

9 Years Later.....

When I started my Ph.D. study in summer 1988, life in the ultrafast scene was much different from what it is now. Working with amplified femtosecond laser systems meant (not only for me) dealing with regular refreshments of dye solutions (with the occasional spilling over floors, optics and clothes), exploding and evaporating electronics in the power supply of the copper vapour laser, or cracked aluminium oxide tubes of the same laser, deteriorating fiber tips, and sometimes – miraculously – a laser system stable enough to do a photon echo experiment on a dye solution, if only the liquid jet would be working....

Around the same time when I was finishing up my Ph.D. study, the first solid-state femtosecond laser systems based on Ti:sapphire had been reported, and then technology went very fast: cavity-dumped Ti:sapphire oscillator systems became an extremely powerful tool in the investigation of optical dephasing and solvation dynamics studies. Rumour says one could run photon echo experiments nowadays fully automated. Experimental schemes such as time-gated photon echo, three pulse photon echo peak shift, and heterodyne detected photon echo, have been demonstrated in the elucidation of the frequency fluctuation correlation function of optical transitions of dye molecules in liquid solution, in protein surroundings, in membranes etc., and even photosynthetic reaction centres where optical chromophores are strongly coupled to each other.

Femtosecond laser systems based on Ti:sapphire are not only powerful because of their stability and extreme bandwidth (and thus the capability of producing ultrashort pulses). Since the demonstration of chirped pulse amplification (CPA) for optical frequencies, very intense femtosecond pulses are generated with CPA-based Ti:sapphire systems. As a result frequency conversion schemes, based on self phase modulation (e.g. in hollow waveguides), optical parametric amplification and sum- and difference frequency mixing, have led to the situation that one can in principle perform ultrafast nonlinear spectroscopy at any frequency, ranging from the near-ultraviolet to the mid-infrared spectral ranges of the electromagnetic spectrum. In the middle of my activities with femtosecond mid-infrared spectroscopy I visited sometimes the field where I came from being involved in work on the connection between hydrogen bonding and solvation dynamics and work on the dephasing and spectral diffusion dynamics of O-H stretching vibrations in hydrogen bonded systems.

When I was in the completion phase of my Ph.D. theory about optical dephasing and solvation dynamics, and in particular its relation to nonlinear spectroscopy had

been around for some years, albeit scattered around in a multitude of papers by several theoreticians. So I decided to write it down in a uniform way in my thesis, thereby relying heavily on the work by Mukamel and co-workers. Halfway through my writing period word got around that a book by Mukamel would appear soon, making my efforts a bit redundant. In the end the book was published two years after my thesis defense, so I guess some people might have taken advantage of my scribbles. In fact, people still refer to my thesis (*“Isn’t that the little booklet with that very red cover?”*) and sometimes even request a copy of it (example: *“You said you would like to have a copy of my thesis, well here it is!”*, with the reply: *“Wait a minute, I already have your thesis, now I recognize that red cover!”*; this apparently happens when one does not remember anymore to whom one has sent the thesis in the first place). The printed version of my thesis has long been out of stock, and I am not planning another order of a few hundred copies at a publisher’s house. However, since I departed for my postdoc-stint at LOA-ENSTA in Palaiseau, the internet phenomenon exploded, with the option of information exchange at low cost level. I wrote my thesis with a Macintosh using Word. The figures were made with an ancient graphics program called Slidewrite, and I just glued the figures onto a print-out of the text. This was sufficient for Krips Repro that printed my thesis in 1993. Naturally I did not bother to save my thesis in a processable format at later times, so converting it in for instance a Word2000 file would be a major project (at least for me). But one could of course scan in the original sheets used by Krips Repro So here it is, my thesis scanned and saved as pdf-file. Never bother the bandwidth needed to download the files, everything on the web keeps expanding anyway...

Added to these comments are my corrections to typos, amendments, mistakes, and blatant errors (underline what you think is the most appropriate). Somehow along the process of delivering such a piece of work one turns blind to the text as printed. Don’t use the equations taken as granted, always find the meaning behind them

I welcome any further comments or corrections one might have; don’t hesitate to notify me.

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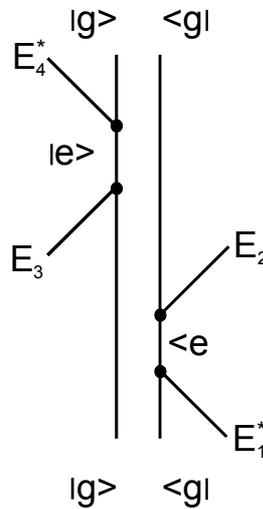
Typos, Corrections, Comments

Chapter 2:

- Page 18: The left hand side of Equation (2.13a) should read: $-\ln \{J(t)\}$
- Page 29: Table 2.1, the real part of the line shape function $g(t)$ for the underdamped oscillator contains a term $[3 - (\gamma/\omega)^2]$ that should be replaced with: $[(\gamma/\omega)^2 - 3]$

Chapter 3:

- Page 45: The most obvious error is of course that made in Figure 3.2, where I erroneously depicted a double-sided Feynman diagram for pathway (II) that is identical to that of pathway (I). The correct diagram for pathway (II) is of course:



- Page 48: Multiply the right hand side of Equations (3.15b) and (3.15c) with the following term: $\exp[-i \omega_3 T - i (\omega_3 + \omega_2) T]$
- Page 56: The remark “It should be mentioned that a fourth diagram appears in case the RLS process occurs in a two level system” is wrong. There is no fourth diagram!

- Page 67: The terms in between the { } brackets in Equation (3.42) should be replaced with: $\{\exp[-g^*(t) - 2i g''(t+\tau) + 2i g''(\tau)] + \exp[-g(t)]\}$

Chapter 4:

- Page 87: Replace $(2\pi c/\omega d)^2$ in the right hand side of Equation (4.8) with the following term: $[(2\pi c/\omega d) - \sin \alpha]^2$

Chapter 6:

- Page 139: Replace the second exponential term on the right hand side of Equation (6.11) with: $\exp[-g^*(t) - 2i g''(t+\tau) + 2i g''(\tau)]$

Chapter 8:

- The fits of the pinacyanol data were performed by using the expressions for the nonlinear response functions R_{I-IV} convoluted with a pulse temporal profile. In these fits I did not realize the additional permutation option between fields E_2 and E_3 , where the interactions E_2 and E_3 may originate from pulse 2 and pulse 3, or from pulse 3 and pulse 2 respectively. I only implemented the first case ($E_2 \leftrightarrow$ pulse 2 and $E_3 \leftrightarrow$ pulse 3). This is the main reason why the response around zero delay is off by a factor of two, as the additional permutation option ($E_2 \leftrightarrow$ pulse 3 and $E_3 \leftrightarrow$ pulse 2) can contribute when pulse 2 and pulse 3 are (nearly) time-coincident. At larger delay times the pulses are well-separated in time, and the order of interactions is clear.
- So why hasn't the results of chapter 8 been published in an ordinary paper? When I left for my postdoc-stint in France I did not expect that it would take so much energy and time to adapt to the french way of life. I had less time to think about the matter, and decided to leave it up for the other team members in Groningen. In addition the e-mail correspondence was just being installed, and not as effective and fast as it is now. Nevertheless at some point I sent a 20⁺-page fax with suggestions to Groningen and was too busy to wait for a prompt response.... Half a year it became clear to me that I had to move on