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# The third- and fifth-order nonlinear Raman response of liquid CS<sub>2</sub> calculated using a finite field nonequilibrium molecular dynamics method

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A finite field molecular dynamics (MD) method has been developed to calculate the off-resonant Raman response of liquids. The method has been used to calculate the third- and fifth-order optical responses of CS<sub>2</sub>. From the third-order response, the intensity of third-order cascading processes has been estimated. The calculated ratio between the fifth-order intensity and the intensity of the third-order cascading processes supports experimental observations, claiming that two-dimensional Raman spectra are dominated by third-order cascading processes. © 2000 American Institute of Physics. [S0021-9606(00)50223-2]

## I. INTRODUCTION

More than 70 years after Raman discovered Raman scattering,<sup>1</sup> Raman spectroscopy has become a widespread technique that is used in many areas of science. In the last decade, the conventional methods, based on determining the characteristics of the spontaneous light scattering spectrum, have been supplemented by a number of femtosecond techniques, relying on stimulated light scattering. In these experiments, which have been extensively applied in experimental studies of the intra- and intermolecular dynamics of liquids and solutions, a short optical pulse perturbs a sample in equilibrium through a Raman interaction. After a period of free evolution another, variably delayed optical pulse is employed to probe the state of the sample. Examples of experiments that are aimed at the low frequency, intermolecular part of the Raman spectrum are the (heterodyned) optical Kerr effect<sup>2,3</sup> and transient grating scattering.<sup>4,5</sup> The main advantage of these time domain methods is that for short enough pulses the excitation occurs impulsively, so that it is possible to observe the induced motions in real time, rather than as a resonance. In particular the initial, short time dynamics can be clearly followed, while that information is hidden in the wings of frequency domain spectra. Despite these operational advantages, however, it should be realized that the information content of time and frequency domain experiments are, in principle, identical. They are both determined by the accessible Raman modes of the liquid and are simply related by Fourier transforms.

Recently, the use of two-dimensional (2D) Raman spectroscopy has been suggested.<sup>6</sup> In these experiments there are two Raman perturbations of the sample, separated by a variable period of free evolution, before the state of the sample is probed after a second independently variable delay. Such experiments are expected to yield considerably more information on the structural dynamics of liquids than the one-dimensional (in either time- or frequency-domain) experi-

ments discussed above. The 2D experiments do not just depend on the overall Raman spectrum of the liquid, but also on dynamical details that give rise to this spectrum. For instance, it should be possible to determine whether the spectra are dominated by ultrafast fluctuations on a local, molecular scale, or by density fluctuations on a much larger length scale.<sup>6,7</sup> In limiting cases this may be described as homogeneous line broadening, arising from the interaction of a system with a fast heat bath, and inhomogeneous line broadening, due to a slowly fluctuating distribution of local environments, respectively. Also, the experiments are expected to be sensitive to mode coupling effects, similar to the well-known coupling effects between spins in 2D-nuclear magnetic resonance (NMR).<sup>8,9</sup>

In the last few years, the 2D off-resonant Raman response has been measured experimentally by various groups.<sup>10-13</sup> The shape of the spectra was not understood until very recently, when Blank *et al.*<sup>13</sup> demonstrated experimentally that the two-dimensional Raman spectrum is dominated by third-order cascade processes. The true fifth-order response that contains all the information about the line broadening and the mode coupling mechanisms is apparently much weaker than these cascading lower-order processes.

The search for the true fifth-order response can be guided by theoretical calculations and simulations. Theory can predict the line shape and intensities of the different types of response and in particular give the intensity ratio between the cascade response and the true fifth-order response.

## II. THEORY

The Raman response can be calculated in four different ways. The most frequently used, to fit experimental results, is based on a phenomenological model, where the many-body motion in the liquid is described by a few Brownian oscillators.<sup>6,14,15</sup> Since the experimental results are not the

true fifth-order response, this method cannot provide useful insight in the dynamics of the liquid that gives rise to the optical response. An alternative approach to this problem is the use of MD simulations that in principle can provide all the information needed to calculate the response functions. This can be done either using the full MD data<sup>16,17</sup> or by using the instantaneous normal mode (INM) approach, where the dynamics is described as motion in harmonic potentials around local structures that are derived from the MD simulation.<sup>18–20</sup> This last approach is only valid for short times, so that, for instance, diffusion cannot be described in this approach. The three methods, described so far, are all based on calculation of the response of the system as a small perturbation from equilibrium, using classical correlation functions.

The third- and fifth-order nonlinear optical response functions  $R^{(3)}$  and  $R^{(5)}$  are related to the quantum mechanical correlation functions of the polarizability tensor elements  $\Pi_{ab}$ :<sup>21,22</sup>

$$R_{abcd}^{(3)}(t_1) = -\frac{i}{\hbar} \text{Tr}(\Pi_{ab}(t_1)[\Pi_{cd}(0), \rho(-\infty)]), \quad (1)$$

$$R_{abcdef}^{(5)}(t_1, t_2) = \left(\frac{i}{\hbar}\right)^2 \text{Tr}(\Pi_{ab}(t_1+t_2) \times [\Pi_{cd}(t_1), [\Pi_{ef}(0), \rho(-\infty)]]), \quad (2)$$

where  $\rho(-\infty)$  is the density matrix of the system at equilibrium. In the classical limit the commutator  $[A, B]$  is replaced by the Poisson bracket  $i\hbar\{A, B\}$ , which gives

$$R_{abcd}^{(3)}(t_1) = \langle \Pi_{ab}(t_1) \{ \Pi_{cd}(0), \rho(-\infty) \} \rangle, \quad (3)$$

$$R_{abcdef}^{(5)}(t_1, t_2) = \langle \Pi_{ab}(t_1+t_2) \times \{ \Pi_{cd}(t_1), \{ \Pi_{ef}(0), \rho(-\infty) \} \} \rangle. \quad (4)$$

The Poisson bracket  $\{A, \rho\}$  is given by  $-\dot{A}\rho/k_B T$ <sup>23,app.8E</sup> where  $\dot{A}$  is the time derivative of  $A$ ,  $k_B$  is Boltzmann's constant and  $T$  is the temperature. Thus, the response functions can be written as

$$R_{abcd}^{(3)}(t_1) = -\frac{1}{k_B T} \langle \Pi_{ab}(t_1) \dot{\Pi}_{cd}(0) \rho(-\infty) \rangle, \quad (5)$$

$$R_{abcdef}^{(5)}(t_1, t_2) = -\frac{1}{k_B T} \langle \Pi_{ab}(t_1+t_2) \times \{ \Pi_{cd}(t_1), \dot{\Pi}_{ef}(0) \rho(-\infty) \} \rangle. \quad (6)$$

Using the general relation  $\{A, B\rho\} = B\{A, \rho\} + \{A, B\}\rho$  and moving the time differentiation in the third-order expression we get the classical correlation function expressions:

$$R_{abcd}^{(3)}(t_1) = \frac{1}{k_B T} \langle \dot{\Pi}_{cd}(t_1) \Pi_{ef}(0) \rho(-\infty) \rangle, \quad (7)$$

$$R_{abcdef}^{(5)}(t_1, t_2) = \left(\frac{1}{k_B T}\right)^2 \langle \Pi_{ab}(t_1+t_2) \times \dot{\Pi}_{cd}(t_1) \dot{\Pi}_{ef}(0) \rho(-\infty) \rangle - \frac{1}{k_B T} \langle \Pi_{ab}(t_1+t_2) \{ \Pi_{cd}(t_1), \dot{\Pi}_{ef}(0) \} \rho(-\infty) \rangle. \quad (8)$$

The Poisson bracket,  $\{\dots, \dots\}$ , in the second term of the fifth-order expression can be written in terms of the differentials with respect to the phase space coordinates,  $p$  and  $q$ :

$$\{ \Pi_{cd}(t_1), \dot{\Pi}_{ef}(0) \} = \sum_i \frac{\partial \Pi_{cd}(t_1)}{\partial q_i(0)} \frac{\partial \dot{\Pi}_{ef}(0)}{\partial p_i(0)} - \frac{\partial \Pi_{cd}(t_1)}{\partial p_i(0)} \frac{\partial \dot{\Pi}_{ef}(0)}{\partial q_i(0)}. \quad (9)$$

These differentials of the polarizabilities with respect to a phase space coordinate pose a problem, since they cannot be calculated straightforwardly from molecular dynamics data. However, they can be rewritten using the chain rule for derivatives, where  $x$  can be any phase space coordinate, both momentum and position, and the summation over  $k$  runs over all possible phase space coordinates.

$$\frac{\partial \Pi_{cd}(t_1)}{\partial x_i(0)} = \sum_k \frac{\partial \Pi_{cd}(t_1)}{\partial x_k(t_1)} \frac{\partial x_k(t_1)}{\partial x_i(0)}. \quad (10)$$

It is possible to calculate this expression, if one knows how a change in the phase space coordinates at one time affects the phase space coordinates at a later time. The  $\partial x_k(t_1)/\partial x_i(0)$  derivatives can be collected in the so-called stability matrix:<sup>22</sup>

$$M_{jk}(t_1, 0) \equiv \left\{ \frac{\partial x_k(t_1)}{\partial x_j(0)} \right\}. \quad (11)$$

This stability matrix contains  $(6 \times N)^2$  numbers, where  $N$  is the number of particles.

Using molecular dynamics all these numbers have to be updated every time step<sup>22</sup> which is very time consuming. Using the INM approach or the Brownian oscillator model the nonlinear response can be calculated analytically, but, as discussed before, this involves approximations of which the validity is unclear.

The fourth way of calculating the response is to directly simulate the actual experimental conditions. In an experiment ultrashort laser pulse pairs excite the Raman active modes in the liquid.<sup>10–13</sup> In the case of a linear molecule this is the same as applying a torque (or more general: a force) on the individual molecules during the short time that the laser pulses interact with the liquid. This torque will tend to align the molecules in the direction of the local electric field, giving rise to different polarizabilities in different directions, i.e., an induced anisotropy,  $\alpha$ . The diagonal elements of the  $\alpha$  tensor are defined from the polarizability tensor elements of the simulation box,  $\Pi_{ab}$ , and the volume of the box,  $V_{\text{box}}$ , as

$$\alpha_{aa} = \frac{\Pi_{aa} - (\Pi_{aa} + \Pi_{bb} + \Pi_{cc})/3}{V_{\text{box}}}. \quad (12)$$

The off-diagonal elements are defined similarly

$$\alpha_{ab} = \frac{\Pi_{ab}}{V_{\text{box}}}. \quad (13)$$

In the third-order experiment, the anisotropy induced by a pulse pair is monitored by a delayed probe pulse. In the fifth-order experiment two laser pulse pairs are used, separated by a delay  $t_1$ . Then, after a second delay  $t_2$  a probe pulse is applied, which generates a signal pulse, which depends on the induced anisotropy of the sample.

This sequence of events is exactly how the calculation in the finite field MD method is performed. When the laser pulse pairs are applied in the experiment a torque is added to the molecules in the simulation, in order to take the combined effect of the two ultrashort optical fields into account. The signal is then calculated by monitoring the induced anisotropy tensor of the simulated molecules.

The third-order response function can be expressed as function of the  $ab$  component of the anisotropy,  $\alpha_{ab}^{(3)}$ , induced by laser fields polarized in the  $d$  and  $c$  directions, and the number density of the liquid

$$R_{abcd}^{(3)}(t) = \frac{\alpha_{ab}^{(3)}(t)}{4\pi\epsilon_0 N E_c E_d}. \quad (14)$$

The fifth-order response function can be found by performing a simulation where the laser pulse pairs are applied twice. The third-order responses from each of the two pulse pairs separately are subtracted from the total signal. This procedure is repeated for different values of delay  $t_1$ , in order to produce the full two-dimensional response.

The essential difference between the correlation function methods and the finite field method is that the full molecular dynamics is used, while avoiding the complications related to the evaluation of the stability matrix Eq. (11). In finite field calculations, first the distortion of the phase space coordinates caused by the applied laser fields is calculated. Subsequently, the field-free evolution of the system is followed, which is equivalent to calculating only the part of the stability matrix that corresponds to the initial distortion. In contrast the whole stability matrix that can describe arbitrary distortions has to be calculated in the correlation function methods.

Cascading signals arise through the combined effect of two third-order processes. They are emitted by the sample in the same direction as the two-dimensional fifth-order signal and have the same overall dependence on laser intensity. Thus, their possible contribution to the overall signal has to be carefully evaluated. In the past, this was done experimentally for sequential third-order processes, which were shown to yield an insignificant contribution to the observed fifth-order signals in CS<sub>2</sub>.<sup>12,23</sup> This is possible because of the selectivity that phase matching provides. Both the fifth-order and the cascade processes obey the same overall phase matching condition, but for the cascade process phase matching requirements related to the intermediate steps are also of importance. Recently it was realized that cascades, built up

from parallel third-order processes may yield significant contributions to the experimentally observed signals, due to insufficient suppression of the intermediate fields.<sup>13,24</sup> Here, we evaluate how selective the phase matching should be in an experiment, in order to suppress any kind of cascade process compared to the true fifth-order signal.

In this study all optical fields were chosen to be polarized in the  $z$  direction. According to the analysis of Tokmakoff<sup>25,26</sup> the ratio between the cascading and the true fifth-order response can be at most a factor of 2 different for other polarization conditions. For simplicity, we omit the polarization indices of the third and fifth-order response functions in the remainder of this article.

Solving the Maxwell equations for the optical fields in the sample and calculating the microscopic response in the simulation box can be separated as long as the size of the simulation box is much smaller than the wavelength of the optical field. The intensity ratio between the two-dimensional fifth-order signal and the cascade processes that are proportional to two third-order signals is then found solving the Maxwell equations for the optical fields using the microscopic third-order response function  $R^{(3)}$ , and the fifth-order response function  $R^{(5)}$  from the simulations. This introduces macroscopic experimental parameters as the optical frequency  $\omega$ , the effective sample thickness  $l$ , the number density  $N$ , the refractive index of the sample  $n_\lambda$ , and the phase mismatch in these coherent nonlinear interactions. In the following expression all phase matching conditions have been included in  $f(\Delta kl)$ :

$$\frac{I_{j,cas}}{I_{j,5th}} \approx \frac{(\pi\omega)^2 l^2}{c^2 n_\lambda^2} N^2 \frac{|R^{(3)}R^{(3)}|^2}{|R^{(5)}|^2} f^2(\Delta kl). \quad (15)$$

Experimental wavelengths of about 620 nm (Refs. 10 and 12) and 800 nm (Ref. 11) have been used with sample thicknesses of 1–2 mm. The number density of pure CS<sub>2</sub> at the simulated conditions is  $9.88 \times 10^{27} \text{ m}^{-3}$ , which is calculated from the experimental density of 1.26 g/ml (Ref. 27) and the refractive index of pure CS<sub>2</sub> is 1.628.<sup>28</sup>  $R^{(3)}$  and  $R^{(5)}$  both depend on time and polarization of the laser fields.

### III. RESULTS

To compare the third-order response functions of the finite field method, described in Sec. II, with the full MD data correlation function approach, MD simulations were performed with a slightly modified version of GROMACS 1.6.<sup>29</sup> The MD box is cubic and contains 256 rigid CS<sub>2</sub> molecules at 1 bar pressure and 298 K, using a Berendsen thermostat<sup>30</sup>. The intermolecular interaction is described using atomic Lennard-Jones potentials from literature, giving a fair description of properties such as density, diffusion constant and neutron and x-ray scattering data.<sup>27</sup> The size of the time steps in the calculations is 10 fs. The experimental molecular polarizability tensor for an oscillating field with a wavelength of 514.5 nm is used.<sup>31</sup> For each Raman event, a 3.83 V/nm (dc) field is applied during one time step. The box polarizability is calculated as a simple sum of the polarizability of the individual molecules, so local field effects are neglected in this study.



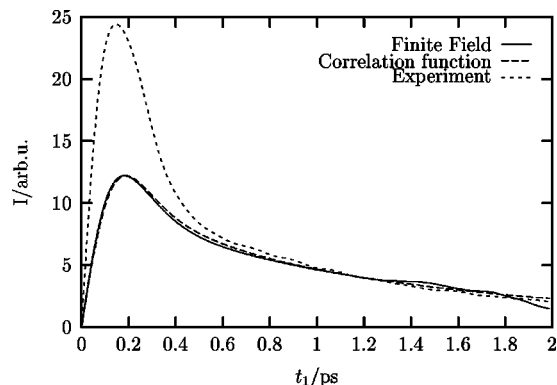


FIG. 1. Third-order Raman response  $R_{zzzz}^{(3)}$  of  $\text{CS}_2$ , calculated using the finite field method and the correlation function method. Experimental results are also shown. For details see text.

The third-order correlation function response was calculated from a single 100 ps MD simulation. The finite field response was obtained from 8000 simulations of 2 ps duration. In Fig. 1 the calculated third-order response functions are compared with each other and with the experimental response function<sup>32</sup>. The highest value of the calculated induced anisotropy  $\alpha^{(3)}$  is  $1.05 \times 10^{-14}$  C/Vm.

In the comparison between the third-order responses, calculated using the full MD correlation function approach and the finite field approach, almost perfect agreement is observed (Fig. 1). The long diffusive tail of the experimentally observed response function is reproduced very well by both calculated response functions. The discrepancy with the experiment at short times is due to the neglect of local field effects. Previous correlation function calculations of the same third-order response function by Geiger and Ladanyi<sup>17</sup> have also shown that the long diffusive tail is well reproduced, even when one omits the local field effects. However, the peak at 200 fs is underestimated by a factor of 2 by not taking these effects into account. The comparison of our results with those of Geiger and Ladanyi<sup>17</sup> indicate that inclusion of local field effects in our calculations will give results in much better agreement with the experiment at short times. This will be treated in a future publication.<sup>33</sup> Here we will concentrate on the ratio between third- and fifth-order responses, in order to be able to estimate the contribution of cascade processes to the fifth-order 2D-Raman response.

The fifth-order response was calculated by averaging over 8000 finite field approach simulations with a duration of 0.75 ps using the same MD simulation conditions as for the third-order response. The result is shown in Fig. 2. The magnitude of noise introduced by the perturbation of the system has been calculated as the spread on the mean value of the response function at each time  $t_2$  for the calculation with  $t_1=0.2$  ps. The highest value of the induced anisotropy  $\alpha^{(5)}$  is  $0.98 \times 10^{-17}$  C/Vm which occurs for  $t_1=0.2$  ps and  $t_2=0.2$  ps.

The intensity ratio of the cascaded and fifth-order response can be estimated from the peak values of the third- and fifth-order response functions in the sample. Using the calculated response function peak intensities we find

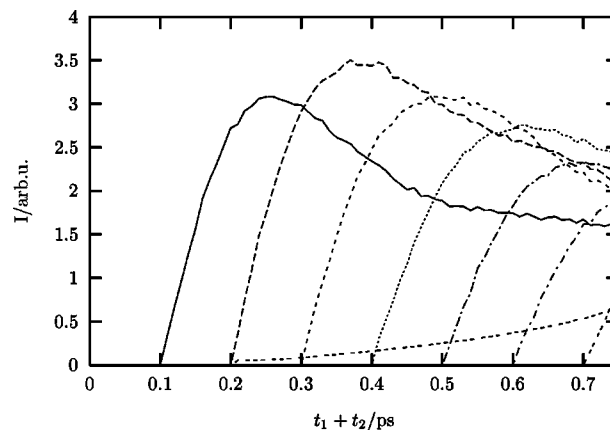


FIG. 2. Fifth-order response  $R_{zzzzzz}^{(5)}$ , calculated using the finite field method. The different lines correspond to different values of  $t_1$ , with  $t_1$  increasing from 0.1 ps in the left trace to 0.7 ps in the right trace in steps of 0.1 ps. The positively inclined line at the bottom signifies the noise level in the calculation with  $t_1$  0.2 ps.

$$\frac{N^2 |R^{(3)} R^{(3)}|^2}{|R^{(5)}|^2} = 0.0104. \quad (16)$$

With this information Eq. (15) gives an approximate intensity ratio of the two types of response of  $4 \times 10^6$  in favor of the third-order cascade processes when a wavelength of 620 nm, a sample size of 1 mm and perfect phase matching,  $f(\Delta kl) = 1$ , is taken. This indicates that the cascade process should be very severely mismatched in phase under experimental conditions, in order to be able to observe the 2D fifth-order Raman signal. Such mismatch was not present in the experiments reported so far.<sup>10-13</sup>

#### IV. CONCLUSIONS

The estimated intensity ratio of 4 million between the third-order cascading processes and the true fifth-order response, in favor of the cascading processes before taking phase matching into account, supports the conclusions of D. A. Blank *et al.*<sup>13</sup> that all reported experimental results of 2D Raman scattering actually dealt with cascading processes, instead.

Although in the present study local field effects are not taken into account, it is not expected that these will change the ratio by orders of magnitude. Work is in progress to include interaction induced effects in the future simulations.<sup>33</sup>

The finite field method used in this study was proven to be reliable. This conclusion is based on the agreement between the third-order response functions calculated with the finite field method and the correlation function method. The finite field method is a bit more time consuming in the present third-order calculations, but this is mainly because the correlation function can be simplified when local field effects are ignored. For the fifth-order response, the finite field method provides a much more efficient alternative to the correlation function approach. The latter is very time consuming when the full MD trajectories are used.

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