Ab initio molecular dynamics of molecules in strong laser fields

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Prof. Smriti Anand                Dr. Jason Sonk
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Background and Motivation

- Photons as reagents for mode selective chemistry
- Rapid intramolecular vibrational redistribution (IVR) defeats mode specificity (~1 ps)
- Critical conditions needed to overcome IVR:
  - Ultrafast excitation
  - Ultrashort reaction times
- Requires the use of intense, ultrafast lasers
- Laser fields of $10^{14}$ W cm$^{-2}$ are strong enough to distort the potential energy surface and to affect the dynamics of molecules
Ab Initio Classical Trajectory on the Born-Oppenheimer Surface Using Hessians

Calculate the energy, gradient and Hessian in the laser field

Solve the classical equations of motion on a local 5th order polynomial surface

Distortion of the PES by a Low Frequency, Strong Laser Field (collaboration with Prof. Wen Li, WSU)

- Laser fields of $10^{14} \text{ W cm}^{-2}$ are strong enough to distort the potential energy surface and to affect the dynamics of molecules
- Wagging tail model for $\text{H}^+$ dissociation in $\text{HCl}^+$
- Wardlaw and coworkers, *JCP* 1995, 102, 7462
  *JCP* 2004, 120, 1279

\[ KE_{\max} \approx 0.25 D_e + 2\sqrt{2D_e U_{pm}} + 8U_{pm} \]

\[ U_{pm} = \frac{E_{\max}^2}{4\mu\omega^2} \]
HCO\(^+\) → H\(^+\) + CO Dissociation in a CW Laser Field (10 μm, 2.9 \times 10^{14} \text{ W cm}^{-2})

Formyl Chloride Cation

Strong field dissociation by ultrashort mid-infrared laser pulses

- Mode selective chemistry
- Dependence of branching ratios on the wavelength and orientation of the field

\[ \text{ClCHO}^+ \rightarrow \text{Cl} + \text{HCO}^+ \ (0.30 \text{ eV}) \]
\[ \rightarrow \text{H} + \text{ClCO}^+ \ (1.26 \text{ eV}) \]
\[ \rightarrow \text{HCl}^+ + \text{CO} \ (1.34 \text{ eV}) \]

Field-free Dissociation Times

\[
\text{ClCHO}^+ \rightarrow \text{Cl} + \text{HCO}^+ \\
\rightarrow \text{H} + \text{ClCO}^+ \\
\rightarrow \text{HCl}^+ + \text{CO}
\]
Dissociation Times with Laser Field

\[ \text{ClCHO}^+ \rightarrow \text{Cl} + \text{HCO}^+ \]
\[ \rightarrow \text{H} + \text{ClCO}^+ \]
\[ \rightarrow \text{HCl}^+ + \text{CO} \]
Dissociation at 7 μm: HCl+ channel

- A closer look at trajectories of the HCl+ channel: C-Cl bond stretch, C-H stretch and rock, followed by H+ migration
Field Orientation Dependency

\[
\text{CIC}H\text{O}^+ \rightarrow \text{Cl} + \text{HCO}^+ \\
\rightarrow \text{H} + \text{ClCO}^+ \\
\rightarrow \text{HCl}^+ + \text{CO}
\]

Relative yields vs. Field direction $\theta$ (degree)
Charge Oscillation ClCHO$^+$ due to the Laser Field

(B)

<table>
<thead>
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<th>Charge</th>
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<tbody>
<tr>
<td>-0.5</td>
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<tr>
<td>0.5</td>
</tr>
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<table>
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<th>Time (fs)</th>
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<tr>
<td>60</td>
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<tr>
<td>80</td>
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<tr>
<td>100</td>
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Bromofluoroform cation ($\text{CF}_3\text{Br}^+$)
Iodobenzene dication ($\text{C}_6\text{H}_5\text{I}^2+$)

- Molecules can be aligned and electric field applied along specific bonds
- Laser parameters
  - Gaussian pulse envelope
  - Number of cycle = 5
  - $E_{max} = 0.07$ and $0.09$ a.u.
  - Wavelength : $4 \sim 10 \text{ \mu m}$

Field directed along a C-F bond of CF$_3$Br$^+$

- C-F avg. stretching: ~7.8 µm (field-free) “near-resonance effect”

- Relative yields
  - 0.07 a.u.
  - 0.09 a.u.
  - F
  - F*
  - Br
  - C-F

Wavelength (µm)
Field directed along a C-Br bond of CF$_3$Br$^+$

- Poor bond selectivity at 0.07 a.u.
- Multi-body dissociation dominant at 10 $\mu$m
Bond Selective Dissociation in Iodobenzene Dication

- A very high degree of spatial alignment can be achieved experimentally for C₆H₅I

<table>
<thead>
<tr>
<th>Field direction</th>
<th>Field strength of 0.09 a.u. at 10 μm</th>
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<tbody>
<tr>
<td></td>
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<tr>
<td>Perpendicular to C-I</td>
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<tr>
<td>Parallel to C-I</td>
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</tr>
<tr>
<td>Along Ortho/Meta C-H</td>
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</table>
CH₃OH⁺ Isomerization Driven by Short, Intense Laser Pulses

- Yamanouchi and co-workers have examined the fragmentation of methanol by intense 800 nm laser pulses
- 40 fs 800 nm pump pulse produces methanol monocation
- probe pulse delayed by 100 – 800 fs generates the dication
- coincidence momentum imaging of CH₃⁺/OH⁺ and CH₂⁺/H₂O⁺ showed that ultrafast CH₃OH⁺ → CH₂OH₂⁺ isomerization during the pulse and slower isomerization occurred after the pulse
- BOMD simulations of isomerization and fragmentation by a 800 nm laser pulse with CAM-B3LYP/6-31G(d)

Simulation of Strong Field Isomerization and Dissociation of CH$_3$OH$^+$

- Classical trajectory calculations of ground state CH$_3$OH$^+$ with CAM-B3LYP/6-31G(d,p) level of theory
- 40 fs 800 nm trapezoidal laser pulse (randomly oriented)
- 0, 0.07 and 0.09 au field strength (corresponds to 0, 0.88×10$^{14}$ and 2.9×10$^{14}$ W/cm$^2$)
- 75, 100, 125 kcal/mol added vibrational energy to simulate extra energy gained on ionization
- 200 trajectories of 400 fs for each case
Potential Energy Surface for CH$_3$OH$^+$

Low energy channels include CH$_2$OH$^+$+ H, HCOH$^+$+ H$_2$ and isomerization (CAM-B3LYP/6-31G(d,p), CBS-QB3 (italics) and CBS-APNO (bold))
Branching Ratios for CH$_3$OH$^+$ Dissociation and Isomerization

- H dissociation most abundant in all cases
- H$_2$ next most abundant channel
- Much less migration and OH dissociation
- Little or no dissociation after migration
C-O dissociation after H migration seen in experiment with intense 800 nm laser pulses but not in simulations for ground state CH$_3$OH$^+$

- With 800 nm laser pulses, some C-O dissociations may occur on excited state surfaces of CH$_3$OH$^+$
- CH$_3$OH$^+$ gains considerable energy from the pulse in experiments but not in adiabatic BOMD simulations
- May be due to non-adiabatic dynamics during the pump intense 800 nm pulse
Isomerization and Dissociation of CH$_3$OH$^+$ by Mid-IR Laser Fields

- At 800 nm, classical dynamics simulations showed that ground state methanol cation gained very little energy from the laser.
- Mid-IR laser pulses can interact directly with the molecular vibrations and are less likely to cause excitation or ionization.
- Studies of ClCHO$^+$, CF$_3$Br$^+$ and C$_6$H$_5$I$^2+$ showed that orientation can enhance specific reactions by mid-IR lasers.
- Simulations using CAM-B3LYP/6-31G(d,p) with a 15 cycle 95 fs 7 μm trapezoidal laser pulse (randomly oriented and C-O aligned) with intensities of 0.88×10$^{14}$ and 1.7×10$^{14}$ W/cm$^2$ (0.05, 0.07 au).
Energy Deposited in CH$_3$OH$^+$ by a 4 cycle 7 μm pulse

Average energy deposited
(random / aligned)
42 / 76 kcal/mol at 0.05 au
81 / 120 kcal/mol at 0.07 au

0.05 au field strength

0.07 au field strength

Infrared spectrum of CH$_3$OH$^+$

- When the laser polarization is aligned with the C-O bond, the vibrational intensities in the mid-IR range are higher and nearly twice as much energy is deposited by the 7 µm pulse.

randomly oriented
C-O aligned

4 cycle 7 µm pulse:
1430 cm$^{-1}$ with
600 cm$^{-1}$ FWHM
Isomerization and Dissociation of CH$_3$OH$^+$ by Mid-IR Laser Fields

- CH$_3$OH$^+$ gains an order of magnitude more energy from a 7 µm pulse than from a 800 nm pulse.
- For a 7 µm pulse, CH$_3$OH$^+$ gains nearly twice as much energy for intensity of $1.7 \times 10^{14}$ W/cm$^2$ than for $0.88 \times 10^{14}$ W/cm$^2$.
- Aligned CH$_3$OH$^+$ gains 50 - 80% more energy than randomly oriented.
  - This is in accord with the higher vibrational intensities in the mid-IR range for aligned CH$_3$OH$^+$.
Comparison of Potential Energy Surfaces for CH$_3$X$^+$ (X = NH$_2$, OH, F)

- Explore effect of changes in potential energy surface (PES) on the reactions driven by the laser field.
- H elimination has lowest barrier in all cases.
- CH$_3$NH$_2^+$ has higher barriers than CH$_3$OH$^+$ and CH$_3$F$^+$.
- Largest change is in C-X dissociation energies.

Randomly oriented and aligned
\( \text{CH}_3\text{NH}_2^+\), \( \text{CH}_3\text{OH}^+\), \( \text{CH}_3\text{F}^+\)
in a 7 \( \mu\text{m} \) Laser Pulse

Field strength (au),
Field alignment (R or A),
X = NH\(_2\), OH, F
Isomerization and Dissociation of CH$_3$NH$_2^+$, CH$_3$OH$^+$ and CH$_3$F$^+$
by 7 $\mu$m Laser Fields

- CH$_3$X$^+$ gains an order of magnitude more energy from a 7 $\mu$m pulse than from a 800 nm pulse
- Aligned CH$_3$X$^+$ gains nearly twice as much energy as randomly oriented
- Energy gained: CH$_3$NH$_2^+$ > CH$_3$OH$^+$ > CH$_3$F$^+$
- CH$_3$NH$_2^+$ less reactive than CH$_3$OH$^+$ and CH$_3$F$^+$ because of higher barriers
- Most abundant reaction path is CH$_2$X$^+$ + H (63%-93%) with 2$^{nd}$ most favorable path HCX$^+$ + H$_2$ (4-33%)
- Only CH$_3$F$^+$ showed C-X cleavage after isomerization
New algorithm for MD in an intense laser pulse


- Algorithm accounts for the variation of the electric field during the integration time step
- Calculate predictor step on a local polynomial surface for the gradient that includes the electric field dependence
- Dipole derivative and polarizability derivative give the dependence of the gradient on the electric field

\[ \tilde{g}(\tilde{x}, \tilde{\varepsilon}(t)) = \tilde{g}(\tilde{x}_1, \tilde{\varepsilon}(t_1)) + \left. \frac{\partial \tilde{g}}{\partial \tilde{x}} \right|_{\tilde{x}_1, \tilde{\varepsilon}(t_1)} (\tilde{x} - \tilde{x}_1) \]

\[ + \left. \frac{\partial \tilde{g}}{\partial \tilde{\varepsilon}} \right|_{\tilde{x}_1, \tilde{\varepsilon}(t_1)} (\tilde{\varepsilon}(t) - \tilde{\varepsilon}(t_1)) \]

\[ + \frac{1}{2} \left. \frac{\partial^2 \tilde{g}}{\partial \tilde{\varepsilon}^2} \right|_{\tilde{x}_1, \tilde{\varepsilon}(t_1)} (\tilde{\varepsilon}(t) - \tilde{\varepsilon}(t_1))^2 \]

where

\[ \frac{\partial \tilde{g}}{\partial \tilde{\varepsilon}} = \frac{\partial^2 E}{\partial \tilde{\varepsilon} \partial \tilde{x}} = \frac{\partial \tilde{\mu}}{\partial \tilde{x}} \]

\[ \frac{\partial^2 \tilde{g}}{\partial \tilde{\varepsilon}^2} = \frac{\partial^3 E}{\partial \tilde{\varepsilon}^2 \partial \tilde{x}} = \frac{\partial \tilde{\alpha}}{\partial \tilde{x}} \]
Corrector step for integrating MD in an intense laser pulse

- calculate corrector step on a distance weighted interpolant surface that includes the electric field
- use velocity Verlet to integrate on the DWI surface ($\delta t=\Delta t/100$)

\[
g(\bar{x}, \bar{E}(t)) = w_1(\bar{x}) \tilde{g}_1(\bar{x}, \bar{E}(t)) + w_2(\bar{x}) \tilde{g}_2(\bar{x}, \bar{E}(t))
\]
\[
w_1(\bar{x}) = \frac{\| \bar{x} - \bar{x}_2 \|^2}{\| \bar{x} - \bar{x}_1 \|^2 + \| \bar{x} - \bar{x}_2 \|^2},
w_2(\bar{x}) = \frac{\| \bar{x} - \bar{x}_1 \|^2}{\| \bar{x} - \bar{x}_1 \|^2 + \| \bar{x} - \bar{x}_2 \|^2}
\]
\[
g_n(\bar{x}, \bar{E}(t)) = \bar{g}(\bar{x}_n, \bar{E}(t_n)) + \frac{\partial \bar{g}}{\partial \bar{x}} \bigg|_{\bar{x}_n, \bar{E}(t_n)} (\bar{x} - \bar{x}_n) + \frac{1}{2} \frac{\partial^2 \bar{g}}{\partial \bar{x}^2} \bigg|_{\bar{x}_n, \bar{E}(t_n)} (\bar{x} - \bar{x}_n)^2
\]
\[
+ \frac{\partial \bar{g}}{\partial \bar{E}} \bigg|_{\bar{x}_n, \bar{E}(t_n)} (\bar{E}(t) - \bar{E}(t_n)) + \frac{1}{2} \frac{\partial^2 \bar{g}}{\partial \bar{E}^2} \bigg|_{\bar{x}_n, \bar{E}(t_n)} (\bar{E}(t) - \bar{E}(t_n))^2
\]

- Hessians are updated (CFD-Bofill\(^1\)) and are recalculated only every 20 steps
- 3\(^{rd}\) derivatives approximated by the finite difference of the two Hessians

\(^1\) Wu, Rahman, Wang, Louderaj, Hase, Zhuang JCP 2010, 133, 074101
Effect of dipole and polarizability derivatives on a HCO$^+$ trajectory
($2.9 \times 10^{14}$ W cm$^2$, CW, $\Delta t=0.25$ fs)

Hessian Updating

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<tr>
<th>$\Delta t$</th>
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<th>n=20</th>
<th>n=30</th>
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<tr>
<td>0.10 fs</td>
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<td>0.50 fs</td>
<td>34.75</td>
<td>34.81</td>
<td>34.87</td>
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Electronic Response of Molecules
Short, Intense Laser Pulses

- Non-linear response – cannot be treated by perturbation theory
- rt-TD-HF and rt TD-DFT: real time integration of the HF or KS equations
  \[ i \hbar \frac{dP(t)}{dt} = [F(t), P(t)] \]
- TD-CI: integration of the time dependent Schrodinger equation expanded in terms of the field-free ground and excited states
  \[ i\hbar \frac{d\Psi}{dt} = \hat{H}\Psi \]
  \[ \Psi(t) = \sum C_i(t) \psi_i \]
  \[
  \begin{bmatrix}
    \frac{dC_1}{dt} \\
    \frac{dC_2}{dt} \\
    \vdots \\
    \frac{dC_n}{dt}
  \end{bmatrix}
  =
  \begin{bmatrix}
    \omega_1 + \tilde{E}(t) \cdot \tilde{\mu}_{11} & \tilde{E}(t) \cdot \tilde{\mu}_{12} & \cdots & \tilde{E}(t) \cdot \tilde{\mu}_{1n} \\
    \tilde{E}(t) \cdot \tilde{\mu}_{21} & \omega_2 + \tilde{E}(t) \cdot \tilde{\mu}_{22} & \cdots & \tilde{E}(t) \cdot \tilde{\mu}_{2n} \\
    \vdots & \vdots & \ddots & \vdots \\
    \tilde{E}(t) \cdot \tilde{\mu}_{n1} & \tilde{E}(t) \cdot \tilde{\mu}_{n2} & \cdots & \omega_n + \tilde{E}(t) \cdot \tilde{\mu}_{nn}
  \end{bmatrix}
  \begin{bmatrix}
    C_1 \\
    C_2 \\
    \vdots \\
    C_n
  \end{bmatrix}
  \]
- Requires the energies of the field-free states, \( \omega_i \), and their transition dipoles, \( \mu_{ij} \)
- Need to limit the expansion to a subset of the excitations (e.g. single excitations)
- Excited states calculated by CIS, CIS(D), EOM-CCSD, RPA, TD-DFT
Strong Field Ionization using Complex Absorbing Potentials

- Ionization corresponds to exciting an electron into an unbound continuum state
- Standard molecular orbital calculations with atom-centered basis functions cannot represent unbound electrons
- Add an complex potential outside the valence region to absorb the unbound electron density

\[ i \frac{\partial \Psi(t)}{\partial t} = \hat{H}_{el} - \bar{\mu} \bar{E}(t) - i \hat{V}_{abs} \]
Hydrogen atom in a constant field

- Ramp up the field gradually to its maximum value
- Dipole moment reaches a constant value
- The complex absorbing potential causes the norm of the wavefunction to decay exponentially
- The decay rate corresponds to the ionization rate

Hydrogen atom ionization rate as a function of field strength

Ionization rates using complex absorbing potentials compared to accurate, grid-based calculations
Ionization rate of $\text{H}_2^+$ as a function of bond length

As the bond length is stretched, the ionization rate increases due to charge resonance enhanced ionization (CREI). Using gaussian basis functions (suitable for many electron systems).

Accurate grid-based method
Bandrauk and co-workers (only suitable for 1 and 2 electron systems)
Ionization of HCl\(^+\) as a function of bond length

(a) Lowest 6 excited states for field free HCl\(^+\)
(b) Ionization rates for 800 nm (0.057 au)
(c) Ionization rates for 1064 nm (0.043 au)

Blue - aug-cc-pVTZ
Green - aug-cc-pVTZ plus absorbing basis at bond midpoint
Red - aug-cc-pVTZ plus absorbing basis on H and Cl
Ionization of HCO$^+$ as a function of bond length

(a) Lowest 6 excited states for field free HCO$^+$
(b) ionization rates for 800 nm (0.057 au)
(c) ionization rates for 1064 nm (0.043 au)

Blue - aug-cc-pVTZ
Green - aug-cc-pVTZ plus absorbing basis at bond midpoint
Red - aug-cc-pVTZ plus absorbing basis on H and Cl
Ground state and $\sigma \rightarrow \sigma^*$ state populations for (a) HCl$^+$ and (b) HCO$^+$

Similar to H$_2^+$, a charge-resonance enhanced ionization mechanism contributes to the increased ionization rate as the bonds are elongated.
Ionization of Ethylene, Butadiene and Hexatriene

- 7 cycle 800 nm cosine squared, $0.88 \times 10^{14}$ W/cm$^2$
- TD-CIS with complex absorbing potential using aug-cc-pVTZ basis plus 3 s, 2 p, 3 d and 1 f diffuse functions on each atom

C$_2$H$_4$ – 1849 states
C$_4$H$_6$ – 5468 states
C$_6$H$_8$ – 10897 states

Ionization of Ethylene, Butadiene and Hexatriene

Number of states used in the TD-CI propagation can be reduced

States with energies greater than 5 au do not contribute to the ionization rate
Orientation Dependence of Ionization Rate for Ethylene, Butadiene, Hexatriene
Angular Dependence of Ionization Rate for Butadiene
Acknowledgements

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