Impulsive temporally two-dimensional Raman scattering
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Chapter 6
Analysis of nonlinear optical contributions to temporally two-dimensional Raman scattering

6.1 Introduction

As we saw in the last chapter nonresonant third-order experiments yield the total spectral density associated with the low-frequency intermolecular motions in liquids. They do not provide direct information about the time scales of the underlying microscopic processes. In particular, it is not possible to separate homogeneous and inhomogeneous contributions to the overall line width. Moreover, the coupling mechanisms between different modes as well as the microscopic origin of the optical response cannot be identified. Therefore, it has been proposed by Tanimura and Mukamel [1] to use the fifth-order nonlinear optical response to probe these details of the nuclear dynamics. Their key article on this subject was followed by a number of theoretical [2,3] and experimental [4-11] papers.

The principle of the temporally two-dimensional (2D) fifth-order Raman experiment is shown in Fig. 6.1. together with the two beam configurations (I) and (II), which were used by us experimentally [7,9] and will be discussed in detail below. Two excitation pulse pairs, separated by a variable delay $T_1$, are followed by a probe pulse after an independently variable delay $T_2$. In a transient grating scattering (TGS) experiment, the two pulse pairs scatter the probe in the directions $k_i = k_p + k_1 - k_f$ and $k_i = k_p + k_2 - k_f$, designated by the + signs in Fig. 6.1.(I) and (II). These signals provide information on the one-time correlation function of the polarizability, analogous to the OHD-OKE response discussed in the previous chapter. In contrast to the latter experiment, the TGS signal is measured background-free, i.e., the response is given by the square of the polarization. The delay dependence of the corresponding third-order response was discussed in the previous chapter. Additional third-order signals are observed when the probe pulse overlaps in time with the first or second pulse pair, or by the interaction between the pulses
of the two pairs. The 2D fifth-order response, which contains the desired information on the two-time correlation function of the polarizability, is observed in the direction $k_5 = k_1 - k_2 + k_3 + k_{pr}$.

The phase matching configuration is chosen such that the fifth-order signal is emitted in a unique direction, to allow for spatial filtering. Still, the main problem in this degenerate experiment is to separate the weak fifth-order signal from other contributions. One obvious test is the requirement that the observed signal depends on all five pulses. As will be shown in detail below, there are several processes such as interfering [12] or sequential [5,8,9,11,13,14] third-order response, scattering due to hyperpolarizabilities [7,8,9,11], and higher-order Bragg diffraction [15,16], that involve all five pulses and that may, in general, contribute to the observed

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Fig. 6.1: Principle of a 2D fifth-order Raman scattering experiment, where the two delays $T_1$ and $T_2$ are varied. The polarizations of the pulse pairs (1', 1'') and (2', 2''), the probe (pr) and the fifth-order signal (5) are indicated by H (horizontal) and V (vertical). The configurations (I) and (II) are shown for the incoming pulses and the signals as they leave the sample. In configuration (I) the five incoming beams follow different paths whereas pulses 1' and 2', and pulses 1'' and 2'', respectively, follow the same path in configuration (II). The 2D Raman signal is symbolized by $\square$. Some of the third-order signals are also shown: the transient grating signals induced by one of the pulse pairs and the probe are found in the directions $k_3$, indicated by $\circ$. The intermediate third-order signals that are involved in the sequential processes discussed in the text, are depicted by $\blacklozenge$. The position of the second-order Bragg diffraction is represented by $\bullet$. The position of the second-order Bragg diffraction is represented by $\bullet$. 

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signals. Since they do not carry the desired information, they are often considered as artefacts. To avoid any misinterpretations the origin of the measured response will be characterized carefully; a detailed discussion of the fifth-order dynamics will be given in the next chapter.

This chapter is organized as follows: The temporally two-dimensional fifth-order signal of neat CS$_2$, a typical example for the traces obtained by this technique is presented in Sec. 6.2. In Secs. 6.3 and 6.4, these results are used to investigate whether possible third- and fifth-order artefacts occur in our experiments. Although artefacts do occur, especially when one of the two delay times is zero, the desired 2D fifth-order effect provides the largest contribution to the fifth-order nonlinear optical response of this liquid. In one of the two beam configurations discussed in detail the signal is intrinsically heterodyned by another fifth-order process. This method provides a higher sensitivity but the observed response is partly determined by the temporal shape of the local oscillator as will be demonstrated in Sec. 6.4. Some concluding remarks are presented in Sec. 6.5.

6.2 Time-domain 2D Raman scattering signal of neat CS$_2$

The 2D fifth-order Raman signal of neat CS$_2$ along the two time axes is shown in Figs. 6.2 and 6.3. It was measured using beam configuration (I) of Fig. 6.1. In Fig. 6.2 the $T_2$-dependence for $T_1 = 0$ fs, i.e., when both pulse pairs arrive at the same time, is compared to the third-order TGS signal. In contrast to the TGS signal the fifth-order signal possesses hardly any instantaneous component. It exhibits a finite rise time of approximately 180 fs that is slightly shorter than that of the TGS signal. The tail of the fifth-order signal is much weaker and it decays much faster than the TGS one. The decay constants of approximately 100 and 800 fs, respectively, differ by almost one order of magnitude.

In Fig. 6.3 the $T_1$ dependence is shown for $T_2 = 170$ fs. This signal is measured by varying

![Fig. 6.2: The $T_2$-dependence of the 2D fifth-order Raman response for $T_1 = 0$ fs (solid line) and third-order TGS signal (dots) of CS$_2$. Consult text for details.](image)
the delay of the first pulse pair compared to the second pulse pair and the probe. Note that for 
\(-T_2 < T_1 < 0\) (i.e., \(T_1\) between 0 and \(-170\) fs in Fig. 6.3), both \(T_1\) and \(T_2\) change, since pulse pair 1 then arrives after pulse pair 2, and their roles are inverted [8]. From Fig. 6.3 it is clear that the signal trace along \(T_1\) consists of three parts: (i) a very large pulsewidth-limited peak at zero delay, (ii) a fast nonexponential decay at delays smaller than 1 ps, and (iii) an exponential tail with a decay time of 800 fs at longer delays. This shape qualitatively resembles the third-order transients, as measured by transient grating scattering [17,18] or optical Kerr effect measurements [19,20]. However, here the maximum of the signal occurs at (or very near) \(T_1 = 0\), while in third-order experiments the maximum is reached at a delay of 200 fs due to the inertial character of the nuclear response. For a detailed discussion of the third-order response consult chapter 5.

![Graph showing the delay dependence of the 2D fifth-order Raman response for \(T_1=170\) fs (solid line) and third-order TGS signal (dots) of \(\text{CS}_2\). At short times both signals shown in the inset on a linear scale, are dominated by a strong nonexponentially decaying contribution. On a ps time scale the signals decay exponentially with the same time constant of about 800 fs. The traces have been scaled to have the same amplitude in the tail.](image)

Fig. 6.3: The \(T_1\)-dependence of the 2D fifth-order Raman response for \(T_1=170\) fs (solid line) and third-order TGS signal (dots) of \(\text{CS}_2\). At short times both signals shown in the inset on a linear scale, are dominated by a strong nonexponentially decaying contribution. On a ps time scale the signals decay exponentially with the same time constant of about 800 fs. The traces have been scaled to have the same amplitude in the tail.
6.3 Third-order artefacts

Artefacts in fifth-order nonlinear optical experiments arise through unaccounted contributions, which may partly be due to third-order effects. The amplitudes of all signals add up at the detector, leading to cross terms, which depend on all five pulses and both delay times. An example of this effect is shown in Fig. 6.4. The signals were measured in the direction designated by the + sign using configuration (II). The interaction of the probe pulse with both pulse pairs separately generates two spatially overlapping third-order signals, which have a fixed phase relation, since the pulse pairs were generated interferometrically. For details we refer the reader to chapter 4. When both pulse pairs are modulated with different frequencies and the signal is processed at the sum or difference frequency, only the cross term of the two interfering third-order amplitudes is recorded. Hence, the signals depicted in Fig. 6.4 depend on all five pulses and both delay times. However, they contain only one-dimensional dynamic information, and have nothing to do with the fifth-order 2D Raman effect.

Stray light from such third-order sources may affect the observed fifth-order signals. For the particular polarization conditions investigated here (see Sec. 4.4 and Fig. 6.1) the polarization of the interfering third-order signals is orthogonal to that of the 2D Raman response, so it is easily recognized. However, when the probe pulse overlaps with either the first or the second pulse pair, many more third-order grating scattering signals are emitted. Some of them are shown in Fig. 6.1. Pulse-width limited transients at \( T_1 = 0 \) or \( T_2 = 0 \) should therefore be considered suspect, and be checked on the properties expected for fifth-order signals. True 2D Raman signals should (i) depend on all five pulses; (ii) obey a fifth-power laser intensity dependence; (iii) be emitted in the correct phase-matched direction; (iv) have the correct vertical polarization state. Although these requirements seem very selective, third-order transients can still cause artefacts to occur.

The observed power dependence, signal direction and polarization are also found when the signal is due to a sequence of two independent third-order processes. In our case, the most important of these processes, shown schematically in Fig. 6.5, involves the diffraction of pulses \( k_z \) and \( k_x \) by the grating induced by the first pulse pair. These intermediate signals are emitted in the directions \( k_{i'} = k_z + (k_{i''} - k_z) \) and \( k_{i} = k_z + (k_{i''} - k_z) \), respectively. When the intensity of these signals is high enough, a second third-order process will occur, in which the intermediate signals form a grating with pulses \( k_y \) and \( k_z \). The probe is then scattered in the directions \( k_{seq} = k_{pr} + (k_{seq} - k_z) \) and \( k_{seq} = k_{pr} + (k_{seq} - k_z) \). This leads to the same overall phase matching condition as for the fifth-order signal, so irrespective of the beam geometry, \( k_{seq} = k_z \) always holds.

The only way to suppress these sequential effects is to choose the beam geometry such that the phase matching condition for one or both of the two sequential third-order processes is not fulfilled. For the configurations (I) and (II) of Figs. 6.1 the mismatch \( |\Delta k| \) for the generation of the intermediate fields is about 38 rad mm\(^{-1}\), which leads to mismatch factors \( |\Delta k|/\pi = 12 \) and 24 for the experimental sample thicknesses of 1 = 1 and 2 mm. So, the phase-match condition \( |\Delta k|/\pi < 1 \) is clearly violated; the intensity of the third-order signals \( k_x \) and \( k_z \) is expected to be weaker by at least two orders of magnitude. Since a similar factor holds for the second third-order process, the intensity of the sequential signal is reduced considerably.

Whether this phase mismatch is sufficient to suppress the sequential process compared to
the 2D fifth-order Raman scattering effect, cannot be easily predicted, since the absolute magnitudes of the third- and fifth-order susceptibilities are not known. However, this can be determined from the shape of the signals of Figs. 6.2 and 6.3. A sequence of two third-order processes follows along both time coordinates the third-order transient grating scattering signal, similar to the interference effect shown in Fig. 6.4. As discussed in Sec. 6.2, this is in particular not the case for the $T_5$-dependent signal of Fig. 6.2, that lacks any diffusive tail. Therefore we can conclude that sequential processes contribute negligibly for our experimental arrangements, in which rather large angles between the beams and a reasonably thick sample were used, cf. chapter 4.

Another way to investigate the relative importance of this cascaded fifth-order process was proposed by Tokmakoff and Fleming [8]. They compared the intensity of the intermediate signals in the directions $k_z$ and $k_0$ with that of the fifth-order signal in the direction $k_x$. Since the latter was much larger than the intermediate signals, they could exclude sequential processes in their signal analysis.

A third method to investigate the role of these processes was proposed already in the early seventies by Lukasik and Ducuing [13]. They pointed out that a true fifth-order process depends on the square of the concentration of solute molecules while for a sequence of two third-order processes, that each scale quadratically, a fourth-order power law is expected. This argument has later also been invoked by Ivanecky and Wright [14] in their investigation of intramolecular vibrations in toluene, and by Tominaga and Yoshihara [5] who studied the low-frequency intermolecular modes of CS$_2$ in various cosolvents. It should be noted, however, that the low-frequency spectrum in molecular liquids may be partly caused by many-body effects as was discussed in Sec. 5.5. These collision- and interaction-induced effects exhibit a different concentration dependence [21] which may complicate a quantitative analysis.
When the probe pulse overlaps in time with the first pulse pair, indeed a sequential third-order effect occurs, which gives rise to a small signal in the $T_2$ dependent scan at $T_2 = -T_1$. In the first third-order process, pulse 1" and the probe form a grating, that causes self diffraction in the direction $k_i = 2k_1 - k_{pr}$. Due to the small angle between these two pulses, this is a rather efficient process. A second grating, formed by this intermediate signal and pulse 1', then scatters pulse 2" after a delay $T_1$ in the direction of the fifth-order signal. As can be seen in the traces of Fig. 6.6, this is a rather small effect that is easily recognized, because the signal occurs only for this specific delay time, where there is no fifth-order signal present.

### 6.4 Fifth-order artefacts

Now that third-order effects were shown to have small influence, it remains to determine whether the signals of Figs. 6.2, 6.3 and 6.6 are completely due to the 2D Raman process depicted in Fig. 6.1. When the full nonresonant fifth-order response is worked out, additional terms with the same phase matching condition are found, that result from electronic hyperpolarizabilities [3]. This is analogous to the situation in third-order response, where next to the delayed nuclear response a pulse-width limited transient at zero delay is found due to the first electronic hyperpolarizability. In the fifth-order response three additional processes occur, which were discussed in chapters 2 and 3. They are shown in an energy level diagram in Fig. 6.7. The importance of these processes, compared to the 2D Raman effect, is determined by the values of the (hyper)polarizabilities, which depend on the employed optical frequencies and the polarization conditions of the incoming beams [16]. Since the frequency dependence of these
Fig. 6.6: 2D Raman signal of CS$_2$ along $T_2$ for $T_1=0, 100, 200, 300, 400, 500$ and 1000 fs (bottom to top). At $T_2=-T_1$ there is a small pulsewidth-limited peak due to a sequence of two third-order processes. A detailed discussion of the fifth-order signal will be given in chapter 7.

hyperpolarizabilities is not exactly known, we will use the experimental fifth-order results to estimate the relative contributions of these effects.

Process (a) of Fig. 6.7 is of purely electronic origin and therefore instantaneous when nonresonant optical fields are used. It is expected to show up as a pulsewidth-limited feature at zero delay in a $T_2$-scan for a fixed delay $T_1=0$. Since there is hardly any such feature present in Fig. 6.2, it can be concluded that process (a) is not very efficient at this laser wavelength and in this sample.

Process (b) starts with an instantaneous four-photon interaction, which excites a nuclear coherence via the coordinate dependent electronic hyperpolarizability (hyper Raman scattering). Note that a similar process generates an instantaneous signal component at zero delay in the third-order response (cf. Fig. 2.2). Then, however, the coordinate independent electronic hyperpolarizability (hyper Rayleigh scattering) determines the instantaneous signal. In the fifth-order process, the signal is generated by a normal Raman interaction after a single nuclear propagation time $T_2$. Therefore, the response is related to the one-time correlation function of the first hyperpolarizability and the linear polarizability.

In configuration (I) process (b) can contribute only when both pulse pairs overlap. It therefore provides an excellent explanation for the pulsewidth-limited peak at zero delay in the $T_1$-scan shown in Fig. 6.3. Within this interpretation the 2D Raman effect and process (b) both also should contribute to the $T_2$-dependent signal at $T_1=0$ (see Fig. 6.2). Since that trace shows only a sub-ps response, we can conclude that the one-time correlation function of the first hyperpolarizability and the linear polarizability is not sensitive to diffusive decay. In configuration
Fig. 6.7: Next to the 2D-Raman effect depicted in Fig. 6.1 electronic hyperpolarizabilities in principle also contribute to the fifth-order response. Process (a) is due to subsequent excitation and deexcitation of two virtual states, indicated by the dashed lines. For large detuning from electronic resonances, this process is instantaneous. In process (b) a nuclear coherence is excited by the coordinate dependent part of the electronic hyperpolarizability. The nuclear coherence is monitored after a single propagation time by normal Raman scattering. Process (c) is the mirror image of process (b), i.e. the normal Raman scattering is followed by an instantaneous four-photon process.

(II) process (b) contributes to the signal even when $T_2 \neq 0$, due to the interaction of each pulse pair separately with the probe pulse, since $k = k_p + (k_1 - k_1) + (k_2 - k_2) = k_p + 2(k_1 - k_1) = k_p + 2(k_2 - k_2)$. As will be discussed below, this may give rise to interference effects that modify the appearance of the two-dimensional fifth-order response.

Process (c) of Fig. 6.7 is almost the mirror image of (b). It also contains a two-photon and a four-photon interaction, and may contribute when the probe pulse coincides with the second pulse pair. However, in this case the four-photon interaction is expected to be much weaker than for process (b), due to the different polarization conditions of the participating optical fields (VVHV instead of VVHH). In principle, this process could give rise to a pulse-width limited transient at $T_2 = 0$ for configurations (I) and (II). The shoulder, which was indeed sometimes observed at $T_2 = 0$, can be attributed to imperfect polarization and could be reduced considerably by fine adjustment of the beams.

Aside from artefacts due to hyperpolarizabilities, the 2D Raman signal can be obscured by higher-order Bragg diffraction. In general, a grating with wave vector $\mathbf{q}$ scatters the probe pulse in the directions $k_p \pm n \mathbf{q}$ where $n$ is an integer denoting the diffraction order [15]. In transient grating experiments usually the $n=1$ diffraction (first-order Bragg) is measured [17,18]. In the fifth-order experiment two gratings with wave vectors $\mathbf{q}_1 = \mathbf{k}_1 - \mathbf{k}_1$, and $\mathbf{q}_2 = \mathbf{k}_2 - \mathbf{k}_2$, are induced. When the 2D Raman signal coincides with one or more higher-order ($n > 1$) diffraction signals, this may cause unwanted signal contributions.

In configuration (I) the 2D Raman signal may be mixed with the fourth-order diffraction ($n=4$) of the grating induced by the second pulse pair. Using single modulation of the probe, this
Fig. 6.8: $T_2$-dependent fifth-order signals for $T_1 = 500$ fs, measured with configuration (II) and modulation of only the probe pulse. Three fifth-order traces are shown: from only the first pulse pair (dashed), from the 1.75 times weaker second pulse pair (dotted), and from all five pulses together (solid). The enhancement around $T_2 = 700$ fs is not only due to the (five pulse) 2D-Raman signal, but also to the interference term between the 2D-signal and the signal from the second pulse pair only. Since the latter does not depend on the delay $T_1$, it acts as a local oscillator for the five-pulse signal when this delay is varied. For details, see text.

ninth-order nonlinear signal should be present even in absence of the first pulse pair. It was not found experimentally, due to the very small value of this high-order susceptibility. The first pulse pair and the probe cannot produce diffraction in the direction $k_5$.

In configuration (II) second-order diffraction ($n=2$) by either of the two gratings is emitted in the direction of the 2D Raman response. This fifth-order signal can be due to the processes of Figs. 6.6.b and/or 6.1 with $T_1 < \tau_{\text{pulse}}$. As shown in Fig. 6.8, it is indeed observed when only one of the pulse pairs and the probe are present. When all pulses are present, the signal after the second pulse pair increases substantially due to both the desired 2D Raman signal and its interference with the fifth-order signal of the pulses $k_2$, $k_2'$, and $k_5$ alone. When both pulse pairs are modulated and the signal is processed at the sum frequency, as was done in Ref. 7, the true 2D Raman signal will be processed, but also the interference term. Thus, the fifth-order signal of pulses $k_3$, $k_2'$, and $k_5$ acts as local oscillator, with a fifth-order power dependence, no dependence on the delay $T_1$ and a strong dependence on $T_2$. When the delay $T_1$ is increased, the ratio of the 2D Raman intensity and the interference term rapidly decreases until finally only the interference term is detected, which is proportional to the amplitude of the 2D Raman signal. The resulting slower decay along $T_1$ has the advantage that the measurement can be extended to larger delay times [7], but the disadvantage that its shape along $T_2$ is affected by the temporal profile of the fifth-order local oscillator. Hence, any change of shape of the 2D Raman signal along $T_2$ as a function of $T_1$ cannot be recorded very sensitively.

In a recent paper by Tokmakoff et al. [10] it was shown that the 2D fifth-order Raman signal can be intrinsically heterodyned by a third-order TGS signal. This method provides a larger sensitivity when compared to the homodyne detection of, e.g., configuration (I). However, the signal is then determined by the third-order response, which serves as a local oscillator, and by
the desired fifth-order response. The interpretation of the experimental results is then less straightforward. Therefore, in the next chapter we will discuss results obtained in configuration (I) where local oscillators play no role.

6.5 Summary

Various possible contributions to the signal in fifth-order impulsive stimulated scattering experiments have been discussed. The most important contribution arises from a temporally 2D Raman process, which is related to the two-time correlation function of the polarizability. This property contains valuable information on the microscopic dynamics of the sample. When the beam configuration is chosen adroitly, sequences of third-order processes only play a minor role. It was shown that they show up in our experiments only when the probe pulse overlaps with the first pulse pair. This does not influence the overall signal shapes, but gives rise to a small artefact at negative delay $T_2=−T_1$ where fifth-order 2D Raman signals are absent.

Depending on the beam geometry, the 2D five-pulse Raman signals are mixed with fifth-order contributions that depend on the interaction of a single pulse pair with the probe. This leads to heterodyned detection that may improve the accuracy of the $T_1$-dependent experiment. However, it distorts the shape of the signal along the $T_2$-coordinate, since the local oscillator sets a time window for the heterodyne detection. The phase matching condition can be chosen such that the two fifth-order signals are emitted in different directions, so that this interference effect does not occur.

Processes involving electronic hyperpolarizabilities may be important in fifth-order Raman experiments. In particular, when one of the delay times is zero they can lead to additional signal contributions. These processes can be partly suppressed by choosing appropriate polarization conditions of the optical pulses. In our case, a pulselength-limited peak at zero delay in the $T_1$-scan can be explained by four-photon scattering, followed by a Raman interaction after a delay $T_2$.
References