Toward **molecular switches and biochemical detectors employing adaptive femtosecond-scale laser pulses**

Petra Sauer and Roland E. Allen, Institute for Quantum Studies and Physics Department, Texas A&M University

- **Cis to trans (and trans to cis) photoisomerization of azobenzene**, with nuclear motion allowing extra electronic transitions for pulse durations > about 50 fs

- **Photoinduced ring-opening (and ring-closing) in a model dithienylethene**

- **Response of dipicolinic acid to femtosecond-scale laser pulses**, including excited states and nuclear motion (with Yuri Rostovtsev)
Representative applications: azobenzene

### Holographic data storage

**Peptide oligomers for holographic data storage**

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

Rolf Nylund Laboratory, DK-3000 Aarhus, Denmark

Several classes of organic materials, such as azobenzene-based liquid-crystal polymers and photochromic polymers, 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 reliable holographic data storage applications. The feasibility of our approach is based on the structural properties of peptide-like molecules, which allow for all-optical control of the chromophores, and thereby optimization of the optical properties of the recording medium. Here, we show that holographic recording with large first-order diffraction efficiencies up to 50% can be written and erased optically in oligomer films without the use of micromirrors. The holograms also exhibit good thermal stability, and are erased after heating to 100°C for one minute. Straightforward extension of this peptide-based strategy to other molecular structures should optimize the design and fabrication of a wide range of optical materials with potentially useful optical properties.

**Nature** - Vol. 363 - 10 October 1993

### Light-driven molecular switch

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

C. Zhang, †M.-H. Du, ‡H.-P. Cheng, ‡X.-G. Zhang, †A. E. Rubloff, † and J. L. Reinecke

†Department of Physics and Quantum Theory Project, University of Florida, Gainesville, Florida 32611, USA
‡Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6772, USA

May 31, 2000

We apply a first-principles approach to study a light-responsive molecular switch. The molecule comprises the switch, which can convert between a home and an off configuration upon photoexcitation. We find that the relaxation dynamics of the molecule are such that the system has potential applications as a molecular device. A detailed analysis of the overtone structure of the excited states 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 "low-mode" storage technique (in which only the thermal energy of lower light is used in the recording process and hence information is stored as a physical change of the storage media that are used in current optical technology) has been limited by the distinct properties of light, and the alternative "photonic" (in which information is stored in a photo-induced electrical change of the storage media) has attracted attention recently for high-density storage. The most promising candidates for realizing this mode seem to be photocatalysts and photovoltaic cells, but these have some inherent drawbacks. Here we present a novel "photonic" technique that uses the photochemical properties of a Langmuir-Blodgett film as an actuating mechanism. The method can be interconvertible photochemically or electrochemically between three chemical states, and this three-state system is shown to provide a potential storage mechanism that allows for high-density storage capacity, remote-function memory and non-destructive information readout.

**Nature** - Vol. 347 - 18 October 1990

### Liquid Crystal Display

**Optical Switching and Image Storage by Means of Liquid Crystals**

Tomoko Ikeda & Jiro Fujisawa

Department of Physics and Quantum Theory Project, University of Florida, Gainesville, Florida 32611, USA

NATURE - VOL 363 - 10 October 1993

### Nanomechanical Device

**Single-Molecule Optomechanical Device**

Thorsten Hugel, †Nobu Takahashi, †Anna Cattani, †Luis Moroder, †Markus Seitz, †Harmann E. Gaub

†ETH Zurich, Institute of Nanoscience and Technology, Zurich, Switzerland

May 31, 2000

Light-powered molecular machines are conjectured to be essential constituents of future nanoelectromechanical systems. As a model for such systems, we have synthesized a polymer of bistable photoreactive azobenzene molecules. 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 Photoreponsive Surface**

Kunihiko Ichimura, †Sang-Keun Oh, Masaru Nakagawa

†Department of Physics and Quantum Theory Project, University of Florida, Gainesville, Florida 32611, USA

NATURE - Vol. 363 - 10 October 1993

The precise control 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 proteins. We describe a general approach for manipulating allosteric control using optical switches. Our strategy is compiled by a light-controlled allosteric switch to control the activity of a protein. The allosteric interaction is illustrated with a montage of proteins containing a light-activated switch. The enzyme is an aldolase, the allosteric switch is a single-molecule allosteric control using optical switches. The optical control is achieved by the use of a photoresponsive surface that can be used to control the activity of an enzyme without the need for an external optical input. The system is an example of how allosteric control can be achieved in a simple and general manner.
One major result from these simulations -- we find that photochemical reactions involve:

» **multiple steps**
(e.g., first $S_0 \rightarrow S_1$, and subsequently $S_0 \rightarrow S_2$ because nuclei move, or first $S_2 \rightarrow S_1$ and then $S_1 \rightarrow S_0$ for later de-excitation of the molecule)

» **multiple excitations**
(e.g., linear combination of $S_0$, $S_1$, $S_2$, $S_3$)

» **multiple configuration coordinates**
(e.g., rotational dihedral angle *and* length of central bond)

In the present picture, with configuration interaction neglected,  

**$S_0$ is the ground state**  

**$S_1$ is the excitation of one electron from HOMO to LUMO**  
(highest occupied molecular orbital to lowest unoccupied molecular orbital)  

**$S_2$ is the excitation of one electron from HOMO-1 to LUMO**  
(from next-to-highest occupied molecular orbital)  

**$S_3$ is the excitation of two electrons from HOMO to LUMO**
We call our technique **semiclassical electron-radiation-ion dynamics (SERID)** to emphasize the limiting approximations:

The radiation field and nuclear motion are both treated classically, and the ion cores are regarded as inert (with only the valence electrons included in the dynamics).

Recall, however, that one still observes “n-photon” and “n-phonon” processes in a semiclassical treatment. Also, the nuclear motion is treated correctly on reasonably short time scales (e.g., picoseconds).

List of approximations in present calculations:
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 density-functional 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.
Coupled dynamics of electrons and ions in matter subjected to an intense laser pulse

(1) Generalized Ehrenfest theorem for ion dynamics:

\[
M \ddot{X} = - \sum_j \Psi_j^\dagger \cdot \frac{\partial H}{\partial X} \cdot \Psi_j - \frac{\partial U}{\partial X}
\]  

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

\[
i\hbar \frac{\partial \Psi_j}{\partial t} = H(t) \cdot \Psi_j
\]

Density-functional-based parameterization of the electronic Hamiltonian \(H\) and the effective repulsive potential \(U\):

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

\[ H_{\alpha\beta}(l, l') = H_{\alpha\beta}^0(l, l') \exp \left( \frac{ie}{\hbar c} A \cdot (R_l - R_{l'}) \right) \]  \hspace{1cm} (3)

where \( R_l \) = position of \( l \)th ion and \( \alpha \) labels orbital

(4) Cayley algorithm for electron dynamics:

\[ \Psi_j(t + \Delta t) = (1 + iH\Delta t/2\hbar)^{-1} \cdot (1 - iH\Delta t/2\hbar) \cdot \Psi_j(t) \]  \hspace{1cm} (4)
Ehrenfest's theorem states that

\[ M \frac{d^2 \hat{X}}{dt^2} = -\frac{\partial \mathcal{H}}{\partial \hat{X}} \]

where \( \hat{X} \) is the operator corresponding to any nuclear coordinate, \( M \) is the corresponding mass, and \( \mathcal{H} \) is the full Hamiltonian for all particles in the molecule. If the electrons are treated in a time-dependent self-consistent field picture, and the one-electron wavefunctions are represented in terms of localized basis functions, one obtains

\[ M \frac{d^2 \hat{X}}{dt^2} = -\sum_j \bar{\psi}_j^+ (t) \cdot \frac{\partial \mathcal{H}(t)}{\partial \hat{X}} \cdot \bar{\psi}_j (t) - \frac{\partial U_{rep}}{\partial \hat{X}}. \]

Since quantum fluctuations, in the present context, are typically smaller than 0.05 Å for C and smaller than 0.10 Å even for H, it is a reasonable approximation to expand in a Taylor series about the expectation value:

\[ \frac{\partial \mathcal{H}(t)}{\partial \hat{X}} = \left[ \frac{\partial \mathcal{H}(t)}{\partial \hat{X}} \right]_{\hat{X} = \langle \hat{X} \rangle} + \left[ \frac{\partial \mathcal{H}(t)}{\partial \hat{X}} \right]_{\hat{X} = \langle \hat{X} \rangle} (\hat{X} - \langle \hat{X} \rangle) + O\left( (\hat{X} - \langle \hat{X} \rangle)^2 \right). \]

With \( X \equiv \langle \hat{X} \rangle \), and with terms that are second-order in the quantum fluctuations neglected, we then take the expectation value to obtain the equation used for the nuclear motion:

\[ M \frac{d^2 X}{dt^2} = -\sum_j \bar{\psi}_j^+ (t) \cdot \frac{\partial \mathcal{H}(t)}{\partial X} \cdot \bar{\psi}_j (t) - \frac{\partial U_{rep}}{\partial X}. \]
photoisomerization of azobenzene

\[ \Delta E_{\text{cis to trans}} \approx 0.50 \text{ eV} \]

\[ E(TS) \approx 1.00 \text{ eV} \]
What is already known about the isomerization process:

- Photoisomerization quantum yields for $S_1$ >> than for $S_2$ [P. Bortolus and S. Monti, J. Phys. Chem. 83, 648 (1979)].
- Dominant isomerization product from cis state forms within 170 fs, and from trans state within 320 fs [T. Naegele et al., Chem. Phys. Lett. 272, 489 (1997)].
- First configuration interaction calculations indicated an “inversion pathway” for $S_1$ excitation (which involves opening a CNN bond angle, with planar motion) and a “rotation pathway” for $S_2$ excitation (which involves rotation through the central CNNC dihedral angle) [S. Monti et al, Chem. Phys. 71, 87 (1982)].
- Later calculations suggest that “rotation pathway” is most probable mechanism for both [T. Ishikawa et al, J. Chem Phys. 115, 7503 (2001)].
SERID calculated molecular orbital structure

CIS

TRANS
SERID results for $S_1$ excitation: electron dynamics during excitation

Prepare state with an ultrashort 10 fs (FWHM) pulse, so that ion core motion during excitation is minimal, and transition is thus predominantly HOMO to LUMO.

laser pulse duration (FWHM) = 10 fs, photon energy = 3.55 eV, fluence = 0.28 kJ/m$^2$, $T = 0$ K
Electron dynamics following HOMO to LUMO excitation

Between ~ 50 and 100 fs, a series of avoided crossings leads to the transfer of ~ 0.6 electrons downward from LUMO to HOMO.
The SERID simulations indicate rotational pathway rather than inversion pathway for $S_1$ excitation.
SERID results for $S_2$ excitation: electron dynamics during excitation

Prepare excited state with an ultrashort 10 fs (FWHM) pulse, so that nuclear motion during excitation is minimal, and transition is predominantly HOMO-1 to LUMO.

laser pulse duration (FWHM) = 10 fs, photon energy = 4.18 eV, fluence = 0.15 kJ/m$^2$, T = 0 K
Electron dynamics following HOMO-1 to LUMO excitation

At about 780 fs, a HOMO-1/HOMO avoided crossing leads to a transfer of roughly 0.60 holes up from the HOMO-1 into the HOMO. A subsequent HOMO/LUMO avoided crossing at about 900 fs then transfers ~ 0.7 electrons down from the LUMO into the HOMO.
SERID results for $S_2$ excitation: nuclear dynamics

The SERID simulations indicate rotational mechanism for $S_2$ excitation, occurring in the excited state, followed by return to the ground state.
Excitation with 100 fs (FWHM) pulse: electron dynamics during excitation

Longer pulse initially excites electrons from HOMO to LUMO. As nuclei move, electrons are excited from HOMO-1 to LUMO.

laser pulse duration (FWHM) = 100 fs, photon energy = 3.55 eV, fluence = 0.47 kJ/m², T = 0K
Excitation with 100 fs (FWHM) pulse: nuclear dynamics during excitation
Excitation with 100 fs (FWHM) pulse: electron dynamics after excitation

At about 260 fs, an avoided crossing between HOMO-1 and HOMO leads to a transfer of roughly 0.70 holes up into the HOMO. A subsequent series of HOMO-LUMO avoided crossings, between 340 fs and 550 fs, transfer ~ 0.3 electrons down into the HOMO.
Excitation with 100 fs (FWHM) pulse: nuclear dynamics after excitation

Depopulation of the excited states occurs as the isomerization proceeds along a rotational pathway.
Summary for azobenzene isomerization

- An ultrashort 10 fs (FWHM) pulse matched to the HOMO-LUMO energy gap excites electrons from HOMO to LUMO. Isomerization proceeds along a rotational pathway. An avoided crossing between HOMO and LUMO, approximately halfway between cis and trans geometries, transfers the electronic population back into the ground state.

- An ultrashort 10 fs (FWHM) pulse, matched to the HOMO-1 to LUMO energy gap, excites electrons predominantly from HOMO-1 to LUMO. Isomerization again proceeds along a rotational pathway. An avoided crossing between HOMO-1 and HOMO near the trans configuration transfers hole population from HOMO-1 to HOMO. A later avoided crossing between HOMO and LUMO transfers electrons to the HOMO.

- A longer 100 fs (FWHM) laser pulse matched to the HOMO-LUMO energy gap excites electrons from both HOMO-1 and HOMO into the LUMO. The second excitation is due to nuclear motion during pulse excitation. An avoided crossing between HOMO-1 and HOMO near the cis configuration transfers hole population from HOMO-1 to HOMO. A subsequent HOMO-LUMO avoided crossing halfway between cis and trans configurations transfers electron population back into the ground state.
Lower fluence $\rightarrow$ no isomerization: electron dynamics

No HOMO-1/HOMO avoided crossing $\Rightarrow$ no transfer of holes from HOMO-1 to HOMO. Then high occupancy of HOMO $\Rightarrow$ no transfer of electrons from LUMO to HOMO, despite HOMO/LUMO avoided crossings.
Lower fluence → no isomerization: nuclear dynamics

Similar behavior as with more intense laser pulse, except amplitude of oscillations not as large. Molecule never reaches geometry required for HOMO-1/HOMO avoided crossing.
The dithienylethene model system consists of both closed and open forms. Both forms have $C_2$ symmetry. The barrier height is much larger than the open-closed energy difference.

Both forms can be interconverted under visible light or UV light.
SERID calculated molecular orbital structure

$\Delta E_g = 1.53 \text{ eV}$

$\Delta E_g = 3.14 \text{ eV}$
Electron dynamics during excitation

Initial excitation is from HOMO into LUMO. Nuclear motion subsequently permits additional excitations out of HOMO-1 and into LUMO+1.

**orbital population**

**orbital energy**

pulse duration (FWHM) = 150 fs,
\( \hbar \omega = 1.8 \text{ eV}, \quad F = 0.44 \text{ kJ/m}^2, \quad T = 300 \text{ K} \)
Nuclear dynamics during excitation

- C\textsubscript{c}-C\textsubscript{c} bond length
- C\textsubscript{a}-C\textsubscript{a} bond length
- C\textsubscript{b}-C\textsubscript{a}-C\textsubscript{a}-C\textsubscript{b} angle
- C\textsubscript{a}-C\textsubscript{b} bond length
Electron dynamics leading to bond breakage

At ~ 785 fs: electron transfer from LUMO+1 to LUMO

At ~ 960 fs: hole transfer from HOMO-1 to HOMO and electron transfer from LUMO+1 to LUMO
Electron dynamics following bond breakage

Between ~ 1 ps and 4 ps, a series of avoided crossings between HOMO and LUMO return molecule to the ground state.
Nuclear dynamics following excitation

**$C_c - C_c$ bond length**

**$C_b - C_a - C_a - C_b$ angle**

Bond breaks at ~ 1 ps

Ring opening, followed by rotation about central dihedral angle, until molecule returns to ground state at ~ 4 ps.
Nuclear dynamics following excitation (continued)

**$C_a-C_a$ bond length**

- Tendency toward double bond after final HOMO-LUMO exchange of electron occupancy

**$C_a-C_b$ bond length**

- Tendency toward single bond after final HOMO-LUMO exchange
Summary of ring-opening mechanism

- Laser pulse, matched to the HOMO-LUMO energy difference, initially excites electrons from HOMO to LUMO.

- Nuclear motion subsequently permits excitations out of HOMO-1 and into LUMO+1.

- After laser pulse excitation, an avoided crossing between HOMO-1 and HOMO transfers holes into the HOMO. An avoided crossing between LUMO+1 and LUMO transfers electrons into LUMO.

- Following these population transfers, ring-opening occurs at ~ 1 ps.

- A series of HOMO-LUMO avoided crossings, which occur between ~ 1ps and 4 ps, transfer electronic population back to the ground state.
dipicolinic acid (DPA): electronic and vibrational response
Overview of the parameterization scheme
for nitrogen and oxygen

We scale the density-functional-based hydrogen and carbon pairwise interactions to include interactions with nitrogen and oxygen.

Parameterization scheme consists of two parts:

I. Electronic Properties

Diagonal Hamiltonian matrix elements ($H_{ii}$) scaled to the s and p atomic energies of the new atom

Diagonal elements of the overlap matrix ($S_{ii}$) unchanged (equal to 1)

Off-diagonal elements of the Hamiltonian scaled so that the energy eigenvalue difference of the active space region equals the energy difference calculated using DFT. The off-diagonal elements of the overlap matrix are left unchanged.

II. Structural Properties

The repulsive potential is scaled to match the structural properties (i.e. bond lengths and vibrational frequencies) of the diatomic molecule corresponding to a given pairwise interaction.
Parameterization scheme: electronic properties

Schematic illustration for parameterizing nitrogen-nitrogen interactions starting with carbon-carbon interactions:

\[ C_2 (N_2) \]

\[ H_{ij} = \langle i | H | j \rangle \quad \text{and} \quad S_{ij} = \langle i | j \rangle \]

Eigenvalues of \( \vec{H} \cdot \vec{\psi} = \varepsilon \vec{S} \cdot \vec{\psi} \)
Parameterization scheme: structural properties

We then scale the effective nuclear repulsive potential:

\[ V_{\text{new}}(r_{\text{new}}) = (c_0 + c_1 r)V_{\text{old}}(r_{\text{old}}) . \]

The constants \(c_0\) and \(c_1\) are determined from the equilibrium conditions

\[ \left( \frac{dE_{\text{rep}}}{dr} + \frac{dE_{\text{elec}}}{dr} \right)_{r=r_0} = 0 \quad \text{and} \quad \left( \frac{d^2E_{\text{rep}}}{dr^2} + \frac{d^2E_{\text{elec}}}{dr^2} \right)_{r=r_0} = M \omega^2 \]

where the derivatives of the electronic energy are determined numerically from the scaled Hamiltonian and the overlap matrix:

\[ \frac{\partial E_{\text{elec}}}{\partial x} = \sum_n \Psi_n^\dagger \left( \frac{\partial H}{\partial x} - \varepsilon_n \frac{\partial S}{\partial x} \right) \Psi_n f(n) \]

\[ \frac{\partial^2 E_{\text{elec}}}{\partial x^2} = 2 \sum_n \sum_{m \neq n, \varepsilon_m \neq \varepsilon_n} \left| \Psi_n^\dagger \left( \frac{\partial H}{\partial x} - \varepsilon_n \frac{\partial S}{\partial x} \right) \Psi_m \right|^2 f(n) + \sum_n \Psi_n^\dagger \left( \frac{\partial^2 H}{\partial x^2} - 2 \frac{\partial \varepsilon_n}{\partial x} \frac{\partial S}{\partial x} - \varepsilon_n \frac{\partial^2 S}{\partial x^2} \right) \Psi_n f(n) \]
### Results of the parameterization for various diatomics

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<th>Property</th>
<th>Exp.</th>
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In all cases the experimental bond lengths and frequencies were taken from the CRC Handbook of Chem. and Phys. (2004) online, the binding energies from Herzberg, *Spectra of Diatomic Molecules* (1989) and the excitation energies from a B3LYP//aug-cc-pVQZ calculation, except for the hydride bond lengths, which were taken from Sun et al, *J. Chem Phys.* 74, 6842 (1981), and the excitation energy of N2, which was calculated without diffuse functions.
Parameterization applied to the equilibrium states of the azabenzences

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<th>SERID (Å)</th>
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<td>C-H</td>
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Parameterization applied to the equilibrium states of various oxygen-containing molecules

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<tr>
<th>Molecule</th>
<th>Bond</th>
<th>SERID (Å)</th>
<th>Exp. (Å)</th>
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<td>Acetaldehyde$^1$</td>
<td>C$_b$-O</td>
<td>1.208</td>
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</tr>
<tr>
<td></td>
<td>C$_a$-C$_b$</td>
<td>1.520</td>
<td>1.501</td>
</tr>
<tr>
<td></td>
<td>C$_a$-H</td>
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<td>1.114</td>
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<td></td>
<td>C$_b$-H</td>
<td>1.097</td>
<td>1.086</td>
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<td>C-H</td>
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<td>O$_a$-H</td>
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<td>1.086</td>
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<td></td>
<td>C$_b$-H</td>
<td>1.096</td>
<td>1.090</td>
</tr>
</tbody>
</table>

$^2$ Herzberg, Spectra of Diatomic Molecules (1989)
Summary of Parameterization Scheme

➤ Hamiltonian and overlap matrix elements scaled to the electronic properties for the relevant pairwise interaction.

➤ Effective nuclear repulsion then scaled to the equilibrium bond lengths and vibrational frequencies of the diatomic molecule corresponding to the desired pairwise interaction.

➤ Parameterization scheme yields bond lengths for larger molecules that are normally within 2-3% of the experimental bond lengths (and within 5% in every case).
We obtained the equilibrium configuration of DPA through a 2000 fs simulation in which the velocity of each atom was reduced by 0.3% at each time step.
### Nuclear equilibrium properties

#### Bond lengths

<table>
<thead>
<tr>
<th>Bond</th>
<th>SERID (Å)</th>
<th>MCSCF/6-21G (Å) *</th>
</tr>
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<tr>
<td>N-C&lt;sub&gt;a&lt;/sub&gt;</td>
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<td>C&lt;sub&gt;a&lt;/sub&gt;-C&lt;sub&gt;b&lt;/sub&gt;</td>
<td>1.401</td>
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<td>C&lt;sub&gt;b&lt;/sub&gt;-C&lt;sub&gt;c&lt;/sub&gt;</td>
<td>1.394</td>
<td>1.395</td>
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<td>C&lt;sub&gt;a&lt;/sub&gt;-C&lt;sub&gt;d&lt;/sub&gt;</td>
<td>1.509</td>
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<td>C&lt;sub&gt;d&lt;/sub&gt;-O&lt;sub&gt;a&lt;/sub&gt;</td>
<td>1.260</td>
<td>1.216</td>
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<td>C&lt;sub&gt;d&lt;/sub&gt;-O&lt;sub&gt;b&lt;/sub&gt;</td>
<td>1.327</td>
<td>1.336</td>
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<tr>
<td>H&lt;sub&gt;a&lt;/sub&gt;-O&lt;sub&gt;b&lt;/sub&gt;</td>
<td>0.948</td>
<td>0.955</td>
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<td>1.096</td>
<td>1.070</td>
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<td>H&lt;sub&gt;c&lt;/sub&gt;-C&lt;sub&gt;c&lt;/sub&gt;</td>
<td>1.096</td>
<td>1.071</td>
</tr>
</tbody>
</table>

#### Key Normal Modes Excited During Laser Pulse Simulation

<table>
<thead>
<tr>
<th>Description</th>
<th>SERID (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>B3LYP/cc-pVDZ (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
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</thead>
<tbody>
<tr>
<td>Ring stretch</td>
<td>702</td>
<td>640</td>
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<tr>
<td>Ring breathe</td>
<td>1070</td>
<td>1012</td>
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<td>1625</td>
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<tr>
<td>Ring stretch</td>
<td>1738</td>
<td>1632</td>
</tr>
</tbody>
</table>

**Electronic equilibrium properties**

<table>
<thead>
<tr>
<th>Level</th>
<th>SERID (eV)</th>
<th>B3LYP/cc-pVDZ (eV)</th>
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</thead>
<tbody>
<tr>
<td>HOMO-3</td>
<td>-7.79</td>
<td>-8.42</td>
</tr>
<tr>
<td>HOMO-2</td>
<td>-7.20</td>
<td>-7.77</td>
</tr>
<tr>
<td>HOMO-1</td>
<td>-7.05</td>
<td>-7.75</td>
</tr>
<tr>
<td>HOMO</td>
<td>-6.89</td>
<td>-7.35</td>
</tr>
<tr>
<td>LUMO</td>
<td>-2.86</td>
<td>-2.01</td>
</tr>
<tr>
<td>LUMO+1</td>
<td>-2.59</td>
<td>-1.89</td>
</tr>
<tr>
<td>LUMO+2</td>
<td>-0.35</td>
<td>+0.37</td>
</tr>
<tr>
<td>LUMO+3</td>
<td>+0.99</td>
<td>+1.33</td>
</tr>
</tbody>
</table>

HOMO-2, HOMO-1, and HOMO nearly degenerate
LUMO and LUMO+1 nearly degenerate

SERID: $\Delta E_{\text{gap}} = 4.03$ eV
DPA subjected to a (010) polarized pulse matched to the HOMO-2 to LUMO+1 transition frequency

Laser Pulse Parameters:

\[ t_{\text{pulse}} \text{ (FWHM)} = 5 \text{ fs} \]
\[ A_0 = 0.13 \text{ G cm} \]
\[ E = 4.61 \text{ eV} \]
(010) polarization

\[ A(t) = A_0 \cos \left( \frac{\pi (t - t_{\text{pulse}} / 2)}{t_{\text{pulse}}} \right) \sin(\omega t) \]
Normalized frequency spectrum after completion of laser pulse

The two peaks with the largest intensity correspond to two ring breathing modes.
Absorption spectrum

Experiment

~ 270 nm

Fig. 1. Absorption spectra of 10 μM DPA in water at pH 2.0 (-----), and DPA− (----), and CaDPA in HEPES buffer at pH 7.5 (-----).


Molecular orbitals involved in transitions

\[ \pi \rightarrow \pi^* \text{ at } 231 \text{ nm (y-dipole)} \]

\[ \pi \rightarrow \pi^* \text{ at } 246 \text{ nm (x-dipole)} \]

Artificially broadened spectrum:

\[
\alpha(\omega) = \sum_{i=1}^{n} \frac{f_i \Gamma_i}{(\omega - \Omega_i)^2 - \Gamma_i^2}
\]

- \(f_i\) = oscillator strength
- \(\Omega_i\) = transition frequency
- \(\Gamma_i\) = half-width of transition
- \(n \leftrightarrow\) all transitions from filled to unfilled orbitals

\[ n \rightarrow \pi^* \text{ at } 298 \text{ nm} \]
SERID calculated transitions

Choose short pulse in order to excite a wide possible range of transitions.

\[ E = 4.03 \text{ eV} \]
\[ t_{\text{pulse}} \text{(FWHM)} = 5 \text{ fs} \]
\[ \text{polarization is (100)} \]
\[ T = 0 \text{ K} \]
transition from HOMO-2 to LUMO
\[ (E = 4.34 \text{ eV}, \lambda = 286 \text{ nm}) \]

\[ E = 4.03 \text{ eV} \]
\[ t_{\text{pulse}} \text{(FWHM)} = 5 \text{ fs} \]
\[ \text{polarization is (010)} \]
\[ T = 0 \text{ K} \]
transition from HOMO-2 to LUMO+1
\[ (E = 4.61 \text{ eV}, \lambda = 269 \text{ nm}) \]
SERID excitation spectrum with frozen nuclei

\[ \alpha(\omega) = 1.130 e^{-\left(\frac{\hbar \omega - 4.339 \text{eV}}{0.028 \text{eV}}\right)^2} \]

\[ \alpha(\omega) = 1.020 e^{-\left(\frac{\hbar \omega - 4.613 \text{eV}}{0.028 \text{eV}}\right)^2} \]

\[ A(t) \propto \cos\left(\frac{\pi}{2t_{\text{pulse}}} \left( t - \frac{t_{\text{pulse}}}{2} \right) \right) \]
\[ I(t) \propto \cos^2\left(\frac{\pi}{2t_{\text{pulse}}} \left( t - \frac{t_{\text{pulse}}}{2} \right) \right) \]

\[ \Delta t \sim \frac{t_{\text{pulse}}}{4} = 25 \text{ fs} \]
\[ \Delta E \Delta t \sim \hbar \]
\[ \Delta E \sim 0.026 \text{ eV} \]

\( (1\ 0\ 0) \)

\( (0\ 1\ 0) \)
SERID calculated excitation spectrum with nuclear motion at 0 K
fluence = $1.80 \times 10^{-3}$ kJ/m$^2$ and (1 0 0) polarization

$$\alpha(\omega) = 0.383 \ e \left( \frac{\hbar \omega - 4.289 \text{eV}}{0.033 \text{eV}} \right)^2$$

As absorption increases, the transition energy decreases, causing
- shift to lower frequencies
- plateau region for higher frequencies
- abrupt cut-off for lower frequencies
SERID calculated excitation spectrum about 4.34 eV with $T = 300$ K

fluence $= 1.80 \times 10^{-3}$ kJ/m$^2$ and (1 0 0) polarization

Low energy sidebands due to excitation out of HOMO-1 and HOMO orbitals

High energy sidebands due to excitations to LUMO+1 orbital.

$$\alpha(\omega) = 0.323 e \left( \frac{\hbar \omega - 4.301 \text{eV}}{0.095 \text{eV}} \right)^2$$
Comparison of excitation spectra

Nuclear motion decreases, shifts, and broadens the absorption spectra.
SERID calculated excitation spectrum about 4.61 eV with $T = 300$ K
fluence $= 1.80 \times 10^{-3}$ kJ/m$^2$ and (0 1 0) polarization

Steady increase in absorption with increasing frequency, due to excitations from orbitals below HOMO-2.

\[
\alpha(\omega) = 0.195 \left( \frac{\hbar \omega - 4.645 \text{ eV}}{0.266 \text{ eV}} \right)^2
\]
Full SERID calculated excitation spectrum

Gaussian fit (sum of x- and y- polarized fits):

\[ \alpha(\lambda) = 0.10 e \left( \frac{\lambda - 270.1 \text{ nm}}{10.29 \text{ nm}} \right)^2 + 0.16 e \left( \frac{\lambda - 288.3 \text{ nm}}{6.43 \text{ nm}} \right)^2 \]

Conclusions for DPA spectrum

- Predominant feature of the theoretical absorption spectrum of DPA consists of two closely spaced $\pi$ to $\pi^*$ transitions, one with an electric dipole moment in the $x$-direction and one in the $y$-direction.

- Our SERID method qualitatively reproduces key features of the absorption spectrum, as seen experimentally and as calculated with density functional theory.

- Width of excitation spectrum is due to motion of the nuclei, which cause a change in the excitation energy, and additionally permit excitation to and from other molecular orbitals.
A final reminder of our motivation: 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 studies of the kind reported here.

---

**Summary of the processes studied**

- **Cis to trans (and trans to cis) photoisomerization of azobenzene**, with nuclear motion allowing extra electronic transitions for pulse durations > about 50 fs

- **Photoinduced ring-opening (and ring-closing) in a model dithienylethene**

- **Response of dipicolinic acid to femtosecond-scale laser pulses**, including excited states and nuclear motion