

Laser Coherent Control of Quantum Dynamics at the CSIR: NLC

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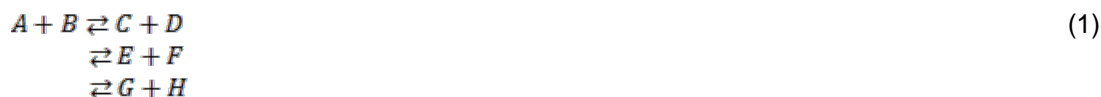
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Abstract

Coherent control of quantum dynamics in optical, molecular and biological systems is a rapidly advancing field with many possible applications. This field of study was originally motivated by the goal of steering photoreactions into specific reaction channels. The principle used is controlled interference of the quantum wave functions via time domain shaped ultra-short pulses. The time/frequency product of a pulse is a constant, determined by Heisenberg's uncertainty principle, therefore, a short time pulse results in a pulse that has a broad frequency bandwidth. In addition, there is a fixed phase relation between the various frequency components that constitute the pulse. Time domain beam shaping allows the modification of the phase and amplitude in the frequency domain of the Fourier transform that constitute the pulse and then transforming back to the time domain. This has the effect of shaping the pulse in time. Various techniques of laser coherent control exist, but they all depend on manipulating the phase and amplitude of the laser pulse, which controls the quantum dynamics via the interference of the quantum wave functions. This paper will give an introduction to coherent control, specifically with regards to optical, molecular and biological systems, as well as an overview of the various coherent control experiments at the CSIR National Laser Centre (NLC).

1. Introduction

Consider the following chemical reaction:



The branching ratio of the various reactions can be written as x:y:z, where for example x is the sum of the number of C and D molecules and similarly for y and z. It is obvious that it would be advantageous if some form of control of the branching ratios were possible, since this would allow a form of control on the outcome of the reaction. In "classical" equilibrium chemistry these branching ratios are controlled via the various reaction constants. These reaction constants are determined by the Arrhenius equation which can be written as:

$$k = Ae^{-E_a/RT} \tag{2}$$

A is called the pre-exponential factor and E_a is called the activation energy. As can be seen from the equation, the reaction constant is dependent on the temperature. Thus changing the reaction temperature

allows a form of control of the reaction. However, the Arrhenius equation assumes thermal equilibrium between all the degrees of freedom of the molecule and the level of control is limited.

The invention of the laser resulted in the availability of light, with among other properties, that of high intensity and at the same time a narrow spectral bandwidth. The idea was to use this narrow spectral bandwidth to selectively excite a specific vibrational mode of a molecule. It was postulated that this could lead to the control of chemical reactions using only the laser light. It is important to explain why it was thought that this could lead to a new form of reaction control. When a molecule is heated by a normal thermal source, such as a Bunsen burner, the energy of the molecule is distributed equally among all its degrees of freedom. This is the result of the equipartition theorem. A molecule has 3 translational, 2 rotational and $3N-5$ vibrational degrees of freedom, here N is the number of atoms in the molecule. Thus, in a polyatomic molecule most of the thermal energy of the molecule is distributed among the various vibrational modes. The dissociation of a thermally heated molecule is a statistical process and the weakest bond has the largest probability of breaking. If a specific vibrational mode of a molecule could be excited without exciting others, then that bond can be broken. This would, therefore, allow much more control of the reaction paths. The idea was to tune the laser to a specific resonance of a vibrational mode and then, via a multi-photon process, break this specific bond. This approach is referred to as mode selective chemistry. It was expected that this would lead to new and novel chemical reactions that would not normally occur under thermal equilibrium. However, it was found experimentally that this does not work. The reason is the so-called inter-vibrational relaxation (IVR). IVR is caused by the fact that a molecule is not a harmonic oscillator, but rather an anharmonic oscillator. This means that the various vibrational modes are coupled. If one vibrational mode is excited, others will very quickly start vibrating in sympathy, due to the coupling of the modes. The timescale of IVR is in the region of 100s of femtoseconds to picoseconds. Thus, this process is much faster than the time duration of narrow band laser pulses, which are in the region of nanoseconds. The result was that no laser control was possible and the reaction dynamics was similar to a thermally heated molecule.

The invention of the femtosecond laser offered the possibility of exciting the molecule at timescales which are shorter than the IVR time, again offering the possibility of laser control of the chemical reaction dynamics. However, there was one problem: the Fourier relation between the time duration and bandwidth of the laser dictates that a short pulse laser necessarily has a broad bandwidth. For a 100 fs laser, this bandwidth typically spans the resonance frequency of more than one vibrational transition. This means that it would not be possible to mode-selectively excite a specific vibrational mode without, at the same time, also exciting a different mode. The breakthrough that was developed is so-called coherent control. Coherent control uses the quantum mechanical properties of the molecule, as well as some fundamental quantum mechanical principles. The way that it works is as follows: Suppose that there are more than one path to reach a final state. According to quantum theory, if there are multiple pathways from an initial state to a final product state then one cannot tell, even in principle, which path was taken. In such a case, there will be interference between the molecular quantum wave functions that was generated by the different pathways. This means that the quantum wave functions in the product state, produced by the different pathways, will interfere much the same as normal waves that took different paths will interfere. One criteria for interference is that the process is coherent, i.e. there must be a fixed phase relation between the different pathways. Hence the term coherent control. Thus, by controlling the phase of the different pathways, certain reaction channels can be optimized. Considering a normal wave interference experiment, such as that shown in Figure 1, will help with the understanding of the process. Figure 1 is a simple, two-slit experiment, where two slits are illuminated by a coherent laser beam. Interference from the two beams exiting from the two slits will produce the familiar bright and dark fringes. This is the well-known Young's double slit experiment. The setup at the bottom of Figure 1 one is different, since a phase difference of π was introduced in the bottom slit. The result is a shift in the bright fringes as shown in the Figure. Hence, control was exercised by introducing a phase difference in the one path. Similarly, phase differences induced by the laser pulse are used to control the population in specific vibrational levels in a specific vibrational mode.

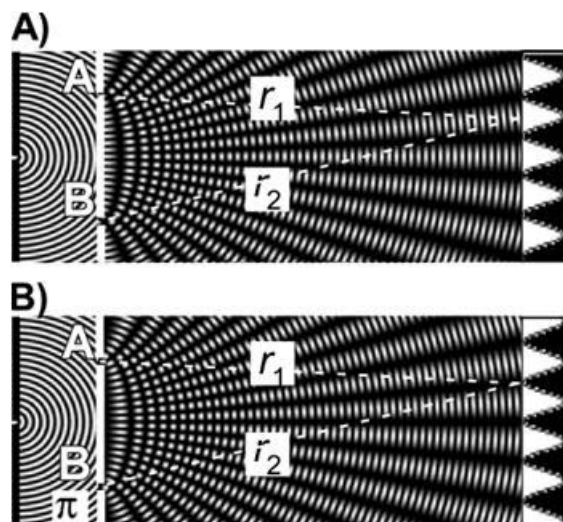


Figure 1. Two examples of Young's 2-slit interference experiment. In example A) there is no phase difference between the waves emerging from slits A and B. In version B) a pi phase difference is introduced in slit B. This causes a shift in the position of the bright fringes.

The question now is how phase could be transferred to different pathways in a molecule using a femtosecond laser beam? As mentioned, a femtosecond laser beam has a broad bandwidth. The result is that different pathways could be excited simultaneously. If a pulse is shaped in time, then different frequency components that make up the pulse, will have different phase values. This is a fundamental property which comes directly from Fourier analysis. Different pathways will have different excitation frequencies and thus quantum wave functions produced by the different pathways will have different phases and will thus interfere. Constructive interference can be used to maximize a certain population level, while destructive interference will similarly minimize certain population levels. The result is that control is possible at a time scale that is less than the typical IVR times.

One further problem remains. Ab Initio calculation of the required pulse shapes for optimizing a certain population level is, in most instances, extremely difficult and most of the time impossible. The reason for this is the extremely complicated molecular Hamiltonians. The breakthrough came with the idea of Rabitz[1], namely to use a learning algorithm to determine the correct pulse shape. This is shown schematically in Figure 2. The principle is as follows: An initial population of various laser pulses is randomly generated. Experiments are performed using these various pulses. A diagnostic technique is used to measure the outcome of the interaction of these pulses with the molecular system. A certain measure is used to indicate the effectiveness of a specific pulse. For example, a specific vibrational level population is measured. An optimization algorithm is then used to iteratively optimize this. Typically genetic algorithms are used. The molecule is thus treated as a black box and the feedback loop and optimization algorithm are used to optimize a certain population level. This avoids the problem of calculating the complicated Hamiltonians. This process is shown schematically in Figure 2.

2. Coherent control of the vibrational ground state of a molecule

Most of the work in coherent control currently starts at the ground electronic state, then excites the molecule to the excited electronic state with a shaped pulse before using a dump pulse to prepare it in a specific ground vibrational state. This is the so called pump dump experiment. One of the reasons for doing this is that these transitions are usually in the near-IR. Lasers and beam shaping techniques are readily available in the near-IR. However, this process has a few disadvantages, one being that it is difficult to limit the excitation to the lower vibrational levels of the molecule. The higher vibrational levels have a much faster IVR rate than the lower ones, which, to an extent, negates the advantages of using

short pulses. The IVR rate of the lower vibrational rates of a molecule are relatively long, i.e. 100s of picoseconds. It would seem, therefore, to be advantageous to excite only the lower vibrational levels of the vibrational ground state of the molecule. The disadvantage is that this would require beam shaping in the far-IR. This is not readily available. Published experimental and theoretical results of exciting lower vibrational states of molecules are not available in the literature. It is, thus, also not clear that it would be possible to use coherent control by addressing only the lowest vibrational modes of a molecule.

A two-pronged approach is therefore being followed at the CSIR's NLC. Firstly, a theoretical model was developed to test the feasibility of the process and, secondly, a process of shaping pulses in the far-IR is being developed. This paper concentrates on the first part, i.e. the development and testing of the process using a computer model.

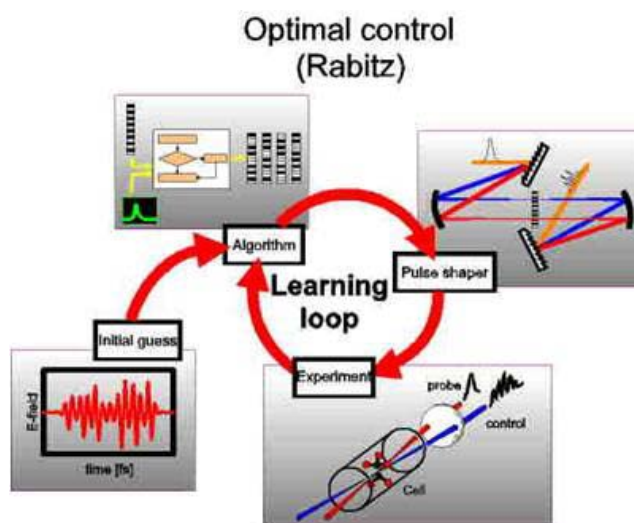


Figure 2. Schematic diagram of optimal control of a chemical reaction via time domain beam shaping and optimization, using a learning algorithm. Source: H Rabitz, Princeton University.

3. Vibrational control model

The selective excitation of an arbitrary vibrational level of a polyatomic molecule, without passage through an intermediary electronic excited state, was modeled. This was achieved by simulating the interaction of a shaped, femtosecond pulse with one vibrational mode of a polyatomic molecule. The carrier frequency of the pulse is chosen near resonant to the ground-to-first-excited vibrational transition of the vibrational mode, and the pulse shape is optimized via closed-loop feedback. The simulation concentrates on the first few vibrationally excited states, since the density of states is still low, thus ensuring that the inter-vibrational decoherence time is relatively long compared to the pulse length.

While various molecules were investigated, this study focuses on a hexafluoride molecule for which detailed spectroscopic data for the ν_3 vibrational mode is available [2]. A multilevel model was developed and can be adapted for any number of levels. A schematic diagram of the multi-level model of the molecule is shown in Figure 3.

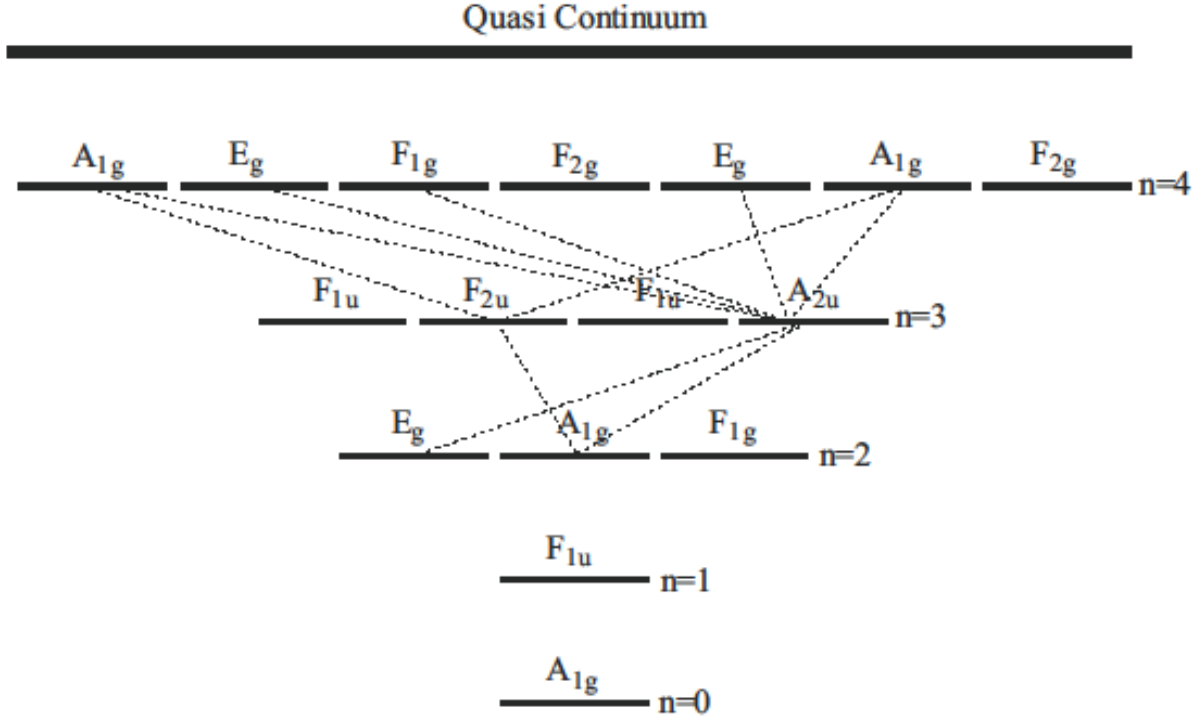


Figure 3. Schematic diagram of the vibrational level diagram of the molecule that was used in the simulation. The ground state of the molecule is triply degenerate. Anharmonic splitting of the excited levels are shown. The broken lines indicate forbidden transitions.

The model reported here was limited to a vibrational quantum number of 4. The spectroscopic data included anharmonic splitting as well as forbidden transitions. The effect of rotational levels was not included. A density matrix approach was followed because this will allow for the introduction of dephasing of the coherent excitation via thermalizing collisions with the reservoir, as well as inter-vibrational relaxation. The time evolution of the density matrix is given by the Von Neumann equation [3]:

$$\frac{d\rho_{ab}}{dt} = -\frac{i}{\hbar} \sum_{i=1}^N (\rho_{ib} I_{ai} e^{i\omega_{ai}t} - \rho_{ai} I_{ib} e^{-i\omega_{bi}t}) \quad (3)$$

where,

$$\omega_{ab} = \omega_a - \omega_b \quad (4)$$

ρ_{ab} gives the elements of the density matrix, ω_a the frequencies of the individual vibrational levels, and I_{ab} the matrix elements of the interaction Hamiltonian [4] which include the detailed time dependence of the shaped femtosecond pulse.

4. Simulation results

A transform limited 350 femtosecond laser pulse with a fluence of 1600 J/m² was used as an initial pulse. Pulse shaping via a Liquid Crystal Modulator (LCM) was simulated by taking the Fourier transform of the input pulse and dividing the spectrum in 640 (the number of pixels in the LCM) equal parts before applying an amplitude and phase mask. The pulse is then inverse Fourier transformed back to the time domain and applied to the molecules using equation (3). The population in each of the vibrational levels is a sum of the

populations in the various anharmonic splitting components of the corresponding vibrational quantum number. The genetic algorithm minimizes a fitness function defined as $1-p$, where p is the population in the target vibrational level. In this example the vibrational chosen for optimization was level 2.

The time evolution of the populations in the various vibrational levels of a molecule excited by the initial transform limited pulse is shown in Figure 3. As can be seen, the population in the targeted vibrational level 2 is approximately 20 percent, or 0.2. Figure 4 gives the population dynamics of the vibrational levels when the laser is excited by a pulse as optimized using a feedback loop and a genetic algorithm. The population in the targeted vibrational level 2 is now approximately 85 percent. This is a significant improvement on the 20 percent of the non-optimized case and illustrated clearly that coherent control has a significant influence on the process. The initial transform-limited pulse, as well as the shaped pulse determined by the genetic algorithm, are shown together in Figure 5. The Frequency Resolved Optical Gating (FROG) traces of the transform-limited pulse, as well as that of the shaped pulse, is shown in Figures 6 and 7. The fitness factor as a function of the generation is shown in Figure 9.

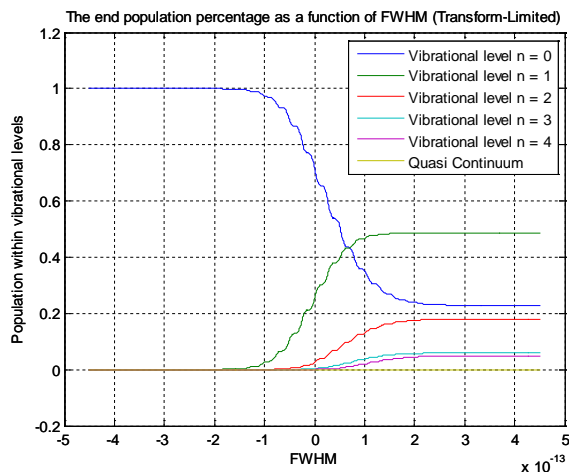


Figure 4. Time evolution of the various vibrational levels of a molecule excited with a transform limited pulse. The target level for optimization was level 2. The population after the transform limited pulse is less than 0.2.

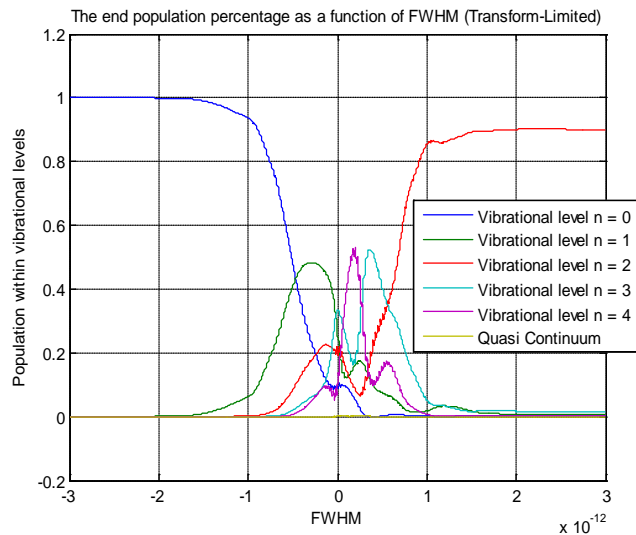


Figure 5. Time evolution of the various vibrational levels of a molecule excited by the optimum pulse as determined by the feedback loop and genetic algorithm. The population of the level 2 is now approximately 0.9, which is considerably higher than the 0.2 of the non-optimized pulse of Figure 3.

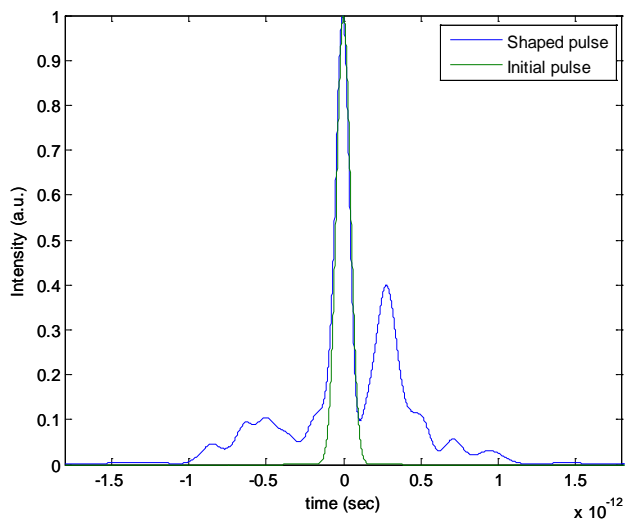


Figure 6. Intensity envelopes of the transform-limited starting pulse as well as that of the optimized shaped pulse.

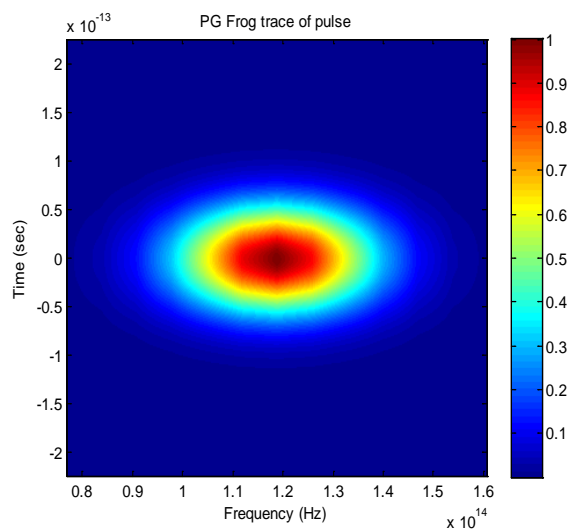


Figure 7. Frog trace of the non-optimized pulse.

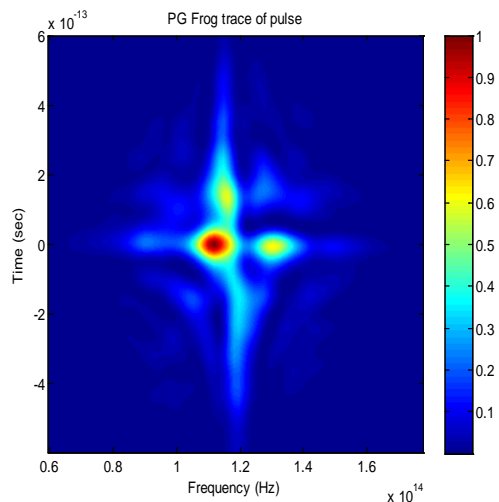


Figure 8. Frog trace of the optimized pulse.

5. Conclusion and suggestions for future work

This work demonstrates that shaped femtosecond pulses can selectively excite vibrational levels in the ground electronic state of polyatomic molecules, without recourse to an auxiliary excited electronic level. This opens up the possibility of novel mode selective chemistry. Excitation of most molecules in the ground vibrational state requires shaped pulses in the mid-IR range. We are currently in the process of developing techniques to generate shaped pulses in this range via difference frequency mixing techniques. Initial simulations indicate that the pulse shaping is reasonably well preserved, even if the shaping is carried out before frequency mixing.

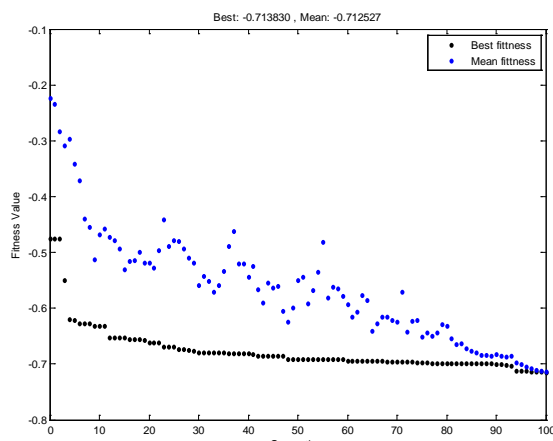


Figure 9. Fitness function as a function of population generation.

6. References

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