Electronic and structural response of materials to fast intense laser pulses, including light-induced superconductivity

Roland E. Allen
Department of Physics and Astronomy, Texas A&M University, College Station, Texas 77843

ABSTRACT

This is a very brief discussion of some experimental and theoretical studies of materials responding to fast intense laser pulses, with emphasis on those cases where the electronic response and structural response are both potentially important (and ordinarily coupled). Examples are nonthermal insulator-to-metal transitions and light-induced superconductivity in cuprates, fullerenes, and an organic Mott insulator.
Keywords: ultrafast, laser pulse, bandgap collapse, insulator-to-metal transition, semiconductor, high-temperature superconductor, cuprate, fullerene, light-induced superconductivity

1. INTRODUCTION

It is a remarkable fact that carefully designed pump-probe experiments, using wavelengths from infrared to X-ray, can be used to characterize and even control a wide variety of properties in important materials. Here we very briefly review a few narrow topics in this vast area of current research, with an even more narrow selection of important results.

2. ULTRAFAST BANDGAP COLLAPSE IN SEMICONDUCTORS

Experimental studies of ultrafast bandgap collapse in semiconductors like GaAs[1-3] indicated a nonthermal transition from semiconducting to metallic phases, and this was confirmed by the theoretical studies[4-8], as illustrated in Figs. 1-3.

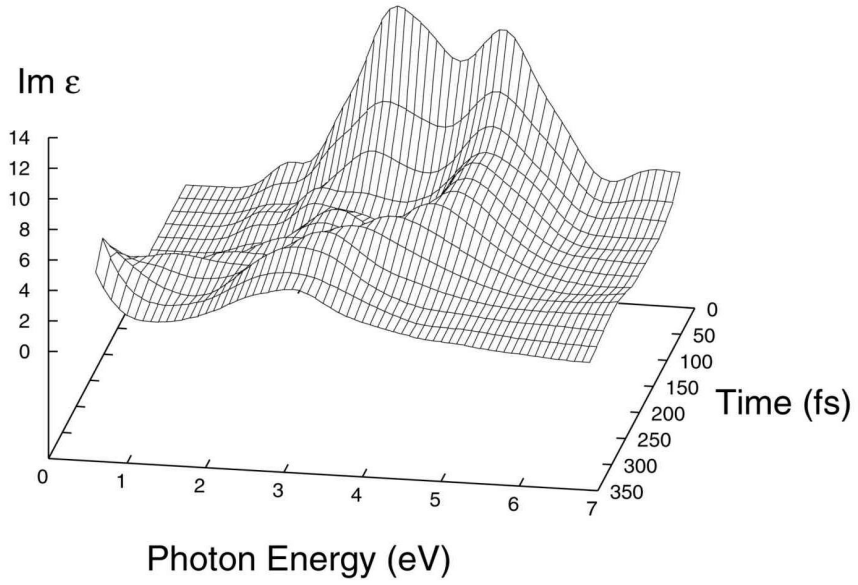

Figure 1. The imaginary part of the time-dependent dielectric function is shown for GaAs after it has been subjected to an ultrafast laser pulse above the threshold intensity for a nonthermal phase transition due to destabilization of the atomic bonding on a femtosecond time scale. The results of this simulation agree with the experimental measurements of Mazur and coworkers[1-3], as described in the text. After Dumitrica et al.[7]

Ultrafast Bandgap Photonics, edited by Michael K. Rafailov, Eric Mazur, Proc. of SPIE Vol. 9835, 98351J · © 2016 SPIE
CCC code: 0277-786X/16/$18 · doi: 10.1117/12.2225129

Note three aspects in the behavior of the dielectric function shown in Fig. 1:

(1) There is a loss of the original structural features, signaling a loss of the original tetrahedral bonding in the semiconductor.

(2) The imaginary part of the dielectric function, which measures absorption, becomes nonzero for photon energies below the original band gap energy of about 1.4 eV, In fact, one observes metallic behavior, which demonstrates a complete collapse of the band gap, beyond about 250 fs.

(3) There is a "hump" which persists even after the band gap has collapsed, and which appears to indicate that there are still bonding-to-antibonding transitions, even after the long-range crystalline order has been lost.

Figure 2 shows the corresponding behavior of the nonlinear susceptibility, which probes the atomic structure of the material and is thus complementary to the linear dielectric function, which probes the electronic structure.

Notice that $\mathrm{Im}\,\chi^{(2)}$ falls to zero over the entire range of photon energies, signaling a loss of the original symmetry of the GaAs lattice. This is also consistent with the experimental results of Refs. 1-3.

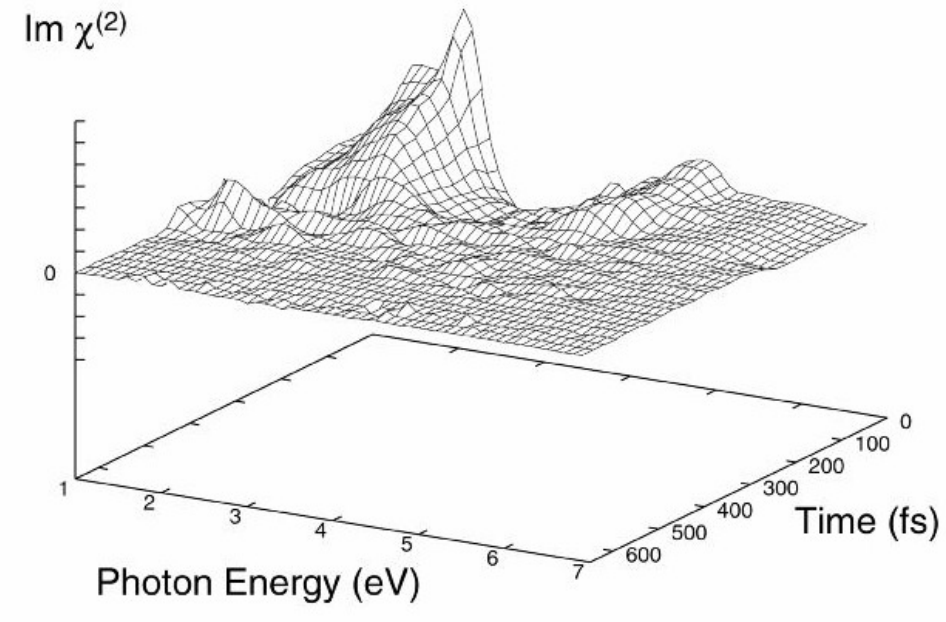

Figure 2. Imaginary part of the time-dependent nonlinear susceptibility for GaAs just above the threshold laser intensity for a nonthermal phase transition. After Dumitrica et al. [6]

The power of realistic simulations is that one can study the behavior of the system in microscopic detail, as well as obtaining the quantities, like those in Figs. 1 and 2, which are experimentally accessible. For example, Fig. 3 shows how rapidly the atoms move from their initial positions following femtosecond-scale laser pulses for which the amplitude of the electric field is given by A; $A = 1.0$ corresponds to a fluence of $0.815\,\mathrm{kJ/m^2}$ for a full-width-at-half-maximum duration of 70 femtoseconds (which was used in the simulations of Figs. 1-3).

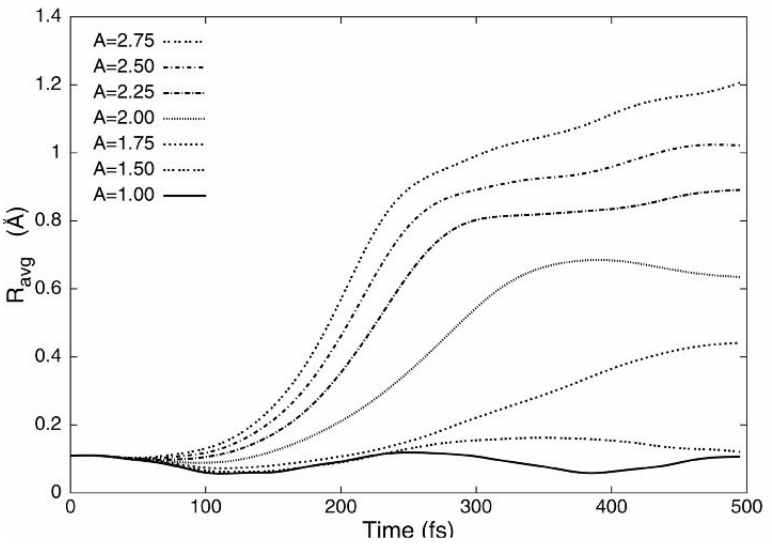

Figure 3. Average displacement of GaAs atoms from their equilibrium positions for various intensities of the applied laser pulse. The nonthermal transition clearly occurs above A = 1.50 gauss cm. After Dumitrica et al.[7]

3. C_{60} AND GRAPHENE

Figure 4 represents experimental observations of excitation of the breathing mode in C_{60} buckyballs by an ultrafast laser pulse. In Figure 5, both the breathing mode and the pentagonal pinch mode at higher frequency were observed.

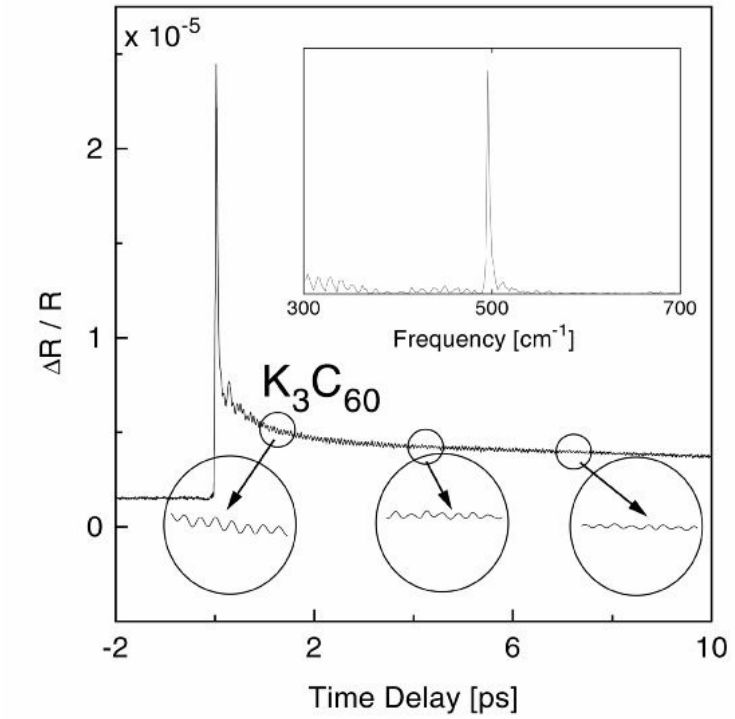

Figure 4. Observation of phonon oscillations in K_3C_{60} at 300 K. The pump-probe data were taken in reflectivity with a single wavelength pump-probe setup having a time resolution of about 20 fs. The larger inset shows the Fourier transform power spectrum with a sharp peak at 492.5 inverse centimeters. After Fleischer et al.[9]

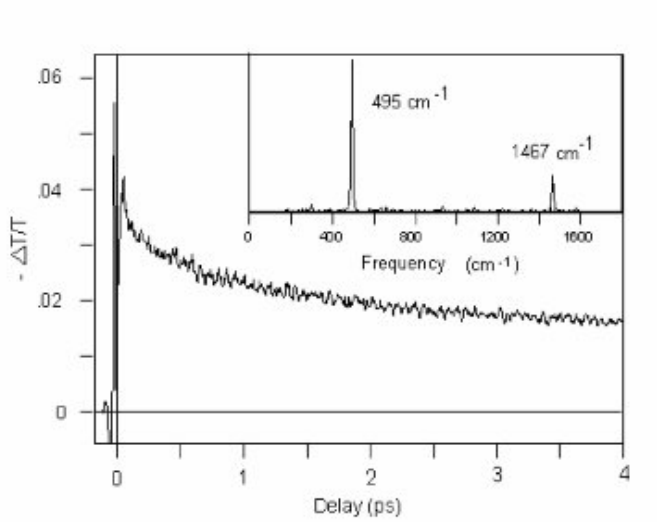

Figure 5. Light-induced negative differential transmittance of a C_{60} thin film detected at 580 nm as a function of time delay between 12 fs pump and probe pulses centered on 620 nm. The Fourier power spectrum of the oscillatory part of the response is shown in the inset. After Dexheimer et al.[10]

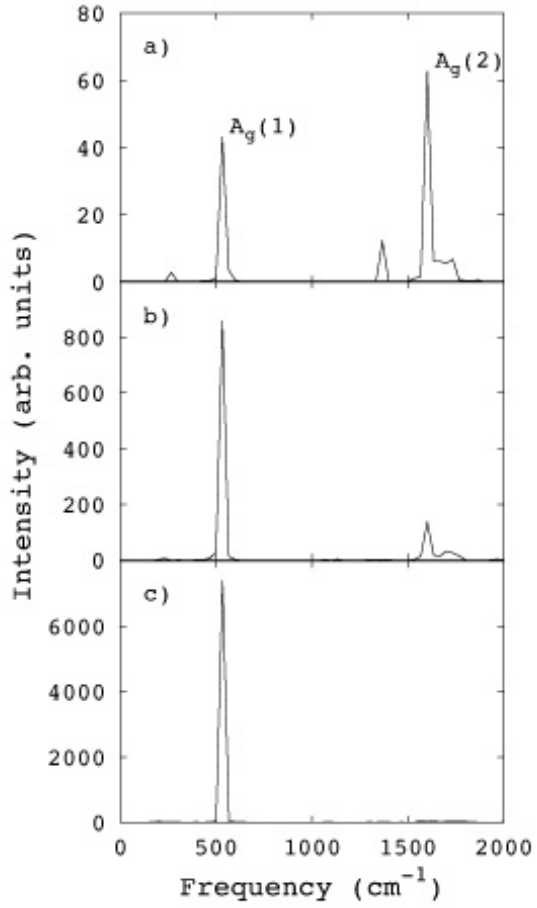

Figure 6. Vibrational spectrum of C_{60} after being subjected to a 10 fs FWHM, 2.0 eV laser pulse with a fluence of (a) 0.06 kJ/m^2, (b) 0.10 kJ/m^2, and (c) 0.16 kJ/m^2. After Torralva et al. [11]

As can be seen in Fig. 6, the calculations by Torralva[11] resolve what might appear to be a discrepancy between the results of the two experimental groups, by demonstrating that only the breathing mode is seen at high laser intensity, whereas both the breathing mode and the pentagonal-pinch mode are seen at lower intensity. At still higher intensity, there is fragmentation with the emission of dimers, in agreement with experiment, as shown in Fig. 7.

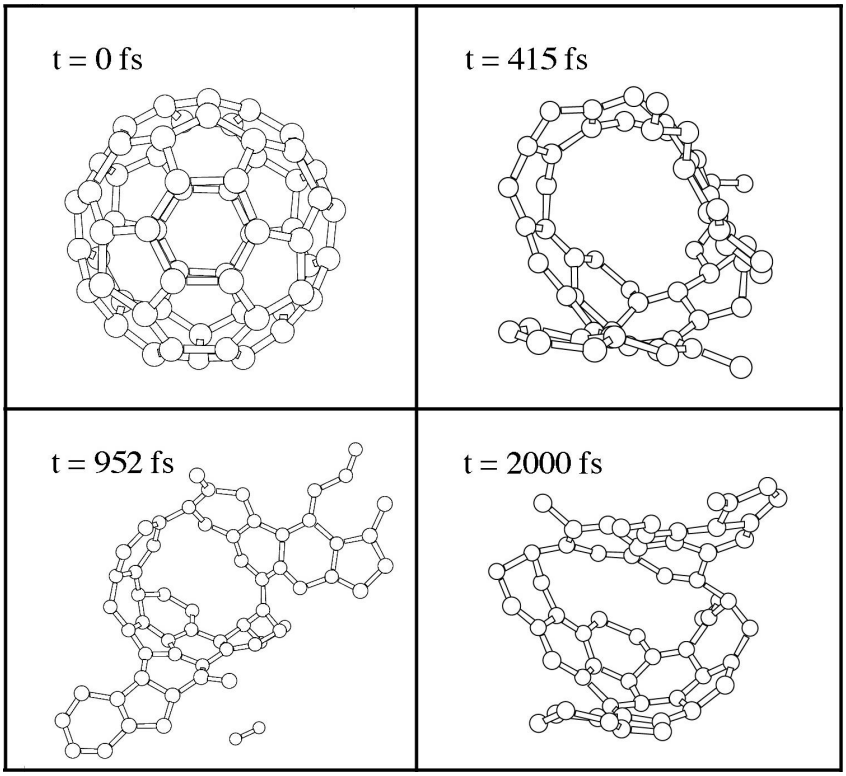

Figure 7. Photofragmentation of a C_{60} molecule. Following a 35 fs, 2.0 eV laser pulse with a fluence of 1.17 kJ per square meter, there are two particularly striking features: The first is the dramatic opening of both ends of the fullerene, accompanied by the breaking of many bonds. The second is the release of a dimer (at t = 952 fs) with a kinetic energy of 0.25 eV, which is slightly more than half the value reported for the experiments (Hohmann et al., Z. Phys. D. 33, 143 (1995)). Following emission of the dimer, the remaining 58 atoms tend to move back toward one another and reform bonds with both hexagons and pentagons. After Torralva et al. [11]

The related work of Zhao et al.[13] and Jiang et al.[14] demonstrated the potential for enhancing the relative response of selected modes by the proper choice of pulse duration and the interval between applied sequential pulses. One motivation is to emphasize those modes which might be most useful for identification of a chemical species or biological agent. Figure 8 demonstrates such enhancement for a C_{60} molecule: In (a), the originally small response of the Ag(1) mode becomes totally dominant. In (b), the Hg(1) mode is dominant. In (c), the Hg(1) mode is almost completely suppressed, with the combined Ag(1) and Hg(4) modes enhanced.

Figure 9 shows an interesting discovery of Long et al. [15] These simulations – which, like all the others discussed in this section, are density-functional-based – demonstrated that atomic hydrogen can be encapsulated in C_{60} via collisions of either H or H_2 with a C_{60} molecule whose breathing mode has been properly excited by an optimized femtosecond-scale laser pulse. The basic mechanism is a "breathing trap'', with the C_{60} first expanding, to admit the H, and then contracting, to contain it.

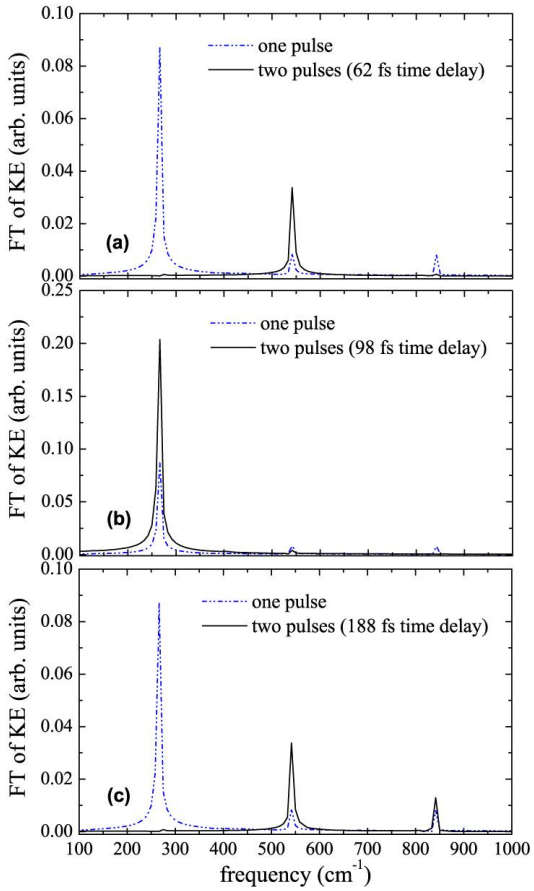

Figure 8. Fourier transform of total kinetic energy of C_{60} after two 26 fs (FWHM) 1500 nm pulses separated by various time delays. After Jiang et al.[14], following the work of Zhao et al.[13]

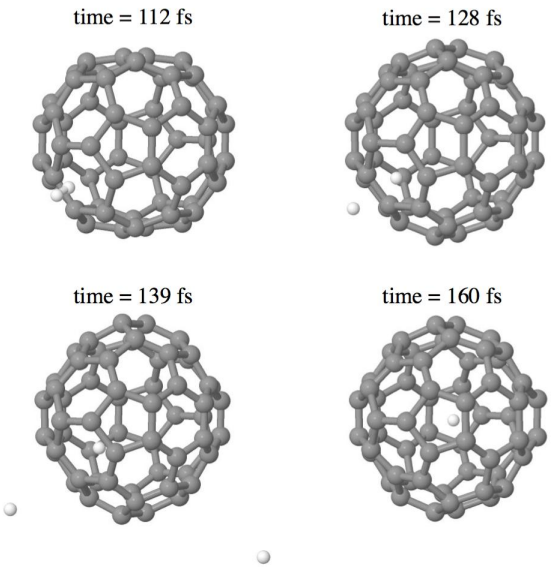

Figure 9. An H_2 molecule is incident on a C_{60} molecule whose breathing mode has been excited by a femtosecond-scale laser pulse. One H atom rebounds but the other is encapsulated in the C_{60} cage. This observation provides a proposal for encapsulation of H, which has not yet been achieved through other means. After Long et al. [15]

Figure 10 illustrates a remarkable discovery of Zhibin Lin[16]: In our technique, electrons equilibrate with each other in about 100 femtoseconds, because they are indirectly coupled to each other via the nuclear motion – even though the electronic temperature is one or two orders of magnitude higher than the temperature associated with nuclear motion (and even though correlation effects are omitted in these mean-field calculations). This means the description is physically correct, and also justifies a 2-temperature model for simulations on larger scales.

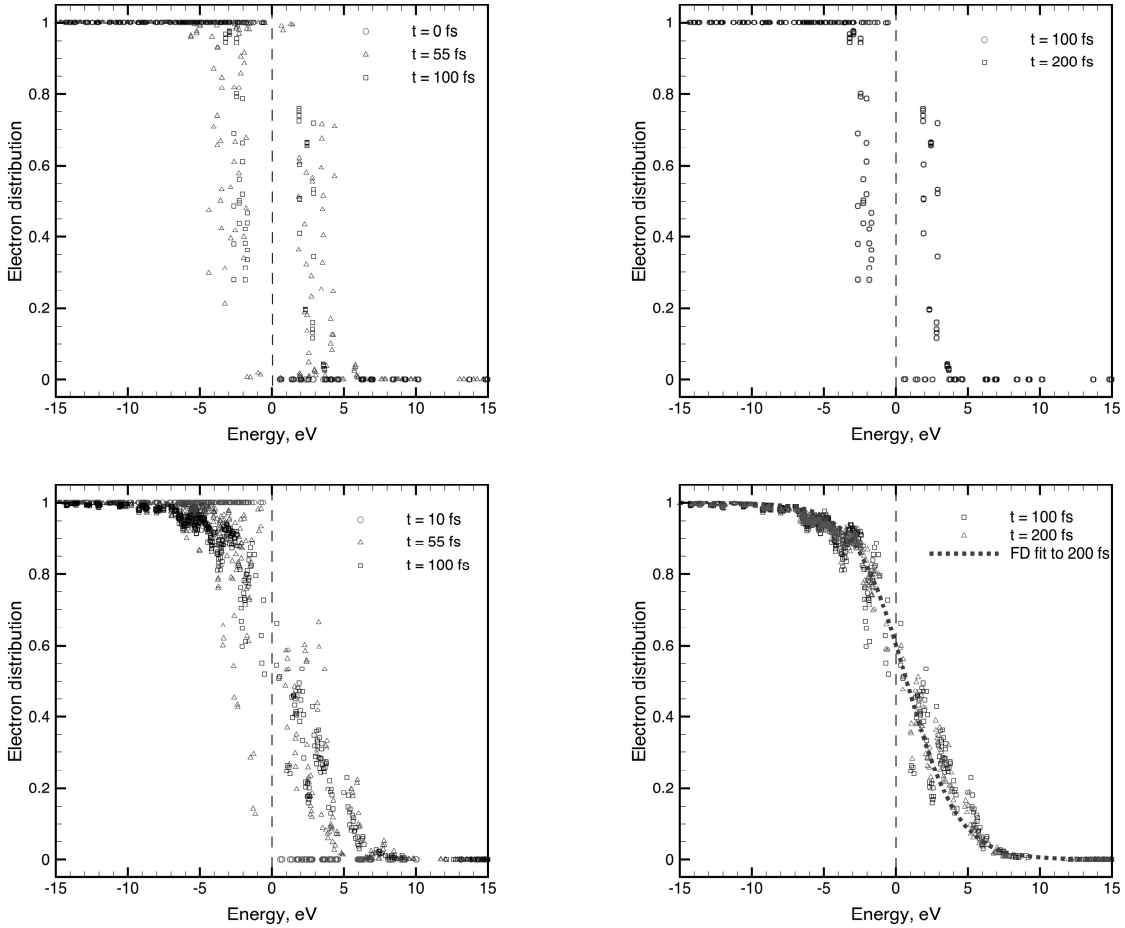

Figure 10. Results for 2-layer graphene: With nuclei frozen, in top panels, electrons fail to equilibrate. But with nuclei permitted to move, in bottom panels, electrons form up into a Fermi-Dirac distribution. After Lin et al.[16]

4. LIGHT-INDUCED SUPERCONDUCTIVITY

Here we use "light" in a very broad sense, to include infrared and terahertz electromagnetic radiation. One can imagine several hypothetical mechanisms for (transient) light-induced superconductivity. An ultrafast laser pulse might lead to, e.g., one of the following on roughly a picosecond time scale:

- elimination of a competing order parameter
- modification of the atomic structure or vibrations
- carrier doping
- modification of the electronic structure

It appears that the group of Cavalleri and coworkers have observed the first two effects, in cuprates[18-21] and K_3C_{60}[22] respectively. Suda et al.[23] appear to have observed the third in a strongly correlated molecular conductor, on a vastly longer time scale (seconds rather than femtoseconds) as shown in Figs. 11 and 12, where isomerization of a spiropyran

monolayer dopes the κ-Br with holes, with both resistance and diamagnetism acting as signatures of induced superconductivity.

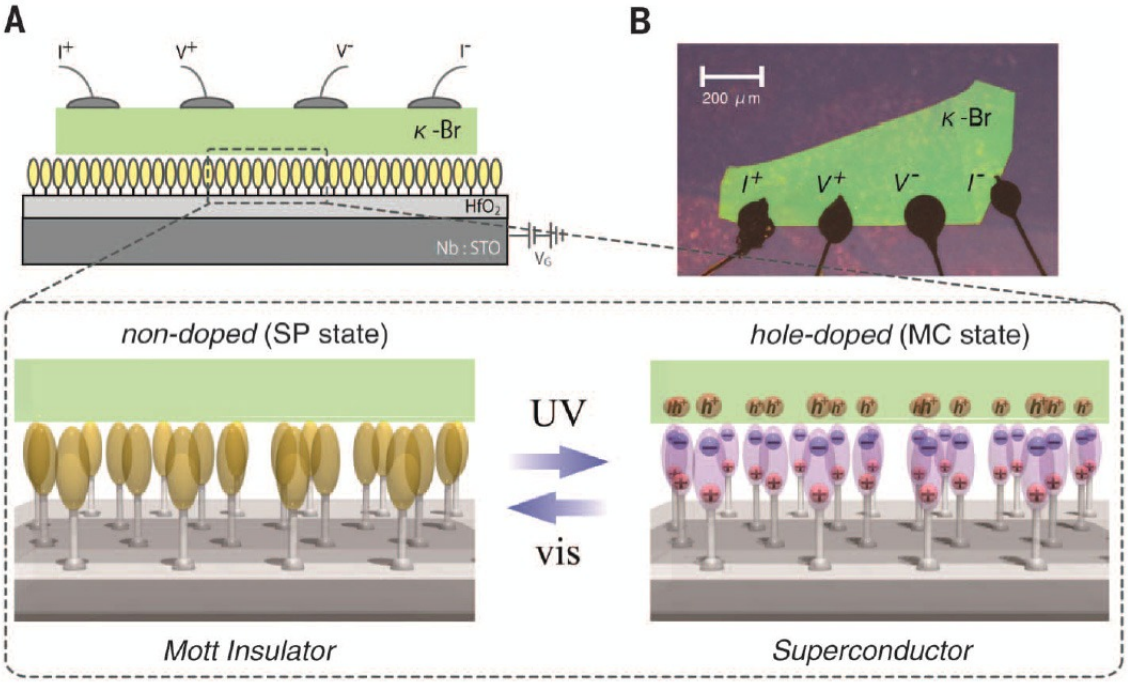

Figure 11. A. The spiropyran (SP) monolayer can isomerize reversibly by UV and visible light irradiation at the interface. This produces an electric field that dopes the κ-(BEDT-TTF)2Cu[N(CN)2]Br – or κ-Br – with holes. B. Optical microscope image of the κ-Br single crystal laminated on the substrate. After Suda et al.[23]

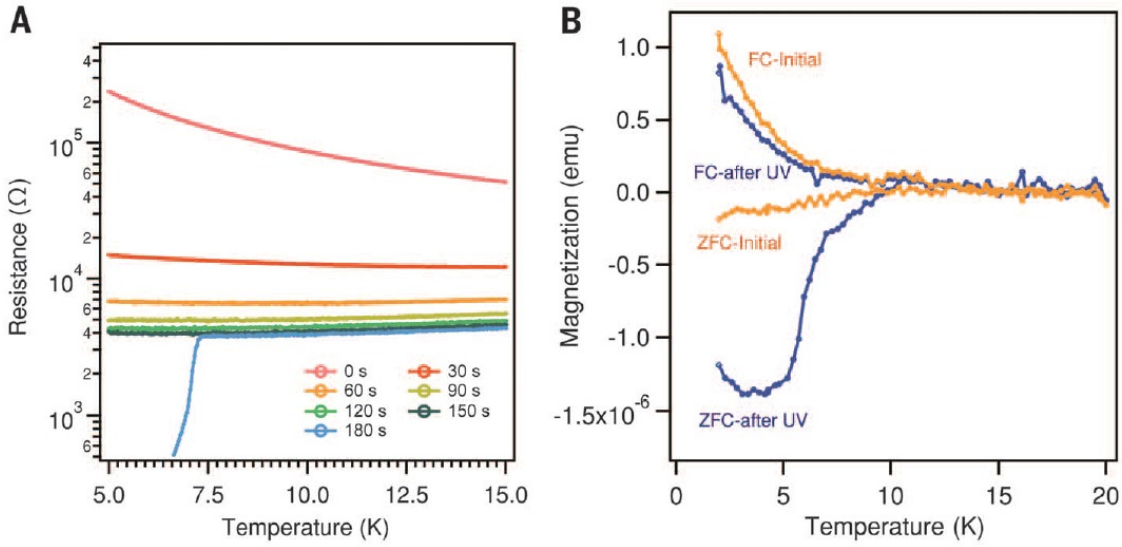

Figure 12. Temperature dependence of the resistance and the magnetization for the κ-Br device. **(A) Resistance versus temperature** after various times of irradiation with UV light. When the irradiation time reached 180 s, the device showed an abrupt resistance drop around 7.3 K. **(B) Magnetic susceptibility** [zero–field-cooled (ZFC) and field-cooled (FC) measurements] in the initial state and UV-irradiated state under a field of 100 Oe. After UV light irradiation, the zero–field-cooled curve was strongly enhanced, implying an increase in the **Meissner effect** and superconducting fraction. After Suda et al.[23]

In Fig. 13, a Josephson plasma resonance edge in the reflectance, near 60 cm^{-1}, is interpreted as a signature of 3D superconductivity in the relevant cuprates, associated with Josephson coupling between CuO_2 planes. It is seen in superconducting $La_{1.84}Sr_{0.16}CuO_4$ ($LSCO_{0.16}$), for example, but not in the non-superconducting phases of this material or $La_{1.675}Eu_{0.2}Sr_{0.125}CuO_4$ ($LESCO_{1/8}$). The interpretation is shown in the schematic drawing of Fig. 14, which depicts for $La_{1.875}Ba_{0.125}CuO_4$ the charge, spin, and lattice arrangement within a CuO_2 plane and set of planes in the stripe-ordered, low-temperature tetragonal (LTT) phase below 55 K. Cu atoms are blue and oxygen atoms red. Holes form stripes which separate domains of oppositely phased antiferromagnetic domains, with spins indicated by arrows. The stripe orientation of periodic CuO_2 planes rotates by 90° between layers. Then, when an ultrafast laser pulse is applied, melting of the stripes permits coherent 3D superconductivity, according to this interpretation.

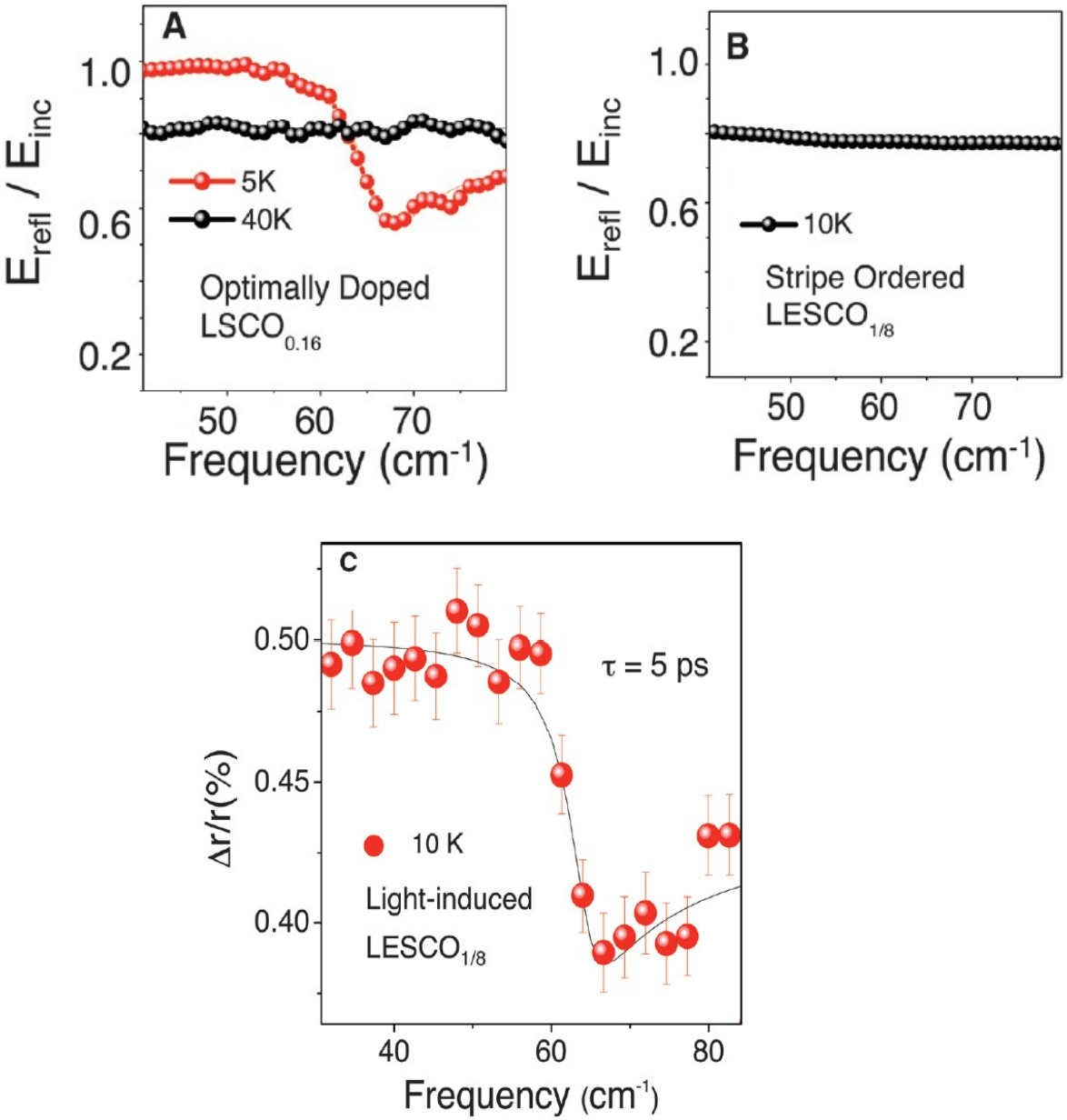

Figure 13. Evidence for transient light-induced superconductivity in $La_{1.675}Eu_{0.2}Sr_{0.125}CuO_4$: Josephson plasma resonance edge in the reflectance, near 60 cm^{-1}, as seen in superconducting $La_{1.84}Sr_{0.16}CuO_4$ but not in the non-superconducting phases of this material or $La_{1.675}Eu_{0.2}Sr_{0.125}CuO_4$. After Fausti et al.[18]

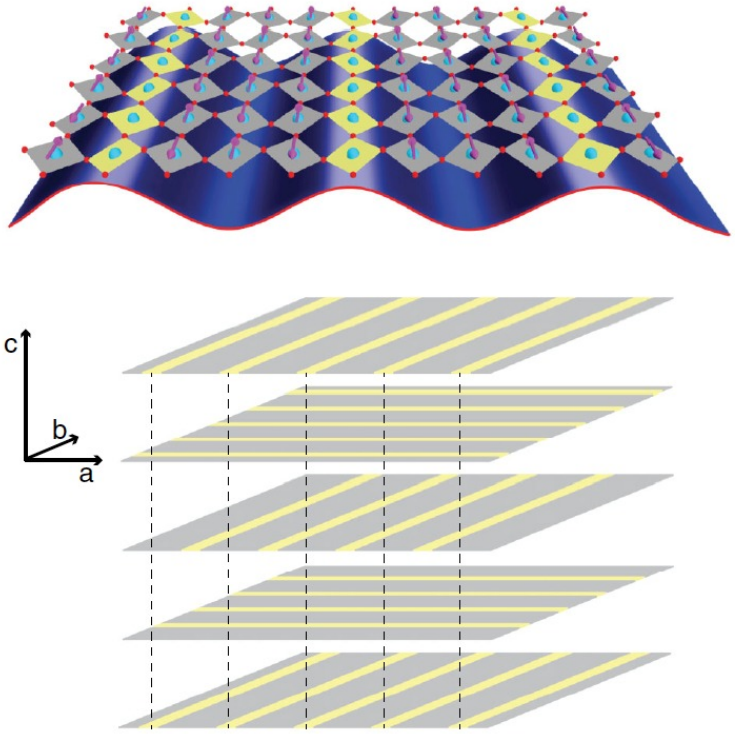

Figure 14. Schematic depiction of $La_{1.875}Ba_{0.125}CuO_4$ charge, spin, and lattice arrangement in the stripe-ordered, low-temperature tetragonal phase. After Fausti et al.[18]

5. CONCLUSION

Here we considered a tiny selection of the ways in which studies of the electronic and structural response to ultrafast laser pulses can elucidate the behavior of important materials. Carefully designed pump-probe experiments can address a vast number of other topics[24] including, e.g., the coupled dynamics of electrons, nuclear motion, and the order parameters associated with magnetism, charge density waves, spin density waves, superconductivity, and even more exotic phases.

We are currently developing a hybrid technique for treating such problems, which combines a density-functional-based approach for the gross electronic structure, on a 1eV energy scale, with semiempirical models for interacting order parameters on a 100 K (or 0.01 eV) scale. A key point is that superconductivity, charge density waves, and spin density waves all involve pairing of electronic states near the Fermi surface, with quasiparticle energies having the basic form $E = \left(\varepsilon^2 + \Delta^2\right)^{1/2}$ (referenced to the chemical potential μ). The order parameter Δ can be determined by a semiempirical free energy, and the scheme can be extended to make everything time-dependent (and to include collective modes). Similar ideas can be used for other magnetic and correlation effects.

REFERENCES

[1] Glezer, E. N., Siegal, Y., Huang, L., and Mazur, E., "The behavior of chi(2) during laser-induced phase transtions in GaAs", Phys. Rev. B 51, 9589 (1995).
[2] Huang, L., Callan, J. P., Glezer, E. N., and Mazur, E., "GaAs under ultrafast excitation: response of the dielectric function", Phys. Rev. Lett., 80, 185 (1998).

[3] Callan, J. P., Kim, A. M.-T., Roeser, C. A. D., and Mazur, E. "Universal dynamics during and after ultrafast laser-induced semiconductor-to-metal transitions", Phys. Rev. B, 64, 073201 (2001).
[4] Graves, J. S., and Allen, R. E., "Response of GaAs to Fast Intense Laser Pulses", Phys. Rev. B 58, 13627 (1998).
[5] Dumitrica, T., Graves, J. S., and Allen, R. E., "Second-Order Susceptibility from a Tight-Binding Hamiltonian", Phys. Rev. B 58, 15340 (1998).
[6] Dumitrica, T. and Allen, R. E., "Time Evolution of Second Order Susceptibility in GaAs following a Fast Intense Laser Pulse", Solid State Commun. 113, 653 (2000).
[7] Dumitrica, T. and Allen, R. E., "Femtosecond-Scale Response of GaAs to Ultrafast Laser Pulses", Physical Review B 66, 081202 (2002).
[8] Dumitrica, T., Burzo, A., Dou, Y., and Allen, R. E., "Response of Si and InSb to Ultrafast Laser Pulses", Physica Status Solidi (b) 241, 2331 (2004).
[9] Fleischer, S. B., Pevzner, B., Dougherty, D. J., Zeiger, H. J., Dresselhaus, G., Dresselhaus, M. S., Ippen, E. P., and Hebard, A. F., "Coherent phonons in alkali metal-doped C_{60}", Appl. Phys. Lett. 71, 2734 (1997).
[10] Dexheimer, S. L., Mittleman, D. M., Schoenlein, R. W., Vareka, W., Xiang, X.-D., Zettl, A., and Shank, C. V., "Ultrafast Dynamics of Solid C_{60}", in *Utrafast Phenomena VIII*, edited by Martin, C. V., Migus, A., Mourou, G. A., and Zewail, A. H. (Springer-Verlag, Berlin, 1993).
[11] Torralva, B., Niehaus, T. A., Elstner, M., Suhai, S., Frauenheim, Th., and Allen, R. E., "Response of C_{60} and C_n to Ultrashort Laser Pulses", Physical Review B 64, 153105 (2001).
[12] Torralva, B. and Allen, R. E., " Mechanisms for Laser Control of Chemical Reactions", Journal of Modern Optics 49, 593 (2002).
[13] Zhou, X., Lin, Z., Jiang, C., Gao, M., and Allen, R. E., "Maximum relative excitation of a specific vibrational mode via optimum laser-pulse duration", Physical Review B 82, 075433 (2010).
[14] Jiang, C., Zhou, X., Xie, R., Li, F., and Allen, R. E., "Selective control of vibrational modes with sequential femtosecond-scale laser pulses", Chemical Physics Letters 515, 137 (2011).
[15] Long, Z., Zhou, X., Cai, H., Chen, C., Miao, L., and Allen, R. E., "Breathing-trap mechanism for encapsulation of atomic hydrogen in C60", Chemical Physics Letters 583, 114 (2013).
[16] Lin, Z., and Allen, R.E., "Ultrafast equilibration of excited electrons in dynamical simulations", J. Phys. Condens. Matter 21, 485503 (2009).
[17] Dou, Y., Torralva, B., and Allen, R. E., "Interplay of electronic and nuclear degrees of freedom in a femtosecond scale photochemical reaction", Chemical Physics Letters 392, 352 (2004).
[18] Fausti, D., Tobey, R. I., Dean, N., Kaiser, S., Dienst, A., Hoffmann, M. C., Pyon, S., Takayama, T., Takagi, T. H., and Cavalleri, A., "Light-induced superconductivity in a stripe-ordered cuprate", Science **331,** 189 (2011).
[19] Kaiser, S., Hunt, C. R., Nicoletti, D., Hu, W., Gierz, I., Liu, H. Y., Le Tacon, M., Loew, T., Haug, D., Keimer, B., and Cavalleri, A., "Optically induced coherent transport far above T_c in underdoped $YBa_2Cu_3O_{6+\delta}$", Phys. Rev. B 89, 184516 (2014).
[20] Först, M., Tobey, R. I., Bromberger, H., Wilkins, S. B., Khanna, V., Caviglia, A. D., Chuang, Y.-D., Lee, W. S., Schlotter, W. F., Turner, J. J., Minitti, M. P., Krupin, O., Xu, Z. J., Wen, J. S., Gu, G. D., Dhesi, S. S., Cavalleri, A., and Hill, J. P., "Melting of Charge Stripes in Vibrationally Driven $La_{1.875}Ba_{0.125}CuO_4$: Assessing the Respective Roles of Electronic and Lattice Order in Frustrated Superconductors", Phys. Rev. Lett. 112, 157002 (2014).
[21] Först, M., Frano, A., Kaiser, S., Mankowsky, R., Hunt, C. R., Turner, J. J., Dakovski, G. L., Minitti, M. P., Robinson, J., Loew, T., Le Tacon, M., Keimer, B., Hill, J. P., Cavalleri, A., and Dhesi, S. S., "Femtosecond X-rays link melting of charge density wave correlations and light enhanced coherent transport in $YBa_2Cu_2O_{6.6}$", Phys. Rev. B 90, 184514 (2014).
[22] Mitrano, M., Cantaluppi, A., Nicoletti, D., Kaiser, S., Perucchi, A., Lupi, S., Di Pietro, P., Pontiroli, D., Riccò, M., Clark, S. R., Jaksch, D., and Cavalleri, A., "Possible light-induced superconductivity in K_3C_{60} at high temperature", Nature 530, 461 (2016).
[23] Suda, M., Kato, R., and Yamamoto, H. M., "Light-induced superconductivity using a photoactive electric double layer", Science 347, 743 (2015).
[24] See, e.g., *Ultrafast Phenomena XVII*, edited by Chergui, M., Jonas, D., Riedle, E., Schoenlein. R., Taylor, A. (Oxford University Press, 2011).