# Supplementary Information

## I. The theoretical model of the medium:

Each $CCl_4$ molecule is represented by the linear oscillator with C atom in the middle and Cl ($^{35}Cl$ or $^{37}Cl$) atoms on both sides,

with intramolecular harmonic Hamiltonian $H_0 = \frac{1}{2}\sum_{n=1}^{2} k_1 (x_C - x_{C\ln})^2$ , where $x_C$ and $x_{Cl_n}$ denote the small displacements of the appropriate atoms from the equilibrium positions and $k_1$ is the intramolecular force constant. Thus we consider three types of virtual molecules, $^{35}Cl$-C-$^{35}Cl$, $^{37}Cl$-C-$^{37}Cl$, $^{35}Cl$-C-$^{37}Cl$. If we denote $m_{Cl}, m_C$ as the masses of the chlorine and carbon atoms, respectively, $M_i = m_{Cl_{1i}} + m_C + m_{Cl_{2i}}$ as the mass of the i-th molecule, and $\frac{1}{\mu_i} = \frac{1}{m_{Cl_{1i}}} + \frac{1}{m_{Cl_{2i}}}$ as the inverse reduced mass of chlorine atoms in a given molecule, then the general expressions for the normal square frequencies $\omega_\alpha^2$ and the appropriate coordinates $Q(\alpha)$ in a single molecule, found with accuracy to the linear terms $\frac{m_{Cl_2} - m_{Cl_1}}{m_{Cl_1}}$ , are the following:

for symmetric stretching vibration, $\omega_{1i}^2 = \frac{k_1}{2\mu_i}$ , and $Q_{1i} = (x_{Cl_{1i}} - x_{Cl_{2i}}) + \frac{m_C}{4r_i}(x_{Cl_{1i}} + x_{Cl_{2i}} - 2x_{C_i})$ (1)

for asymmetric stretching vibration, $\omega_{2i}^2 = \frac{k_1}{2\mu_i} + \frac{2k_1}{m_C}$ , and $Q_{2i} = (x_{Cl_{1i}} + x_{Cl_{2i}} - 2x_{C_i}) - \frac{m_C}{4r_i}(x_{Cl_{1i}} - x_{Cl_{2i}})$ , (2)

where we have introduced $\frac{1}{r_i} = \frac{1}{m_{Cl_{1i}}} - \frac{1}{m_{Cl_{2i}}}$ , which equals zero for symmetric molecules $^{35}Cl$-C-$^{35}Cl$ and $^{37}Cl$-C-$^{37}Cl$ since $m_{Cl_1} = m_{Cl_2}$ . For asymmetric molecule $^{35}Cl$-C-$^{37}Cl$ the ratio $\frac{m_{Cl_2} - m_{Cl_1}}{m_{Cl_1}} \approx 0.06$ . The symmetric stretching vibration of such oscillators corresponds to the $\nu_1$ fundamental in $CCl_4$ molecule and is Raman active. The asymmetric vibration in a linear symmetric molecule is Raman inactive.

We assume the medium as a set of linear dimers composed of two molecules defined above.

where the interaction Hamiltonian between the closest chlorine atoms belonging to different molecules i,j, is given in a form $H_I = \frac{1}{2}\sum_{i \neq j} k_2 (x_{Clj} - x_{Cli})^2$ and $k_2$ denotes the intermolecular force constant. We will denote the k-th dimer as $d_k$.

Equations of motions in harmonic approximation for small atomic displacements from the equilibrium positions in the *k-th* dimer are the following:

$$
\begin{aligned}
m_{Cl_{11}} \ddot{x}_{Cl_{11}} &= k_1 (x_{C_1} - x_{Cl_{11}}) \\
m_C \ddot{x}_{C_1} &= k_1 (x_{Cl_{11}} + x_{Cl_{21}} - 2x_{C_1}) \\
m_{Cl_{21}} \ddot{x}_{Cl_{21}} &= -k_1 (x_{Cl_{21}} - x_{C_1}) + k_2 (x_{Cl_{12}} - x_{Cl_{21}}) \\
m_{Cl_{12}} \ddot{x}_{Cl_{12}} &= k_1 (x_{C_2} - x_{Cl_{12}}) - k_2 (x_{Cl_{12}} - x_{Cl_{21}}) \\
m_C \ddot{x}_{C2} &= k_1 (x_{Cl_{12}} + x_{Cl_{22}} - 2x_{C2}) \\
m_{Cl_{22}} \ddot{x}_{Cl_{22}} &= k_1 (x_{C_2} - x_{Cl_{22}})
\end{aligned} \qquad (3)
$$

where for clarity we have omitted the index *k* at each displacement.

For each dimmer we introduce new coordinates being the combinations of the displacements. We will number the considered vibrations with index α. Four of them are the amplitudes of normal vibrations of the left, $Q(\alpha_1) \equiv Q_{11}$ and $Q(\alpha_2) \equiv Q_{21}$, and of the right, $Q(\alpha_3) \equiv Q_{12}$ and $Q(\alpha_4) \equiv Q_{22}$, single molecules, defined by Eq.(1) and Eq.(2) respectively. Then, there is the amplitude of the intermolecular interaction $Q(\alpha_5) = Q_5$, corresponding to the out of phase displacement of the whole molecules:

$$Q_5 = x_{Cl_{11}} + \frac{m_{Cl_{21}}}{m_{Cl_{11}}} x_{Cl_{21}} + \frac{m_C}{m_{Cl_{11}}}(x_{C_1} - x_{C_2}) - \frac{m_{Cl_{12}}}{m_{Cl_{11}}} x_{Cl_{12}} - \frac{m_{Cl_{22}}}{m_{Cl_{11}}} x_{Cl_{22}} \tag{4}$$

and the condition of the center of mass frame of reference:

$$0 = x_{Cl_{11}} + \frac{m_{Cl_{21}}}{m_{Cl_{11}}} x_{Cl_{21}} + \frac{m_C}{m_{Cl_{11}}}(x_{C_1} + x_{C_2}) + \frac{m_{Cl_{12}}}{m_{Cl_{11}}} x_{Cl_{12}} + \frac{m_{Cl_{22}}}{m_{Cl_{11}}} x_{Cl_{22}} \tag{5}$$

The dynamics of the dimers, subjected to the interaction of the incident pump pulse, is described by the set of equations of motion for these five amplitudes with damping term and the driving force $f(\alpha) = P^{(1)}_{kl}(\alpha) F_k F_l(t)$, where $P^{(1)}_{kl}(\alpha)$ denotes the first derivative of the medium polarizability with respect to the appropriate normal amplitude $Q(\alpha)$ and $F_k(t) = ((\varepsilon_0 + 2)/3) E^{pump}_k(t)$. We have assumed the optical pump field to have a Gaussian envelope, $E^{pump}_i(t) = E_i e^{-(t/2\Delta t)^2} e^{i\omega t}$; $\Delta t$ is the pulse width, $\omega$ is the central frequency, and the pump optical field is linearly polarized.

The equations of motion for each dimer, with accuracy to the terms linear in $\frac{1}{r_i}$ are the following:

$$\begin{aligned}
\ddot{Q}_{11} &= -\frac{k_1}{2\mu_1} Q_{11} - \Gamma_1 \dot{Q}_{11} - \frac{k_2}{m_{Cl_{21}}}\left(1 - \frac{m_C}{4r_1}\right)(x_{Cl_{12}} - x_{Cl_{21}}) + f(\alpha_1) \\
\ddot{Q}_{21} &= -\left(\frac{k_1}{2\mu_1} + \frac{2k_1}{m_C}\right) Q_{21} - \Gamma_2 \dot{Q}_{21} + \frac{k_2}{m_{Cl_{21}}}\left(1 + \frac{m_C}{4r_1}\right)(x_{Cl_{12}} - x_{Cl_{21}}) + f(\alpha_2) \\
\ddot{Q}_{12} &= -\frac{k_1}{2\mu_2} Q_{12} - \Gamma_3 \dot{Q}_{12} - \frac{k_2}{m_{Cl_{12}}}\left(1 + \frac{m_C}{4r_2}\right)(x_{Cl_{12}} - x_{Cl_{21}}) + f(\alpha_3) \\
\ddot{Q}_{22} &= -\left(\frac{k_1}{2\mu_2} + \frac{2k_1}{m_C}\right) Q_{22} - \Gamma_4 \dot{Q}_{22} - \frac{k_2}{m_{Cl_{12}}}\left(1 - \frac{m_C}{4r_2}\right)(x_{Cl_{12}} - x_{Cl_{21}}) + f(\alpha_4) \\
\ddot{Q}_5 &= 2\frac{k_2}{m_{Cl_{11}}}(x_{Cl_{12}} - x_{Cl_{21}}) - \Gamma_5 \dot{Q}_5 + f(\alpha_5)
\end{aligned} \tag{6}$$

where $(x_{Cl_{12}} - x_{Cl_{21}})$ is the combination of normal amplitudes:

$$\begin{aligned}
x_{Cl_{12}} - x_{Cl_{21}} = &-\frac{m_{Cl_{11}}}{2}\left(\frac{1}{M_1} + \frac{1}{M_2}\right) Q_5 + \frac{1}{2M_1}\left(2m_{Cl_{11}} + m_C - \frac{m_C^2}{4r_1}\right) Q_{11} - \frac{m_C}{M_1}\left(1 + \frac{2m_{Cl_{11}} + m_C}{4r_1}\right) Q_{21} \\
&+ \frac{1}{2M_2}\left(2m_{Cl_{22}} + m_C + \frac{m_C^2}{4r_2}\right) Q_{12} + \frac{m_C}{M_2}\left(1 - \frac{2m_{Cl_{22}} + m_C}{4r_2}\right) Q_{22}
\end{aligned} \tag{6a}$$

Thus, we can see that in asymmetric dimers the frequency of each considered intermolecular mode is blue shifted proportionally to *k*$_2$.

In the case of symmetric dimers composed of two identical molecules, $\mu_1 = \mu_2 = \mu$, $M_1 = M_2 = M$ and $r_1 = r_2 = r$, the sum and the difference of intramolecular normal amplitudes describe the in-phase and out-of-phase vibrations of both molecules, respectively. If we put $\Gamma_1 = \Gamma_3$ and $\Gamma_2 = \Gamma_4$, the appropriate equations have the form:

- for in-phase symmetric vibration $Q_1 = (Q_{11} + Q_{12})/2$,

$$\ddot{Q}_1 = -\frac{k_1+k_2}{2\mu}Q_1 - \Gamma_1\dot{Q}_1 + \frac{k_2}{2\mu\ M}\Big[(\Delta m\ + m_C/4r)Q_2 + 2m_C(1-\Delta m/4r)Q_3 + (Mm_C/2r)Q_4 + 2m_{Cl_{11}}Q_5)\Big] + f_1 \tag{7a}$$

- for out-of-phase symmetric vibration $Q_2 = (Q_{11} - Q_{12})/2$ ,

$$\ddot{Q}_2 = -\left(\frac{k_1}{2\mu} + \frac{k_2\Delta m}{2Mr}\right)Q_2 - \Gamma_1\dot{Q}_2 + \frac{k_2}{2r\ M}(MQ_1\ - 2m_CQ_3 - 2m_{Cl_{11}}Q_5) + f_2 \tag{7b}$$

- for out-of-phase asymmetric vibration $Q_3 = (Q_{21} - Q_{22})/2$

$$\ddot{Q}_3 = -\left(\frac{k_1}{2\mu} + \frac{2k_1}{m_C} + \frac{k_2m_C}{M\mu}\right)Q_3 - \Gamma_2\dot{Q}_3 + \frac{k_2}{2M\mu}(MQ_1 - (\Delta m + m_C/4r)Q_2 - (Mm_C/4r)Q_4 - 2m_{Cl_{11}}Q_5) + f_3 \tag{7c}$$

- for in-phase asymmetric vibration $Q_4 = (Q_{21} + Q_{22})/2$ ,

$$\ddot{Q}_4 = -\left(\frac{k_1}{2\mu} + \frac{2k_1}{m_C}\right)Q_4 - \Gamma_2\dot{Q}_4 + \frac{k_2}{2Mr}(-2m_CQ_3 + MQ_1 - \Delta mQ_2 - 2m_{Cl_{11}}Q_{5s}) + f_4 \tag{7d}$$

- for intermolecular out-of-phase vibration

$$\ddot{Q}_5 = -\frac{2k_2}{M}Q_5 - \Gamma_5\dot{Q}_5 + \frac{2k_2}{Mm_{Cl_{11}}}(MQ_1 - (\Delta m + m_C^2/4r)Q_2 - 2m_CQ_3 - (Mm_C/4r)Q_4 + f_5 \tag{7e}$$

where $M = m_C + m_{Cl_1} + m_{Cl_2}$ , $\mu$ , $\Delta m\ = m_{Cl_2} - m_{Cl_1}$ and $r$ , respectively, are specified for a given symmetric dimmer. $f_1 = (f(\alpha_1) + f(\alpha_3))/2;\ f_2 = (f(\alpha_1) - f(\alpha_3))/2;\ \ f_3 = (f(\alpha_2) - f(\alpha_4))/2;\ \ f_4 = (f(\alpha_2) + f(\alpha_4))/2;\ \ f_5 = f(\alpha_5)$ . The index *k* numbering the dimers has been omitted.

In order to find the first order derivatives of the medium polarizability with respect to vibrational amplitudes, $P_{kl}^{(1)}(\alpha)$ , we have calculated the polarizabilities of all dimers, applying the Silberstein model[34]:

$$P_{rr} = \sum_{n=1}^{6} \alpha^{eff}(n) \quad , \tag{8}$$

where with accuracy to the terms of order of $\frac{\alpha}{r_{nn'}^3}$ we have taken the effective polarizabilities in the form;

$$\alpha^{eff}(n) = \alpha(n)\left(1 + \frac{\alpha(n-1)}{r_{n,n-1}^3} + \frac{\alpha(n+1)}{r_{n,n+1}^3}\right) \tag{8a}$$

with $r(n,n') = r_0(n,n') + x_n - x_{n'}$ . We have applied the values of undisturbed polarizabilities, $\alpha_C = 0.88\cdot 10^{-24}cm^3$ for carbon atom and $\alpha_{Cl} = 1.91\cdot 10^{-24}cm^3$ for chlorine atom, from reference [34], assuming that $\alpha_{^{35}Cl} = \alpha_{^{37}Cl}$, and the equilibrium distance between carbon and chlorine atoms is the same as in CCl$_4$ molecule, $r_0(C,Cl) = 1.7\cdot 10^{-8}cm$ , taken from ref.[10]. The value of total polarizability of CCl$_4$ molecule, calculated on the base of Eq.(8) and Eq.(8a) , $\alpha_{CCl_4} = \alpha_C^{eff} + 4\alpha_{Cl}^{eff} = 10.28\cdot 10^{-24}cm^3$ , is in a good agreement with the calculated and observed ones[34].

The first order derivatives, $P_{ii}^{(1)}(\alpha)$ , derived for our model of the medium, present in the above equations of motion, are the dimer polarizability derivatives averaged over all possible directions of dimer with respect to the direction of the external electric field. In Eqs (6) they are the following:

$$\begin{aligned}
P_{ii}^{(1)}(\alpha_1) &= 9\left(\frac{\alpha_C\alpha_{Cl}}{r_0{}^4(C,Cl)} - \frac{\alpha_{Cl}^2}{2r_0^4(Cl_{21},Cl_{12})M_1}(2m_{Cl_{11}} + m_C - m_C^2/4r_1)\right)\\
P_{ii}^{(1)}(\alpha_2) &= 9\left(-\frac{\alpha_C\alpha_{Cl}}{r_0^4(C,Cl)}\frac{m_C}{4r_1} + \frac{\alpha_{Cl}^2}{r_0^4(Cl_{21},Cl_{12})}\frac{m_C}{M_1}(1+(2m_{Cl_{11}} + m_C)/4r_1)\right)\\
P_{ii}^{(1)}(\alpha_3) &= 9\left(\frac{\alpha_C\alpha_{Cl}}{r_0{}^4(C,Cl)} - \frac{\alpha_{Cl}^2}{2r_0^4(Cl_{21},Cl_{12})M_2}(2m_{Cl_{22}} + m_C + m_C^2/4r_2)\right)\\
P_{ii}^{(1)}(\alpha_4) &= 9\left(-\frac{\alpha_C\alpha_{Cl}}{r_0^4(C,Cl)}\frac{m_C}{4r_2} - \frac{\alpha_{Cl}^2}{r_0^4(Cl_{21},Cl_{12})}\frac{m_C}{M_2}(1-(2m_{Cl_{22}} + m_C)/4r_2)\right)\\
P_{ii}^{(1)}(\alpha_5) &= 9\frac{\alpha_{Cl}^2\ m_{Cl_{11}}}{2r_0^4(Cl_{21},Cl_{12})}\left(\frac{1}{M_1}+\frac{1}{M_2}\right)
\end{aligned} \tag{9}$$

where in the SI units the formulas should be multiplied by the factor $4\pi\varepsilon_0$ **.** If we substitute $r_0(Cl_i,Cl_j) = 4\cdot 10^{-8}cm$ **,** we can estimate that in our model the contributions of the symmetric stretching modes $\alpha_1,\alpha_3$ are about 100 times stronger than of the other modes. In the symmetric dimers, Eqs.(7), only the in phase symmetric stretching mode, $P_{ii}^{(1)}(1) = (P_{ii}^{(1)}(\alpha_1) + P_{ii}^{(1)}(\alpha_3))/2 = 2.33\cdot 10^{-16}cm^2$ , the out of phase asymmetric stretching mode $P_{ii}^{(1)}(3) = (P_{ii}^{(1)}(\alpha_2) - P_{ii}^{(1)}(\alpha_4))/2 = 0.025\cdot 10^{-16}cm^2$ , the in phase asymmetric stretching mode, $P_{ii}^{(1)}(4) = (P_{ii}^{(1)}(\alpha_2) + P_{ii}^{(1)}(\alpha_4)/2 = -0.009\cdot 10^{-16}\ cm^2$, and the intermolecular vibration are Raman active. The out of phase symmetric stretching mode is Raman inactive, since $P_{ii}^{(1)}(2) = (P_{ii}^{(1)}(\alpha_1) - P_{ii}^{(1)}(\alpha_3))/2 = 0$ .

## II. Evolution of the dynamic Raman spectrum

Calculating the Fourier transform of the time resolved signal we start our analysis with certain delay, at least 400 fs, in order to neglect the electronic part of the signal. In Fig.1, below, we present how the Raman spectrum of the $\nu_1$ vibration in $CCl_4$, obtained as a Fourier transform of the time domain signal, depends on this time delay. It can be seen that the background composed of the overtone and combination bands decays within 1ps, whereas the fundamental lines remain almost unchanged. Such a result is in agreement with the results of time domain higher-order nonlinear spectroscopy by K. Tominaga and K.Yoshihara[34], who have detected the decoherence times of the higher-order lines to be much shorter than of the fundamental lines.

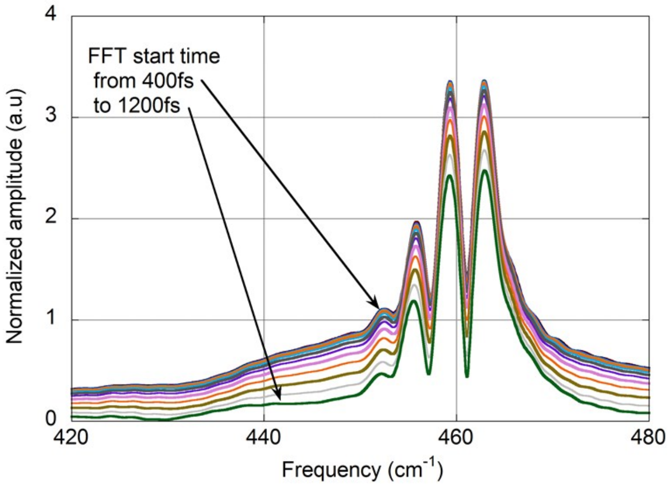
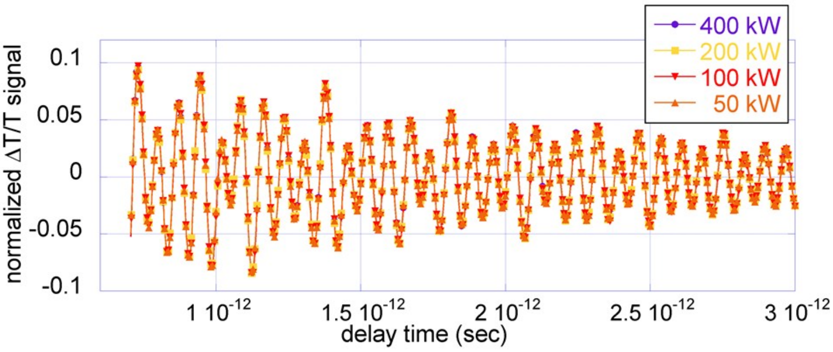


*Fig.1. FFT of the time domain transient transmission signal for different start times for the signal analysis. Fig.3b in the paper corresponds to the 1 ps start time.*

## III. Pump power dependence

In order to establish, if the relaxation of the medium, studied in our paper, might be affected by other nonlinear processes due to pump pulse, we have repeated the experiment for four values of the pump power. The extended fragments of time domain $\Delta T/T$ signals for all powers are shown in Fig.2a. The signals were normalized with respect to the electronic part of the response and extended in order to show that there are no discrepancies among them. Fourier transforms for all cases, were taken for the 0.4ps- 40ps time range. Fig.2b shows the isotopically split $\nu_1$ band. It is very important to notice that for all pump powers the ratios of the sub-peaks in the spectrum of $\nu_1$ vibration are the same, and different than in spontaneous Raman spectrum.

a)



b)

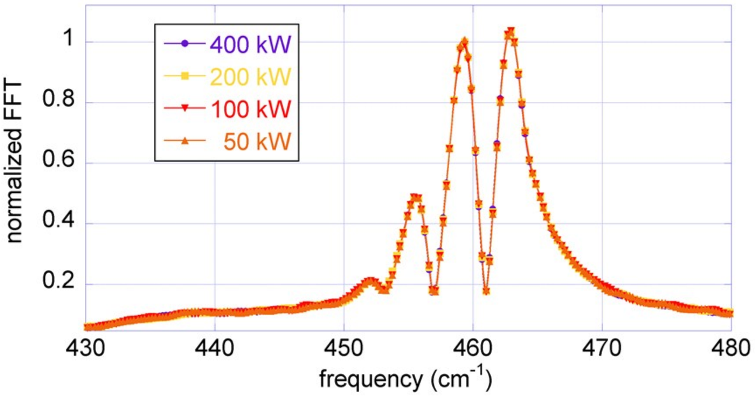


Fig.2. a) Fragment of time domain signal (the whole signal is shown in Fig.2a in the manuscript) in pure $CCl_4$ for four values of the pump power applied; b) $\nu_1$ band in pure $CCl_4$, obtained as FFT of the time domain signals for four values of the pump power applied , normalized with respect to the middle peak.