

Optical Control of Chemical Systems

Ryan Choi 2023

Abstract

Chemical reactions can be controlled in many ways, such as reagent selection and temperature. These macroscopic methods of regulation are good for controlling and investigating reactions in bulk; however, even more precise control is possible with electromagnetic radiation. Light is frequently used in chemistry through spectroscopy, with which we can make observations about our system of interest, but we are not limited to only making measurements. With the advancement of laser technology, we can also control chemical processes using ultrashort laser pulses.

Introduction: Tannor-Rice Control Method

The Tannor-Rice method is an early method to control simple chemical reactions. Though it has been succeeded by more sophisticated schemes such as STIRAP control, it illustrates fundamental principles of optical control. This introduction will provide a conceptual overview of the method.

The goal behind the Tannor-Rice method is to steer a chemical reaction into producing a specified product. In terms of a potential energy "landscape," the reactants could end up in a variety of product stable states separated by potential energy barriers. This method involves electronic (and vibronic) excitation of the reactant molecule with a short laser pulse, on the order of femtoseconds, which produces a localized wave packet on the excited state surface. As time passes, the wave packet propagates on the excited state surface, and by careful timing of a second pulse, one can select the products when the wave packet is aligned with the desired state.

Optical control of chemical reactions was not feasible until the invention of ultrashort laser pulses. Pulses on the order of femtoseconds is necessary for a few reasons. First, the propagation of the wave packet on the excited state surface occurs on such a timescale, so naturally, temporally precise optics are needed. Second, energy dissipates from the excited state quickly. Lastly, a short pulse localized in space will be spectrally broad due to the uncertainty relation. This, combined with the Franck-Condon relation, helps produce a localized wavepacket when the pump pulse is delivered.

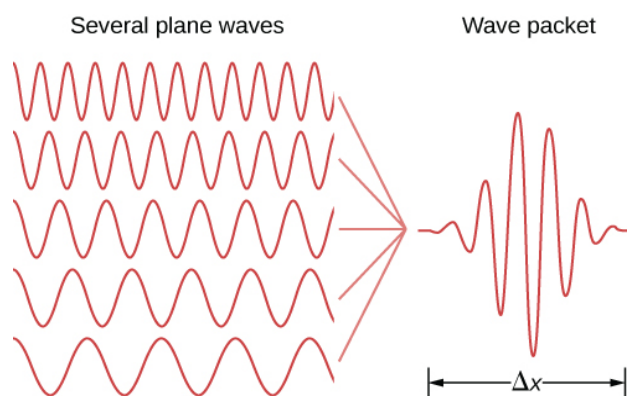


Figure 1. Illustration of highly localized but spectrally broad wavepacket. (Licensed under Creative Commons, [3])

The Frank-Condon relation describes the probability of a vibrational transition from an initial state i to a final state f when an electronic transition occurs.

$$P_{i,f} = |\langle \psi_f | \mu | \psi_i \rangle|^2$$

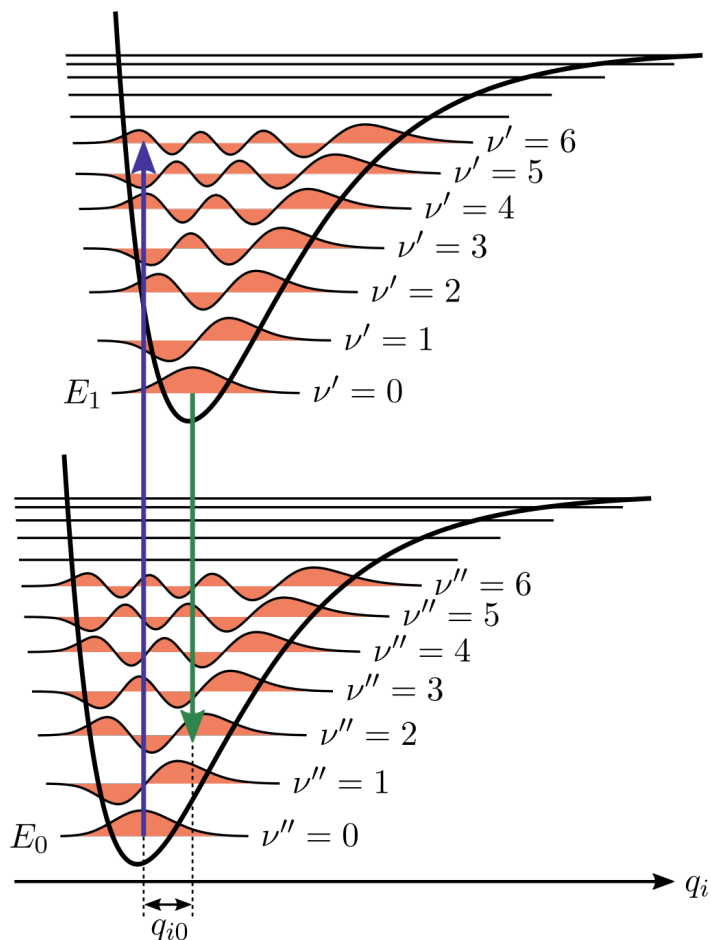
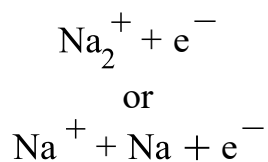


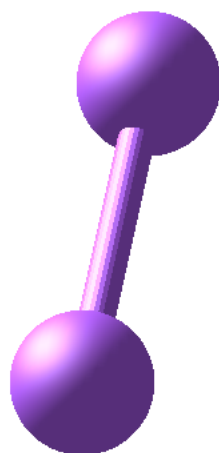
Figure 2. Illustration of Franck-Condon principle. (Licensed under Creative Commons, [4])

With a ultrashort laser pulse, we can coherently excite multiple vibrational states at once, creating a wavepacket. This then propagates on the excited state surface.

To illustrate how the Tannor-Rice control method works, we can take a look at an example. One of the first reactions to be optically controlled was the photodissociation of Na_2 , which can form two different products:



- > *with(QuantumChemistry)*
[*AOLabels, ActiveSpaceCI, ActiveSpaceSCF, AtomicData, BondAngles, BondDistances, Charges, (2.1)*
ChargesPlot, ContractedSchrodinger, CorrelationEnergy, CoupledCluster, DensityFunctional,
DensityPlot3D, Dipole, DipolePlot, Energy, ExcitationEnergies, ExcitationSpectra,
ExcitationSpectraPlot, ExcitedStateEnergies, ExcitedStateSpins, ExcitonDensityPlot,
ExcitonPopulations, ExcitonPopulationsPlot, FullCI, GeometryOptimization, HartreeFock,
Interactive, Isotopes, MOCoefficients, MODiagram, MOEnergies, MOIntegrals,
MOOccupations, MOOccupationsPlot, MOSymmetries, MP2, MolecularData,
MolecularDictionary, MolecularGeometry, NuclearEnergy, NuclearGradient,
OscillatorStrengths, Parametric2RDM, PlotMolecule, Populations, Purify2RDM, RDM1,
RDM2, RTM1, ReadXYZ, Restore, Save, SaveXYZ, SearchBasisSets, SearchFunctionals,
SkeletalStructure, SolventDatabase, Thermodynamics, TransitionDipolePlot,
TransitionDipoles, TransitionOrbitalPlot, TransitionOrbitals, Variational2RDM,
VibrationalModeAnimation, VibrationalModes, Video]
- > *na2 := [{"Na", 0, 0, 0}, {"Na", 0, 0, 3.079}]*
na2 := [{"Na", 0, 0, 0}, {"Na", 0, 0, 3.07900000}] (2.2)
- > *PlotMolecule(na2)*



To see how this reaction is controlled, we can look at the potential energy surfaces of several electronic excited states of Na_2 . Refer to Figure 3, on page 53, in reference [5] for the following description.

Starting at the ground state, we can use laser pulses to excite the molecule to the $2^1\Pi_g$ state, which is where we have the opportunity to influence the reaction. With a spectrally broad laser pulse, one can coherently excite multiple vibrational states, forming a wave packet. Upon excitation to the $2^1\Pi_g$ state, the wave packet will be localized to the left turning point of the curve (the bottom of arrow 1). Since the wavefunction for the ground state Hamiltonian is not a stationary state of an excited state Hamiltonian, the wave packet will time evolve and move towards the right turning point of the curve (the bottom of arrow 2).

Eventually, the wave packet will decohere, but before it does so, we can deliver a final laser pulse to select the desired product. Exciting the molecule when the wave packet is under arrow 1 will yield the diatomic ion, since the wave packet can "settle" into the well of the $2^2\Sigma_g^+$ state. Exciting the molecule when the wave packet is under arrow 2 will yield the dissociated ionized product, since the wave packet will travel outwards towards increasing bond length. Arrow 3 shows that one can excite the diatomic ion to produce the dissociated product. In literature, the first laser pulse(s) are referred to as the "pump," and the final laser pulse that determines the product is called the "dump" or the "probe." Figure 4 from reference [5] shows how the delay between the pump and dump pulses selects for one product, with the periodic nature corresponding to the wave packet oscillating back and forth between the two turning points.

Theory

To mathematically represent the Tannor-Rice method, we will start with a coupled system of differential equations representing the time-dependent Schrödinger equations of a ground state and an excited state. The Hamiltonian of the entire system will contain the Hamiltonians of the ground and excited states, as well as the interaction of the transition dipole moment with an electromagnetic field, $\epsilon(t)$. It is convenient to write the Hamiltonian as a matrix.

$$\hat{H} = \begin{bmatrix} \hat{H}_g & \mu \cdot \epsilon(t) \\ \mu \cdot \epsilon(t) & \hat{H}_e \end{bmatrix} \quad (1)$$

The coupled differential equations are written with this matrix.

$$i\hbar \frac{\partial}{\partial t} \begin{bmatrix} \psi_g \\ \psi_e \end{bmatrix} = \begin{bmatrix} \hat{H}_g & \mu \cdot \epsilon(t) \\ \mu \cdot \epsilon(t) & \hat{H}_e \end{bmatrix} \begin{bmatrix} \psi_g \\ \psi_e \end{bmatrix} \quad (2)$$

The system will start in the ground state, so we will set the wavefunction to be $\psi_g(0)$ when $t = 0$. We

can then write equation (2) in integral form.

$$\Psi_g(t) = e^{\frac{-i}{\hbar} \hat{H}_g t} \Psi_g(0) - \frac{i}{\hbar} \int_{-\infty}^t e^{\frac{-i}{\hbar} \hat{H}_g (t-t')} \mu \cdot \varepsilon(t') \Psi_e(t') dt' \quad (3)$$

$$\Psi_e(t) = - \frac{i}{\hbar} \int_{-\infty}^t e^{\frac{-i}{\hbar} \hat{H}_e (t-t')} \mu \cdot \varepsilon(t') \Psi_g(t') dt' \quad (4)$$

We can use second-order time-dependent perturbation theory to derive an expression for the motion of the wavefunction. First, equation (4) is set to the following.

$$\Psi_e(t_2) = - \frac{i}{\hbar} \int_{-\infty}^{t_2} e^{\frac{-i}{\hbar} \hat{H}_e (t_2-t_1)} \mu \cdot \varepsilon(t_1) \Psi_g(0) e^{-i\omega t_1} dt_1 \quad (5)$$

Then, within perturbation theory, the ground state wavefunction is:

$$\Psi_g^{(2)}(t) = - \frac{1}{\hbar^2} \int_{-\infty}^t \int_{-\infty}^{t_2} e^{\frac{-i}{\hbar} \hat{H}_g (t-t_2)} \mu \cdot \varepsilon(t_2) e^{\frac{-i}{\hbar} \hat{H}_e (t_2-t_1)} \mu \cdot \varepsilon(t_1) \Psi_g(0) e^{-i\omega t_1} dt_1 dt_2 \quad (6)$$

This equation represents the ground state wavefunction evolving on the ground state potential energy surface from $t=0$ to $t=t_1$, then transitioning instantaneously to the excited state surface where it evolves from $t=t_1$ to $t=t_2$. Lastly, the wavefunction relaxes back to the ground state where it evolves from $t=t_2$ onwards (until time t). As t increase beyond the times when the transitions occurred, the system will enter one of the product states, and a projection operator onto that state can be used to find the probability of forming that product.

Because the dump pulse determines product selection, an important question is what the optimal dump pulse shape should be given a certain pump pulse. If we have two discrete initial and final states, χ_i and χ_f

f ,

with $\phi_i = \mu \chi_i$ and $\phi_f = \mu \chi_f$, then the probability of a transition between the initial and final states is determined by:

$$P_{ij} \propto \left| \int_{-\infty}^{\infty} \int_{-\infty}^t \phi_f^* \varepsilon_2(t) e^{\frac{-i}{\hbar} \hat{H}(t-s)} \varepsilon_1(s) \phi_i dt ds \right|^2 \quad (7)$$

A normalization constraint is also enforced, since there is a finite number of photons in the pulse.

$$\int_{-\infty}^{\infty} |\epsilon_2(t)|^2 dt = 1 \quad (8)$$

At this point, Tannor and Rice's derivations use variational analysis to determine the optimal pulse shape. The following functional, using equations (7) and (8), is maximized.

$$I = \left| \int_{-\infty}^{\infty} \int_{-\infty}^t \phi_f^* \epsilon_2(t) e^{\frac{-i}{\hbar} \hat{H}(t-s)} \epsilon_1(s) \phi_i dt ds \right|^2 + \lambda \left[\int_{-\infty}^{\infty} |\epsilon_2(t)|^2 dt - 1 \right] \quad (9)$$

The resulting equation is:

$$\epsilon_2^*(t) = \frac{f(t)}{\sqrt{\int_{-\infty}^{\infty} |f(t)|^2 dt}} \quad (10)$$

where $f(t)$ is defined as follows.

$$f(t) = \int_{-\infty}^t \phi_f^* e^{\frac{-i}{\hbar} \hat{H}(t-s)} \epsilon_1(s) \phi_i dt \quad (11)$$

$f(t)$ can be interpreted as a convolution of the pump pulse and the time-evolving wavepacket, and one is trying to maximize the response of the system via the dump pulse.

Applications

Optical manipulation of quantum systems on nanosecond or femtosecond scales has opened the door for useful technologies. One notable example is pump-probe spectroscopy, in which one is not necessarily attempting to control a chemical system, but investigating its properties. The transmission of the probe pulse in response to the pump pulse can reveal the identity of a sample, characterize nanostructures, and track reaction dynamics. This technique has advantages such as high chemical selectivity and the ability to detect weakly fluorescent molecules. It also has promising applications in biological imaging, since it is a nonlinear optical technique and thus less affected by the thickness of the medium, namely tissue.

Stimulated Raman adiabatic passage (STIRAP) is another optical control scheme that has applications in trapped, ultracold molecular systems, such as Bose-Einstein condensates, which have interesting properties. These ultracold systems are usually formed from atoms using laser-cooling, but the same techniques cannot be directly applied to diatomic molecules because the energy from photons can be absorbed into rotational and vibrational channels. With STIRAP, one can prepare diatomics in their

rotational-vibrational ground state, overcoming this difficulty. Optics are also used to control ultracold qubits in quantum computers.

Conclusion

The Tannor-Rice method is a foundational method that introduces how one can control chemical reactions with optics. By delivering an appropriately timed dump pulse after a pump pulse, the reaction can be directed into a specific product. Beyond the Tannor-Rice method, many other optical methods are used for precise control and measurement of quantum systems.

References

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