JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

ARTICLE

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Photoinduced $\pi-\pi^*$ Band Gap Renormalization in Graphite

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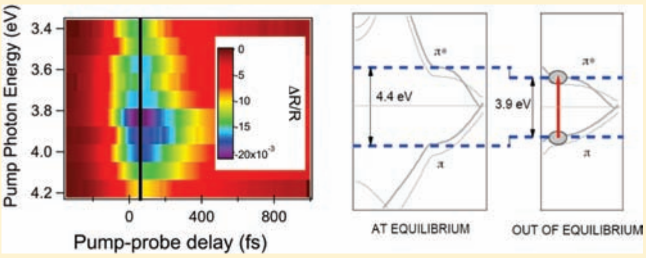
ABSTRACT: As is well-known, the character of the π orbitals is of paramount importance for the chemical properties of the carbon allotropes and their derived compounds. While at equilibrium the nature of these orbitals is well understood, their photoinduced nonequilibrium behavior is under investigation. Here, we demonstrate that when a UV-laser pulse excites a carrier density larger than 10% of the π^* density of state in graphite, a renormalization of the $\pi-\pi^*$ band gap takes place. This result has been achieved by detecting the transient reflectivity and the associated decay time of an infrared probe following the excitation of a UV pump pulse tuned across the $\pi-\pi^*$ absorption resonance. The pump photon energy at which both the transient reflectivity and the decay time are maximum is downshifted by 500 meV with respect to the relative absorption maximum at equilibrium. This finding is interpreted as a transient $\pi-\pi^*$ band gap shrinking of similar magnitude, near the M point of the Brillouin zone.



INTRODUCTION

In the past few decades, several new carbon allotropes have been discovered,[1−5] while in the last several years, very important behavior has been revealed about the structural properties of carbon compounds excited by an ultrashort and intense light pulse.[6−11] These important findings will set the path for new discoveries about the photochemical properties of carbon-based materials. However, we first need a clear understanding of the interaction between an intense ultrashort light pulse and carbon-based compounds. The challenging mechanisms at the origin of this interaction rely on the fact that when an intense femtosecond laser pulse is absorbed by a solid, the electrons and the lattice are driven out of equilibrium, and both screening effects and rearrangement of the lattice occur because of the excitation of a large fraction of the valence electrons to the conduction band.[12−16]

These processes are well-known in semiconductors, where the absorption of an ultrashort and intense light pulse suddenly modifies the charge distribution, switching on screening effects resulting from Coulomb and exchange forces, while inducing a narrowing of the band gap (band gap renormalization, BGR).[17] Typically by exciting about 10% of the valence electrons, the lattice is destabilized and the band gap shrinks and eventually collapses to zero. This effect can be clearly revealed by detecting the nonequilibrium dielectric function, which exhibits a metallic character on a time-scale of 100−200 fs.[17−19] For these reasons, semiconductors have been the preferred materials for such studies.[12]

Instead, in semimetals and gap-less compounds, such as graphite, the response to a sudden photoexcitation process, together with out of equilibrium behavior, remains unclear. Recently, time-resolved electron diffraction and scanning tunneling microscopy studies on graphite[7−9] have shown that intense infrared (IR) femtosecond laser pulses can induce a new transient phase characterized by a pseudo sp^3-bonding configuration, but overall different from the known phases of diamond. The interplay between the dynamics of the structural changes induced by IR pulses and the reorganization of orbital charge has been also investigated by femtosecond electron energy loss spectroscopy and ab initio calculations.[6,10,11,20]

Because of the peculiar electronic structure of graphite, it could be interesting to study the photoexcitation with ultrashort coherent pulses in the ultraviolet (UV) spectral region. Here, we show that, when an UV-ultrashort optical pump excites about 2 × 10^{21} electrons/cm^3 across the $\pi-\pi^*$ band gap near the M point of the Brillouin zone (BZ), significant variations of the graphite optical properties occur. This transient change of the dielectric function takes place within 150 fs of the pump-pulse excitation and is consistent with a ∼500 meV gap renormalization of the π bands.

Previous transient optical measurements on graphite[21] suggest the existence of a weak BGR in graphite (about 30 meV). This interesting, but limited information, has been obtained from experiments carried out using ultrashort IR pulses (800 nm, 1.55 eV). However, at these photon energies, the favorable coupling of the photoexcited carriers with a subset of high energy optical phonons (i.e., strongly coupled optical phonons, SCOP[22,23]) can

Received: December 22, 2010
Published: March 31, 2011

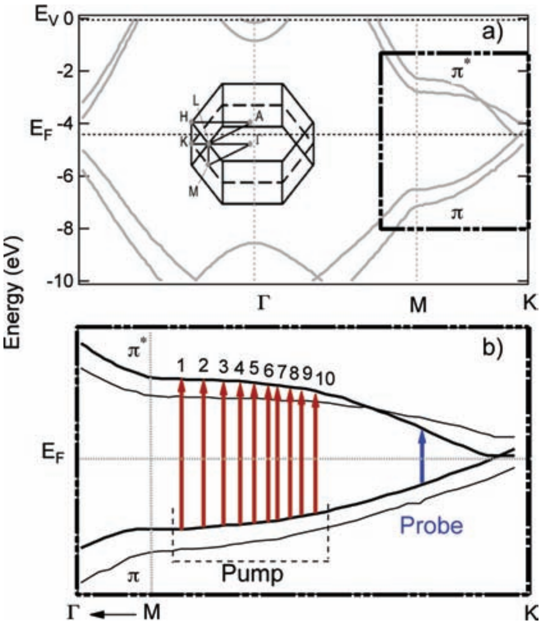


Figure 1. (a) Graphite electronic structure taken from ref 27. The energies refer to the vacuum level $E_V = 0$. (b) Sketch of the transient reflectivity experiment. The laser pump photon energy is tuned across the numbered optical transitions (from 3.4 to 4.2 eV) close to the M-point of the graphite Brillouin zone. For each pump photon energy, the reflectivity of the probe, with a photon energy fixed at 1.5 eV, is acquired at different pump probe delay times (see Figure 2).

induce significant structural changes, preventing the detection of the bare electronic response.[20] By contrast, UV light pulses tuned across the $\pi-\pi^*$ optical resonance near the M point of the Brillouin zone (BZ) excite carriers whose relaxation does not involve significant SCOP effects. These experimental conditions allow the transient optical signal to be a straightforward fingerprint of the evolving electronic structure. Moreover, at these photon energies, the strength of the electric dipole oscillator is expected to be larger than in the IR spectral region, inducing a significant π band structure rearrangement.[24−26]

Therefore, the novelty of our time-resolved optical pump−probe experiment consists of studying the transient electronic structure of a highly oriented pyrolytic graphite sample (HOPG) using a 3.4−4.2 eV tunable photon pump, while setting a spectator probe at 1.55 eV photon energy. Using this experimental approach, we are able to induce and reveal a strong BGR effect in a semimetal such as graphite.

■ EXPERIMENTAL DETAILS

The measurements are performed on a freshly cleaved HOPG sample using an amplified Ti:Sapphire laser system capable of delivering 150 fs light pulses at 1 kHz repetition rate, of 1 mJ energy at λ = 790 nm. A traveling wave optical parametric amplifier is then used to generate photons in the 1160−1460 nm (0.85−1.07 eV) spectral range. By quadrupling the output of the parametric amplifier, it is possible to span the photon energy from 3.4 to 4.2 eV. The resulting UV pulses (150 fs, 1−10 nJ), after being focused into a spot of 100 μm × 100 μm (equivalent to a laser fluence of 2.5 mJ/cm^2), are used to excite the HOPG sample. The transient optical reflectivity is measured by taking the difference between the probe reflectivity with and without the pump pulse. Optical absorption measurements with a continuous wave (CW) source were performed using a spectrometer.

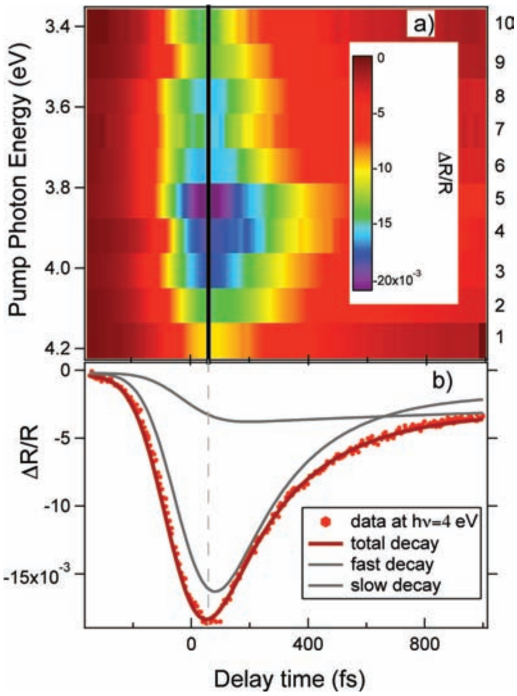


Figure 2. (a) Transient reflectivity spectra collected by tuning the pump photon energy from 3.4 to 4.2 eV and the probe photon energy fixed at 1.5 eV, as reported in Figure 1. The pump fluence is 2.5 mJ/cm^2. (b) A representative analysis carried out on the transient reflectivity spectra to obtain information about the relaxation dynamics. The data are fitted with two exponential curves convolved with a Gaussian to take into account the laser pulsewidth.

■ RESULTS AND DISCUSSION

In the infrared and ultraviolet (IR-UV) spectral range, the possible bulk-band optical excitations in graphite are prevalently transitions between the $\pi-\pi^*$ bands (see Figure 1a). At the K point of the reciprocal space, the electronic band structure displays a vanishing density of states (DOS) and a vanishing energy gap between the valence and conduction bands that shows, for a single layer, an identical linear k dispersion of the two π bands.[27] At the M point of the Brillouin zone, graphite behaves as a semiconductor. The electronic structure displays a van Hove singularity in the joint DOS (JDOS), which is at the origin of a maximum in the absorption spectrum ($\pi-\pi^*$ resonance at 4.4 eV). In Figure 1b, the red arrows represent the pump photon energies tuned from 3.4 to 4.2 eV, close to the M point of the BZ at equilibrium, that is, where the imaginary part ($\varepsilon_2(\omega)$) of the graphite dielectric function has a maximum.

The probe transient reflectivity (TR) experimental data, taken at constant pump fluence and probe photon energy fixed at $h\nu$ = 1.55 eV, are shown in a colormap image in Figure 2a. Under these experimental conditions, the effects correlated to the population relaxation[28] excited by the laser pump (3.4−4.2 eV) can be, in fact, excluded in the probe reflectivity signal at 1.55 eV, because the decay of the carriers from the M-point toward the K-point near the Fermi level is unlikely, due to energy and momentum conservation.[29]

To investigate the relaxation dynamics, each spectrum reported in Figure 2a is fitted by two exponential functions convolved with a Gaussian to account for the laser pulse-width. In Figure 2b, the analysis of the decay times on a representative spectrum collected with the pump photon energy at 4 eV clearly shows both a fast ($\tau_1 \approx 200$ fs) and a slow ($\tau_2 \approx 2$ ps) decay process, as will be discussed later.

It is rather important to note that the maximum variation of $\Delta R/R_{\max}$ and the longest τ_1 decay time are detected at about 3.9 eV.

Because of the functional form of the reflectivity of solids at equilibrium,[30] changes in the reflectivity signal are related to fractional change in both the real and the imaginary part of the dielectric function ($\Delta R = \Delta R(\Delta\varepsilon_1,\Delta\varepsilon_2)$). Previous measurements on graphite show that TR signal is mainly dominated by the fractional change in the imaginary part of the dielectric function $\Delta\varepsilon_2$ at the probe photon energy:[28]

$$\frac{\Delta R(h\nu_{\text{probe}})}{R(h\nu_{\text{probe}})} \propto \frac{\Delta\varepsilon_2(h\nu_{\text{probe}})}{\varepsilon_2(h\nu_{\text{probe}})} \tag{1}$$

Hence, within the actual experimental conditions, the observed transient fractional variations of the reflectivity can originate only by transient modifications in the graphite dielectric function, which depend solely on the interaction between light and graphite electronic structure. Moreover, at constant pump fluence, the transient probe reflectivity variation, $\Delta R/R$, is only determined by the pump absorption.

As a consequence of this model, the transient band structure changes are linked to the excited carriers density ($N(E)$), which is proportional to the pump pulse of fluence F, assuming an absorption coefficient $\alpha(h\nu_{\text{pump}})$:

$$\int_0^{\infty} N(E)\,\mathrm{d}E = \frac{(1 - R(h\nu_{\text{pump}}))F\alpha(h\nu_{\text{pump}})}{(h\nu_{\text{pump}})} \tag{2}$$

Under these assumptions, the maximum of the transient reflectivity $\Delta R/R_{\max}$ signal should be expected when the pump photon energy matches the energy of the $\pi-\pi^*$ excitations at the M-point of the BZ, where the absorption is maximum. At equilibrium, this energy is found to be 4.4 eV,[24] which is in good correspondence to the relative maximum of the imaginary part of the dielectric function ($\varepsilon_2(\omega)$) (Figure 3a).

A plot of $\Delta R/R_{\max}$ versus pump photon energy (Figure 3b) exhibits a maximum at 3.9 eV, 500 meV lower than the equilibrium value, implying that also the transient $\varepsilon_2(\omega)$ maximum is shifted downward by the same amount. This finding is regarded as a clear evidence that the $\pi-\pi^*$ energy gap in graphite undergoes a band gap renormalization (BGR) when the estimated density of the photoexcited carriers is $2 \times 10^{21}/\text{cm}^3$.[31]

To avoid artifacts due to the quality of HOPG sample, absorption measurements at equilibrium are carried out on the same HOPG sample used in the TR experiments. Figure 3a shows the spectrum of the CW-absorbance, defined as $-\ln(I_T/I_0)$, where I_T is the transmitted intensity and I_0 is the incident intensity, along with the $\varepsilon_2(\omega)$ reported by Taft et al.[25] In agreement with the literature, the maximum of the absorption is detected at 4.4 eV.

Further evidence of the observed BGR effect is provided by the study of the relaxation times. The TR spectra are well fitted by two different decay times (Figure 2). The fast decay time ($\tau_1 = 200$ fs) is mainly due to electron–electron interactions, whereas the slow decay ($\tau_2 = 2$ ps) time is ascribed to the electron–phonon relaxation. These dynamics have to be compared to transient measurements performed by exciting the hot electron population close to the Fermi level (photon energy pump at 1.5 eV). Under this condition, the electron–electron scattering yields a thermalization of the excited electron population within 30 fs,[21] relaxation mechanisms through SCOP assisted processes last for few hundreds of a femtosecond, whereas decay times on the picosecond time scale are attributed to photoinduced structural instabilities launched in the material.[20]

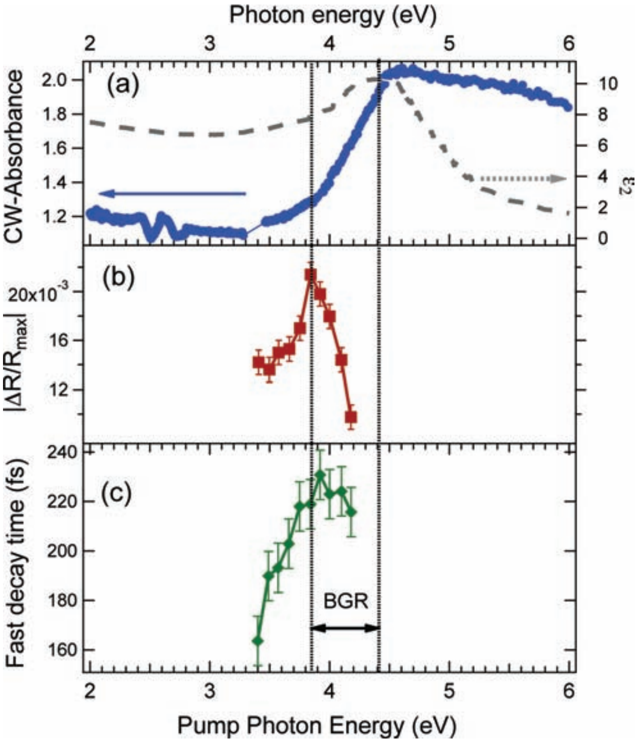


Figure 3. (a) Absorbance spectrum on graphite together with the imaginary part ($\varepsilon_2(\omega)$) of the graphite dielectric function from ref 25. The maximum at 4.4 eV is due to the strong M-point optical transition. (b) The maximum of the transient reflectivity spectra shown in Figure 2 versus the laser pump photon energy. (c) Dependence of the fast decay time on the laser pump photon energy. The shift between the maximum of the $\Delta R/R_{\max}$ signal and the fast decay time with respect to that of $\varepsilon_2(\omega)$ represents the band gap renormalization value.

In Figure 3c, the dependence of the fast decay time on the laser pump photon energy is shown. The fast decay time increases with the photon energy up to 3.9 eV. Previous theoretical and experimental studies[29,32] have shown that the lifetime of the excited carriers in graphite strongly depends on the wave vector of the Brillouin zone. In contrast to electrons decaying from other regions of the band structure, electrons excited at the M point have comparatively long lifetimes. The dynamics of the TR signal are sensitive to the electronic band structure changes that depend on the lifetime of the excited carrier density. Therefore, a maximum of the TR decay time is expected at the M point optical transition energy where the carriers have a longer lifetime. The presence of a decay time maximum red-shifted of 500 meV with respect to the M optical transition at equilibrium represents the second experimental evidence of the π band gap shrinkage. The same shift of both the $\Delta R/R$ signal and the decay time maximum is the fingerprint of a photoinduced renomalization of the π band at the M point, as sketched in Figure 4.

In a phenomenological picture, the BGR effect can be explained by considering that, during the near-resonant pump

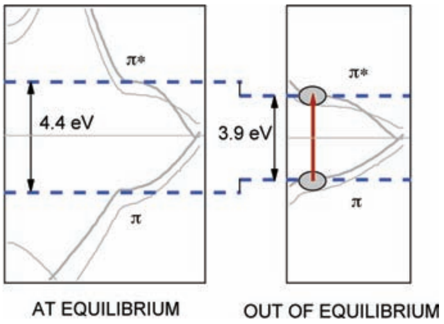


Figure 4. Sketch of the $\pi-\pi^*$ band gap renormalization in graphite.

laser pulsewidth, the excited carriers continue to modify the graphite band structure, altering the dielectric function and shifting the absorption peak about 500 meV toward the lower photon energies. This absorption shift can be monitored by the variation of the probe reflectivity, while the pump photon energy is tuned across the $\pi-\pi^*$ transition.

At a laser pump fluence of ~2.5 mJ/cm^2 and photon energy of 4.0 eV, the carrier density excited in the π^* band is 10%[31] of the density of states around the M-point at equilibrium (1.8×10^{22} electrons/cm^3).[27] Hence, under the present experimental conditions, when 2×10^{21} electrons/cm^3 are injected into the π^* band, the $\pi-\pi^*$ gap shrinks by 500 meV within 150 fs. These findings are in agreement with BGR observed in semiconductors when a carrier density of 10^{21} electrons/cm^3 is induced by optical excitations.[17] Unfortunately, the experimental conditions prevented changing the laser pump fluence to verify the dependence of the BGR value on the excited carrier density.

The present results can be fitted in a more general scenario, where the nonequilibrium structural properties of graphite produced by ultrafast coherent light excitations are considered. At the present, most of the studies reported in the literature concern experiments performed at 800 nm[7−9] or in the THz spectral region.[33] At these photon energies, the $\pi-\pi^*$ excitations are close to the K-point of the graphite band structure (see Figure 1b), where a selective coupling of the excited carriers to coherent phonons (SCOP) takes place in 100−500 fs.[20] Such structural vibrations could also modify the equilibrium optical properties of graphite. Single color pump−probe experiments at 800 nm (1.5 eV) show a change of the sign of the transient probe transmissivity ($\Delta T/T$). These findings have been the matter of two alternative interpretations.[20,21] The first ascribes the change of the transient transmission sign to SCOP-induced oscillations of the graphene planes along the *c*-axis, the second to a weak BGR effect (30 meV) that leads to a red-shift of the interband absorption. Unfortunately, by photoexciting the graphite in the near IR, it is not possible to decouple the electronic excitations from the SCOP effects. Instead, this is possible using near-UV photons. At these photon energies, in fact, transient changes of the dielectric function are mostly induced by $\pi-\pi^*$ excitations near the M-point where the electron−SCOP coupling is weak. This phenomenological picture explains the strong BGR observed in the present experiment. In addition, the dynamics of the BGR suggest that electron−electron interactions, rather than structural effects, induce the band gap shrinkage. Very likely, this discovery discloses new photoinduced properties of graphite different from those observed in the IR regime. Further structural dynamical studies, using laser pulses in the UV regime (around 4−4.5 eV), can help clarify this question.

■ CONCLUSION

We report a careful and novel study of the transient electronic structure induced in graphite by an ultrashort and intense UV laser pulse. The experiment has been performed using time-resolved optical spectroscopy employing as a pump an ultrashort laser pulse tunable in the 3.4−4.2 eV photon energy region and as a probe the fundamental emission of a Ti:sapphire amplified laser. By tuning the pump photon energy across the graphite van Hove singularity and exciting ~2×10^{21} electrons/cm^3 across the $\pi-\pi^*$ band gap at the M point of the BZ, we clearly show that a significant variation of the equilibrium graphite dielectric function occurs. This transient dielectric function alteration, occurring within the 150 fs of the pump-pulse excitation, can be reconciled with a 500 meV gap renormalization of the π bands. Finally, this significant transient rearrangement of the electronic structure of graphite is expected to be central to novel chemical properties, leading to new studies and applications.

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■ ACKNOWLEDGMENT

F.P. thanks the MIUR for supporting this work under contracts FIRB-RBNE0155X7 and PRIN 2008JWKYXB.

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