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EXECUTIVE SUMMARY OF THE THESIS

Two dimensional electron spectroscopy of graphene nanoribbons: modeling and experiment

LAUREA MAGISTRALE IN ENGINEERING PHYSICS - INGEGNERIA FISCA

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Academic year: 2022-203

1. Introduction

Material science at the nano and molecular scale has witnessed significant advancements in the last decades, offering a myriad of opportunities to tailor nanostructures for diverse applications. The confinement of graphene within a few nanometers has led to the creation of a finite band gap in its electronic structure. This development makes the resulting nanographenes exceptionally promising for various optoelectronic applications [1]. This master's thesis focuses on a particularly promising nanographene structure with optoelectronic properties suitable for lasing. The molecular nanostructure is a Dibenzo[hi,st]ovalene functionalized with two mesityl groups and two chlorine atoms (DBOVMes-Cl), and it has been studied using advanced ultrafast spectroscopy techniques. Nanographene derivatives have a strong vibrational-electronic (vibronic) coupling. Vibrational modes coupled to electronic states have been suggested to drive ultrafast radiationless decays in biological as well as synthetic molecular systems, so that understanding the nuclear and electronic degrees of freedom interplay is crucial to describe the photophysical properties of the molecule.

To comprehensively describe the vibrational modes and quantify the contribution of each electronic state to the vibronic interplay, the thesis employs advanced spectroscopy techniques. Two-dimensional electron spectroscopy (2DES) emerges as a powerful time-resolved spectroscopical tool, offering high temporal and frequency resolution, which allows to provide real time tracking of energy/charge transfer processes real time, and to unveil the origin and role of molecular excited and ground state vibrations. To unveil from a 2DES experiment such rich information, a plethora of interpretative models can be applied. In this work, the modeling and simulation have been addressed contextually with the experimental part.

This Master thesis is divided in four main chapters. In Chapter 1 the theoretical framework for multi dimensional spectroscopy is first given. Additionally the simulations equations are introduced with an emphasis on the assumptions needed for each derivation. Chapter 2 starts with a brief description of the 2DES experimental set up. Then simulation methodological approach was discussed. In the third chapter a deep characterization of the model is presented.

The predicting capabilities, the parameter dependence and the physical meaning of the model are assessed supported by plenty of simulated 2DES maps and parameter dependence plots. Chapter 4 presents the DBOVMes-Cl experimental data along with its simulated counterpart. A systematic comparison between the two is therefore proposed, validating the presented model while corroborating with the experiment based claims.

2. Experiment:

Like no other third order non linear spectroscopy technique, 2D spectroscopy disentangles the temporal and frequency resolution limit imposed by the Fourier theory. 2DES allows indeed to resolve dynamics with a time resolution of tens of femtoseconds (fs) and contextually being able to build a correlation spectrum between the excitation and the detection frequencies. In 2D spectroscopy the system is let to interact with three distinct time-delayed pulses. The third order polarization it then recorded through an optical heterodyne detection measurement. The emitted field caused by the non linear polarization interferes with a fourth phase-coherent light pulse, called the local oscillator (LO). This chain of interactions defines three subsequent time intervals t_1, t_2 and t_3 , namely the delay of one interaction to its prior. A spectrometer records then the signal, performing a Fourier transform from t_3 to ω_3 . With spectral interferometry the non linear polarization can be retrieved as $P^{(3)} = (t_1, t_2, \omega_3)$. Furthermore, by means of a second Fourier transform in respect to t_1 , the signal can be expressed as $P^{(3)} = (\omega_1, t_2, \omega_3)$. The interpretation for this complex function is no trivial and it relies on considering ω_1 the excitation frequency, while ω_3 being the detection frequency. $P^{(3)}$ represents then a collection of transient absorption (or transmission) spectra, each related to a specific excitation frequency ω_1 [2].

For the second transformation to be meaningful, the measure requires interferometric stability between pairs of excitation pulses phase locked within a small fraction of their carrier wavelength. This can be insured in different ways working with infrared light, but in the visible spectrum region it could be very difficult to achieve. In the ultra fast laboratory of

Politecnico di Milano the pulses interferometric stability is achieved thanks to the Translating-Wedge-Based Identical Pulses eNcoding System (TWINS) [3].

3. Modeling:

The modeling of the system response in terms of 2DES experiment proceeded with subsequent generalization. This method worked as a natural didactic exercise, but also to highlight the physical assumptions and the consequent relations that brought to the final simulation equations. Starting from a two level system, the model has been developed, for certain cases, to include a third energy level so that a photo induced absorption signal could be simulated as well. The first introduced model was developed along S.Mukamel book "Principles of Non Linear Spectroscopy" [4] and it is based on the Brownian oscillator model. In this context, quite general stochastic assumptions were made to describe the sample-environment interaction as a phonon bath coupling. The case of a continuous of overdamped Brownian oscillators was chosen to describe the bath so that the interaction operator and thus the consequent response functions were analytically derived. From a phenomenological picture, the model enables to predict and explain with simple parameters several experimental evidences like the spectral diffusion, the Stokes shift and the decoherence decay.

The second model focuses instead on coherent vibrations and nucleus-electron interplay within the response function. In a fully adiabatic fashion the Hamiltonian is thus changed to include a vibrational terms that relates a certain displacement 'z' to its relative electronic state [5]. The model describes the vibrational field on its coherent state basis, and it uses the time evolution and the displacement operator to derive in a very general way the response function for the M-th order response functions of a N-th level system. The equations for the vibrational third order response of a two level system were then added to the simulation environment and because of the adiabatic hypothesis it is possible to combine vibrational and electronic response functions by the mean of a simple product of each contribution. The full model stands on the high

temperature limit so it is able to simulate most of ambient temperature experiments, but it can be easily generalized for every temperature and initialization state. The complete model is then able to describe and predict oscillatory dynamics along the population time (t_2) as well as vibrational replica in the 2D spectra. Out of the four response functions computed, here the example of the rephasing photo bleaching contribution is reported:

$$R_1^{(3,e)} = \left(\frac{i}{\hbar}\right)^3 \mu^4 e^{-\frac{i}{\hbar}(\epsilon_1 - \epsilon_0)(t_1 + t_3)} \exp(-g(t_1) - g^*(t_3) - f_+(t_1, t_2, t_3)) \quad (1)$$

$$f_+(t_1, t_2, t_3) = g^*(t_2) - g(t_1 + t_2) - g^*(t_2 + t_3) + g(t_1 + t_2 + t_3) \quad (2)$$

$$g(t) = \frac{2\lambda k_B T \tau_C^2}{\hbar} [\exp(-t/\tau_C) + t/\tau_C - 1] - i\lambda \tau_C [\exp(-t/\tau_C) + t/\tau_C - 1] \quad (3)$$

$$R_1^{(3,v)} = \exp[z^2(-2 + e^{-i\Lambda_{111}} + e^{i\Lambda_{010}} + e^{i\Lambda_{001}} + e^{-i\Lambda_{100}} - e^{i\Lambda_{011}} - e^{i\Lambda_{110}})] \quad (4)$$

$$\Lambda_{p_1, p_2, p_3} \equiv \frac{\epsilon_v}{\hbar} (p_1 t_1 + p_2 t_2 + p_3 t_3) \quad (5)$$

$$S^{(3)} \propto \sum_{i=1}^4 [R_i^{(3,e)} R_i^{(3,v)} - (R_i^{(3,e)} R_i^{(3,v)})^*] \quad (6)$$

The modeling has proven to be effective, so that both the line shapes and the t_2 dynamics could be simulated to replicate similar enough replicas. This is quite extraordinary considering the model is based on a simple adiabatic two level system coupled with a stochastic phonon bath.

4. Experimental results:

The DBOV experimental results show indeed a strong vibronic interplay. While exciting the sample with visible light, oscillations and vibronic replica are visible in the spectra. In the investigated spectrum region, the molecule shows a strong positive peak around 2.0eV caused by an overlap of the photo bleaching and the stimulated emission signals. Looking at the

lineshape evolution time scale and its broadening factors more physical properties could be inferred. The broadening of the line shape, and its evolution along t_2 , can be used to derive the exciton coherence time and the intensity and the correlation time of the phonon bath coupling. Using the formalism of the models applied, the correlation time constant is found to be about 80fs. This leads to assuming a small reorganization energy λ too, in particular for the simulation λ was set at 0.05eV. This is also supported by the almost invisible Stokes shift measured withing the 2D spectrum. Even though the lack of a distinguishable stimulated emission peak for the 0-0 transition could be supported by an overall quenching of the stimulated emission, the presence of such contribution it is supported by the presence of the cross peaks. The cross peaks, in facts, stand in this case for the transitions involving vibrational overtones, mainly the 0-1 and 1-0 transitions. In general the cross peaks above the main one are due to ground state modes, while the ones below are indication of excited state modes. Thanks to the simulation it is possible to verify the claim very effectively by plotting alternatively only the photo bleaching or the stimulated emission 2DES signals, as respectively Fig. 1a and Fig. 1b shows.

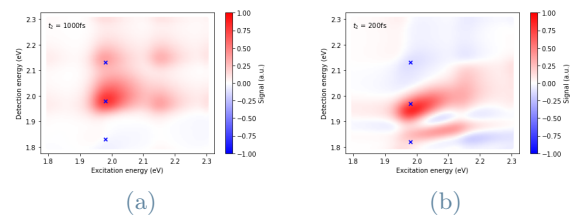


Figure 1: Simulated 2D spectra of the photo bleaching (a) and the stimulated emission (b) contributions.

Moreover the position of the cross peaks determines the energy of the vibrational mode causing the cross peaks, in this case it was esteemed to be 0.18eV. Two less energetic vibrational modes, at 0.015eV and 0.043eV, are also present but their cross peaks fall in the broadening of the main peak. Their evidence was found taking the Fourier transform along the population time. In accord with the data of the transform amplitude, the mode at 0.043eV showed three times the intensity of the least energetic mode. Looking at the t_2 dynamics for a fixed pair of

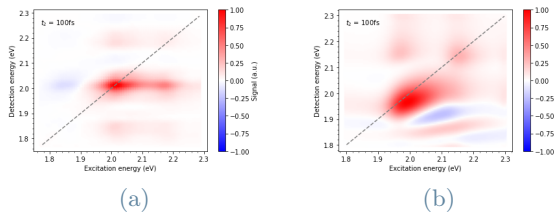


Figure 2: a): DBOV-Mes-Cl 2DES experimental spectrum b):the simulated replica for a population time delay of $t_2 = 100fs$.

spectral coordinates the oscillation due to the $0.043eV$ mode is indeed dominant, and the oscillations contained in Figure 3b show a period of $95fs$ compatible with the energy of such mode. Moreover Figures 3a 3b contain evidence of an almost perfect counter phase relation between the dynamics of two spectral coordinates taken across the main peak. This relation is confirmed by the simulated dynamics in Figure 3d. While it is expected for an ideal dynamical system with a pole, its an exceptional result finding such a clear evidence in a much more complex experimental case. To resemble the experimental restraints, the simulated signal has been filtered with a low pass filter to cut out the high frequency contribution from the mode causing the cross peaks in the map. Additionally the same phase relation is found across the first stimulated emission cross peak and the first photo bleaching cross peak, respectively in Figure 3e and in Figure 3f. The study of dynamics at the two cross peaks offer a new discussion point about the nature of the vibrational mode. Oscillation in Fig.3e are found to be much more intense than the one in Fig.3f. Therefore, it can be inferred that for the vibrational mode at $0.043eV$ the dominant contribution comes from the excited state. This does not seem to be also the case for the highest energy vibrational mode at $0.18eV$, in fact the cross peaks are in looking to the experimental maps comparable in intensity.

5. Conclusions

In conclusion, this master's thesis presents a step forward in to the exploration of nanographene structures, particularly focusing on a detailed 2DES analysis of a DBOV derivative. By combining experimental and modeling approaches, this research thesis contributes to advancing

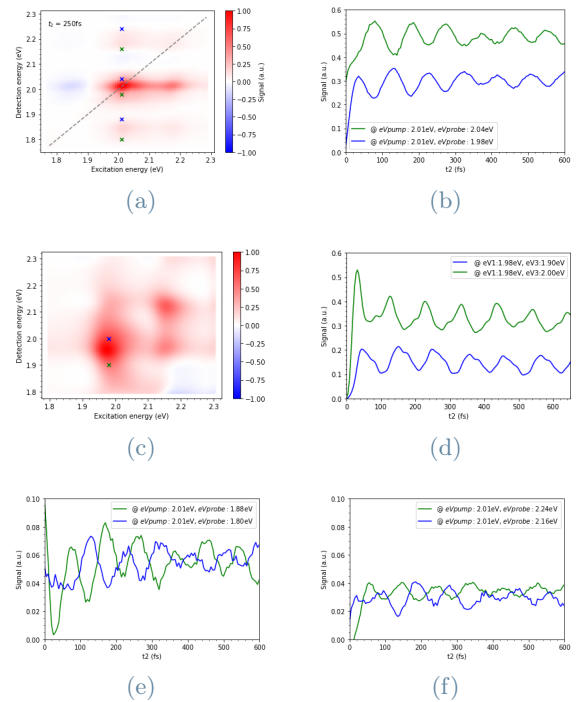


Figure 3: (a)the DBOV experimental map for $t_2 = 250fs$ and its simulated counter part (c).(b)the t_2 dynamics of two spectral coordinates, taken across the main peak, show an almost perfect counter phase relation. Simulated dynamics matches in the overall functional behavior and the counter phase relation (d). The same kind of study for spectral coordinates across the first stimulated emission cross peak (e) and the first photo bleaching cross peak (f).

the understanding of vibronic interactions and their potential role played for designing materials with tailored functional properties. The presented evidences argue for a greater involvement of the excited state to the vibrational mode in the respect to the ground state. This can have profound implications in processes like energy and charges transfer within the molecule. Eventually different DBOV substituent atoms and geometry could be studied to best engineer the molecule and understand the effects and interaction behind some properties. Regarding the model and simulation, various implementation approaches are possible. The first logical step is to generalize the vibrational model to a multiple level system. A further step would be then introducing a non-adiabatic term in the Hamiltonian to derive more general response functions and a more capable simulation environment.

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