A Laser, a Genetic Algorithm and Some Molecules: Ingredients for Controlled Photchemistry

Rajarshi Guha

Penn State University

Overview

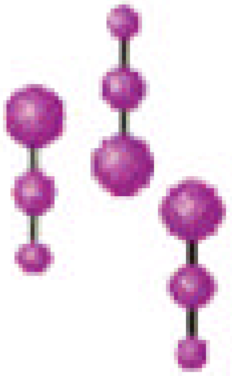
- A review of laser power & effects on molecules
- Photochemical reactions with strong & weak field lasers
- Designing a laser pulse and using a genetic algorithm (GA) to control sequences of pulses
- Experimental results

A Brief History of Laser Power

- The first lasers were continous with powers of the order 10^3 W
- Q switching allows nanosecond pulses and powers up to 10^6 W
- Mode locking creates picosecond pulses and powers up to 10^9 W
- Further increases in power were achieved by chaining laser amplifiers
- Chirped Pulse Amplification achieves sub picosecond pulses and petawatt powers (10^{15} W)

The Effects of Power

- Alignment



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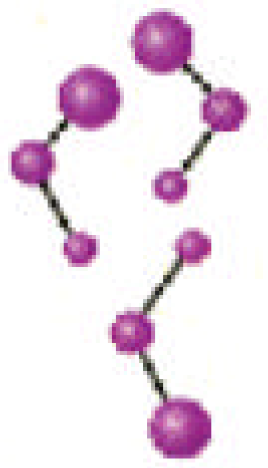
[a] K. Yamanouchi, *Science*, **2002**, 295, 1659

The Effects of Power



- Alignment
- Deformation

K. Yamanouchi, *Science*, **2002**, 295, 1659

The Effects of Power

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- Coulomb explosion

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The Effects of Power

- Alignment
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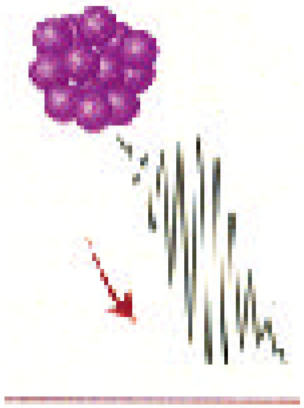
- Coulomb explosion
- X-ray emission



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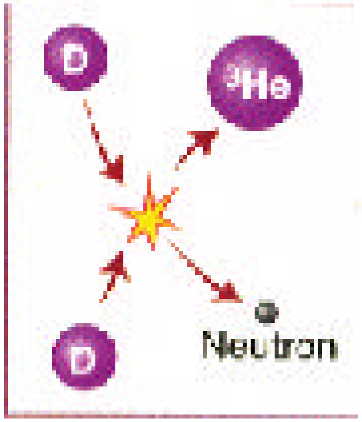
The Effects of Power



- Alignment
- Deformation
- Coulomb explosion
- X-ray emission
- Nuclear reaction

K. Yamanouchi, *Science*, **2002**, 295, 1659

Dressing a PES

- Laser fields of $\mathbf{10^{14}}$ to $\mathbf{10^{15}\ W/cm^2}$ can mix electronic states
- Effectively, the PES is deformed
- Controlling the deformation leads to controlling the direction of nuclear motion
- Selective bond breaking may be achieved

Photochemical Reactions

- Usually employs weak field lasers
- The laser must be tuned to the molecular resonance
- Limited to reactions where bond dissociation energies are less than $\sim$50 kcal/mol
- Due to IVR, selective bond breaking is difficult
- We thus lose control over the reaction after initial irradiation

Strong Field Lasers

- Intensities are of the order of $\mathbf{10^{13}\ W/cm^2}$
- Leads to Stark shifting & multiphoton excitation
- Multiple eigenstates are brought into resonance
- Bandwidth restriction removed

Controlled Radiation Fields

- Such fields have been generated mainly in NMR experiments
- Various waveforms have been developed to:
  - Excite small regions of a spectrum
  - Suppress solvent peaks

Designing a Laser Pulse

- Designing a laser pulse for reaction control is more complex than modulating RF waves
- Requires knowledge of the *complete* Hamiltonian

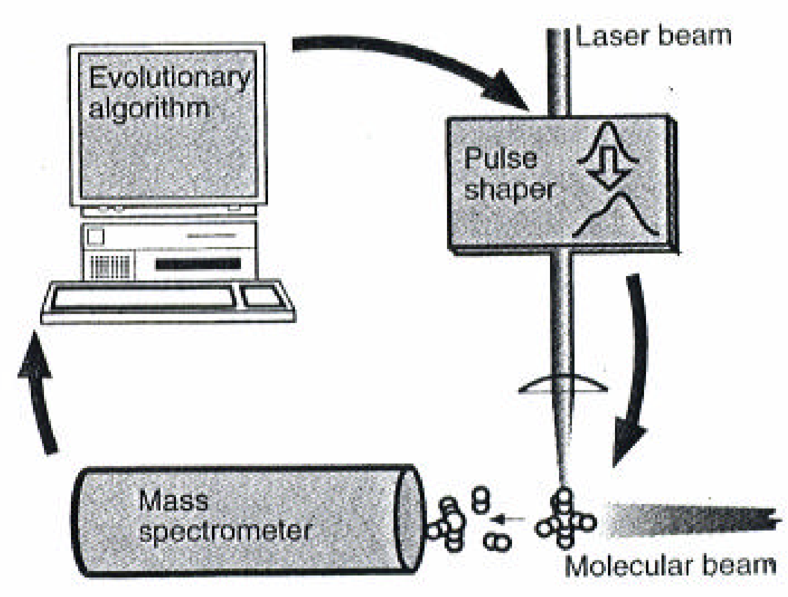
Designing a Laser Pulse

- Problems:
  - Intense laser fields cannot be treated as perturbations
  - Complete Hamiltonians are generally not available
  - The calculated field must account for errors in the Hamiltonian & actual beam
- Numerical design of a pulse is unfeasible

Closed Loop Methods

- An iterative method to reach an optimal state
  - Perturb the system
  - Observe the effect(s) of the perturbation
  - Modify the perturbation and repeat
- Stop when the system is in the required state
- This has been implemented using a GA as the controlling mechanism

Designing a Laser Pulse



- Solution - Analog Computation:
  - Use the laser itself as a *computer*!
  - Apply a field to the molecules
  - Analyze products
  - The report is then used to modify the laser field

A. Assion et al, *Science*, **1998**, 282, 919

Using a GA to Design Pulses

- Split a laser beam into 128 bands
- Each band can have its phase & amplitude modulated
- Modulation is achieved by mutations and crossover within a population of beams
- After modulation, the bands are recombined to give the unique pulse

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R.J. Levis et al, *Science*, **2001**, 292, 709

The GA Details

- Groups of 16 neighboring pixels are tied together, giving a genome with 16 active sites
- Initial population consists of 40 randomly generated pulses
- Fields are propagated using proportional selection
- New fields are generated by cross over and mutation

Mechanisms of Control

- Two possible control mechanisms can occur:
    - Trivial Control
    - Non Trivial Control

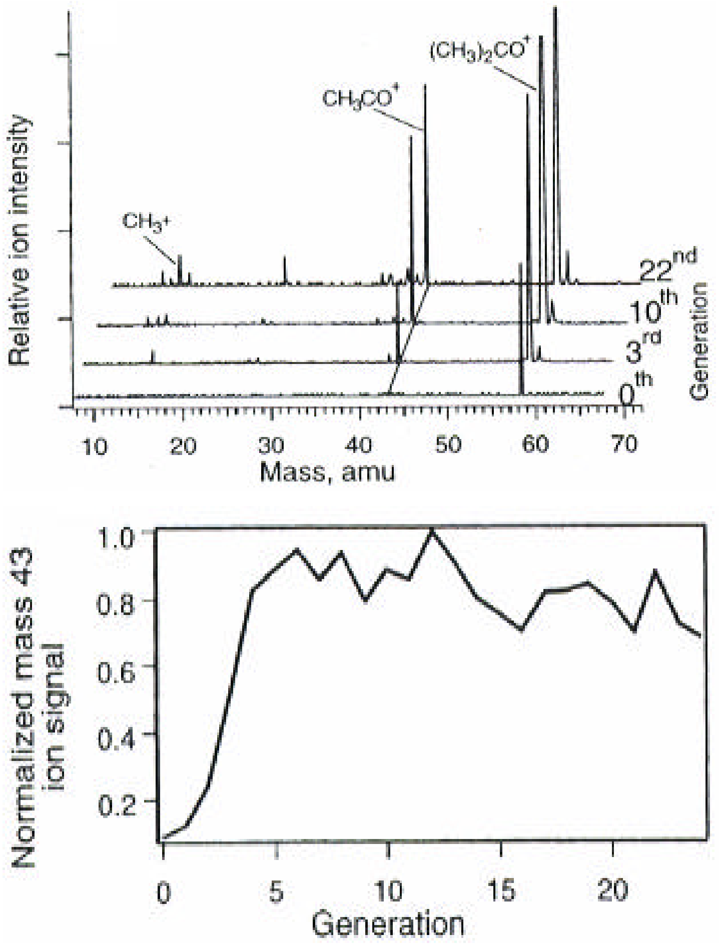
Mechanisms of Control

- Trivial Control
  - Due to simple intensity or pulse duration effects
- Non Trivial Control
  - Due to interaction of the laser pulse with the molecular wavepacket
  - Thus, dependant on the shape of the pulse

Mechanisms of Control

- The nature of control can be verified experimentally
- Ion yields from traditional and pulse shaping experiments are compared
- Pulse shaped experiements should not be signifcantly affected by pulse intensity or duration.

Catching the Signal

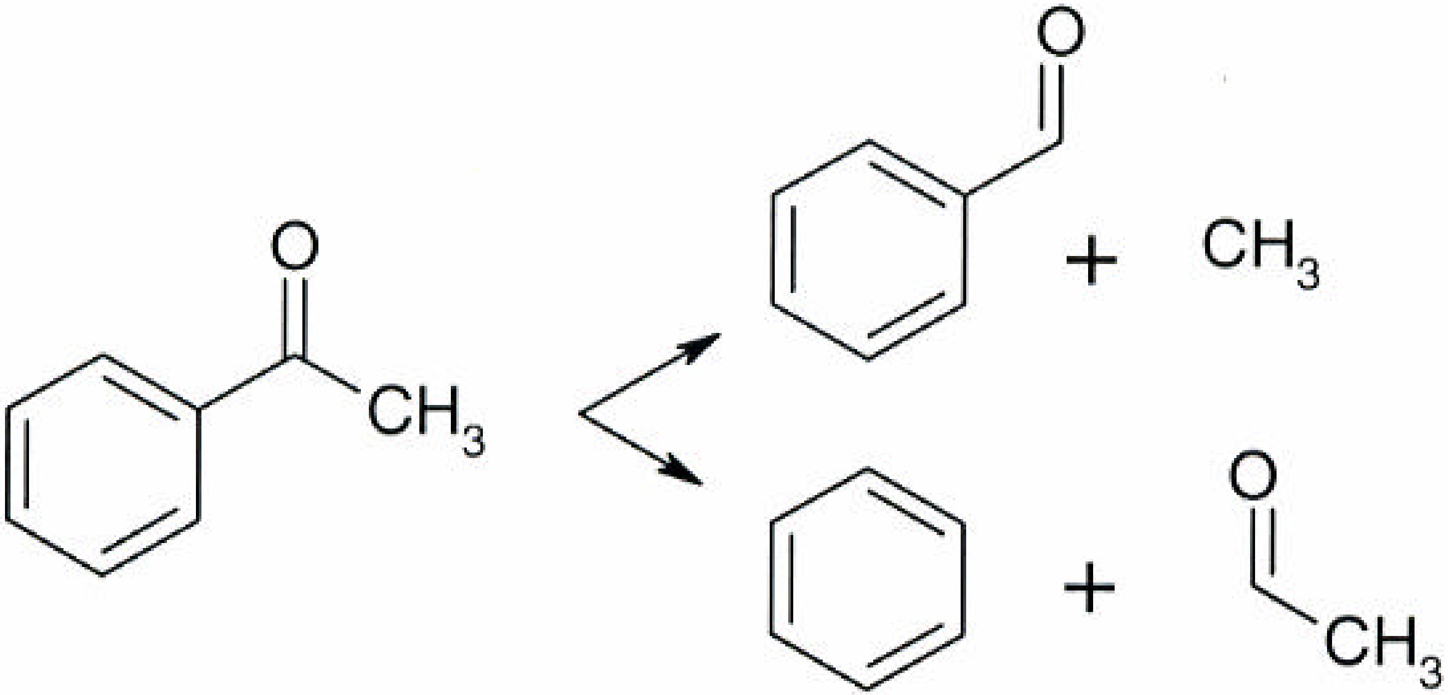


- The initial $\mathrm{CH_3CO^+}$ signal is nearly invisible
- The GA is able to pick it out and hence maximize it
- The signal increases rapidly and then plateaus - variations are due to random change.

R.J. Levis et al, *Science*, **2001**, 292, 709

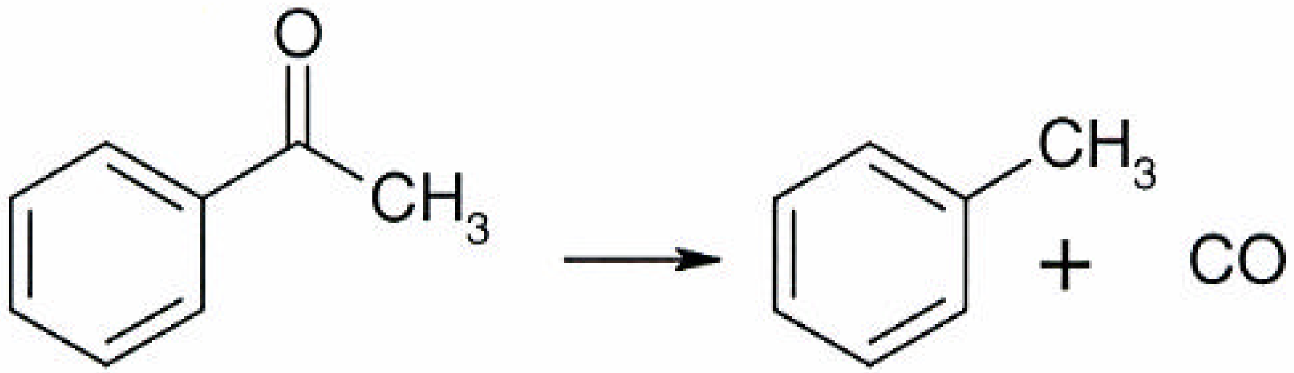
Acetophenone Reactions

- Acetophenone can undergo cleavage in two possible ways:



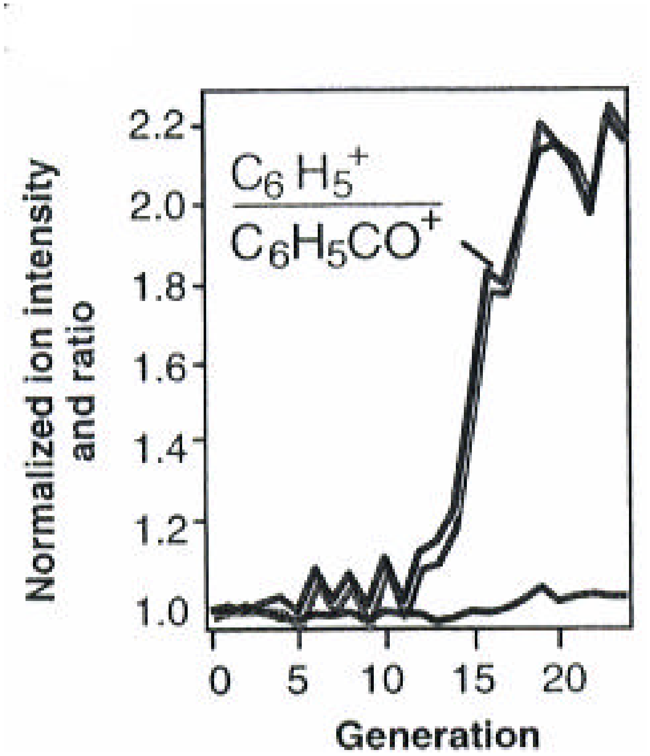
Acetophenone Reactions

- Acetophenone can also undergo a rearrangement to generate toluene



- It was possible to experimentally specify which path would be followed

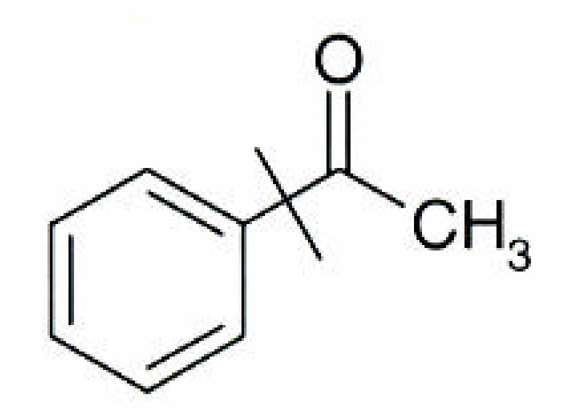
Dissociative Cleavages

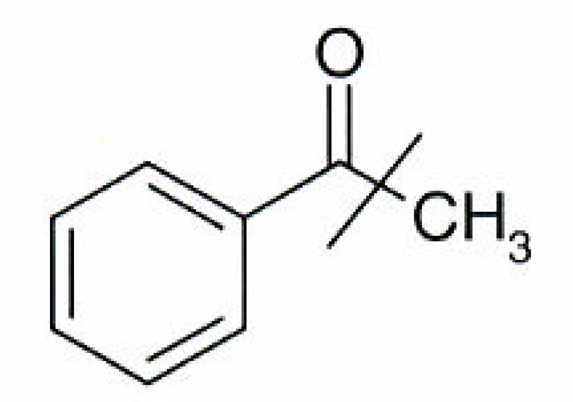


- By setting the goal to maximization of the $C_6H_5^+/C_6H_5CO^+$ ratio, we are specifying cleavage of the phenyl group
- The $C_6H_5CO^+$ signal remains relatively constant

R.J. Levis et al, *Science*, **2001**, 292, 709

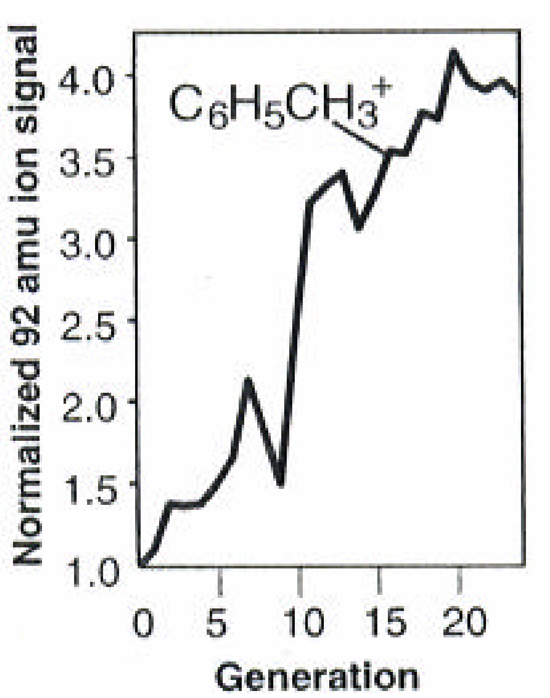
Interesting Features





- The $\mathbf{Ph - COCH_3}$ bond energy is ∼100 kcal/mol
- The $\mathbf{CH_3 - COPh}$ bond energy is ∼85 kcal/mol
- We are thus able to guide a reaction along an energetically unfavorable pathway

Dissociative Rearrangement



- Tradition EI mass spectrum of acetophenone does not exhibit a toluene signal
- The TOF mass spectrum contains a toluene signal
- Hence, it is possible to instruct the GA to maximize the toluene pathway

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R.J. Levis et al, *Science*, **2001**, 292, 709

Nature of Control

- In this case, control is non trivial:
  - Unlikely that trivial control could increase the phenyl intensity but keep that of phenylcarbonyl constant
  - Increasing pulse duration and lower intensities both decreased ion intensity monotonically in reference experiments.
  - No such correlation in pulse shaped experiments.

Conclusions

- A laser can indeed be *taught* to control the dynamics of a reaction
- *A priori* knowledge of the molecular PES or Hamiltonian is not required
- It is possible to drive a reaction in specific directions - cleavage or dissociation in this case
- Reactions with high dissociation energies can be optically controlled