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# Note: Inverted time-ordering in two-dimensional-Raman-terahertz spectroscopy of water

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In a previous paper,[1] we have studied the 2D-Raman-THz response of liquid water, based on an all-atom molecular dynamics (MD) simulation. This novel two-dimensional spectroscopy is designed to directly work in the low-frequency spectral range of the *inter*molecular degrees of freedom of water. Its information content is similar to 2D-Raman[2–9] or 2D-THz spectroscopy,[10] but the experimental implementation should be easier. In 2D-Raman-THz spectroscopy, a near-infrared laser pulse excites a coherence of an intermolecular vibrational mode through a Raman process (see Fig. 1(b)). After time $t_1$, the THz pulse interrogates the molecular system again and switches it into another coherence, which is finally read out at time $t_1 + t_2$ by the emission of a THz field. It is this switching between coherences which ultimately allows one to measure couplings and correlations between the various degrees of freedom of the system under study.

In the present note, we explore the inverted time-ordered pulse sequence, in which the first coherence is generated by a direct THz excitation, while the switching of coherences is achieved by a Raman interaction (Fig. 1(a)). The dependence of the polarizibility on the nuclear coordinates is expected to be more nonlinear compared to that of the dipole moment. Both pulse sequences involve a two-quantum transition for the switching of coherences, which requires such an electrical anharmonicity. Since the second interaction in the inverted pulse sequence is the one with the larger nonlinearity, one might expect that it reveals more of the couplings and correlations between the various degrees of freedom. The second motivation for looking at the inverted time-ordered response function lies in the fact that in an experimental realization of 2D-Raman-THz spectroscopy, where the laser pulses will not be infinitely short, one will convolute over both response functions during pulse overlap, so both will be needed for a modeling of an experimental result.

The response function of the original pulse sequence is[1]

$$R^{(I)}(t_2, t_1) \propto \mathrm{Tr}\{\mu(t_2 + t_1)[\mu(t_1), [\mathbf{\Pi}(0), \rho_{\mathrm{eq}}]]\}, \qquad (1)$$

where $[.., ..]$ is a commutator, $\Pi(t)$ and $\mu(t)$ are polarizibility and dipole operators, respectively, and $\rho_{\mathrm{eq}}$ the equilibrium density matrix. For the inverted time-ordered response function, this is changed to

$$R^{(II)}(t_2, t_1) \propto \mathrm{Tr}\{\mu(t_2 + t_1)[\mathbf{\Pi}(t_1), [\mu(0), \rho_{\mathrm{eq}}]]\}. \qquad (2)$$

The hybrid equilibrium-non-equilibrium approach introduced by Tanimura and co-workers[8] is used to compute this response function from an all-atom MD simulation:

$$R^{(II)}(t_2, t_1) \propto \langle(\mu_+(t_2) - \mu_-(t_2))\dot{\mu}(-t_1)\rangle_{nonequ}. \qquad (3)$$

Here, the average is taken over an ensemble of non-equilibrium trajectories, and $\mu_+(t_2)$ and $\mu_-(t_2)$ refer to the dipole moments at time $t_2$ obtained after perturbing the momenta of the individual atoms by $\pm \Delta p_i$, respectively, at time $t = 0$. This perturbation now requires the calculation of the forces on the individual water molecules upon acting of a short electric field pulse on the polarizibility tensor (rather than the dipole moment). All other simulation details, in particular the MD protocol, the parametrization for the calculation of the dipole moment and the polarizibility tensor of the simulation box and the electric field strength are the same as in Ref. 1.

Fig. 1(c) shows the response function $R^{(II)}$ calculated in this way and combines it with $R^{(I)}$ in Fig. 1(d). The time-axis $t_1$ has been inverted for $R^{(II)}$ to emphasize the continuity of the overall response function with $R^{(I)}(t_1 = 0, t_2) = R^{(II)}(t_1 = 0, t_2)$ for all $t_2$. This continuity is, of course, expected as both response functions are supposed to be the same when the THz and the Raman-pulses coincide with $t_1 = 0$. However, given the fact that Eq. (3) and its counterpart for $R^{(I)}$ (Ref. 1) require the evaluations of different derivatives, the continuity serves as a good consistency check of the numerical procedures.

Most interesting is the signature of an echo along the diagonal in the inverted THz-Raman-THz sequence along the diagonal for $t_1 = t_2$ (Fig. 1(c), label *). An echo arises when a coherence dephases very quickly, and then rephases upon a second perturbation. Traces of a photon echo appear in simulations of 2D-Raman spectroscopy, but only when approximating the signal with instantaneous or quenched normal modes.[3,6] The photon echo gets completely blurred in 2D-Raman spectroscopy when all the dynamic effects of a fully anharmonic MD force field are included. To our knowledge, the echo signal in Fig. 1(c) is the clearest signature of that kind observed so far for a fully anharmonic MD simulation, highlighting the potential that lies in the THz-Raman-THz pulse sequence. The reason for the larger sensitivity to an echo might be the following: Assuming that the dependence of the polarizibility $\mathbf{\Pi}$ on nuclear coordinates $q$ is more nonlinear than that of the dipole moment $\mu$, the THz-Raman-THz sequence is dominated by the term $\mathrm{Tr}\{q(t_2 + t_1)[q^2(t_1), [q(0), \rho_{\mathrm{eq}}]]\}$, where the $q^2(t_1)$-term is responsible for a two-quantum transition. Indeed, it has been
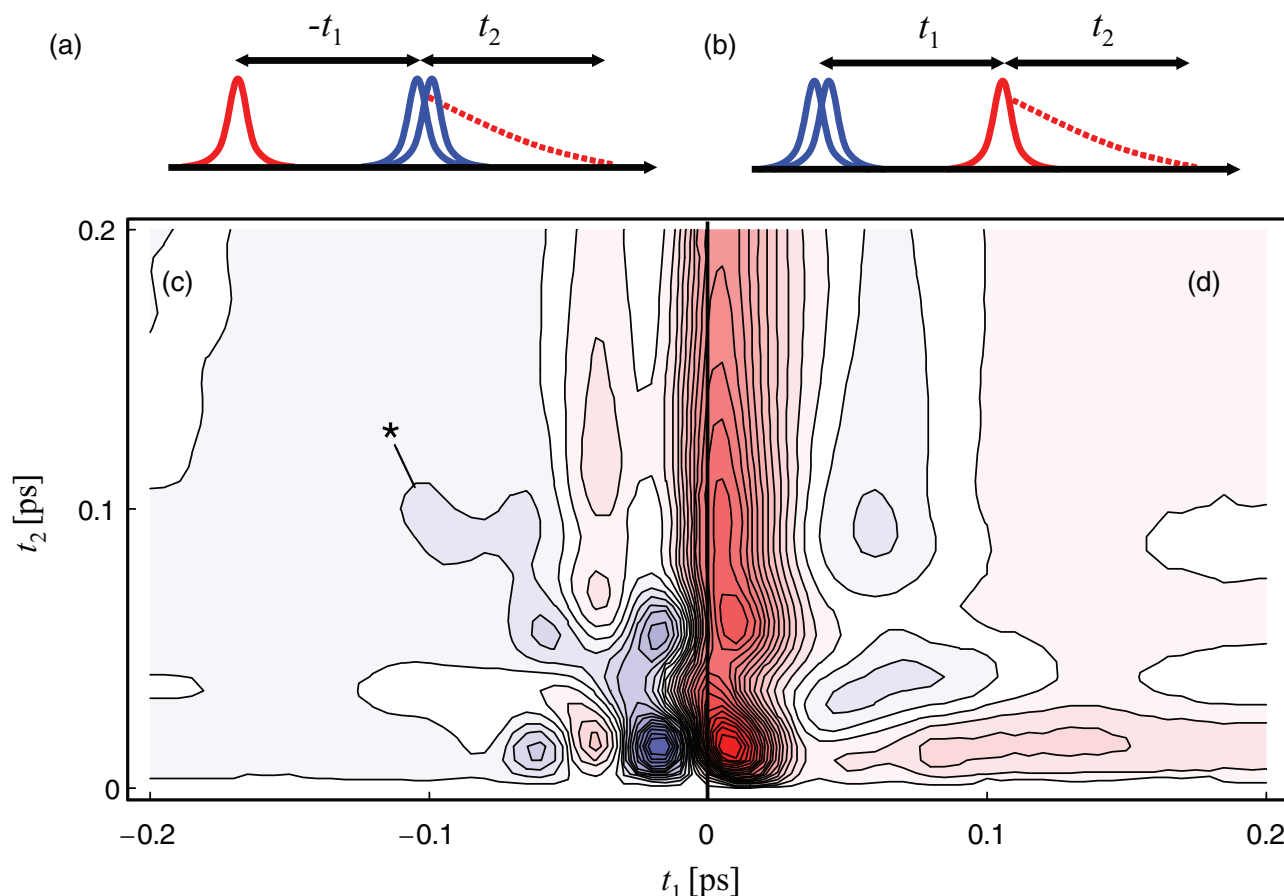
FIG. 1. (a) The inverted pulse sequences and (b) the original pulse sequence of Ref. 1. A red pulse depicts a THz field, a pair of blue pulses depicts the two fields necessary to achieve a Raman transition. Panels (c) and (d) show the response functions according to Eqs. (1) and (2), respectively, where red and blue colors depict response of opposite sign. The response function $R^{(I)}$ in panel (d) is adapted from Ref. 1. The time-axis $t_1$ has been inverted in panel (c) to emphasize the continuity of the overall response function at $t_1 = 0$. The feature labeled with an asterisk (*) indicates an echo.

shown that this term dephases as a function of $(t_1 - t_2)$, i.e., forms an echo at $t_1 = t_2$ (Ref. 4) (the mechanism for the formation of an echo is different from resonant 2D spectroscopy, where two phase-conjugate pathways exist). On the other hand, the term $\mathrm{Tr}\{q^2(t_2 + t_1)[q(t_1), [q(0), \rho_{eq}]]\}$ contributes equally strongly in the Raman-Raman-Raman sequence of 2D-Raman spectroscopy. The latter does not switch coherences after time $t_1$, but is superimposed and hence might blur the echo. Even worse, in our original Raman-THz-THz sequence $R^{(I)}$, this second term dominates. Another possible explanation for the different responses might be connected to non-coincidence effect we have identified for the librational mode,[1] in which case Raman and THz transitions are mutually exclusive to a certain extent. Calculating the various signals based on a normal mode analysis will clarify this effect.

We conclude that indeed the inverted pulse sequence more sensitively measures the coupling between the various degrees of freedom of water. Simulations of that kind, on the one hand, will guide the design of an experimental implementation of 2D-Raman-THz spectroscopy, and on the other

hand, will contribute to validating the water model on which the simulation is based, once experimental data are available. Should one observe an echo, it will give unprecedented insights into water structure and dynamics.

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