Spatial Spectral Interferometry and Compressed Sensing Detection in Single-Shot 2DFT Spectroscopy

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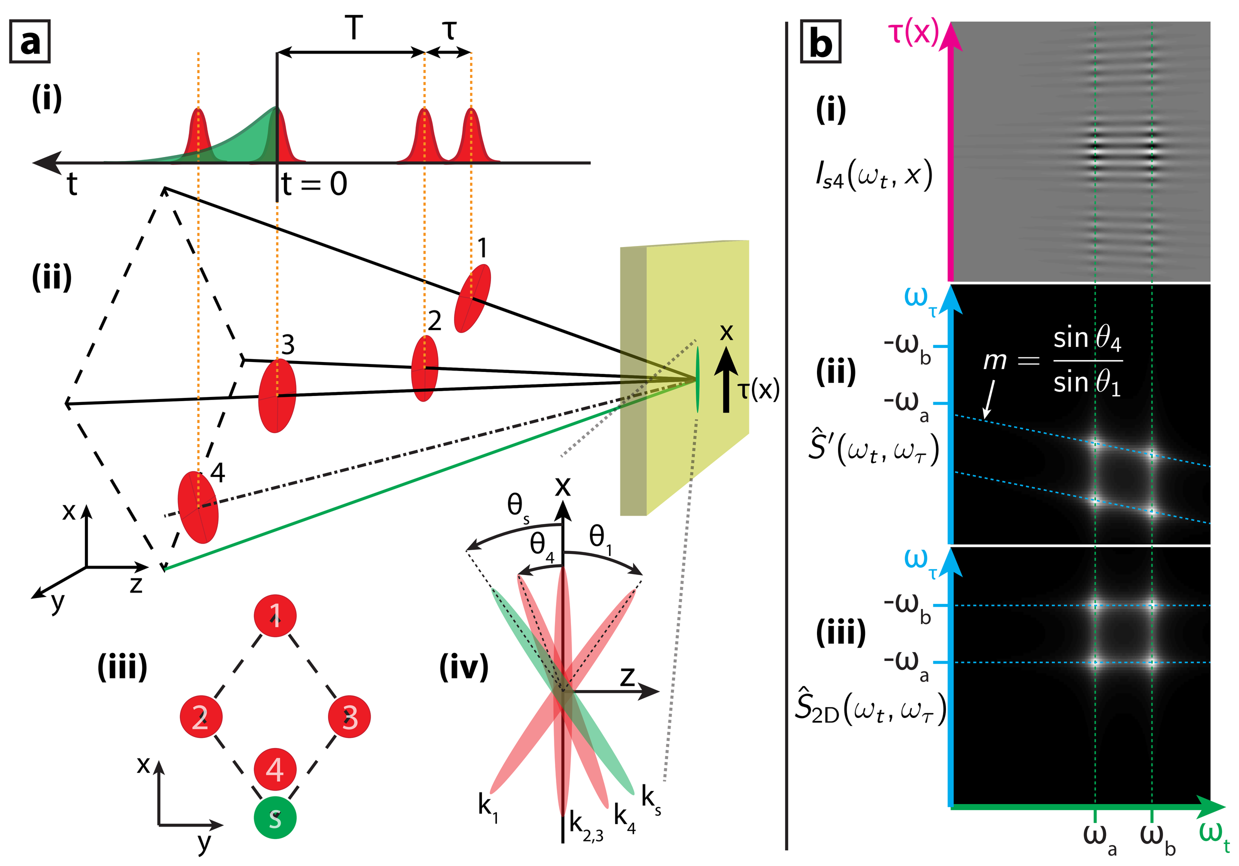
Spatial Spectral Interferometry*

Introduction

Multidimensional spectroscopies have the power to uncover coupling in complex systems of electronic and vibrational transitions. In particular, two-dimensional Fourier-transform (2DFT) spectra contain the frequency correlation of dipole oscillations between two time intervals (τ and t) separated by a waiting time (T) with molecule-limited frequency and time resolution. Peak amplitudes and beatings in the spectrum expose population kinetics and coherent coupling between states. Of particular interest are off-diagonal cross peaks, which mark coupled transitions, yielding valuable molecular information including vibronic coupling and energy transfer dynamics.

Experiment



a) In GRadient-Assisted Photon Echo Spectroscopy (GRAPES), a three pulse sequence is focused to a line in the sample, exciting a third-order polarization that subsequently radiates a signal field. The signal is detected by spectral interferometry using a fourth beam as the reference field.

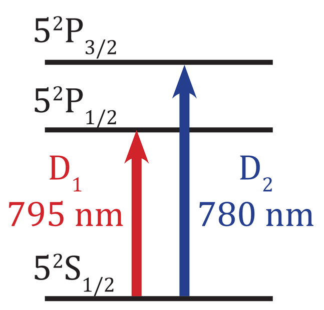
b.i) By tilting beam 4 relative to the signal, spatial interference fringes appear in the spatial spectral interferogram.

b.ii) The resulting peaks in the 2DFT spectrum are shifted from their expected locations by a frequency-dependent factor.

b.iii) Multiplying the interferogram by the factor below corrects for the signal–reference tilt.

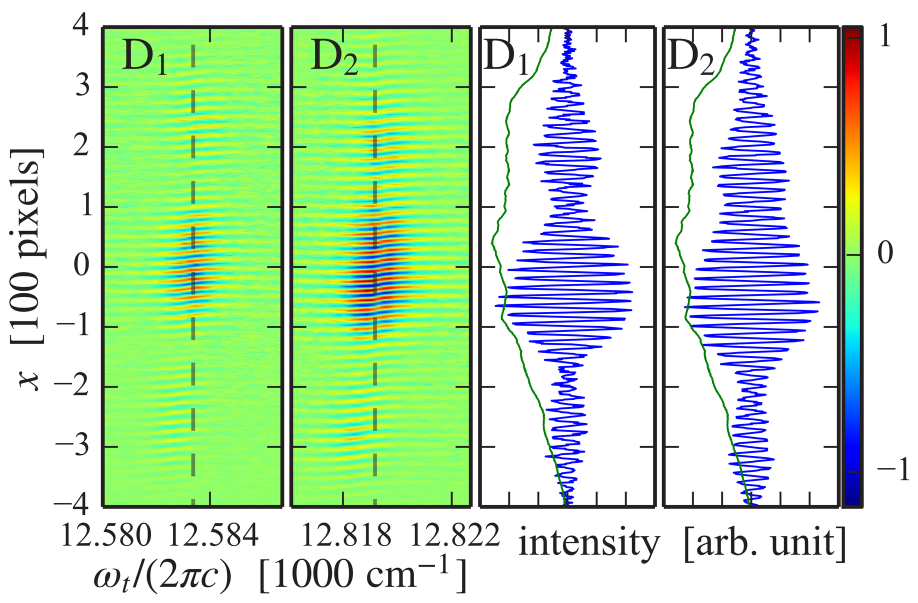
$$\tilde{I}^c_{s4}(\omega_t, x) = I_{s4}(\omega_t, x)\exp\{[k_4(\omega_t) - k_3(\omega_t)]\cdot x\}$$

Rubidium Vapor



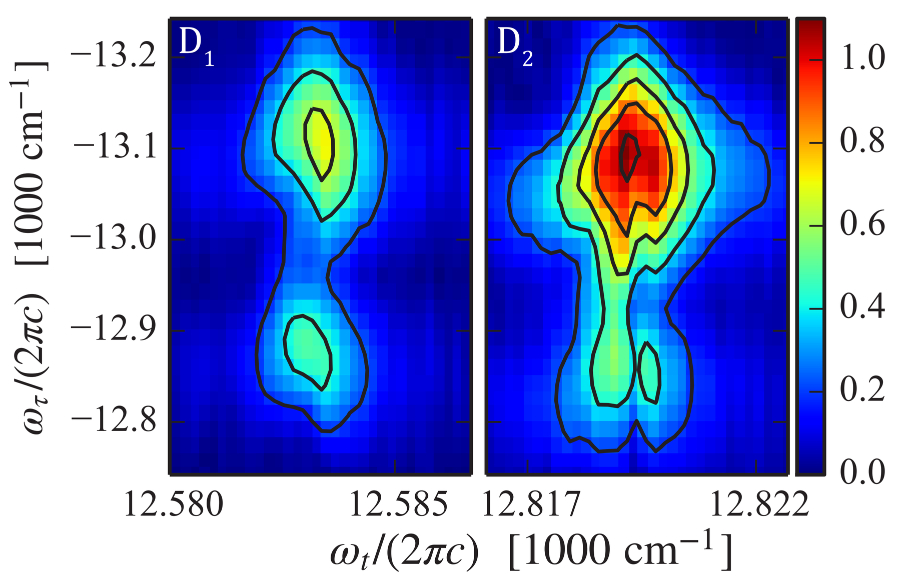
The D lines of atomic rubidium vapor are exceptionally narrow, having linewidths of only ~0.3 cm^{-1} when broadened by 650 Torr of neon buffer gas.

Interferogram



Spatial spectral interferograms exhibit beating between signal radiated at the D_1 and D_2 transition frequencies.

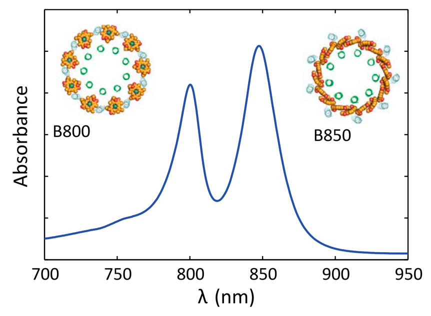
2DFT Spectrum



The 2DFT spectrum contains two diagonal peaks and two corresponding off-diagonal cross peaks, as expected for transitions linked by a common ground state.

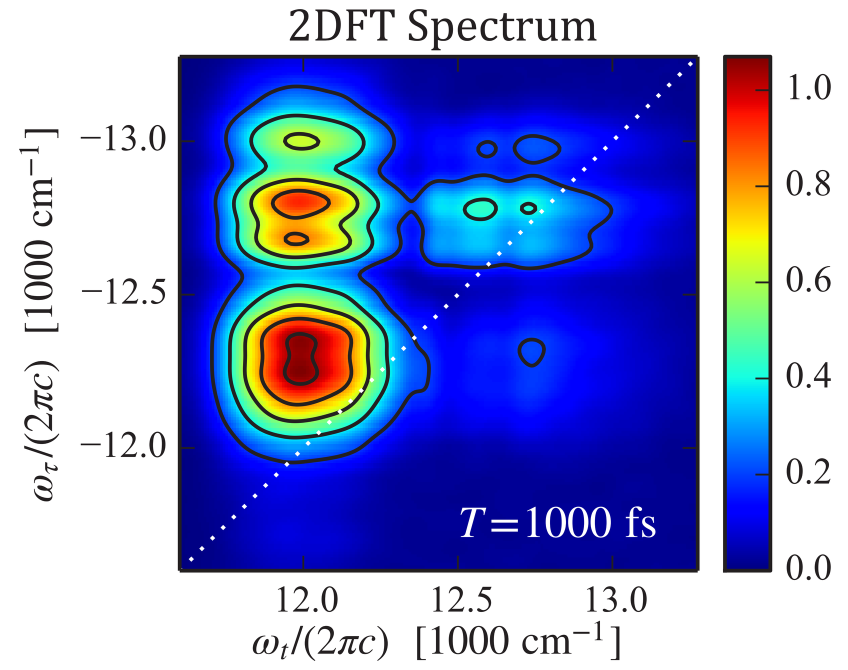
Signal reabsorption is responsible for the peak distortions present near the D_2 detection frequency.

LH2



The light harvesting protein complex LH2 has two electronic transitions in the near infrared: B800 at 800 nm and B850 at 850 nm. Although the excited states of these transitions are delocalized on separate chromophore ring structures, energy transfer between rings occurs on a ~1 ps timescale.

2DFT Spectrum



By a waiting time of T = 1 ps, the higher energy B800 diagonal peak has lost much of its amplitude to the above-diagonal cross peak, a signature of energy transfer.

Conclusions

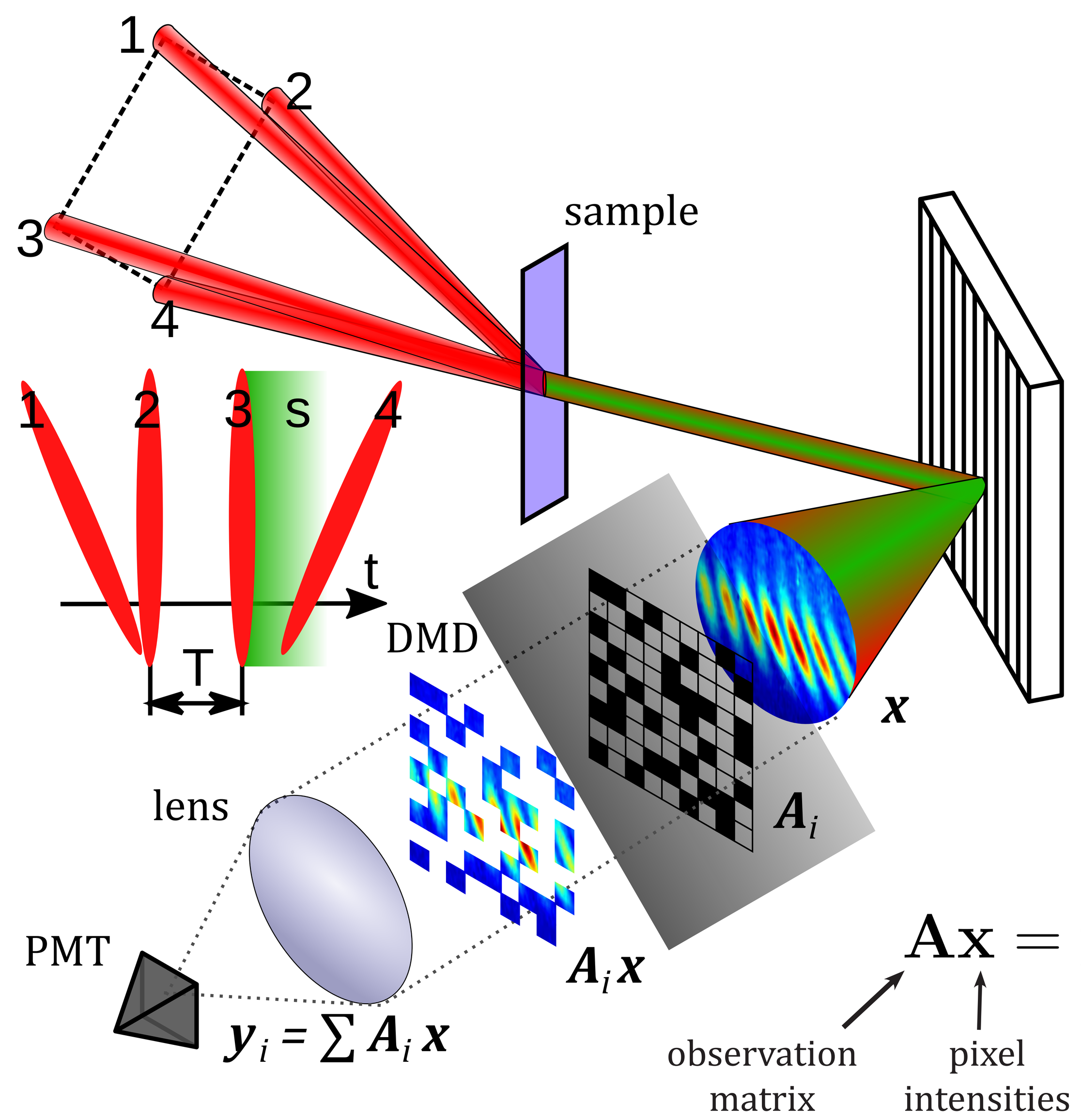
Spatial spectral interferometry:

- eliminates the frequency resolution limitations of Fourier-transform spectral interferometry, enabling study of narrow rubidium vapor D lines;
- improves sensitivity due to higher spectrograph throughput (no need to resolve narrow interference fringes);
- enhanced flexibility with the ability to optimize frequency resolution versus sensitivity.

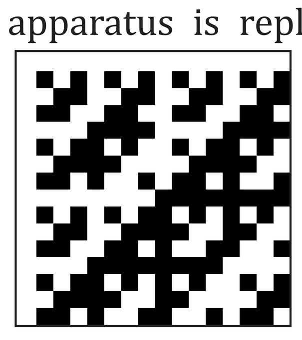
*Spencer, A. P., Spokoyny, B. & Harel, E. Enhanced-Resolution Single-Shot 2DFT Spectroscopy by Spatial Spectral Interferometry. *J. Phys. Chem. Lett.* 945–950 (2015).

Compressed Sensing Detection†

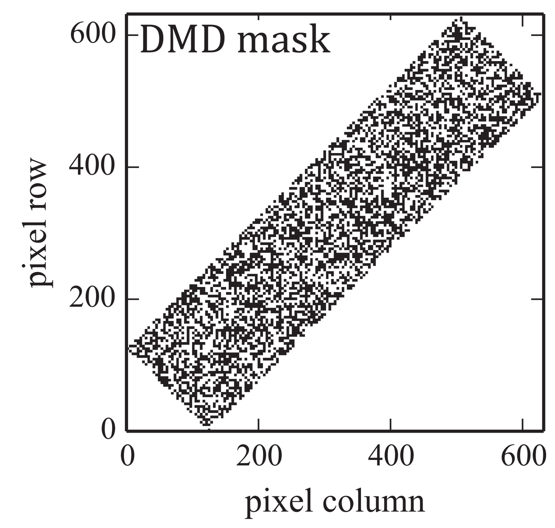
Experiment

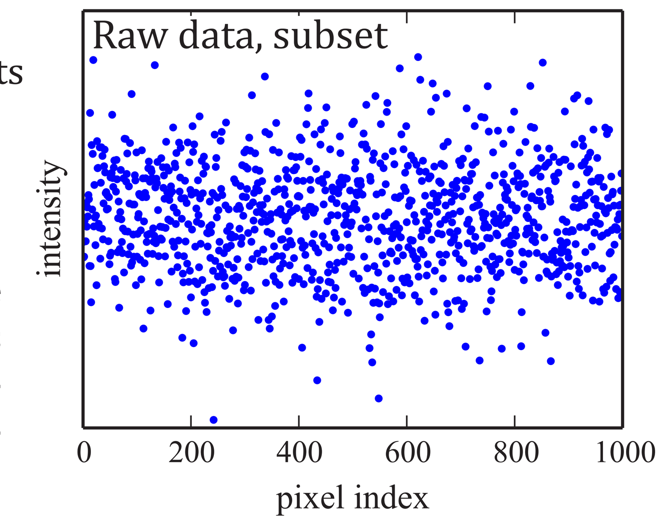


To implement compressed sensing (CS) detection, the 2D array detector used in a standard GRAPES apparatus is replaced by a digital micromirror device (DMD) and single-element photomultiplier tube (PMT), enabling arbitrary sampling of the spatial spectral interferogram image at the output of the spectrometer.



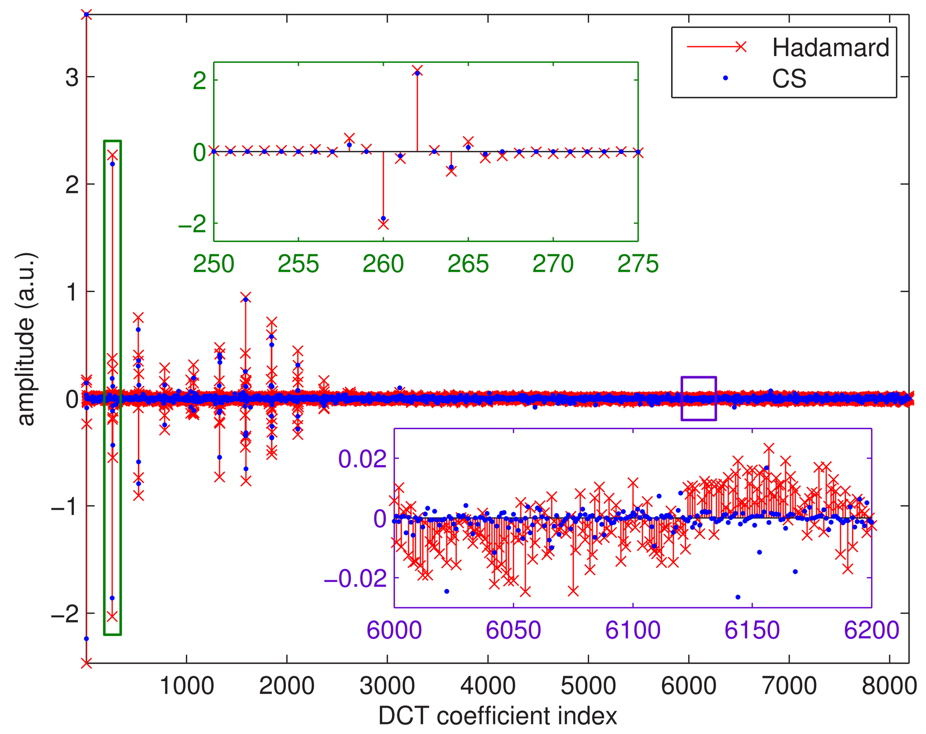
H_{16} matrix





Results

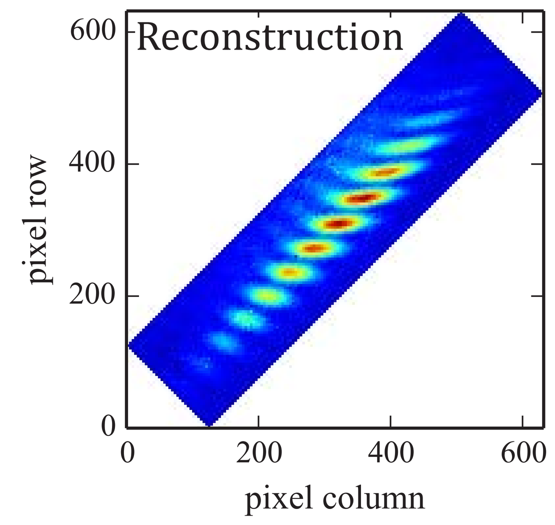
DCT of Pixel Data

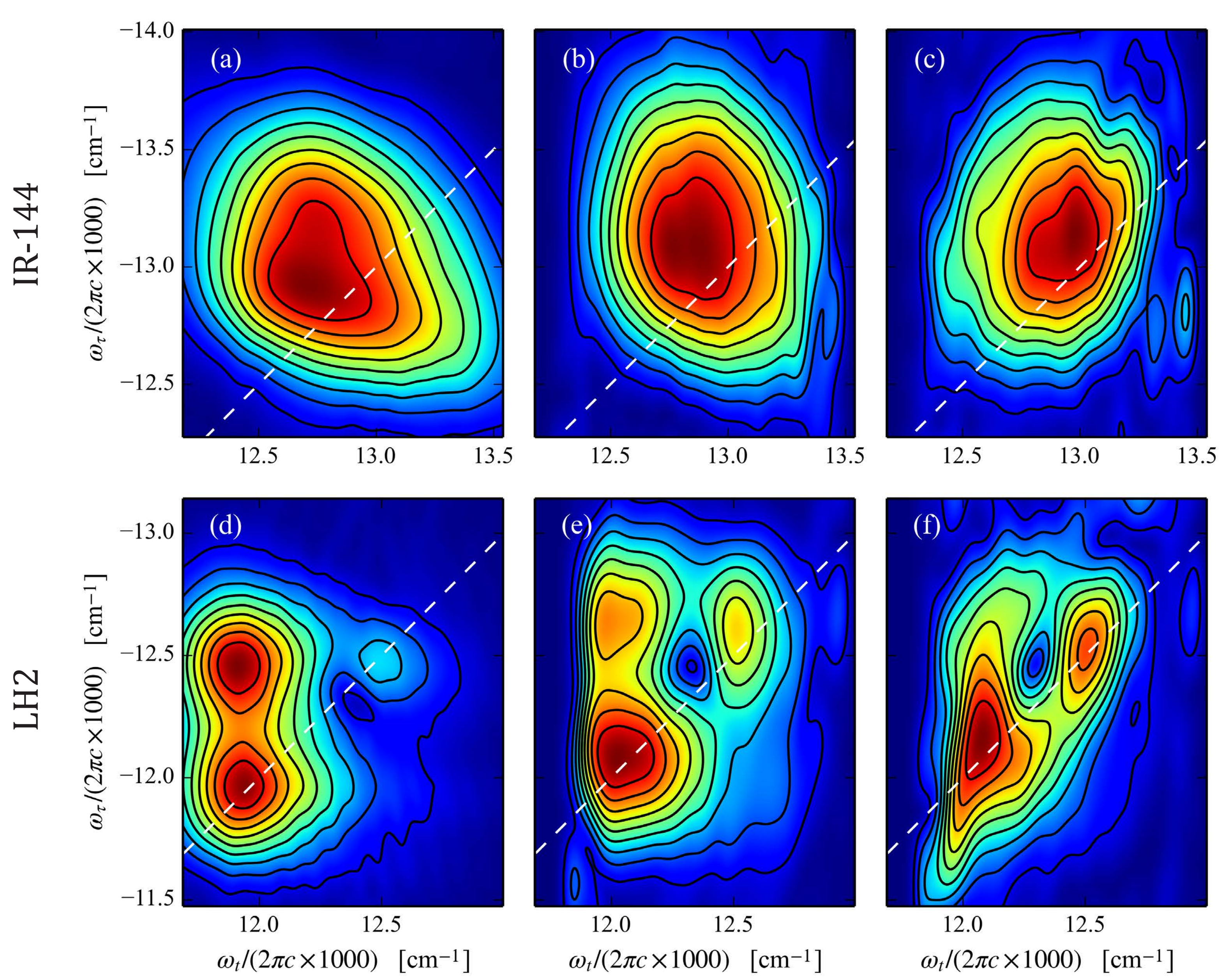


The discrete cosine transform (DCT) was used as the sparsifying transform for compressed sensing.

The CS reconstruction compares well to the DCT of the Hadamard reconstruction.

CS does not recover the low-lying high frequency components of the DCT that are attributable to noise (purple inset).





Conclusions

Both Hadamard and CS reconstructions produce 2DFT spectra that match the peak locations of spectra acquired using a traditional 2D array detector.

Peak shapes and amplitudes are somewhat distorted, partly due to DMD mask area restrictions.

A CS algorithm is able to reproduce the Hadamard reconstruction with only 10–15% as many measurements (i.e., ~10× sub-Nyquist sampling).

†Spencer, A. P., Spokoyny, B., Ray, S., Sarvari, F. & Harel, E., submitted.