Close collisions in the two-dimensional Raman response of liquid carbon disulfide

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The fifth-order 2D Raman response of a liquid is calculated taking all possible interaction induced effects into account. Next to dipole-induced dipole interactions, close collision effects due to induced multipoles and electron overlap are found to give a significant contribution to the response of liquid carbon disulfide. A correct prediction of the spectrum is impossible, when these effects are not properly taken into account. The calculated response is found to be in good agreement with some of the most recent experiments.

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I. INTRODUCTION

In the liquid phase, where the molecules constantly touch each other, the low frequency dynamics is dominated by complex many-body interactions. These dynamics have been studied experimentally through, for example, time resolved third-order Raman response.[1,2] Various theoretical models[3–5] have been used in the interpretation of these signals that can roughly be split in two parts. The subpicosecond response is mainly due to interaction-induced effects while a slowly decaying response is caused by the diffusive realignment of the molecules. The interaction-induced effects have traditionally been taken into account through the dipole-induced dipole model.[2,3] In an earlier study[6] we showed that this model is insufficient and that induced multipoles play an important role in the generation of the Raman signal. Furthermore, overlapping electron clouds were also found to give a small contribution to the third-order Raman response.

Unfortunately the dynamic information revealed by the third-order response is limited and it is not possible to distinguish between different relaxation mechanisms. Therefore Tanimura and Mukamel[7] suggested using 2D fifth-order Raman as a means to obtain more detailed information on the relaxation. It was soon realized that the fifth-order technique also makes the observation of mode coupling possible as in 2D NMR.[8–10] In addition, the fifth-order response can be expected to be highly affected by interaction induced effects. Calculations have shown that both dipole-induced dipoles[11] and induced multipoles[12] strongly contribute to the fifth-order response.

Experimentally the fifth-order response has been a big challenge to measure. In these temporally 2D experiments five optical pulses are employed. Two pulse pairs separated by a first variable delay t_1 excite the sample and after a second time delay t_2 a fifth- pulse generates the polarization that is emitted as a signal. In 1999 it was shown that all experiments performed till then were contaminated by third-order cascaded response.[13] This experimental observation was later supported by our theoretical estimations of the intensity ratios.[11,14] Since then, Tokmakoff and co-workers claimed to have measured the $\chi^{(5)}_{zyzzyz}$ polarization component of the response using an heterodyne detection technique.[15] Recently Kubarych *et al.*[16] employed a multi-color technique that effectively suppresses the cascaded response. Also Kaufman *et al.*[17] have recently claimed to have measured the true fifth-order response.

Theoretically the fifth-order response was calculated with various methods. First the response was modelled using Brownian oscillator models,[18,8,19,20] but their use is limited to fitting experimental data and investigating phenomenological effects. Later the instantaneous normal mode (INM) approach[12,21,22] was used, but this method has problems describing the long time behavior of the response. This was evident for example in calculations on liquid xenon,[22–24] where the INM response was compared to fifth-order response calculated with the very time consuming full molecular dynamics time correlation function method. The complexity of this full MD time correlation function method limited the calculations to include only 32 atoms.[24,25]

The finite field method, developed by us[11,14] uses the full molecular dynamics data too, but this nonequilibrium method simulates the experiment directly and gives a much more efficient way to calculate the fifth-order response than the correlation function method.

Various mode coupling models have also been used to calculate the fifth-order response.[26,27] These methods all rely on approximations of the motion in the liquid and their value still has to be proven.

In the Sec. II a description of an improved version of the finite field method, effectively eliminating higher order response contributions, will be given. Models for the first-order susceptibility that includes interaction induced effects to various levels of sophistication will be briefly summarized in Sec. III. The simulated fifth-order responses will be presented and discussed in Sec. IV and finally the conclusions will be presented in Sec. V.

II. THE FINITE FIELD METHOD

The idea behind the finite field method is to simulate the optical experiment by explicitly applying the forces, originating from the interaction between the optical fields and the liquid. This is done for the two excitation pulse pairs, separated by a first variable delay t_1. The polarizability of the

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sample is then evaluated as a function of the second time delay t_2. This allows one to calculate the fifth-order response, avoiding the time consuming calculation of the 2D time-correlation functions.

In the original calculations with the finite field method[14,11] the fifth-order response was obtained from a simulation in which pulse pairs were applied at two times (0 and t_1) resulting in a susceptibility $\chi^{(1)}_{ab;cd;ef}$ containing both first, third and fifth-order contributions. Here a through f denote the polarization directions of the involved electrical fields. The first and third-order contributions were then removed using the results from simulations with one field pair applied at time 0 or t_1 ($\chi^{(1)}_{ab;cd;00}$ or $\chi^{(1)}_{ab;00;ef}$) and without any applied fields ($\chi^{(1)}_{ab;00;00}$). Furthermore, the calculated response was corrected for the strength and duration of the fields:

$$\chi^{(5)}_{abcdef}(t_1,t_2)=\frac{\chi^{(1)}_{ab;cd;ef}+\chi^{(1)}_{ab;00;00}-\chi^{(1)}_{ab;cd;00}-\chi^{(1)}_{ab;00;ef}}{E_cE_dE_eE_f(\Delta t)^2}. \tag{1}$$

Alternatively the fifth-order response can be obtained from four simulations all with fields applied at two times (0 and t_1). In these calculations the polarization direction of one of the fields is inverted resulting in an inversion of the applied force. The four calculations all contain the fifth-order response as well as third-order contributions, but with different signs in the different calculations. This allows to isolate the fifth-order response and at the same time eliminate all contributions arising from an uneven number of pulse pairs (order $4n+3,\ n\in\mathcal{N}$). Denoting the polarization direction inverse to direction d, $\bar{d}$ the fifth-order response is

$$\chi^{(5)}_{abcdef}(t_1,t_2)=\frac{\chi^{(1)}_{ab;cd;ef}+\chi^{(1)}_{ab;c\bar{d};e\bar{f}}-\chi^{(1)}_{ab;c\bar{d};ef}-\chi^{(1)}_{ab;cd;e\bar{f}}}{4E_cE_dE_eE_f(\Delta t)^2}. \tag{2}$$

This inverted force method will be applied in order to eliminate artifacts due to higher order response. It allows the use of stronger laser fields in the simulations.

III. SUSCEPTIBILITY MODELS

A hierarchy of models will be applied to approximate the first-order susceptibility, where each model includes the interaction induced effects on a different level of complexity. The molecular model (MOL) only accounts for the contributions from individual molecule polarizabilities.[14] Local dipole fields generated by induced dipoles on neighboring molecules are taken into account in the dipole-induced dipole (DID) model. This model has been applied in most theoretical studies.[3,21,25,11] Since the molecules have an extended structure, induced multipoles also influence the susceptibility. This can be accounted for by using a model with atomic polarizabilities (POL) instead of molecular ones. Previously, we showed that such a model accounts well for the polarizability in the third-order Raman response.[6] Similar models have been used in other studies of the third- and fifth-order Raman response.[5,28,12]

When molecules are touching each other, their electron clouds overlap. This also affects the polarizability which can be taken into account in an approximate way by using the direct reaction field model (DRF).[29,30] In this model a set of screening functions damp the interaction as the atoms start overlapping, assuming that the electron clouds are well described by exponentially decaying densities. A thorough description of how the first-order susceptibility can be calculated using this model can be found in our earlier paper considering the effects in the third-order Raman response.[6]

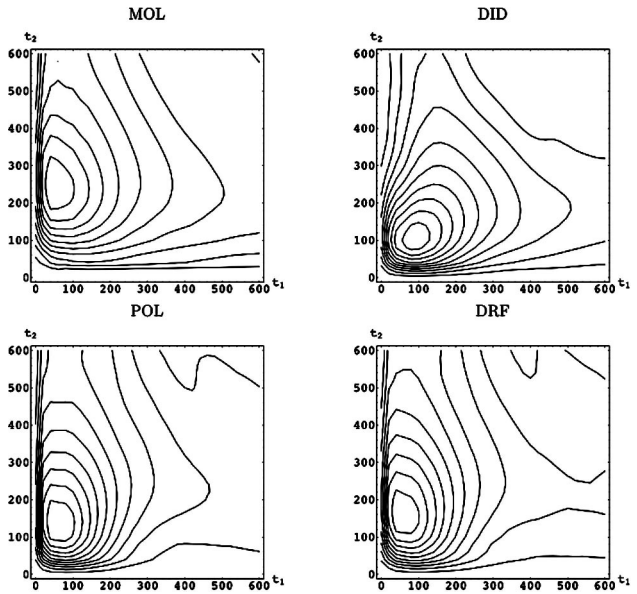

FIG. 1. The all polarized 2D Raman response $\chi^{(5)}_{zzzzzz}$ in the MOL, POL, DID, and DRF models. The time is given in fs.

Applying these four different models and comparing the results allows to examine the origin of the fifth-order response. This will contribute significantly to an interpretation of the 2D spectra.

IV. RESULTS AND DISCUSSION

The fifth-order Raman response was simulated using finite field molecular dynamics simulations based on the inverted force method [Eq. (2)]. This was done using a simulation box containing 64 carbon disulfide molecules. In earlier studies[11] employing the DID model 256 molecules were used, but no difference was observed when we limited ourselves to using 64 molecules. The carbon disulfide molecules are kept rigid and the isothermal-isobaric ensemble procedure by Berendsen *et al.*[31] is used. With the DRF model the fifth-order Raman response was calculated from 4000 different starting configurations, using a laser strength of 1.915 V/Å. The response was calculated for times t_1 and t_2 between 0 and 600 fs, with 20 fs resolution. For comparison, the MOL, DID, and POL model responses were calculated under the same conditions, but with a slightly lower laser strength of 1.724 V/Å for the MOL and DID models. In the DID calculations only 2000 starting configurations were needed. The calculated responses for the $\chi^{(5)}_{zzzzzz}$ and $\chi^{(5)}_{mmzzzz}$ polarization directions are shown in Figs. 1 and 2.

For the $\chi^{(5)}_{zzzzzz}$ component the molecular (MOL) response

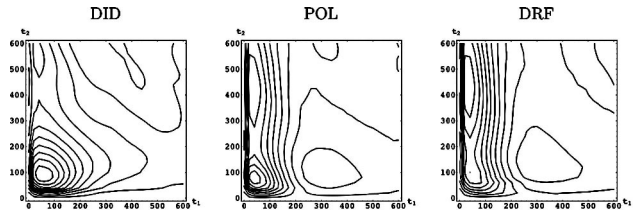

FIG. 2. The $\chi^{(5)}_{mmzzzz}$ 2D Raman response in the DID, POL and DRF models, where *m* denotes the magic angle compared to the *z* axis. The time is given in fs.

is somewhat elongated along the t_2 axis. The response found with the DID model is more symmetric, while the POL and DRF model results are even more stretched out along the t_2 axis than the pure molecular response. In the third-order response the close collisions were seen to counteract the effect of the dipole-induced dipoles. This also seems to be the case in the fifth-order response, but in fifth-order the POL model stretches the response even further along the t_2 axis than the molecular model does. Slight differences are also observed between the POL and DRF model, showing that electron cloud overlap is of some importance.

In the $\chi^{(5)}_{mmzzzz}$ response, the signal is independent of the individual molecular orientations and therefore the MOL model does not give rise to optical response at all. As might be expected for a signal that is solely dependent on interaction induced effects, the differences between the DID, POL, and DRF models are even more pronounced, as shown in Fig. 2. The DID response is rather symmetrical, while the POL and DRF responses show a ridge along the t_2 axis. This clearly demonstrates that the close collision effects are of crucial importance in the fifth-order response. The effect of electron cloud overlap is clearly visible in the area where t_1 and t_2 are 100 fs. A peak is seen in the DID and POL results, while this is not observable in the DRF response where the electron overlap is taken into account.

At present we can only speculate on the detailed interpretation of the spectrum. The long ridges along the t_2 axis were also found phenomenologically in a model suggested by Steffen and Duppen,[19] involving fast phase relaxation during the first time delay and slow population relaxation during the second time delay. This model is briefly described in the Appendix. In the low frequency homogeneous line broadening limit of this model ($\omega \ll \Delta \ll \Lambda$) a ridge along the t_2 axis is found. When the frequency, the fluctuations of the frequency and the timescale of these fluctuations are of the same order of magnitude ($\omega \approx \Delta \approx \Lambda$) a more peaklike structure of the response is observed. However, the true many-body response is more complicated than suggested by this phenomenological model.

It is essential to understand why the DID response is rather symmetric while the DRF response is highly asymmetric. The only difference between these two models is the distance and orientation dependence of the polarizability.[6] This indicates that different dimer configurations are responsible for the rather symmetric part of the response and the ridge along the axis. It is reasonable that the nature of the response depends on the distance and orientation between the molecules, since the intermolecular forces experienced in

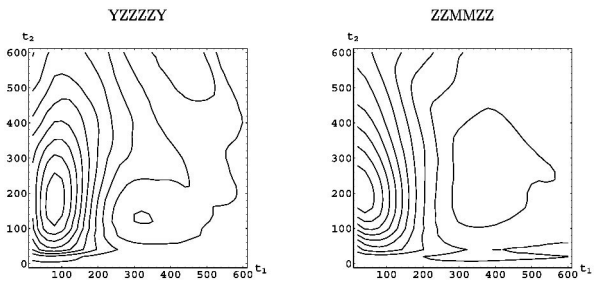

FIG. 3. The $\chi^{(5)}_{zyzzzy}$ and $\chi^{(5)}_{zzmmzz}$ 2D Raman response in the DRF model, where *y* and *m* denotes an axis perpendicular to the *z* axis and an axis forming the magic angle with the *z* axis, respectively. The time is given in fs.

different configurations will be very different. More investigations will be needed to give an exact interpretation of the observed spectral features.

The multicolor experiments published recently[16,32] are in good qualitative agreement with the simulated results reported here. In these experiments the cascaded processes are severely suppressed by the phase mismatch. For the $\chi^{(5)}_{zzzzzz}$ component a long tail along the t_2 (τ_4) axis is observed in very good agreement with the response calculated with the DRF model. Furthermore, the observed signal along the diagonal vanishes very fast, just as in the calculated response.

In order to compare with the experiment performed by Golonzka *et al.*[15] we have calculated the $\chi^{(5)}_{zyzzzy}$ component employing the DRF model. This calculated response is shown in Fig. 3. A ridge is found along the t_2 axis where t_1 is 100 fs. In the experiment a similar ridge is found but at a value of t_1 of around 200 fs.

In recent theoretical[25] and experimental studies[17] nodal lines in the $\chi^{(5)}_{zzzzzz}$ response of CS_2 were reported, which occur on the t_2 axis. Such features are not observed in the multi-color experiments by Kubarych[16,32] nor in the present simulations. In their simulations, Saito and Ohmine[25] used a flexible molecule model, where a rigid model is used in the present study. However, this flexibility was found to be of minor importance to the observed spectrum.[33] Also, the microcanonical ensemble was employed, where we use the isothermal-isobaric ensemble consistent with the experimental conditions.

The use of the isothermal-isobaric ensemble is, in principle, not perfect, since artifacts might be introduced by the Berendsen procedures that are applied to keep the temperature and pressure constant.[31] In order to check whether such artifacts are present, the time constant of calculations, performed in the pressure conserving scheme, was varied. This did not give rise to changes in the simulated fifth-order response along the t_2 axis. Calculations at constant energy instead of temperature did not show any difference either. From these observations we conclude that the isothermal-isobaric ensemble can be confidentially used to represent the experimental conditions of the fifth-order experiments.

An alternative way to mimic the experimental conditions is to do the simulations in the microcanonical ensemble with several initial conditions, selected from a distribution that is canonical, and then average the results. However, this

method also has disadvantages, since it does not allow local fluctuations of the density unless the simulation box is taken to be very large. In our nonequilibrium simulations, energy is transferred to the system when the laser fields are applied. In a simulation with constant energy, this amount of excess energy is not allowed to dissipate out of the system again, as it does from the sample in the laboratory. If the time scales of the energy dissipation and the density fluctuations are much larger than that of the dynamical motions that are the subject of investigation, very little or no difference should be observed between the simulated results of the two methods just discussed.

Both experimentally[17] and theoretically[25] the $\chi^{(5)}_{zzmmzz}$ component was reported. For comparison we have calculated this component too employing the DRF model for calculating the susceptibility (Fig. 3). This calculated response resembles the experimental observations[17] well at first sight, but the peak on the t_2 axis is positive in the calculations and negative in the experiment. Furthermore the calculated peak stretches out to 200 fs along t_1, where the experimental peak only stretches out to 100 fs.

The harmonic oscillator model of Steffen and Duppen[19] cannot account for nodes along the t_2 axis as shown in the Appendix. This means that any such nodal structure must arise from anharmonicities or couplings not taken into account in that model. More sophisticated quantum Fokker-Planck equation models have been reported, but these do not seem to produce nodes on the t_2 axis of the fifth-order response either.[20] Okumura and Tanimura developed models taking small anharmonicities into account[18,8] showing strong influence on the relaxation rates along the two axis, but again no observation of nodes along the t_2 axis were reported.

V. CONCLUSIONS

In this study we showed that induced multipole interactions and electron overlap effects are very important in the fifth-order Raman response of liquid carbon disulfide. These effects are even more pronounced than in the third-order Raman response[6,34] changing the shape from peaklike to ridgelike. This change in character is more pronounced in the $\chi^{(5)}_{mmzzzz}$ component than in the $\chi^{(5)}_{zzzzzz}$ component. It proves that the fifth-order Raman response is a sensitive tool for the investigation of many-body interactions. The response thus provides important clues on details in the intermolecular motion.

The calculated $\chi^{(5)}_{zzzzzz}$ response was found to be in good agreement with the signals experimentally observed by Kubarych *et al.*[16] Furthermore, the observed spectral features seem to be in reasonable agreement with phenomenological models.[19] In contrast, the calculated response does not seem to concur with the observations by Kaufman *et al.*[17] nor the calculations by Saito and Ohmine.[25] It might be possible that specific couplings between translational and rotational degrees of freedom play a role, as suggested by the authors.[33]

For the $\chi^{(5)}_{zyzzzy}$ component reasonable agreement was found with the experiment by Golonzka *et al.*[15] and for the $\chi^{(5)}_{zzmmzz}$ component some resemblance with the experiment by Kaufman *et al.*[17] was observed, but with a unexplained difference in the sign.

The calculated response gives a reasonable description of most experiments, but some differences are observed in the timescales. It should be remembered that the fifth-order response is sensible to anharmonicities and couplings[7–9,18] that may not be well described by the simple force field employed here. This might provide an explanation for the observed deviations in the details of the spectra.

Still further research is required in order to give a clear interpretation of the spectra and establish consensus between the experimental and theoretical results. This will allow fifth-order Raman spectroscopy to become a useful method for studying the complicated motion of liquids.

APPENDIX

Steffen and Duppen[19] examined a harmonic oscillator model allowing line broadening due to fluctuation of the frequency of the oscillator. In this model the line shape function $g(t)$ was given by

$$g(t)=\frac{\Delta^2}{\Lambda^2}(e^{-\Lambda t}+\Lambda t-1). \tag{A1}$$

Here Δ denotes the root mean square of the frequency fluctuations and Λ^{-1} denotes the correlation time of these fluctuations. The frequency of the oscillator is denoted ω. In the inhomogeneous limit $\Delta \gg \Lambda$ and in the homogeneous limit $\Delta \ll \Lambda$. The fifth-order Raman response in this model is[19]

$$\begin{aligned}\chi^{(5)}(t_1,t_2)=&e^{-2g(t_1)-2g(t_2)+g(t_1+t_2)}\cos[\omega(t_1-t_2)]\\&-e^{-g(t_1+t_2)}\cos[\omega(t_1+t_2)]+e^{-g(t_1)}\cos[\omega t_1]\\&-e^{-2g(t_2)-2g(t_1+t_2)+g(t_1)}\cos[\omega(t_1+2t_2)].\end{aligned} \tag{A2}$$

Using this general result the fifth-order Raman response along the t_2 axis can be expressed as

$$\chi^{(5)}(0,t_2)=1-e^{-4g(t_2)}\cos(2\omega t_2). \tag{A3}$$

This function can never become negative as long as t_2 and Λ are both positive and the model can therefore not account for a node on the positive part of the t_2 axis.

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