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

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1 Introduction

The interaction of light with matter has been an intensely studied area - both theoretically and experimentally. Lasers are one of the most important tools for such experimental research. Progress in this area has been linked to the evolving capabilities of lasers. There are two features of lasers that are of importance in the study of light matter interactions - the pulse duration and intensity. Rapid improvements in these two features have allowed scientists to probe regimes where molecular interactions can be observed on molecular timescales. However, though these features allow us to observe molecular phenomena, manipulation of these features does not allow us to reach our ultimate goal, viz. control of molecular phenomena. To have such control one must look at another feature of lasers - the shape of the pulse itself.

1.1 Speed and Power

Since the invention of the pulsed laser in the 1960's, the peak power capabilities of lasers have increased by successive orders of magnitudes. This has been achieved by various methods. The first lasers were free running, with durations of microseconds and peak powers in the kilowatt range. In 1962 modulation of the laser cavity quality factor (Q switching) enabled the same amount of energy to be released on nanosecond time scales, thus raising the power output to the megawatt range. The next increase in power was achieved with the technique of mode locking which enabled generation of pulses in the pico second time frame, thus giving peak powers in the gigawatt range. Further increases in output energy were made by chains of laser amplifiers.

However, at these extreme intensities, the index of refraction of the gain media becomes linearly proportional to the intensity, which can be described by the equation,[1]

$$n = n_0 + n_2 I \tag{1}$$

where n_0 is the index of refraction at low intensities, n_2 is the nonlinear index of refraction, I is the intensity and n is the observed index of refraction. Additional nonlinear problems include self focusing, filamentation and self phase modulation[2] occur. Such non linear optical responses can distort or even break the laser beam. The only way around this problem was to increase the beam diameter. As a result, though pulse durations decreased over the years, the peak power output remained relatively constant.

However, a major advancement was made in the mid 1980's with the development of chirped pulse amplification (CPA), whereby an extremely short duration laser pulse is first stretched, amplified and then recompressed. The net result of this technique was peak powers in the terawatt (and even petawatt) range could be generated for pulses of sub pico second durations.

1.2 High Intensity Lasers & Molecules

Given such ultra intense lasers, what can be done with them? Below intensities of 10^{12} W/cm^2 (the peturbative regime), weak interactions with light causes atoms and molecules to absorb one or more photons. However it is beyond this regime that many interesting phenomena may be observed. The range of intensities between 10^{12} and 10^{17} W/cm^2 are termed the Coulombic regime, as the laser energy is nearly equal to the binding energy of the valence electrons. Around 10^{12} W/cm^2, molecular alignment is observed - molecules become aligned with the laser polarization due to the torque that is generated between the non resonant light fields and the induced dipole moment of the molecule.[3] An example of such molecular alignment in CO_2 has been reported by Hoshina *et al.*[4,5]

One of the most interesting phenomena from a chemists point of view occurs in the range of 10^{14} to 10^{15} W/cm^2. In this regime, a strong mixing of electronic states of a molecule is seen to occur. Since the electronic states of a molecule define its potential energy surface (PES), lasers of such intensity provide a means to deform molecular PES's. Such control over the molecular PES provides a means to control the fate of the molecule in a reaction. Controlling reactions with the help of *light dressed* PES's will be discussed in more detail in a later section.

Beyond peak intensities of 10^{15} W/cm^2 , molecular deformation is observed - linear molecules become bent and bent molecules become stretched.[3] Such phenomena have been ascribed to the formation of new adiabatic internuclear potentials arising from avoided crossings between *dressed* molecular electronic states.[6] During such geometrical deformation, tunneling ionization[7,8] occurs. This is a phenomenon where electrons can escape by tunneling through the deformed Coulombic barrier. This results in singly and multiply ionized (intact) ions.[9] After formation of such ions, strong Coulombic repulsive force cause an abrupt fission of chemical bonds (known as Coulomb explosion).[8,10] Characterization of the resultant fragments by methods such as mass resolved momentum imaging[6] and coincidence momentum imaging[11] allow for the determination of the structure of the parent ions.

We thus see that ultra intense laser fields provide us with a tool to probe and control molecular phenomena. In the following sections I discuss the use of intense laser fields in modifying PES's and controlling chemical reactions.

2 Laser Control of Reactions

Organic chemistry is replete with reactions whose products are the result of irradiation. The product distribution in these cases is controlled by tuning a monochromatic laser source to the excited state of a precursor molecule.[12] The most important feature of this form of manipulation is that after the irradiation there is no more control over the outcome of the reaction. However, in many cases one would like to channel a reaction into a state which might be thermally inaccessible or guide the final distribution of products along a certain path. Thus the ultimate aim would be to control the fate of a reaction in real time. This has been achieved by using closed loop methods using intense lasers. In one set of experiments organometallic clusters were selectively cleaved.[13] In another case, a number of experiments were formed with acetone, triflouroacetone and acetophenone.[12] Both cleavage and rearrangements were exhibited. In both experiments, the closed loop method utilized a genetic algorithm (GA) to enable the laser to learn the photodynamics of the reaction.

2.1 Closed Loop Methods

The concept of a laser being able to learn how to control a reaction was first proposed by Judson *et al.*[14] in 1992. There have been a number of theoretical studies which attempted to design laser sequences to control reactions[15,16] and other molecular processes.[17] However, theoretical methods face a number of computational stumbling blocks. The Hamiltonians under consideration have a large number of degrees of freedom, all of which need to be controlled simultaneously. Furthermore, even though it has been shown that under appropriate conditions[15] a laser field can be used to drive a reaction in a specified direction, to achieve this goal, one requires the complete Hamiltonian for the system. Such Hamiltonians are usually unavailable for systems larger than a few atoms. In addition, the generation of the laser beam itself is subject to laboratory error. The net result is that the fields generated from approximate Hamiltonians will not be able to account for the errors in the Hamiltonian and the beam itself.

The use of a GA coupled to a laser to generated tailored pulses was first demonstrated experimentally by Bardeen*et al.* [17] where they were able to optimize the electronic population transfers in a laser dye molecule. Schemes to implement control of chemical reactions were proposed by Judson *et al.*[12,14] and Aisson *et al.*[13] All the above mentioned schemes attempt to solve the Schrödinger equation. However, rather than attempting a numerical evaluation, they use a laser coupled to a learning algorithm creating a system which effectively acts as an analog computer. The laser (along with detection apparatus) acts as an input/output system that is able to report the effects of a field on the molecules. When coupled with a learning mechanism (a genetic algorithm in this case), the scheme allows for the recognition of patterns and thus leads to the design of a new set of fields to be applied to the molecules. Successive iterations cause the system to converge to the desired state - in this case, the desired products.

Thus information about the molecular potential energy surfaces or Hamiltonians are no longer required. The main requirement for such a procedure is the rapid generation of laser pulses. With the development of femtosecond lasers, experimental demonstrations of the theoretical concepts has been achieved.

2.2 Strong Field versus Weak Field Photochemistry

In general photochemical reactions employ weak field continuous lasers. As a result the laser must be precisely tuned to the molecular resonance. Matters can be improved by using weak field pulsed beams. However, the low bandwidth around the laser frequency does not provide much control. In addition intra molecular vibrational relaxation (IVR) leads to the rapid dissipation of the incident energy. As a result controlled cleavage of specific bonds is difficult to achieve. Using strong field pulses (10^{13} W/cm^2) reduces the need for precise tuning required to match resonance frequencies. This is due to the fact that Stark shifting[18] and multi photon excitation shifts multiple eigenstates into resonance. As a result, bandwidth restrictions are effectively removed.

The application of strong field pulsed beams to organic molecules results in a wide variety of products ranging from ionized molecules to decomposition fragments. The rapid generation of such strong field pulses and observations of their interaction with molecules allows the GA to generate optimal electric fields which can guide the reaction to the desired product.

2.3 Mechanisms of Control

Photochemical reactions employing intense laser beams are usually controlled by one of two mechanisms - trivial or non trivial control.[12] Trivial control implies that the observed photochemistry arises from simple intensity or pulse duration effects. In other words, the shape of the pulse itself does not have any significant effect. Non trivial control occurs when the pulse shape interacts with the molecular wave packet. In such cases the nature of the products and their distribution is sensitive to the time dependant structure of the pulse shape. The type of control being exerted can be studied by comparing relative and absolute ion yields versus generation (in a GA) to those obtained by traditional intensity and pulse duration experiments.[12] Experiments[12] were conducted to determine whether pulse shaping (i.e. non trivial control) rather than intensity / duration effects were guiding reactions along specific paths.

3 Designing a Learning Laser System

A learning laser system has been demonstrated by Levis *et al.* [12] The basic idea was to generate a series of shaped pulses by modulating the phase and amplitude of the beam. The modulation (or design of the pulse shape) was controlled by a GA. Each pulse was then allowed to interact with the reactant molecules and the products of irradiation were recorded. By detecting specific cleavages or rearrangements, those fields which produced the desired effects were carried over to successive generations, serving as a guide for the creation of new pulses. After a number of iterations, the guided shaping of pulses converged to an optimal pulse which maximized the generation of a specific product.

3.1 Experimental Setup

The experimental setup involved the successive generation of unique time dependant electric fields by splitting a laser beam into 128 discrete frequency bands using a liquid crystal spatial light modulator (SLM). Each band was independently altered by means of a pair of SLM's and a polarizer. Recombination of the modulated components resulted in a unique time dependant electric field. During the experiment the SLM was controlled by a GA. The algorithm controlled the voltages that determined the phase and amplitude of the components which in turn determines the form of the final pulse. For the setup described there were 256 voltages to be controlled. A constraint imposed was that groups of 16 neighboring pixels were linked to each other. This resulted in the genome having 16 variable sites. In each generation proportional selection was used to select the fittest fields. New fields were created using cross over and mutation. A population of 40 pulses was used to search for the optimal pulse for a specific reaction. The initial pulses were randomly generated and were focused on the reactant molecules. The products of the irradiation were analyzed with a time of flight (TOF) mass spectrometer. The TOF spectra were signal averaged 8 times.

4 Results

Three sets of experiments were run to investigate various features of the learning scheme described above. The experiments indicated that the GA was indeed optimizing the pulses to generate specific products in a given reaction. Furthermore, it was possible to direct the GA to optimize in favor of dissociative rearrangements or cleavages. Finally, comparing the results obtained with traditional experiments indicated that it was the pulse shape that was interacting with the evolving molecular wave packet, rather than simple intensity effects, to generate the observed results.

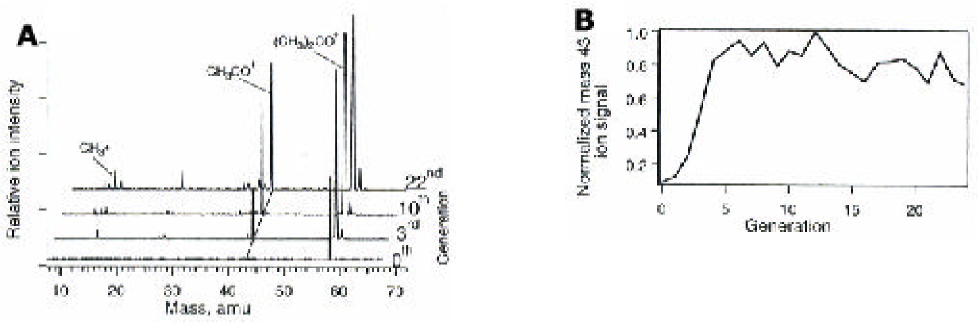

Figure 1: **A**. Mass spectra of acetone for successive generations. **B**. CH_3CO^+ signal as a function of generation.[12]

4.1 Exercising the GA

The first set of experiments attempted to maximize the generation of CH_3CO^+ fragments from acetone.

The results indicated that the GA did indeed optimize the pulses so as to maximize the CH_3CO^+ signal in the TOF spectra. Figure 1A is a plot showing the mass spectrum of the sample versus the generation. In the first few generations the CH_3CO^+ signal is hardly observable but is sufficiently strong to be picked out by the GA. Once selected, the signal increases rapidly until it reaches a more or less steady value. Subsequent changes in the signal were due to random mutations and cross overs. Figure 1B shows the variation in the CH_3CO^+ signal as a function of generation. This experiment shows that it is possible for a closed loop method to optimally control dissociation. Furthermore, as can be seen from the figures above, the method allows the manipulation of the mass spectrum by designing pulses.

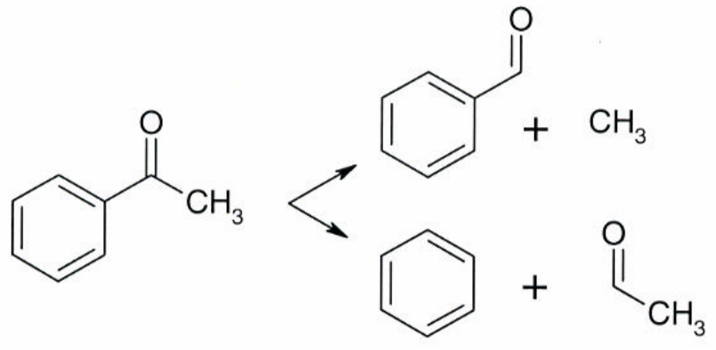

Figure 2: Cleavage of Acetophenone

4.2 Determining the Type of Control

As mentioned in Section 2.3, control in photochemical reactions can be trivial or non trivial. An example of an experiment which attempted to determine the nature of control in the closed loop learning scheme involved the dissociation of acetophenone.[12] The experiment involved the optimization of the $C_6H_5CO^+/C_6H_5^+$ ratio and vice versa. In the former case, the optimization led to the preferential cleavage of the methyl species and in the latter it led to the preferential cleavage of the phenyl species. The scheme is shown in Fig. 2 point to note in both cases was the fact that the ratio was increased by increasing the phenyl ion intensity while keeping the phenylcarbonyl intensity more or less constant. This is interesting due to the fact that the bond energy for phenyl-carbonyl bond is $\sim$100 Kcal/mol and that for the methyl-phenylcarbonyl bond is $\sim$85Kcal/mol.

The action of non trivial control was evidenced by the fact that in the reference experiments (no pulse shaping) the absolute ion intensities decreased monotonically with increase in pulse duration or decrease in pulse intensity. Such a relationship was not seen in the case where the pulse was shaped. Another indication of non trivial control was that in the reference ex-

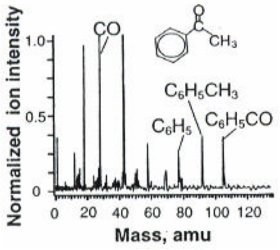

Figure 3: TOF mass spectrum of acetophenone[12]

periments, changes in intensity altered the $C_6H_5^+/C_6H_5CO^+$ ratio by 1.5; the process however required a change in the $C_6H_5CO^+$ ion intensity of one order of magnitude. The closed loop experiment however, showed a quadruple increase in the ratio with no accompanying change in the $C_6H_5CO^+$ intensity.

4.3 Dissociative Rearrangement

Both the previous experiments involved dissociative cleavage of the parent molecule. However rearrangements are also possible. This has been observed in the strong field photochemistry of acetophenone. Traditional EIMS experiments on acetophenone do not exhibit any toluene signals. However a signal for $C_6H_5CH_3^+$ can be seen in the TOF mass spectrum (Fig. 3) when a strong field is used. This observation indicated that maximization of the toluene signal should be possible. Indeed, when the GA was programmed to optimize the signal, the ion yield increased 4 times.[12] The increase of the $C_6H_5CH_3^+$ signal versus the generation can be seen in Fig. 4.

5 Conclusion

Lasers have come to play an important role in numerous fields of chemistry. However, in many cases, involving the probing of chemical reactions, it is a relatively crude tool. With the

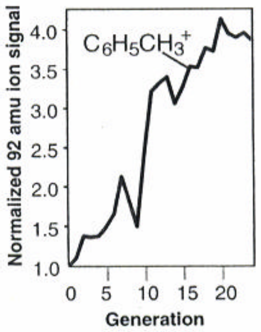

Figure 4: Increase of toluene signal versus generation[12]

development of ultra intense, high speed lasers, high energy regimes of molecules are open to exploration; regimes where new photochemical products may be observed, which may not be the case for the usual weak field lasers.

However, the ultimate goal is to be able to control the path and hence outcome of a reaction. Together with high power lasers and a learning algorithm as described above, such control is now available. Pathways involving cleavage or rearrangement can be specified at will. Even energetically unfavorable pathways can be selected over more favorable ones.

The intense laser fields discussed here cause a large distortion in the eigenstates of the molecules and result in highly nonlinear electron dynamics. However the learning algorithm is able to pick out features of the pulses that cause selective cleavage and rearrangments, without a priori knowledge of the molecular potential energy surface or Hamiltonian.

Thus, not only do ultra intense lasers open up new regimes of molecular energies to study, coupling such laser systems with learning algorithms allows for the exploration of molecular reactivity control mechanisms.

References

1. Mourou, G. A.; Barty, C. P.; Perry, M. D. *Phyics Today* **1998,** 22.
2. Milonni, P. W.; Eberly, J. H. *Lasers;* Wiley-Interscience, John Wiley & Sons: New York, 1988.
3. Yamanouchi, K. *Science* **2002,** *295,* 1659.
4. Hoshina, K.; Yamanouchi, K.; Ohshima, T.; Ose, Y.; Todokoro, H. *Chem. Phys. Lett.* **2002,** *353,* 33.
5. Hoshina, K.; Yamanouchi, K.; Ohshima, T.; Ose, Y.; Todokoro, H. *Chem. Phys. Lett.* **2002,** *353,* 27.
6. Hishikawa, A.; Iwamae, A.; Yamanouchi, K. *Phys. Rev. Lett.* **1999,** *83,* 1127.
7. Zon, B. *J. Exp. Theo. Phys.* **2000,** *91,* 899.
8. Ledingham, K.; Singhal, R.; Smith, D.; McCanny, T.; Graham, P.; Kilic, H.; Peng, W.; Wang, S.; Langley, A.; Taday, P.; Kosmidis, C. *J. Phys. Chem. A* **1998,** *102,* 3002.
9. Ledingham, K.; Smith, D.; Singhal, R.; T., M.; Graham, P.; Killic, H.; Peng, W.; Langley, A.; Taday, P.; Kosmidis, C. *J. Phys. Chem. A* **1999,** *103,* 2952.
10. Poth, L.; Castleman, A. J. *J. Phys. Chem. A* **1998,** *102,* 4075.
11. Hasegawa, H.; Kishikawa, A.; Yamanouchi, K. *Chem. Phys. Lett.* **2001,** *349,* 57.
12. Levis, R. J.; Menkir, G. M.; Rabitz, H. *Science* **2001,** *292,* 709.

13. Assion, A.; Baumert, T.; Bergt, M.; Brixner, T.; Kiefer, B.; Seyfried, V.; Strehle, M.; Gerber, G. *Science* **1998,** *282,* 919.

14. Judson, R. S.; Rabitz, H. *Phys. Rev. Lett.* **1992,** *68,* 1500.

15. Shi, S.; Rabitz, H. *J. Chem. Phys.* **1990,** *92,* 364.

16. Tannor, D.; Rice, S. *J. Chem. Phys.* **1985,** *83,* 5013.

17. Bardeen, C.; Yaokvlev, V.; Wilson, K.; Carpenter, S.; Weber, P.; Warren, W. *cpl* **1997,** *280,* 151.

18. McIlrath, T.; Bucksbaum, P.; Freeman, R.; Bashkansky, M. *Phys. Rev. A* **1987,** *35,* 4611.