

Effect of Alkali Doping on the Structural Stability of Solid C₃₆

A. Zettl, C. Piskoti, Jeffery C. Grossman, Marvin L. Cohen,
and Steven G. Louie

Department of Physics, University of California at Berkeley, and
Materials Sciences Division, Lawrence Berkeley National Laboratory,
Berkeley, CA 94720 U.S.A.

Abstract

We demonstrate that alkali-doping C₃₆ solids causes the C₃₆ cage molecules to be bonded less strongly to each other in the solid. Laser irradiation mass spectroscopy experiments show that for pure C₃₆ solid, no isolated C₃₆ subunits are observed in the ablated material, while for potassium-doped C₃₆, isolated C₃₆ molecules are readily produced by laser irradiation. Theoretical modelling shows that charge transfer from the alkali to the C₃₆ molecules greatly hinders C₃₆ dimer formation, consistent with these experiments.

In sharp contrast to the behavior of van der Waals solids formed from the more inert higher fullerenes such as C₆₀, the carbon-cage molecules in solid C₃₆ are tightly held together with covalent-like bonds. This relatively strong bonding configuration may have distinct advantages for practical applications. On the other hand, the same bonding character also makes it difficult to dissociate solid C₃₆ into its constituent C₃₆ molecules. Isolating individual C₃₆ molecular species from each other or from other molecular or atomic units is often desirable if not absolutely necessary for certain purification or characterization purposes.

In the original arc synthesis of C₃₆ molecules and solids, it was found that arc-generated carbon "soot" contained a sizable fraction of C₃₆ molecules¹. These species were identified by time-of-flight mass spectroscopy. In the mass spectroscopy method, a film of the fullerene-containing soot is irradiated by photons from a nitrogen laser, and the ejected material is ionized and accelerated through a mass spectrometer. The fact that this rather "violent" laser ablation works at all for C₃₆ is somewhat surprising; one might expect that the laser photons would break apart the C₃₆ molecules before pulling them intact from the solid. One possible reason for the success of the method is that the substantial amounts of amorphous carbon and higher-order fullerenes surrounding the C₃₆ molecules in the unpurified soot act as an energy absorbing and isolation matrix.

CP486, *Electronic Properties of Novel Materials— Science and Technology of Molecular Nanostructures*,
edited by H. Kuzmany, J. Fink, M. Mehring, and S. Roth
© 1999 American Institute of Physics 1-56396-900-9/99/\$15.00

We here investigate the influence of a matrix on the laser-induced dissociation of solid C₃₆. We find that without an isolation matrix, lone C₃₆ molecules cannot easily be extracted from the solid via laser irradiation. We then show that introducing alkali metal into the C₃₆ solid prior to laser irradiation does allow for clean and highly efficient C₃₆ ablation from the solid. A theoretical investigation of C₃₆ intermolecular interactions indicates that uncharged C₃₆ molecules easily bond to one another to form dimers, while negatively charged C₃₆ molecules have a substantially higher energy barrier for dimerization and a higher bound state energy. These findings are consistent with the experimental laser-induced dissociation results on pure and alkali-doped solid C₃₆.

Pure C₃₆ samples were prepared using variations on a previously described method¹. 6mm POCO graphite rods were arced in a 400 torr He atmosphere using approximately 50A DC at 20-25V. The resulting sublimation product was brushed from the walls and loaded into a soxhlet extractor where higher fullerenes (C₆₀, C₇₀, etc) were removed by extraction with toluene. The C₃₆ was then extracted using pyridine. Care was taken to keep all materials under an argon atmosphere throughout all purification steps, and all solvents used were first dried by distilling over sodium.

Fig. 1a shows a laser desorption/ionization mass spectrum (negative ion acceleration configuration) of the purified C₃₆ solid. The laser wavelength is 337.1 nm with intensity close to threshold for observing a signal in the mass spectrum. The observed spectrum shows a very broad mass distribution peaked at about 120 carbon atoms. A sharp rise in the mass peak occurs at about 70-75 carbon atoms, which could be a signature of dimerized C₃₆ units. Conspicuously absent, however, is a peak that would correspond to 36 carbon atoms. Indeed, from Fig. 1 alone one might conclude that this sample contains no C₃₆ molecules whatsoever!

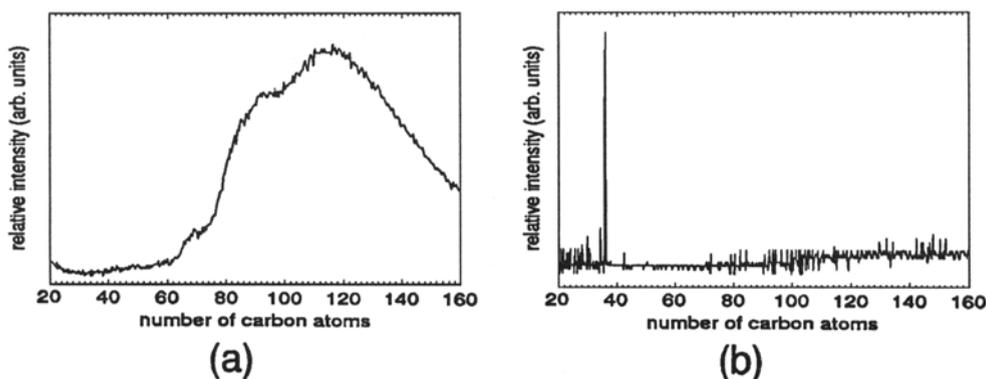


Fig. 1 Mass spectrum for a) pure C₃₆ solid and b) K-doped C₃₆ solid.

Our interpretation is that the sample used for Fig. 1 does contain C_{36} but that it is simply too pure. The highly reactive C_{36} molecules have bonded strongly to each other (i.e. the material has polymerized). With no matrix present to isolate the molecules or to aid in energy dispersal, no individual C_{36} molecules can be readily ablated. This underscores the utility of an additional matrix in mass spectroscopy studies of solid C_{36} .

To further support the conjecture of strong spontaneous bonding in a purified C_{36} solid, we have prepared a sample exactly as that used for Fig. 1a (i.e. a highly purified sample), but then added potassium to the solid. The potassium insertion was accomplished via a low temperature liquid ammonia technique to be described in detail elsewhere².

Fig. 1b shows the time-of-flight mass spectrum of the K_xC_{36} compound. The spectrum shows a large reduction in the higher mass distribution of Fig. 1a, as well as a dramatic and very sharp peak at exactly at 36 carbon atoms, i.e. at C_{36} . The introduction of potassium into the C_{36} solid system clearly allows the solid to give up isolated, in-tact C_{36} molecules quite readily upon laser irradiation. The absence of a higher mass distribution in Fig. 1b also suggests that this distribution (seen in Fig. 1a) originates from C_{36} dimers and other fragments of polymerized C_{36} solid. Potassium-doping of C_{36} provides the cleanest and most direct source of pure and isolated C_{36} molecules that we have found.

We now investigate theoretically how potassium or charge transfer may facilitate dissociation of the C_{36} solid into independent C_{36} molecules. For simplicity, we examine the related "inverse" problem of C_{36} dimer formation, both for case of two neutral C_{36} molecules and for the case of two negatively charged C_{36} molecules. LDA calculations^{3,4} have been performed for various intermolecular separations. At each point, a full structural optimization was carried out with the constraint of fixed intermolecular bond distance.

Fig. 2 shows the results of the calculation. The solid circles (with solid line) are for the neutral molecules. As the neutral molecules are brought closer together, the onset of an attractive, van der Waals type interaction appears at around 4.5\AA . The total energy possesses a shallow minimum at about 3.0\AA , and at 2.6\AA separation a small barrier of order 0.1eV is encountered before the dimer begins to covalently bond, reaching a stable minimum at 1.6\AA . We do not consider the small barrier at 2.6\AA to be important; it may be due to technical limitations of the calculations, and in any case it occurs below the reactant energy. For neutral C_{36} molecules, spontaneous polymerization is favored.

The solid squares (with dashed line) in Fig. 2 represent a similar calculation for two C_{36}^- molecules (the resulting dimer thus has a charge of -2). The total energy in this case suggests that extra charge substantially inhibits dimer formation. The two

negatively charge molecules experience an electrostatic $1/r$ repulsion as they approach one another, which accounts for the fact the fact that at 8\AA separation the dimer is more than 1 eV unbound. At the equilibrium distance of 1.6\AA the charged system is energetically bound by roughly 0.4eV ; however, to reach this minimum the system must pass through an unfavorable barrier which is 0.35eV above the energy at 8\AA separation and 1.5\AA above the energy of two isolated C_{36}^- molecules. These results help account for the experimental findings that charged C_{36} molecules (the charging resulting from alkali introduction) are less likely to be found in a strongly-bonded state. Interestingly, these findings for C_{36} are exactly the opposite to those for C_{60} , where charging the molecules actually enhances polymerization.

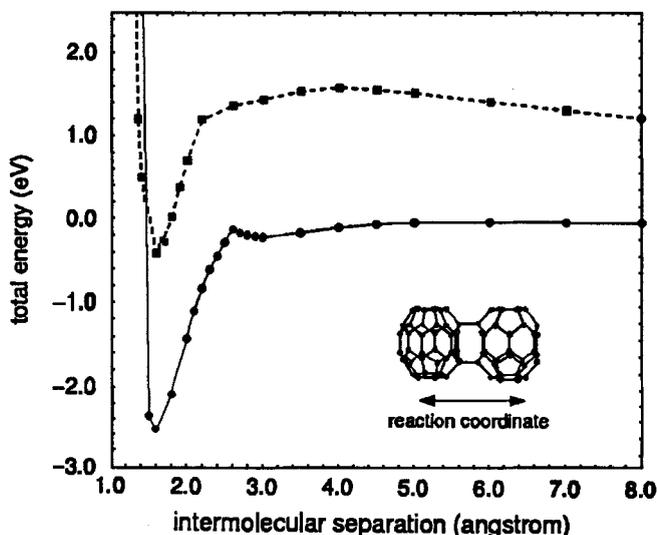


Fig. 2 Calculated total energy for dimer formation for neutral (solid circles) and charged (solid squares) C_{36} molecules.

This research was supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

References

1. C. Piskoti, J. Yarger, and A. Zettl, *Nature* **393**, 771 (1998); J.C. Grossman, M. Cote, S.G. Louie, and M.L. Cohen, *Chem. Phys. Lett.* **284**, 644 (1998); M. Cote, J.C. Grossman, M.L. Cohen, and S.G. Louie, *Phys. Rev. Lett.* **81**, 697 (1998)
2. C. Piskoti, J. Grossman, M.L. Cohen, S.G. Louie, and A. Zettl (to be published)
3. J.C. Grossman, C. Piskoti, S.G. Louie, M.L. Cohen, and A. Zettl (to be published)