

Optical Multidimensional Spectroscopy of Atomic Vapor

Hebin Li¹, Galan Moody^{1,2}, Alan D. Bristow¹, Mark E. Siemens¹, and Steven T. Cundiff^{1,2}

¹JILA, National Institute of Standards and Technology, and University of Colorado, Boulder, CO 80309-0440, USA

²Department of Physics, University of Colorado, Boulder, CO 80309-0440, USA

Abstract. Optical single- and double-quantum three-dimensional Fourier-transform spectra are obtained for atomic vapors. We show that three-dimensional spectra can be used to identify the Hamiltonian of complex systems and to reveal the nature of many-body interactions.

Advances in preparing cold atoms and molecules provide a unique and controllable environment for experiments in the virtual absence of thermal motion. In contrast, an ensemble of thermalized atoms (an atomic vapor) at ambient or higher temperatures represents a more natural scenario which is shared by many processes such as DNA folding and photosynthesis. It is important to understand the optical response due to fundamental processes such as interatomic interactions in an atomic vapor in order to gain insights for more complex systems.

Predicting and controlling optical responses and other quantum phenomena requires knowledge of the system Hamiltonian. In coherent control [1], for example, the information about contributing pathways or the underlying Hamiltonian is essential for achieving deterministic control and for improving the performance of optimal control approaches. The Hamiltonian of complex systems, especially the effects of inter-particle interactions and coupling to the environments, can only be determined experimentally. The greatest challenge is how to isolate each single quantum pathway so that the information can be unambiguously identified for each particular process. Here we report an experimental approach to determine a full Hamiltonian by using optical three-dimensional Fourier-transform (3DFT) spectroscopy [2]. 3DFT spectra contain full information of the third-order optical response, while the contributions from different pathways are isolated such that the components of the Hamiltonian can be determined. Moreover, double-quantum 3DFT spectra provide information about interatomic interactions by isolating spectral contributions due to collective resonances of atoms.

Optical multidimensional spectra are generated from three-pulse transient four-wave mixing (TFWM) experiments. The JILA-MONSTR [3] provides four phase-stabilized 100 fs laser pulses in the box geometry. Three pulses with wave vectors \mathbf{k}_A , \mathbf{k}_B , and \mathbf{k}_C are incident on the sample to generate a TFWM signal in the direction $\mathbf{k}_S = -\mathbf{k}_A + \mathbf{k}_B + \mathbf{k}_C$. The fourth pulse is routed around the sample and later combined with the signal for spectral interferometry. We denote the time delay between the first and second pulses as τ , between the second and third pulses as T and the emission time as t . The TFWM signal is recorded in the frequency domain while scanning one or two time delays. Multidimensional spectra are generated by Fourier

This is an Open Access article distributed under the terms of the Creative Commons Attribution License 2.0, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

transforming the signal with respect to the time delays. Scanning either τ or T generates two-dimensional Fourier-transform (2DFT) spectra, while a 3DFT spectrum can be obtained by scanning both τ and T . The experiments are performed with atomic vapors held in thin titanium cells with two sapphire windows. The spectral lines are broadened by a 1550 torr argon buffer gas. The atomic density can be adjusted by changing the cell temperature. An important advantage of 2DFT spectra is the ability to dissect quantum pathways by unfolding a one-dimensional spectrum onto a 2D plane. However, in most cases, the quantum pathways are only partially separated in a 2DFT spectrum. In order to completely isolate the quantum pathways, the spectrum can be further unfolded in a 3DFT spectrum with three frequency dimensions corresponding to three time delays (τ , T and t). Here we demonstrate both single- and double-quantum 3DFT spectra.

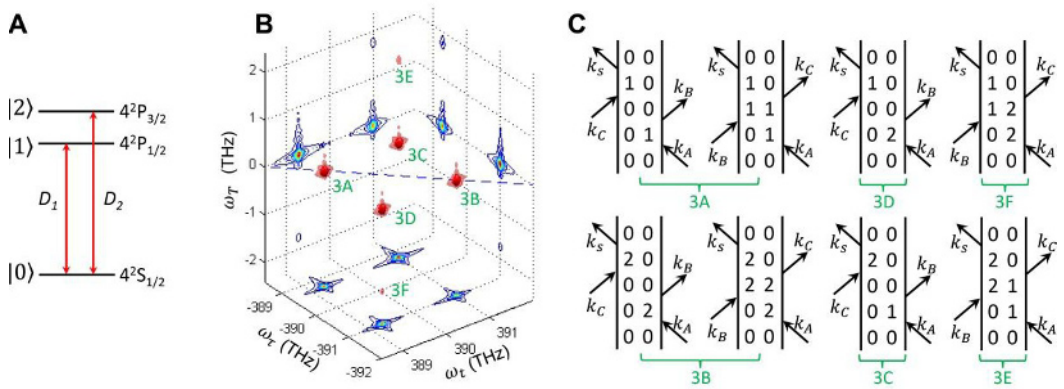


Fig. 1. (A) Energy level scheme of potassium atom. (B) 3D rephasing spectrum with 2D projections. (C) Double-sided Feynman diagrams representing all quantum pathways and the corresponding peaks in the spectrum.

The single-quantum 3DFT spectra are obtained with a potassium (K) vapor. The relevant energy levels of the K atom are shown in Fig. 1A. The laser is tuned to cover both D_1 and D_2 transitions which are coupled through a common ground state. With the conjugated pulse (k_A) arriving first, a 3DFT rephasing spectrum, as shown in Fig. 1B, can be obtained. The spectrum is visualized as isosurfaces (red), a 3D analog of 2D contour lines. Compared to 2D spectra, the 3D spectrum is further unfolded in the third frequency dimension. The contributions from the zero-quantum coherences are isolated from the off-diagonal peaks on the $\omega_T = 0$ plane.

A 3D spectrum contains the full information of the system's third-order optical response. As illustrated in Fig. 1B, projecting a 3D spectrum onto different 2D planes reconstructs various 2D spectra [4] including the ones that are not accessible by conventional 2D spectroscopy. More importantly, the spectral contributions from different pathways shown in Fig. 1C are completely isolated. In the spectrum, four peaks (3D-F) that are not on the diagonal line each represents a single pathway, while the two peaks (3A-B) on the diagonal line each include two pathways which describe equivalent processes in a closed system. Therefore, the information on a particular physical process can be retrieved by analyzing a single 3D spectral peak. The position, strength and lineshape of all 3D peaks can be used to determine the system's energy levels, dipole moments and relaxation rates. These are all components that are needed to identify the system's full Hamiltonian including the relaxation matrix.

Additionally, the Hamiltonian of a ladder system can be determined through double-quantum 3DFT spectra. In a ladder energy level scheme shown in Fig. 2A, the system's Hamiltonian includes double-quantum coherences which contribute to the TFWM signal in the direction k_S if the conjugated pulse (k_A) arrives at the sample last. A rubidium (Rb) vapor is used and the laser is tuned to the D_2 line such that the double-quantum state $5D$ is also excited.

The double-quantum 3DFT spectrum of the Rb vapor is shown in Fig. 2B. All peaks are located on the gray plane corresponding to the single-quantum resonant frequency. Peaks I and II represent the pathways involving double-quantum coherences between states $|2\rangle$ and $|0\rangle$. However, the double-quantum coherence frequency of peak III is twice the energy difference between states $|1\rangle$ and $|0\rangle$, which does not correspond to a real energy state. This peak is attributed to the collective resonances of two atoms induced by the dipole-dipole interaction [5]. In the joint Hilbert space of the two atoms, the double-quantum state represents two atoms in their individual singly-excited states. The double-quantum coherence involving such a state contributes to the signal if the two atoms interact with each other. Peak III indicates the dipole-dipole interaction between Rb atoms and might reveal the nature of many-body interactions in atomic vapor.

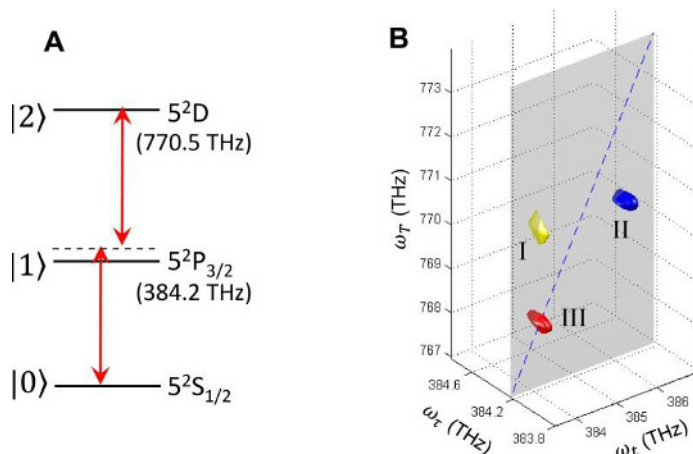


Fig. 2. (A) Energy level scheme of rubidium atom. (B) Double-quantum 3DFT spectrum of a rubidium vapor.

In summary, optical multidimensional spectroscopy can provide complete and well-isolated information of the third-order optical response of an atomic vapor. The information can be used to fully characterize the Hamiltonian of complex systems including many-body interactions, which is useful for predicting and controlling their quantum mechanical behaviors.

References

- [1] H. Rabitz, R. de Vivie-Riedle, M. Motzkus, and K. Kompa, "Chemistry - whither the future of controlling quantum phenomena?" *Science* **288**, 824 (2000).
- [2] H. Li, A.D. Bristow, M.E. Siemens, G. Moody, and S.T. Cundiff, "Experimental determination of Hamiltonian via optical 3D Fourier-transform spectroscopy," Submitted.
- [3] A.D. Bristow *et al.*, "A versatile ultra-stable platform for optical multidimensional Fourier-transform spectroscopy," *Rev. Sci. Instrum.* **80**, 073108 (2009).
- [4] X. Dai, A.D. Bristow, D. Karaiskaj, and S.T. Cundiff, "Two-dimensional Fourier-transform spectroscopy of potassium vapor," *Phys. Rev. A* **82**, 052503 (2010).
- [5] X. Dai, M. Richter, H. Li, A.D. Bristow, C. Falvo, S. Mukamel, and S.T. Cundiff, "Two-dimensional double-quantum spectra reveal collective resonances in an atomic vapor," *Phys. Rev. Lett.* **108**, 193201 (2012).