

Viewpoint

Distinguishing between molecules that look the same

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Published June 22, 2009

Different molecules with nearly identical absorption spectra can be distinguished with the help of shaped laser pulses and adaptive algorithms.

Subject Areas: **Optics, Chemical Physics**

A Viewpoint on:

Quantum Control of Tightly Competitive Product Channels

Matthias Roth, Laurent Guyon, Jonathan Roslund, Véronique Boutou, Francois Courvoisier, Jean-Pierre Wolf and Herschel Rabitz

Phys. Rev. Lett. **102**, 253001 (2009) – Published June 22, 2009

Optical spectroscopy is a remarkably powerful tool that can be used to discriminate between samples that have very similar physical properties. But what do you do if two molecules or samples you want to discriminate between absorb and emit at the same frequencies? In a paper published in *Physical Review Letters*, Matthias Roth, Jonathan Roslund, and Herschel Rabitz of Princeton University, Laurent Guyon, Véronique Boutou, and Francois Courvoisier at Université Lyon, and Jean-Pierre Wolf at the University of Geneva demonstrate an approach to this problem based on “coherent control” [1]. They make use of shaped ultrafast lasers and an adaptive algorithm that controls the pulse shapes to distinguish between two different molecules with identical absorption and emission spectra. Their work illustrates the power of using controlled quantum interference to discriminate between similar systems.

The field of coherent control was born just over 20 years ago and has grown rapidly since then [2–5]. The basic idea is to coax an atom or molecule toward a specific desired target state using interference between different “pathways,” just as light that takes different pathways in an optical interferometer can interfere to produce large or small intensities at the output. Rather than different pathways in physical space, as in an optical interferometer, the pathways in coherent control represent different trajectories in a quantum mechanical phase space (that is, the space in which all possible quantum states of the system are represented). The phase between two different lasers can be adjusted to achieve constructive interference in a target state of a molecule, while maintaining destructive interference into other final states of the same or another molecule. It is as if one is performing a double slit experiment inside the molecule and controlling the phase acquired in passing through one of the slits. Controlling the relative phase of the light through the two slits determines the posi-

tion of bright and dark fringes in the far field. An important early coherent control experiment demonstrated how the phase between two lasers could be used to control the outcome of a simple chemical reaction [6].

While one can control the intensity of light at a given point in a double slit experiment, the extension to multiple slits allows for arbitrary control over the far field light pattern, just as Fourier synthesis with many frequency components allows for creating complicated wave forms in time. Adjusting the position of the slits for an N slit diffraction experiment controls the relative phase of the light passing through them, and adjusting the size of the slits controls the amplitude of the light passing through them. Shaped ultrafast laser pulses, which offer control over hundreds of independent frequencies in the Fourier domain, have enabled coherent control to move from “double slit experiments” to “ N slit experiments” [7]. With detailed control over many spectral components in the applied electric field, and thus control over many interfering pathways in a molecule, the range of systems that have been controlled and the level of control possible has grown enormously [8]. However, if there is a large number of control parameters and molecular degrees of freedom, it is generally not possible to determine *a priori* what pulse shapes (spectral phases and amplitudes) are optimal for a given control experiment.

In order to overcome this hurdle, Rabitz and Judson proposed using experimental feedback to discover optimal pulse shapes for controlling where the absorbed energy goes in a molecule [9]. The idea was to “let the molecule design an optimal laser pulse itself.” In their approach, a learning algorithm on a computer controls the selection of pulse shapes, which are experimentally evaluated by illuminating the sample with them. Measurements of the fraction of molecules that actually enter the target state (e.g., a dissociative product from the

parent molecule or the fluorescence from an excited- to ground-state transition) are used to evaluate the pulse shapes in the collection. The learning algorithm takes the best pulse shapes and combines them to create new ones. This process is iterated (that is, the process runs in a “closed loop”) until the target state yield does not improve over several iterations. Experiments making use of this approach have ranged from controlling high-order harmonic generation in an atomic gas to controlling molecular fragmentation [10, 11].

As coherent control aims to selectively prepare target molecular states, it is a natural tool for molecular discrimination. However, the limits of discrimination, particularly in very demanding situations, have not been explored in detail. Among other challenges, theoretical work has addressed the separation of molecules that differ only by their handedness (enantiomers) [12]. Experiments have looked at selectively ionizing diatomic molecules composed of different isotopes [13, 14] and selecting for fluorescence from two different dye molecules in solution excited via two-photon absorption [15]. The experiments on diatomic molecules made explicit use of the isotope-dependent molecular dynamics initiated by an unshaped “pump” pulse to discriminate between molecules with a separate unshaped “probe” pulse. Since the molecules under study were simple and the dynamics calculable, the shaping of the total applied electric field could be limited to producing two pulses and varying the delay between them. The dye molecule experiment made use of feedback and pulse shaping to optimize the discrimination between fluorescence between the two samples. Feedback was necessary given the complexity of the molecular system in solution.

Roth *et al.* have combined the pump-probe approach with closed loop optimization to perform “optimal dynamic discrimination,” which allows them to distinguish between large molecules with identical absorption and emission spectra in solution. It is “optimal” because the laser pulses used for discrimination are optimized using experimental feedback, and “dynamic” because the discrimination relies on measurement of a time-dependent quantum state.

The basic idea is illustrated in Fig. 1, which shows a simple cartoon of the excitation and probing of the molecules on an excited-state potential energy surface. Each surface shows the potential energy of the molecule as a function of two vibrational coordinates for the excited electronic state. The shaped ultraviolet pump pulse excites a portion of the ground-state vibrational wave function to the excited electronic state of the molecule, where the vibrational wave function evolves since it is not at the minimum (equilibrium position) of the excited-state energy surface. The potential energy surfaces of the two molecules [flavin mononucleotide (FMN) and riboflavin (RBF)] are similar, but have subtle differences due to their slightly different molecular structure. The evolution of the wave function is very sensitive to the details of the energy surface, and

thus the dynamics in RBF can be slightly different than in FMN, leading the two wave functions excited by a shaped pulse to travel along slightly different paths. By probing the molecule (exciting a portion of the wave function to a third electronic state with unshaped infrared pulses) when the wave functions for the two molecules are in slightly different locations, Roth *et al.* are able to measure a significant difference in the depleted fluorescence yield from the intermediate excited state to the ground state. This allows them to discriminate between the two systems well beyond the noise in the measurement.

The probing can be regarded as a projection of the vibrational wave function from one electronic state to another. The fluorescence from the intermediate state is depleted in proportion to the fraction of the wave function that is projected onto the third electronic state. This projection is sensitive to the phase and amplitude of the initial wave function excited by the shaped pulse because the time resolution of the probe pulse makes the projection spatially selective. Since the phase and amplitude of the wave function prepared by the shaped pump pulse dictate the shape of the wave function at later times, the fluorescence depletion can be sensitive to the phase and amplitude of the initial wave function on the intermediate potential energy surface. Thus the detected fluorescence is different for FMN and RBF, despite their nearly identical absorption spectra.

The observation by Roth *et al.* that molecular dynamics can be optimized for discrimination is an important one that opens up the field to many applications, including molecule-selective biological imaging, composition analysis, and new forms of pulse shape spectroscopy, which, as in nuclear magnetic resonance, may provide more information than is available with conventional absorption spectroscopy.

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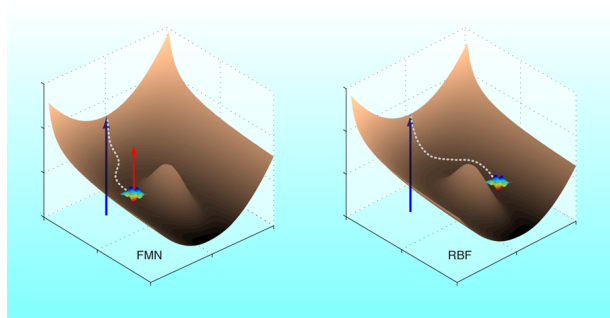


FIG. 1: Schematic illustration of dynamic discrimination for two molecules with identical static absorption spectra. Similar but slightly different potential energy surfaces (which display energy versus two vibrational coordinates in the molecule) are shown for the two molecules FMN and RBF. A shaped UV pump pulse launches a tailored wave function on the potential energy surface of each molecule (large blue arrow). The wave functions evolve on the excited state surface (dotted white line) and are shaped (via the shaped UV laser pulse) to maximize the differences between them when the probe pulse arrives. The unshaped infrared probe pulse (small red arrow) transfers a portion of the wave function for one molecule (FMN in this case) to a final state from which fluorescence is not detected (small red arrow). The wave function in the other molecule (RBF) is in a different location when the probe pulse arrives, and it is therefore not transferred to the final state, leading to a larger fluorescence signal. A different shaped UV pulse can reverse the situation, leading to suppression of RBF fluorescence relative to FMN. (Illustration: Alan Stonebraker)

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About the Author

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Thomas Weinacht received his Ph.D. in 2000 from the University of Michigan. His research interests are in strong field coherent control and ultrafast spectroscopy. He has been a professor of Physics at Stony Brook University since 2002.