Response of Dipicolinic Acid Molecules $\text{C}_5\text{H}_3\text{N}(\text{COOH})_2$ to Ultrafast Laser Pulses

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Overview

I. Description of semiempirical electron-radiation-ion dynamics (SERID)

II. Parameterization scheme for nitrogen- and oxygen-containing molecules

III. Equilibrium properties of dipicolinic acid (DPA)

IV. DPA subjected to short laser pulse with a frequency matched to the HOMO-LUMO gap energy

V. DPA subjected to a short laser pulse with a frequency matched to the transition with the largest oscillator strength
Electron dynamics: Time-dependent Schrödinger equation in a nonorthogonal basis

\[ i\hbar \frac{\partial \Psi_j}{\partial t} = S^{-1}H \Psi_j \]

Evolution of electronic states: Modified Cayley algorithm

\[ \Psi_j(t + \Delta t) = (1 + \frac{i}{2\hbar}L)^{-1}(1 - \frac{i}{2\hbar}L)\Psi_j(t) \]

\[ L = \int_{t}^{t+\Delta t} H(t + \Delta t)dt \]

SERID Description: Classical Part

Ion core dynamics: Generalized Ehrenfest Theorem

\[ M_i \ddot{X}_{i\alpha} = \frac{1}{2} \sum_j \Psi_j^+ \left( \frac{\partial H}{\partial X_{\alpha}} - i\hbar \frac{\partial S}{\partial X_{\alpha}} \right) \Psi_j + \text{h.c.} - \frac{\partial U_{\text{rep}}}{\partial X_{i\alpha}} \]

Electron coupling to the radiation field: Time-dependent Peierls substitution

\[ H_{ab} (\mathbf{X} - \mathbf{X}') = H_{ab}^0 (\mathbf{X} - \mathbf{X}') \exp \left[ \frac{i q}{\hbar c} \mathbf{A}(t)(\mathbf{X} - \mathbf{X}') \right] \]

Ionic motion algorithm: Velocity Verlet algorithm

\[ \ddot{\mathbf{R}}_i(t + \Delta t) = \ddot{\mathbf{R}}_i(t) + \frac{1}{2} \left[ \dddot{\mathbf{R}}_i(t + \Delta t) + \dddot{\mathbf{R}}_i(t) \right] \Delta t \]
Overview of the Parameterization Scheme for Nitrogen and Oxygen

Need to scale the hydrogen and carbon pairwise interactions from the Frauenheim group to include interactions with nitrogen and oxygen.

Parameterization scheme composed of two parts:

I. Electronic Properties

On-diagonal Hamiltonian matrix elements \( (H_{ii}) \) scaled to the atomic s and p energies of the new atom

On-diagonal elements of the overlap matrix \( (S_{ii}) \) set to 1 (complete overlap)

Off-diagonal elements of the Hamiltonian \( (H_{ij}) \) scaled so that the energy eigenvalue difference of the active space region equals the energy difference calculated using a DFT calculation. The off-diagonal elements of the overlap matrix \( (S_{ij}) \) are left alone

II. Nuclear Properties

The repulsive potential is scaled to match the atomic equilibrium properties (i.e. bond lengths and vibrational frequencies) of the diatomic molecule corresponding to the pairwise interaction in question
Parameterization Scheme: Electronic Properties

Graphic illustration for parameterizing a nitrogen-nitrogen interaction from a carbon-carbon interaction:

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

\[ H \Psi = \varepsilon S \Psi \]
Parameterization Scheme: Nuclear Properties Part I

Original effective nuclear repulsion has the form:

\[ V_r = \sum_{n=2}^{9} a_n (r_{\text{cut-off}} - r)^n \]

Where \( r_{\text{cut-off}} \) is the cut-off value for the repulsive potential and the \( a_n \) are what we must determine for the new pairwise interactions.

We scale the atomic distances by:

\[ r_{\text{new}} = \frac{r_{\text{old}}}{\beta} \]

where:

\[ \beta = \frac{r_{o,\text{old}}}{r_{o,\text{new}}} \]
We then scale the nuclear repulsive potential so that:

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

And determine the constants \( c_0 \) and \( c_1 \) from the equilibrium conditions that:

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

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

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

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

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Scale Factor</th>
<th>Property</th>
<th>Exp.</th>
<th>SERID</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
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<td>5.74</td>
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<tr>
<th>Molecule</th>
<th>Scale Factor</th>
<th>Property</th>
<th>Exp.</th>
<th>SERID</th>
</tr>
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<td></td>
<td>( \Delta E_g ) (eV)</td>
<td>7.09</td>
<td>10.54</td>
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</table>

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-ccpVQZ calculation, except for the hydride bond lengths, which were taken from Sun et al, *J. Chem Phys.* 74 (1981) 6842, and the excitation energy of N₂, which was calculated without diffuse functions.
### Parameterization Applied to the Equilibrium State of the Azabenzenes

<table>
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<tr>
<th>Molecule</th>
<th>Bond</th>
<th>Exp. (Å)</th>
<th>SERID (Å)</th>
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<tbody>
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<td>1.394</td>
</tr>
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</tr>
<tr>
<td></td>
<td>C-H</td>
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<td>pyridazine²</td>
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<td>1.336</td>
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<tr>
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<td>N-C_a</td>
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<td>1.362</td>
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<td>C_b-C_a</td>
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<td>1.395</td>
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<td>C_b-H</td>
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<td>1.396</td>
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<tr>
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<td>1.362</td>
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<td>C_b-C_c</td>
<td>1.393</td>
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<td>1.096</td>
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<td>triazine⁴</td>
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<td>1.358</td>
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<tr>
<td></td>
<td>C-H</td>
<td>1.084</td>
<td>1.084</td>
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</table>

Parameterization Applied to the Equilibrium States of Various Oxygen-containing Molecules

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Bond</th>
<th>Exp. (Å)</th>
<th>SERID (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂¹</td>
<td>C-O</td>
<td>1.177</td>
<td>1.162</td>
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<tr>
<td>H₂O¹</td>
<td>O-H</td>
<td>0.979</td>
<td>0.957</td>
</tr>
<tr>
<td>Acetaldehyde¹</td>
<td>Cₐ-O</td>
<td>1.208</td>
<td>1.216</td>
</tr>
<tr>
<td></td>
<td>Cₐ-Cₜ</td>
<td>1.520</td>
<td>1.501</td>
</tr>
<tr>
<td></td>
<td>Cₐ-H</td>
<td>1.146</td>
<td>1.114</td>
</tr>
<tr>
<td></td>
<td>Cₜ-H</td>
<td>1.097</td>
<td>1.086</td>
</tr>
<tr>
<td>Acetic Acid²</td>
<td>C-C</td>
<td>1.531</td>
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</tr>
<tr>
<td></td>
<td>C-Oₐ</td>
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</tr>
<tr>
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<td>C-Oₜ</td>
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<td>1.364</td>
</tr>
<tr>
<td></td>
<td>C-H</td>
<td>1.099</td>
<td>1.100</td>
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<tr>
<td></td>
<td>Oₐ-H</td>
<td>0.965</td>
<td>0.971</td>
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<td>Furan¹</td>
<td>Cₜ-Cₜ</td>
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<td>1.431</td>
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<td>C-H</td>
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<td>1.086</td>
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<td>Ethanol²</td>
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<tr>
<td></td>
<td>Cₜ-H</td>
<td>1.096</td>
<td>1.090</td>
</tr>
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</table>

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

I. Hamiltonian and overlap matrix elements scaled to the electronic properties of the desired pairwise interaction

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

III. Parameterization scheme yields bond lengths for larger molecules that are normally within 2-3% (not greater than 5%) of the experimental bond lengths
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 6-31G (Å)</th>
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<tbody>
<tr>
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<tr>
<td>C(_a)-C(_b)</td>
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<td>C(_a)-C(_d)</td>
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<td>C(_d)-O(_a)</td>
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<td>C(_d)-O(_b)</td>
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<td>H(_c)-C(_c)</td>
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## Key Normal Modes Excited During Laser Pulse Simulation

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<thead>
<tr>
<th>Description</th>
<th>SERID (cm(^{-1}))</th>
<th>B3LYP//cc-pVDZ (cm(^{-1}))</th>
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<tbody>
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<td>640</td>
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<td>Ring breathe</td>
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<td>1012</td>
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## Electronic Equilibrium Properties

### Levels and Energies

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<th>Level</th>
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<th>B3LYP//c-pVDZ (eV)</th>
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</thead>
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<tr>
<td>LUMO+3</td>
<td>+0.99</td>
<td>+1.33</td>
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</table>

**ΔE_{gap} = 4.03 eV**

- HOMO-2, HOMO-1 and HOMO nearly degenerate
- LUMO and LUMO+1 nearly degenerate
Laser Pulse Matched to HOMO-LUMO Gap Applied in the (010)-Direction

Primary excitation from HOMO-2 to LUMO+1 during application of laser pulse

Laser Pulse Parameters:
\[ t_{\text{pulse}}(\text{FWHM}) = 5 \text{ fs} \]
\[ A_0 = 0.65 \text{ G cm} \]
\[ \omega = 4.03 \text{ eV} \]
\[ P = (010)444 \]
Laser Pulse Matched to HOMO-LUMO Gap Applied in the (100)-Direction

Primary excitation from HOMO-2 to LUMO during application of laser pulse

Laser Pulse Parameters:
\( t_{\text{pulse}} (\text{FWHM}) = 5 \text{ fs} \)
\( A_0 = 0.65 \text{ G cm} \)
\( \omega = 4.03 \text{ eV} \)
\( P = (100) \)
Comparison of SERID with TDDFT

TDDFT B3LYP/cc-pVDZ results in for the first two transitions with significant oscillator strengths:

<table>
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<tr>
<th>Transition</th>
<th>Frequency (eV)</th>
<th>Oscillator Strength</th>
<th>x-Electric Dipole Moment (au)</th>
<th>y-Electric Dipole Moment (au)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO-2 to LUMO+1</td>
<td>5.07</td>
<td>0.0631</td>
<td>0.7130</td>
<td>0.0000</td>
</tr>
<tr>
<td>HOMO-2 to LUMO</td>
<td>5.46</td>
<td>0.0875</td>
<td>0.0000</td>
<td>-0.8091</td>
</tr>
</tbody>
</table>

TDDFT and SERID calculations both show that the first two significant transitions are from the HOMO-2 to the LUMO+1 and the HOMO-2 to the LUMO, although the x and y polarized character of the LUMO and LUMO+1 levels are reversed.
DPA Subject to a (010)-Polarized Pulse Matched to the HOMO-2 to LUMO+1 Transition Frequency

Laser Pulse Parameters:

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

\[ A(t) = A_0 \cos \left( \frac{\pi (t - t_{\text{pulse}} / 2)}{t_{\text{pulse}}} \right) \sin(\omega t) \]
Normalized Frequency Spectrum After Completion of Laser Pulse

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

1036 cm$^{-1}$

1270 cm$^{-1}$
Overview of the Electronic Structure

HOMO-3 through LUMO+3 Energy Levels

HOMO-3 through LUMO+3 Occupation

Initial transition is from the HOMO-2 level to the LUMO+1 level. Through a series of avoided crossings and subsequent electron transitions, the HOMO levels is depopulated and the LUMO level is populated.
A series of electron transitions between the HOMO-2 and HOMO-1 levels occur between 13.9 fs and 415.0 fs, leaving the HOMO-1 level as the primarily depopulated level. From 330 fs until 550 fs, the HOMO level slowly becomes depopulated as HOMO-1 level becomes repopulated. From 550 fs until the end of the simulation, the HOMO level is the only significantly depopulated level.
A Closer Look at the LUMO and LUMO+1 Levels

Energy Levels

Percent of Level Occupancy

A series of electron transitions between the LUMO and LUMO+1 levels occur between 13.5 fs and 70.2 fs, leaving the excited electrons primarily in the LUMO level. After this time, the electron population is almost entirely located in the LUMO level for the remainder of the simulation.
First LUMO+1 to LUMO transition and first HOMO-2 to HOMO-1 transition.

Only HOMO is deoccupied and only LUMO is occupied.

Last LUMO+1 to LUMO transition.
Internuclear Distances Between Breathing Ring Atoms

Period of oscillation $\sim 32$fs
This corresponds roughly to the breathing mode at 1036 cm$^{-1}$

red = 1
green = 2
blue = 3
I. SERID predicts an equilibrium geometry and vibrational frequencies for DPA that are in reasonable agreement with other \textit{ab initio} methods.

II. SERID and TDDFT predict excited state transitions from the HOMO-2 to both the LUMO and LUMO+1 levels. The two methods disagree on the ordering of the LUMO and LUMO+1 states, but these are nearly degenerate.

III. SERID predicts a series of avoided crossings between the nearly degenerate HOMO-2, HOMO-1 and HOMO levels and between the LUMO and LUMO+1 levels after the completion of the laser pulse.

IV. The SERID calculations show that a breathing mode, with a frequency of 1036 cm\(^{-1}\) is the dominant mode excited by a 5 fs (FWHM) laser pulse matched to the HOMO-2 to LUMO+1 energy difference.