) Thornton, E. R. *J. Am. Chem. Soc.* **1962**, *84*, 2474-2475.