

Sled-Type Motion on the Nanometer Scale: Determination of Dissipation and Cohesive Energies of C₆₀

R. Lüthi,* E. Meyer, H. Haefke, L. Howald, W. Gutmannsbauer, H.-J. Güntherodt

The tribological properties of C₆₀ on the mesoscopic scale were investigated with a scanning force microscope, which allowed simultaneous measurements of normal and lateral forces under ultrahigh-vacuum conditions. Islands of C₆₀, deposited on NaCl(001), could be moved by the action of the probing tip in a controlled way. Different modes of motion, such as translation and rotation, were observed. An extremely small dissipation energy of about 0.25 millielectron volt per molecule and a cohesive energy of 1.5 electron volts were determined in these nanometer-scale experiments. The corresponding shear strength of 0.05 to 0.1 megapascal was smaller by one order of magnitude than typical values of boundary lubricants. For C₆₀ on graphite, disruption of the islands was observed and collective motion of the islands could not be achieved. These results could find use in the field of nanotechnology; for example, C₆₀ islands could be developed into a sled-type transport system on the nanometer scale.

The mechanical properties of fullerenes have attracted much attention in the scientific community. The nearly spherical shape and low surface strength of fullerenes are believed to be the essential ingredients for a material that could play a role as important as Teflon (polytetrafluoroethylene). Theoretical studies of these materials have predicted an exceptional rigidity (1) and load-bearing capacity (2). Experimental studies on a macroscopic scale have shown (3) that the tribological properties of C₆₀ films are strongly dependent on the preparation conditions. Rather high wear rates are observed on films that are sublimed from solution, whereas ion-bombarded films exhibit improved wear lifetime. The friction of these ion-bombarded films is comparable to that of solid lubricants, such as MoS₂ or graphite.

Recently, scanning tunneling microscopy (STM) was used to move atoms and molecules in a controlled way (4). Normal force F_N and lateral force F_L can be measured during the modification process with a modified scanning force microscope (SFM), termed a friction force microscope (FFM) (5). We have developed an ultrahigh-vacuum (UHV) FFM, based on laser-beam deflection (6), that can be used for in situ study of the samples (7).

We used C₆₀ powder (purity, 99.99%; MER Corporation, Tucson, Arizona). Before deposition, we purified the powder by removing organic solvents in the effusion cell at 375°C for 5 hours. The C₆₀ films were grown by vapor deposition onto NaCl(001) and highly oriented pyrolytic graphite

(HOPG), both of which were freshly cleaved under UHV conditions. The substrate was maintained at room temperature. Nominal film thicknesses ranged from 0.5 to 3 monolayers (ML), which were obtained at a rate of 0.1 ML min⁻¹. The film thickness and deposition rate were controlled by a water-cooled quartz oscillator. The films were characterized by topographic images, where is-

lands of 2 to 5 ML were observed. Both NaCl and C₆₀ could be resolved on the atomic scale. Lattice constants were found to be in agreement with the bulk values (8). Terraces were atomically smooth, and no additional roughness was observed for all films studied. The base pressure in our UHV chamber was below 5×10^{-11} mbar, which guaranteed that the surface remained clean during the experiments. The friction coefficient at the interface between the probing tip (oxidized Si) and the C₆₀ islands was 0.15 (9). This value is in agreement with the values found by Bhushan *et al.* (10) but deviates from the results of Mate (11) (both of these experiments were performed at ambient pressure). The differing value of Mate (0.8) is probably related to a different film growth mode, as pointed out by Bhushan *et al.* (3, 10), which causes a larger ploughing component of the lateral forces. Microscopic experiments at the interface between the probing tip and C₆₀ have demonstrated that films of high quality are reasonable solid film lubricants but do not exhibit unusual behavior. We show below that the tribological behavior at the interface between C₆₀ and NaCl(001) is unexpected.

A sequence of 530 nm by 530 nm SFM images of C₆₀ islands grown on a NaCl(001) substrate (Fig. 1) represents a top view of the sample surface recorded at constant normal force. Applied normal

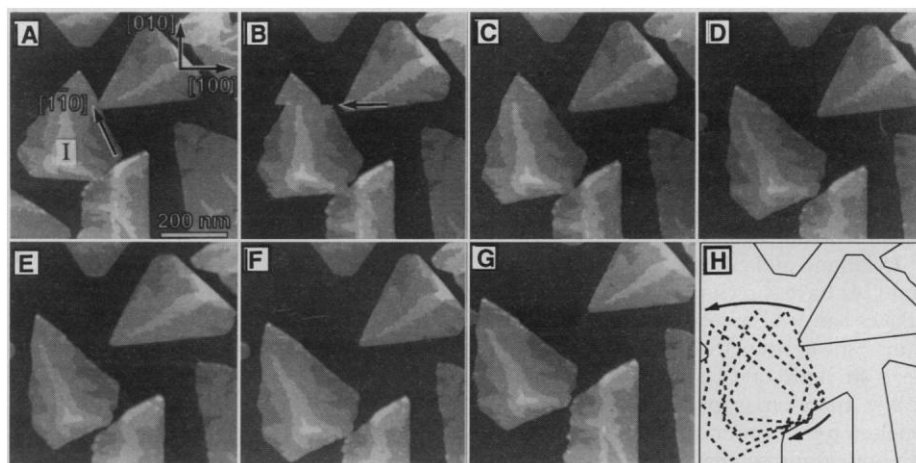


Fig. 1. (A through G) A sequence of 530 nm by 530 nm top-view SFM images of C₆₀ on NaCl(001). The dark areas correspond to the NaCl(001) substrate, and the bright areas are assigned to C₆₀ islands. The crystallographic directions of the NaCl substrate are indicated at the top right in (A). A C₆₀ island [labeled as I in (A)] is moved successively (A to G) by the controlled action of the probing tip without destroying the island as an entity. The image shown in (B) represents a snapshot of a typical shear event when an island is moved during the scan process [indicated with an arrow in (B)]. Two types of island motion are identifiable in the image sequence: First, a (nearly continuous) rotation, and second, a translation from one location to another. The C₆₀ island is rotated counterclockwise by $\sim 3^\circ$ (A) $\rightarrow$ (B), $\sim 9^\circ$ (B) $\rightarrow$ (C), and $\sim 13^\circ$ (C) $\rightarrow$ (D). From (E) to (G), the orientation of the C₆₀ island is unchanged (the in-plane angle between [110] of the C₆₀ island and [010] of NaCl is $\sim 52^\circ$) and is translated laterally until it is blocked by the left adjacent C₆₀ island. (H) A summary of the movement of the C₆₀ island (dashed lines). In this FFM study, microfabricated *n*-doped Si cantilevers of rectangular shape (normal and torsion spring constant of 0.04 and 17.4 N/m, respectively) were used (20). During imaging, applied normal forces ranged from 1 to 2 nN (21). In order to obtain maximum sensitivity in the lateral force signal, the scan angle was chosen perpendicular to the long axis of the cantilever.

Institute of Physics, University of Basel, Klingelbergstrasse 82, CH-4056 Basel, Switzerland.

*To whom correspondence should be addressed.

forces between the probing tip (oxidized Si) and the sample ranged from 1 to 2 nN. When the force was increased from 2 to 10 nN, the lateral force on impact with the step edge was sufficient to move the C_{60} island as an entity in a controlled way and without destroying it (compare Fig. 1, A through G). The actual lateral force needed to move an island is proportional to the area and depends on the location on the substrate. On flat terraces the islands can be easily moved, whereas at step edges the lateral force is higher or the motion is even inhibited.

Some representative profiles from dozens of different modification processes obtained by moving C_{60} islands on a step-free area are shown in Fig. 2A. When the probing tip came in contact with the perimeter of the island, the lateral force increased to $F_{L(max)}$, at which point the force stored in the cantilever deflection was large enough to move the island. The force decreased to an average minimum value $F_{L(avg)}$ during sliding. When the island approached an imperfection on the substrate, the lateral force increased again until the island stopped sliding and the tip could rise over the island edge. If we take into account the contact area A of a C_{60} island, the shear strength τ can be determined from the lateral force F_L according to $\tau = F_L/A$. For island I (in Fig. 1A) with $A = 7.5 \times 10^4 \text{ nm}^2$, we found that the shearing started at a shear strength of 0.1 MPa and decreased to 0.05 MPa during sliding. These values are about one order of magnitude less than typical shear strengths of conventional lubricants, such as cadmium arachidate (12). We also investigated C_{60} on graphite, where disruption of the islands was observed and collective motion of the islands could not be achieved (Fig. 3).

Several mechanisms can be invoked to explain the differing shear strengths:

1) Hirano and Shinjo (13) and McClelland (14) have shown that incommensurate surfaces can lead to very small, if not vanishing, shear strengths. The fact that the shear strength of C_{60} on NaCl is much weaker than on graphite leads us to the conclusion that commensurability is not the only important parameter. Apparently, the bonding between C_{60} and the substrate can change the frictional behavior drastically.

2) The creation and movement of dislocations can influence shear strengths. However, recent molecular dynamics simulations have shown that the formation of dislocations is energetically unfavorable for nanometer-sized objects (15). Therefore, we assume that the islands are moved as an entity. Thus, the dissipation energy (0.25 meV per molecule), determined by dividing the product of shear force and distance by the number of molecules, is a meaningful number.

3) The rotation of C_{60} molecules at the

interface might be a relevant parameter to explain the shear strength. The spinning inhibits the formation of direction-dependent bonding and minimizes stick-slip (14, 16). Experiments by Altman and Colton

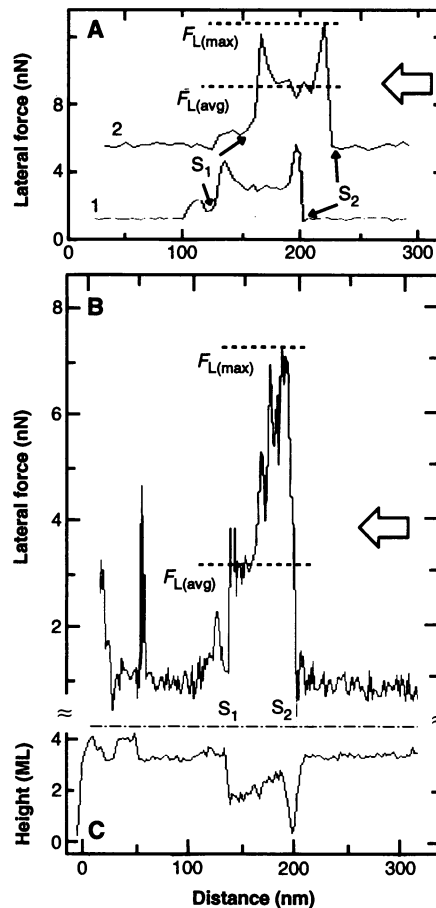


Fig. 2. (A) Movement of free islands (curves 1 and 2): Two representative snapshots of shear events of free C_{60} islands are shown (curve 2 is slightly offset). The shear event takes place between positions S_1 and S_2 . The outlined arrow indicates the scan direction. The maximum lateral force $F_{L(max)}$ represents the amount of force necessary to overcome static friction of the C_{60} island on the NaCl substrate and decreases to $F_{L(avg)}$, the kinetic friction. Taking into account the area of the moved island (island I in Fig. 1A), we could determine a shear strength τ ranging from 0.1 MPa (at the start of shear) to 0.05 MPa (during sliding) and a dissipation energy of 0.25 meV per molecule per lattice distance. (B and C) Fracture experiments: lateral force data (B) were acquired simultaneously with the topographic profile (C) taken at the position marked by the arrow in Fig. 1B. Before the shear event, the island was coalesced to other islands (compare Fig. 1A). The common boundary with the neighboring islands was 125 nm in length and 3 ML in height. Analysis of the lateral force data of this shear event yields an estimation for the cohesive energy of C_{60} molecules. The area under the curve from S_1 to S_2 [$F_{L(max)} \rightarrow F_{L(avg)}$] corresponds to the energy that is necessary to separate the C_{60} island from its neighbors, 550 eV. Thus, a cohesive energy of $550 \text{ eV}/(3 \text{ ML by } 125 \text{ nm}) = 1.5 \text{ eV}$ for C_{60} can be derived.

with STM have shown that the spinning strongly depends on the interaction with the substrate (17). The internal structure of C_{60} on gold was observed, which means that the molecules were frozen, whereas the internal structure on a GaAs surface could not be observed. By analogy, the different bonding of C_{60} on graphite and C_{60} on NaCl might lead to a freezing of the rotation of molecules at the interface.

Another important property of a lubricant is its ability to conserve its local order during a sliding process. Therefore, it is important that the cohesive energy is large enough. In some shearing events, we observed the fracture of small parts of islands and the formation of new surfaces. In Fig. 2, B and C, the line section of lateral force data and the topographic profile, respectively, of a fracture experiment are shown. By analogy to the determination of the dissipation energy, the cohesive energy of C_{60} can be derived from the measured lateral forces during fracture. As shown in Fig. 1A, a large surface (125 nm by 3 ML) is created at the island perimeter with a lateral force of 7.5 nN, corresponding to an energy of $0.55 \pm 0.1 \text{ keV}$, which yields to a cohesive energy of $0.55 \pm 0.1 \text{ keV}/(125 \text{ nm} \times 3 \text{ molecules}) = 1.5 \pm 0.3 \text{ eV}$. Theoretical calculations (18) have yielded values of $\sim 2 \text{ eV}$ for the cohesive energy, whereas sublimation experiments at 760 K give a value of 1.6 eV (19). Both values are in good agreement with ours.

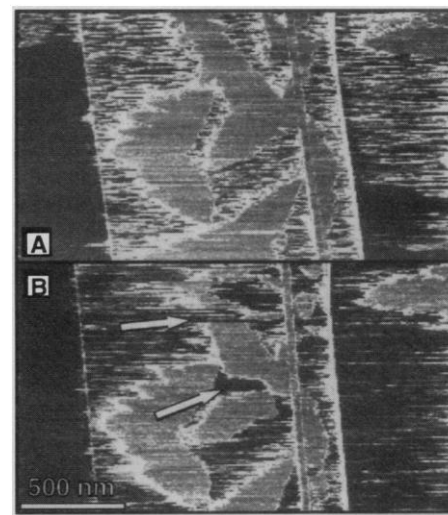


Fig. 3. Friction force maps of C_{60} deposited on HOPG(0001) (A) before and (B) after a local modification experiment. Bright areas are assigned to the C_{60} islands, which we interpret as due to higher friction on the C_{60} islands as compared to the HOPG substrate. Force conditions similar to those applied in the case of C_{60} on NaCl (compare with Figs. 1 and 2) cause damage and wear at the step edges, so-called etching by the action of the tip, revealed as bright streaky lines. However, the C_{60} islands on this substrate could not be moved as single entities by the action of the tip.

The tribological behavior of C_{60} on NaCl(001) is unusual. Extremely low shear strengths of 0.05 to 0.1 MPa are found. The small dissipation energies and the reasonable cohesive energy allow C_{60} islands to move as an entity with small lateral forces. Conceivably, C_{60} islands could be used as transport devices for fabrication processes of nanometer-sized machines, whereby C_{60} islands might play the role of a transport carrier. Larger molecules (biomolecules) could be deposited on such a nanosled and then transported to a desired location.

REFERENCES AND NOTES

1. D. Tománek and M. A. Schluter, *Phys. Rev. Lett.* **67**, 2331 (1991).
2. D. W. Brenner, J. A. Harrison, C. T. White, R. J. Colton, *Thin Solid Films* **206**, 220 (1991); R. C. Mowrey, D. W. Brenner, B. I. Dunlap, J. W. Mintmire, C. T. White, *J. Phys. Chem.* **95**, 7138 (1991).
3. B. Bhushan, B. K. Gupta, G. W. Van Cleef, C. Capp, J. V. Coe, *Appl. Phys. Lett.* **62**, 3253 (1993).
4. D. M. Eigler and E. K. Schweizer, *Nature* **344**, 524 (1990); Y. W. Mo, *Phys. Rev. Lett.* **71**, 2923 (1993); Ph. Avouris and I.-W. Lyo, *Appl. Surf. Sci.* **60-61**, 426 (1992).
5. C. M. Mate, G. M. McClelland, R. Erlandsson, S. Chiang, *Phys. Rev. Lett.* **59**, 1942 (1987).
6. G. Meyer and N. M. Amer, *Appl. Phys. Lett.* **57**, 2089 (1990).
7. L. Howald *et al.*, *ibid.* **63**, 117 (1993).
8. We calibrated the piezoelectric tube scanner in the x, y, and z directions according to the procedure given in a study on the Si(111)7 × 7 surface by operating the multifunctional force microscope in the scanning tunneling mode [see (7)].
9. R. Lüthi *et al.*, *Z. Phys. B* **95**, 1 (1994).
10. B. Bhushan, J. Ruan, B. K. Gupta, *J. Phys. D* **26**, 1319 (1993); B. Bhushan, B. K. Gupta, G. W. Van Cleef, C. Capp, J. V. Coe, *Tribol. Trans.* **36**, 573 (1993).
11. M. Mate, *Wear* **168**, 17 (1993).
12. E. Meyer *et al.*, *Phys. Rev. Lett.* **69**, 1777 (1992); R. M. Overney *et al.*, *Nature* **359**, 133 (1992).
13. M. Hirano and K. Shinjo, *Phys. Rev. B* **41**, 11837 (1990).
14. G. M. McClelland, in *Adhesion and Friction*, M. Grunze and H. J. Kreuzer, Eds., vol. 17 in the Springer Series in Surface Science (Springer, Berlin, 1990), p. 81.
15. J. Belak, D. B. Boercker, I. F. Stowers, *Mater. Res. Soc. Bull.* **18**, 55 (1993); T. Gyalog *et al.*, unpublished material.
16. J. B. Sokoloff, *Phys. Rev. B* **42**, 760 (1990).
17. E. I. Altman and R. Colton, in *Atomic and Nano-meter-Scale Modifications of Materials: Fundamentals and Applications*, Ph. Avouris, Ed. (vol. 239 of the NATO Advanced Study Institutes Series, Kluwer Academic, London, 1993), pp. 303-313.
18. Ph. Lambin, A. A. Lucas, J.-P. Vigneron, *Phys. Rev. B* **46**, 1794 (1992).
19. C. Pan, M. P. Sampson, Y. Chai, R. H. Hauge, J. L. Margrave, *J. Phys. Chem.* **95**, 2944 (1991).
20. Cantilevers supplied by O. Ohlsson of Nanosensors, Aidingen, Germany.
21. The normal force was deduced with respect to the point at which the tip jumps off the surface.
22. We thank Ch. Gerber, D. Anselmetti, P. Chaudari, H.-P. Lang, V. Thommen-Geiser, and H. R. Hidber who contributed to many stimulating and clarifying discussions. We thank H. Breitenstein, A. Tonin, and R. Maffioli for their technical help. We thank R. Hofer and D. Brodbeck for providing us with user-friendly software. We are especially grateful to J. Frommer who motivated one of us (R.L.) with donations of vitamin C. Supported by the Swiss National Science Foundation and the Kommission zur Förderung der wissenschaftlichen Forschung.

8 August 1994; accepted 14 October 1994

Crystal Structure of the Catalytic Domain of HIV-1 Integrase: Similarity to Other Polynucleotidyl Transferases

Fred Dyda,* Alison B. Hickman,* Timothy M. Jenkins, Alan Engelman, Robert Craigie, David R. Davies†

HIV integrase is the enzyme responsible for inserting the viral DNA into the host chromosome; it is essential for HIV replication. The crystal structure of the catalytically active core domain (residues 50 to 212) of HIV-1 integrase was determined at 2.5 Å resolution. The central feature of the structure is a five-stranded β sheet flanked by helical regions. The overall topology reveals that this domain of integrase belongs to a superfamily of polynucleotidyl transferases that includes ribonuclease H and the Holliday junction resolvase RuvC. The active site region is identified by the position of two of the conserved carboxylate residues essential for catalysis, which are located at similar positions in ribonuclease H. In the crystal, two molecules form a dimer with an extensive solvent-inaccessible interface of 1300 Å² per monomer.

Integration of HIV DNA into the host genome is an essential step in the viral replication cycle (1). The enzyme responsible for integration, HIV integrase, has no known functional analog in human cells and is therefore a particularly attractive target for the design of antiviral agents. The three-dimensional structures of two other essential HIV enzymes, reverse transcriptase and protease, have been determined and much progress has been made toward the structure-based design of effective inhibitors, particularly with protease (2).

HIV DNA integration occurs through a defined set of DNA cutting and joining reactions. In the first step of the integration process, 3' processing, two nucleotides are removed from each 3' end of the blunt-ended viral DNA made by reverse transcription. A subsequent DNA strand transfer reaction covalently joins the recessed 3' ends of the viral DNA to the 5' ends of the target DNA at the site of integration. Purified HIV integrase carries out these reactions in vitro with either Mg^{2+} or Mn^{2+} as a cofactor (Fig. 1). Integrase cleaves two nucleotides from the 3' ends of DNA substrates that mimic the viral DNA ends and also inserts the processed ends into other DNA molecules that serve as targets for strand transfer (3). When presented with a DNA substrate that mimics the product of DNA strand transfer, integrase can catalyze an apparent reversal of the strand transfer reaction, termed disintegration (4). In this reaction, the viral DNA end segment of the substrate is liberated and the target DNA segment is sealed.

Several lines of evidence point to a com-

mon active site for all three catalytic activities. Three highly conserved amino acid residues in the central core domain of HIV-1 integrase, Asp⁶⁴, Asp¹¹⁶, and Glu¹⁵², the D,D-35-E motif, are observed in the integrase proteins of retroviruses and retrotransposons as well as in the transposase proteins of some prokaryotic transposons (5-7). In general, mutation of any one of these residues abolishes all enzyme activities (6-9). Stereochemical analysis of the 3' processing and DNA strand transfer reactions also indicates that each occurs through a one-step transesterification mechanism (10). In the 3' processing reaction, integrase activates the phosphodiester bond at the site of cleavage to nucleophilic attack by various nucleophiles (10, 11). The DNA strand transfer reaction may occur by a similar mechanism, with integrase playing the additional role of positioning the 3'-OH end of the viral DNA for nucleophilic attack on a phosphodiester bond in the target DNA (10).

While the full-length integrase protein (288 residues) is required for 3' processing and DNA strand transfer activities (9, 12, 13), the central core domain can carry out the disintegration reaction and therefore contains the catalytic site for polynucleotidyl transfer (14). The precise roles of the NH₂- and COOH-terminal domains in the 3' processing and DNA strand transfer reactions are not known, although the COOH-terminal domain binds to DNA nonspecifically (12, 15, 16).

Previous attempts to crystallize HIV-1 integrase have been obstructed by its poor solubility (17). In an attempt to circumvent this problem, we undertook a systematic replacement of the hydrophobic residues in the core domain of HIV-1 integrase (residues 50 to 212) (18). The single amino acid substitution of Lys for Phe¹⁸⁵ resulted in a

Laboratory of Molecular Biology, NIDDK, NIH, Bethesda, MD 20892-0560, USA.

*These two authors contributed equally to this work.

†To whom correspondence should be addressed.