Lineshape Analysis of Double-Quantum Multidimensional Coherent Spectra

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Double-quantum two-dimensional coherent spectroscopy (MDCS) is a powerful optical method that is used to study optical properties of atomic and complex molecular systems and semiconductor materials. Double-quantum 2D spectra and particularly the peak lineshapes on the spectra can also provide information about many-body interactions. We model 2D spectra by solving the optical Bloch equations and show the effects of correlation between coupled resonances, which also explains the discrepancies between the experimental results reported by multiple groups.

I. INTRODUCTION

In the past two decades multidimensional coherent spectroscopy (MDCS) [1, 2] has become a powerful and routine technique for studying optical properties and ultrafast dynamics of atomic/molecular samples and semiconductor materials [2–7]. MDCS is based on concepts of Nuclear Magnetic Resonance experiments that is widely used for determining the molecular structure [8]. A simplified schematic diagram of multidimensional coherent spectroscopy is shown in Fig. 1 (a). A sequence of three pulses (A, B, C) incident on the sample of interest generates a four-wave mixing (FWM) signal which is then heterodyne detected, using a local oscillator pulse, as a function of the delays between the excitation pulses. Experimentally, the separation of the FWM and linear signals are performed either utilizing a “Box” geometry [9] or a co-linear geometry [10, 11] and phase-cycling schemes (each excitation pulse is frequency tagged and the signal is detected at $f_{\text{sig}} = -f_a + f_b + f_c$ frequency) as shown in Fig. 1 (b) and (c). The recorded time domain interferogram is then Fourier transformed with respect to the time delays between the incident pulses and over the time period during which the signal is emitted to generate a multidi- mensional coherent spectrum.

In MDCS, a multidimensional coherent spectrum generated by different pulse ordering provides different spectroscopic information. For example: if the first pulse is the phase conjugated pulse ($A^*, B, C$) (which is also called as the photon echo excitation scheme [12]) then the corresponding multidimensional spectrum (also referred to as a single-quantum 2D spectrum) provides both the homogeneous and inhomogeneous linewidths of the sample and they can be extracted simultaneously [13]. On the other hand if the complex phase-conjugated pulse arrives last ($B, C, A^*$) then the corresponding 2D spectrum (also referred to as a double-quantum 2D spectrum) can probe weak many-body interactions (for example long-range dipole-dipole interactions) [14–18]. In addition, peak lineshapes on a two-dimensional spectrum provide extremely valuable information. For example, one can determine a correlation function [19] (which is related to the spectral diffusion) by measuring the ellipticity of the elongated peaks on a single quantum two dimensional spectrum as a function of the time delay between B and C pulses [20, 21]. We note that over the years several methods have been developed to interpret lineshapes of single-quantum multidimensional coherent spectra [13, 20–22].

On the other hand, the literature is not consistent about peak lineshapes (elongation) on double-quantum coherent spectra which is also very important as they provide insight about the underlying physics of the many-body interactions. In double-quantum 2D spectra the elongation of the peaks along the diagonal suggests that there is correlation between excitation and emission frequencies. However, theoretically it has been shown that peaks are expected to be elongated and no correlation parameter was included in the calculation [18]. Furthermore, there were several 2D experiments performed both on semiconductor materials and atomic samples that didn’t show any peak elongation [14, 18, 23–25]. There were also experiments performed on atomic and molecular samples where the elongated peaks were observed [17, 26].

In [17] we briefly explained the experimental results using a simple model. In this paper we show the full theoretical model, which could also shed light on the inconsistencies between the results mentioned above. This simple model will help interpret experimental 2D spectra. In the next section we will discuss the concept of double-quantum multidimensional coherent spectroscopy. In section III we will show our model and the results of our simulation and in section IV we will conclude our observation.

II. GENERATION OF A FWM SIGNAL IN DOUBLE-QUANTUM TWO-DIMENSIONAL COHERENT SPECTROSCOPY

As described above, double-quantum two dimensional coherent spectroscopy uses the pulse sequence where the
FIG. 1. (a) Schematic diagram of multidimensional coherent spectroscopy. In the figure the photon echo excitation sequence is displayed. Pulse A* creates a coherence between the ground and excited states. Pulse B converts the coherence into the population state and then pulse C converts it back to the coherence between and the ground and excited states which emits a Four-Wave-Mixing (FWM) signal. The signal is detected with a local oscillator pulse. (b) and (c) shows the detection of the FWM signal using a "box" and the co-linear geometry, respectively. |g⟩ and |e⟩ correspond to ground and excited excited states, respectively.

phase conjugated pulse arrives last. Pictorially the generation of a FWM signal in a simple three-level system is shown in Fig. 2 (a). The first pulse excites a coherence between the ground and singly excited states and then the same pulse (or different pulse if three pulses are used) excites the coherence between the ground state and the doubly excited state (also referred to as a double-quantum coherence). The last pulse then puts the system either back into the coherence between the ground and the singly excited states or into the coherence between the singly excited and doubly excited states. The final coherence then radiates the FWM signal that is detected. From this diagram it is clear that double-quantum MDCS is used to probe doubly excited states in the sample, however it can provide even more important information if applied to samples that do not have double excited states (or they are outside the bandwidth of the laser pulses). In that case the generation of a FWM signal can be described by combining two 2-level systems as shown in Fig. 2 (b) which clearly shows a doubly excited state. In Fig. 2 (c) we show the double-sided Feynman diagrams of the pathways that are contributing in the generation of the FWM signal. However, if there is no interaction between these two 2-level systems then the contributions have the same strength and the opposite sign (I-IV positive, II-III negative) and hence they cancel each other. If we include many-body interactions (for example long range dipole-dipole interactions between two 2-level atoms) then singly and doubly excited states experience slight energy shifts or changes in the line-width (Fig. 2 (d)). The changes break the symmetry between the contributions in Fig. 2 (c) which leads to the generation of a FWM signal. We note that the FWM signal is only due to the interactions (even a small interaction strength is enough to break the symmetry between the contributions) and hence double-quantum MDCS is a very sensitive and powerful tool for probing many-body interactions.

III. SIMULATION AND RESULTS

To study the peak behavior of double-quantum 2D spectra we solved the optical Bloch equations for two coupled 3-level V-type systems. The energy level diagram of two combined V-type systems (without interaction) is shown in Fig. 2 (e) which can also be described as superposition of the states created by coupled 2-level systems shown in Fig. 2 (e, 1,2,3,4). In our simulation we used delta-function pulses and at first we treated the systems to be homogeneously broadened. Under these conditions the third order polarization (one of the pathways) for figure Fig. 2 (e(1)) created by the sequence of MDCS pulses (Fig. 2 (a)) is:

$$P(t, \tau) = (-i/\hbar)^3 \mu_{ge}^4 \text{Exp}[i\omega t - i\omega_\tau \tau - \gamma t - \gamma_\tau \tau]$$
FIG. 2. (a) Double-quantum excitation scheme. (b) energy level diagram of two combined two-level systems without interaction. (c) Double-sided Feynman diagrams contributing for the generation of the FWM signal. (d) energy level diagram of two combined two-level systems with interaction. ∆1 and ∆2 energy shifts due to interaction. Dotted lines show the shifted energy states. (e) Energy level diagram of two combined V-type systems which is also represented as a superposition of states created by two-level systems (1), (2), (3) and (4). |g⟩, |e⟩ and |f⟩ correspond to ground, excited and doubly excited states, respectively.

energy shifts Δ1 and Δ2 (described below) for the single and double excited states (Fig. 2 (d)).

To model a real system, inhomogeneous broadening was incorporated into the simulation by integrating the polarization over a generalised two-dimensional Gaussian function [27]:

\[
f(x, y) = \frac{1}{2\pi \sigma_x \sigma_y \sqrt{1 - \rho^2}} e^{-\left(\frac{(x - \nu_x)^2 - 2\rho(x - \nu_x)(y - \nu_y) + (y - \nu_y)^2}{2(1 - \rho^2)}\right)}
\]

(2)

where \(\nu_x, \nu_y, \sigma_x, \sigma_y\) correspond to the centers and widths of two interacting inhomogeneously broadened resonances and \(\rho\) is a correlation parameter. \(\rho=1, \rho=0,\) and \(\rho=-1\) implies that the resonances are perfectly correlated, uncorrelated and anti-correlated, respectively.

The integration yields

\[
P(t, \tau) = (-i\hbar)^3 \mu_{ge}^4 \exp[i\omega t - i\omega t \tau - \gamma t \tau - 2\gamma t \tau - \frac{1}{2}(t^2(\sigma_A^2 + \sigma_I^2) + 2\rho\sigma_A\sigma_I) - 2t(\rho\sigma_A\sigma_I + \sigma_I^2) + t^2\sigma_I^2)]
\]

(3)

If we assume that \(\sigma_A=\sigma_I \equiv \sigma\) and include the energy shifts due to interactions \(\omega_I = \omega_{ge} + \Delta_1\) and \(\omega_I = 2\omega_{ge} + \Delta_2\) (where \(\omega_{ge}\) is the transition frequency between the ground and the excited states), then all the polarization terms that are contributing in the generation of the FWM signal for the system shown in Fig. 2 (e(1)) are
performed on Doppler broadened atomic samples that showed that the peaks were not elongated along the diagonal line (the elongation was obscured and the peaks were elongated more along the vertical line) [14, 23]. But in the experiments an argon (Ar) buffer gas was introduced into the gas cell to artificially broaden (collisional broadening) the resonances to match the spectrometer resolution. To model the case we increased the decay rates (by a factor of 20 which is similar to the values of their experimental parameters) in our simulation. The results that are plotted in Fig. 3(f) show that even with the high degree of correlation (\( \rho = 0.75 \)), peaks now are elongated along the vertical line which is similar to the results observed in [14, 23].

Our model can be extended to semiconductor materials as well. For quantum wells (and quantum dots) \( \rho \) is expected to be close to zero (or partially correlated). This is because in semiconductor materials a double-quantum FWM signal is due to the coupling of the excitons that are located in nearby quantum wells and the thickness of wells are most likely random. In this case the peaks are expected to be elongated along the diagonal (ellipticity = 0.5) but the experiments showed that the peaks are tilted toward the vertical axis [24, 25]. This can be explained with the fact that unlike atomic systems, the excitons experience additional dephasing due to excition-exciton and exciton- free carrier scattering (which is a strong function of the temperature) reported in [18]. This scattering causes the 2D peaks to be tilted similarly to the results that we showed for atomic systems in Fig. 3(f).

IV. CONCLUSION

In this work we theoretically investigated the line-shapes of double-quantum two-dimensional coherent spectra. We studied two coupled V-type systems and simulated the spectra by solving the optical Bloch equations. We showed that peak line-shapes describe how the resonances (from each system) are correlated and give insight into the mechanism of many-body interactions. We applied our model to Doppler-broadened atomic samples and explained the discrepancies between the experi-
Emission frequency $\omega - \omega_{\text{ref}}$ [GHz]

Double quantum frequency $2(\omega - \omega_{\text{ref}})$ [GHz]

$\rho = -0.9$

$\rho = -0.6$

$\rho = 0.0$

$\rho = 0.6$

$\rho = 0.9$

$\rho = 0.75$

(a) (b) (c) (d) (e) (f)

FIG. 3. Simulation results. (a) $\rho = -0.9$ (b) $\rho = -0.6$, (c) $\rho = 0.0$, (d) $\rho = 0.6$, (e) $\rho = 0.9$, (f) $\rho = 0.75$ and increased decay rate. $\omega_{\text{ref}}$ arbitrary optical frequency. Color scale shows normalized signal magnitude.

tal results reported in [14, 17, 23]. We also discussed the expected peak lineshapes (and correlation) of 2D spectra generated in semiconductor materials and explained the difference between our theoretical results and the experimental results reported in [18, 24]. We hope that the MDCS community will benefit with this simple method when interpreting double-quantum correlation coherent spectra. We also hope that the model will help the MDCS community understand the many-body interactions better, particularly the dipole-dipole interaction that plays the crucial role for photosynthesis and the formation of complex molecules.

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