CHEMICAL PHYSICS

Taking six-dimensional spectra in finite time

Clever data acquisition can probe how vibrations couple to electronic states in molecules

By **Joseph Goodknight** *and* **Alan Aspuru-Guzik**

Pump-probe spectroscopies use ultrafast laser pulses to excite molecules, and then probe them with a time-delayed pulse. If more laser pulses are used, information beyond excited-state spectra can be gained. For example, four-pulse techniques can explore how vibrations or electronic excited states are coupled. However, adding even more pulses usually comes at a price—that of very long experimental times to collect all of the data. Spencer *et al.* (*1*) now report on a six-pulse laser spectroscopy that obtains intricate details on the coupling between electronic states to vibrational motions, a key issue in the observation of quantum coherence in proteins (*2*–*5*). This method takes advantage of the ingenious gradient-assisted photon-echo spectroscopy (GRAPES) developed (*6*) for four-pulse spectroscopy that speeds acquisition times by tilting the beams to introduce time delays and sampling along a line rather than a point.

In so-called two-dimensional (2D) spectroscopy, two time dimensions are scanned, one between the two pumps and the other between the two probes. A "map" is generated of the energy flow in the system as a function of time. As laser pulses become faster, the energy range they must cover necessarily increases because of the uncertainty principle. Thus, probing a typical vibration transition requires a pulse about 100 fs long, but probing a molecular electronic transition requires a pulse closer to 50 fs long. Thus, 2D optical spectroscopy first addressed the coupling of chemical vibrations (*7*). As faster pulses were developed, electronic energy transfer could be probed, for example, in photosynthetic light-harvesting systems (*2*–*4*).

The experiments on photosynthetic complexes suggested that in certain cases, electronic excited states might be in a quantum coherent superposition that lasted long enough to transport energy like a wave, instead of like a particle–which would be slower–through an array of chromophores. If true, biomolecular engineering for sustaining wavelike transport would be of interest for basic and applied research. One use could be better light-collection devices. Other studies, however, have emphasized the role of molecular vibrations to explain these observations (*5*). To help settle these long-standing discussions, new spectroscopic techniques that extract more information need to be developed.

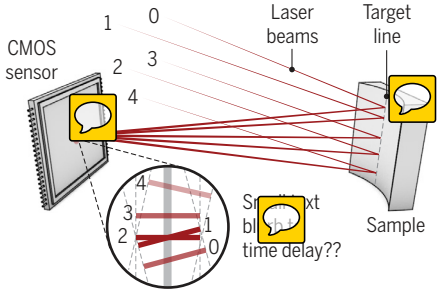
The GAMERS method (gradient-assisted multidimensional electronic Raman spectroscopy) may provide a way to resolve this matter by adding another pulse to a 2D electronic spectroscopy. This additional pulse controls the initial vibrational state of the molecule. During the time between the first and the second pulse, the vibrational state changes. By looking at the subsequent changes to the electronic coupling based on the starting vibrational state, GAMERS could determine how vibrations change the electronic coupling, which is not generally directly obtained from other spectroscopies.

With a traditional setup, simiar data collection would take more than 1 week, and lasers are not guaranteed to be stable for that long. Instead of delaying two beams by physically changing the beam path and measuring in the same location, GRAPES tilts the two beams relative to each other (see the figure) and takes the detection as a 2D image, thus performing all of the necessary experiments at once and drastically reducing the time to solution. GAMERS uses the GRAPES technique for the delay between the middle two pulses, thereby reducing the acquisition time from ~1 week to mere hours. The complex multidimensional spectroscopic signals acquired may yield intricate details on the coupling of electronic states to nuclear vibrational motion. The quantum of perovskite solar cells (*8*), singlet-fission materials (*9*), quantum nanostructures (*10*), and photosynthestic complexes (*2*) all exhibit details of the electronic-vibrational interactions that require further exploration.

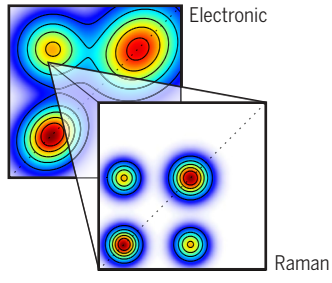
There are some drawbacks,. The GAMERS protocol requires a molecular vibration that is Raman active, which is not always the case. There is also theoretical work needed to understand precisely what information GAMERS encodes. It may be particularly useful to consider GAMERS in the context of quantum-process tomography (*11*), as the addition of more pulses makes the experiment probe more elements of the quantum process matrix. ■

Faster spectra collection

The method of Spencer et al. speed up pump-probe data collection that can interrogate how vibrations between atoms connect to the electronic bonding states in molecules.



Lines and mirrors
Five separate laser pulses focusing in to the target. The tilt between beams 1 and 2, shown in the circular inset, create a time delay.



Spectra within spectra
Each point in the electronic spectrum collected in two dimensions in effect contains a Raman spectrum in two imdensions [where the w;s are...

Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA 02138, USA. Email: alan@aspuru.com

GRAPHIC: C. BICKEL/*SCIENCE*

REFERENCES

1. A. P. Spencer, W. O. Hutson, E. Harel, *Nat. Commun.* **8**, 14732 (2017).
2. G. S. Engel *et al.*, *Nature* **446**, 782 (2007).
3. G. D. Scholes *et al.*, *Nature* **543**, 647 (2017).
4. J. Huh *et al.*, *J. Am. Chem. Soc.* **136**, 2048 (2014).
5. V. Tiwari, W. K. Peters, D. M. Jonas, *Proc. Natl. Acad. Sci. U.S.A.* **110**, 1203 (2013).
6. E. Harel, A. F. Fidler, G. S. Engel, *J. Phys. Chem. A* **115**, 3787 (2011).
7. M. Khalil, N. Demirdöven, A. Tokmakoff, *J. Phys. Chem.* A **107**, 5258 (2003).
8. H. Zhou *et al.*, *Science* **345**, **542** (2014).
9. W.-L. Chan, J. R. Tritsch, X.-Y. Zhu, *J. Am. Chem. Soc.* **134,** 18295 (2012).
10. J. Bylsma *et al.*, *Phys. Rev. B* **86**, 125322 (2012).
11. J. Yuen-Zhou, J. J. Krich, M. Mohseni, A. Aspuru-Guzik, *Proc. Natl. Acad. Sci. U.S.A.* **108**, 17615 (2011).

10.1126/science.aan2842