J|A|C|S COMMUNICATIONS

Quantum Study of Laser-Induced Initial Activation of Graphite-to-Diamond Conversion

Angela Acocella,[†] Fabrizio Carbone,[‡] and Francesco Zerbetto*,[†]

Dipartimento di Chimica "G. Ciamician", Università di Bologna, Via F. Selmi 2, 40126, Bologna, Italy, and DPMC, University of Geneva, 24 Quai Ernest-Ansermet, 1211 Geneva 4, Switzerland

Received March 31, 2010; E-mail: angela.acocella@gmail.com; fabrizio.carbone@epfl.ch; francesco.zerbetto@unibo.it

Abstract: Recently (*Science* **2009**, *325*, 181), femtosecond-resolved electron energy loss spectroscopy (FEELS) was used to map the structural changes of graphite upon laser irradiation, revealing the change from sp^2 to sp^3, i.e., diamond-like, hybridization. With a laser excitation energy of 2.39 eV and a fluence of 1.5 mJ/cm^2, the most pronounced changes were observed in $\sim$180 fs, a time similar to the temporal resolution of the technique. The presence of the laser field turns the electronic wavefunction into a wavepacket whose quantum dynamics governs the onset of the structural rearrangement. Density functional theory calculations with a quantum propagator that include the laser field show that the charge density of graphite expands between the layers in an ultrafast process of the order of $\sim$10 fs. Calculations as a function of the field/fluence further show different values of the maximum bond order reached at the stationary state. The experimentally used value is at the crossover between two regimes. It is tempting to associate the second regime with the electron organization necessary to achieve ablation or melting. The application of the model demonstrates its potential for examining the dynamical nature of the charge density and chemical bonding as it forms.

Mapping the dynamics of the electron density variation with atomic-scale resolution is now feasible.[1,2] Sophisticated techniques allow visualizing changes with resolutions of femtoseconds and millielectronvolts. In graphite, theoretical and experimental investigations[3,5] revealed that optical excitation generates a non-equilibrium state that evolves on a time scale of 10−500 fs as a function of the laser fluence. Optical pump−probe experiments showed that the ultrafast response occurs in 30−50 fs.[6] The optical transmission through graphite films increases upon laser excitation.[6] The increased transmission persists at probe wavelengths different from those of laser excitation, which suggests a complex reorganization of the electron density as the origin of the increase. The behavior is similar to that of graphite compressed by hydrostatic pressure, which shows an increase in the optical transmission that is particularly strong during the transformation into diamond.[7] Very recently, femtosecond-resolved electron energy loss spectroscopy (FEELS) was used to map the structural changes in graphite, revealing the compression and subsequent expansion of layers upon irradiation.[8,9] The breathing correlates with the direction of change from sp^2 to sp^3, i.e., diamond-like, hybridization. The most pronounced changes were observed in $\sim$180 fs, a time similar to the temporal resolution of the technique.

In the present work, we report time-dependent quantum mechanical calculations of the onset of the sp^2-to-sp^3 electron density reorganization induced by electromagnetic radiation that drives the interlayer dynamics in graphite. A quantum-mechanical time-dependent propagator evolves the electronic wavefunction of graphite, which is described with periodic boundary conditions. The propagator, proposed by Allen and co-workers,[10] is a function of the graphite Hamiltonian plus the electromagnetic field, F:

$$\Psi(t + \Delta t) = \left(\frac{1 + iH\Delta t}{2\hbar}\right)^{-1}\left(\frac{1 - iH\Delta t}{2\hbar}\right)\Psi(t) \qquad (1)$$

where Ψ is the electronic wavefunction, Δt is the time step set to 0.4 atomic units or $\sim$10 attoseconds, and H is the total Hamiltonian, $H = H_0 + F\mu \cos(\omega t)$, where μ is the matrix of the dipole moments between crystal atomic orbitals and ω is the frequency of the laser excitation energy. At $t = 0$, Ψ is an eigenstate of the crystal electronic Hamiltonian, H_0. At $t \neq 0$, the perturbation of the field makes Ψ no longer an eigenfunction of H; i.e., it is not in a stationary state and becomes a wavepacket. The nuclear geometries are frozen during the electron wavepacket dynamics so that the pure propensity of the graphite-to-diamond transition is calculated. The coefficients of $\Psi(t)$ are updated at each time step. The approach has been successfully used by us to investigate the dynamics of photoinduced dissociation,[11] nonlinear optical properties,[12] and single-photon and multiphoton excitations.[13]

The graphite-to-diamond transformation occurs via highly symmetric paths,[14,15] both from the hexagonal Bernal structure to hexagonal diamond and from the rhombohedral structure to cubic diamond. We investigate the initial step of both photoconversion paths by monitoring the interlayer bond order during the quantum dynamics. The frequency ω of the field was set to the experimental laser excitation energy of 2.39 eV,[8,9] and the fluence was set to the experimentally reported value of 1.5 mJ/cm^2;[8] the direction of the field was parallel to the z axis of the cell. The ground electronic states of the two graphite structures were calculated with the Gaussian 09 suite of programs,[16] at Heyd-Scuseria-Ernzerhof/6-31G* level of theory,[17] which has been thoroughly tested for graphitic materials.[17] Both unit cells consisted of 16 carbon atoms, figure S1 Supporting Information. The inter/intra cell bond order, BO, was calculated from the density matrix P, following Wiberg definition.[18−21]

Application of eq 1 in the absence of the electric field produces stable bond orders. Switch off of the field leaves the system in a nonstationary state, Figure S2 Supporting Information, that can collapse to an eigenstate in the presence of an external perturbation. The in-layer bond order obtained for the graphite ground state, at time $t = 0$, is 1.23, which is smaller than the value of 1.33 that one expects for a C−C bond length of 1.4210 Å.[21] The lower value is due to the conjugation of the C−C bonds in crystalline graphite, which enhances the electronic density between atoms that are not translationally equivalent. The interlayer bond order analysis performed during the time-propagation shows that the transforma-

---

[†] Università di Bologna.
[‡] University of Geneva.

10.1021/ja102497z

tion from graphite to diamond is practically insensitive to the type of stacking and that the two paths are equivalent when the sp^3 bonds start to form, confirming previous local density-functional theory calculations.[15]

The stationary state is reached in ∼10 fs. The final interlayer bond order of ∼0.17 corresponds to an interlayer distance ∼2.1 Å (calculated from the relationship between bond order and bond length suggested by Pauling).[22] The sp^3 structure starts to form at a distance of ∼1.8 Å,[14] the present effect is in the *prebonding* regime. An interlayer bond length of about 1.9 Å for a transient graphite structure was also found in a recent study[4] carried out with combined time-dependent density functional/molecular dynamics simulations with excitation energies of 30 keV. The timescale of the reorganization of the electronic wavefunction is also similar to that found in previous molecular dynamics simulations at tight binding level that focused on the range of energies typical of ablation (2.0 eV/atom).[3]

Figure 1 shows the intra- and interlayer dynamics of the bond order of two pairs of atoms, one in-layer, the other between layers. The presence of the field triggers a transfer of bonding density from the layer to the interlayer region. The calculated variation of the radial density and the final interlayer distances, calculated by the Pauling equation,[22] are given as figures S4 and S5 in the Supporting Information.

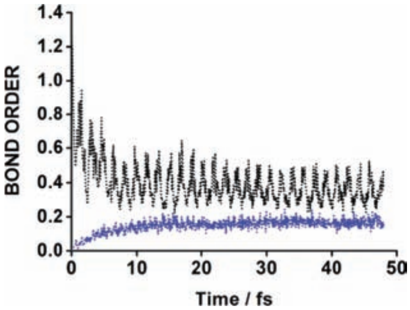

Figure 1. Intra- (black line) and interlayer (blue line) bond order dynamics of hexagonal graphite under the effect of the electromagnetic radiation. The bond order is calculated for a pair of atoms either in-layer or between layers.

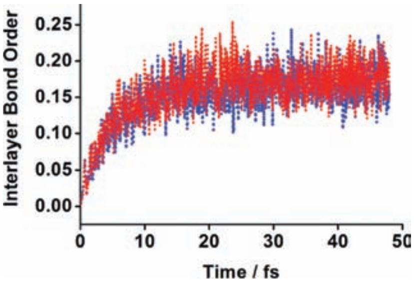

Figure 2. Time evolution of the bond order between interlayer atoms in adjacent planes in hexagonal graphite (blue line) and in rhombohedral graphite (black line).

The results of Figures 1 and 2 are obtained with the fluence and frequency used in the FEELS experiments,[8] which correspond to an electric field of 4.94 V/Å. A higher value of 5.3 mJ/cm^2 was used elsewhere.[9] Figure 3 shows the values of the bond order reached at the stationary state as a function of the field/fluence. The experimental value is at the crossover between two regimes. It is tempting to associate the second regime to the electron organization that is necessary to achieve ablation or melting.

The calculations provide insight into the dynamics of the electron density and demonstrate that, before the graphite structure starts deforming, the charge density expands between layers in a ultrafast process of the order of ∼10 fs. The application of the model demonstrates its potential for examining the dynamical nature of the charge density and chemical bonding as it forms. It will be of interest to expand the analysis in terms of the electronic fluxes that take place between individual occupied and unoccupied crystal orbitals to obtain further information into the dynamical processes of bonding.[23]

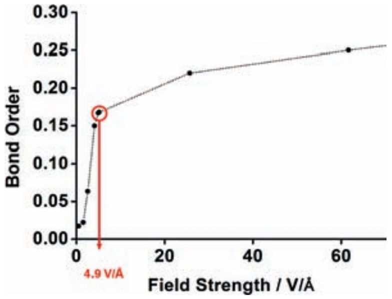

Figure 3. Bond order reached at the stationary state as a function of the field. The dots are the calculated values. The lines are used to assist the eye.

Acknowledgment. We are grateful to Drs. Chong-Yu Ruan and David Tomanek for useful e-mail correspondence.

Supporting Information Available: Figure S1, two views of the unit cells; Figure S2, effect of switching off the field at various times; Figure S3, pictorial representation of the electron density dynamics; Figure S4, interlayer variation in time of the radial density; Figure S5, interlayer separation that can be reached at each time given the calculated bond order. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Ferenc, K.; Misha, I. *Rev. Mod. Phys.* **2009**, *81*, 163.
(2) Zewail, A. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 2586.
(3) Jeschke, H. O.; Garcia, M. E.; Bennemann, K. H. *Phys. Rev. Lett.* **2001**, *87*, 015003.
(4) Raman, K. R.; Murooka, Y.; Yang, T.; Berber, S.; Tomanek, D. *Phys. Rev. Lett.* **2008**, *101*, 077401.
(5) Carbone, F.; Baum, P.; Rudolf, P.; Zewail, A. H. *Phys. Rev. Lett.* **2008**, *100*, 035501.
(6) Breusing, M.; Ropers, C.; Elsaesser, Th. *Phys. Rev. Lett.* **2009**, *102*, 086809.
(7) Utsumi, W.; Yagi, T. *Science* **1991**, *252*, 1542.
(8) Carbone, F.; Kwon, O.-H.; Zewail, A. H. *Science* **2009**, *325*, 181.
(9) Carbone, F.; Barwick, B.; Kwon, O.-H.; Park, H. S.; Baskin, J. S.; Zewail, A. H. *Chem. Phys. Lett.* **2009**, *468*, 107.
(10) Allen, R. E. *Phys. Rev. B* **1994**, *50*, 18629.
(11) Jones, G. A.; Acocella, A.; Zerbetto, F. *J. Phys. Chem. A* **2008**, *112*, 9650.
(12) Jones, G. A.; Acocella, A.; Zerbetto, F. *Theor. Chem. Acc.* **2007**, *118*, 99.
(13) Acocella, A.; Jones, G. A.; Zerbetto, F. *J. Phys. Chem. A* **2006**, *110*, 5164.
(14) Fahy, S.; Louie, S. G.; Cohen, M. L. *Phys. Rev. B* **1986**, *34*, 1191.
(15) Fahy, S.; Louie, S. G.; Cohen, M. L. *Phys. Rev. B* **1987**, *35*, 7623.
(16) Frisch, M. J.; et al. *Gaussian 09*, Revision A.1; Gaussian, Inc: Wallingford CT, 2009.
(17) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. *J. Chem. Phys.* **2003**, *118*, 8207; **2006**, *124*, 219906. Izmaylov, A. F.; Scuseria, G. E.; Frisch, M. J. *J. Chem. Phys.* **2006**, *125*, 104103. Heyd, J.; Scuseria, G. E. *J. Chem. Phys.* **2004**, *121*, 1187. Heyd, J.; Peralta, J. E.; Scuseria, G. E. *J. Chem. Phys.* **2005**, *123*, 174101. Brothers, E. N.; Izmaylov, A. F.; Normand, J. O.; Barone, V.; Scuseria, G. E. *J. Chem. Phys.* **2008**, *129*, 011102. Barone, V.; Peralta, J. E.; Wert, M.; Heyd, J.; Scuseria, G. E. *Nano Lett.* **2005**, *5*, 1621. Barone, V.; Peralta, J. E.; Scuseria, G. E. *Nano Lett.* **2005**, *5*, 1830. Barone, V.; Hod, O.; Scuseria, G. E. *Nano Lett.* **2006**, *6*, 2748.
(18) Bridgeman, A. J.; Cavigliasso, G.; Ireland, L. R.; Rothery, J. *J. Chem. Soc., Dalton Trans.* **2001**, 2095.
(19) Wiberg, K. A. *Tetrahedron Lett.* **1968**, *24*, 1083.
(20) Kalinowski, J. A.; Lesyng, B.; Thompson, J. D.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. A* **2004**, *108*, 2545.
(21) Bochicchio, R. C.; Reale, H. F. *J. Phys. B: At. Mol. Opt. Phys.* **1993**, *26*, 4871.
(22) Pauling, L. *The nature of the Chemical Bond*, 3rd ed.: Cornell University Press: Ithaca, NY, 1960.
(23) Bressler, C.; Abela, R.; Chergui, M. *Z. Kristallogr.* **2008**, 223.

JA102497Z