



Preface

Preface to special issue “Douwe Alle Wiersma – 30 years of molecular photon echo spectroscopy”



Douwe Alle Wiersma, whose scientific achievements are being honoured with this special issue, was born on January 8, 1943 in Amsterdam, the Netherlands. He grew up in the northern part of the Netherlands, and pursued undergraduate and Ph.D. studies at the Department of Chemistry of the University of Groningen in the Netherlands. Under the guidance of his thesis advisor Jan Kommandeur (see Chemical Physics special issue on nonradiative processes [1]) he completed his Ph.D. study in 1969, entitled “Photochromism through photodissociation; an ESR and optical study”. He then joined the research group of Robin M. Hochstrasser at the University of Pennsylvania, Philadelphia, USA as a postdoctoral member in the years 1969–1971, where he performed experiments on electronic excited states. In 1971 he was invited to return to Groningen by Jan Kommandeur to start his own research team as assistant professor in the Laboratory for Physical Chemistry. Here Douwe contributed to the increasingly extraordinary world fame of the Department of Physical Chemistry at the University of Groningen, which consisted of, besides the gas phase cluster group of

Jan Kommandeur, the molecular dynamics group of Herman J. C. Berendsen and Wilfred F. van Gunsteren, the NMR group of Rob Kaptein and the solid state chemistry group of George A. Sawatzky. Douwe’s increasingly important scientific output was matched with his academic status, as he was promoted to associate and to full professor in 1977 and 1981, respectively.

Douwe continued to produce work on the structure of electronic excited states of aromatic molecules using optical and magnetic resonance spectroscopy together with Jan H. Meyling, Hendrik Veenfliet and Jan H. Lichtenbelt throughout the seventies. His major breakthrough, however, came with a series of papers describing photon echo measurements published between 1976 and 1987. The photon echo technique has been reported for the first time by the group of Sven R. Hartmann in 1964 [2] and the technique has been explored and expanded on by Hartmann and many others on atomic and molecular systems in the gas phase and simple ions in the solid phase. Its magnetic resonance counterpart, the spin echo, dates back more than a decade earlier by Erwin L. Hahn [3], who also came up

with the name “echo” to describe the recurrences in time of macroscopic magnetization/polarization, induced by a rephasing pulse on an inhomogeneously broadened system prepared initially in a coherent superposition by a first pulse. Douwe’s photon echo projects remained his key research activities from then onwards, while initiating other research directions in the course of time.

In the first phase on echo research Douwe and his team members Thijs J. Aartsma, Wim H. Hesselink, Jos. B.W. Morsink, Laurens W. Molenkamp and Koos Duppen applied the photon echo technique on various molecular mixed crystals [4,5], on semiconductors [6] and on molecules in polymer matrices [7]. Picosecond dye laser systems were used to perform these measurements at low temperatures using cryostats, facilitating the detection of pico to nanosecond dephasing dynamics of the electronic transitions of aromatic molecules, such as pentacene doped in naphthalene, from which the homogeneous broadening component in the spectral line breadth can be grasped. The photon echo technique was further developed with picosecond echo detection through optical mixing [8], the discovery of the accumulated photon echo, where a much stronger echo signal is generated by the laser pulse trains on ground state frequency gratings after accumulation of excited state population in a bottleneck state [9], and with two colour photon echoes [10]. Douwe explored together with Harmen de Vries the method of hole burning to obtain complementary information on homogeneous broadening in molecular mixed crystals [11,12]. A more thorough understanding of the underlying broadening mechanisms being dictated by the frequency fluctuation correlation function was pursued with Philipus de Bree [13]. Finally a clear description of the tight connection between transient grating and photon echo spectroscopy was published in the mid eighties by Koos Duppen and Douwe. Here they showed that time-resolved four wave mixing experiments can be considered as forms of ultrafast holography, where e.g. signals in transient grating spectroscopy are caused by spatial population modulations, and in photon echo spectroscopy are induced by frequency population gratings [14,15].

Besides research on dephasing dynamics of molecular electronic transitions transient coherent Raman spectroscopy on molecular systems was pursued with H.M.M. (Ben) Hesp, Koos Duppen, Howard B. Levinsky and Daniel P. Weitekamp in the early 1980s. Douwe in addition collaborated with Hans-Peter Trommsdorff and Michael D. Fayer during sabbatical intermissions in 1982 and 1983, and with Arnold J. Hoff (together with Stephen A. Meech) on bacterial reaction centres in the mid eighties [16].

After a phase of reflection Douwe initiated new rounds of scientific research in the later eighties. The first dealt with the optical dynamics of chromophores in molecular glasses and proteins at low temperatures, a continuation of the initial work on amorphous systems initiated with Molenkamp [7], to which Hans C. Meijers, Otto Berg, Daan Thorn Leeson and Kees Lazonder contributed. Here the structural dynamics of the glass or protein surround-

ings is probed on time scales ranging from femtoseconds to seconds (or longer) [17–19]. The conclusions from this research, in accordance with those of Michael D. Fayer and others, are that at low temperatures only limited regions of the energy landscape, approximated as a distribution of two-level systems, play a role in the dephasing and spectral diffusion. At higher temperatures, approximating the glass transition temperature and beyond, the impact of the structural dynamics of a glass is caused by browsing more extended regions of the energy landscape, and a description using a collection of damped harmonic oscillators may be more appropriate.

A second line of research involved the spectroscopy of strongly electronically coupled molecular systems, where individual chromophores form excitonic states with new energy level schemes, strongly altered electronic transition frequencies and cross sections, accompanied by different dephasing and radiative dynamics, as compared to those of uncoupled molecules. This line of research was initiated on J aggregates in glasses together with Steven de Boer and Kees J. Vink [20,21], came to fruition in a combined experimental and theoretical approach together with Henk Fidler and Jasper Knoester [22,23], and was augmented with James R. Durrant, Johannes Moll and Eric O. Potma. From these studies it became clear how the interplay between excitation coupling strengths and static and dynamic disorder determine the outcome of the observed linear and nonlinear spectroscopic response. The observation of the one- to two-exciton transitions with two-colour pump-probe spectroscopy has also received broad attention [24]. Additional studies include J aggregates in Langmuir–Blodgett monolayers (with Jacob Terpstra) and J aggregates in liquid solution (with Mirjam van Burgel and Koos Duppen). Twenty years after the first report, the key role of this line of research is evident in the understanding of exciton delocalisation and excitation transport dynamics in light harvesting complexes.

A third line of research initiated in the late eighties involved the optical dephasing and solvation dynamics of dye molecules in liquid solution at ambient temperatures, for which in the first round Koos Duppen, Foppe de Haan and myself contributed. This research had only become possible with the advent of femtosecond dye laser technology (as developed by the Bell laboratory group led by Charles V. Shank, who also reported the first photon echo on a dye molecule in solution in 1989). The merit of work by Douwe’s team lies in the first clear demonstration of nonMarkovian optical dynamics in solution, using resonance light scattering [25] and photon echo measurements [26]. The key role played by the underlying frequency fluctuation correlation function (with effective temporal characteristics ranging from tens of femtoseconds to several picoseconds) in dictating optical line shapes and photon echo signals became clear by use of the pioneering theoretical work by Phillip W. Anderson and Ryogo Kubo in explanation of the experiments, as well as using the major body of work on nonlinear spectroscopy by the group of

Shaul Mukamel. A tight connection between optical dephasing (loss of coherence of the optical excitation) and solvation (the solvent shell rearrangements induced by the optical excitation) can be made, thus linking the achievements by Douwe's group with those obtained on solvation dynamics by Paul F. Barbara, Graham R. Fleming, Mark Maroncelli, Norbert F. Scherer, James T. Hynes and many others. Special attention deserves the report on the method of chirped four wave mixing [27] where an alternative form of coherent Raman scattering is described, and a conclusive report on this first round of work on dephasing and solvation dynamics in liquid solution in a Chemical Physics special issue on dissipative dynamics [28].

Despite earlier efforts by Edward W. Castner Jr. and Jacob J. Korpershoek on synchronously pumped dye laser technology the second phase of research on dephasing and solvation in liquid solution could only really be started with the implementation of solid state femtosecond laser technology, enabling a extremely versatile approach to measure the ultrafast nonlinear optical response. In particular the development of a cavity-dumped 13 fs Ti:sapphire oscillator [29] and pulse compression down to 5 fs [30] have had a major impact in the ultrafast optics and ultrafast spectroscopy communities. Wim P. de Boei and Maxim S. Pshenichnikov contributed to the development of phase-locked heterodyne-detected photon echo [31], femtosecond time-gated photon echo [32], and the echo peak shift [33] (which was in parallel published on by the Fleming group) as means to grasp the frequency fluctuation correlation function. Later team members Michel F. Emde, Andreas Kummrow, Andrius Baltuška and Maxim S. Pshenichnikov explored the optical dynamics of the hydrated electron, that exhibits even faster dynamics than those typical of molecular chromophores in solution. The conclusions of the second phase of research on dephasing and solvation in liquids have been summarized in a review published in 1998 [34].

In addition to these three above-mentioned activities initiated since the late eighties additional projects involved the nonlinear response of molecules in front of a mirror caused by local field effects (with Gerard Cnossen and Karel E. Drabe) and ultrafast photochemistry (with Egbert Lenderink, Frank P.X. Everdij and Koos Duppen).

A major change in Douwe's activities commenced in 1998 when he accepted the dean position of the natural science department of the University of Groningen, which was – due to diminishing student numbers and increasingly tighter budgetary constraints – a challenge in itself. He moved in addition into two new research directions, which dealt again with the spectroscopy of molecular vibrations.

Pioneering work on ultrafast infrared photon echo spectroscopy has been pursued by Michael D. Fayer (first picosecond IR echo reported in 1993), Robin M. Hochstrasser (first femtosecond IR echoes on molecules in liquid solution, and development of heterodyne-detected multidimensional IR spectroscopy in 1998), and Thomas Elsaesser (first IR two pulse echo and three pulse echo peak shift

on the OH stretching vibration of water in 2001–2002). It is thus of no surprise that IR photon echoes became part of Douwe's interest, as evidenced by the report on heterodyne-detected IR photon echo of water in 2003 [35]. While many groups work intensively on the dynamics of hydrogen bonded water, Douwe together with Sergei Yermenko, Dan Cringus and Maxim S. Pshenichnikov contributed to this, sometimes in collaboration with the group of Peter Vöhringer.

A research activity on bioimaging with potential to reach unexplored territories was initiated with Wim P. de Boei in 1998. Transient confocal imaging of molecular vibrations with coherent Stokes Raman scattering by Eric O. Potma was used to visualise intracellular hydrodynamics of water in single living cells [36]. After this fluorescence imaging experiments of biomembrane systems were performed with Nicoletta Kahya.

In closing, one can state that many researchers have benefited strongly from the foundations on photon echo spectroscopy and on nonlinear spectroscopy of excitonic molecular systems laid down by Douwe. This special issue, dedicated to Douwe, contains an impressive collection of work by many (former) group members of Douwe and by his scientific colleagues, reverberating the research topics Douwe has worked on during his career. I cordially thank the contributors to this special issue and expect that achievements made by Douwe in the last 30 years will proliferate in the work by others in many years to come.

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