Selective Excitation of a Vibrational Level within the Electronic Ground State of a Polyatomic Molecule with Ultra Short Pulses

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Abstract: Coherent control of the upper vibrational level populations in the electronic ground state of a polyatomic molecule was simulated. Results indicate that selective excitation of a specific upper state level is possible.

1. Theoretical background

The selective excitation of an arbitrary vibrational level of a polyatomic molecule, without passage through an intermediary electronic excited state is demonstrated. This was achieved by simulating the interaction of a shaped, femtosecond pulse with one vibrational mode of the molecule.

While various molecules were investigated this study focuses on various spherical top molecules for which spectroscopic data for the vibrational modes are available in literature. A density matrix approach was followed. The time evolution of the density matrix is given by the Von Neumann equation [1]

$$\frac{d\rho_{ab}}{dt} = \frac{-i}{\hbar}\sum_{l=1}^{N}(\rho_{lb}I_{al}e^{i\omega_{b,l}t} - \rho_{al}I_{lb}e^{-i\omega_{b,l}t}) \qquad (1)$$

where,

$$\omega_{a,b} = \omega_a - \omega_b. \quad , \qquad (2)$$

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 [2] which include the detailed time dependence of the shaped femtosecond pulse.

2. Simulation results

A transform limited 150 femtosecond laser pulse with a fluence of 600 J/m^2 was used as an initial pulse. Pulse shaping via a Liquid Crystal Modulator (LCM) was simulated. The pulse found is applied to the molecules using equation (1). A genetic algorithm is then used to maximize the population in the chosen vibrational level. In this case the target level was vibrational level n=2.

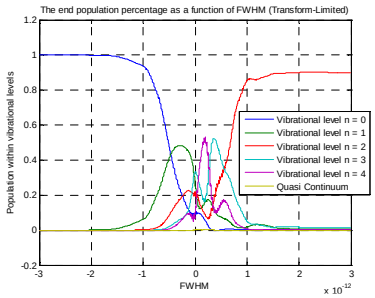

Fig. 1: Population dynamics of the various vibrational levels up to vibrational quantum number 4. The population associated with each vibrational quantum number is a sum of the populations in the various anharmonic splitting components.

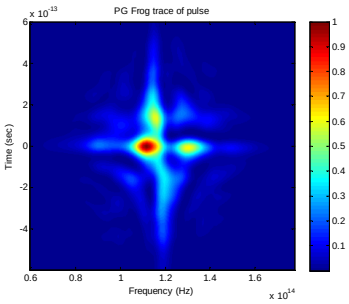

Fig. 2: The PG (polarization-gate) FROG of the shaped pulse.

3. Conclusion and 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.

4. References

[1] Claude Cohen-Tannoudji, Bernard Diu and Franck Laloë, *Quantum Mechanics*, (Wiley-VCH, 2005),Chap. 3.
[2] Rodney Loudon, *The Quantum Theory of Light (*Oxford science publication,1983*)*,Chap. 2