

## Bulk Production of a Strong Covalently Linked (C<sub>60</sub>H<sub>x</sub>)<sub>2</sub> Dimer

Yury V. Vasil'ev,<sup>\*,†</sup> Sotirios G. Kotsiris,<sup>†</sup> Igor O. Bashkin,<sup>\*,‡</sup> Vladimir E. Antonov,<sup>‡</sup>  
Alexander P. Moravsky,<sup>§</sup> and Thomas Drewello<sup>\*,†</sup>

*Department of Chemistry, University of Warwick, Coventry CV4 7AL, England, U.K., Institute of Solid State Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow District, RU, and Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow District, RU.*

*Received: April 5, 2005; In Final Form: May 17, 2005*

The high-pressure treatment of C<sub>60</sub> in an H<sub>2</sub> atmosphere at high temperatures leads to the efficient formation of a covalently bound dimer and some oligomeric species. The resulting hydrogenated C<sub>120</sub> is an example of the bulk production of covalently bound derivatized fullerene cores. Matrix-assisted laser desorption/ionization in conjunction with reflectron time-of-flight mass spectrometry has been applied to the product analysis. The dissociation pattern of selected C<sub>120</sub>H<sub>2x</sub><sup>+</sup> ions ( $x > 30$ ) indicates the dimeric structure of (C<sub>60</sub>H<sub>x</sub>)<sub>2</sub>, as opposed to a giant hydrofullerene species possessing a fused C<sub>120</sub> core. However, the results also clearly indicate a much stronger bonding (multiple  $\sigma$  bonding) between the C<sub>60</sub>H<sub>x</sub> units than present in cycloaddition products. Evidence of a covalently linked dimer was obtained in labeling experiments, on the basis of which any laser-induced gas-phase aggregation of the C<sub>60</sub>H<sub>x</sub> monomer during the analysis is discounted.

### Introduction

On the basis of potential uses as conductors or nanowires, fullerene polymers have attracted significant attention. The direct linking of fullerenes such as C<sub>60</sub> and C<sub>70</sub> via [2 + 2] addition, resulting in the formation of polymers, has been achieved by applying UV–vis irradiation<sup>1–3</sup> and high-pressure/high-temperature treatments.<sup>4–7</sup> The three-dimensional arrangement of potentially reactive double bonds leads to differently structured polymers and cross-linking.<sup>8</sup> More selective ways to polymerize C<sub>60</sub> and C<sub>70</sub> have been reported. The high-pressure/high-temperature treatment of a co-crystallate of C<sub>60</sub> and a calixarene (in which the C<sub>60</sub> molecules are aligned in linear columns) leads to the formation of linear chain (C<sub>60</sub>)<sub>n</sub> polymers.<sup>9</sup> The dimer<sup>10</sup> and trimer<sup>11</sup> of C<sub>60</sub> have been produced in a mechanochemical solid-state reaction using high-speed vibration milling of the fullerene in the presence of a catalyst. Although the mixed dimer of C<sub>60</sub> and C<sub>70</sub> could be prepared in the same manner,<sup>12</sup> there was no indication of the formation of the C<sub>70</sub> dimer using this method. Interestingly, the high-pressure dimerization of C<sub>70</sub> led to the selective formation of only one of five possible [2 + 2] addition isomers of (C<sub>70</sub>)<sub>2</sub>.<sup>13</sup>

The polymerization of derivatized fullerenes, where the repeat units would consist of directly bound fullerene cores which would still possess exohedrally attached ligands, represents a challenging task. The chemical modification of the carbon surface of a fullerene polymer is of interest in order to alter its material properties; however, any synthetic approach in this

direction faces considerable problems.<sup>14</sup> Either the polymerization has to be carried out without releasing the attached ligand or chemical reactions using a pure fullerene polymer must not affect the  $\sigma$ -bonds that link the fullerene units. These requirements are difficult to meet, as the most thermally labile bonds must remain intact. The present paper reports the successful production of (C<sub>60</sub>H<sub>x</sub>)<sub>n</sub> oligomers (where  $x > 30$  and  $n \leq 4$ ) following high-pressure/high-temperature treatment of C<sub>60</sub> in a hydrogen atmosphere and the structural characterization of the dimer by mass spectrometry. The product analysis was carried out by means of matrix-assisted laser desorption/ionization (MALDI) mass spectrometry. Ion dissociation experiments conducted with the hydrogenated dimer, in conjunction with isotopic labeling experiments involving the deuterated counterpart, provide supporting evidence for the covalent linking of two essentially intact hydrofullerene entities. The comparison with other dimeric fullerene derivatives and related cycloaddition products reveals that the bonding between the two C<sub>60</sub>H<sub>x</sub> moieties is stronger than for a [2 + 2] or [2 + 4] cycloaddition and that a giant hydro[120]fullerene structure can be equally discounted. Interestingly, a recent investigation into the hydrofullerenes derived by high-pressure/high-temperature treatment of C<sub>60</sub> with hydrogen reports the detection of a dimeric species in one of the studied samples.<sup>15</sup> Unfortunately, no further insight into elemental composition, structural features, and actual origin of this species could be provided.

### Experimental Section

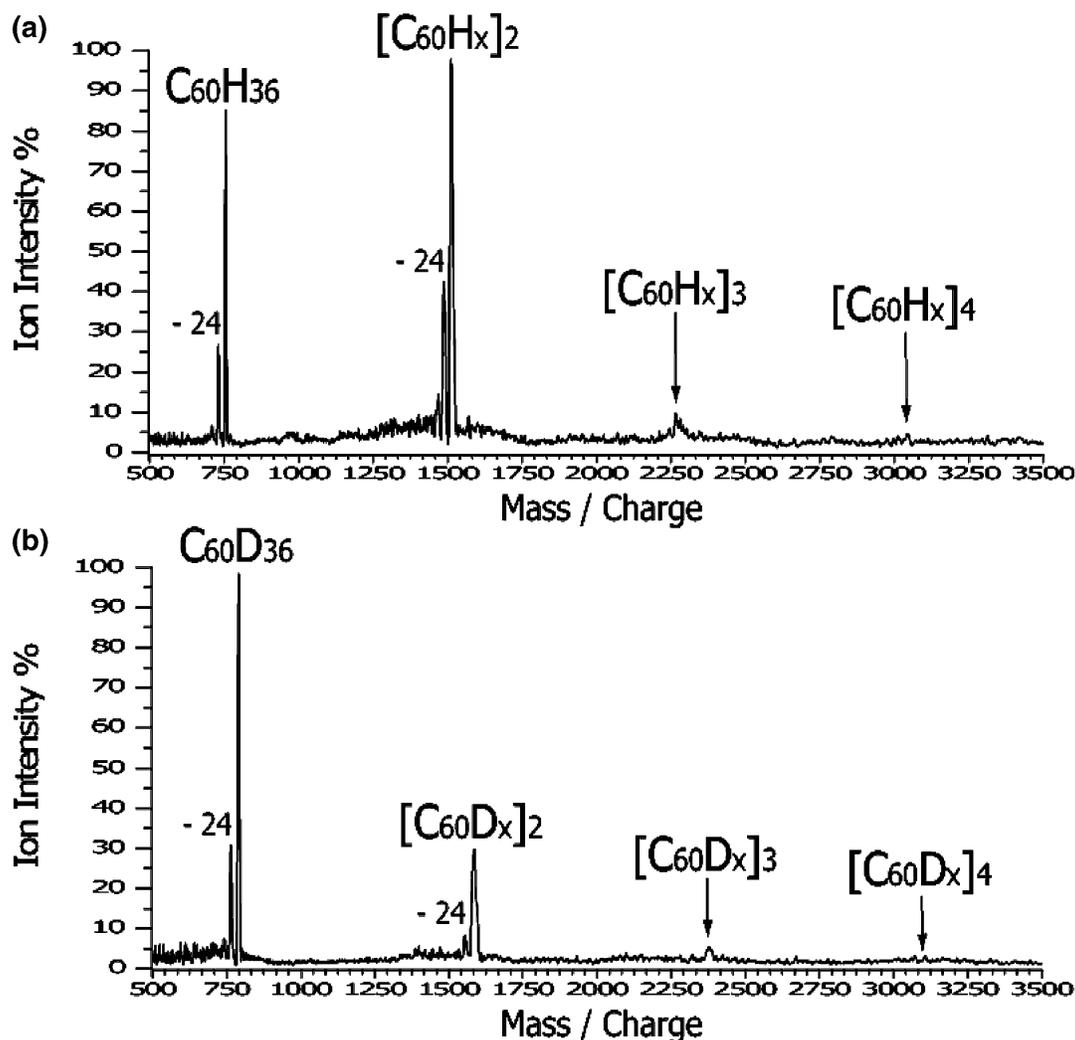
C<sub>60</sub> powder (99.99% purity with respect to C<sub>70</sub>) was prepared as described elsewhere<sup>4</sup> and sublimed at temperatures of up to 870 K in a dynamic vacuum at a pressure lower than 10<sup>-5</sup> Torr. The material was then brought to bulk polycrystalline state by sublimation in an evacuated quartz tube at 870–920 K. For the

\* To whom correspondence should be addressed. E-mail: Y.V.V., y.vasilev@oregonstate.edu; I.O.B., bashkin@issp.ac.ru; T.D., t.drewello@warwick.ac.uk.

<sup>†</sup> University of Warwick.

<sup>‡</sup> Institute of Solid State Physics, Russian Academy of Sciences.

<sup>§</sup> Institute of Problems of Chemical Physics, Russian Academy of Sciences.

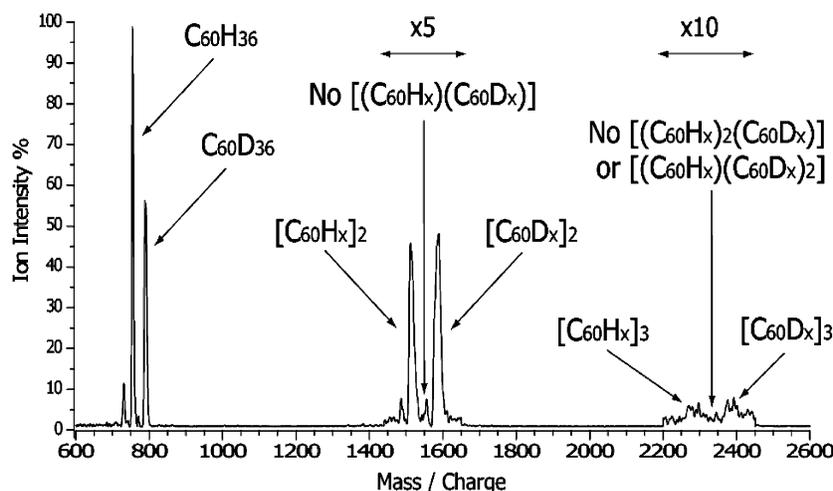


**Figure 1.** Positive-ion MALDI mass spectrum of the reaction product derived from high-pressure/high-temperature treatment of C<sub>60</sub> in H<sub>2</sub> (a) and D<sub>2</sub> (b) atmospheres, revealing oligomeric forms of (C<sub>60</sub>H<sub>x</sub>)<sub>n</sub> and (C<sub>60</sub>D<sub>x</sub>)<sub>n</sub> with  $x > 30$  and  $n \leq 4$ .

synthesis of hydrofullerites, 100 mg of C<sub>60</sub> was encased into ampules (made of copper or lead) together with AlH<sub>3</sub> at approximately the same weight. A thin Pd foil separated the two reagents. At a pressure of 7 kbar and temperatures higher than 450 K, AlH<sub>3</sub> decomposes and functions as a convenient source of hydrogen. Under these conditions, the hydrogen can penetrate the Pd foil, whereas Cu and Pb are less permeable for hydrogen, thus preventing the loss of hydrogen during further treatment. The amount of hydrogen in the ampules corresponded to a ratio of H/C<sub>60</sub>  $\geq$  90, so that hydrogen was always present in excess during the experiments. The assembled ampules were compressed using a toroid-type high-pressure device and subjected to a two-stage high-temperature treatment at a pressure of 30 kbar. The samples were initially maintained at 620  $\pm$  10 K for a period of 24 h. After this first stage, the reaction was usually not completed, as was concluded from the nonuniform color changes. In a second stage, the samples were kept for varying times at fixed temperatures ranging from 620 to 770 K. The time of this treatment varied from 24 h at lower temperatures to 6 h at higher temperatures and resulted in products that were uniformly white in color. Deuterated analogues were prepared by the same method using AlD<sub>3</sub>. Solid-state characterization of materials produced by similar means has been detailed elsewhere.<sup>16,17</sup>

For the MALDI analysis, 1 mg of the solid product (from the high-pressure/high-temperature treatment of C<sub>60</sub> in H<sub>2</sub>) was

taken up in 1 mL of tetrahydrofuran (THF). The resulting sample slurry was then mixed with a matrix solution, consisting of 1 mg of matrix in 1 mL of THF in a molar matrix-to-analyte ratio of 20:1. In contrast to earlier MALDI investigations of hydrofullerenes,<sup>18,19</sup> DCTB (for IUPAC name and structure, see refs 20 and 21) was used here as the MALDI matrix.<sup>20</sup> Recent experiments revealed the superior performance of DCTB as a matrix material for MALDI of a large variety of fullerene derivatives.<sup>21–23</sup> The DCTB matrix features low-threshold laser fluences<sup>20,23</sup> and a favorable thermochemistry<sup>23</sup> for the formation of most fullerene-related ions. This in turn leads to enhanced signal and less fragmentation. When calculating the matrix-to-analyte ratio, it was assumed that the analyte consisted entirely of C<sub>60</sub>H<sub>36</sub>. The matrix/analyte solution was deposited onto a stainless-steel target slide and dried in a cold air stream prior to the introduction into the ion source of the mass spectrometer. All experiments were conducted using a commercially available reflectron time-of-flight mass spectrometer (Kompact MALDI IV, Kratos, Manchester, U.K.). The instrument is equipped with a nitrogen laser at 337 nm with a pulse length of 3 ns. Ions are accelerated by a continuous potential difference of 20 kV. An ion gate precedes the reflectron in the linear flight tube and is employed for the deflection of unwanted ions, allowing the selection of ions of interest for fragmentation studies. A more comprehensive description of the experimental setup has been published elsewhere.<sup>24</sup> Each mass spectrum shown here repre-



**Figure 2.** Positive-ion MALDI mass spectrum of a target mixture containing the hydrogenated and deuterated products of the respective high-pressure/high-temperature reactions of  $C_{60}$  in  $H_2$  and in  $D_2$ .

sents the accumulation of 200 spectra, each acquired after a single laser shot. The resolving power in the present experiments did not exceed 500, and the mass accuracy varied from  $\pm 1$  to  $\pm 5$  amu.

## Results and Discussion

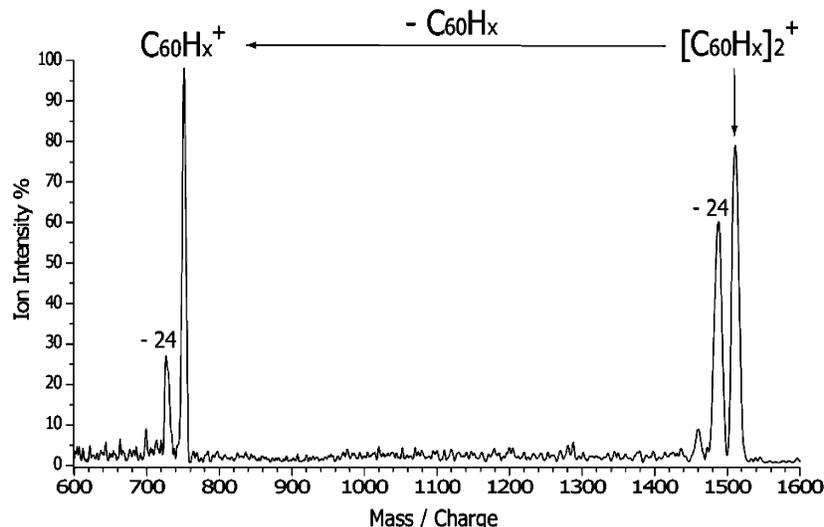
Mass spectrometry-based experiments have been of prime importance for the analysis and physicochemical characterization of derivatized fullerenes. The mechanism of transfer of the solid hydrofullerene into the gas phase has proven crucial for successful analysis, as the facile loss of initially attached hydrogen can hinder the establishment of the exact hydrogen attainment. The use of MALDI with  $C_{60}H_{36}$  produces  $C_{60}H_{35}^+$  as the quasi-molecular ion.<sup>18</sup> The ion formation can be controlled in such a way that further unwanted dissociations of both neutrals and ions can be prevented.<sup>18,19</sup> Although the understanding of the formation mechanism of the quasi-molecular ion is not well-developed at present, its presence is indicative of the hydrogen attainment of the neutral. Consequently, MALDI is applied in this investigation as the method of choice for the analysis of the hydrofullerenes. For the formation of negative ions in conjunction with laser desorption, see ref 25.

The positive-ion MALDI mass spectrum of the products resulting from high-pressure/high-temperature treatment of  $C_{60}$  in  $H_2$  atmosphere is shown in Figure 1a. The signal assigned to  $C_{60}H_{36}$  is centered at  $m/z$  755/756 and is accompanied at higher masses by abundant signals relating to the dimer and, to a lesser extent, by signals for the trimer and the tetramer. While the mass accuracy in these experiments was sufficient to confidently assign signals within the monomer region, the higher-mass region was affected by a mass uncertainty of approximately  $\pm 5$  amu. Although it was therefore not possible to reveal the exact hydrogen content of the dimer, the findings clearly indicate that about 70 hydrogen atoms are still attached to the dimer. This conclusion has been confirmed by the investigation of the corresponding deuterated species (Figure 1b) that resulted from the reaction of  $C_{60}$  in a  $D_2$  atmosphere. The deuterated species in Figure 1b display exactly the mass shifts that are expected for their assignment as the deuterated counterparts of the  $(C_{60}H_x)_n$  oligomers observed in Figure 1a. This also confirms that each oligomer in Figure 1a incorporates multiple  $C_{60}$  units. Any significant contribution of alternative elemental compositions, whereby a carbon atom was replaced by 12 hydrogen atoms, would have resulted in higher mass shifts than observed

in Figure 1b, as the deuterated species would have revealed an additional mass shift of 12 Da for each replaced carbon atom. However,  $C_{60}$  is not the only carbon core involved. The monomer and dimer signals in Figure 1a are both accompanied by a satellite peak which is 24 mass units lower in mass. This mass difference corresponds to  $C_2$ , as the corresponding deuterated species in Figure 1b are also spaced by 24 mass units. A comprehensive investigation into the dissociation behavior of ionized hydrofullerenes<sup>26</sup> revealed that the  $C_2$  loss channel is unimportant for both neutral and ionized  $C_{60}H_x$  (with  $x = 18-36$ ). The dissociations of ionized  $C_{60}H_x$  (with  $x = 18-36$ ) are characterized by loss of alkyl units ( $C_nH_m$  with  $n = 1, 2, 3, \dots$ ) rather than  $C_2$  losses.<sup>26</sup> Consequently, it must be assumed that this "impurity" originates from the actual sample. In fact, it has been recently suggested that prolonged hydrogenation of  $C_{60}$  at elevated temperatures and pressures may lead to the bulk production of "fragmented fullerenes" such as  $C_{58}H_x$ .<sup>27</sup> Since this species is not accessible via  $C_2$  loss from  $C_{60}H_x$ , it has to be concluded that the low-mass satellites in the monomer and dimer region (Figure 1a) incorporate a  $C_{58}H_x$  entity which has been formed during the synthesis.

Although the MALDI mass spectrum indicates the detection of abundant quantities of dimeric hydrofullerenes, the actual origin of this dimer remains to be identified. Direct laser desorption of pure fullerenes leads predominantly to their efficient fusion into larger (giant) fullerenes,<sup>28-30</sup> whereas the "softer" MALDI process can readily promote the aggregation of a suitable fullerene derivative into oligomeric forms. Recent examples include the formation of  $(C_{60})_2O_n$ <sup>31</sup> and  $(C_{70})_2O_n$ ,<sup>32</sup> formed in the MALDI process from the respective monomeric fullerene oxides. These experiments strongly indicated that the resulting dimers possess the same structural features as macroscopic  $(C_{60})_2O$ .<sup>33,34</sup> It is therefore necessary to establish the origin of the  $C_{120}H_{2x}$  dimer observed in the present investigation either as the result of a laser-induced gas-phase reaction or as a genuine product of the high-pressure/high-temperature synthesis. For this purpose, a MALDI target was prepared using a mixture of the reaction product that resulted from the treatment of  $C_{60}$  with  $H_2$  and the product that resulted when using  $C_{60}$  and  $D_2$ .

The intention of this experiment is it to evaluate the extent to which laser-induced dimerization takes place, as indicated by the abundance of the mixed dimer ion,  $(C_{60})_2H_xD_x^{*+}$ . The resulting positive-ion MALDI mass spectrum is depicted in



**Figure 3.** Positive-ion dissociation mass spectrum of the size-selected dimer  $(C_{60}H_x)_2^{2+}$ , featuring the formation of monomeric  $C_{60}H_x^{+}$  product ions.

Figure 2. The signals corresponding to the hydrogenated and deuterated  $C_{60}$  monomers appear in a ratio of approximately 3:2, while the respective dimeric ion signals show a ratio of roughly 1:1. This variation may be attributed to slight variations in the composition of the two mixed reaction products or might indicate different stabilities of the two isotopomeric dimers. The vital observation is, however, that a signal indicative of a mixed dimer,  $(C_{60})_2H_xD_x^{2+}$ , is not present. If the dimer formation was caused exclusively by gas-phase aggregation of the hydrogenated and deuterated monomers which are observed in a ratio of 3:2 (Figure 2), and assuming equal rates for the formation of the three different dimeric species, the formation of  $(C_{60})_2H_x^{2+}/(C_{60})_2H_xD_x^{2+}/(C_{60})_2D_x^{2+}$  would have resulted in a ratio of 9:12:4. Alternatively, the ratio of 1:1, as observed in Figure 2 for the hydrogenated and deuterated dimer ions, would afford an abundance of the mixed dimer which is twice as high as the one observed for each of the unmixed dimers. In either case, a significant abundance of the mixed dimer would be expected, but is not observed. The entire absence of the corresponding signal serves to counter the hypothesis that dimer formation is caused by gas-phase aggregation. This in turn establishes the hydrogenated  $C_{120}$  species as a genuine reaction product present within the sample.

In the following, experiments are discussed which are aimed at the structural characterization of the  $(C_{60}H_x)_2$  dimer. The essential issue addressed here concerns the formation of a dimeric  $(C_{60}H_x)_2$  in its intrinsic sense as two connected, intact units, as opposed to the formation of a giant, hydrogen-containing  $C_{120}$  core. The unimolecular decay behavior of ionized hydrofullerenes, such as  $C_{60}H_{18}$  and  $C_{60}H_{36}$ , features (in addition to the loss of hydrogen) the efficient loss of neutral hydrocarbon entities.<sup>26</sup> In analogy, a giant  $C_{120}$  hydrofullerene ion can be expected to feature similar dissociations, whereas a dimeric structure would most likely undergo a pronounced fission reaction, leading to a charged monomer and a neutral monomer. The fragmentation behavior of the ionized dimer was therefore studied in a post-source decay (PSD) experiment,<sup>21</sup> in which the dimer ion is selected using the ion gate located in the linear flight part preceding the reflectron of the mass spectrometer; the latter subsequently achieves a separation of fragment and undissociated parent ions. The resulting daughter ion spectrum is shown as Figure 3.

The selectivity of the ion gate for the isolation of a particular ion of interest is approximately  $\pm 44$  amu in the mass range

under investigation. Therefore, both  $C_{120}H_x^{2+}$  and the low-mass satellite  $C_{118}H_x^{2+}$  are simultaneously selected (Figure 3). Although the selectivity is poor, it is sufficient to prevent any monomeric component that might have been generated in the ion source from reaching the detector. However, an abundant signal at approximately 750 Da is observed in the monomer mass region. The mass accuracy in this experiment amounts to about  $\pm 5$  Da so that this finding clearly indicates that a decomposition of the  $C_{120}H_x^{2+}$  dimer ion has taken place into a neutral component and an ionic component which are approximately equal in size. The monomeric  $C_{60}H_x^{+}$  fragment is again accompanied by the  $C_{58}H_x^{+}$  satellite 24 mass units below, the most likely origin of which is the decomposition of the co-selected  $C_{118}H_x^{2+}$ , which therefore possesses a  $(C_{58}H_x)(C_{60}H_x)$  structure.

The close similarity of the monomer region in the MALDI mass spectrum in Figure 1a with the corresponding fragmentation pattern of the dimer (Figure 3) indicates that dissociation of the oligomeric species may be an important source of the observed monomers. Unfortunately, the present experiments do not allow one to decide to which extent decomposition might have influenced the appearance of the MALDI mass spectrum in Figure 1a.

Finally, further structural information can be derived from the comparison of related fullerene derivatives studied under identical experimental conditions. In separate investigations, we have studied the MALDI behavior of fullerene compounds that feature similar or even stronger bonding between their entities compared with an assumed [2 + 2] cycloaddition motif within  $(C_{60}H_x)_2$ . These samples included the [4 + 2] cycloaddition product of anthracene and  $C_{60}$ ,<sup>35</sup> the  $(C_{70})_2$  dimer, featuring a [2 + 2] cycloaddition motif,<sup>13</sup> and the  $\sigma$ -CC bonded  $(C_{59}N)_2$  azaheterodimer.<sup>36</sup> None of these molecules provides under comparable MALDI conditions a detectable molecular ion in the positive ion mode. This in turn provides a clear indication that the  $(C_{60}H_x)_2$  dimers must possess a higher bond dissociation energy than these reference compounds. This discounts a linkage of both moieties via [2 + 2] cycloaddition. Consequently, one must conclude that the two  $C_{60}H_x$  units in  $(C_{60}H_x)_2$  are linked via multiple bonds that are strong enough to allow the transfer of the intact dimer into the gas phase, while both entities retain their structural integrity. Interestingly, stable dumbbell-like  $(C_{60})_2$  dimers of this type have been proposed in computational studies.<sup>37</sup>

## Conclusion

High-pressure/high-temperature treatment of C<sub>60</sub> in an H<sub>2</sub> atmosphere leads to the formation of oligomeric hydrofullerenes. MALDI experiments, in conjunction with isotopic labeling and selected ion dissociations, reveal a dumbbell-like (C<sub>60</sub>H<sub>x</sub>)<sub>2</sub> structure. However, while retaining their integrity, both entities are linked by strong covalent bonding, exceeding the bond dissociation energy of single  $\sigma$ -CC bonded and cycloaddition dimers.

**Acknowledgment.** The work at Warwick was financially supported by The Leverhulme Trust. S.G.K. is grateful to Warwick University for a fully funded studentship. The high-pressure experiments were supported by the RFBR (grant no. 02-02-16859) and by the Russian program "Fullerenes and Atomic Clusters". The authors are indebted to Dr. N. Chronakis, Prof. M. Orfanopoulos, Dr. S. Lebedkin, Prof. M. M. Kappes, and Prof. A. Hirsch for providing samples for separate investigations, which allowed insight into the bonding situation of the dimeric hydro[60]fullerene.

## References and Notes

- (1) Rao, A. M.; Zhou, P.; Wang, K.; Hager, G. T.; Holden, J. M.; Wang, Y.; Lee, W.; Bi, X.; Eklund, P. C.; Cornett, D. S.; Duncan, M. A.; Amster, I. J. *Science* **1993**, *259*, 955.
- (2) Burger, B.; Winter, J.; Kuzmany, H. Z. *Physica* **1996**, *101*, 227.
- (3) Ata, M.; Kurihara, K.; Takahashi, N. *J. Phys. Chem. B* **1997**, *101*, 5.
- (4) Bashkin, I. O.; Rashchupkin, V. I.; Gurov, A. F.; Moravsky, A. P.; Rybchenko, O. G.; Kobelev, N. P.; Soifer, Ya. M.; Ponyatovsky, E. G. *J. Phys.: Condens. Matter* **1994**, *6*, 7491.
- (5) Iwasa, Y.; Arima, T.; Fleming, R. M.; Siegrist, T.; Zhou, O.; Haddon, R. C.; Rothberg, L. J.; Lyons, K. B.; Carter, H. L., Jr.; Hebard, A. F.; Tycko, R.; Dabbagh, G.; Krajewski, J. J.; Thomas, G. A.; Yagi, T. *Science* **1994**, *264*, 1570.
- (6) Rao, A. M.; Eklund, P. C.; Hodeau, J.-L.; Marques, L.; Nunez-Regueiro, M. *Phys. Rev. B* **1997**, *55*, 4766.
- (7) Iwasa, Y.; Furudate, T.; Fukawa, T.; Ozaki, T.; Mitani, T.; Yagi, T.; Arima, T. *Appl. Phys. A* **1997**, *64*, 251.
- (8) Sundqvist, B. *Adv. Phys.* **1999**, *48*, 1; and references therein.
- (9) Sun, D.; Reed, C. A. *Chem. Commun.* **2000**, 2391.
- (10) Wang, G.-W.; Komatsu, K.; Murata, Y.; Shiro, M. *Nature (London)* **1997**, *387*, 583.
- (11) Komatsu, K.; Fujiwara, K.; Murata, Y. *Chem. Lett.* **2000**, *9*, 1016.
- (12) Komatsu, K.; Fujiwara, K.; Murata, Y. *Chem. Commun.* **2000**, 1583.
- (13) Lebedkin, S.; Hull, W. E.; Soldatov, A.; Renker, B.; Kappes, M. M. *J. Phys. Chem. B* **2000**, *104*, 4101.
- (14) Segura, J. L.; Martín, N. *Chem. Soc. Rev.* **2000**, *29*, 13; and references therein.
- (15) Talyzin, A. V.; Sundqvist, B.; Shulga, Y. M.; Peera, A. A.; Imus, P.; Billups, W. E. *Chem. Phys. Lett.* **2004**, *400*, 112.
- (16) Kolesnikov, A. I.; Antonov, V. E.; Bashkin, I. O.; Li, J. C.; Moravsky, A. P.; Ponyatovsky, E. G.; Tomkinson, J. *Physica B* **1999**, *263–264*, 436.
- (17) Bashkin, I. O.; Antonov, V. E.; Kolesnikov, A. I.; Ponyatovsky, E. G.; Mayers, J.; Parker, S. F.; Tomkinson, J.; Moravsky, A. P.; Shulga, Yu. M. *Mol. Mater.* **2000**, *13*, 251.
- (18) Rogner, I.; Birkett, P.; Campbell, E. E. B. *Int. J. Mass Spectrom.* **1996**, *156*, 103.
- (19) Vasil'ev, Y.; Wallis, D.; Nüchter, M.; Ondruschka, B.; Lobach, A. S.; Drewello, T. *Chem. Commun.* **2000**, 1233.
- (20) Ulmer, L.; Mattay, J.; Torres-Garcia, H. G.; Luftmann, H. *Eur. J. Mass Spectrom.* **2000**, *6*, 49.
- (21) Brown, T.; Clipston, N. L.; Simjee, N.; Luftmann, H.; Hungerbühler, H.; Drewello, T. *Int. J. Mass Spectrom.* **2001**, *210/211*, 249.
- (22) Fati, D.; Leeman, V.; Vasil'ev, Y. V.; Drewello, T.; Leyh, B.; Hungerbühler, H. *J. Am. Soc. Mass Spectrom.* **2002**, *13*, 1448.
- (23) Streletskii, A. V.; Ioffe, I. N.; Kotsiris, S. G.; Barrow, M. P.; Drewello, T.; Strauss, S. H.; Boltalina, O. V. *J. Phys. Chem. A* **2005**, *109*, 714.
- (24) Barrow, M. P.; Drewello, T. *Int. J. Mass Spectrom.* **2000**, *203*, 111.
- (25) Vasil'ev, Y.; Absalimov, R. R.; Nasibullaev, S. K.; Lobach, A. S.; Drewello, T. *J. Phys. Chem. A* **2001**, *105*, 661.
- (26) Möder, M.; Nüchter, M.; Ondruschka, B.; Czira, G.; Vékey, K.; Barrow, M. P.; Drewello, T. *Int. J. Mass Spectrom.* **2000**, *195/196*, 599.
- (27) Talyzin, A. V.; Tsybin, Y. O.; Peera, A. A.; Schaub, T. M.; Marshall, A. G.; Sundqvist, B.; Mauron, P.; Züttel, A.; Billups, W. E. *J. Phys. Chem. B* **2005**, *109*, 5403.
- (28) Yeretzian, C.; Hansen, K.; Diederich, F.; Whetten, R. L. *Nature (London)* **1992**, *359*, 44.
- (29) Shvartsburg, A. A.; Hudgins, R. R.; Dugourd, Ph.; Jarrold, M. F. *J. Phys. Chem. A* **1997**, *101*, 1684.
- (30) Shvartsburg, A. A.; Pederson, L. A.; Hudgins, R. R.; Schatz, G. C.; Jarrold, M. F. *J. Phys. Chem. A* **1998**, *102*, 7919.
- (31) Barrow, M. P.; Tower, N. J.; Taylor, R.; Drewello, T. *Chem. Phys. Lett.* **1998**, *293*, 302.
- (32) Al-Jafari, M. S.; Barrow, M. P.; Taylor, R.; Drewello, T. *Int. J. Mass Spectrom.* **1999**, *184*.
- (33) Lebedkin, S.; Ballenweg, S.; Gross, J.; Taylor, R.; Krätschmer, W. *Tetrahedron Lett.* **1995**, *36*, 4971.
- (34) Taylor, R.; Barrow, M. P.; Drewello, T. *J. Chem. Soc., Chem. Commun.* **1998**, 2497.
- (35) Chronakis, N.; Orfanopoulos, M. *Tetrahedron Lett.* **2001**, *42*, 1201.
- (36) Berthold, N.; Hirsch, A. *Chem. Commun.* **1996**, 1421.
- (37) Gal'pern, E. G.; Stankevich, I. V.; Chistyakov, A. L.; Chernozatonskii, L. A. *Chem. Phys. Lett.* **1997**, *269*, 85.