

Supplementary Information

I. Spontaneous Raman spectra of C_2Cl_4

For comparison we present also the spontaneous Raman spectra in order to find out what is the role of coherent excitation of molecules. The spontaneous Raman scattering spectra were acquired applying NXR-FT Raman Module Nicolette 6700 FT-IR spectrometer with a pump wavelength of $1\mu m$. The spectra were recorded in backward scattering geometry with a resolution of $1cm^{-1}$, for two configurations of polarizers, parallel (H) and perpendicular (V). There are five Raman active vibrational modes, i.e. three of them of A_g symmetry; $\nu_1=1571cm^{-1}$, $\nu_2=447cm^{-1}$ and $\nu_3=237cm^{-1}$ and two of them, $\nu_4=347cm^{-1}$ of B_{1g} and $\nu_5=512cm^{-1}$ of B_{2g} symmetry^{9,15,16}. Two last modes are not visible in the isotropic configuration:

$$I_{iso} = I_{HH} - \frac{4}{3}I_{HV} \quad (1)$$

Besides that in the isotropic part of the spectrum I_{iso} the influence of rotational dynamics of molecules is excluded. On the other side the anisotropic Raman line profiles $I_{aniso} = I_{HV}$ are dependent on molecular anisotropy. In Fig.S1 we present the Raman spectrum of intramolecular vibrations in the frequency range $150 - 600cm^{-1}$. We are not interested in higher frequency vibrations since they are not observed in our time resolved experiments. It can be seen that the isotropic signal, obtained according to Eq.1, contains only three peaks assigned to modes of A_g symmetry; around $447cm^{-1}$, around $237cm^{-1}$ and a small peak at $464cm^{-1}$. The first two correspond to fundamental vibrations of a C_2Cl_4 molecule, i.e. ν_2 is as the symmetric C-Cl stretching vibration in the plane of molecule ($\nu-CCL$)¹¹, and ν_3 is the symmetric CCl_2 deformation ($\delta-CCL_2$)¹¹. The small third peak has been identified as the overtone ($2\nu_3$)^{10,11} and does not occur in the anisotropic spectrum. In contrast to the ν_3 fundamental, the ν_2 one has a very weak anisotropic contribution, which is apparent in the I_{HV} signal in

Fig.S1. The depolarization ratios $\rho_{457} = \frac{I_{HV}}{I_{HH}} = 0.08$ and $\rho_{237} = \frac{I_{HV}}{I_{HH}} = 0.66$ obtained from the spectra in Fig.S1 are in good agreement with the results of other authors^{8,11,14}.

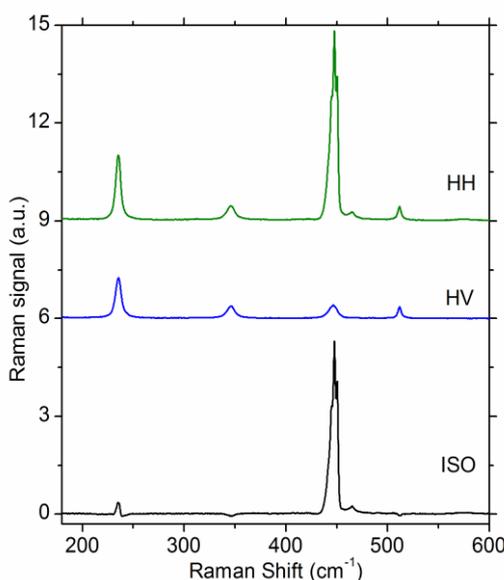


Fig.S1. Raman spectrum of C_2Cl_4 for two polarization configurations: the top spectrum (HH) was obtained for parallel polarizations of the scattered and incident light waves; the middle spectrum (HV) was obtained for perpendicular polarizations of the scattered and incident light waves; the bottom spectrum was obtained by subtraction of the middle spectrum from the top one according to Eq.1.

The depolarization ratios of two depolarized lines $\rho_{347} = \frac{I_{HV}}{I_{HH}} = 0.77$ and $\rho_{512} = \frac{I_{HV}}{I_{HH}} = 0.73$, are also close to the results of other authors^{8,11,14}. The isotropic part, shown in Fig.S2, exhibits evident splitting of the bands due to natural abundance

of chlorine isotopes. It can be seen even in a very weak 237cm^{-1} peak, shown in Fig.S3. The frequency spacing between succeeding peaks results from mass differences of ^{35}Cl and ^{37}Cl isotopes. According to the formula²⁵ $\Delta\omega_\lambda = \omega_\lambda \left(\frac{m_{^{37}\text{Cl}} - m_{^{35}\text{Cl}}}{8m_{^{35}\text{Cl}}} \right)$ it is estimated to be 3cm^{-1} for 447cm^{-1} band and 1.64cm^{-1} for 237cm^{-1} band.

Thus, the isotope fine structure of the Raman band is the most apparent for the ν_2 symmetrical stretching vibration. We have performed the curve-fit analysis of the 447cm^{-1} band, as shown in the bottom plot of Fig.S2. The contributions of particular isotopologues have been fitted by Gaussian-Lorentzian curves. It means that in the stochastic response the frequency modulations due to the distribution of the surrounding molecules is significant^{26,33}. The obtained amplitudes and life times of succeeding vibrations, calculated from the line peak widths, are shown in Table 1 of the main text.

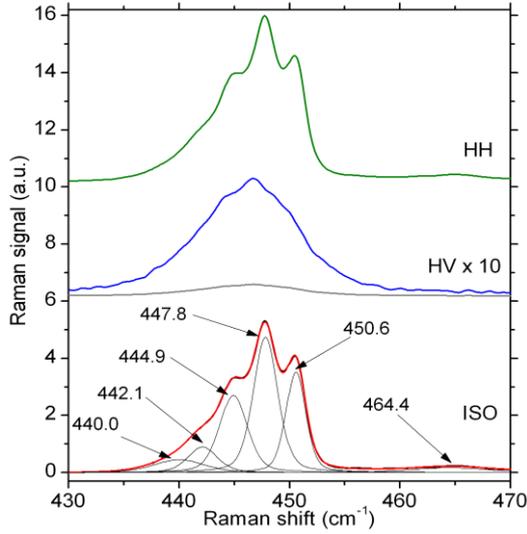


Fig.S2. Raman spectrum of the ν_2 fundamental obtained as the enlarged part of spectra in Fig.S1. In the bottom isotropic spectrum the black line is the experimental curve and the red line is the fit curve. The fine continuous lines show contributions of particular isotopologues. In the middle spectrum the grey line shows the real magnitude of the peak.

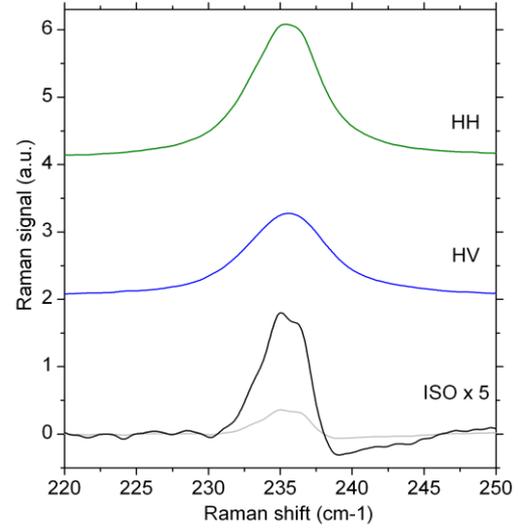
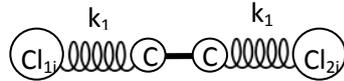


Fig.S3. Raman spectrum of the ν_3 fundamental obtained as the enlarged part of spectra in Fig.1. In the bottom spectrum the grey line shows the real magnitude of the peak.

II. The theoretical model of the medium:

Each C_2Cl_4 molecule is represented by a linear oscillator with two C atoms in the middle and Cl (^{35}Cl or ^{37}Cl) atoms on both sides. Since we do not see C-C stretching vibration in our time resolved measurements, for simplicity we assume that C-C bond is rigid:



We consider only longitudinal vibrations in line of the interatomic bonds. Thus, the intramolecular harmonic Hamiltonian has the form $H_0 = \frac{1}{2} \sum_{n=1}^2 k_1 (x_C - x_{\text{Cl}_n})^2$, 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, $^{35}\text{Cl-C-C-}^{35}\text{Cl}$, $^{37}\text{Cl-C-C-}^{37}\text{Cl}$, $^{35}\text{Cl-C-C-}^{37}\text{Cl}$. If we denote m_{Cl_i} , m_C as the masses of the chlorine and carbon atoms,

respectively, $M_i = m_{\text{Cl}_{1i}} + 2m_C + m_{\text{Cl}_{2i}}$ as the mass of the i -th molecule, and $\frac{1}{\mu_i} = \frac{1}{m_{\text{Cl}_{1i}}} + \frac{1}{m_{\text{Cl}_{2i}}}$ as the inverse reduced mass

of chlorine atoms in a given i -th molecule, then the general expressions for the normal square frequencies ω_λ^2 and the

appropriate coordinates q_λ in a single molecule, found with accuracy to the linear terms $\frac{m_{\text{Cl}_2} - m_{\text{Cl}_1}}{m_{\text{Cl}_1}}$, are the following:

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

for asymmetric stretching vibration, $\omega_{2i}^2 = \frac{k_1}{2\mu_i} + \frac{k_1}{m_C}$, and $q_{2i} = (x_{Cl_{1i}} + x_{Cl_{2i}} - 2x_{C_i}) - \frac{m_C}{\rho_i} (x_{Cl_{1i}} - x_{Cl_{2i}})$, (3)

where we have introduced $\frac{1}{\rho_i} = \frac{1}{m_{Cl_{1i}}} - \frac{1}{m_{Cl_{2i}}}$, which equals zero for symmetric molecules $^{35}\text{Cl-C-C-}^{35}\text{Cl}$ and $^{37}\text{Cl-C-C-}^{37}\text{Cl}$

since $m_{Cl_1} = m_{Cl_2}$. For asymmetric molecule $^{35}\text{Cl-C-C-}^{37}\text{Cl}$ the ratio $\frac{m_{Cl_2} - m_{Cl_1}}{m_{Cl_1}} \approx 0.06$. The symmetric stretching

vibration of such oscillators is Raman active and can correspond to both $\nu_2=447\text{cm}^{-1}$ and $\nu_3=237\text{cm}^{-1}$ fundamentals in C_2Cl_4 molecule for the appropriate k_1 values, which are assumed in our model as $k_1 \equiv k_{12} = m_{^{35}\text{Cl}}(2\pi\nu_2)^2$ or

$k_1 \equiv k_{13} = m_{^{37}\text{Cl}}(2\pi\nu_3)^2$. The asymmetric vibration in a linear symmetric molecule is Raman inactive.

We assume the medium as a set of dimers composed of two molecules parallel to each other:

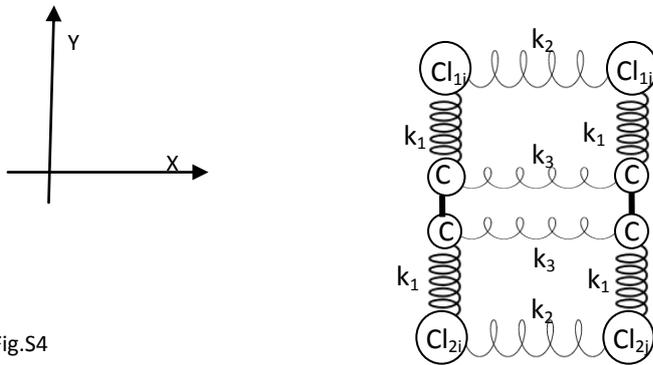


Fig.S4

where the interaction between the closest chlorine and carbon atoms belonging to different molecules i, j , is considered.

We have denoted the axes (x, y) of the momentary frame of reference connected with a dimer. In our simplified model we consider rigid-linear molecules, which means that we do not take into account intramolecular vibrations perpendicular to the molecular line. Then the intramolecular displacements of atoms along the molecular axes become directed along y axis

$\vec{y}_i = [0, y_i]$ and intramolecular Hamiltonian has the form $H_0 = \frac{1}{2} \sum_{i,n=1}^2 k_1 (y_{C_i} - y_{Cl_{ni}})^2$, where $i=1,2$ numbers molecules and

$n=1,2$ numbers Cl atoms in a molecule. The interaction Hamiltonian between atoms belonging to different molecules, $i \neq j$, results from expansion of pair Lennard-Jones potential in power series with respect to small atomic displacements. In our dimer we have $\bar{r}(Cl_{1i}, Cl_{1j}) = \bar{r}_0(Cl_i, Cl_j) + \Delta\bar{r}_{ij} = [R + \Delta x_{ij}, \Delta y_{ij}]$, and similarly for $\bar{r}(Cl_{2i}, Cl_{2j})$ and $\bar{r}(C_i, C_j)$. The equilibrium vector between atoms belonging to different i and j molecules has only x component, $\bar{r}_0(Cl_i, Cl_j) = \bar{r}_0(C_i, C_j) = [R, 0]$. In order to get the influence of transversal interactions on intramolecular vibrations, in the interaction Hamiltonian we have taken into account higher order anharmonic mixed terms:

$$H_I = \frac{1}{2} \sum_{\substack{i \neq j \\ s=1,2}} \left(k_2 (x_{Cl_{sj}} - x_{Cl_{si}})^2 + k_3 (x_{C_{sj}} - x_{C_{si}})^2 + (k_2/R)(x_{Cl_{sj}} - x_{Cl_{si}})(y_{Cl_{sj}} - y_{Cl_{si}})^2 + (k_3/R)(x_{C_{sj}} - x_{C_{si}})(y_{C_{sj}} - y_{C_{si}})^2 \right)$$

where k_2 denotes the intermolecular Cl-Cl force constant and k_3 denotes the intermolecular C-C force constant.

We will denote the l -th dimer as d_l , the left molecule with $j=1$ and the right molecule with $j=2$.

II.1. Equations of motions for small atomic displacements from the equilibrium positions in the l -th dimer are the following:

- for intramolecular displacements (in these equations both carbon atoms belonging to the same molecule have the same displacements):

$$\begin{aligned}
m_{Cl_{11}} \ddot{y}_{Cl_{11}} &= k_1(y_{C_1} - y_{Cl_{11}}) + k_2(x_{Cl_{12}} - x_{Cl_{11}})(y_{Cl_{12}} - y_{Cl_{11}}) / R \\
2m_C \ddot{y}_{C_1} &= k_1(y_{Cl_{11}} + y_{Cl_{21}} - 2y_{C_1}) + k_3(x_{C_{22}} + x_{C_{12}} - x_{C_{11}} - x_{C_{21}})(y_{C_2} - y_{C_1}) / R \\
m_{Cl_{21}} \ddot{y}_{Cl_{21}} &= -k_1(y_{Cl_{21}} - y_{C_1}) + k_2(x_{Cl_{22}} - x_{Cl_{21}})(y_{Cl_{22}} - y_{Cl_{21}}) / R \\
m_{Cl_{12}} \ddot{y}_{Cl_{12}} &= k_1(y_{C_2} - y_{Cl_{12}}) - k_2(x_{Cl_{12}} - x_{Cl_{11}})(y_{Cl_{12}} - y_{Cl_{11}}) / R \\
2m_C \ddot{y}_{C_2} &= k_1(y_{Cl_{12}} + y_{Cl_{22}} - 2y_{C_2}) - k_3(x_{C_{22}} + x_{C_{12}} - x_{C_{11}} - x_{C_{21}})(y_{C_2} - y_{C_1}) / R \\
m_{Cl_{22}} \ddot{y}_{Cl_{22}} &= k_1(y_{C_2} - y_{Cl_{22}}) - k_2(x_{Cl_{22}} - x_{Cl_{21}})(y_{Cl_{22}} - y_{Cl_{21}}) / R
\end{aligned} \tag{4a}$$

for displacements along x axis we remain only harmonic terms (in these equations the carbon atoms belonging to the same molecule may have different displacements):

$$\begin{aligned}
m_{Cl_{11}} \ddot{x}_{Cl_{11}} &= k_2(x_{Cl_{12}} - x_{Cl_{11}}) \\
m_C \ddot{x}_{C_{11}} &= k_3(x_{C_{12}} - x_{C_{11}}) \\
m_C \ddot{x}_{C_{21}} &= k_3(x_{C_{22}} - x_{C_{21}}) \\
m_{Cl_{21}} \ddot{x}_{Cl_{21}} &= k_2(x_{Cl_{22}} - x_{Cl_{21}}) \\
m_{Cl_{12}} \ddot{x}_{Cl_{12}} &= -k_2(x_{Cl_{12}} - x_{Cl_{11}}) \\
m_C \ddot{x}_{C_{12}} &= -k_3(x_{C_{12}} - x_{C_{11}}) \\
m_C \ddot{x}_{C_{22}} &= -k_3(x_{C_{22}} - x_{C_{21}}) \\
m_{Cl_{22}} \ddot{x}_{Cl_{22}} &= -k_2(x_{Cl_{22}} - x_{Cl_{21}})
\end{aligned} \tag{4b}$$

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

For each l -th dimer we introduce new coordinates being the combinations of the displacements. We will number the considered vibrations with index $\lambda=1,2,3,4,5,6,7,8,9,10,11,12$. Four of them are the amplitudes of normal vibrations of single molecules:

$$\begin{aligned}
Q_1 = q_{11} &= (y_{Cl_{11}} - y_{Cl_{21}}) + \frac{m_C}{\rho_1} (y_{Cl_{11}} + y_{Cl_{21}} - 2y_{C_1}); & Q_3 = q_{12} &= (y_{Cl_{12}} - y_{Cl_{22}}) + \frac{m_C}{\rho_2} (y_{Cl_{12}} + y_{Cl_{22}} - 2y_{C_2}); \\
Q_2 = q_{21} &= (y_{Cl_{11}} + y_{Cl_{21}} - 2y_{C_1}) - \frac{m_C}{\rho_1} (y_{Cl_{11}} - y_{Cl_{21}}); & Q_4 = q_{22} &= (y_{Cl_{12}} + y_{Cl_{22}} - 2y_{C_2}) - \frac{m_C}{\rho_2} (y_{Cl_{12}} - y_{Cl_{22}})
\end{aligned}$$

Then, there is the amplitude of the intermolecular interaction Q_5 , corresponding to the out of phase displacement of the whole molecules along y axis:

$$Q_5 = y_{Cl_{11}} + \frac{m_{Cl_{21}}}{m_{Cl_{11}}} y_{Cl_{21}} + \frac{2m_C}{m_{Cl_{11}}} (y_{C_1} - y_{C_2}) - \frac{m_{Cl_{12}}}{m_{Cl_{11}}} y_{Cl_{12}} - \frac{m_{Cl_{22}}}{m_{Cl_{11}}} y_{Cl_{22}} \tag{5a}$$

and the out of phase displacement of the whole molecules along x axis:

$$Q_6 = x_{Cl_{11}} + \frac{m_{Cl_{21}}}{m_{Cl_{11}}} x_{Cl_{21}} + \frac{m_C}{m_{Cl_{11}}} (x_{C_{11}} + x_{C_{21}} - x_{C_{12}} - x_{C_{22}}) - \frac{m_{Cl_{12}}}{m_{Cl_{11}}} x_{Cl_{12}} - \frac{m_{Cl_{22}}}{m_{Cl_{11}}} x_{Cl_{22}} \tag{5b}$$

Along x axis we introduce normal variables for the whole dimer:

$$\begin{aligned}
Q_7 &= (x_{Cl_{11}} + x_{C_{11}} - x_{Cl_{21}} - x_{C_{21}} - x_{Cl_{12}} - x_{C_{12}} + x_{Cl_{22}} + x_{C_{22}}) / 2\sqrt{2}; \\
Q_8 &= (x_{Cl_{11}} + x_{C_{11}} - x_{Cl_{21}} - x_{C_{21}} + x_{Cl_{12}} + x_{C_{12}} - x_{Cl_{22}} - x_{C_{22}}) / 2\sqrt{2}; \\
Q_9 &= (x_{Cl_{11}} + x_{Cl_{21}} + x_{Cl_{12}} + x_{Cl_{22}} - (x_{C_{11}} + x_{C_{21}} + x_{C_{12}} + x_{C_{22}})) / 2\sqrt{2}; \\
Q_{10} &= (x_{Cl_{11}} + x_{Cl_{21}} - x_{Cl_{12}} - x_{Cl_{22}} - (x_{C_{11}} + x_{C_{21}} - x_{C_{12}} - x_{C_{22}})) / 2\sqrt{2};
\end{aligned}$$

$$\begin{aligned}
Q_{11} &= (x_{Cl_{11}} - x_{C_{11}} - x_{Cl_{21}} + x_{C_{21}} + x_{Cl_{12}} - x_{C_{12}} - x_{Cl_{22}} + x_{C_{22}}) / 2\sqrt{2}; \\
Q_{12} &= (x_{Cl_{11}} - x_{C_{11}} - x_{Cl_{21}} + x_{C_{21}} - x_{Cl_{12}} + x_{C_{12}} + x_{Cl_{22}} - x_{C_{22}}) / 2\sqrt{2};
\end{aligned} \tag{6}$$

The conditions of the center of mass frame of reference have the form:

$$\begin{aligned}
0 &= x_{Cl_{11}} + \frac{m_{Cl_{21}}}{m_{Cl_{11}}} x_{Cl_{21}} + \frac{m_C}{m_{Cl_{11}}} (x_{C_{11}} + x_{C_{21}} + x_{C_{12}} + x_{C_{22}}) + \frac{m_{Cl_{12}}}{m_{Cl_{11}}} x_{Cl_{12}} + \frac{m_{Cl_{22}}}{m_{Cl_{11}}} x_{Cl_{22}} \\
0 &= y_{Cl_{11}} + \frac{m_{Cl_{21}}}{m_{Cl_{11}}} y_{Cl_{21}} + \frac{2m_C}{m_{Cl_{11}}} (y_{C_1} + y_{C_2}) + \frac{m_{Cl_{12}}}{m_{Cl_{11}}} y_{Cl_{12}} + \frac{m_{Cl_{22}}}{m_{Cl_{11}}} y_{Cl_{22}}
\end{aligned} \tag{7}$$

The model simplifies if we consider the rigid plane molecules. Then $Q_9 = Q_{10} = Q_{11} = Q_{12} = 0$, and there are possible only the following combinations of displacements:

$$1) x_{Cl_{11}} = x_{Cl_{21}} = x_{C_{11}} = x_{C_{21}} \equiv x_1; \quad x_{Cl_{12}} = x_{Cl_{22}} = x_{C_{12}} = x_{C_{22}} \equiv x_2,$$

what corresponds to translational vibrations of the whole molecules. The out-of-phase vibration is defined by

$$\bar{Q}_6 = (x_1 - x_2) = \frac{m_{Cl_{11}}}{2} \left(\frac{1}{M_1} + \frac{1}{M_2} \right) Q_6.$$

2) $x_{Cl_{11}} = -x_{Cl_{21}}$; $x_{Cl_{12}} = -x_{Cl_{22}}$ and $x_{C_{11}} = -x_{C_{21}}$; $x_{C_{12}} = -x_{C_{22}}$ what corresponds to oscillations of molecules around their centers of mass. It becomes obvious if we put $x_{Cl_{11}} \equiv r_0 \Theta_1$, $x_{Cl_{12}} \equiv r_0 \Theta_2$ and $x_{C_{11}} \equiv r_{10} \Theta_1$, $x_{C_{12}} \equiv r_{10} \Theta_2$, where

$r_0 = r_0(C, Cl) + r_{10}$ and $r_{10} = \frac{1}{2} r_0(C, C)$ are the distances of chlorine and carbon atoms from the center of mass of a

molecule, respectively, and Θ_i denotes the angular displacement of molecular line from the dimer y axis. Then we have

and $Q_7 = (x_{Cl_{11}} + x_{C_{11}} - x_{Cl_{12}} - x_{C_{12}}) / 2 \equiv (r_0 + r_{10})(\Theta_1 - \Theta_2) / 2$ - out of phase oscillations

$Q_8 = (x_{Cl_{11}} + x_{C_{11}} + x_{Cl_{12}} + x_{C_{12}}) / 2 \equiv (r_0 + r_{10})(\Theta_1 + \Theta_2) / 2$ - in phase oscillations.

Then from Eqs.(6) we have:

$$\begin{aligned}
x_{Cl_{11}} - x_{Cl_{12}} &= 2\bar{Q}_7 \left(\frac{m_{Cl_{21}} + m_C}{M_1} + \frac{m_{Cl_{22}} + m_C}{M_2} \right) + \bar{Q}_6 - 2\bar{Q}_8 \left(\frac{m_{Cl_{21}} - m_{Cl_{11}}}{M_1} - \frac{m_{Cl_{22}} - m_{Cl_{12}}}{M_2} \right) \\
x_{Cl_{21}} - x_{Cl_{22}} &= -2\bar{Q}_7 \left(\frac{m_{Cl_{11}} + m_C}{M_1} + \frac{m_{Cl_{12}} + m_C}{M_2} \right) + \bar{Q}_6 - 2\bar{Q}_8 \left(\frac{m_{Cl_{21}} - m_{Cl_{11}}}{M_1} - \frac{m_{Cl_{22}} - m_{Cl_{12}}}{M_2} \right),
\end{aligned} \quad \text{and}$$

where we have introduced the denotations: $\bar{Q}_7 = Q_7 \left(1 + \frac{r_{10}}{r_0} \right)^{-1}$ and $\bar{Q}_8 = Q_8 \left(1 + \frac{r_{10}}{r_0} \right)^{-1}$.

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 eight amplitudes with a damping term and the driving force $f_\lambda = P_{kl}^{(1)}(\lambda) F_k F_l(t)$,

where $P_{kl}^{(1)}(\lambda)$ denotes the first derivative of the medium polarizability with respect to the appropriate normal amplitude

Q_λ and $F_k(t) = ((\epsilon_0 + 2)/3) E_k^{pump}(t)$. We have assumed the optical pump field to have a Gaussian envelope,

$E_i^{pump}(t) = E_i e^{-(t/2\Delta t)^2} e^{i\omega t}$; Δt is the pulse width, ω is the central frequency, and the pump optical field is linearly polarized.

The equations of motion for all modes in a dimer, $Q_1 = q_{11}, Q_2 = q_{21}, Q_3 = q_{12}, Q_4 = q_{22}, Q_5, Q_6, Q_7, Q_8$, with accuracy to $\frac{1}{\rho_i}$ terms, are the following:

$$\begin{aligned}
Q''_1 &= -\frac{k_1}{2\mu_1}Q_1 - \Gamma_1 Q'_1 - \frac{k_2}{2R\mu_1} \left(2\bar{Q}_7(Q_2 - Q_4 - 2(y_{C_2} - y_{C_1})) + \bar{Q}_6(Q_3 - Q_1) \right) \\
&\quad - \frac{k_2}{2R\rho_1} \left(2\bar{Q}_7(Q_1 + Q_3) + \bar{Q}_6(Q_4 - Q_2 + 2(y_{C_2} - y_{C_1})) \right) + f_1 \\
Q''_2 &= -\left(\frac{k_1}{2\mu_1} + \frac{k_1}{m_C} \right) Q_2 - \Gamma_2 Q'_2 + \frac{k_2}{2R\mu_1} \left(2\bar{Q}_7(Q_1 - Q_3) - \bar{Q}_6(Q_4 - Q_2 + 2(y_{C_2} - y_{C_1})) \right) \\
&\quad + \frac{k_2}{2R\rho_1} \left(2\bar{Q}_7(Q_4 - Q_2 + 2(y_{C_2} - y_{C_1})) - \bar{Q}_6(Q_1 + Q_3) \right) + \frac{k_3}{m_C} \bar{Q}_6(y_{C_2} - y_{C_1}) + f_2 \\
Q''_3 &= -\frac{k_1}{2\mu_2}Q_3 - \Gamma_3 Q'_3 + \frac{k_2}{2R\mu_2} \left(2\bar{Q}_7(Q_2 - Q_4 - 2(y_{C_2} - y_{C_1})) + \bar{Q}_6(Q_3 - Q_1) \right) \\
&\quad + \frac{k_2}{2R\rho_2} \left(2\bar{Q}_7(Q_1 + Q_3) + \bar{Q}_6(Q_4 - Q_2 + 2(y_{C_2} - y_{C_1})) \right) + f_3 \\
Q''_4 &= -\left(\frac{k_1}{2\mu_2} + \frac{k_1}{m_C} \right) Q_4 - \Gamma_4 Q'_4 - \frac{k_2}{2R\mu_2} \left(2\bar{Q}_7(Q_1 - Q_3) - \bar{Q}_6(Q_4 - Q_2 + 2(y_{C_2} - y_{C_1})) \right) \\
&\quad - \frac{k_2}{2R\rho_2} \left(2\bar{Q}_7(Q_4 - Q_2 + 2(y_{C_2} - y_{C_1})) - \bar{Q}_6(Q_1 + Q_3) \right) - \frac{k_3}{m_C} \bar{Q}_6(y_{C_2} - y_{C_1}) + f_4 \\
Q''_5 &= 2 \frac{k_2}{m_{Cl_{11}}} \left(2\bar{Q}_7(Q_1 - Q_3) + \bar{Q}_6(Q_2 - Q_4) \right) - \frac{2k_3 + 4k_2}{m_{Cl_{11}}} \bar{Q}_6(y_{C_2} - y_{C_1}) - \Gamma_5 Q'_5 + f_5 \\
\bar{Q}''_6 &= -(2k_2 + 2k_3) \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \left(\bar{Q}_6 - 2\bar{Q}_7 \left(\frac{m_{Cl_{11}} m_{Cl_{21}}}{\rho_1 M_1} + \frac{m_{Cl_{12}} m_{Cl_{22}}}{\rho_2 M_2} \right) - 2\bar{Q}_8 \left(\frac{m_{Cl_{11}} m_{Cl_{21}}}{\rho_1 M_1} - \frac{m_{Cl_{12}} m_{Cl_{22}}}{\rho_2 M_2} \right) \right) - \Gamma_6 \bar{Q}'_6 + f_6 \\
Q''_7 &= -\left[k_2 \left(\frac{1}{\mu_1} + \frac{1}{\mu_2} \right) \left(\frac{m_C + m_{Cl_{11}}}{M_1} + \frac{m_C + m_{Cl_{12}}}{M_2} \right) + k_2 \left(\frac{1}{m_{Cl_{11}}} + \frac{1}{m_{Cl_{12}}} \right) \left(\frac{m_{Cl_{21}} m_{Cl_{11}}}{\rho_1 M_1} + \frac{m_{Cl_{12}} m_{Cl_{22}}}{\rho_2 M_2} \right) + \frac{2k_3 r_{10}}{m_C r_0} \right] \bar{Q}_7 + \\
&\quad - k_2 \left(\frac{1}{\rho_1} - \frac{1}{\rho_2} \right) \bar{Q}_6 - \Gamma_7 Q'_7 + f_7 \\
Q''_8 &= -k_2 \left(\frac{1}{\mu_1} - \frac{1}{\mu_2} \right) \left[\left(\frac{m_{Cl_{11}} m_{Cl_{21}}}{\rho_1 M_1} - \frac{m_{Cl_{12}} m_{Cl_{22}}}{\rho_2 M_2} \right) \bar{Q}_8 - \bar{Q}_6 \right] - k_2 \left[\left(\frac{1}{\mu_1} - \frac{1}{\mu_2} \right) \left(\frac{m_C + m_{Cl_{11}}}{M_1} + \frac{m_C + m_{Cl_{12}}}{M_2} \right) \right] \bar{Q}_7 - \Gamma_8 Q'_8 + f_8
\end{aligned} \tag{8}$$

where $(y_{C_2} - y_{C_1})$ is the combination of normal amplitudes:

$$\begin{aligned}
y_{C_2} - y_{C_1} &= -\frac{m_{Cl_{11}}}{2} \left(\frac{1}{M_1} + \frac{1}{M_2} \right) Q_5 + \frac{1}{2M_1} (m_{Cl_{11}} - m_{Cl_{21}}) Q_1 + \frac{1}{2M_1} (m_{Cl_{11}} + m_{Cl_{21}}) Q_2 \\
&\quad - \frac{1}{2M_2} (m_{Cl_{12}} - m_{Cl_{22}}) Q_3 - \frac{1}{2M_2} (m_{Cl_{12}} + m_{Cl_{22}}) Q_4
\end{aligned} \tag{8a}$$

It can be seen that the equation of motion for Q_7 describes librations of molecules within the dimer with frequency dependent on the intermolecular interaction coefficients k_2 and k_3 . In asymmetric dimers the frequency of in-phase libration Q_8 is proportional to $\frac{1}{\rho_i^2}$. On the other hand, in symmetric dimers the equation for Q_8 describes free rotation of both molecules. If the displacements of both molecules are equal it corresponds to free rotation of the dimer.

In the case of symmetric dimers composed of two identical molecules, $\mu_1 = \mu_2 = \mu$, $M_1 = M_2 = M$ and $\rho_1 = \rho_2 = \rho$, 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 $\bar{Q}_1 = (q_{11} + q_{12})/2 = (Q_1 + Q_3)/2$,

$$\bar{Q}''_1 = -\frac{k_1}{2\mu} \bar{Q}_1 - \Gamma_1 \bar{Q}'_1 + \bar{f}_1 \quad (9a)$$

- for out-of-phase symmetric vibration $\bar{Q}_2 = (q_{11} - q_{12})/2 = (Q_1 - Q_3)/2$,

$$\bar{Q}''_2 = -\frac{k_1}{2\mu} \bar{Q}_2 - \Gamma_1 \bar{Q}'_2 - \frac{k_2}{2R\mu} (2\bar{Q}_7 \bar{Q}_3) - \bar{Q}_6 \bar{Q}_2 - \frac{k_2}{2R\rho} (2\bar{Q}_7 \bar{Q}_1 - \bar{Q}_2 \bar{Q}_3) + \bar{f}_2 \quad (9b)$$

- for out-of-phase asymmetric vibration $\bar{Q}_3 = (q_{21} - q_{22})/2 = (Q_2 - Q_4)/2$

$$\bar{Q}''_3 = -\left(\frac{k_1}{2\mu} + \frac{k_1}{m_C}\right) \bar{Q}_3 - \Gamma_2 \bar{Q}'_3 + \frac{k_2}{2R\mu} (2\bar{Q}_7 \bar{Q}_2 + \bar{Q}_6 \bar{Q}_3) + \frac{k_2}{2R\rho} (2\bar{Q}_7 \bar{Q}_3 - \bar{Q}_6 \bar{Q}_1) + \frac{k_3}{m_C} \bar{Q}_6 (y_{C_2} - y_{C_1}) + \bar{f}_3 \quad (9c)$$

- for in-phase asymmetric vibration $\bar{Q}_4 = (q_{21} + q_{22})/2 = (Q_2 + Q_4)/2$,

$$\bar{Q}''_4 = -\left(\frac{k_1}{2\mu} + \frac{k_1}{m_C}\right) \bar{Q}_4 - \Gamma_2 \bar{Q}'_4 + \bar{f}_4 \quad (9d)$$

- for intermolecular out-of-phase vibration

$$Q''_5 = 2 \frac{k_2}{m_{Cl_1}} (2\bar{Q}_7 Q_2 + \bar{Q}_6 Q_3) - \frac{2k_3 + 4k_2}{m_{Cl_1}} \bar{Q}_6 (y_{C_2} - y_{C_1}) - \Gamma_5 Q'_5 + f_5 \quad (9e)$$

where $M = 2m_C + m_{Cl_1} + m_{Cl_2}$, μ , $\Delta m = m_{Cl_2} - m_{Cl_1}$ and r , respectively, are specified for a given symmetric dimer.

$\bar{f}_1 = (f_1 + f_3)/2$; $\bar{f}_2 = (f_1 - f_3)/2$; $\bar{f}_3 = (f_2 - f_4)/2$; $\bar{f}_4 = (f_2 + f_4)/2$. The index l numbering the dimers has been omitted.

$$\bar{Q}''_6 = -\frac{2(2k_2 + 2k_3)}{M} \bar{Q}_6 - \Gamma_6 \bar{Q}'_6 + f_6$$

$$Q''_7 = -\left[4 \frac{k_2}{\mu} + \frac{2k_3 r_{10}}{m_C r_0}\right] \bar{Q}_7 - \Gamma_7 Q'_7 + f_7 \quad (9f)$$

$$Q''_8 = -\Gamma_8 Q'_8 + f_8$$

It can be seen in Eqs.(9) that the in-phase vibrations in symmetric dimers are unaffected by intermolecular interactions. The equation for Q_8 describes free rotation of both molecules.

II. 2. Polarizability

In order to find the first order derivatives of the medium polarizability with respect to vibrational amplitudes, $P_{kl}^{(1)}(\lambda)$, we have calculated the polarizabilities of all dimers, applying the Silberstein model²⁸:

$$P_{rs} = \sum_{n=1}^6 \alpha_{rs}^{eff}(n), \quad (10)$$

where with accuracy to the terms of order of $\frac{\alpha^2}{r_{nn'}^6}$ we have taken the effective polarizabilities in the form;

$$\alpha_{rs}^{eff}(n) = \alpha(n) \left\{ \delta_{rs} + \sum_{n'} \frac{\alpha(n')}{r_{nn'}^3} \left[3 \frac{r_{r,nn'} r_{k,nn'}}{r_{nn'}^2} - \delta_{rk} \right] \left[\delta_{ks} + \sum_{n''} \frac{\alpha(n'')}{r_{n'n''}^3} \left(3 \frac{r_{s,n'n''} r_{k,n'n''}}{r_{n'n''}^2} - \delta_{ks} \right) \right] \right\} \quad (10a)$$

with $r_{k,nn'} = r_{0k}(n, n') + \Delta r_{k,nn'}$, and $\alpha(n)$ denotes the polarizability of the n -th atom. The summation is performed over the nearest neighbors. We have applied the values of undisturbed polarizabilities, $\alpha_C = 0.88 \cdot 10^{-24} \text{ cm}^3$ for carbon atom and $\alpha_{Cl} = 1.91 \cdot 10^{-24} \text{ cm}^3$ for chlorine atom, from reference [28], assuming that $\alpha_{35Cl} = \alpha_{37Cl}$, and the equilibrium distances between carbon and chlorine atoms, $r_0 = r_0(C, Cl) = 1.7 \cdot 10^{-8} \text{ cm}$ and two carbon atoms, $r_{01} = r_0(C, C) = 1.3 \cdot 10^{-8} \text{ cm}$, are the same as in C_2Cl_4 molecule taken from refs.[10, 11].

II.2.1 For isotropic dimer polarizability, $P_{iso} = \frac{1}{3}(P_{xx} + P_{yy} + P_{zz})$, the dependence on atomic displacements appears

only in terms of order of $\frac{\alpha^2}{r_{nn'}^6}$. The first order derivatives of isotropic polarizability do not vanish only for in-phase

symmetric stretching vibrations, $Q_1 = q_{11}$ and $Q_3 = q_{12}$ (in asymmetric dimers) or \bar{Q}_1 (in symmetric dimers), and for intermolecular translational mode Q_6 . The fit of the TT signal in Fig.1. was obtained applying formula:

$$P_{iso}^{(1)} = P_{iso}^{(1)}(1)(Q_1 + Q_3) + P_{iso}^{(1)}(6)Q_6 \quad (11)$$

where

$$P_{iso}^{(1)}(1) = P_{iso}^{(1)}(3) = -\frac{12}{r_0^4} \left(\frac{\alpha_C \alpha_{Cl}^2 + \alpha_C^2 \alpha_{Cl}}{r_o^3} + \frac{\alpha_C^2 \alpha_{Cl}}{r_{o1}^3} - \frac{\alpha_C \alpha_{Cl}^2 + \alpha_C^2 \alpha_{Cl}}{R^3} \right) \quad (11a)$$

$$P_{iso}^{(1)}(6) = -\frac{12}{R^4} \left(\frac{2\alpha_{Cl}^3 + \alpha_C^3}{R^3} + 2 \frac{\alpha_C \alpha_{Cl}^2 + \alpha_C^2 \alpha_{Cl}}{r_0^3} \right)$$

where r_0 denotes the length of the C-Cl bond and R is the distance between the molecular centers of mass in Fig.S4. In the SI units the formulas should be multiplied by the factor $4\pi\epsilon_0$. Eq.(11) shows why the isotropic response obtained in time

resolved TT spectroscopy, $R_{iso} \propto 3 \frac{N}{V} (P_{iso}^{(1)})^2$, where N/V is the number density of dimers, includes only two symmetric

polarized vibrations. Since the sums of amplitudes ($Q_1 + Q_3$) in asymmetric dimers exhibit the small dependence on k_2 , proportional to $1/r$, (Eq.(8)), and in symmetric dimers there is no dependence at all, Eq.(9), the TT signal is almost not

influenced by intermolecular vibrations. For atomic polarizabilities $\alpha_C = 0.88 \cdot 10^{-24} \text{ cm}^3$ and $\alpha_{Cl} = 1.91 \cdot 10^{-24} \text{ cm}^3$, the inter-atomic distances $r_0 = r_0(C, Cl) = 1.7 \cdot 10^{-8} \text{ cm}$, $r_{01} = r_0(C, C) = 1.3 \cdot 10^{-8} \text{ cm}$ and

$r_0(Cl_i, Cl_j) = r_0(C_i, C_j) = R = 4 \cdot 10^{-8} \text{ cm}$, the calculated values of the isotropic dimer polarizability derivatives are the

following: $P_{iso}^{(1)}(1) = -2.2 \cdot 10^{-16} \text{ cm}^2$, $P_{iso}^{(1)}(6) = 0.1 \cdot 10^{-16} \text{ cm}^2$. It can be seen that the contribution of intramolecular stretching vibrations is dominating in the isotropic response of C_2Cl_4 liquid.

II.2.2. The anisotropic part of the dimer polarizability exhibits the dependence on atomic displacements already in terms

of order of $\frac{\alpha}{r_{nn'}^3}$ (see Eq.(10a):

$$P_{aniso} = \frac{1}{3} \sum_{n,n'} \frac{\alpha(n)\alpha(n')}{r^5(n,n')} \begin{bmatrix} 3x^2 - r^2 & 3xy & 0 \\ 3xy & 3y^2 - r^2 & 0 \\ 0 & 0 & -r^2 \end{bmatrix}, \text{ where } x, y \text{ are the components of vector } \vec{r}(n, n') \text{ and}$$

$$r \equiv r(n, n') = \sqrt{x^2 + y^2}.$$

The first order derivatives of anisotropic polarizability of a dimer for particular modes have the form:

$$P_{aniso}^{(1)}(1) = \frac{2\alpha(Cl)\alpha(C)}{r_0^4} \begin{bmatrix} 1 & 0 & 0 \\ 0 & -2 & 0 \\ 0 & 0 & 1 \end{bmatrix} + \frac{(2\alpha^2(Cl) + \alpha^2(C))(m_{Cl_{11}} - m_{Cl_{21}})}{M_1 R^4} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (12a)$$

$$P_{aniso}^{(1)}(2) = \frac{(-4m_C \alpha^2(Cl) + (m_{Cl_{11}} + m_{Cl_{21}})\alpha^2(C))}{M_1 R^4} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (12b)$$

$$P_{aniso}^{(1)}(3) = \frac{2\alpha(Cl)\alpha(C)}{r_0^4} \begin{bmatrix} 1 & 0 & 0 \\ 0 & -2 & 0 \\ 0 & 0 & 1 \end{bmatrix} - \frac{(2\alpha^2(Cl) + \alpha^2(C))(m_{Cl_{12}} - m_{Cl_{22}})}{M_2 R^4} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (12c)$$

$$P_{aniso}^{(1)}(4) = \frac{(4m_C \alpha^2(Cl) - (m_{Cl_{21}} + m_{Cl_{22}})\alpha^2(C))}{M_2 R^4} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (12d)$$

$$P_{aniso}^{(1)}(5) = -\frac{m_{Cl_{11}}(2\alpha^2(Cl) + \alpha^2(C))}{R^4} \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (12e)$$

$$P_{aniso}^{(1)}(6) = \frac{4\alpha(Cl)\alpha(C)}{r_0^4} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} + \frac{(4\alpha^2(Cl) + 2\alpha^2(C))}{R^4} \begin{bmatrix} -2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}; \quad P_{aniso}^{(1)}(7) = 0 \quad (12f)$$

$$P_{aniso}^{(1)}(8) = \left(\frac{4\alpha(Cl)\alpha(C)}{r_0^4} + \frac{2\alpha^2(C)}{r_0^4} \right) \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (12g)$$

For symmetric dimers the following derivatives have simpler forms:

$$P_{aniso}^{(1)}(\bar{Q}_1) = \frac{2\alpha(Cl)\alpha(C)}{r_0^4} \begin{bmatrix} 1 & 0 & 0 \\ 0 & -2 & 0 \\ 0 & 0 & 1 \end{bmatrix}; \quad P_{aniso}^{(1)}(\bar{Q}_2) = \frac{(2\alpha^2(Cl) + \alpha^2(C))(m_{Cl_1} - m_{Cl_2})}{MR^4} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}; \quad P_{aniso}^{(1)}(\bar{Q}_4) = 0$$

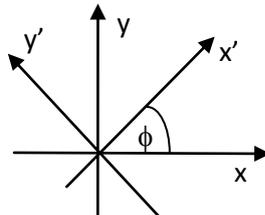
$$P_{aniso}^{(1)}(\bar{Q}_3) = \frac{(4m_C \alpha^2(Cl) - (m_{Cl_1} + m_{Cl_2})\alpha^2(C))}{MR^4} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}; \quad P_{aniso}^{(1)}(Q_5) = -\frac{2m_{Cl_1}(2\alpha^2(Cl) + \alpha^2(C))}{MR^4} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$P_{ij, aniso}^{(1)}(\text{dim } er) = \sum_{\lambda=1}^8 P_{ij, aniso}^{(1)}(\lambda) Q_\lambda$$

In the dimer model presented here the libration Q_7 is Raman inactive, $P_{aniso}^{(1)}(Q_7) = 0$, which is not in agreement with experimental results. In the next section we show the low frequency libration contribution in OKE spectrum. In order to correct our model, just with respect to this vibration we would have to add the third molecule parallel to both previous ones. In such a configuration two side molecules librate in-phase and the middle one out-of-phase. The contribution from this vibration equals $P_{aniso}^{(1)}(Q_8)$.

The anisotropic response obtained in OKE spectroscopy is proportional to products $\langle P_{II}^{(1)}(\lambda) P_{JJ}^{(1)}(\lambda) \rangle$, where I, J denote the axes of the laboratory frame of reference and the averaging is performed over all possible directions of dimer axes. Assuming that the light wave propagates along Z axis and the electric field of the pump pulse is polarized along X axis, we look for the differences $\langle P_{XX}^{(1)}(\lambda) P_{XX}^{(1)}(\lambda) \rangle - \langle P_{YY}^{(1)}(\lambda) P_{XX}^{(1)}(\lambda) \rangle$.

Let us consider the simplest configuration, in which the dimer axes (x,y) are rotated around Z axis with respect to the



laboratory frame of reference (X, Y) :

Then the dimer polarizability derivative for each mode, in laboratory frame of reference, has the form:

$$P_{aniso}^{(1)}(\lambda) = \begin{bmatrix} P_{xx}^{(1)} \cos^2 \Phi + P_{yy}^{(1)} \sin^2 \Phi - P_{xy}^{(1)} \sin 2\Phi & (P_{xx}^{(1)} - P_{yy}^{(1)}) \sin 2\Phi / 2 + P_{xy}^{(1)} \cos 2\Phi & 0 \\ (P_{xx}^{(1)} - P_{yy}^{(1)}) \sin 2\Phi / 2 + P_{xy}^{(1)} \cos 2\Phi & P_{xx}^{(1)} \sin^2 \Phi + P_{yy}^{(1)} \cos^2 \Phi + P_{xy}^{(1)} \sin 2\Phi & 0 \\ 0 & 0 & P_{zz}^{(1)} \end{bmatrix} \quad (13)$$

If we take into account that molecules rotate simultaneously with vibrations, then the rotation angle is time dependent, $\Phi(t)$, and the nuclear part of the OKE response takes the form:

$$\Delta n_{XX} - \Delta n_{YY} \propto \frac{N}{V} \sum_{\lambda} \{ (P_{xx}^{(1)}(\lambda) - P_{yy}^{(1)}(\lambda)) \cos 2\Phi(t) - 2P_{xy}^{(1)}(\lambda) \sin 2\Phi(t) \} Q_{\lambda}(t) \quad (14)$$

Substituting solutions $Q_{\lambda}(t)$ of Eqs. (8) or Eqs.(9) into Eq.(14) we get the final form of the OKE signal:

$$\Delta n_{XX} - \Delta n_{YY} \propto \frac{N}{V} \sum_{\lambda} \{ (P_{xx}^{(1)}(\lambda) - P_{yy}^{(1)}(\lambda))^2 \langle \cos 2\Phi(t) \cos^2 \Phi(0) \rangle + 2(P_{xy}^{(1)}(\lambda))^2 \langle \sin 2\Phi(t) \sin 2\Phi(0) \rangle \} F_{\lambda}(t) \quad (15)$$

where $F_{\lambda}(t) = \int_{-\infty}^t G_{\lambda}(t-t') |E_X|^2(t') dt'$ and $G_{\lambda}(t-t')$ is the Green's function for the appropriate Eq.(7) for $Q_{\lambda}(t)$. The

rotational correlation functions were shown¹⁹ to decay in time as $e^{-\frac{t}{\tau_{rot}}}$. Formula (15) was used to fit OKE signal in Fig.3.

In symmetric dimers the calculated contributions of particular modes in Eq. (15) are the following:

for the in-phase symmetric stretching vibration: $(P_{xx}^{(1)} - P_{yy}^{(1)}) \langle \bar{Q}_1 \rangle = 1.2 \cdot 10^{-16} \text{ cm}^2$; the out-of phase symmetric vibration is

Raman active only for asymmetric molecules $m_{Cl1} \neq m_{Cl2}$: $P_{xy}^{(1)} \langle \bar{Q}_2 \rangle = 0.00007 \cdot 10^{-16} \text{ cm}^2$;

for the out-of-phase asymmetric vibration: $P_{xy}^{(1)} \langle \bar{Q}_3 \rangle = 0.005 \cdot 10^{-16} \text{ cm}^2$;

the in-phase asymmetric vibration is Raman inactive: $P_{ij}^{(1)} \langle \bar{Q}_4 \rangle = 0$;

for the translational nonlinear vibration: $P_{xy}^{(1)} \langle \bar{Q}_5 \rangle = 0.023 \cdot 10^{-16} \text{ cm}^2$;

for translational vibration: $P_{xy}^{(1)} \langle \bar{Q}_6 \rangle = 0.9 \cdot 10^{-16} \text{ cm}^2$ and $(P_{xx}^{(1)} - P_{yy}^{(1)}) \langle \bar{Q}_6 \rangle = 0.06 \cdot 10^{-16} \text{ cm}^2$;

and for rotational vibration: $P_{xy}^{(1)} \langle \bar{Q}_8 \rangle = 1.35 \cdot 10^{-16} \text{ cm}^2$.

In asymmetric dimers the calculated contributions of particular modes in Eq. (15) are the following:

for Q_1 mode: $(P_{xx}^{(1)} - P_{yy}^{(1)}) \langle 1 \rangle = 1.2 \cdot 10^{-16} \text{ cm}^2$ and $P_{xy}^{(1)} \langle 1 \rangle = 0.00007 \cdot 10^{-16} \text{ cm}^2$;

for Q_3 mode: $(P_{xx}^{(1)} - P_{yy}^{(1)}) \langle 1 \rangle = 1.2 \cdot 10^{-16} \text{ cm}^2$ and $P_{xy}^{(1)} \langle 1 \rangle = -0.00007 \cdot 10^{-16} \text{ cm}^2$;

for Q_2 and Q_4 modes: $P_{xy}^{(1)} \langle 2 \rangle = -P_{xy}^{(1)} \langle 4 \rangle = 0.005 \cdot 10^{-16} \text{ cm}^2$.

It can be seen that, in our model, the main contribution to the OKE spectrum comes from the in-phase symmetric stretching vibrations ν_2 and ν_3 , in the range $200\text{-}600 \text{ cm}^{-1}$, and from rotational and translational vibrations in the low frequency part of the spectrum, $\nu < 100 \text{ cm}^{-1}$. Full OKE spectrum is shown in Fig.S7 below.

III. Polarizability tensors for real C_2Cl_4 molecule

In order to differentiate the contributions of both A_{1g} intramolecular modes, $\nu_2=447 \text{ cm}^{-1}$ and $\nu_3=237 \text{ cm}^{-1}$, in both isotropic and anisotropic responses, we have to calculate first order derivatives of the molecular polarizability of the real C_2Cl_4 molecule. We assume that the molecule lies in (y,z) plane (see Fig.S5), perpendicular to the dimer plane shown in Fig.S4. Black circles denote C atoms and white circles denote Cl atoms. For simplicity we assume that the angle between CCl bonds and y axis equals 60° .

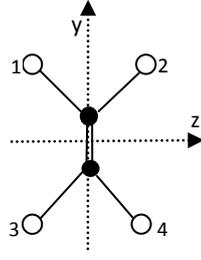


Fig.S5

Polarizability tensor of C_2Cl_4 molecule, calculated on the basis of Eq.(10) and Eq.(10a), has the form:

$$P_{mol} = \begin{bmatrix} 9.33 & & \\ & 11.46 & \\ & & 17.64 \end{bmatrix} \cdot 10^{-24} \text{ cm}^3, \text{ which gives the average value } \bar{\alpha}_{mol} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 = 12.8 \cdot 10^{-24} \text{ cm}^3.$$

The derivatives for particular modes are calculated as³⁹ $P_{rs}^{(1)}(\lambda) = \frac{1}{\sqrt{N}} \sum_{k,n} P_{rs,k}^{(1)}(n) e_k(\lambda/n)$, where $e_k(\lambda/n)$ denotes the k-th component of the displacement vector of n-th atom in a mode λ and $P_{rs,k}^{(1)}(n)$ is the first order polarizability derivative over the k-th component of the n-th atom displacement.

$$\text{For } 447 \text{ cm}^{-1} \text{ mode: } \bar{e}(v_2/1) = \frac{1}{2} \begin{pmatrix} 0 \\ 1 \\ -\sqrt{3} \end{pmatrix}; \bar{e}(v_2/2) = \frac{1}{2} \begin{pmatrix} 0 \\ 1 \\ \sqrt{3} \end{pmatrix}; \bar{e}(v_2/3) = \frac{1}{2} \begin{pmatrix} 0 \\ -1 \\ -\sqrt{3} \end{pmatrix}; \bar{e}(v_2/4) = \frac{1}{2} \begin{pmatrix} 0 \\ -1 \\ \sqrt{3} \end{pmatrix}$$

$$\text{for } 237 \text{ cm}^{-1} \text{ mode: } \bar{e}(v_2/1) = \frac{1}{2} \begin{pmatrix} 0 \\ -\sqrt{3} \\ -1 \end{pmatrix}; \bar{e}(v_2/2) = \frac{1}{2} \begin{pmatrix} 0 \\ -\sqrt{3} \\ 1 \end{pmatrix}; \bar{e}(v_2/3) = \frac{1}{2} \begin{pmatrix} 0 \\ \sqrt{3} \\ -1 \end{pmatrix}; \bar{e}(v_2/4) = \frac{1}{2} \begin{pmatrix} 0 \\ \sqrt{3} \\ 1 \end{pmatrix}$$

The calculated matrices of polarizability derivatives are the following:

$$P^{(1)}(v_2) = \begin{bmatrix} -2.0785 & & \\ & -0.096 & \\ & & -3.177 \end{bmatrix} \cdot 10^{-16} \text{ cm}^2 \quad \text{and} \quad P^{(1)}(v_3) = \begin{bmatrix} 0 & & \\ & 2.076 & \\ & & -2.814 \end{bmatrix} \cdot 10^{-16} \text{ cm}^2$$

The calculated first order derivatives of the isotropic polarizability, $P_{iso} = \frac{1}{3}(P_{xx} + P_{yy} + P_{zz})$ are the following:

$P_{iso}^{(1)}(v_2) = 1.78 \cdot 10^{-16} \text{ cm}^2$ and $P_{iso}^{(1)}(v_3) = 0.25 \cdot 10^{-16} \text{ cm}^2$, which justifies small contribution of the 247 cm^{-1} mode in the isotropic Raman and TT spectra.

Anisotropic contributions, visible in OKE response, are the following:

$$\begin{aligned} (P_{xx}^{(1)} - P_{yy}^{(1)})(v_2) &= -1.98 \cdot 10^{-16} \text{ cm}^2 & (P_{xx}^{(1)} - P_{yy}^{(1)})(v_3) &= -2.076 \cdot 10^{-16} \text{ cm}^2 \\ (P_{xx}^{(1)} - P_{zz}^{(1)})(v_2) &= 1.1 \cdot 10^{-16} \text{ cm}^2 & (P_{xx}^{(1)} - P_{zz}^{(1)})(v_3) &= 2.814 \cdot 10^{-16} \text{ cm}^2 \\ (P_{zz}^{(1)} - P_{yy}^{(1)})(v_2) &= -3.081 \cdot 10^{-16} \text{ cm}^2 & (P_{zz}^{(1)} - P_{yy}^{(1)})(v_3) &= -4.89 \cdot 10^{-16} \text{ cm}^2 \end{aligned} \quad \text{and}$$

OKE response is proportional to $R_{OKE} \approx \frac{2}{15} \left[(P_{xx}^{(1)} - P_{yy}^{(1)})^2 + (P_{xx}^{(1)} - P_{zz}^{(1)})^2 + (P_{zz}^{(1)} - P_{yy}^{(1)})^2 \right]$. Thus,

$R_{OKE}(v_2) \approx 1.94 \cdot 10^{-32} \text{ cm}^4$ and $R_{OKE}(v_3) \approx 4.82 \cdot 10^{-32} \text{ cm}^4$, which means higher contribution of v_3 mode.

IV. Optical Kerr Effect time signal and the FFT of time signal

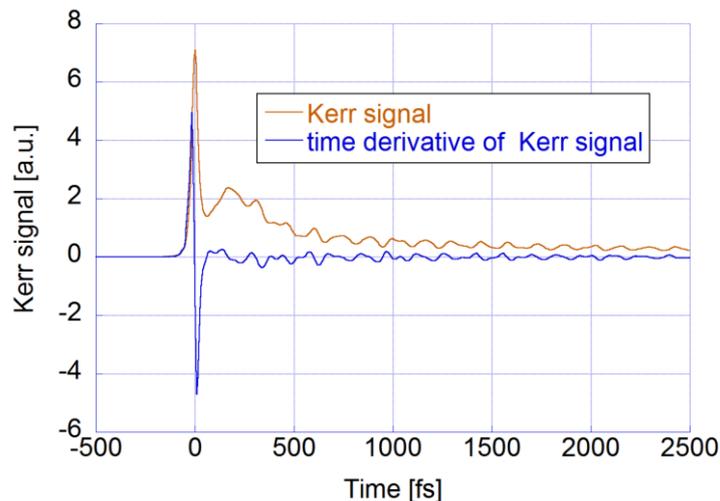


Fig.S6. OKE time resolved signal for C_2Cl_4 liquid and time derivative of OKE signal

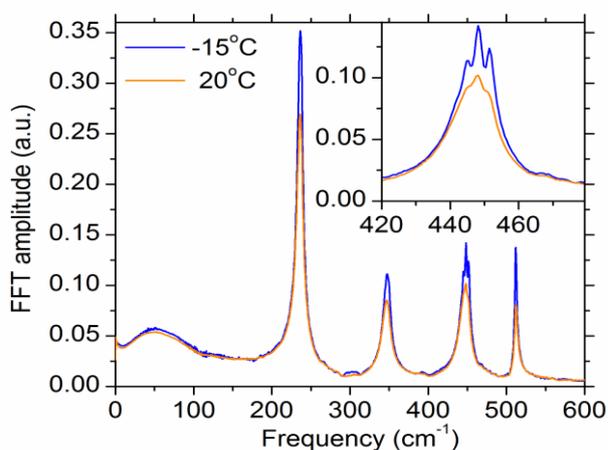


Fig.S7. FFT of the time signal obtained in the Optical Kerr Effect spectroscopy in the frequency range $0-600\text{cm}^{-1}$, for two temperatures.

In Fig. S7 we can see the low frequency feature of the spectrum, which reflects the contribution of librational and translational intermolecular vibrations. At low temperature the isotope splitting of the symmetric ν_2 vibrational band becomes apparent for two consistent reasons: the vibrational life time gets longer with lowering temperature^{39,40} and free rotation of molecules is restricted due to stronger intermolecular interactions. The latter reason means that the rotational life time tends to infinity.

39. W. Gadomski and B. Ratajska-Gadomska, Phys. Rev. A, 1986, 34, 1277;

40. V. M. Kenkre, A. Tokmakoff, and M. D. Fayer, J. Chem. Phys., 1994, 101 (12), 10618

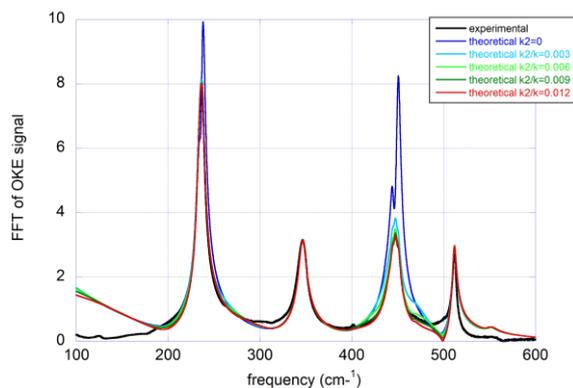


Fig.S8. The dependence of the FFT of the time domain OKE signal on intermolecular interactions, force constant k_2 .

This picture supports our explanation of windowed FFT spectra in Fig.8 (in the main manuscript) and in the section below. Diminishing of intermolecular interactions shows the same tendency as succeeding spectra in Fig.8. It means that fine structure of ν_2 band appears when the local structure of molecules and their mutual interactions diminish.

V. Windowed Fourier Transform Spectra in Log scale

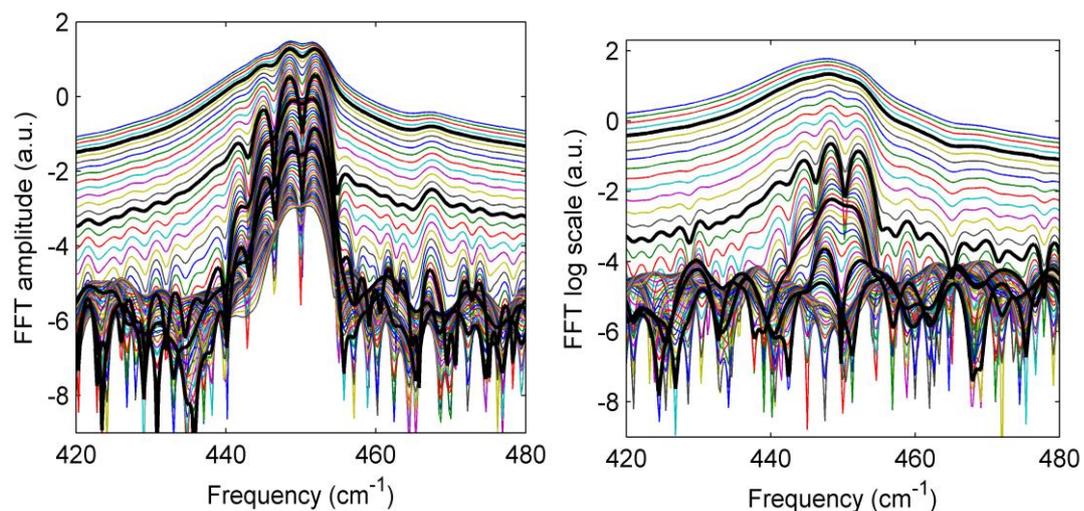


Fig.S9. The ν_2 band. Time series of the FFTs, in the log scale, of the time domain signals in Fig.4 (in the main manuscript), TT signal, (left plot) and in Fig.6 (in the main manuscript), OKE signal, (right plot).

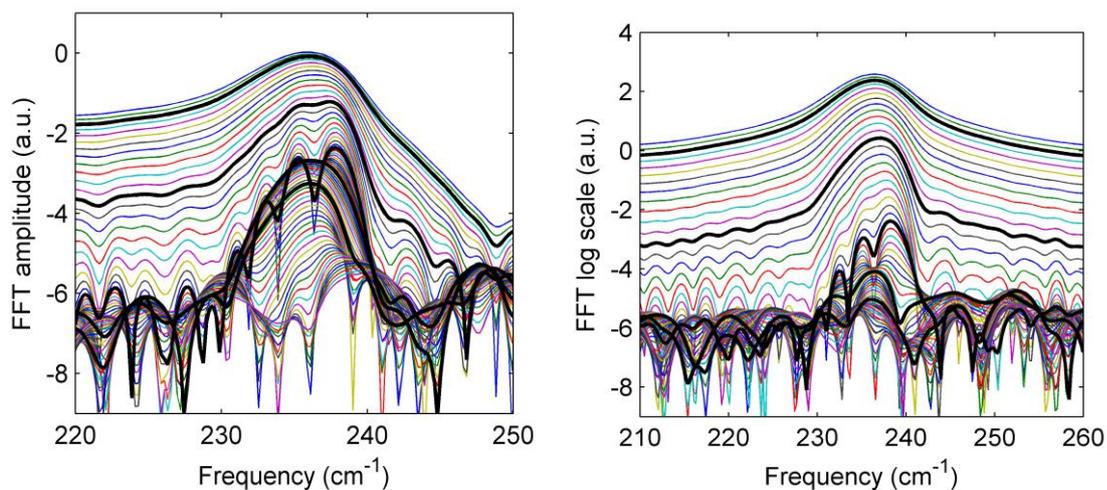


Fig.S10. The ν_3 band. Time series of the FFTs, in the log scale, of the time domain signals in Fig.4(in the main manuscript), TT signal, (upper plot) and in Fig.6(in the main manuscript), OKE signal, (bottom plot).