Supercomputing studies of light-matter interactions
in materials and molecules

Roland E. Allen
Physics Department, Texas A&M University

Supercomputing is required for an understanding of systems and phenomena with many degrees of freedom, which are too complex to be treated analytically, and which are too rich in detail to be fully accessible to experiment.

Our specific emphasis here is on the response of important systems in physics, chemistry, biology, electronics, and materials science to ultrafast (femtosecond-scale) laser pulses.

Dr. Zhibin Lin: graphene, silicon, metals, development of new methods

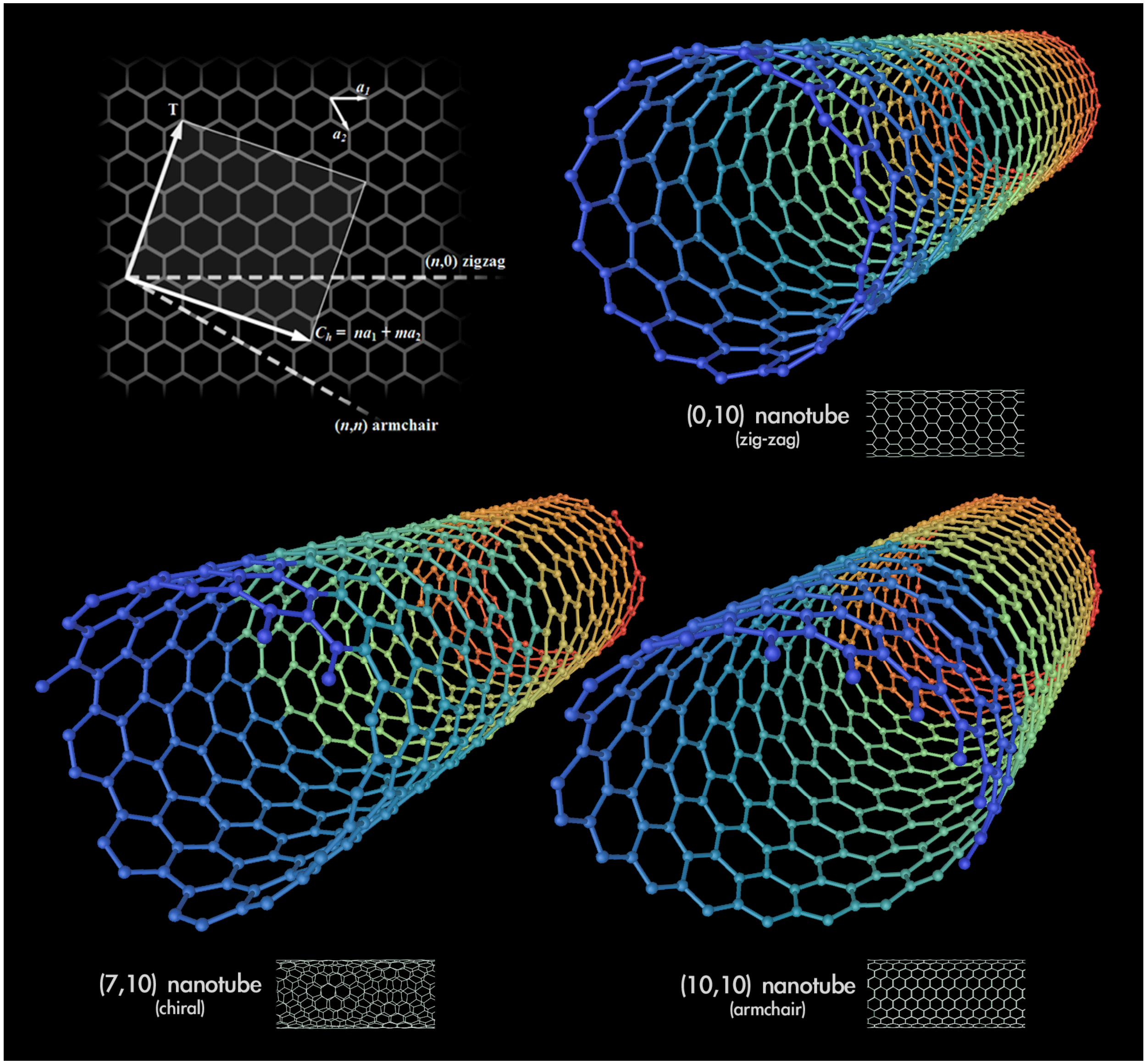
Chenwei Jiang: photoisomerization, photocyclization, C_{60} vibrational & electronic response

Dr. Xiang Zhou: carbon nanotubes – vibrational and electronic response, H_2 storage

Meng Gao: carbon nanotubes with new techniques, including electron-electron interactions

earlier work: John Graves, Ben Torralva, Traian Dumitrica, Andrea Burzo, Yusheng Dou, Petra Sauer

(also John Ruihua Xie, Shahram Khosravi, Qingsheng Gao, Robert Hamilton)



Types of single-wall carbon nanotubes.

From http://commons.wikimedia.org/wiki/File:Types_of_Carbon_Nanotubes.png.

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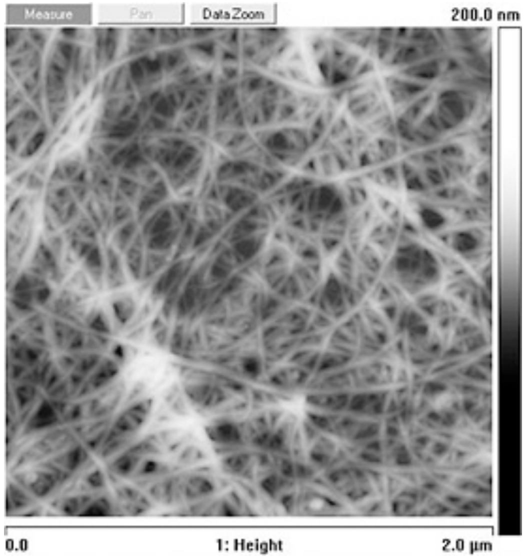
Carbon nanotubes have an extremely wide variety of potential applications in electronics, composite materials, energy conversion, energy storage, sensors, field emission displays, and radiation sources.

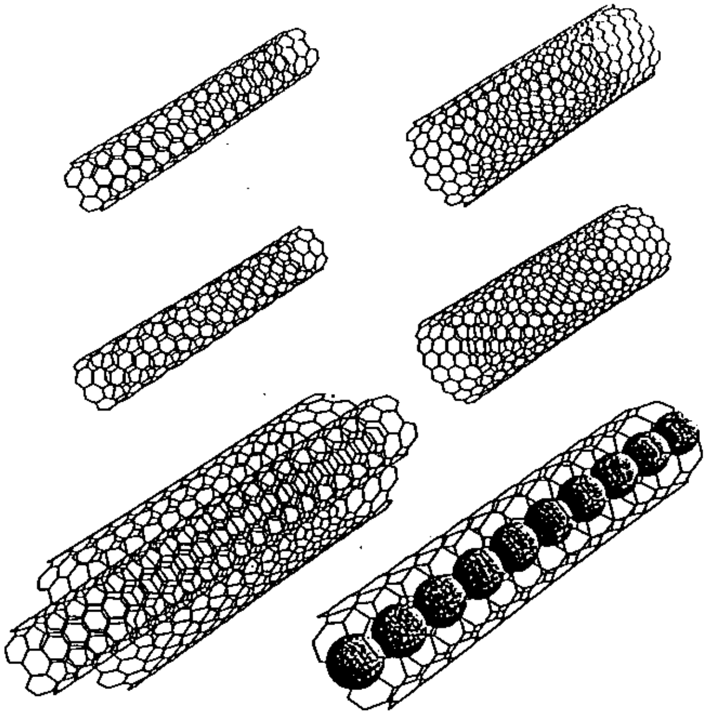
They have extraordinary strength, unique electrical properties, high thermal conductivity, and even the ability to emit light.

They also come in many different varieties – single-walled, double-walled, multiwalled, with a range of diameters and chiralities.



AFM image of carbon nanotubes.

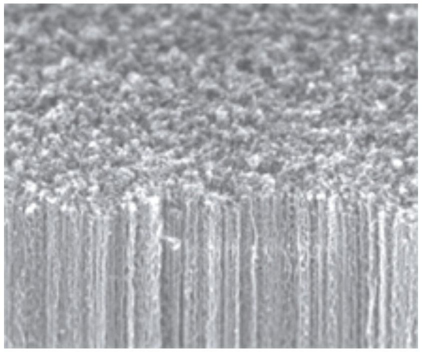
From http://www.nrel.gov/pv/measurements/atomic_force.html/.
Credit: National Renewable Energy Laboratory.



Examples of carbon nanotube structures.

From http://www.wtec.org/loyola/nano/04_03.htm.

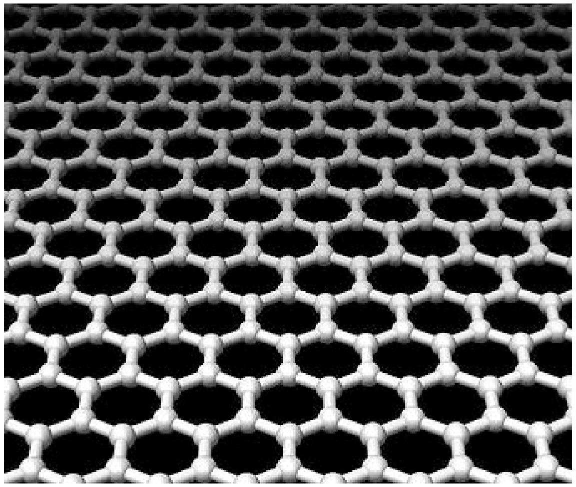
Credit: Donald M. Cox, Exxon Research and Engineering.



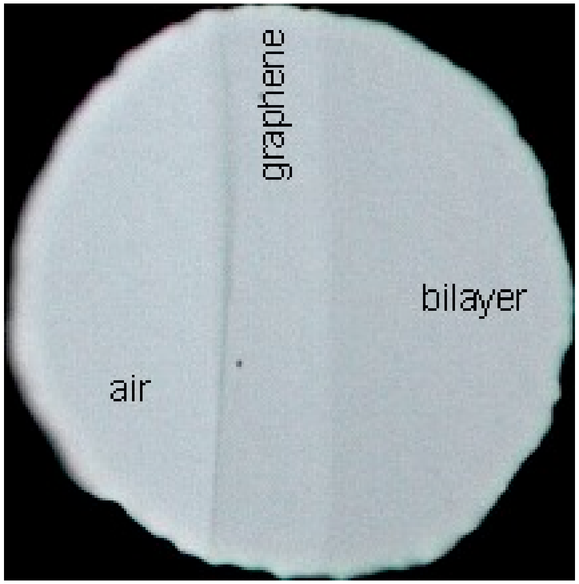
Scanning electron microscope image of an array of vertical carbon nanotubes doped with nitrogen.

From http://www.technologyreview.com/energy/22074/.
Credit: Science.

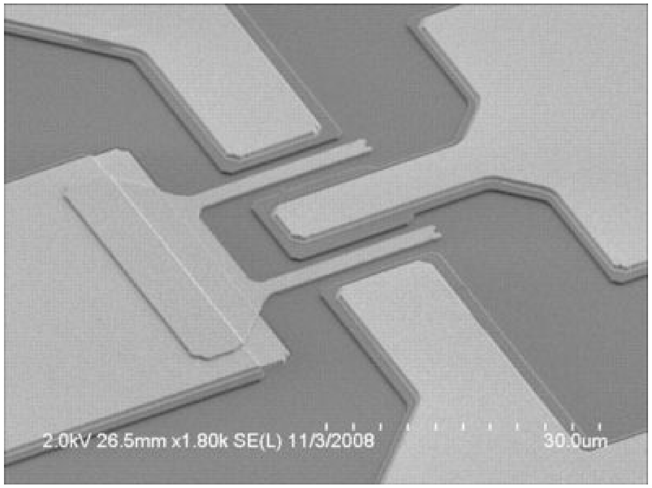
Graphene has even greater promise for some applications.



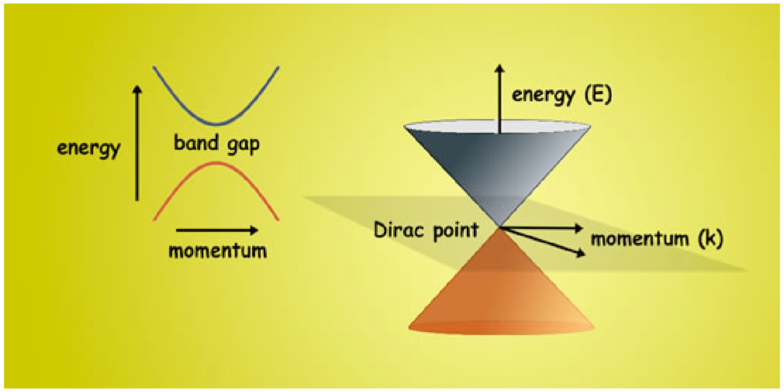
Graphene is an atomic-scale honeycomb lattice made of carbon atoms. Measurements have shown that graphene has a breaking strength 200 times greater than steel, making it the strongest material ever tested.
Figure and text from http://en.wikipedia.org/wiki/Graphene.



Photograph of graphene in transmitted light. This one atom thick crystal can be seen with the naked eye because it absorbs approximately 2.3% of white light.
Figure and caption from http://en.wikipedia.org/wiki/Graphene.



HRL Laboratories demonstrated the first graphene field-effect transistors (FETs) using epitaxial graphene film operating in the radio frequency (RF) range.
From http://www.nanotech-now.com/news.cgi?story_id=31577.

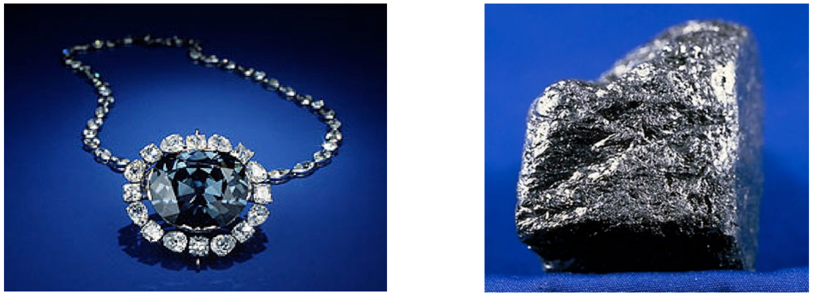


The band structure of a representative three-dimensional solid (left) is parabolic, with a band gap between the lower-energy valence band and the higher-energy conduction band.

The energy bands of two-dimensional graphene (right) are smooth-sided cones, which meet at the Dirac point.

These are energy-momentum relationships of quasiparticles behaving as if they were massless electrons – so-called Dirac fermions.

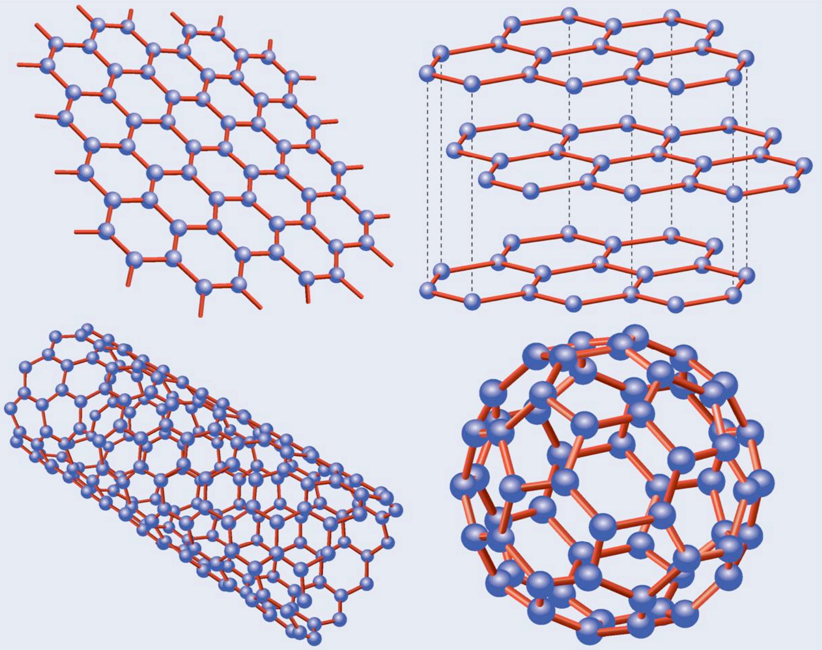
From http://www.lbl.gov/Science-Articles/Archive/ALS-graphene.html.
Credit: Lawrence Berkeley National Laboratory Research News



The forms of carbon known before 1985:
left, diamond (the Hope Diamond) – right, graphite

From http://www.sciencenewsforkids.org/articles/20081217/Feature1.asp.
Credits: left, The Smithsonian Institution – right, U.S. House of Representatives

2 Graphene: mother of them all



Graphene (top left) consists of a 2D hexagonal lattice of carbon atoms. Each atom is covalently bonded to three others; but since carbon has four valence electrons, one is left free – allowing graphene to conduct electricity. Other well-known forms of carbon all derive from graphene: graphite is a stack of graphene layers (top right); carbon nanotubes are rolled-up cylinders of graphene (bottom left); and a buckminsterfullerene (C_{60}) molecule consists of graphene balled into a sphere by introducing some pentagons as well as hexagons into the lattice (bottom right).

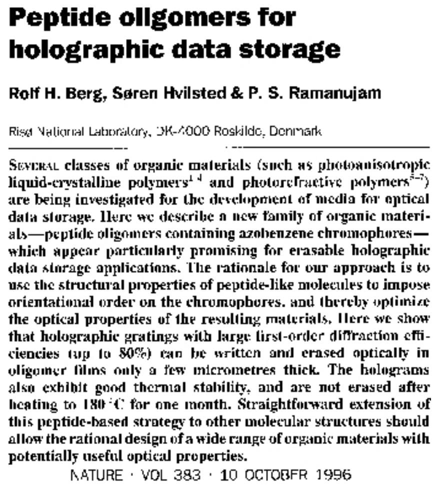
Graphene was discovered in 2004 by Andre Geim's group at Manchester University in England.

Among the potential applications are electronic devices such as atomically thin transistors, electronic waveguides, and sensitive chemical sensors.

Figure and text from http://physics.bu.edu/%7Eneto/.
Credit: A. H. Castro Neto, F. Guinea, and N. M. R. Peres, Physics World, November 2006.

Representative applications of molecular switching: azobenzene

Holographic data storage



Peptide oligomers for holographic data storage

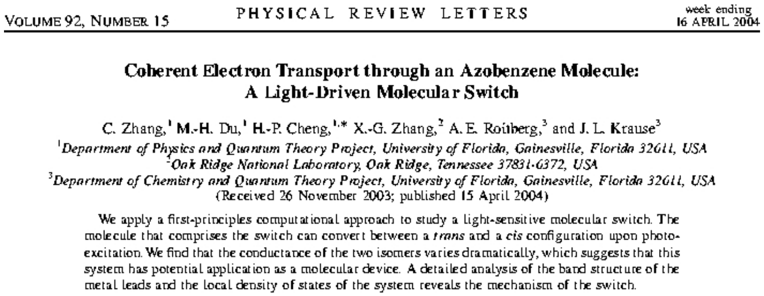
Rolf H. Berg, Søren Hvilsted & P. S. Ramanujam

Risø National Laboratory, DK-4000 Roskilde, Denmark

SEVERAL classes of organic materials (such as photoanisotropic liquid-crystalline polymers[1-4] and photorefractive polymers[5-7]) are being investigated for the development of media for optical data storage. Here we describe a new family of organic materials—peptide oligomers containing azobenzene chromophores—which appear particularly promising for erasable holographic data storage applications. The rationale for our approach is to use the structural properties of peptide-like molecules to impose orientational order on the chromophores, and thereby optimize the optical properties of the resulting materials. Here we show that holographic gratings with large first-order diffraction efficiencies (up to 80%) can be written and erased optically in oligomer films only a few micrometres thick. The holograms also exhibit good thermal stability, and are not erased after heating to 180 °C for one month. Straightforward extension of this peptide-based strategy to other molecular structures should allow the rational design of a wide range of organic materials with potentially useful optical properties.

NATURE · VOL 383 · 10 OCTOBER 1996

Light-driven molecular switch



VOLUME 92, NUMBER 15 PHYSICAL REVIEW LETTERS week ending 16 APRIL 2004

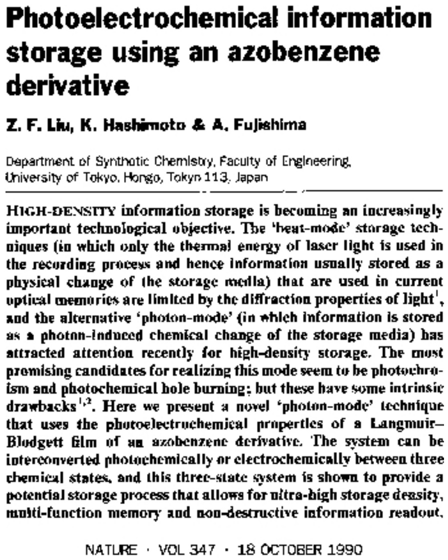
Coherent Electron Transport through an Azobenzene Molecule: A Light-Driven Molecular Switch

C. Zhang,[1] M.-H. Du,[1] H.-P. Cheng,[1,*] X.-G. Zhang,[2] A. E. Roitberg,[3] and J. L. Krause[3]

[1]*Department of Physics and Quantum Theory Project, University of Florida, Gainesville, Florida 32611, USA*
[2]*Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6372, USA*
[3]*Department of Chemistry and Quantum Theory Project, University of Florida, Gainesville, Florida 32611, USA*
(Received 26 November 2003; published 15 April 2004)

We apply a first-principles computational approach to study a light-sensitive molecular switch. The molecule that comprises the switch can convert between a *trans* and a *cis* configuration upon photoexcitation. We find that the conductance of the two isomers varies dramatically, which suggests that this system has potential application as a molecular device. A detailed analysis of the band structure of the metal leads and the local density of states of the system reveals the mechanism of the switch.

Photoelectrochemical Storage



Photoelectrochemical information storage using an azobenzene derivative

Z. F. Liu, K. Hashimoto & A. Fujishima

Department of Synthetic Chemistry, Faculty of Engineering, University of Tokyo, Hongo, Tokyo 113, Japan

HIGH-DENSITY information storage is becoming an increasingly important technological objective. The 'heat-mode' storage techniques (in which only the thermal energy of laser light is used in the recording process and hence information usually stored as a physical change of the storage media) that are used in current optical memories are limited by the diffraction properties of light[1], and the alternative 'photon-mode' (in which information is stored as a photon-induced chemical change of the storage media) has attracted attention recently for high-density storage. The most promising candidates for realizing this mode seem to be photochromism and photochemical hole burning; but these have some intrinsic drawbacks[1,2]. Here we present a novel 'photon-mode' technique that uses the photoelectrochemical properties of a Langmuir–Blodgett film of an azobenzene derivative. The system can be interconverted photochemically or electrochemically between three chemical states, and this three-state system is shown to provide a potential storage process that allows for ultra-high storage density, multi-function memory and non-destructive information readout.

NATURE · VOL 347 · 18 OCTOBER 1990

Liquid Crystal Display

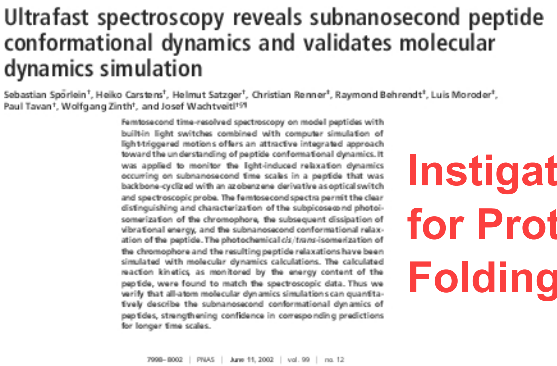
Optical Switching and Image Storage by Means of Azobenzene Liquid-Crystal Films

Tomiki Ikeda* and Osamu Tsutsumi

Liquid crystals are promising materials for optical switching and image storage because of their high resolution and sensitivity. Azobenzene liquid crystals (LCs) have been developed, in which azobenzene moieties play roles as both mesogens and photosensitive chromophores. Azobenzene LC films showed a nematic phase in trans isomers and no LC phase in cis isomers. Trans-cis photoisomerization of azobenzene with a laser pulse resulted in a nematic-to-isotropic phase transition with a rapid optical response of 200 microseconds.

SCIENCE • VOL. 268 • 30 JUNE 1995

Instigator for Protein Folding



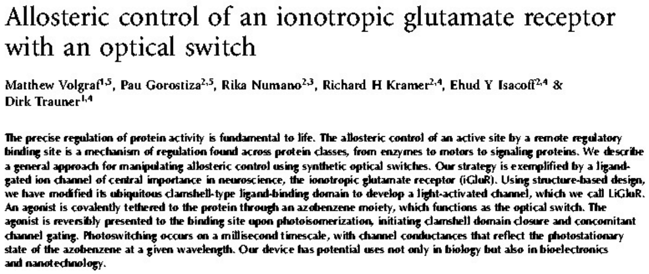
Ultrafast spectroscopy reveals subnanosecond peptide conformational dynamics and validates molecular dynamics simulation

Sebastian Spörlein[†], Heiko Carstens[†], Helmut Satzger[†], Christian Renner[†], Raymond Behrendt[†], Luis Moroder[†], Paul Tavan[†], Wolfgang Zinth[†], and Josef Wachtveitl[†§¶]

Femtosecond time-resolved spectroscopy on model peptides with built-in light switches combined with computer simulation of light-triggered motions offers an attractive integrated approach toward the understanding of peptide conformational dynamics. It was applied to monitor the light-induced relaxation dynamics occurring on subnanosecond time scales in a peptide that was backbone-cyclized with an azobenzene derivative as optical switch and spectroscopic probe. The femtosecond spectra permit the clear distinguishing and characterization of the subpicosecond photoisomerization of the chromophore, the subsequent dissipation of vibrational energy, and the subnanosecond conformational relaxation of the peptide. The photochemical *cis/trans*-isomerization of the chromophore and the resulting peptide relaxations have been simulated with molecular dynamics calculations. The calculated reaction kinetics, as monitored by the energy content of the peptide, were found to match the spectroscopic data. Thus we verify that all-atom molecular dynamics simulations can quantitatively describe the subnanosecond conformational dynamics of peptides, strengthening confidence in corresponding predictions for longer time scales.

7998–8002 | PNAS | June 11, 2002 | vol. 99 | no. 12

Control of Protein Activity

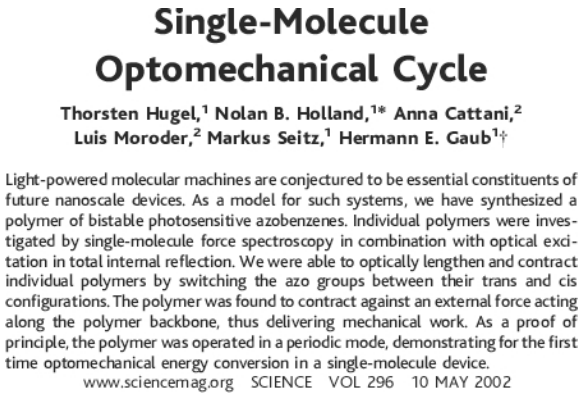


Allosteric control of an ionotropic glutamate receptor with an optical switch

Matthew Volgraf[1,5], Pau Gorostiza[2,5], Rika Numano[2,3], Richard H Kramer[2,4], Ehud Y Isacoff[2,4] & Dirk Trauner[1,4]

The precise regulation of protein activity is fundamental to life. The allosteric control of an active site by a remote regulatory binding site is a mechanism of regulation found across protein classes, from enzymes to motors to signaling proteins. We describe a general approach for manipulating allosteric control using synthetic optical switches. Our strategy is exemplified by a ligand-gated ion channel of central importance in neuroscience, the ionotropic glutamate receptor (iGluR). Using structure-based design, we have modified its ubiquitous clamshell-type ligand-binding domain to develop a light-activated channel, which we call LiGluR. An agonist is covalently tethered to the protein through an azobenzene moiety, which functions as the optical switch. The agonist is reversibly presented to the binding site upon photoisomerization, initiating clamshell domain closure and concomitant channel gating. Photoswitching occurs on a millisecond timescale, with channel conductances that reflect the photostationary state of the azobenzene at a given wavelength. Our device has potential uses not only in biology but also in bioelectronics and nanotechnology.

Nanomechanical Device



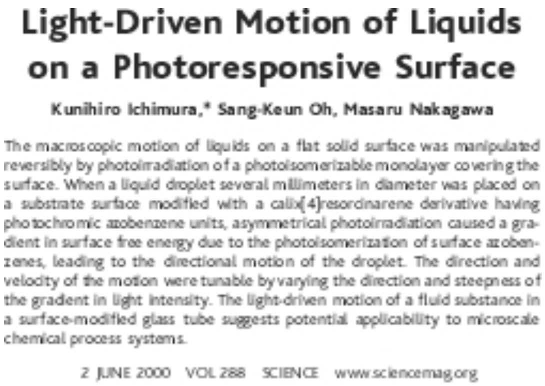
Single-Molecule Optomechanical Cycle

Thorsten Hugel,[1] Nolan B. Holland,[1*] Anna Cattani,[2] Luis Moroder,[2] Markus Seitz,[1] Hermann E. Gaub[1†]

Light-powered molecular machines are conjectured to be essential constituents of future nanoscale devices. As a model for such systems, we have synthesized a polymer of bistable photosensitive azobenzenes. Individual polymers were investigated by single-molecule force spectroscopy in combination with optical excitation in total internal reflection. We were able to optically lengthen and contract individual polymers by switching the azo groups between their trans and cis configurations. The polymer was found to contract against an external force acting along the polymer backbone, thus delivering mechanical work. As a proof of principle, the polymer was operated in a periodic mode, demonstrating for the first time optomechanical energy conversion in a single-molecule device.

www.sciencemag.org SCIENCE VOL 296 10 MAY 2002

Droplet Driver



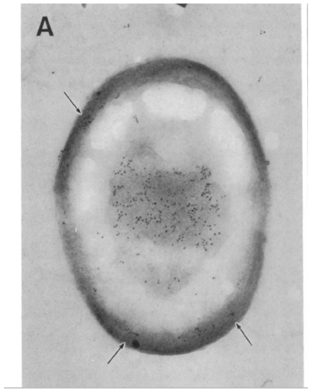
Light-Driven Motion of Liquids on a Photoresponsive Surface

Kunihiro Ichimura,* Sang-Keun Oh, Masaru Nakagawa

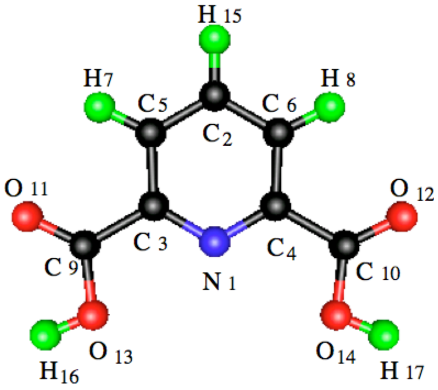
The macroscopic motion of liquids on a flat solid surface was manipulated reversibly by photoirradiation of a photoisomerizable monolayer covering the surface. When a liquid droplet several millimeters in diameter was placed on a substrate surface modified with a calix[4]resorcinarene derivative having photochromic azobenzene units, asymmetrical photoirradiation caused a gradient in surface free energy due to the photoisomerization of surface azobenzenes, leading to the directional motion of the droplet. The direction and velocity of the motion were tunable by varying the direction and steepness of the gradient in light intensity. The light-driven motion of a fluid substance in a surface-modified glass tube suggests potential applicability to microscale chemical process systems.

2 JUNE 2000 VOL 288 SCIENCE www.sciencemag.org

Scully et al. propose detection of pathogens like anthrax with femtosecond-scale laser pulses.

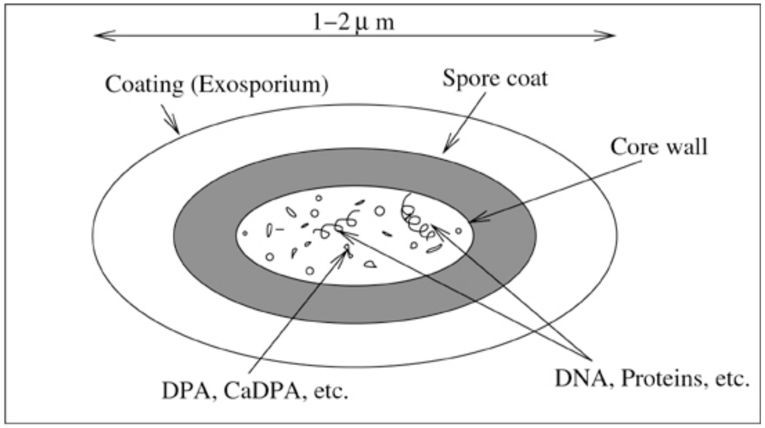


bacterial spore



dipicolinic acid is ~ 5-15 % of dry spore weight (in compounds)

[figure from Xie, Smith, and Allen]

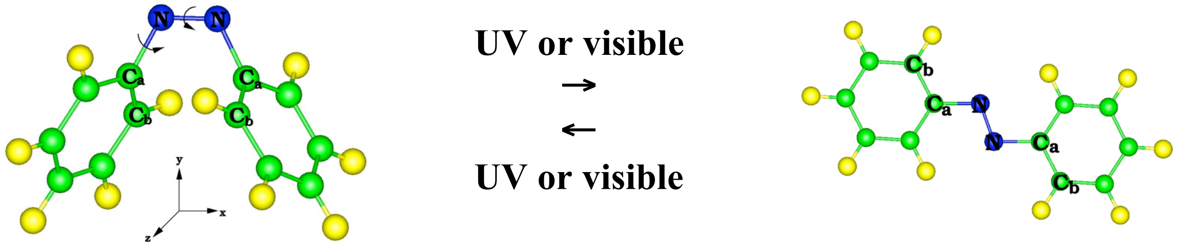


Schematic depiction of an anthrax spore, after M. O. Scully, G. W. Kattawar, R. P. Lucht, T. Opatrny, H. Pilloff, A. Rebane, A. V. Sokolov, and M. S. Zubairy, PNAS 99, 10994 (2002).

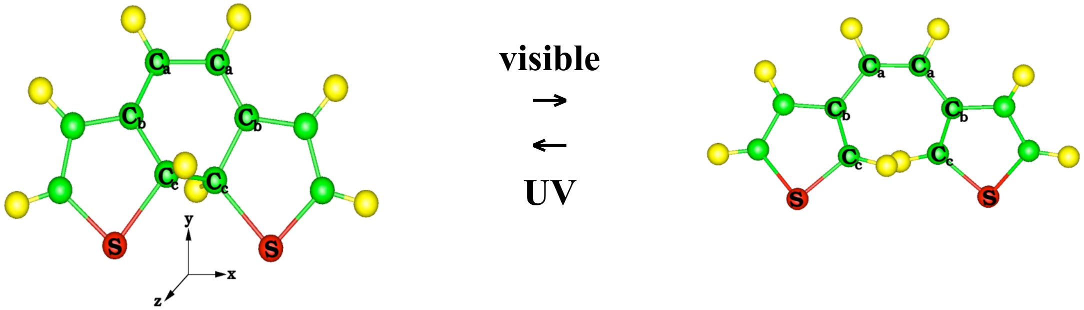
Dipicolinic acid (DPA) and its salts (e.g. Ca-DPA) are contained in the core and are in contact with the spore-specific DNA ribosomes and cell proteins.

Some processes previously studied (by Yusheng Dou & Petra Sauer)

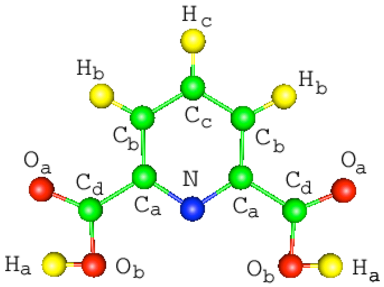
- Photoisomerization of azobenzene



- Photoinduced ring-opening



- Response of dipicolinic acid



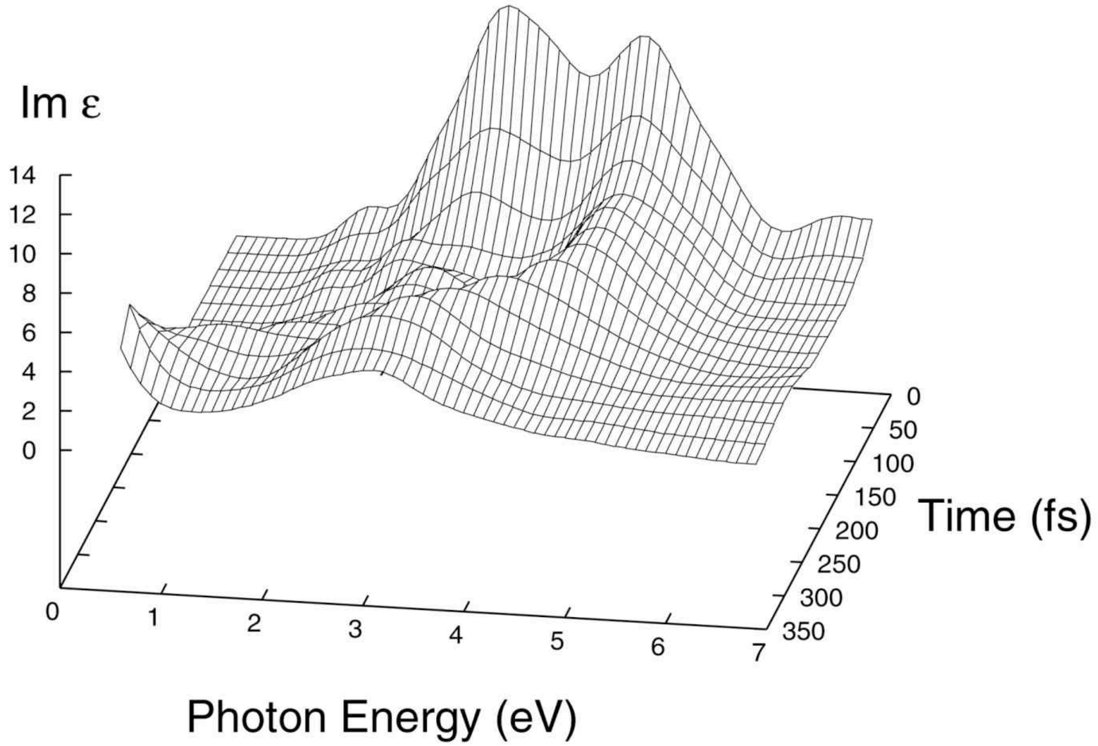
Although real applications (such as molecular switches and biochemical detectors) will involve adaptive techniques -- with femtosecond-scale laser pulses whose durations, photon energies, fluences, shapes, etc. are tailored for specific applications -- as well as larger systems, one needs an understanding of the rich interplay of electronic and nuclear dynamics to guide more empirical approaches. This understanding can be obtained through detailed dynamical simulations.

One can examine microscopic quantities in great detail during a computer simulation, but one should also calculate the quantities that are directly accessible to experiment.

Example: dielectric function probes electronic structure

- **In this figure, the time-dependent dielectric function is shown for GaAs after it has been subjected to a 70 fs laser pulse above threshold intensity.**
- **The behavior here signals a nonthermal phase transition, due to destabilization of the atomic bonding on a femtosecond time scale.**

[after Dumitrica, Graves, and Allen]

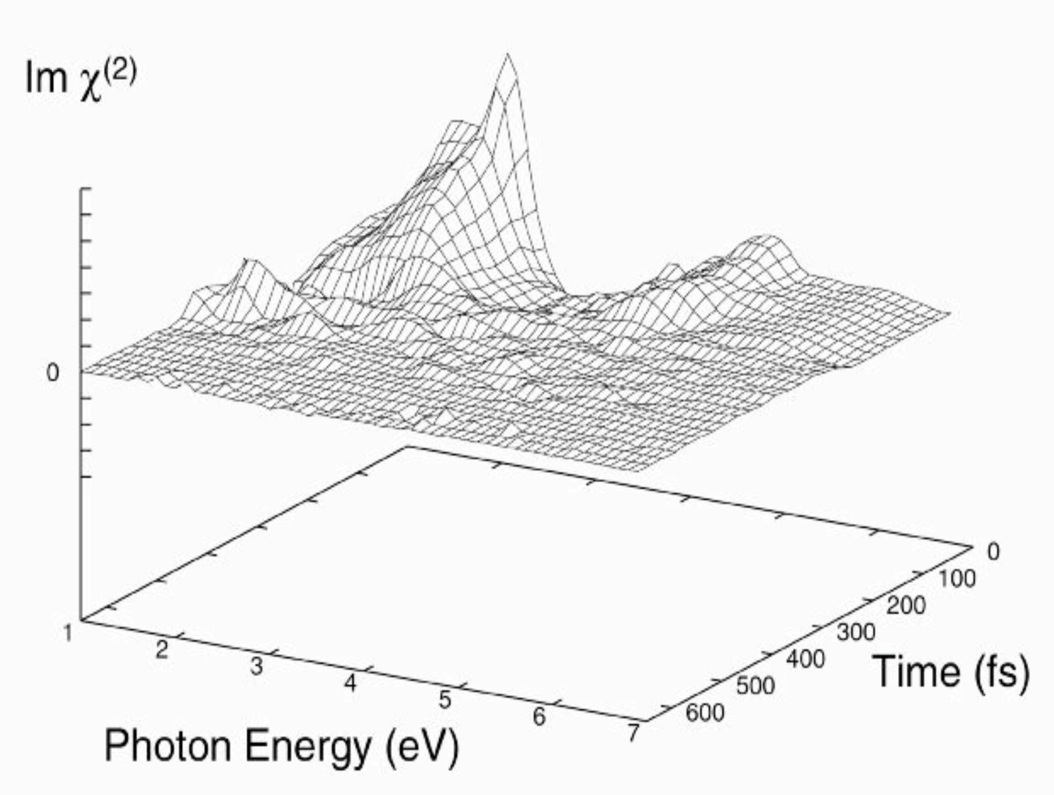


Several groups have studied such transitions experimentally in a variety of materials: c-GaAs, a-GaAs, Si, InSb, a-GeSb, Te, etc.

Another example: nonlinear susceptibility shows atomic structure

Time-dependent nonlinear susceptibility for GaAs just above the threshold laser intensity for a nonthermal phase transition.

- The nonlinear susceptibility probes the atomic structure of the material, and is thus complementary to the linear dielectric function, which probes the electronic structure.
- Notice that the nonlinear susceptibility falls to zero over the entire range of photon energies, signaling a loss of the original symmetry of the GaAs lattice.

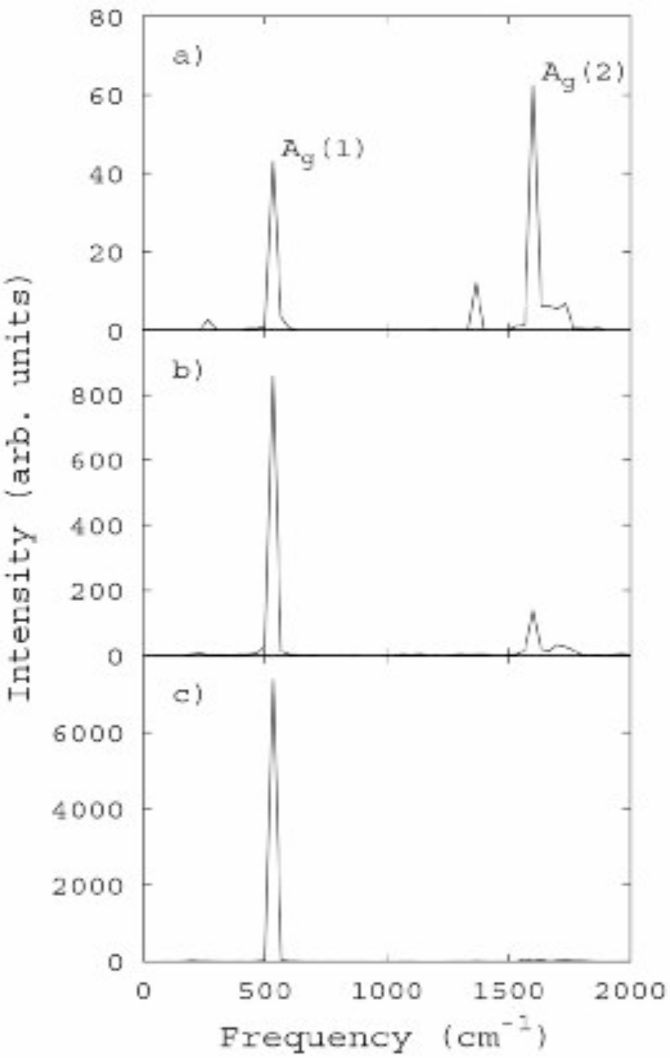


[after Dumitrica, Graves, and Allen]

C_{60} vibrations after ultrafast laser pulse

Our simulations resolved what might appear to be a discrepancy between the results of 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.

After B. Torralva, T. A. Niehaus, M. Elstner, S. Suhai, Th. Frauenheim, and R. E. Allen, Physical Review B 64, 153105 (2001): 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.



In recent work, Chenwei Jiang, for C_{60}, and Xiang Zhou, for carbon nanotubes, have discovered that several laser pulse parameters strongly control the vibrational response: duration, photon energy, and intensity (plus possibly polarization and phase).

Trans-to-cis isomerization of stilbene following an ultrafast laser pulse

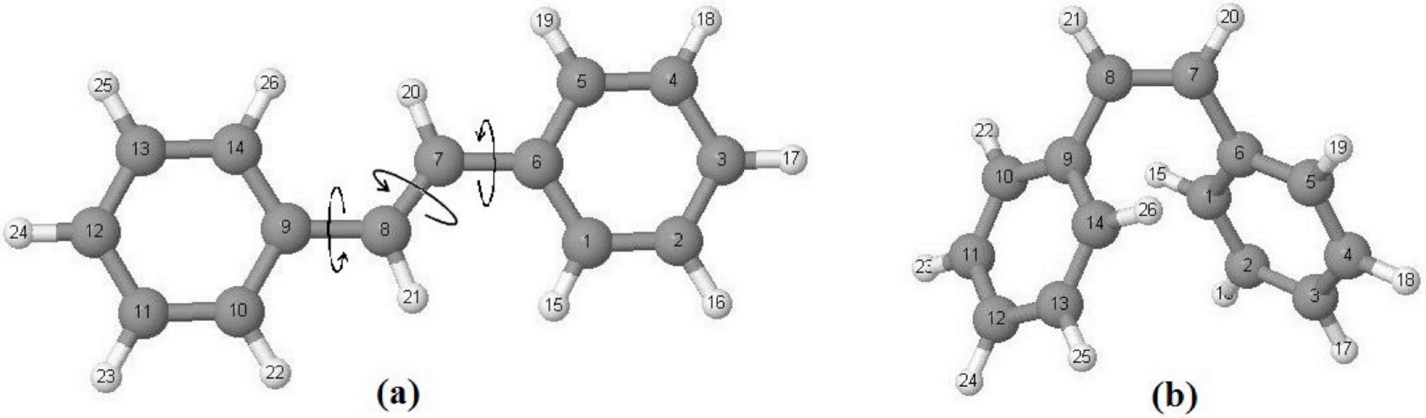
Chenwei Jiang, Ruihua Xie, Fuli Li, and Roland E. Allen (Chemical Physics Letters, in press)

(1) Electronic excitation by the laser pulse weakens the central C-C bond, and also excites vibrations of this bond.

(2) Vibrational energy redistribution then leads to rotation about the bond, resulting in isomerization.

(3) Finally, electronic de-excitation at an avoided crossing (near a conical intersection) restores the molecule to the electronic ground state.

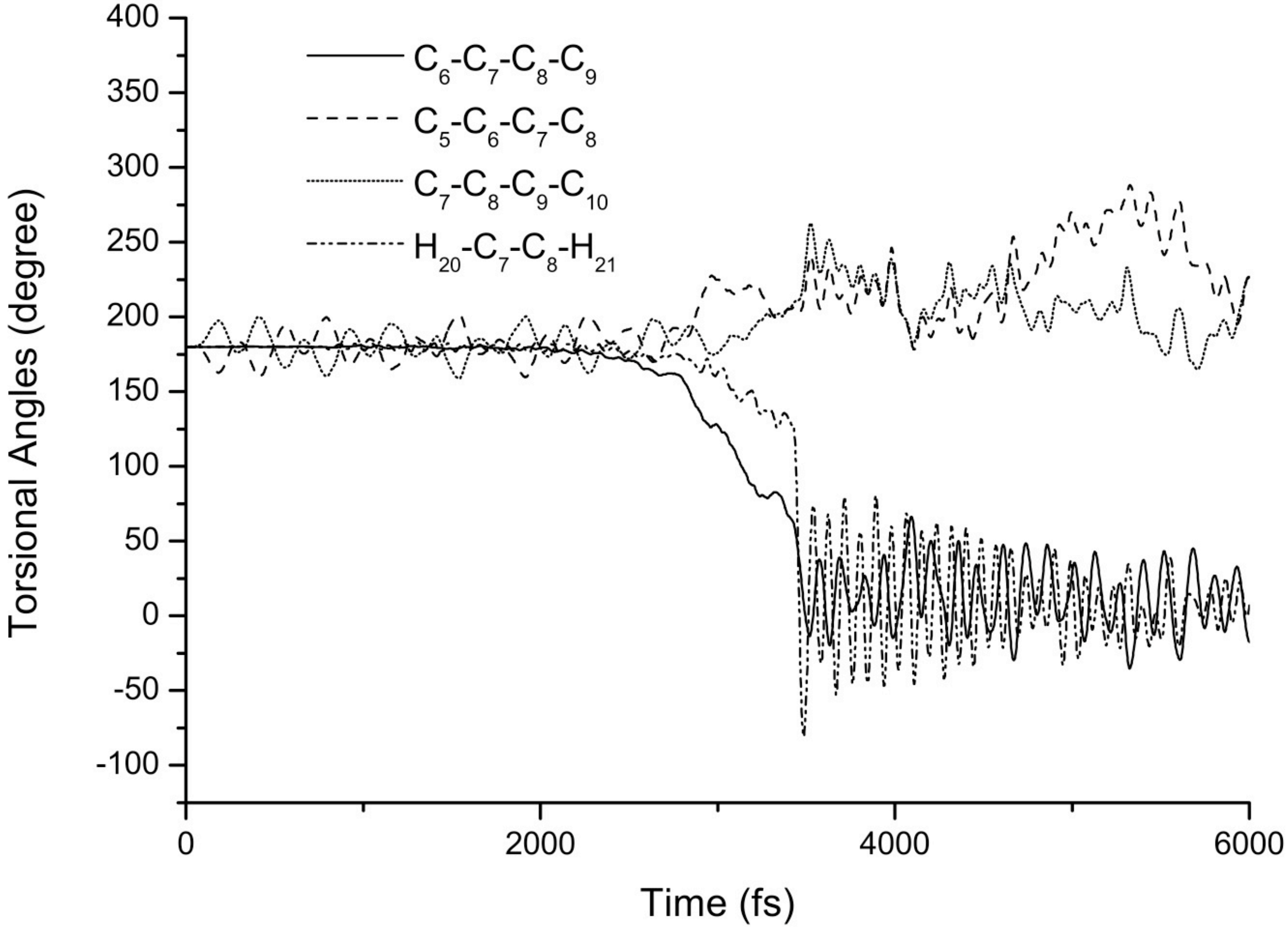
These dynamical simulations demonstrate complexity in the details, and reveal supporting roles for other degrees of freedom, such as torsional motion about the C-C side bonds.



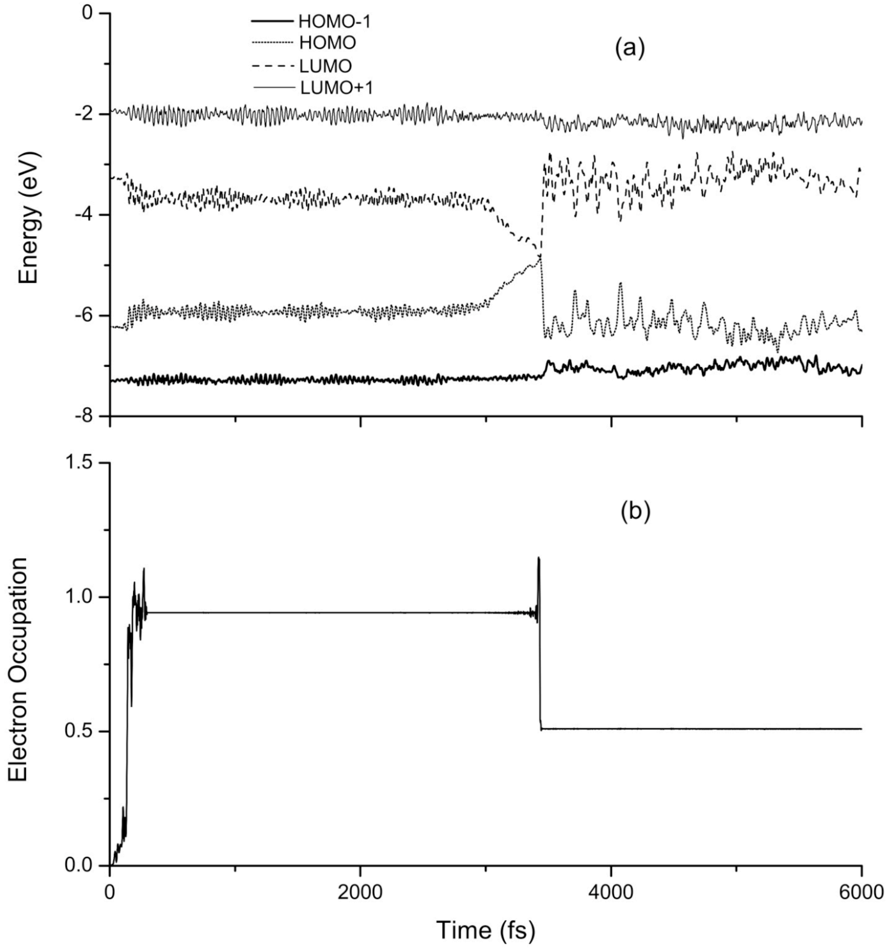
(a) (b)

After about 2800 femtoseconds, vibrational energy is redistributed from stretching of the central C-C bond to rotation around this bond.

The other relevant rotations involved in isomerization are excited at the same time.

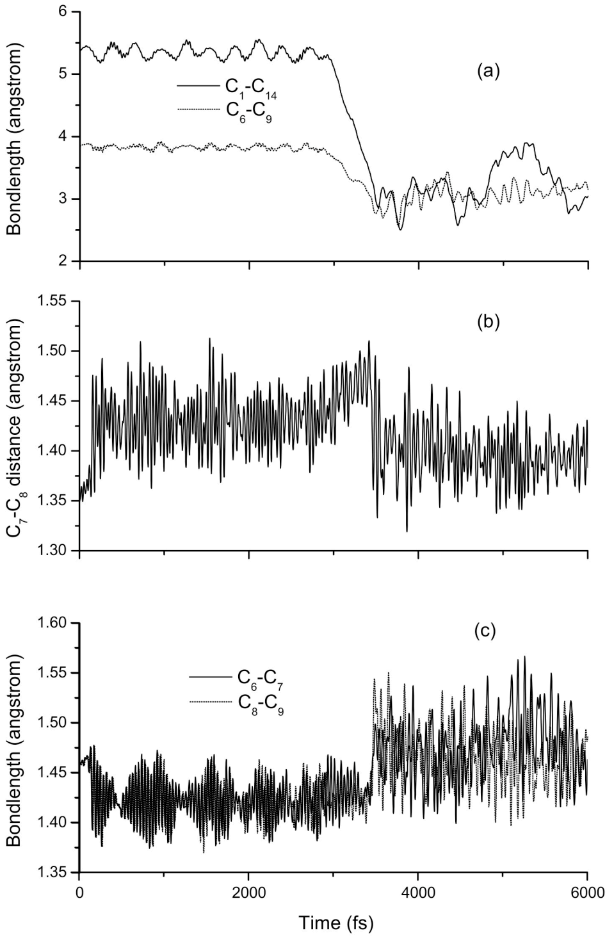


At an avoided crossing, electronic transitions automatically occur, with a transfer of electron population from the lowest initially unoccupied molecular orbital (LUMO) to the highest initially occupied molecular orbital (HOMO). This stabilizes the new structure.

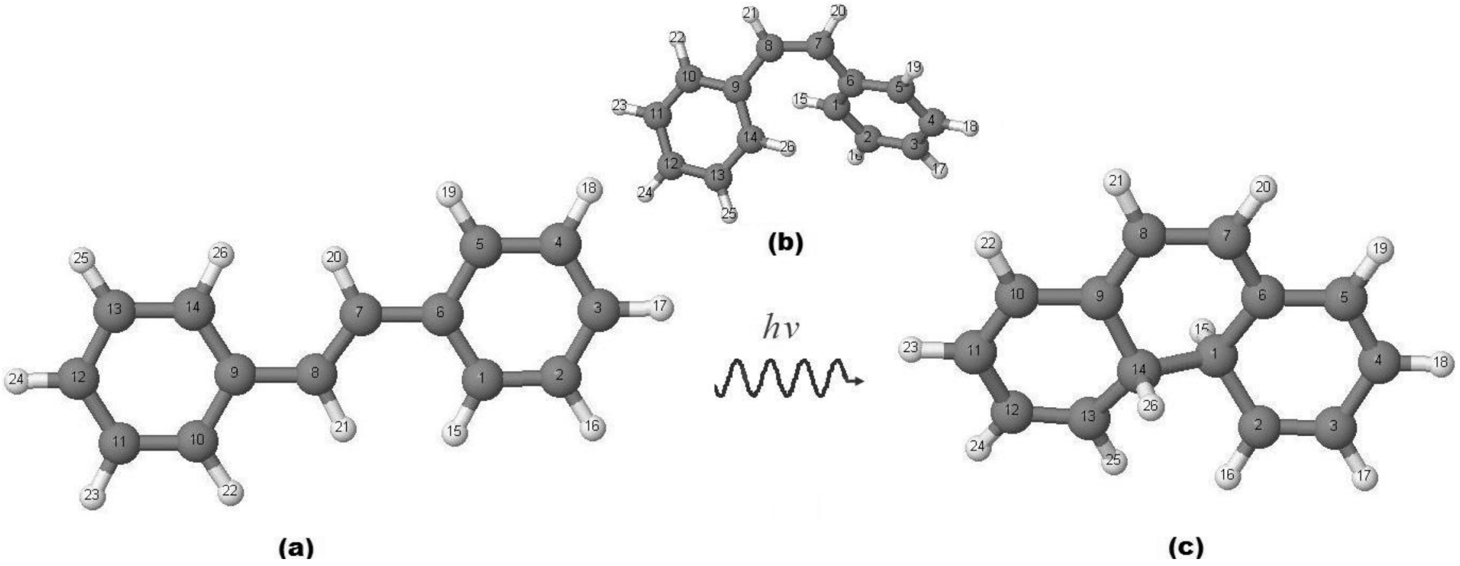


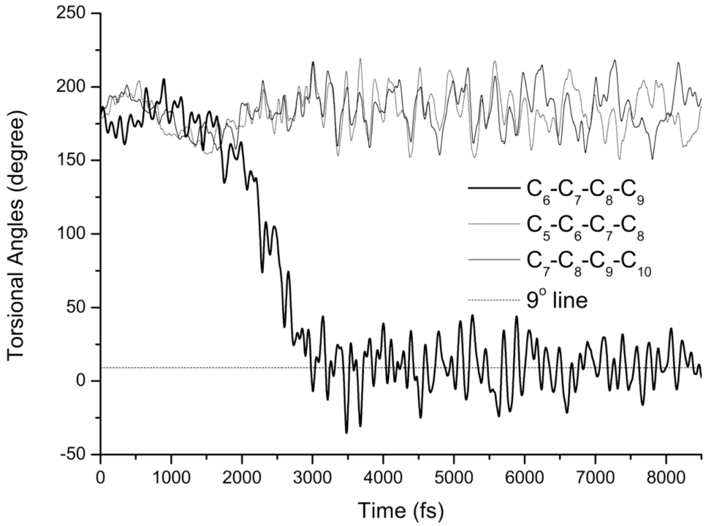
The distances between side-ring carbon atoms decrease, again demonstrating isomerization.

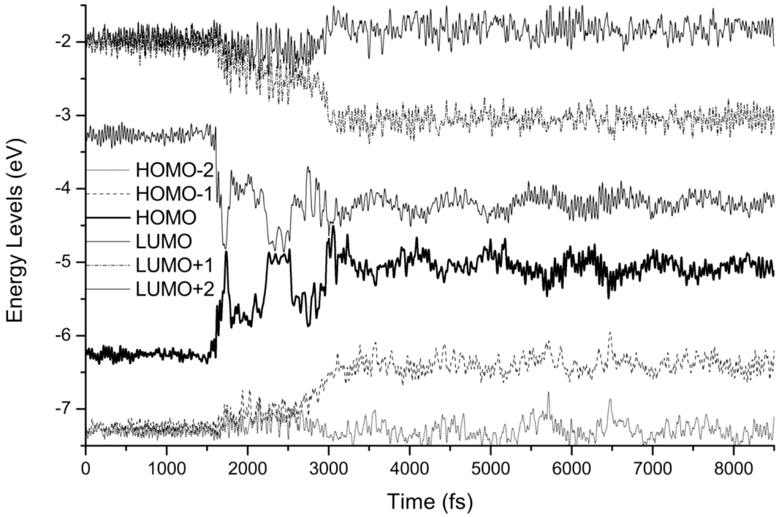
In addition, the central C-C bond is restored to an effective double bond (which is shorter and stronger) while the side-ring C-C bonds are also restored to their original length.



Chenwei Jiang again: photocyclization (ring closing) of trans-stilbene







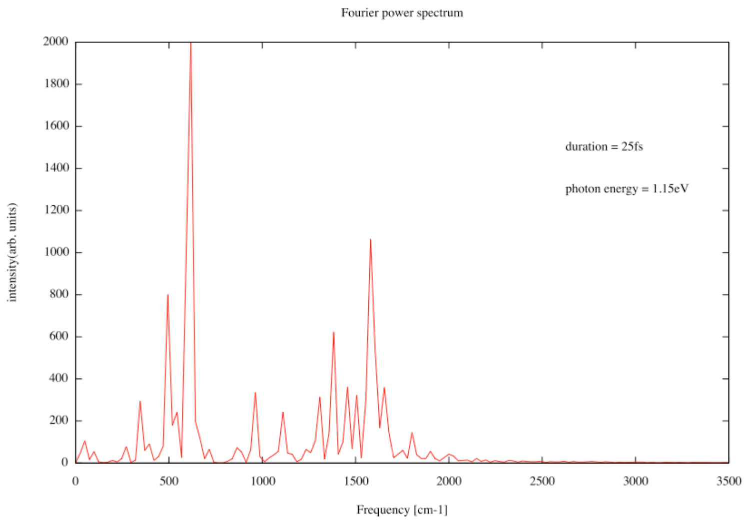
The rotation and bond formation are completed in 3 picoseconds.

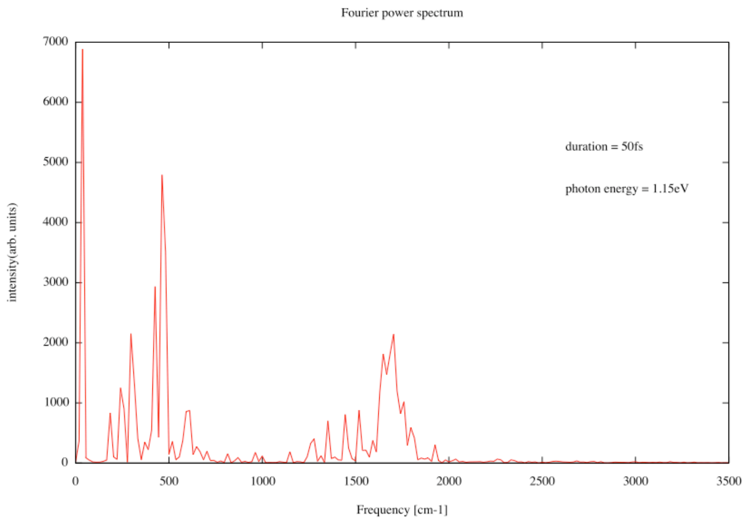
Again, at avoided crossings there are downward electronic transitions.

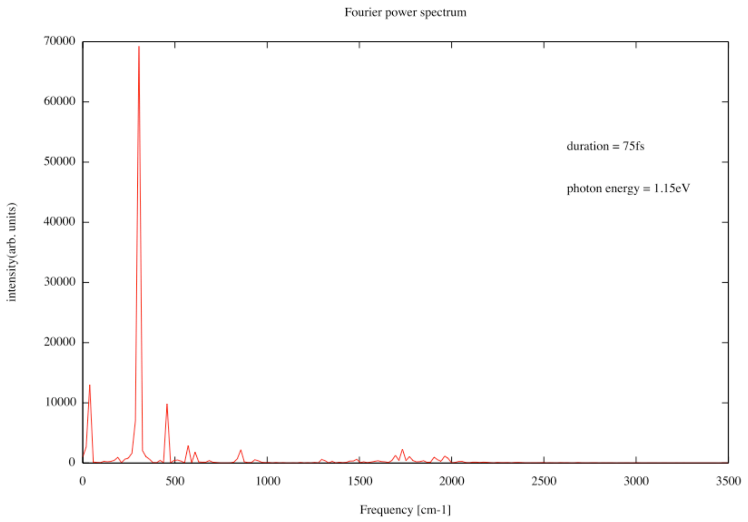
Calculation by Dr. Xiang Zhou of the vibrational response of a carbon nanotube to laser pulses with different durations (full width at half maximum): 25, 50, 75, 100 femtoseconds.

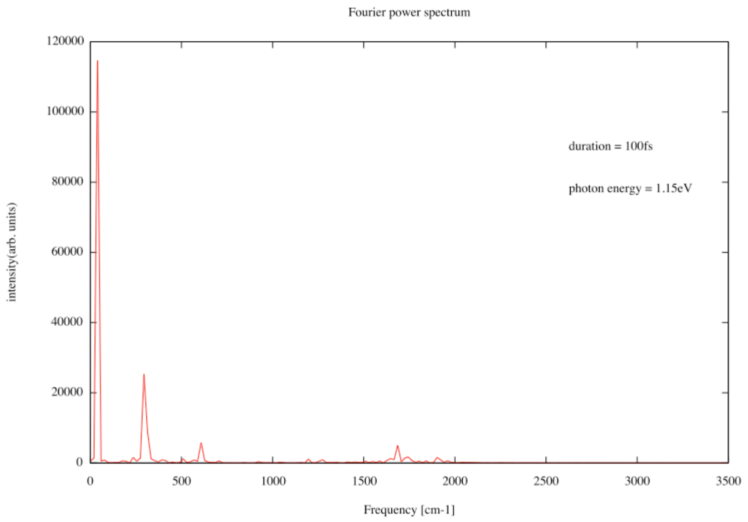
In each case, the photon energy is matched to the energy of the lowest excited state.

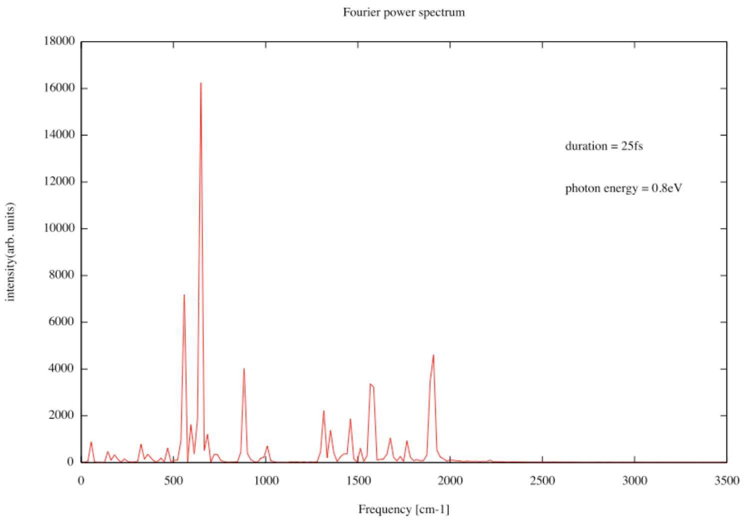
Note that a factor-of-4 increase in the pulse duration produces a factor-of-1000 increase in the excitation of the lowest frequency "radial breathing" mode.

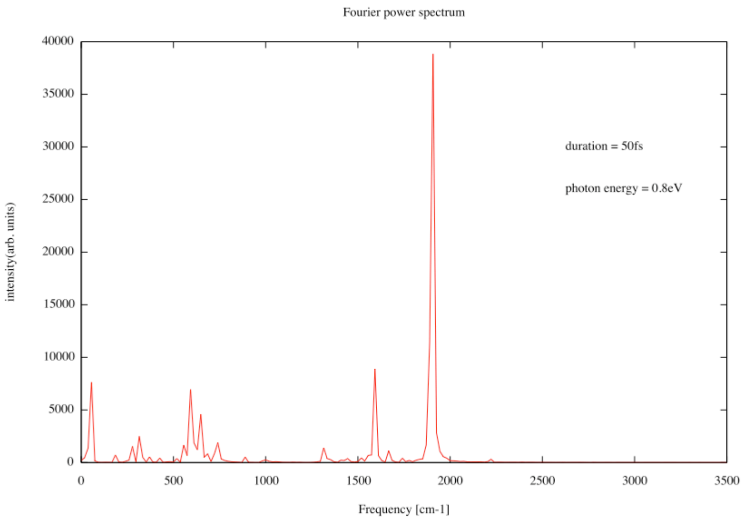


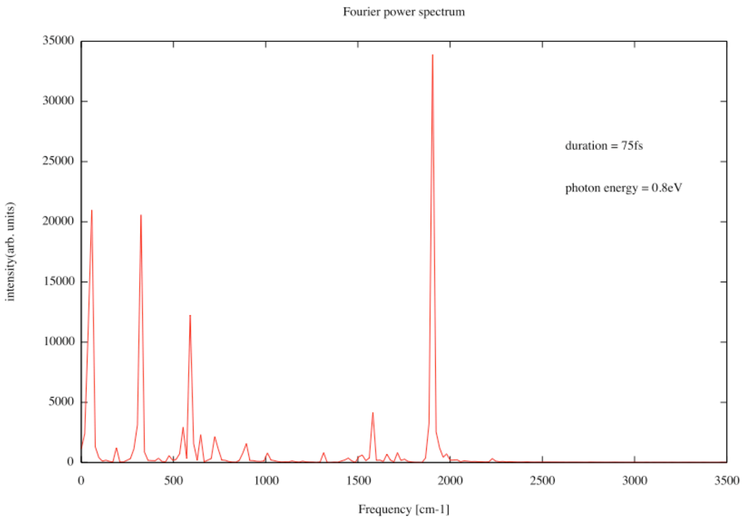


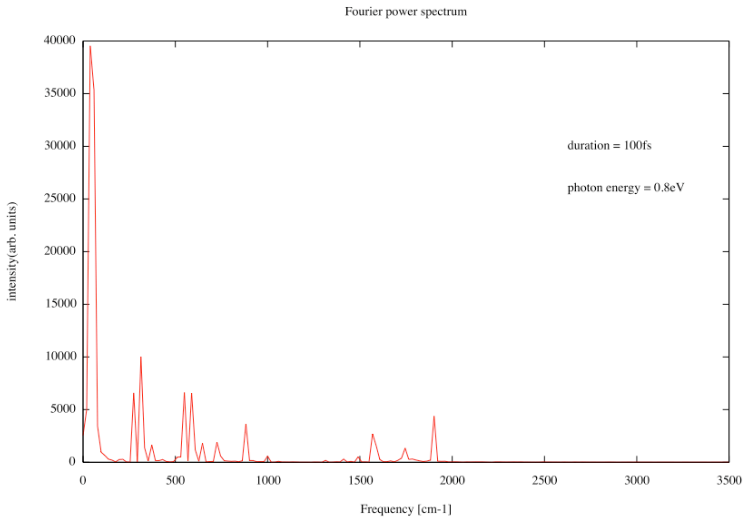












A remarkable fact: For a photon energy *out of resonance* with the excitation energy, there is still an enormous enhancement of the vibrational response for the lowest-frequency mode when the duration is changed from 25 to 100 femtoseconds.

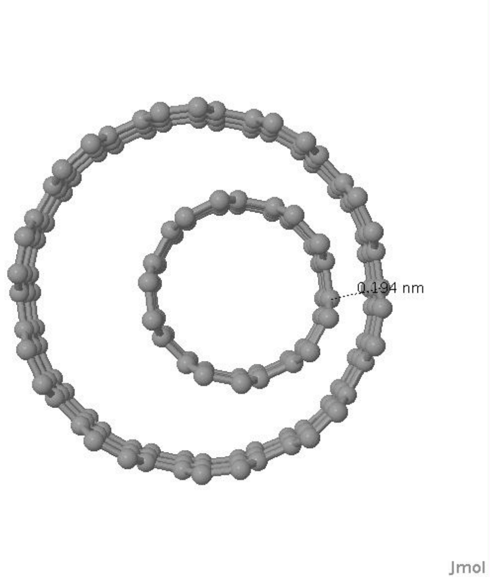
Since there is little electronic excitation in this case, the vibrations must be induced by transient oscillations of the electrons during application of the laser pulse.

All these results are relevant to laser control at the nanoscale.

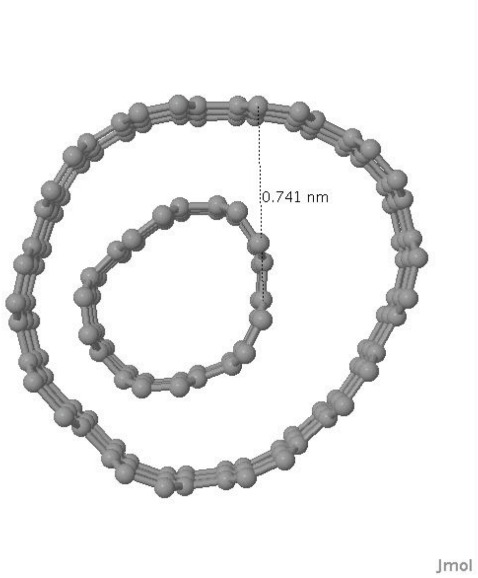
Meng Gao: Outer wall set rotating in double-wall nanotube (with period of 1 picosecond).

Simulations of this kind will help to understand various potential applications.

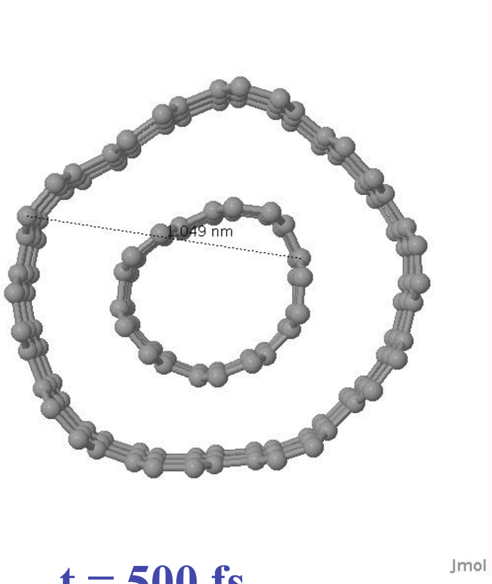
One lesson from all these simulations:
The perfect symmetries that one often imagines do not really occur in nature.



t = 0

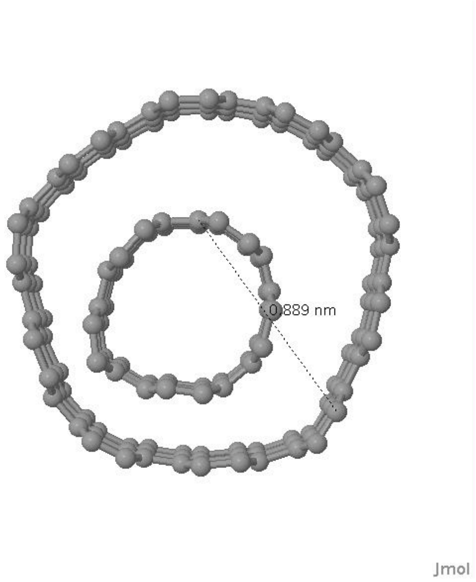


t = 250 fs



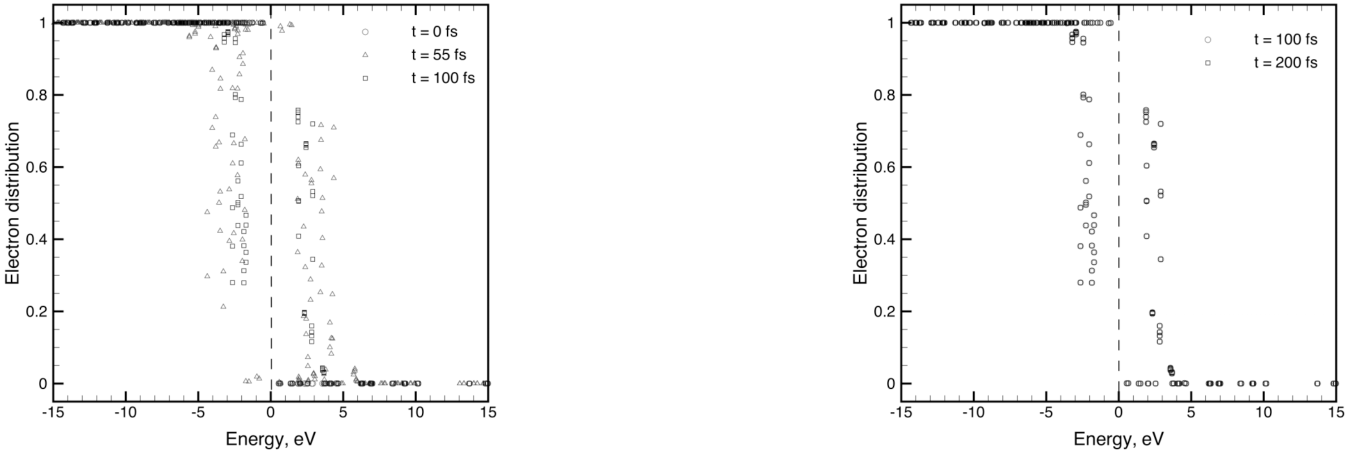
t = 500 fs

t = 750 fs

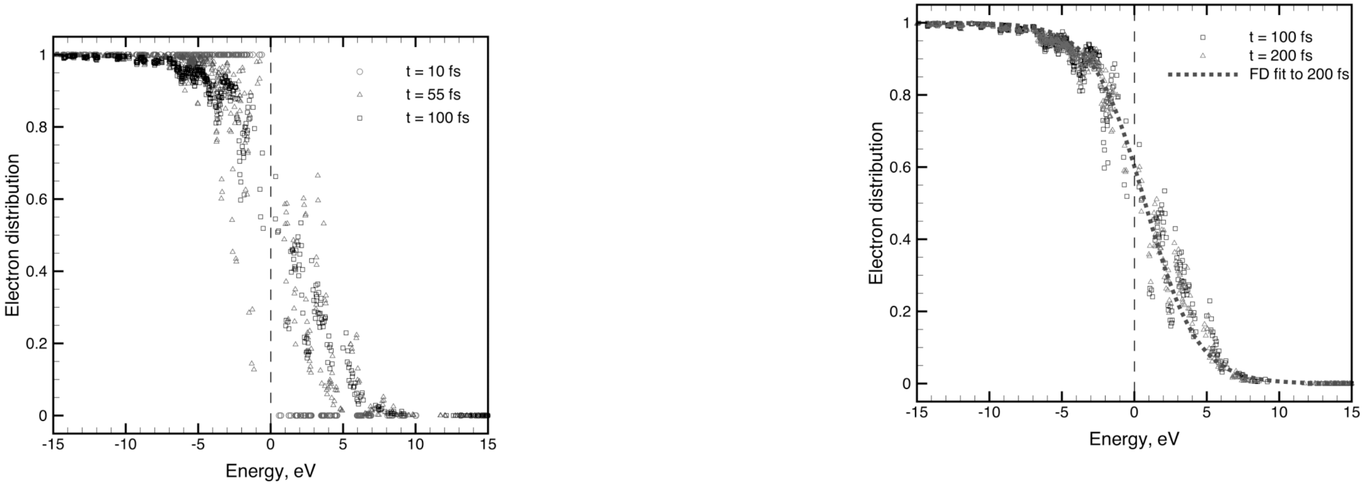


t = 1000 fs

Dr. Zhibin Lin has made a remarkable discovery: **In our technique, electrons equilibrate with each other in about 100 femtoseconds, because they are coupled to the nuclear motion – even though the electronic temperature is one or two orders of magnitude higher than the temperature associated with the nuclear motion. This means the description is physically correct, and also justifies a 2-temperature model for simulations on larger scales.**



Results shown are for 2-layer graphene: With nuclei frozen, electrons fail to equilibrate.



With nuclei permitted to move, electrons equilibrate and form up into a Fermi-Dirac distribution.

How the simulations are performed: ion and electron dynamics

Coupled dynamics of electrons and ions in matter subjected to an intense laser pulse

(1) Generalized Ehrenfest theorem for ion dynamics:

$$M\ddot{X} = -\sum_j \mathbf{\Psi}_j^\dagger \cdot \frac{\partial \mathrm{H}}{\partial X} \cdot \mathbf{\Psi}_j - \frac{\partial U}{\partial X} \tag{1}$$

(2) Time-dependent self-consistent field picture for electron dynamics:

$$i\hbar\partial\mathbf{\Psi}_j/\partial t = \mathbf{H}(t) \cdot \mathbf{\Psi}_j \tag{2}$$

How the simulations are performed: coupling of electrons to laser pulse

(3) Time-dependent Peierls substitution for coupling of electrons to radiation field:

$$H_{\alpha\beta}(l,l') = H^0_{\alpha\beta}(l,l')\ exp(\frac{ie}{\hbar c}\mathbf{A}\cdot(\mathbf{R}_l - \mathbf{R}_{l'})) \tag{3}$$

where $\mathbf{R}_l$ = position of lth ion and α labels orbital

(4) Cayley algorithm for electron dynamics:

$$\mathbf{\Psi}_j(t+\Delta t) = (\mathbf{1} + i\mathbf{H}\Delta t/2\hbar)^{-1}\cdot(\mathbf{1} - i\mathbf{H}\Delta t/2\hbar)\cdot\mathbf{\Psi}_j(t) \tag{4}$$

Semiclassical Electron-Radiation-Ion Dynamics (SERID)

Original approximations (with several now being relaxed):

1. **The atomic nuclei are treated as positive point charges.**
2. **The treatment is nonrelativistic.**
3. **The nuclear motion is treated classically.**
4. **The radiation field is treated classically.**
5. **The electrons are treated in a time-dependent mean-field picture, with many-body effects neglected.**
6. **Only the valence electrons are treated, with the inner electrons plus nucleus represented as an inert core.**
7. **The basis functions are atomic orbitals.**
8. **The spin-orbit interaction, exchange interaction, and other spin-dependent interactions are neglected.**
9. **The calculations are not explicitly self-consistent,and there is no explicit Coulomb repulsion.**
10. **The Hamiltonian matrix elements and core-core repulsion are determined from calculations involving pairs of atoms.**
11. **The Peierls substitution is used to couple the electrons to the radiation field.**
12. **The influence of a larger environment is not included.**

Note that, even with approximations 3 and 4, one still observes “n-photon” and “n-phonon” absorption and stimulated emission processes.

Broad Context

- **The response of matter to fast intense laser pulses is still a current frontier of science.**
- **New discoveries often result from the ability to explore a new regime. Here one is exploring short time scales (below one hundred femtoseconds), high radiation intensities (above one terawatt/cm^2), and complex systems (with many atoms).**
- **The standard approximations of theoretical physics and chemistry break down under these conditions, and both electrons and ions exhibit new kinds of behavior.**
- **Computer simulations show processes in microscopic detail, and reveal properties that are experimentally inaccessible.**

Simple approximations are valid only for simple systems. To understand more general phenomena, we need (supercomputing) calculations which transcend conventional approximations.