2D Spectroscopy Simplified

Insights into the fundamental photonic properties of MoS_2 monolayers and perovskite films hold promise for solar, LED and laser diode applications.

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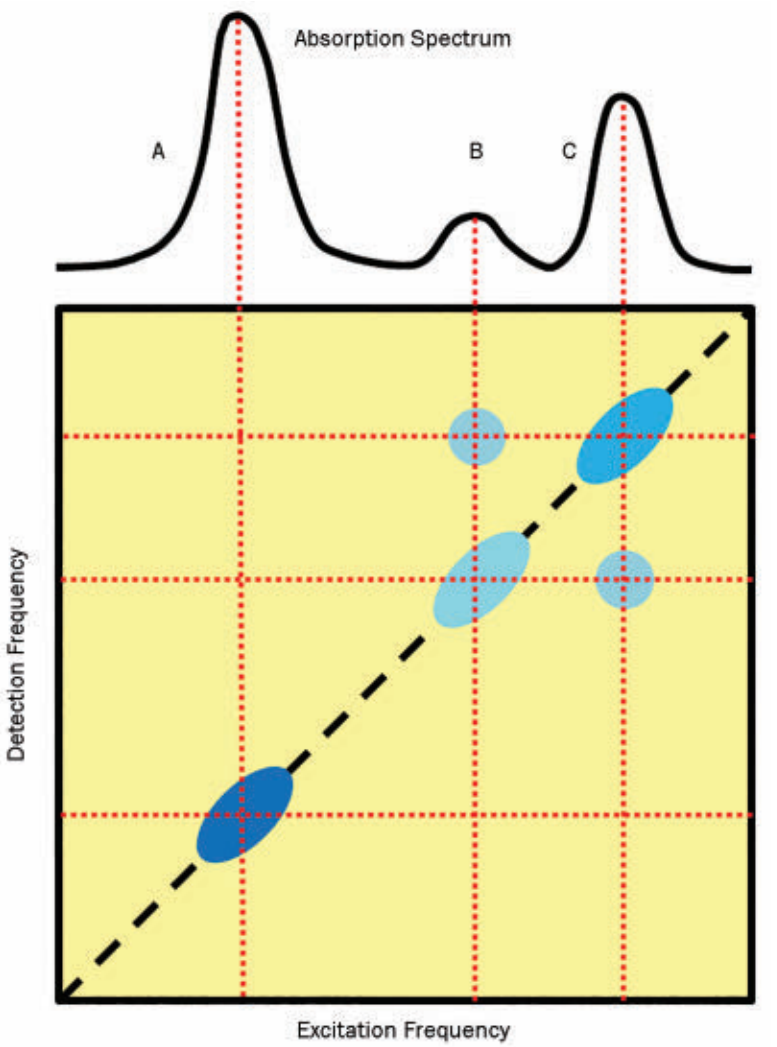
The many forms of conventional or linear spectroscopy such as vibrational, electronic and terahertz all involve measuring light absorption or an emission signal as a function of wavelength to yield information about the structure of the sample being interrogated. In recent years, two-dimensional spectroscopy methods have been developed where the signal is plotted as a function of two different frequencies. This provides unique structural and dynamic information about samples, ranging from model photosynthesis systems to nanomaterials, enzymes, proteins, surface catalysts and semiconductors. Two-dimensional spectroscopy is now yielding findings on two material systems of particular interest to the photonics industry, namely molybdenum disulfide (MoS_2) monolayers and perovskite films.



Fleming group, UC Berkeley

Figure 1. A two-dimensional spectroscopy data plot of a mixture of two compounds. The diagonal plot is equivalent to a conventional linear spectrum. The presence of off-diagonal peaks indicates peaks that are coupled in some way. Here, peak A is due to one of the chemical species, and B and C are both due to the other molecule and so are linked with each other.

2D spectroscopy basics

The one-dimensional or the linear spectrum of a model system consisting of a mixture of two materials contains resonances where the light frequency is coincidental with the energy interval between different stationary states in the sample (Figure 1). In infrared absorption spectra — usually Fourier transform IR — these peaks are due to excitation of different vibrations in the sample. In electronic spectra, for example fluorescence excitation spectra, the peaks are due to transitions between different electronic states.

Scientists use this data to understand the structure of molecules, complexes and other systems. However, this steady state data contains very limited temporal information. The use of flash lamps and pulsed lasers can often extend linear spectroscopy to show the timescale over which one state of the system evolves into another. While this is obviously useful, these pump-probe type studies are, at best, like a series of still photographs and don't resolve the details of how that transition took place. Linear spectroscopy also doesn't indicate which peaks are related to each other — even something as simple as whether two peaks are from the same molecule in a mixed sample (Figure 1).

Two-dimensional spectroscopy can answer these questions and provides both unique structural and detailed kinetic information. This data is invaluable for research in biophysics in the areas of drug binding and membrane dynamics, as well

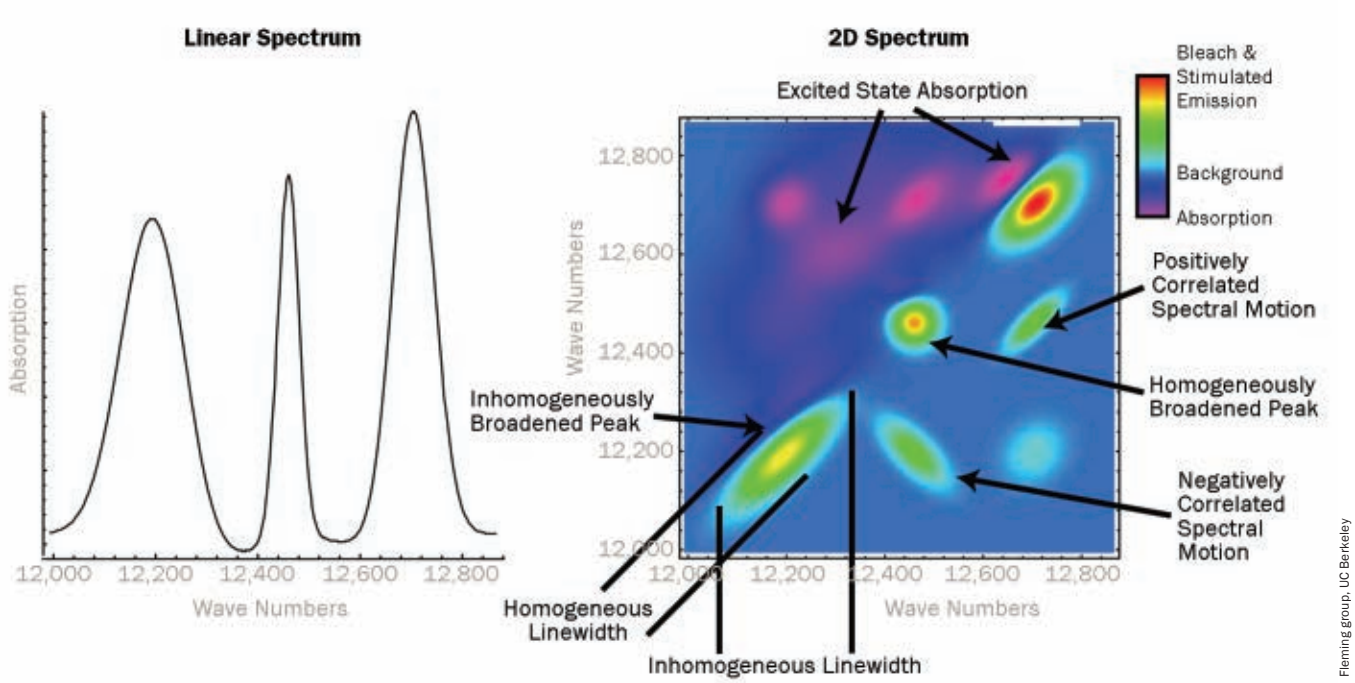


Figure 2. A 2D electronic spectrum potentially contains many different types of information.

as materials science related to developments in OLEDs and new photovoltaics.

Two-dimensional spectroscopy involves measuring an optical signal as a function of two optical frequencies. The data is then usually presented as 2D contour plots, where color and color intensity are often used to represent phase and amplitude. When both optical frequencies are the same, it is equivalent to simply exciting and probing the sample with degenerate light, and the resulting diagonal plot is identical to the one-dimensional spectrum. But if two peaks in the spectrum are coupled in some way, then they will give rise to off-diagonal peaks.

The simplest case involves two different chemicals mixed in a diluted solution or trapped in a solid. The UV-VIS absorption spectrum consists of several peaks due to both molecules. If two peaks are due to electronic transitions involving the same molecule — particularly the same part of that molecule — then exciting one transition with light could cause a change in the excitation signal for the other transition. This could manifest as a frequency shift, broadening or cross-section change, which would show up as cross peaks in a 2D plot. And, the intensity of the cross peaks reveals how strongly the two vibrations are connected. Cross peaks can also occur because of different types of interactions between two nearby molecules, for example in dye aggregates or between pigments in a photosynthetic protein.

Another advantage of 2D spectroscopy is the ability to derive the intrinsic upper state coherence time by measuring the observed linewidth in the anti-diagonal direction, i.e., perpendicular to the diagonal spectrum. Knowing this so-called homogeneous linewidth is critical to the operation of every type of laser and LED, as well as to the efficiency of solar cells. It's also a key number in photosynthetic systems, both natural and man-made. Several other different types of data can also be extracted from 2D electronics spectra (Figure 2).

The first 2D spectroscopy measurements were made directly in the frequency domain by using a tunable narrow line laser to laboriously record a spectrum at many different frequencies of a second laser. Today, most 2D spectroscopy measurements are made in the time domain and converted to the frequency domain using simple Fourier transform (FT) algorithms. Instead of using light at one frequency, coherent pulses of broadband light are used so that all frequencies are recorded simultaneously. Data is measured as a function of the time between the pulses and FT converted into the frequency domain, giving the excitation frequency axis. The emission frequency is simply measured by dispersing the signal in a spectrometer. A total of three pulses are therefore needed — two for excitation and one for detection or emission — leading to increased experimental complexity, but justified by a valuable trove of unique data.

2D electronic spectroscopy

In principle, the core concepts in 2D spectroscopy can be implemented for a range of different spectroscopic signal types. Two-dimensional infrared spectroscopy (2DIR), for instance, is used to study vibrations and bonding. In contrast, 2D electronic spectroscopy (2D ES) involves correlations between electronic transitions, i.e., when electrons are excited to higher energy states in chromophores or conduction bands in the case of solid-state materials. 2D EIR is a hybrid form that looks at links between vibrational (i.e., infrared) and electronic excitations. Even sum frequency generation (SFG) mixing signals can be studied in a 2D format.

Researchers in photochemistry, photobiology, nanotechnology and photonic device development are often interested in electronic spectroscopy. Professor Graham Fleming at the University of California, Berkeley, has pioneered the field of 2D electronic spectroscopy.

Fleming uses the technique to study electronic coupling between chromophores and energy transfer. A simplified schematic of Fleming's setup (Figure 3) shows how four different light pulses are all derived from the same broadband femtosecond source using a simple diffractive optical element. (The fourth pulse is used for heterodyne detection.)

This approach "guarantees a stable signal phase against environmental vibration," Fleming said. His group disperses the final signal in a spectrometer to directly obtain the emission frequency information. Three of the four laser pulses are passed through a pair of glass wedges so that they can independently vary their phase relative to the fourth pulse, which is used for heterodyning detection. "This gives us three time intervals that can each provide some very interesting data," Fleming said.

In particular, this allows Fleming and his team to monitor the energy flow and find the energy transfer timescales. By putting waveplates in the beam paths, they also measure the angle between transition dipole moments, thus providing a sensitive measure of the nature and the geometry of the excited states.

"Polarization-dependent 2D spectroscopy is also a useful tool for decongesting crowded 2D spectra, by selectively enhancing and suppressing cross-peak signals corresponding to different pathways of energy flow," he added.

At the heart of the Fleming lab setup is a one-box femtosecond amplifier (a 6-W Coherent Astrella), which the researchers use to pump a home-built, noncollinear optical parametric amplifier (NOPA) where the center wavelength can be tuned for different experiments.

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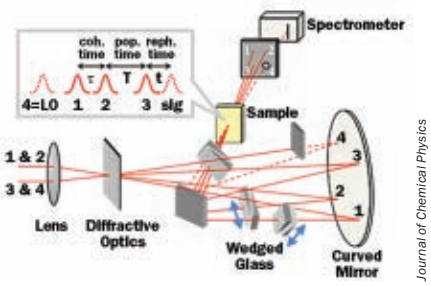

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Figure 3. In the Fleming group's 2D electronic spectroscopy setup, the time delay between different broadband pulses can be independently varied. These delays are not shown to scale. The short interval τ is varied using precision glass wedges. The longer interval T is varied using a mechanical translation stage. A Fourier transform is performed with respect to t by the spectrometer and the data is recorded in the frequency domain.

Fleming explained the choice of laser amplifier: "In four-wave mixing experiments like these, we need substantial femtosecond power because we start by dividing the beam into four separate pulses. Plus, the nature of the technique means the signal levels are low and have a strong nonlinear dependence on laser power," he said.

Depending on the signal-to-noise ratio, experiments can sometimes last tens of hours for averaging. During this time, the group needs very stable laser performance. And lastly, the experimental setup is necessarily a bit complex, so they need a simple-to-operate laser tool that allows the focus to be on the experiment rather than laser adjustment.

Perovskite thin films

Perovskite thin films have recently garnered attention because of their potential for superior photovoltaic devices. A key driver in wider adoption of solar power is to lower the true cost; the goal is actually to reach parity with the cost of grid electricity derived from combustion of fossil fuels.

Today, most solar cells are based on crystalline silicon, which has two well-known drawbacks, namely fabrication cost and a maximum total conversion efficiency (watts of electrical power out vs. watts of absorbed solar power in) of less than 20 percent. A key component in the cost is the use of thick silicon. In contrast, thin-film solar cells such as those based on copper indium gallium selenide (CIGS), have much lower fabrication and material costs, but unfortunately they exhibit efficiency of just a few percent. However, perovskite films offer the potential of lower fabrication costs and high efficiency. In fact, perovskite prototypes have already demonstrated efficiencies as high as 22 percent with even higher values theoretically possible.

The term "perovskite" actually refers to a class of several different crystalline materials. Methlyammonium lead iodide was the first to be investigated for solar use, and more recently, researchers are looking at eliminating the use of environmentally toxic lead, possibly by switching to tin, for this green energy application.

Daniele Monahan, a graduate student in the Fleming group, noted that 2D electronic spectroscopy is a useful tool for investigating semiconductor materials such as perovskite films where the fundamental physics is still not well understood. The group is studying the connections between phonons (quantized lattice vibrations) and free carriers created by light absorption in $CH_3NH_3PbI_3$.

"One of the things we are studying is the fate of 'hot carriers,'" Monahan said. "When a solar cell absorbs a photon that is in excess of the bandgap energy, then this excess energy persists for a finite time in the form of a hot carrier.

"In regular solar cells, this excess energy quickly decays to background heat and is therefore lost. But in perovskite, we know that the lifetime of the hot carriers can be as long as a microsecond. If this hot carrier energy can be harvested in some way, then that will greatly increase overall efficiency," she said.

The group's preliminary research indicates that while perovskite materials nominally have a direct bandgap, in thin films there is evidence of an indirect component, she said, with phonons staying coherent for a long time.

MoS_2 monolayers

MoS_2 and related compounds (WS_2, $MoSe_2$) in the monolayer form are photoluminescent materials with strong potential for next-generation LEDs as well as possibly lasers and even photovoltaics. Monolayers of these materials are studied

for this purpose. The monolayers can be produced by either chemical vapor deposition or by the tape exfoliation method pioneered for graphene.

Liang Guo, a post-doc in the Fleming group, is using the 2D electronic spectroscopy setup to study monolayer samples of MoS_2 produced by chemical vapor deposition.

"MoS_2 has two different excitation modes in the visible, leading to species designated exciton A and exciton B," Guo said. "We can examine coupling between these two modes, and also obtain the intrinsic linewidth of both excitons. We see strong cross-peaks in our preliminary data plots which indicate the role of many body effects consistent with reduced dielectric screening."

This reduced dielectric screening is of interest because it should theoretically allow future designers of LEDs, and possibly laser diodes, the ability to shift the emission profile of monolayers simply by depositing them on different materials.

As Fleming's group's work has revealed, 2D spectroscopy is proving itself as a powerful technique that delivers unique information that justifies its experimental complexity. While there are several different approaches to building a 2D spectrometer, they all require a femtosecond amplifier with at least one broadband OPA. The development of one-box integrated ultrafast amplifiers provides turnkey sources that eliminate virtually all the complexity formerly associated with generating femtosecond pulses for these experiments. This, in turn, is enabling scientists across numerous disciplines to use 2D spectroscopy to probe material systems for important applications in energy, light sources and other disciplines.

Meet the authors

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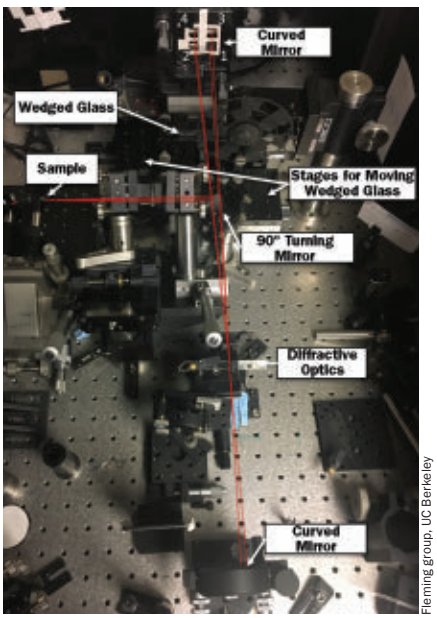

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The key elements in the manipulation of the multiple ultrafast pulses for 2D electronic spectroscopy can be seen here. The beam paths are illustrated by red lines.