PRAMANA — journal of physics

Vol. 82, No. 2
February 2014
pp. 249–253

Quantum coherent control of the vibrational dynamics of a polyatomic molecule using adaptive feedback control of a femtosecond laser

L R BOTHA[1,*], L E DE CLERCQ[3], A M SMIT[1], N BOTHA[1], E RONANDER[2] and H J STRYDOM[2]

[1]CSIR, National Laser Centre, Meiring Naude Road, Gauteng, Pretoria, RSA
[2]Klydon, Meiring Naude Road, Gauteng, Pretoria, RSA
[3]Institute of Quantum Electronics, ETH Zürich, Schafmattstrasse 16, 8093 Zürich, Switzerland
*Corresponding author. E-mail: Lrbotha@csir.co.za

DOI: 10.1007/s12043-013-0671-8; ***e*Publication:** 12 February 2014

Abstract. We simulate adaptive feedback control to coherently shape a femtosecond infrared laser pulse by means of a 4f-spatial light modulator in order to selectively excite the rovibrational modes of a polyatomic molecule. We preferentially populate an arbitrarily chosen upper rovibrational level by only employing these tailored temporally shaped pulses. A second laser would then allow for mode selective chemistry to interact selectively with the excited population. Alternatively the excited molecules enhanced reactivity could be exploited for selective chemistry.

Keywords. Molecules; femtosecond lasers; quantum coherent control; adaptive feedback control; molecular vibrational modes; spatial light modulator; genetic algorithm

PACS Nos 33.80.–b; 82.53.–k

1. Introduction

Various techniques can be utilized to prepare atoms or molecules in well-defined quantum states. An example is Rabi-cycling using the so-called π-pulses [1]. However, this technique is sensitive to various parameters pulse intensity, centre frequency of the pulse and the variable Doppler shift of the spectra of the interacting molecules, making it difficult to use this in practical applications. Techniques based on adiabatic processes are more robust, but the adiabatic requirements [2] limit the type of pulses that can be utilized and limits the control function space. Therefore, only limited control is possible under the adiabatic conditions. In the 1980s, Tannor *et al* [3] as well as Brumer and Shapiro [4] developed laser-based coherent control techniques that could be applied to chemical reaction product control as well as for preparing selective quantum states. Judson and Rabitz [5] suggested a method based on a measurement and adaptive feedback control (AFC)

to produce an optimum laser pulse to control quantum systems. In a recent article [6] it was shown that different coherent control schemes are unified on a fundamental level. The method that was used in this study is a simulation of AFC applied to the interaction of a shaped femtosecond pulse with a multilevel quantum mechanical system; the multilevel system that was used was a specific vibrational mode of a polyatomic molecule. The objective was to show that an arbitrarily chosen upper vibrational level, in the ground electronic state of the molecule, could be preferentially populated. This would then allow mode selective chemistry by applying a second laser that interacts with the excited population but not with the ground state population or alternatively the enhanced reactivity of the excited molecule could be utilized for selective chemistry [7].

2. Theory

A model was developed to describe the kinetics of a single vibrational mode of a polyatomic molecule. UF_6 is a well-studied molecule and detailed spectroscopy of the higher vibrational levels has been published, see for example [8,9]; therefore UF_6 was used in this model. The Von Neumann equation in the interaction picture was used to describe the dynamics of density matrix elements, ρ_{ij} of the different levels in a specific vibrational mode, in this case the υ_3 mode [10].

A set of simultaneous differential equations describing the kinetics of the laser/molecule interaction was solved numerically. The electric field used in the simulation

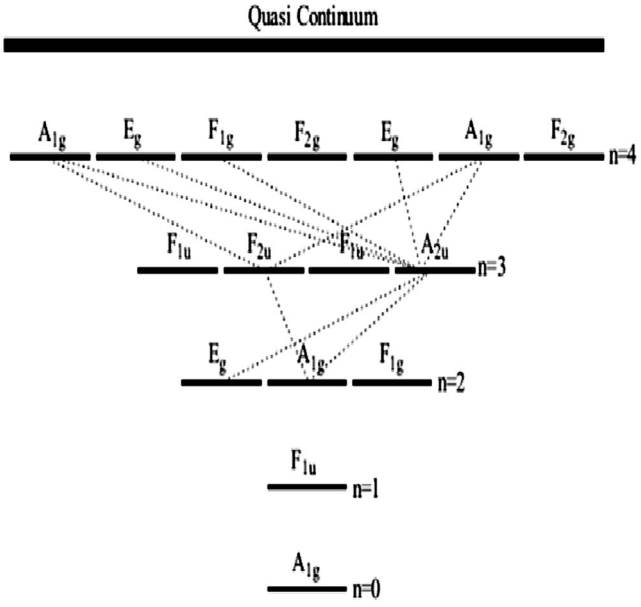

Figure 1. The level structure used in this study. Shown in the figure are the principal quantum numbers, n, as well as the anharmonic splitting of these levels for which there is a small difference in transition frequency. The broken lines represent forbidden transitions [8].

was a shaped ultrashort laser pulse. Time domain beam shaping was simulated by Fourier transforming the laser pulse, and a masking function was then applied in the frequency domain and after that the pulse was inversely Fourier transformed back to the time domain. The masking function allowed changing the phase and amplitude of the pulse at various discrete frequency values. In this particular case the frequency domain was divided into 640 discrete units to correspond to a specific type of spatial light modulator. At each of these 640 points the amplitude and phase could be varied independently. Therefore, the structure of the system (genotype) consists of two strings of 640 different features (genes) that can take values from 0 to 1 in the case of the amplitude and 0 to 2π in the case of the phase. A Matlab© genetic algorithm was used to optimize the pulse shape. The population in an arbitrarily chosen vibrational level was selected as the objective function. For this study, the population in a specific level was defined as a sum of the populations in all the levels with the same principal vibrational quantum number, n, in figure 1.

3. Results

A 150 fs pulse with a fluence of 600 J/m^2 was used as an initial pulse. It was assumed that the initial pulse was transform limited and that the carrier frequency is that of the, $n = 0$ to

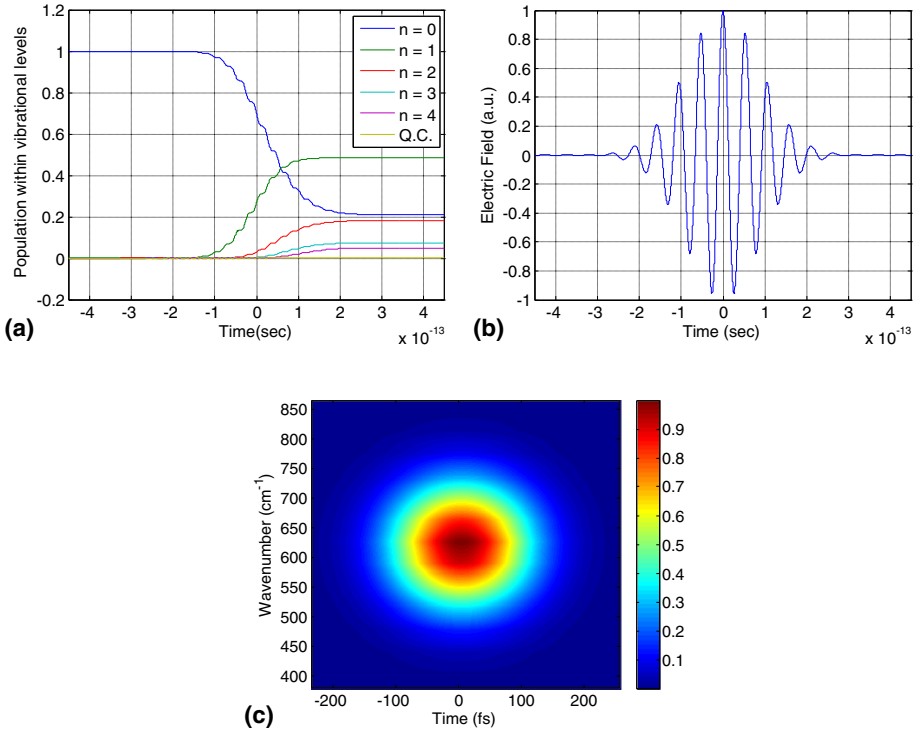

Figure 2. Interaction of a transform limited pulse with the polyatomic molecule. (**a**) Population dynamics, (**b**) electric field and (**c**) Husimi distribution.

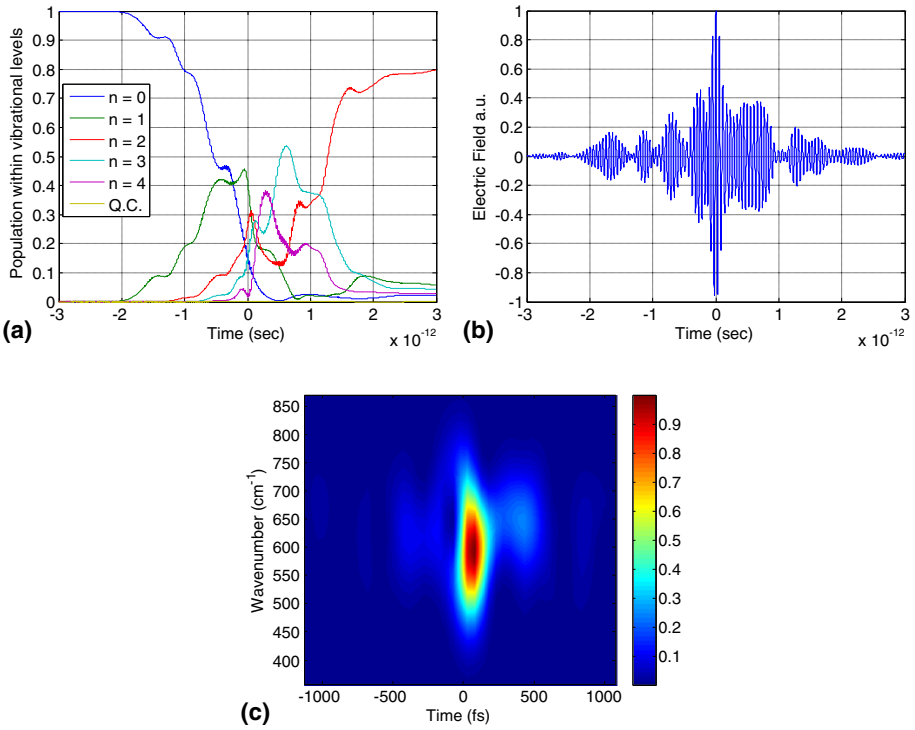

Figure 3. Amplitude and phase shaping. (**a**) Population dynamics, (**b**) electric field and (**c**) Husimi distribution.

$n = 1$ transition. During the simulation the total pulse energy was kept constant ensuring that the shaped pulses had the same energy as the initial pulse. The interaction of this pulse with the molecule was used as a reference. Figure 2 gives the population as distributed amongst the various levels, i.e. the levels with the same principal quantum number, n, after interacting with the transform limited pulse. The percentage of population after the interaction with the laser pulse, in level 2, i.e., vibrational state, $n = 2$, is 18% of the initial population. The time-dependent electric field and the Husimi distribution of it are also shown. From the Husimi distribution it is clear that there is symmetry in both time and frequency as would be expected from a transform limited pulse. The population dynamics and the obtained shaped pulse are shown in figure 3. In this case 80% of the initial population was in the targeted vibrational state, $n = 2$, more than 350% better than that obtained with an unshaped pulse.

4. Conclusion

A model was developed to describe the interaction of a shaped femtosecond pulse with a multilevel molecular system. A feedback loop in combination with a genetic algorithm and time domain beam shaping was used to optimize the population in an arbitrarily

chosen vibrational level. The population excited into this chosen vibrational level by an unshaped pulse was used as a benchmark. In this case the level with two vibrational quanta, i.e. level 2 was chosen. After interaction with the unshaped pulse the population in the level was 18% of the total. Time domain shaping using a combination of phase and amplitude shaping was then used to find optimum population fractions. All three produced significantly higher population fractions than the unshaped pulse. The maximum population in level 2 obtained was when both phase and amplitude shaping was allowed. The value obtained was close to 80% of the initial population.

References

[1] N V Vitanov, T Halfmann, B W Shore and K Bergmann, *Annu. Rev. Phys. Chem. J.* **52**, 763 (2001)
[2] D J Tannor, *Introduction to quantum mechanics, a time dependent perspective* (University Science Books, Sausalito, 2007)
[3] R Kosloff, D J Tannor and S A Rice, *J. Chem. Phys.* **85**, 5805 (1986)
[4] P Brumer and M Shapiro, *Annu. Rev. Phys. Chem.* **43**, 257 (1992)
[5] R S Judson and H Rabitz, *Phys. Rev. Lett.* **68**(**10**), 1500 (1992)
[6] A P Pechen, C Brif, R Wu, R Chakrabarti and H Rabitz, *Phys. Rev. A* **82**, 30101 (2010)
[7] D R Killelea, V L Campbell, N S Shuman and A I Uzt, *J. Phys. Chem. C* **112**, 9822 (2008)
[8] V N Bagratasvili, V S Letokhov, A A Makarov and E A Ryabov, (Harwood Academic Publishers, London, 1984)
[9] L Halonen and M S Child, *J. Chem. Phys.* **79**, 559 (1983)
[10] L E De Clercq, L R Botha, E G Rohwer, H Uys and A Du Plessis, *Proc. SPIE* **7925** (2011)