

Ab initio molecular dynamics of molecules in strong laser fields

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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 10¹⁴ 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





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

10

- Laser fields of 10¹⁴ W cm⁻² are strong enough to distort the potential energy surface and to affect the dynamics of molecules
- Wagging tail model for 0.4H⁺ dissociation in HCl⁺ • Wardlaw and coworkers_ 0.2Energy (a.u.) *JCP* **1995**, *102*, 7462 *JCP* **2004**, *120*, 1279 0 $KE_{\rm max} \approx 0.25 D_{\circ}$ -0.2 $+2\sqrt{2D_eU_{pm}}$ -0.4 $+8U_{pm}$ 0 $\mathbf{2}$ 8 6 R (a.u.) $U_{pm} = E_{max}^2 / 4\mu\omega^2$



HCO⁺ \rightarrow H⁺ + CO Dissociation in a CW Laser Field (10 µm, 2.9×10¹⁴ 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

 $\begin{array}{l} \text{ClCHO}^+ \rightarrow \text{Cl} + \text{HCO}^+ \ (0.30 \text{ eV}) \\ \rightarrow \text{H} + \text{ClCO}^+ \ (1.26 \text{ eV}) \\ \rightarrow \text{HCl}^+ + \text{CO} \ (1.34 \text{ eV}) \end{array}$

Lee, S. K.; Suits A. G.; Schlegel, H. B.; Li, W. *J. Phys. Chem. Lett.* 2012, *3*, 2541



Field-free Dissociation Times





Dissociation Times with Laser Field





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





Charge Oscillation ClCHO+ due to the Laser Field



Time (fs)



Bromofluoroform cation (CF₃Br⁺) Iodobenzene dication (C₆H₅I²⁺)

F C F

 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 : $4 \sim 10 \ \mu m$

Lee, S. K.; Schlegel, H. B.; Li, W. J. Phys. Chem. A 2013, 117, 11202



Field directed along a C-F bond of CF₃Br⁺



0.07 a.u. 0.09 a.u. → F → F ···•· F* → Br → Br

Br

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





Bond Selective Dissociation in Iodobenzene Dication

• A very high degree of spatial alignment can be achieved experimentally for C_6H_5I



Field direction -	Field strength of 0.09 a.u. at 10 µm				
	Ι	Ortho H	Meta H	Para H	No Rx
Perpendicular to C-I	0	13	15	0	73
Parallel to C-I	0	0	0	100	0
Along Ortho/Meta C-H	0	0	59	40	0



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 CH_3^+/OH^+ and CH_2^+/H_2O^+ showed that ultrafast $CH_3OH^+ \rightarrow CH_2OH_2^+$ 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)

B. Thapa, H.B. Schlegel, J. Phys. Chem. A, 2014, 118, 1769



Simulation of Strong Field Isomerization and Dissociation of CH₃OH⁺

- Classical trajectory calculations of ground state CH₃OH⁺ 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/cm²)
- 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 CH₃OH⁺



Low energy channels include CH_2OH^+ + H, HCOH⁺+ H₂ and isomerization (CAM-B3LYP/6-31G(d,p), CBS-QB3 (italics) and CBS-APNO (bold))



Branching Ratios for CH₃OH⁺ Dissociation and Isomerization

- H dissociation most abundant in all cases
- H₂ next most abundant channel
- Much less migration and OH dissociation
- Little or no dissociation after migration





Isomerization and Dissociation of CH₃OH⁺ by Intense 800 nm Laser Fields

- C-O dissociation after H migration seen in experiment with intense 800 nm laser pulses but not in simulations for ground state CH₃OH⁺
- With 800 nm laser pulses, some C-O dissociations may occur on excited state surfaces of CH_3OH^+
- CH₃OH⁺ 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 CH₃OH⁺ 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⁺, CF₃Br⁺ and C₆H₅I²⁺ 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 0.88×10¹⁴ and 1.7×10¹⁴ W/cm² (0.05, 0.07 au)



Energy Deposited in CH₃OH⁺ by a 4 cycle 7 µm pulse





Infrared spectrum of CH₃OH⁺



• 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 μ m pulse



Isomerization and Dissociation of CH₃OH⁺ by Mid-IR Laser Fields

- CH_3OH^+ gains an order of magnitude more energy from a 7 μ m pulse than from a 800 nm pulse
- For a 7 μ m pulse, CH₃OH⁺ gains nearly twice as much energy for intensity of 1.7×10¹⁴ W/cm² than for 0.88×10¹⁴ W/cm²
- Aligned CH₃OH⁺ gains 50 80% more energy than randomly oriented
 - This is in accord with the higher vibrational intensities in the mid-IR range for aligned CH₃OH⁺



Comparison of Potential Energy Surfaces for $CH_3X^+(X = NH_2, OH, F)$

- 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
- CH₃NH₂⁺ has higher barriers than CH₃OH⁺ and CH₃F⁺
- Largest change is in C-X dissociation energies



B. Thapa, H.B. Schlegel, J. Phys. Chem. 2014, 118, 10067-72





Isomerization and Dissociation of CH₃NH₂⁺, CH₃OH⁺ and CH₃F⁺ by 7 µm Laser Fields

- CH_3X^+ gains an order of magnitude more energy from a 7 μ m pulse than from a 800 nm pulse
- Aligned CH_3X^+ gains nearly twice as much energy as randomly oriented
- Energy gained: $CH_3NH_2^+ > CH_3OH^+ > CH_3F^+$
- CH₃NH₂⁺ less reactive than CH₃OH⁺ and CH₃F⁺ because of higher barriers
- Most abundant reaction path is $CH_2X^+ + H$ (63%-93%) with 2nd most favorable path HCX⁺ + H₂ (4-33%)
- Only CH₃F⁺ showed C-X cleavage after isomerization



New algorithm for MD in an intense laser pulse

HBS J. Chem. Theory Comput., 2013, 9, 3293

- 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

$$\vec{g}(\vec{x}, \vec{\varepsilon}(t)) = \vec{g}(\vec{x}_1, \vec{\varepsilon}(t_1)) + \frac{\partial \vec{g}}{\partial \vec{x}} \bigg|_{\vec{x}_1, \vec{\varepsilon}(t_1)} (\vec{x} - \vec{x}_1)$$

$$+\frac{\partial \vec{g}}{\partial \vec{\varepsilon}}\Big|_{\vec{x}_{1},\vec{\varepsilon}(t_{1})}(\vec{\varepsilon}(t)-\vec{\varepsilon}(t_{1})) +\frac{1}{2}\frac{\partial^{2}\vec{g}}{\partial \vec{\varepsilon}^{2}}\Big|_{\vec{x}_{1},\vec{\varepsilon}(t_{1})}(\vec{\varepsilon}(t)-\vec{\varepsilon}(t_{1}))^{2}$$

where
$$\frac{\partial \vec{g}}{\partial \vec{\varepsilon}} = \frac{\partial^2 E}{\partial \vec{\varepsilon} \partial \vec{x}} = \frac{\partial \vec{\mu}}{\partial \vec{x}}$$
 $\frac{\partial^2 \vec{g}}{\partial \vec{\varepsilon}^2} = \frac{\partial^3 E}{\partial \vec{\varepsilon}^2 \partial \vec{x}} = \frac{\partial \underline{\alpha}}{\partial \vec{x}}$



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 ($\delta t = \Delta t/100$)

$$\begin{split} \vec{g}(\vec{x},\vec{\varepsilon}(t)) &= w_1(\vec{x})\vec{g}_1(\vec{x},\vec{\varepsilon}(t)) + w_2(\vec{x})\vec{g}_2(\vec{x},\vec{\varepsilon}(t)) \\ w_1(\vec{x}) &= |\vec{x} - \vec{x}_2|^2 / (|\vec{x} - \vec{x}_1|^2 + |\vec{x} - \vec{x}_2|^2), w_2(\vec{x}) = |\vec{x} - \vec{x}_1|^2 / (|\vec{x} - \vec{x}_1|^2 + |\vec{x} - \vec{x}_2|^2) \\ \vec{g}_n(\vec{x},\vec{\varepsilon}(t)) &= \vec{g}(\vec{x}_n,\vec{\varepsilon}(t_n)) + \frac{\partial \vec{g}}{\partial \vec{x}} \Big|_{\vec{x}_n,\vec{\varepsilon}(t_n)} (\vec{x} - \vec{x}_n) + \frac{1}{2} \frac{\partial^2 \vec{g}}{\partial \vec{x}^2} \Big|_{\vec{x}_n,\vec{\varepsilon}(t_n)} (\vec{x} - \vec{x}_n)^2 \\ &+ \frac{\partial \vec{g}}{\partial \vec{\varepsilon}} \Big|_{\vec{x}_n,\vec{\varepsilon}(t_n)} (\vec{\varepsilon}(t) - \vec{\varepsilon}(t_n)) + \frac{1}{2} \frac{\partial^2 \vec{g}}{\partial \vec{\varepsilon}^2} \Big|_{\vec{x}_n,\vec{\varepsilon}(t_n)} (\vec{\varepsilon}(t) - \vec{\varepsilon}(t_n))^2 \end{split}$$

- Hessians are updated (CFD-Bofill¹) and are recalculated only every 20 steps
- 3rd 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 (2.9×10¹⁴ W cm², CW, Δt=0.25 fs)





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 $i \hbar dP(t)/dt = [F(t), P(t)]$
- TD-CI: integration of the time dependent Schrodinger equation expanded in terms of the field-free ground and excited states

$$i\hbar d\Psi / dt = \hat{H}\Psi$$

$$\Psi(t) = \sum C_i(t) \psi_i$$

$$i\hbar \begin{bmatrix} dC_1 / dt \\ dC_2 / dt \\ \vdots \\ dC_n / dt \end{bmatrix} = \begin{bmatrix} \omega_1 + \vec{E}(t) \cdot \vec{\mu}_{11} & \vec{E}(t) \cdot \vec{\mu}_{12} & \cdots & \vec{E}(t) \cdot \vec{\mu}_{1n} \\ \vec{E}(t) \cdot \vec{\mu}_{21} & \omega_2 + \vec{E}(t) \cdot \vec{\mu}_{22} & \vec{E}(t) \cdot \vec{\mu}_{2n} \\ \vdots & \ddots & \vdots \\ \vec{E}(t) \cdot \vec{\mu}_{n1} & \vec{E}(t) \cdot \vec{\mu}_{n2} & \cdots & \omega_n + \vec{E}(t) \cdot \vec{\mu}_{nn} \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \\ \vdots \\ C_n \end{bmatrix}$$

- Requires the energies of the field-free states, ω_i , and their transition dipoles, μ_{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 a 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

$$\dot{t}\frac{\partial\Psi(t)}{\partial t} = \hat{H}_{el} - \vec{\mu}\vec{E}(t) - i\hat{V}_{abs}$$





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



Krause, P.; Sonk, J. A.; Schlegel, H. B. J. Chem. Phys. 2014, 140, 174113



Hydrogen atom ionization rate as a function of field strength





Ionization rate of H₂⁺ as a function of bond length

As the bond length is stretched, the ionization rate increases due to charge resonance enhanced ionization (CREI)

Accurate grid-based method Bandrauk and co-workers (only suitable for1 and 2 electron systems) Using gaussian basis functions (suitable for many electron systems)









Time-dependent excited state populations of HCl⁺ and HCO⁺

Ground state and $\sigma \rightarrow \sigma^*$ state populations for (a) HCl⁺ and (b) HCO⁺

Similar to H_2^+ , a chargeresonance enhanced ionization mechanism contributes to the increased ionization rate as the bonds are elongated





Ionization of Ethylene, Butadiene and Hexatriene



Krause, P.; Schlegel, H. B. J. Chem. Phys. 2014, 141, 174104



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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