

Advances in nonlinear optical spectroscopies: a historical perspective of developments and applications presented at ECONOS

Johannes Kiefer,^{a,b,c,*} Arnulf Materny,^d Julian Moger,^e Herman L. Offerhaus,^f Peter P. Radi,^g Andreas Volkmer^h and Aleksei M. Zheltikov^{i,j}

This article reviews the contributions to the special issues of the annual European Conference on Nonlinear Optical Spectroscopy (ECONOS) since its establishment in 2002. The review does not only highlight the developments of the scientific areas related to nonlinear optical spectroscopy in Europe but also shows how different sub-fields evolved globally because ECONOS evolved as an international meeting attracting participants from all over the world. Four main topical categories are identified: (1) theoretical and instrumental developments, (2) applications to gas-phase and combustion systems, (3) applications to condensed phase matter, and (4) development and applications of micro-spectroscopy methods. Copyright © 2015 John Wiley & Sons, Ltd.

Keywords: ECONOS; nonlinear optical spectroscopy; four-wave mixing

Introduction

The special nature and unique characteristics of the nonlinear interaction of optical fields with matter offers access to a wealth of information about chemical composition, structure, and symmetry properties of matter in the gas and condensed phase, which is exploited in nonlinear optical spectroscopies and gives rise to the high popularity of their various technological implementations in the physical and life sciences, medicine, and in engineering.

The annual European Conference on Nonlinear Optical Spectroscopy (ECONOS) is devoted to different aspects in the rapidly expanding field of nonlinear optical spectroscopy. ECONOS emerged in 2002 to widen the agendas of the former annual European Coherent Anti-Stokes Raman Scattering (CARS) workshops (held since 1982), and since has been covering all forms of nonlinear optical spectroscopy in the frequency- and time-domain, theoretical and experimental studies, and applications. The main topics include coherent Raman spectroscopies, four-wave mixing and different third-order (or higher) responses and related techniques, the physical and chemical processes defining the spectral signatures in different media, as well as their combination with optical microscopy. Contributions on applications in physics, chemistry, engineering, biomedical research, and other interdisciplinary areas are covered. The main objective of this conference series has been to ascertain scientific exchange and to foster discussions between experts in the research field and users of nonlinear optical spectroscopies.

One feature of ECONOS/ECW is the annual special issue in the *Journal of Raman Spectroscopy*, which contains selected contributions to the conference in the form of full papers. Those papers have to pass the normal peer-review procedure of the journal in order to qualify for publication. The entity of special issues represents a means of historic timeline highlighting the trends and

topical developments in the field. Wolfgang Kiefer, an initiator and frequent participant of ECONOS/ECW and the former editor-in-chief of *Journal of Raman Spectroscopy*, supported and promoted the idea of a special issue, and he helped to establish it in the year of the very first ECONOS meeting in 2002. Since then, the conference and the special issue have gone from strength to strength, and all previous and current guest editors are delighted to present this review of the developments to date. It is embedded

* Correspondence to: Johannes Kiefer, Technische Thermodynamik, Universität Bremen, Badgasteiner Str 1, Bremen, 28359, Germany.
E-mail: jkiefer@uni-bremen.de

a Technische Thermodynamik, Universität Bremen, Bremen, Germany

b School of Engineering, University of Aberdeen, Aberdeen, UK

c Erlangen Graduate School in Advanced Optical Technologies, Universität Erlangen-Nürnberg, Erlangen, Germany

d Department of Physics and Earth Sciences, Jacobs University Bremen, Bremen, Germany

e Department of Physics and Medical Imaging, University of Exeter, Exeter, UK

f Optical Sciences Group, University of Twente, Enschede, The Netherlands

g Paul Scherrer Institute, Villigen, 5232, Switzerland

h 3rd Institute of Physics, University of Stuttgart, Pfaffenwaldring 57, Stuttgart, 70569, Germany

i Department of Physics and Astronomy, Texas A&M University, College Station, TX, USA

j International Laser Center and Department of Physics, M. V. Lomonosov State University, Moscow, Russia

in a joint special issue on the occasion of Wolfgang Kiefer's 75th birthday and ECONOS 2015.

Overview and statistics

The ECONOS special issues to date contained 14 papers on average. The annual numbers are presented in Fig. 1. In this overview, we give the entity of papers a structure by classifying them into four categories: (1) theoretical and instrumental developments, (2) gas-phase applications, (3) condensed-phase applications, and (4) microscopy applications. However, it should be noted that many of the papers are interdisciplinary work and fit several of these categories. This interdisciplinary character is a key feature of ECONOS as a vehicle for exchange between different scientific communities working with the same or similar analytical tools that are all based on the principles of nonlinear optical spectroscopy. This spirit of the meeting led to the establishment of numerous collaborations and exciting developments.

Figure 1 does not only show the total numbers of published papers in the ECONOS special issues but also reveals the trends in the topical areas. For example, it can be clearly seen that over time the number of contributions focusing on gas-phase applications decreased while the area of microscopy increased. The yearly variation of the topics discussed during the conferences also can be explained by the specific interests of the local organizers, who decide on invited speakers. As aforesaid, many papers cannot be assigned to one category unambiguously, and hence the data in the figure should be seen as a rough indication and not be over-interpreted.

The substantial increase in the number of articles devoted to microscopy applications in the special issue of 2009 reflects the first joint meeting of ECONOS with the primary European Conference on Coherent Anti-Stokes Raman Scattering Microscopy held the year before in Igls, Austria.^[1] The rapid developments in nonlinear optical microscopies have occupied a significant part of succeeding ECONOS programs ever since.

Figure 2 shows the geographical distribution of the papers. For the classification, the home institution of the corresponding authors was taken as the relevant measure. However, it should be noted that a significant fraction of the articles are authored by researchers from multiple countries. Although organized by the European community and held in different places throughout Europe each year, colleagues from all over the world are actively

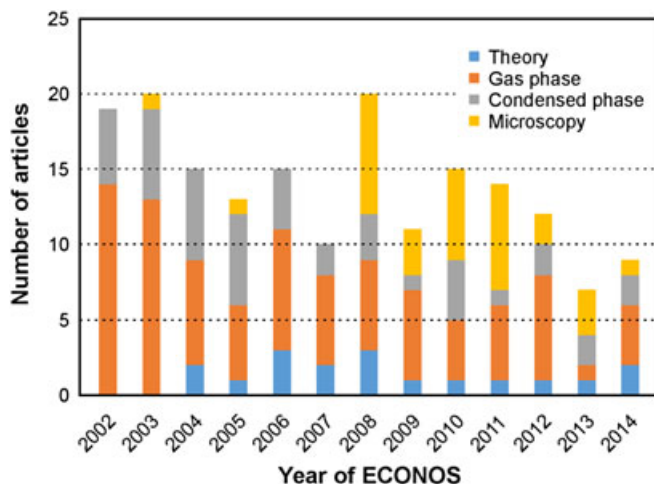


Figure 1. Number of papers in the annual special issue.

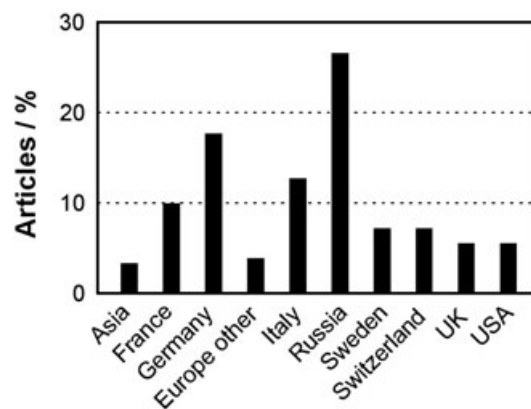


Figure 2. Geographical distribution of the papers. The home institution of the corresponding author was taken as measure.

participating at and contributing to ECONOS. Within Europe, the geographical distribution of the number of articles published in ECONOS special issues reveals contributions from a broad range of countries, with France, Germany, Italy, Russia, Sweden, Switzerland, and the UK leading the crowd. In our view, this for the most part reflects the scientific expertise in research on nonlinear optical spectroscopies accumulated over decades in these nations.

In the following, we review the papers and structure this article with respect to the four categories introduced above. The fundamentals of the individual methods are not introduced in detail, as this would go beyond the scope of this article. Descriptions can be found in a number of books^[2–5] and review articles.^[6–8]

Theoretical and instrumental developments

Fundamental investigations of the interactions of light and matter were presented in a number of papers. This includes studies of the possibilities of controlling atoms and molecules by such interactions. In general, the light–matter interactions are described in terms of a polarization $P(\omega)$ that is induced by an electromagnetic wave with electric field amplitude E and frequency ω in a medium, according to the wave equation derived from Maxwell's equations

$$\nabla^2 E(\omega) = \frac{1}{c^2} \frac{\partial^2 E(\omega)}{\partial t^2} + \mu_0 \frac{\partial^2 P(\omega)}{\partial t^2} \quad (1)$$

where c is the speed of light, t is the time, and μ_0 is the permeability. The polarization gives rise to a multitude of optical responses, which can be summarized phenomenologically as

$$P(\omega) = \epsilon_0 \cdot \sum_i \chi^{(i)} E(\omega)^i \quad (2)$$

where ϵ_0 is the permittivity and $\chi^{(i)}$ is the susceptibility of the order i . All phenomena that can be described by the higher order terms of Eq. (2) (i.e. $i > 1$) are considered nonlinear and involve multiphoton interactions with a medium.

Egorova *et al.*^[9] analyzed two-photon transitions in isotropic molecular gases and developed a refined theory of scattering taking into account virtual electric quadrupole and magnetic dipole transitions. Interesting phenomena were found, when resonant and off-resonant excitations were compared as the interference caused by the fields emitted by the multipoles disappear in the resonance case. Akimov *et al.*^[10,11] proposed a bichromatic spectroscopy method to study Raman transitions in Rubidium atoms. They

showed that transitions with differential frequencies of the order of some hundred terahertz can be excited coherently.

Nichelatti *et al.*^[12] studied the generation of optical signals starting with an ideal point source and proceeding to clusters of point sources, and eventually to a collection of point sources embedded in a layered medium. They proposed a unified formalism that allows the evaluation of light emitted from a volume and show the implications for CARS microscopy. Another theoretical study of CARS spectroscopy in complex media was presented by Ooi,^[13] who developed a microscopic theory of the scattering in mesoscopic particles. He found that the interference between the linear and the nonlinear response of the medium results in an angular dependence of the detected CARS spectrum. This was shown for laser pulses with arbitrary spectral and temporal shape. However, the influence of the laser pulse shape on the signal is an important issue in many experiments. This has been studied in detail by Marrocco, who analyzed the effects of spectral^[14] and temporal^[15] laser profiles on CARS signals.

Such temporal and spectral profiles become very important when the laser pulses become short. Especially in the femtosecond regime, the shaping of pulses has been established as a common approach to control the interactions of optical fields with quantum states of molecules.^[16] Nonlinear spectroscopy with chirped pulses has therefore been a very hot topic at ECONOS over the last decade. Zheltikov^[17] studied the rotational Raman response of molecular gases when excited by shaped pulses. For this purpose, an analytical model was developed to show that molecular rotations can be efficiently driven by optimally time-ordered pulse sequences. Materny and co-workers^[18] studied the effects of modulating the phase and amplitude of the driving laser pulses on the resulting CARS spectra. A systematic analysis showed that the timing of the dispersed pulse segments has the largest potential for optimization using a feedback-control approach. In a follow-up study,^[19] they applied this method to achieve selective excitation or suppression of vibrational modes in gases and liquids. Such control under high field strengths was investigated in theory and experiment by Gräfe *et al.*^[20] They demonstrate control over the dynamics of a molecular system via a non-adiabatic passage in molecular iodine. Furthermore, they explored possibilities of utilizing such techniques for initiating and monitoring chemical reactions. An adiabatic passage based method was also used by Malinovsky^[21] to maximize the CARS coherence.

Another feature of carefully shaped pulses is the possibility to do single-beam CARS. Motzkus and co-workers^[22] developed a theoretical method to optimize the pulse shape *a priori* for a given experiment. Such an optimization is particularly interesting when sensitive samples such as biological tissue are studied as the risk of photo-damage is minimized. The same group showed that a single-beam CARS setup can be used to effectively suppress interferences from two-photon fluorescence.^[23] Moreover, their approach allowed to reconstruct the Raman signal from the CARS signal even in the presence of significantly stronger fluorescence interferences. Cicerone and co-workers have also investigated the retrieval of Raman spectra from CARS data based on fast Fourier transforms.^[24] In a later work, they further developed their approach into a time-domain Kramers–Kronig transform and compared it with prior phase-retrieval work based on the maximum-entropy method,^[25] which they found to perform equally well.^[26]

The development and implementation of experimental methods and new instrumentation are a key aspect in advancing the field of nonlinear spectroscopy. Many of the studies mentioned previously and those to be mentioned in subsequent sections were based on new experimental approaches. On the other hand, only a few

articles on instrumental developments have been published in the ECONOS special issues. Vereshchagin *et al.*^[27] presented a non-collinear parametric amplifier for the generation of broadband laser pulses in the picosecond regime. This device is a useful alternative to dye lasers in CARS experiments. Mallick *et al.*^[28] combined a narrowband picosecond laser with a supercontinuum light source to realize an ultrafast Raman loss spectroscopy setup. Their paper lays out instrumental and methodological aspects.

Applications to gas-phase and combustion systems

CARS spectroscopy

Gas-phase and combustion diagnostics have a long tradition at the ECONOS and the ECW. In particular, CARS spectroscopy in the frequency and time domain has been presented with the aim of measuring parameters such as temperature and chemical composition, or to study molecular physics such as collisional effects. In order to derive quantitative information from an experimental CARS spectrum, the common procedure is to compare it with a series of simulated spectra calculated for conditions similar to the experiment and systematic variations of the parameters of interest, e.g. the temperature.^[4] This however implies, first, that the experiment must be controlled precisely in order to feed reliable numbers into the numerical code and, second, that the underlying model is accurate and takes all relevant physical phenomena into account. Hence, there is significant room for developments on both the theoretical and the experimental side.

Modeling gas-phase CARS spectra

Molecular collisions have a direct effect on the spectral line shape, and thus, the development of collisional models has been a very active area of research. For instance, the understanding of the broadening of nitrogen lines in environments of practical interest is the key to perform accurate temperature measurements in air-fed combustion systems. Bonamy and co-workers have been leading in the theoretical development of linewidth models. In collaboration with experimentalists they studied collisions of molecular nitrogen with a number of partners such as H₂,^[29–32] CO,^[30] CO₂,^[30] H₂O,^[30] O₂,^[30] C₂H₂,^[33] and collisions with itself,^[29,30] over wide temperature and pressure ranges. In recent years, nitrogen collisions have been studied using time-domain CARS with femtosecond lasers. Femtosecond-CARS offers the advantage of avoiding interferences from the non-resonant background signal, and the signal decay in the time domain translates into a linewidth in the frequency domain in a straightforward manner. This was utilized by Knopp *et al.*,^[34] who studied collisional effects at pressures between 0.2 and 5 bar. Wrzesinski *et al.*^[35] extended the pressure range to 50 bar and concluded that the signal behavior in the first few picoseconds after the Raman coherence is excited can be utilized for accurate thermometry at high pressure.

The other molecule that is frequently utilized for thermometry is hydrogen. H₂ is not only a common fuel, e.g. in rocket engines, but also an intermediate species in hydrocarbon flames. Vereshchagin *et al.* did a series of interferometric measurements of H₂ line shapes under different conditions^[36] including high temperature^[37,38] and pressure.^[39] The benefit of interferometry is the high spectral resolution that can be obtained and hence allows accurate line shape determination. As aforesaid, another possibility to measure line widths is the measurement of decay times in the time-domain. This

was demonstrated by Motzkus and co-workers^[40] in binary mixtures of hydrogen with helium and nitrogen. Arakcheev *et al.* studied collisional effects of hydrogen in pure hydrogen^[41,42] and mixtures with helium^[41] at low (80 and 85 K) and room temperatures (296 K). They observed decay rates of the signal that suggested a narrowing of the spectral lines according to the Dicke effect.

Further molecules that were studied in terms of collisional effects include carbon dioxide and acetylene. CO₂ is a common product in hydrocarbon combustion, while acetylene represents a fuel for welding torches and an intermediate species in virtually all hydrocarbon flames.^[43,44] Morozov *et al.* investigated collisional effects on the Fermi-dyad in the CO₂ spectrum. They were able to identify different channels of collision-induced relaxation.^[45] In follow-up papers they studied the collisional effects in greater detail focusing on the individual lines of the Fermi-dyad.^[46,47] Collisions of carbon dioxide and acetylene with helium were studied by Buldyreva *et al.*,^[48] who tackled the common problem of having relatively large particles perturbed by comparatively small particles using a semi-classical treatment.

Another important aspect in the development of models for calculating CARS spectra is the coupling between molecular rotations and vibrations. A common approach to take ro-vibrational effects into account is the introduction of the Herman–Wallis factor.^[49] Marrocco studied the limitations of this approach and found that for small molecules such as hydrogen, inaccuracies of the order of 10% in the line intensity are observed while larger molecules like nitrogen showed smaller deviations.^[50] He compared the effects on vibrational CARS thermometry of nitrogen with a rigid rotor approximation, which neglects ro-vibrational coupling, and found deviations of a few percent.^[51] In vibrational CARS of oxygen the systematic errors especially at high temperature led to the conclusion that advanced models of the Herman–Wallis factor are required in order to ensure accurate temperature measurements.^[52] Follow-up work by Marrocco and collaborators analyzed the effects of the Herman–Wallis factor on rotational CARS thermometry of nitrogen^[53] and oxygen,^[54] and considered the effects of rotation–vibration coupling in time-resolved CARS thermometry,^[55] and in the light of simultaneous temperature and species concentration measurements.^[56,57]

CARS combustion diagnostics

CARS measurements in combustion, in particular for thermometry, used to be the main topic of the European CARS Workshop before the establishment of ECONOS in 2002. An overview of these activities was presented by Stricker *et al.*^[58] in the 2003 special issue of the Journal of Raman Spectroscopy. They showed how CARS matured from an academically interesting technique with a potential for measurements in combustion environments to the most established optical thermometry tool in the gas phase. Of course, the success story of CARS combustion diagnostics continued at ECONOS, at which contributions from quite a few groups around the world were presented.

The temperature remains the key parameter to be determined in combustion-related CARS experiments. Clauss *et al.* and collaborators applied hydrogen CARS thermometry to combustion systems of relevance to rocket engines. They studied cryogenic liquid oxygen and gaseous oxygen-fed hydrogen^[59,60] and hydrocarbon^[60–62] flames operated under extreme conditions. They achieved measurements at pressures as high as 20 MPa and temperatures as high as 3000 K.

In nonstationary combustion environments, the measurement of a single parameter at a time, however, may not be sufficient for a systematic characterization. The application of dual-pump CARS facilitates the determination of the concentrations of selected species^[63] in addition to the temperature. In Europe and in the context of ECONOS, Seeger *et al.* were driving the development of this version of CARS. Using a standard Nd:YAG laser, as well as a broadband and a tunable narrowband dye laser, they performed simultaneous measurements of the temperature and concentrations of N₂, O₂, and CO in a partially premixed model flame.^[64] A similar approach was used to extend the list of species to hydrogen.^[65] The benefit of measuring H₂ and CO in partially premixed hydrocarbon flames is that both species represent the main intermediates in such environments.^[66] As H₂ is a very small molecule, however, its diffusion is much faster and hence the simultaneous determination of H₂ and CO provides important insights into the combustion process.^[67] The difficulty in the evaluation of dual-pump CARS spectra is that the spectroscopy of all the molecules under study must be modeled. To date, this is only possible for small molecules, i.e. diatomic and selected polyatomic species such as CO₂ and acetylene. When larger molecules need to be quantified, an experimental calibration via recording signals in defined mixtures is the method of choice. Beyrau *et al.* demonstrated this approach in simultaneous temperature and fuel/air ratio measurements in an ethylene flame. An extreme application of dual-pump CARS was shown by Braeuer *et al.*,^[68] who used dual-pump CARS for determining the oxygen/nitrogen ratio and the temperature in a diesel-fueled automotive auxiliary heating system that was equipped with small windows. In order to supply sufficiently high pulse energy in the CARS laser beams without damaging the windows, they employed an optical ring-cavity pulse stretcher.^[69,70]

Experimental challenges

Recording CARS spectra in environments like sprays, combustors, and flames always poses a challenge on the experimentalist. Confined systems require windows that may become dirty during the measurement or can be damaged by an optical breakdown. The presence of dust, droplets, and soot may lead to strong interferences obscuring the signal. Also, the particular CARS technique setup, like vibrational or pure rotational CARS,^[71] may reach its limits. Therefore, many contributions have dealt with analyzing these problems and proposing methods to overcome them.

The presence of droplets can lead to strong stimulated Raman scattering (SRS) signals interfering with the desired signal.^[72] Malarski and Leipertz^[73] investigated the SRS in dependence on the laser pulse duration and found that shorter pulse helps to suppress the interfering signal. They concluded that sufficiently short pulses cannot be enhanced in the microcavity of a droplet for geometrical reasons. An issue that arises in flames is spatial averaging *viz.* the presence of hot and cold gases in the CARS measurement volume.^[74] Seeger *et al.*^[75] presented a spectral weighting procedure that enabled the identification of spatial averaging effects in vibrational CARS. A weighting procedure was also developed by Vestin *et al.*^[76] for an improved species concentration measurement using rotational CARS. The same approach enabled the use of rotational CARS at high temperature.^[77] Soot particles represent another challenge. Not only do they emit interferences such as Mie-/Rayleigh scattering, but the interaction with an intense laser beam can lead to laser-induced incandescence^[78] and the production of C₂ radicals.^[79] The latter emit strong signals exactly at the wavelength where the CARS signal of nitrogen is located in the

standard Nd:YAG laser based two-color vibrational CARS experiment. Malarski *et al.*^[80] demonstrated a dual-pump CARS approach to overcome this problem.

As mentioned previously, the modeling of the line profiles is crucial for achieving accurate results. Many experimental problems arise because of effects influencing the linewidth and line position in the spectrum. Seeger *et al.*^[81] studied the effects of pressure on the accuracy of temperature measurements with rotational CARS. Afzelius and Bengtsson investigated the influence of the mode structure of the probe laser.^[82] They concluded that the use of a single-mode laser yields better precision. Nordstrom *et al.*^[83] developed a Fourier-based approach for recording high-resolution vibrational CARS spectra for thermometry applications. This method allowed suppressing a spectral modulation interfering with the CARS signal that leads to inaccuracies observed in the conventional CARS method.

At high temperature in a flame, the gas density is low and the molecules occupy a large number of rotational and vibrational states. Consequently, the signal intensity is low. A common method to overcome this problem is to crank up the laser pulse energy. However, strong electric fields in the probe volume may affect the molecules. Magnotti *et al.*^[84] studied saturation and Stark broadening effects in their dual-pump CARS experiment. They found that temperature measurements are not sensitive to Stark broadening, but saturation effects can play a role when the pump and Stokes lasers exhibit high intensity.

Further exciting developments

The previous sections have shown that most gas-phase applications of CARS focused on the detection of small and well understood molecules such as N₂, H₂, and O₂. Moreover, in most of the work, conventional Q-switched lasers were employed to obtain nanosecond time resolution. Many new developments are meant to overcome the limitations of classical CARS in all dimensions. For example, the use of ultrafast lasers enabled entering the time-domain by separating the excitation of the Raman coherence and the probing.^[85] Nowadays, the combination of time-domain and frequency-domain CARS seems to be the most promising approach as it combines the benefits of the two.^[86–88] This hybrid CARS normally utilizes broadband femtosecond pulses as pump and Stokes, and a narrowband picosecond laser as probe.^[86] Engel *et al.*^[89] employed hybrid CARS for high-speed determination of the composition of binary mixtures. They showed that the time-delayed detection of the signal avoids problems caused by line broadening. In a follow-up paper, Miller *et al.*^[90] presented a method to overcome the limited sensitivity of vibrational fs/ps CARS thermometry of N₂ below 1200 K by spectrally resolving J-dependent rovibrational coherence revivals that occur 32 ps after initial excitation. This makes hybrid vibrational CARS a more general tool for gas-phase diagnostics. Another limitation of many CARS experiments is the lack of spatial flexibility in a sense that the laser beams are guided to the object of investigation by a set of mirrors and prisms. Hence, making changes to the setup often means significant alignment effort. To overcome this limitation, Hsu *et al.*^[91] presented a fiber-based experiment. The fibers allowed the transmission of sufficient laser pulse energy to perform single-shot thermometry.

Other groups extended CARS to new molecules and new pieces of information that can be gained. Bengtsson *et al.* implemented strategies for utilizing the rotational CARS signals of nitrous oxide^[92] and water vapor.^[93] Although both species are not desirable target species, for example, for thermometry, their signals

may interfere with that of nitrogen or oxygen. Hence, being able to predict their contribution to the CARS spectrum is invaluable in reducing the measurement uncertainties. Knopp *et al.*^[94] used fs-CARS to determine the ratio of ortho- and para-states in gaseous deuterium. Their study was performed in the context of the development of an ultra-cold neutron source, for which high amounts of ortho-D₂ are required. Bychkov *et al.*^[95] developed a nonlinear optical activity CARS technique to obtain chiral information in vapor phase systems. For this purpose, they proposed a mechanism for controlling chiral states in molecules with internal rotation employing the coherent quantum entanglement of the rotational–torsional states.

Non-CARS techniques

As indicated in the Theoretical and Instrumental Developments section, the list of nonlinear optical spectroscopy techniques other than CARS is long and so is the number of their applications presented at ECONOS.

Degenerate and two-color four-wave mixing

Degenerate four-wave mixing (DFWM) and two-color four-wave mixing (2C-FWM) are both not only species-selective but highly quantum-state-selective methods. They allow not only the investigation of a number of molecular physics phenomena but also the determination of quantities such as the temperature and the species concentration.^[7] Both methods are fully resonant, which explains the high signal intensities that can be obtained even at low concentration. The fully non-resonant counterpart of DFWM is coherent Rayleigh scattering, which has been employed by Bookey *et al.* for high-resolution spectroscopy.^[96]

Many applications focused on combustion intermediate species either directly in a flame or prepared in a controlled environment, e.g. photolysis of a precursor. In order to obtain laser radiation at the wavelengths in resonance with the species of interest, pulsed dye lasers emitting nanosecond pulses in the visible or ultraviolet spectrum were usually employed. Ewart and co-workers^[97] studied saturation and power broadening effects in DFWM spectra of OH and C₂ radicals in different flames. C₂ in its ionic form was investigated by Tulej *et al.*^[98] using DFWM and 2C-FWM. The ions were provided in a molecular beam prepared by discharging a mixture of acetylene and argon. A similar diagnostic approach was used to study C₃, another combustion intermediate.^[99] Adding two linear methods, laser-induced fluorescence and cavity ring-down spectroscopy, enabled the quantitative measurement of number densities, transition dipole moments, and relaxation rates. 2C-FWM was also applied to the formyl radical, HCO.^[100] HCO was prepared by photo-dissociation of formaldehyde in this study, but it is also a key species in combustion systems, where its concentration indicates the local heat release rate inside the flame front.^[101,102] The dissociation reaction was studied by photo-fragment excitation spectroscopy.^[103] Formaldehyde is an intermediate in flames itself, and it was extensively studied using 2C-FWM^[104] and DFWM.^[105,106] Further combustion intermediates and products of interest were OH and NH radicals^[104] as well as nitrogen dioxide, NO₂.^[107]

Using ultrashort laser pulses for DFWM allows gaining further information as time-resolved signals can be recorded. Femtosecond- and picosecond-DFWM was used in a variety of gases. Again, molecules of combustion interest have been studied frequently. Rouzee *et al.*^[108] carried out a careful analysis of fs-DFWM in CO₂ employing high intensity radiation so that the desired signal was perturbed by a plasma background. They proposed a polarization

technique that allowed suppression of the interference. Polarization-resolved measurements were also performed by Maksyutenko *et al.*,^[109] who studied OH radicals after photolysis of hydrogen peroxide. Knopp *et al.*^[110] used a non-resonant DFWM approach to study molecular oxygen and found that the combined detection in the time and frequency domain can assist in the extraction of physicochemical information. Picosecond lasers were employed for a 2C-FWM study of OH radicals by Chen *et al.*^[111] Their technique enabled direct time-resolved measurements of the collisional state-to-state transfer characteristics in terms of rates and correlation times.

Molecules of atmospheric, biological, and chemical interest have also been investigated by ultrafast DFWM. Liebers *et al.*^[112] studied the vibrational dynamics in excited electronic states of iodine with a pump-probe approach. An initial pump pulse populated an excited state, and the evolution of the resulting wave packet was monitored by DFWM. The process was also modeled, and good agreement with the experimental data was found. Riehn *et al.*^[113] carried out a time-resolved rotational analysis of formic acid and compared their experimental data with computer simulations. Good agreement was found for a non-rigid asymmetric rotor model. A larger molecule *viz.* benzene was under investigation at room temperature and in a supersonic expansion by Matylitsky *et al.*^[114] They concluded that the combination of gas cell and supersonic jet measurements is generally helpful for analyzing the structure of larger and more complex molecules. Pyridine and its derivatives are further aromatic compounds that were studied with fs-DFWM. Doing so, Frey *et al.*^[115] obtained highly accurate values of the ground-state rotational constants.

All the above applications utilized electronic transitions in the visible and ultraviolet spectral range. However, there are many important species, which do not exhibit suitable transitions in this range. Prominent examples are water and many hydrocarbon species. To overcome this problem, these molecules can be probed in the mid-infrared spectral range where they exhibit strong transitions owing to the fundamental modes of their molecular vibrations. Li *et al.* exploited these transitions using IR-DFWM. They demonstrated DFWM of water for flame thermometry^[116] and developed a method for methyl chloride detection in hot gas flows.^[117] The sensitive detection of chlorinated and fluorinated gaseous species is especially important in the context of the combustion and incineration of biomass and waste material, where such species may be emitted to the environment with the exhaust gas.

Polarization spectroscopy

Polarization spectroscopy (PS) is another fully resonant method. Kiefer *et al.*^[118] used a nanosecond dye laser for simultaneously recording PS and laser-induced fluorescence spectra of OH radicals in a model flame. They compared three different strategies for signal evaluation and obtained accurate temperature profiles with two of them, a contour fit of a wider spectral range and a two-line method. Extracting temperature from the linewidth of a single line did not provide sensible results because of the bandwidth of the dye laser. The use of a tunable single-mode laser may for high-resolution spectroscopy resolve such problems as it is better suited for obtaining accurate linewidth information.^[119,120] Faucher and co-workers employed a time-domain version of PS *viz.* femtosecond Raman-induced polarization spectroscopy (RIPS). Their method allowed determination of the chemical composition of ternary and quaternary gas mixtures containing nitrogen dioxide, carbon dioxide, nitrogen, and oxygen.^[121] RIPS temperature measurements

were performed in pure CO₂ and binary mixtures of CO₂ and N₂.^[122] Recent work of the group focused on the study of the molecular physics in mixtures of carbon dioxide and noble gases, taking advantage of a field-free molecular alignment with the femtosecond laser.^[123,124]

Laser-induced gratings

The laser-induced gratings (LIGs) technique represents a very versatile tool for gas-phase analysis and has been employed in an increasing number of practical applications. Hemmerling *et al.*^[125] used the heterodyne detection of electrostrictive LIGs to measure the flow velocity field in the plume of a rocket nozzle. The main purpose of their work was to produce experimental data for the validation of computational fluid dynamics simulations. However, their results also give an impressive demonstration of the application potential of electrostrictive LIGs, a fully non-resonant method. On the other hand, weak resonances were shown to be sufficient to generate thermal LIG signals with high intensity and to perform species-specific measurements. Kozlov and Radi^[126] studied highly excited vibrational overtone and combination bands of methane. They obtained rotationally resolved spectra in the wavelength region between 835 and 895 nm despite the very low absorption cross-sections. The fundamental radiation of a Nd:YAG laser was used to pump overtone and combination bands of propane by Kiefer *et al.*^[127] They performed LIG concentration measurements in a mixture formation process exploiting the temporal profiles of the signal.^[128] Single-shot fuel/air ratio determination was obtained at elevated temperature and pressure, and the results were in good agreement with reference data from Raman spectroscopy. In a follow-up paper, the approach was extended by Roshani *et al.* to determine the fuel vapor concentration and the gas phase temperature simultaneously.^[129] The concept was demonstrated in a flash-boiling propane jet.

Spontaneous Raman scattering techniques

In the interest of scientific discussions, ECONOS is also open to development and applications of linear optical spectroscopy in the form of poster presentations. A small number of spontaneous Raman scattering studies have therefore been included in the special issues. Chrysos *et al.* published a series of papers on collision-induced scattering spectroscopy of carbon dioxide,^[130,131] nitrogen,^[130] and noble gases such as neon^[132,133] and argon.^[131,133,134] Schlüter *et al.* demonstrated the application of a Raman gas analyzer for anesthesia monitoring.^[135]

Applications to condensed phase matter

Liquid and solid materials as well as their combinations represent not only highly interesting but also complicated objects to be investigated by nonlinear optical spectroscopies. The small intermolecular distances in condensed phase matter introduce complexity in terms of molecular interactions that can alter spectral signatures when compared with gas-phase systems.

Water and aqueous solutions of biomolecules

Water has been an interesting and highly active research area for many decades. Bunkin *et al.*^[136] studied the orientational motion of water molecules in the liquid state using a four-wave mixing technique to analyze the Rayleigh wing of the spectrum. In follow-up papers, they extended their technique to the

identification of water isotopes and spin isomers in mixtures of H₂O, D₂O, and HDO.^[137,138]

Aqueous solutions are particularly interesting in the life sciences, e.g. when biologically relevant molecules are dissolved. The above-mentioned Rayleigh-wing four-wave mixing technique was applied to solutions of the enzyme alpha-chymotrypsin.^[139,140] The spectra revealed features that could be interpreted as low-frequency vibrations of the large protein molecule. Akimov *et al.*^[141] developed a third-harmonic generation method utilizing a two-photon resonance of the dye to study the aggregation of dye molecules in aqueous solutions. Such dyes are frequently employed as fluorescence markers in microscopy as they can bind to proteins.^[142] Another dye that is often used as a model biomolecule is beta-carotene. Siebert *et al.*^[143] used a femtosecond pump-CARS scheme to study the internal conversion processes in beta-carotene dissolved in water. For this purpose, the molecules were excited electronically with a pump pulse, and the vibrational redistribution in the ground state was monitored by CARS as a function of time. The detailed investigation allowed the development of a mechanistic model for the repopulation of vibrational states. Konradi *et al.*^[144] used a phase-shaping method in their CARS experiments for coherent control of beta-carotene. This allowed the enhancement and suppression of selected vibrational modes, which was optimized using a feedback-control loop.

Organic and ionic solvents

Sakai *et al.*^[145] studied the low-frequency spectrum of a series of liquids (benzene, pyridine, nitro-benzene, benzyl benzoate, triphenyl phosphite, and salol). For this purpose, they combined ultrafast optical Kerr effect spectroscopy and high-resolution spectroscopy of the spontaneously scattered light. The systematic analysis of the data revealed that the dynamics governing the molecular relaxation in the liquids is non-Markovian. Bunkin *et al.*^[140] utilized the low-frequency spectrum recorded with four-photon Rayleigh-wing spectroscopy for determining the fractal dimensionality in carbon tetrachloride and a series of aqueous solutions. The spectral signatures observed were interpreted as structural differences in the liquids.

At higher frequencies, the vibrational spectrum of solvents was studied by CARS. Munhoz *et al.*^[146] developed a method for determining the Raman depolarization ratio of liquids using a polarization CARS approach. In their scheme, the pump and Stokes lasers can have arbitrary linear polarization, while the signal is analyzed along two perpendicular directions. The concept was proved in toluene and cyclohexane solutions. Kiefer *et al.*^[147] applied femtosecond CARS to an imidazolium ionic liquid. The results suggested that beating pairs of Raman modes typically correspond to either the cation or the anion. Moreover, no evidence for interionic vibrational energy transfer was found despite the fact that the interactions in the ion pair are characterized by strong hydrogen bonds.^[148] A different imidazolium ionic liquid was utilized by Rodriguez as a test case for combined hyper-Rayleigh, hyper-Raman, and spontaneous Raman scattering experiments.^[149] The data suggested the presence of highly correlated imidazolium ionic liquid clusters, involving at least eight ion pairs.

Even higher frequency vibrational modes were studied in the visible spectrum. Manzanares and co-workers^[150] used a thermal lens technique to study overtone CH vibrations of benzene. At cryogenic conditions they compared one- and two-color laser excitation. The fifth vibrational overtone of benzene dissolved in liquefied ethane, krypton, and argon has been recorded at

low concentrations. Experiments with one-color laser excitation turned out to be sensitive enough to detect benzene at parts per million level.

Fluids confined in porous materials

Porous materials have many interesting properties and are frequently used as adsorbents for gases and liquids in chemical and environmental applications. However, the behavior of molecules confined in a micro- or nanoporous material is difficult to investigate. In a series of papers, Arakcheev *et al.* applied CARS to confined carbon dioxide in a systematic manner. They started with an analysis of the Fermi dyad spectrum of pure CO₂ without a porous material. Spectra were recorded along several isotherms near the critical point.^[151] In the next step, CO₂ was confined in a glass matrix with a pore size of 4 nm.^[152] The spectral broadening of the confined CO₂ in the liquid state was found to be not homogeneous in contrast to the bulk fluid. Two main contributions were identified and could be attributed to those molecules in the center of the pores and those located near the walls of the glass material. The CARS spectra could also reveal an alteration of the critical point when CO₂ is confined in a glass matrix.^[153] Interestingly, the spectrum of carbon dioxide condensed in the wider pores was similar to the spectrum at the critical density in the bulk fluid. In contrast, in the narrower pores, the spectrum was found red-shifted indicating a higher density of the confined fluid. Reducing the pore size of the glass enabled an improved investigation of the molecules close to the walls of the pores. With a pore size of 2 nm, it was possible to study the super-monolayer and sub-monolayer coverage.^[154] The experimental results facilitated the characterization and comparison of the spectral properties of gas-like, liquid-like, and surface-adsorbed carbon dioxide.

Confined nitrogen and toluene were studied by Konorov *et al.* using CARS. Polarization-CARS was used to study a toluene solution infiltrated in a porous glass matrix.^[155] The experimental method could selectively and independently address optical nonlinearities of the materials. The rotation of the polarization analyzer with respect to the polarization vectors of the linearly polarized pump fields was found to result in significant deformations of the CARS line profiles. This suggested a change in the ratio of the signal contributions from toluene molecules and the porous glass host. The same group demonstrated a nanoCARS approach to study gaseous nitrogen as well as toluene in the gas- and liquid-phase inside mesoporous silica aerogels.^[156] The theoretical principles of the nanoCARS technique, which must not be mixed up with microscopic versions of CARS, were summarized by Zheltikov.^[157] In contrast to CARS microscopy, which is intended to resolve individual micro-objects, the interferometric nanoCARS technique is not capable of resolving individual nanocrystals in a nanocomposite material. However, it can locally probe the effective-medium linear and nonlinear optical properties of a nanostructure.^[158]

Carbonaceous materials

Carbon structures such as fullerenes and nanotubes have frequently been studied by means of linear and nonlinear optical spectroscopy.^[158–160] Falke *et al.*^[161] combined Raman scattering and UV/Vis absorption spectroscopy with atomic force microscopy to study blends of a polymer and fullerenes. They were able to identify fullerene inclusions in the blends in the Raman spectra.

De Dominicis, Fantoni, and collaborators investigated the nonlinear optical properties of carbon nanotubes (CNTs) in a series of

papers. Nanosecond DFWM was employed to measure the effective third-order nonlinear susceptibility.^[162] Additional scanning electron microscopy experiments allowed establishing a relationship between the nonlinear optical bulk properties and the second-order polarizability coefficient of single nanotubes. Later, they used second-harmonic generation (SHG) to determine the second-order susceptibility tensor.^[163] The first hyper-polarizability of CNTs was also studied theoretically. The effects of electron statistics on the frequency dependence of the hyper-polarizability were analyzed,^[164] as well as finite length effects with respect to the SHG far-field radiation pattern.^[165] The CNT-based generation of the second- and third-harmonic radiation was also demonstrated with femtosecond pulses.^[166] It was concluded that harmonic-generation processes are ideally suited for the nonlinear spectroscopy and structure analysis of CNTs.

Aqueous suspensions of CNTs were studied in the low frequency spectral range by Bunkin and Pershin. The four-wave mixing spectrum below 100 cm^{-1} was used to study hydration layers of water molecules.^[167] Information at higher frequencies was obtained by Raman-induced Kerr effect spectroscopy.^[168] The data from both techniques indicated the formation of hydrogen peroxide molecules at the CNT surface.

Non-carbon powders

Ceramic nanomaterials have a large variety of applications in catalysis and the life sciences.^[169–171] Nanocomposites are of particular interest as they allow tailoring the properties of the materials for a given purpose. Konorov *et al.*^[172] studied the second- and third-harmonic generation in silicon carbide nanopowders embedded in a poly(methyl methacrylate) film using a femtosecond Cr: forsterite laser. A counterintuitive behavior was observed when the nanopowder content in the nanocomposite was varied, which could be explained taking quenching by the absorption of agglomerating nanoparticles into account. The importance of agglomeration was also found in suspensions of titania nanopowders that were studied using coherent Rayleigh scattering by Rondino *et al.*^[173]

Metals and molecules adsorbed at metal surfaces were also studied. Baida *et al.*^[174] combined a spatial modulation linear absorption method with time-resolved nonlinear pump-probe spectroscopy to study individual silver nanoparticles. This allowed the comprehensive optical characterization and an investigation of the particle's acoustic vibrations. The obtained information about the particle size and shape was consistent with the measured vibrational breathing mode period of the particle. Botti *et al.*^[175] utilized the adsorption of traces of explosives on a nanoscale roughened metal surface to obtain high-sensitivity detection because of the plasmonic enhancement. Their surface-enhanced Raman scattering setup allowed the detection of amounts of adsorbed explosives below a nanogram.

Crystals and glasses

Amorphous materials like glass are very common substrates in optics labs, and thus, it is no surprise that their optical properties have been studied by nonlinear optical spectroscopy. Rodriguez^[149] combined hyper-Raman, hyper-Rayleigh, and spontaneous Raman scattering to characterize silica glass. Both the structure and the vibrational dynamics could be analyzed. One finding was that the local structure, referred to as the elementary structural unit, governs the spectroscopic activity. Bunkin *et al.*^[176] studied the low-

frequency spectrum with a four-wave mixing technique. They identified characteristic features on the Rayleigh wing of the spectrum and assigned them to rotations of hydroxyl groups and second sound phonons. Konorov *et al.*^[177] used a femtosecond time-resolved two-photon resonant FWM scheme to study the ultrafast processes triggering photochromic transformations in a three-dimensional polymer matrix. The time-resolved FWM measurements allowed visualization of the build-up of coherences in the photochromic material on the leading edge of the pump pulse and indicated ultrafast phase relaxation on the femtosecond time-scale in the bulk polymeric material.

The nonlinear optical properties of crystalline materials were characterized theoretically and experimentally. Orlov and Polivanov^[178] theoretically studied the influence of the propagation of polaritons on CARS spectra. Support for their theoretical findings was provided by experiments in a BeO crystal. Kitaeva *et al.*^[179] developed omega-k spectroscopy to measure the spatial profiles of the second-order nonlinear optical susceptibility in periodically poled crystals. A comparison was made with experiments using spontaneous parametric down-conversion and second-harmonic generation in a LiNbO₃:Y:Mg crystal. Magnesium doped LiNbO₃ crystals were studied in two further papers of the same group using cascaded coherent Stokes Raman scattering^[180] and a combination of spontaneous parametric down-conversion and near-forward Raman scattering.^[181]

Last but not least, a number of contributions was concerned with the nonlinear optical properties of photonic crystal fibers (PCFs). PCFs are frequently employed to manipulate the characteristics, for example, of a laser beam via nonlinear processes in their highly structured core.^[182,183] Zheltikov demonstrated the potential of a PCF-based light source for CARS and two-photon-resonant sum-frequency generation experiments.^[184] The possibilities of frequency shifting and pulse shaping with PCFs were studied for applications in four-wave mixing spectroscopy by Linik *et al.*^[185] Moreover, a specially structured PCF enabled the generation of mode-separable supercontinuum emission.^[186] The opportunities arising from the application of different spatial and spectral filtering approaches to tailor the output radiation for specific applications were laid out. Another way of controlling the optical properties of a PCF is to fill its hollow spaces with gases or liquids. The same approach can be used for chemical sensing. Konorov *et al.* filled hollow-core PCFs with nitrogen gas and recorded CARS signals of the molecules inside the fiber.^[187,188]

Nonlinear optical microscopy

The development and application of nonlinear optical microscopy techniques have been based upon the vast amount of prior knowledge collected from nonlinear optical spectroscopies in the gas and condensed phases. Their most predominant realizations to date are CARS^[189,190] and SRS microscopy,^[191–194] which have emerged as highly sensitive tools for label-free imaging and micro-spectroscopy with chemical specificity and three-dimensional section capability. While CARS and SRS microscopy provide vibrational image contrast, they have been readily combined with other nonlinear coherent optical image contrast mechanisms, such as SHG, sum-frequency generation, and third-harmonic generation. The combination of these nonlinear optical processes with microscopy has found an ever-increasing interest, which has also been reflected by a number of contributions to ECONOS that focused, on the one hand, on methodological

developments and, on the other hand, on highly interesting applications in the life and material sciences.

Methodological development

Several methodological aspects have been considered theoretically. Marrocco presented a simplified numerical simulation for the description of nonlinear Raman scattering signal generation under conditions of tightly focused laser beams.^[195] A comparison of the proposed method with the full vectorial description revealed a significant speed-up when using the simplified model without any losses of spectroscopic information. A theoretical analysis of the origins of spectral interferences in femtosecond stimulated Raman microscopy was performed by Ploetz *et al.*^[196] They presented a model that includes a contribution from a four-wave mixing process, which experiences a heterodyne amplification and thus interferes with the desired stimulated Raman signal. By means of numerical simulations based on the density matrix model, Beeker *et al.*^[197] theoretically studied two super-resolution CARS microscopy techniques. They proposed that a precise control of the population of the involved vibrational molecular states may achieve a spatial resolution below the diffraction limit.

Such control is normally realized by a tailored shaping of the ultrashort laser pulses. Van Rhijn *et al.*^[198] presented suitable phase-shaping strategies and used an evolutionary algorithm to optimize the chemical selectivity, specificity, and sensitivity. Such a numerical optimization was also introduced by Motzkus and co-workers.^[22] Coherent control through pulse shaping of ultrafast pulses was also the enabling technology for the heterodyne, single-beam CARS microscopy proposed by Müller *et al.*^[199] Using optimized experimental parameters, they obtained high chemical selectivity. Phase shaping also played an important role in the work by Langbein *et al.*,^[200] who theoretically and experimentally investigated the effect of spectral focusing for CARS microscopy with high spectral selectivity. The creation of linearly chirped pulses by propagation through a dispersive glass medium and the limitations due to higher order dispersion were systematically analyzed. A CARS microscopy method employing a wide-field geometry was proposed by Heinrich *et al.*^[201] Using a nanosecond laser source, the concept was demonstrated by fast imaging of oil droplets and sunflower seeds with chemical contrast. Another wide-field CARS configuration was developed by Silve *et al.*,^[202] who employed it for live imaging of cells.

Quite a few articles presented advances of experimental microspectroscopy setups and the involved instrumentation. Furusawa *et al.*^[203] developed a two-beam multiplexed CARS microscopy technique based on a broadband Ti:sapphire oscillator. The spectral structure of the laser pulses led to time-delay-sensitive CARS measurements. A multicolor CARS microscopy based on a tunable picosecond laser light source for the rapid analysis of heterogeneous mixtures was introduced by Garbaciak *et al.*^[204] A color-coding method allowed the meaningful visualization of the complex multidimensional datasets, which was shown for data recorded in a mixture of seven crystalline amino acids. The evaluation of such multidimensional datasets was also the focus of the paper by Masia *et al.*^[205] They developed three algorithms to improve the acquisition and analysis of multicolor CARS images, i.e. a multivariate factorization algorithm improving the ability to identify localized chemical components, a method to recover the full spectral information from a sparse sampled data, and a filter for motion artifacts. Peng *et al.*^[206] proposed a hybrid CARS/coherent Stokes Raman scattering setup for microscopy combining femtosecond excitation

with a narrowband picosecond probe. Another very interesting approach for generating vibrational image contrast was developed by Molotokaite *et al.*,^[207] who exploited the Raman-induced Kerr effect and a balanced-detection technique that remove both linear and nonlinear background signals, provide self-heterodyne amplification of the nonlinear Raman signal, and allow for an intrinsic rejection of laser noise. Another feature is that the signal scales linearly with the sample concentration.

A technique, in which CARS microscopy is performed inside a micro-cavity, was proposed by Marrocco and Nichelatti.^[208] Their theoretical analysis indicated that the cavity will lead to a signal enhancement of one to two orders of magnitude.

A versatile CARS microscope that integrates a number of additional optical imaging modalities was also presented by Downes *et al.*^[209] Besides CARS, their instrument allows imaging of biological samples with differential interference contrast, SHG, sum-frequency generation, one- and two-photon fluorescence, and fluorescence lifetime imaging. Moreover, the combination with an atomic force microscope tip enables imaging with high spatial resolution because of the tip enhancement.

Developments of novel laser light sources

Common to all nonlinear optical microscopy techniques is that ultrashort pulses of high peak powers and moderate average power within a broad range of wavelengths are required for efficient signal generation with high spectral selectivity. The development of new laser light sources and their implementation in microscopy setups have thus been an important driver for advances made in the field. As early as 2003, Yakovlev^[210] proposed a CARS microscope at moderate cost in the order of USD 50k and offering high flexibility.

Leproux *et al.*^[211] demonstrated the use of a new compact supercontinuum source delivering pulses with durations below a nanosecond. This enabled ultra-broadband multiplex CARS imaging of biological samples. Kumar *et al.*^[212] proposed a femtosecond Er:fiber-based oscillator, which has the advantage of being much more compact and versatile while offering almost the same performance like conventional sources for nonlinear Raman microscopy, which are based on sync-pumped, tunable optical parametric oscillators. By using spectral focusing of supercontinuum pulses generated in a PCF that was seeded with femtosecond Ti:sapphire laser pulses, Saint-Jalm *et al.*^[213] presented another approach of a rapidly tunable coherent Raman scattering light source. Marx *et al.*^[214] described an improved light source for femtosecond SRS microspectroscopy. The source delivered both the narrowband pump and the broadband Raman probe pulses. In addition, they discussed the use of different multichannel detectors.

Applications to biological samples

A common application of nonlinear optical microscopy is the label-free imaging of cells and tissues. In particular, most Raman-based bio-imaging applications take advantage of the abundance of C–H stretching vibrations of endogenous lipids. As such, Bonn *et al.*^[215] employed multiplex CARS microscopy for imaging lipid droplets inside cells. Their approach did not only allow visualization of the lipid distribution with chemical contrast but also facilitate gathering information about their physical state. Brackmann *et al.*^[216] also studied lipid droplets in yeast cells using picosecond CARS imaging. A comprehensive dataset with additional two-photon fluorescence images enabled deducing three-dimensional information about

the impact of the nutritional state and the genetic background. Moger and co-workers^[217] presented a multimodal imaging approach combining SRS and two-photon photo-thermal lensing microscopy. This work facilitated simultaneous visualization of cortical microvascular morphology and surrounding cellular structures.

Mortati *et al.*^[218] combined CARS and SHG microscopy to evaluate the production of collagen in living human corneal fibroblasts and mesenchymal stem cells in fibrin hydrogel 3D cultures. They concluded that this multimodal imaging can become a new tool of monitoring the early stages of stem cell differentiation within a three-dimensional scaffold. Further work on stem cell differentiation was presented by Downes *et al.*,^[219] who combined spontaneous Raman scattering and CARS techniques. The same group also proposed a multimodal nonlinear imaging approach for analyzing biological samples, where CARS microscopy was employed to study living cells, the delivery of chemotherapeutic drugs was monitored using CARS and two-photon fluorescence, and adding SHG provided a diagnostic tool for cancer tissue.^[220] The delivery of nanoparticulate drugs was also targeted by Garrett *et al.*,^[221] who proposed a CARS method for imaging nanoparticle drug carriers against a background of biological tissues and cells.

Applications to non-biological samples

Although nonlinear optical imaging in fields other than the life sciences is less common, it can also provide highly interesting insights in the material sciences. For example, Caster *et al.*^[222] employed CARS microscopy for real-time and *in situ* monitoring of the cross-linking of the photoresist material hydrogen silsesquioxane. They studied the process at different temperatures and by inducing it with the help of a high-intensity near-infrared laser. The characteristic Raman bands revealed different stages in the cross-linking. Furusawa *et al.*^[223] utilized a PCF-based supercontinuum light source for broadband CARS microscopy of CNTs. With the help of tip enhancement, they achieved measurements with a spatial resolution of 60 nm. Bratashov *et al.*^[224] used Raman imaging and atomic force microscopy to study the composition, stability, and photo-degradation of polyelectrolyte multilayer microcapsules and coated microparticles. These hollow particles served as containers for phthalocyanine complexes with iron and copper centers. Both complexes are common industrial dyes, and hence, their stability upon exposure to light is of great importance. Fussel *et al.*^[225] applied CARS microscopy to micron-sized drugs in adhesive mixtures for inhalation. Chemically selective imaging enabled the visualization of the distribution of drug particles on the surface of lactose carrier particles. Furthermore, combining CARS with scanning electron microscopy provided chemical and morphological information and thus an unambiguous identification of the spatial drug distribution over the carrier surface.

Conclusion

This article reviewed the contributions published in the ECONOS special issues of the *Journal of Raman Spectroscopy*. The broad applicability of nonlinear optical techniques gives rise to the highly interdisciplinary character of the ECONOS conference, which attracts scientists and engineers of all disciplines every year. This review gives an idea of this unique breadth of topics that were covered in the exciting history of the meeting.

Acknowledgements

The authors, who all served as JRS guest editors for the ECONOS/ECW special issue in the past, would like to thank the former and current editors-in-chief, Wolfgang Kiefer and Larry Nafie, for their continuous support. We would also like to take the opportunity to thank the hundreds of authors and reviewers of manuscripts for their valuable contributions and expertise, which have made this conference series and its published proceedings a success.

References

- [1] A. Volkmer, P. P. Radi, A. M. Zheltikov, A. Zumbusch, *J. Raman Spectrosc.* **2009**, *40*, 712.
- [2] R. W. Boyd, *Nonlinear Optics*, 1st ed., Academic Press, San Diego, **1991**.
- [3] W. Demtröder, *Laser Spectroscopy*, 2nd ed., Springer Verlag, Berlin, New York, **1996**.
- [4] A. C. Eckbreth, *Laser Diagnostics for Combustion Temperature and Species*, 2nd ed., Gordon and Breach, Amsterdam, **1996**.
- [5] H. J. Eichler, P. Günter, D. W. Pohl, *Laser-Induced Dynamic Gratings*, vol. 50, Springer Verlag, Berlin, **1986**.
- [6] S. Roy, J. R. Gord, A. K. Patnaik, *Prog. Energy Combust. Sci.* **2010**, *36*, 280.
- [7] J. Kiefer, P. Ewart, *Prog. Energy Combust. Sci.* **2011**, *37*, 525.
- [8] A. Stampanoni-Panariello, D. N. Kozlov, P. P. Radi, B. Hemmerling, *Appl. Phys. B* **2005**, *81*, 101.
- [9] N. Egorova, A. Kouzov, M. Chrysos, F. Racht, *J. Raman Spectrosc.* **2005**, *36*, 153.
- [10] A. V. Akimov, A. N. Matveev, A. V. Sokolov, V. N. Sorokin, S. I. Kanorsky, N. N. Kolachevsky, *J. Raman Spectrosc.* **2005**, *36*, 123.
- [11] A. V. Akimov, A. N. Matveev, A. V. Sokolov, E. O. Tereshenko, D. A. Kondratjev, V. N. Sorokin, S. I. Kanorsky, N. N. Kolachevsky, *J. Raman Spectrosc.* **2006**, *37*, 712.
- [12] E. Nichelatti, M. Marrocco, R. M. Montereali, *J. Raman Spectrosc.* **2010**, *41*, 859.
- [13] C. H. R. Ooi, *J. Raman Spectrosc.* **2009**, *40*, 174.
- [14] M. Marrocco, *J. Raman Spectrosc.* **2007**, *38*, 1064.
- [15] M. Marrocco, *J. Raman Spectrosc.* **2015**, *46*, 683.
- [16] A. Monmayrant, S. Weber, B. Chatel, *J. Phys. B* **2010**, *43*, 103001.
- [17] A. M. Zheltikov, *J. Raman Spectrosc.* **2008**, *39*, 756.
- [18] J. Konradi, A. Scaria, V. Namboodiri, A. Materny, *J. Raman Spectrosc.* **2007**, *38*, 1006.
- [19] A. Scaria, J. Konradi, V. Namboodiri, A. Materny, *J. Raman Spectrosc.* **2008**, *39*, 739.
- [20] S. Gräfe, D. A. Akimov, B. Böhm, A. M. Zheltikov, M. O. Scully, W. Kiefer, V. Engel, T. Siebert, *J. Raman Spectrosc.* **2007**, *38*, 998.
- [21] V. S. Malinovsky, *J. Raman Spectrosc.* **2009**, *40*, 817.
- [22] A. Wipfler, T. Backup, M. Motzkus, *J. Raman Spectrosc.* **2015**, *46*, 679.
- [23] A. Wipfler, J. Reh binder, T. Backup, M. Motzkus, *J. Raman Spectrosc.* **2013**, *44*, 1379.
- [24] Y. X. Liu, Y. J. Lee, M. T. Cicerone, *J. Raman Spectrosc.* **2009**, *40*, 726.
- [25] E. M. Vartiainen, *JOSA B* **1992**, *9*, 1209.
- [26] M. T. Cicerone, K. A. Amer, Y. J. Lee, E. M. Vartiainen, *J. Raman Spectrosc.* **2012**, *43*, 637.
- [27] A. K. Vereshchagin, K. A. Vereshchagin, V. B. Morozov, V. G. Tunkin, *J. Raman Spectrosc.* **2014**, *45*, 507.
- [28] B. Mallick, A. Lakshmana, S. Umaphathy, *J. Raman Spectrosc.* **2011**, *42*, 1883.
- [29] A. Bohlin, F. Vestin, J. Bonamy, P. Joubert, P.-E. Bengtsson, *J. Raman Spectrosc.* **2010**, *41*, 875.
- [30] A. Bohlin, F. Vestin, P. Joubert, J. Bonamy, P.-E. Bengtsson, *J. Raman Spectrosc.* **2009**, *40*, 788.
- [31] Y. Gao, M. C. Weigl, T. Seeger, A. Leipertz, P. Joubert, J. Bonamy, *J. Raman Spectrosc.* **2009**, *40*, 781.
- [32] P. Joubert, J. Bonamy, L. Gomez, D. Bermejo, *J. Raman Spectrosc.* **2008**, *39*, 707.
- [33] J. Buldyreva, J. Bonamy, M. C. Weigl, F. Beyrau, T. Seeger, A. Leipertz, F. Vestin, M. Afzelius, J. Bood, P.-E. Bengtsson, *J. Raman Spectrosc.* **2006**, *37*, 647.
- [34] G. Knopp, P. Beaud, P. P. Radi, M. Tulej, B. Bougie, D. Cannavo, T. Gerber, *J. Raman Spectrosc.* **2002**, *33*, 861.
- [35] P. J. Wrzesinski, H. U. Stauffer, W. D. Kulatilaka, J. R. Gord, S. Roy, *J. Raman Spectrosc.* **2013**, *44*, 1344.

- [36] K. A. Vereschagin, V. V. Smirnov, O. M. Stel'makh, V. I. Fabelinsky, W. Clauss, D. N. Klimenko, M. Oschwald, A. K. Vereschagin, *J. Raman Spectrosc.* **2005**, *36*, 134.
- [37] K. A. Vereschagin, A. K. Vereschagin, V. V. Smirnov, O. M. Stel'makh, V. I. Fabelinsky, W. Clauss, M. Oschwald, *J. Raman Spectrosc.* **2008**, *39*, 722.
- [38] K. A. Vereschagin, A. K. Vereschagin, V. V. Smirnov, O. M. Stel'makh, V. I. Fabelinsky, W. Clauss, M. Oschwald, *J. Raman Spectrosc.* **2010**, *41*, 897.
- [39] W. Clauss, D. N. Klimenko, M. Oschwald, K. A. Vereschagin, V. V. Smirnov, O. M. Stel'makh, V. I. Fabelinsky, *J. Raman Spectrosc.* **2002**, *33*, 906.
- [40] H. Skenderovic, T. Buckup, W. Wohlleben, M. Motzkus, *J. Raman Spectrosc.* **2002**, *33*, 866.
- [41] V. G. Arakcheev, D. V. Yakovlev, V. B. Morozov, A. N. Olenin, V. G. Tunkin, *J. Raman Spectrosc.* **2003**, *34*, 977.
- [42] V. G. Arakcheev, D. V. Yakovlev, S. Mochalov, V. B. Morozov, A. N. Olenin, V. G. Tunkin, *J. Raman Spectrosc.* **2002**, *33*, 884.
- [43] C. S. McEnally, L. D. Pfeifferle, B. Atakan, K. Kohse-Höinghaus, *Prog. Energy Combust. Sci.* **2006**, *32*, 247.
- [44] H. Richter, J. B. Howard, *Prog. Energy Combust. Sci.* **2000**, *26*, 565.
- [45] V. B. Morozov, S. Mochalov, A. N. Olenin, V. G. Tunkin, A. Kouzov, *J. Raman Spectrosc.* **2003**, *34*, 983.
- [46] V. G. Arakcheev, V. V. Kireev, V. B. Morozov, A. N. Olenin, V. G. Tunkin, A. A. Valeev, D. V. Yakovlev, *J. Raman Spectrosc.* **2007**, *38*, 1038.
- [47] V. G. Arakcheev, V. V. Kireev, V. B. Morozov, A. N. Olenin, V. G. Tunkin, A. A. Valeev, D. V. Yakovlev, *J. Raman Spectrosc.* **2007**, *38*, 1046.
- [48] J. Buldyreva, S. V. Ivanov, L. Nguyen, *J. Raman Spectrosc.* **2005**, *36*, 148.
- [49] R. Herman, R. F. Wallis, *J. Chem. Phys.* **1955**, *23*, 637.
- [50] M. Marrocco, *J. Raman Spectrosc.* **2009**, *40*, 741.
- [51] M. Marrocco, *J. Raman Spectrosc.* **2010**, *41*, 870.
- [52] M. Marrocco, *J. Raman Spectrosc.* **2011**, *42*, 1836.
- [53] A. Bohlin, P.-E. Bengtsson, M. Marrocco, *J. Raman Spectrosc.* **2011**, *42*, 1843.
- [54] A. Bohlin, E. Nordstrom, P.-E. Bengtsson, M. Marrocco, *J. Raman Spectrosc.* **2012**, *43*, 599.
- [55] M. Marrocco, *J. Raman Spectrosc.* **2012**, *43*, 621.
- [56] M. Marrocco, G. Magnotti, A. D. Cutler, *J. Raman Spectrosc.* **2012**, *43*, 595.
- [57] M. Marrocco, *J. Raman Spectrosc.* **2013**, *44*, 1326.
- [58] W. Stricker, R. Luckerath, U. Meier, W. Meier, *J. Raman Spectrosc.* **2003**, *34*, 922.
- [59] D. N. Klimenko, W. Clauss, M. Oschwald, J. Smith, W. Mayer, *J. Raman Spectrosc.* **2002**, *33*, 900.
- [60] V. I. Fabelinsky, V. V. Smirnov, O. M. Stel'makh, K. A. Vereschagin, A. K. Vereschagin, W. Clauss, M. Oschwald, *J. Raman Spectrosc.* **2007**, *38*, 989.
- [61] V. I. Fabelinsky, V. V. Smirnov, O. M. Stel'makh, K. A. Vereschagin, W. Clauss, C. Manfretti, J. Sender, M. Oschwald, *J. Raman Spectrosc.* **2010**, *41*, 890.
- [62] K. A. Vereschagin, V. V. Smirnov, O. M. Stel'makh, V. I. Fabelinsky, W. Clauss, M. Oschwald, *J. Raman Spectrosc.* **2010**, *41*, 902.
- [63] R. P. Lucht, *Opt. Lett.* **1987**, *12*, 78.
- [64] F. Beyrau, A. Datta, T. Seeger, A. Leipertz, *J. Raman Spectrosc.* **2002**, *33*, 919.
- [65] M. C. Weikl, T. Seeger, R. Hierold, A. Leipertz, *J. Raman Spectrosc.* **2007**, *38*, 983.
- [66] J. M. Simmie, *Prog. Energy Combust. Sci.* **2003**, *29*, 599.
- [67] J. C. Sutherland, P. J. Smith, J. H. Chen, *Combust. Theory Model.* **2005**, *9*, 365.
- [68] A. Braeuer, F. Beyrau, M. C. Weikl, T. Seeger, J. Kiefer, A. Leipertz, A. Holzwarth, A. Soika, *J. Raman Spectrosc.* **2006**, *37*, 633.
- [69] J. Kojima, Q.-V. Nguyen, *Appl. Opt.* **2002**, *41*, 6360.
- [70] F. Beyrau, M. C. Weikl, T. Seeger, A. Leipertz, *Opt. Lett.* **2004**, *29*, 2381.
- [71] T. Seeger, A. Leipertz, *Appl. Opt.* **1996**, *35*, 2665.
- [72] T. D. Fansler, S. E. Parrish, *Meas. Sci. Technol.* **2015**, *26*, 012002.
- [73] A. Malarski, A. Leipertz, *J. Raman Spectrosc.* **2008**, *39*, 700.
- [74] T. Parameswaran, D. R. Snelling, *Combust. Flame* **1996**, *106*, 511.
- [75] T. Seeger, M. C. Weikl, F. Beyrau, A. Leipertz, *J. Raman Spectrosc.* **2006**, *37*, 641.
- [76] F. Vestin, M. Afzelius, P.-E. Bengtsson, *J. Raman Spectrosc.* **2005**, *36*, 95.
- [77] F. Vestin, M. Afzelius, H. Berger, F. Chaussard, R. Saint-Loup, P.-E. Bengtsson, *J. Raman Spectrosc.* **2007**, *38*, 963.
- [78] L. A. Melton, *Appl. Opt.* **1984**, *48*, 4473.
- [79] P.-E. Bengtsson, M. Alden, *Combust. Sci. Technol.* **1991**, *77*, 307.
- [80] A. Malarski, F. Beyrau, A. Leipertz, *J. Raman Spectrosc.* **2005**, *36*, 102.
- [81] T. Seeger, F. Beyrau, A. Bräuer, A. Leipertz, *J. Raman Spectrosc.* **2003**, *34*, 932.
- [82] M. Afzelius, P.-E. Bengtsson, *J. Raman Spectrosc.* **2003**, *34*, 940.
- [83] E. Nordstrom, P.-E. Bengtsson, M. Marrocco, *J. Raman Spectrosc.* **2014**, *45*, 489.
- [84] G. Magnotti, A. D. Cutler, G. C. Herring, S. A. Tedder, P. M. Danehy, *J. Raman Spectrosc.* **2012**, *43*, 611.
- [85] J.-C. Diels, W. Rudolph, *Ultrashort Laser Pulse Phenomena: Fundamentals, Techniques, and Applications on a Femtosecond Time Scale*, 2nd revised ed., Academic Press, Burlington, **2006**.
- [86] B. D. Prince, A. Chakraborty, B. M. Prince, H. U. Stauffer, *J. Chem. Phys.* **2006**, *125*, 044502.
- [87] S. Roy, T. R. Meyer, J. R. Gord, *Appl. Phys. Lett.* **2005**, *87*, 264103.
- [88] T. Seeger, J. Kiefer, A. Leipertz, B. D. Patterson, C. J. Kliever, T. B. Settersten, *Opt. Lett.* **2009**, *34*, 3755.
- [89] S. R. Engel, J. D. Miller, C. E. Dedic, T. Seeger, A. Leipertz, T. R. Meyer, *J. Raman Spectrosc.* **2013**, *44*, 1336.
- [90] J. D. Miller, C. E. Dedic, T. R. Meyer, *J. Raman Spectrosc.* **2015**, *46*, 702.
- [91] P. S. Hsu, W. D. Kulatilaka, J. R. Gord, S. Roy, *J. Raman Spectrosc.* **2013**, *44*, 1330.
- [92] A. Bohlin, A. Kindeya, E. Nordstrom, P.-E. Bengtsson, *J. Raman Spectrosc.* **2012**, *43*, 604.
- [93] E. Nordstrom, A. Bohlin, P.-E. Bengtsson, *J. Raman Spectrosc.* **2013**, *44*, 1322.
- [94] G. Knopp, K. Kirch, P. Beaud, K. Mishima, H. Spitzer, P. P. Radi, M. Tulej, T. Gerber, *J. Raman Spectrosc.* **2003**, *34*, 989.
- [95] S. S. Bychkov, B. A. Grishanin, V. N. Zadkov, H. Takahashi, *J. Raman Spectrosc.* **2002**, *33*, 962.
- [96] H. T. Bookey, A. I. Bishop, M. N. Shneider, P. F. Barker, *J. Raman Spectrosc.* **2006**, *37*, 655.
- [97] K. Bultitude, R. T. Bratfalean, P. Ewart, *J. Raman Spectrosc.* **2003**, *34*, 1030.
- [98] M. Tulej, G. Knopp, T. Gerber, P. P. Radi, *J. Raman Spectrosc.* **2010**, *41*, 853.
- [99] M. Tulej, M. Meisinger, G. Knopp, A. M. Walser, T. Gerber, P. P. Radi, *J. Raman Spectrosc.* **2007**, *38*, 1022.
- [100] P. P. Radi, M. Tulej, G. Knopp, P. Beaud, T. Gerber, *J. Raman Spectrosc.* **2003**, *34*, 1037.
- [101] J. Kiefer, Z. S. Li, T. Seeger, A. Leipertz, M. Aldén, *Proc. Combust. Inst.* **2009**, *32*, 921.
- [102] B. O. Ayoola, R. Balachandran, J. H. Frank, E. Mastorakos, C. F. Kaminski, *Combust. Flame* **2006**, *144*, 1.
- [103] M. Tulej, G. Knopp, P. Beaud, T. Gerber, P. P. Radi, *J. Raman Spectrosc.* **2005**, *36*, 109.
- [104] P. P. Radi, A. P. Kouzov, *J. Raman Spectrosc.* **2002**, *33*, 925.
- [105] M. Carpanese, L. De Dominicis, R. Fantoni, *J. Raman Spectrosc.* **2007**, *38*, 1032.
- [106] M. Tulej, M. Meisinger, G. Knopp, A. M. Walser, P. Beaud, T. Gerber, P. P. Radi, *J. Raman Spectrosc.* **2006**, *37*, 680.
- [107] L. De Dominicis, R. Fantoni, *J. Raman Spectrosc.* **2002**, *33*, 896.
- [108] A. Rouzee, V. Renard, S. Guerin, O. Faucher, B. Lavorel, *J. Raman Spectrosc.* **2007**, *38*, 969.
- [109] P. Maksyutenko, P. P. Radi, D. N. Kozlov, A. P. Kouzov, *J. Raman Spectrosc.* **2013**, *44*, 1349.
- [110] G. Knopp, P. P. Radi, D. N. Kozlov, A. P. Kouzov, *J. Raman Spectrosc.* **2011**, *42*, 1848.
- [111] X. Chen, T. B. Settersten, A. P. Kouzov, *J. Raman Spectrosc.* **2009**, *40*, 847.
- [112] J. Liebers, A. Scaria, A. Materny, U. Kleinekathöfer, *J. Raman Spectrosc.* **2009**, *40*, 822.
- [113] C. Riehn, V. V. Matyilitsky, M. F. Gelin, *J. Raman Spectrosc.* **2003**, *34*, 1045.
- [114] V. V. Matyilitsky, W. Jarzeba, C. Riehn, B. Brutschy, *J. Raman Spectrosc.* **2002**, *33*, 877.
- [115] H. M. Frey, A. Müller, S. Leutwyler, *J. Raman Spectrosc.* **2002**, *33*, 855.
- [116] Z. W. Sun, Z. S. Li, B. Li, M. Alden, *J. Raman Spectrosc.* **2011**, *42*, 1828.
- [117] A. L. Sahlberg, J. Zhou, M. Alden, Z. S. Li, *J. Raman Spectrosc.* **2015**, *46*, 695.
- [118] J. Kiefer, A. Meyerhoefer, T. Seeger, A. Leipertz, Z. S. Li, M. Aldén, *J. Raman Spectrosc.* **2009**, *40*, 828.
- [119] J. Kiefer, Z. S. Li, J. Zetterberg, M. Linvin, M. Aldén, *Opt. Commun.* **2007**, *270*, 347.
- [120] K. Richard, P. Manson, P. Ewart, *Meas. Sci. Technol.* **2008**, *19*, 015603.
- [121] H. Tran, B. Lavorel, O. Faucher, R. Saint-Loup, P. Joubert, *J. Raman Spectrosc.* **2002**, *33*, 872.
- [122] H. Tran, B. Lavorel, O. Faucher, R. Saint-Loup, P. Joubert, *J. Raman Spectrosc.* **2003**, *34*, 994.
- [123] T. Vieillard, F. Chaussard, D. Sugny, B. Lavorel, O. Faucher, *J. Raman Spectrosc.* **2008**, *39*, 694.
- [124] F. Chaussard, T. Vieillard, F. Billard, O. Faucher, J. M. Hartmann, C. Boulet, B. Lavorel, *J. Raman Spectrosc.* **2015**, *46*, 691.
- [125] B. Hemmerling, M. Neracher, D. N. Kozlov, W. Kwan, R. Stark, D. Klimenko, W. Clauss, M. Oschwald, *J. Raman Spectrosc.* **2002**, *33*, 912.
- [126] D. N. Kozlov, P. P. Radi, *J. Raman Spectrosc.* **2008**, *39*, 730.
- [127] J. Kiefer, D. N. Kozlov, T. Seeger, A. Leipertz, *J. Raman Spectrosc.* **2008**, *39*, 711.
- [128] T. Seeger, J. Kiefer, M. C. Weikl, A. Leipertz, D. N. Kozlov, *Opt. Express* **2006**, *14*, 12994.
- [129] B. Roshani, A. Flügel, I. Schmitz, D. N. Kozlov, T. Seeger, L. Zigan, J. Kiefer, A. Leipertz, *J. Raman Spectrosc.* **2013**, *44*, 1356.

- [130] S. Benec'h, F. Rachet, M. Chrysos, J. Buldyreva, L. Bonamy, *J. Raman Spectrosc.* **2002**, *33*, 934.
- [131] F. Rachet, M. Chrysos, A. Kouzov, *J. Raman Spectrosc.* **2003**, *34*, 965.
- [132] F. Rachet, M. Chrysos, G. Lothon, R. Moszynski, A. Milet, *J. Raman Spectrosc.* **2003**, *34*, 972.
- [133] S. Dixneuf, M. Chrysos, F. Rachet, *J. Raman Spectrosc.* **2005**, *36*, 139.
- [134] M. Chrysos, S. Dixneuf, *J. Raman Spectrosc.* **2005**, *36*, 158.
- [135] S. Schlüter, F. Kruschke, N. Popovska-Leipertz, T. Seeger, G. Breuer, C. Jeleazcov, J. Schüttler, A. Leipertz, *J. Raman Spectrosc.* **2015**, *46*, 708.
- [136] A. F. Bunkin, A. A. Nurmatov, S. M. Pershin, A. A. Vigin, *J. Raman Spectrosc.* **2005**, *36*, 145.
- [137] A. F. Bunkin, S. M. Pershin, *J. Raman Spectrosc.* **2008**, *39*, 726.
- [138] A. F. Bunkin, S. M. Pershin, A. A. Nurmatov, A. P. Gorchakov, *J. Raman Spectrosc.* **2007**, *38*, 973.
- [139] A. F. Bunkin, A. U. Chikishev, A. P. Gorchakov, A. A. Nurmatov, S. M. Pershin, *J. Raman Spectrosc.* **2006**, *37*, 689.
- [140] A. F. Bunkin, A. P. Gorchakov, A. A. Nurmatov, S. M. Pershin, *J. Raman Spectrosc.* **2006**, *37*, 693.
- [141] D. A. Akimov, A. A. Ivanov, M. V. Alfimov, E. P. Grabchak, A. A. Shtykova, A. N. Petrov, A. A. Podshivalov, A. M. Zheltikov, *J. Raman Spectrosc.* **2003**, *34*, 1007.
- [142] T. D. Slavnova, H. Goerner, A. K. Chibisov, *J. Phys. Chem. B* **2007**, *111*, 10023.
- [143] T. Siebert, R. Maksimenka, A. Materny, V. Engel, W. Kiefer, M. Schmitt, *J. Raman Spectrosc.* **2002**, *33*, 844.
- [144] J. Konradi, A. K. Singh, A. Scaria, A. Materny, *J. Raman Spectrosc.* **2006**, *37*, 697.
- [145] Y. Sakai, J. Watanabe, S. Kinoshita, *J. Raman Spectrosc.* **2013**, *44*, 1369.
- [146] F. Munhoz, S. Brustlein, D. Gachet, F. Billard, S. Brasselet, H. Rigneault, *J. Raman Spectrosc.* **2009**, *40*, 775.
- [147] J. Kiefer, M. Namboodiri, M. M. Kazemi, A. Materny, *J. Raman Spectrosc.* **2015**, *46*, 722.
- [148] M. Namboodiri, M. M. Kazemi, T. Z. Khan, A. Materny, J. Kiefer, *J. Amer. Chem. Soc.* **2014**, *136*, 6136.
- [149] V. Rodriguez, *J. Raman Spectrosc.* **2012**, *43*, 627.
- [150] H. Diez-y-Riega, D. Camejo, C. E. Manzanares, *J. Raman Spectrosc.* **2015**, *46*, 716.
- [151] V. G. Arakcheev, V. N. Bagratashvili, A. A. Valeev, V. M. Gordiyenko, V. V. Kireev, V. B. Morozov, A. N. Olenin, V. K. Popov, V. G. Tunkin, D. V. Yakovlev, *J. Raman Spectrosc.* **2003**, *34*, 952.
- [152] V. G. Arakcheev, V. N. Bagratashvili, S. A. Dubyanskiy, V. B. Morozov, A. N. Olenin, V. K. Popov, V. G. Tunkin, A. A. Valeev, D. V. Yakovlev, *J. Raman Spectrosc.* **2008**, *39*, 750.
- [153] V. G. Arakcheev, V. B. Morozov, *J. Raman Spectrosc.* **2013**, *44*, 1363.
- [154] V. G. Arakcheev, V. B. Morozov, *J. Raman Spectrosc.* **2014**, *45*, 501.
- [155] S. O. Konorov, A. B. Fedotov, I. E. Smirnova, V. P. Mitrokhin, K. Sakoda, D. A. Sidorov-Biryukov, A. M. Zheltikov, *J. Raman Spectrosc.* **2006**, *37*, 663.
- [156] S. O. Konorov, V. P. Mitrokhin, I. V. Smirnova, D. A. Sidorov-Biryukov, A. B. Fedotov, A. M. Zheltikov, *J. Raman Spectrosc.* **2005**, *36*, 171.
- [157] A. M. Zheltikov, *J. Raman Spectrosc.* **2005**, *36*, 176.
- [158] R. Saito, M. Hofmann, G. Dresselhaus, A. Jorio, M. S. Dresselhaus, *Adv. Physiol. Educ.* **2011**, *60*, 413.
- [159] Y. Z. Ma, T. Hertel, Z. V. Vardeny, G. R. Fleming, L. Valkunas, *Carbon Nanotubes*, vol. **111**, **2008** p, 321.
- [160] A. Hartschuh, H. N. Pedrosa, J. Peterson, L. Huang, P. Anger, H. Qian, A. J. Meixner, M. Steiner, L. Novotny, T. D. Krauss, *Chem. Phys. Chem.* **2005**, *6*, 577.
- [161] S. Falke, P. Eravuchira, A. Materny, C. Lienau, *J. Raman Spectrosc.* **2011**, *42*, 1897.
- [162] S. Botti, R. Ciardi, L. De Dominicis, R. Fantoni, L. S. Asilyan, A. Fiori, R. Appolloni, *J. Raman Spectrosc.* **2003**, *34*, 1025.
- [163] L. De Dominicis, R. Fantoni, S. Botti, R. Ciardi, L. S. Asilyan, A. Fiori, S. Orlanducci, *J. Raman Spectrosc.* **2005**, *36*, 165.
- [164] L. De Dominicis, R. Fantoni, *J. Raman Spectrosc.* **2006**, *37*, 669.
- [165] L. De Dominicis, R. Fantoni, *J. Raman Spectrosc.* **2009**, *40*, 840.
- [166] S. O. Konorov, D. A. Akimov, A. A. Ivanov, M. V. Alfimov, S. Botti, R. Ciardi, L. De Dominicis, L. S. Asilyan, A. A. Podshivalov, D. A. Sidorov-Biryukov, R. Fantoni, A. M. Zheltikov, *J. Raman Spectrosc.* **2003**, *34*, 1018.
- [167] A. F. Bunkin, S. M. Pershin, *J. Raman Spectrosc.* **2009**, *40*, 836.
- [168] A. F. Bunkin, S. M. Pershin, *J. Raman Spectrosc.* **2011**, *42*, 1908.
- [169] R. Singh, H. S. Nalwa, *J. Biomed. Nanotechnol.* **2011**, *7*, 489.
- [170] L. Treccani, T. Y. Klein, F. Meder, K. Pardun, K. Rezwan, *Acta Biomater.* **2013**, *9*, 7115.
- [171] Y. Q. Dai, W. Y. Liu, E. Formo, Y. M. Sun, Y. N. Xia, *Polym. Adv. Technol.* **2011**, *22*, 326.
- [172] S. O. Konorov, D. A. Akimov, A. A. Ivanov, M. V. Alfimov, S. V. Zaboltnov, D. A. Sidorov-Biryukov, A. B. Fedotov, A. A. Podshivalov, L. Fornarini, M. Carpanese, M. Avella, M. E. Errico, R. Fantoni, A. M. Zheltikov, *J. Raman Spectrosc.* **2003**, *34*, 999.
- [173] F. Rondino, R. D'Amato, G. Terranova, E. Borsella, M. Falconieri, *J. Raman Spectrosc.* **2014**, *45*, 528.
- [174] H. Baida, D. Christofilos, P. Maioli, A. Crut, N. Del Fatti, F. Vallee, *J. Raman Spectrosc.* **2011**, *42*, 1891.
- [175] S. Botti, L. Cantarini, A. Palucci, *J. Raman Spectrosc.* **2010**, *41*, 866.
- [176] A. F. Bunkin, S. M. Pershin, A. A. Nurmatov, V. Luk'yanchenko, *J. Raman Spectrosc.* **2007**, *38*, 978.
- [177] S. O. Konorov, D. A. Sidorov-Biryukov, I. Bugar, D. Chorvat, D. Chorvat, A. M. Zheltikov, *J. Raman Spectrosc.* **2003**, *34*, 1013.
- [178] S. N. Orlov, Y. N. Polivanov, *J. Raman Spectrosc.* **2002**, *33*, 948.
- [179] G. K. Kitaeva, V. V. Tishkova, A. N. Penin, *J. Raman Spectrosc.* **2005**, *36*, 116.
- [180] G. K. Kitaeva, K. A. Kuznetsov, A. N. Penin, S. V. Solosin, *J. Raman Spectrosc.* **2002**, *33*, 941.
- [181] G. K. Kitaeva, K. A. Kuznetsov, A. V. Shevlyuga, A. N. Penin, *J. Raman Spectrosc.* **2007**, *38*, 994.
- [182] P. Russell, *Science* **2003**, *299*, 358.
- [183] J. C. Knight, *Nature* **2003**, *424*, 847.
- [184] A. M. Zheltikov, *J. Raman Spectrosc.* **2007**, *38*, 1052.
- [185] Y. M. Linik, A. A. Ivanov, D. A. Akimov, M. V. Alfimov, T. Siebert, W. Kiefer, A. M. Zheltikov, *J. Raman Spectrosc.* **2006**, *37*, 705.
- [186] A. B. Fedotov, P. Zhou, A. P. Tarasevitch, K. V. Dukel'skii, Y. N. Kondrat'ev, V. S. Shevandin, V. B. Smirnov, D. Von der Linde, A. M. Zheltikov, *J. Raman Spectrosc.* **2002**, *33*, 888.
- [187] S. O. Konorov, A. B. Fedotov, E. E. Serebryannikov, V. P. Mitrokhin, D. A. Sidorov-Biryukov, A. M. Zheltikov, *J. Raman Spectrosc.* **2005**, *36*, 129.
- [188] S. O. Konorov, D. A. Akimov, A. N. Naumov, A. B. Fedotov, R. B. Miles, J. W. Haus, A. M. Zheltikov, *J. Raman Spectrosc.* **2002**, *33*, 955.
- [189] M. D. Duncan, J. Reintjes, T. J. Manuccia, *Opt. Lett.* **1982**, *7*, 350.
- [190] A. Zumbusch, G. R. Holtom, X. S. Xie, *Phys. Rev. Lett.* **1999**, *82*, 4142.
- [191] E. Ploetz, S. Laimgruber, S. Berner, W. Zinth, P. Gilch, *Appl. Phys. B* **2007**, *87*, 389.
- [192] C. W. Freudiger, W. Min, B. G. Saar, S. Lu, G. R. Holtom, C. He, J. C. Tsai, J. X. Kang, X. S. Xie, *Science* **2008**, *322*, 1857.
- [193] P. Nandakumar, A. Kovalev, A. Volkmer, *New J. Phys.* **2009**, *11*, 033026.
- [194] Y. Ozeki, F. Duke, S. Kajiyama, K. Fukui, K. Itoh, *Opt. Express* **2009**, *17*, 3651.
- [195] M. Marrocco, *J. Raman Spectrosc.* **2010**, *41*, 882.
- [196] E. Ploetz, B. Marx, P. Gilch, *J. Raman Spectrosc.* **2011**, *42*, 1875.
- [197] W. P. Beeker, C. J. Lee, K. J. Boller, P. Gross, C. Cleff, C. Fallnich, H. L. Offerhaus, J. L. Herek, *J. Raman Spectrosc.* **2011**, *42*, 1854.
- [198] A. C. W. van Rhijn, M. Jurna, A. Jafarpour, J. L. Herek, H. L. Offerhaus, *J. Raman Spectrosc.* **2011**, *42*, 1859.
- [199] C. Müller, T. Backup, B. von Vacano, M. Motzkus, *J. Raman Spectrosc.* **2009**, *40*, 809.
- [200] W. Langbein, I. Rocha-Mendoza, P. Borri, *J. Raman Spectrosc.* **2009**, *40*, 800.
- [201] C. Heinrich, C. Meusberger, S. Bernet, M. Ritsch-Marte, *J. Raman Spectrosc.* **2006**, *37*, 675.
- [202] A. Silve, N. Dorval, T. Schmid, L. M. Mir, B. Attal-Trétout, *J. Raman Spectrosc.* **2012**, *43*, 644.
- [203] K. Furusawa, N. Hayazawa, S. Kawata, *J. Raman Spectrosc.* **2010**, *41*, 840.
- [204] E. T. Garbacik, J. L. Herek, C. Otto, H. L. Offerhaus, *J. Raman Spectrosc.* **2012**, *43*, 651.
- [205] F. Masia, A. Karuna, P. Borri, W. Langbein, *J. Raman Spectrosc.* **2015**, *46*, 727.
- [206] J. H. Peng, D. Pestov, M. O. Scully, A. V. Sokolov, *J. Raman Spectrosc.* **2009**, *40*, 795.
- [207] E. Molotokaite, V. Kumar, C. Manzoni, D. Polli, G. Cerullo, M. Marangoni, *J. Raman Spectrosc.* **2013**, *44*, 1385.
- [208] M. Marrocco, E. Nichelatti, *J. Raman Spectrosc.* **2009**, *40*, 732.
- [209] A. Downes, R. Mouras, A. Elfick, *J. Raman Spectrosc.* **2009**, *40*, 757.
- [210] V. V. Yakovlev, *J. Raman Spectrosc.* **2003**, *34*, 957.
- [211] P. Leproux, V. Couderc, A. de Angelis, M. Okuno, H. Kano, H. Hamaguchi, *J. Raman Spectrosc.* **2011**, *42*, 1871.
- [212] V. Kumar, M. Casella, E. Molotokaite, D. Polli, G. Cerullo, M. Marangoni, *J. Raman Spectrosc.* **2012**, *43*, 662.
- [213] S. Saint-Jalm, P. Berto, L. Jullien, E. R. Andresen, H. Rigneault, *J. Raman Spectrosc.* **2014**, *45*, 515.
- [214] B. Marx, L. Czerwinski, R. Light, M. Somekh, P. Gilch, *J. Raman Spectrosc.* **2014**, *45*, 521.
- [215] M. Bonn, M. Müller, H. A. Rinia, K. N. J. Burger, *J. Raman Spectrosc.* **2009**, *40*, 763.
- [216] C. Brackmann, J. Norbeck, M. Akeson, D. Bosch, C. Larsson, L. Gustafsson, A. Enejder, *J. Raman Spectrosc.* **2009**, *40*, 748.

- [217] J. Moger, N. L. Garrett, D. Begley, L. Mihoreanu, A. Lalatsa, M. V. Lozano, M. Mazza, A. Schatzlein, I. Uchegbu, *J. Raman Spectrosc.* **2012**, *43*, 668.
- [218] L. Mortati, C. Divieto, M. P. Sassi, *J. Raman Spectrosc.* **2012**, *43*, 675.
- [219] A. Downes, R. Mouras, P. Bagnaninchi, A. Elfick, *J. Raman Spectrosc.* **2011**, *42*, 1864.
- [220] R. Mouras, G. Rischitor, A. Downes, D. Salter, A. Elfick, *J. Raman Spectrosc.* **2010**, *41*, 848.
- [221] N. L. Garrett, A. Lalatsa, D. Begley, L. Mihoreanu, I. Uchegbu, A. G. Schotzlein, J. Moger, *J. Raman Spectrosc.* **2012**, *43*, 681.
- [222] A. G. Caster, S. Kowarik, A. M. Schwartzberg, O. Nicolet, S. H. Lim, S. R. Leone, *J. Raman Spectrosc.* **2009**, *40*, 770.
- [223] K. Furusawa, N. Hayazawa, F. C. Catalan, T. Okamoto, S. Kawata, *J. Raman Spectrosc.* **2012**, *43*, 656.
- [224] D. N. Baratashov, A. Masic, A. M. Yashchenko, M. F. Bedard, O. A. Inozemtseva, D. A. Gorin, T. Basova, T. K. Sievers, G. B. Sukhorukov, M. Winterhalter, H. Möhwald, A. G. Skirtach, *J. Raman Spectrosc.* **2011**, *42*, 1901.
- [225] A. L. Fussell, F. Grasmeijer, H. W. Frijlink, A. H. de Boer, H. L. Offerhaus, *J. Raman Spectrosc.* **2014**, *45*, 495.