SI 1

FFT analysis of residuals was carried out. The residuals were obtained by fitting kinetic traces by biexponential lows. Also the residuals were determined for rows of **V** matrix determined by singular value decomposition of $\Delta A = \mathbf{U}\,\mathbf{S}\,\mathbf{V}^T$ as shown in the Figure SI 1.1

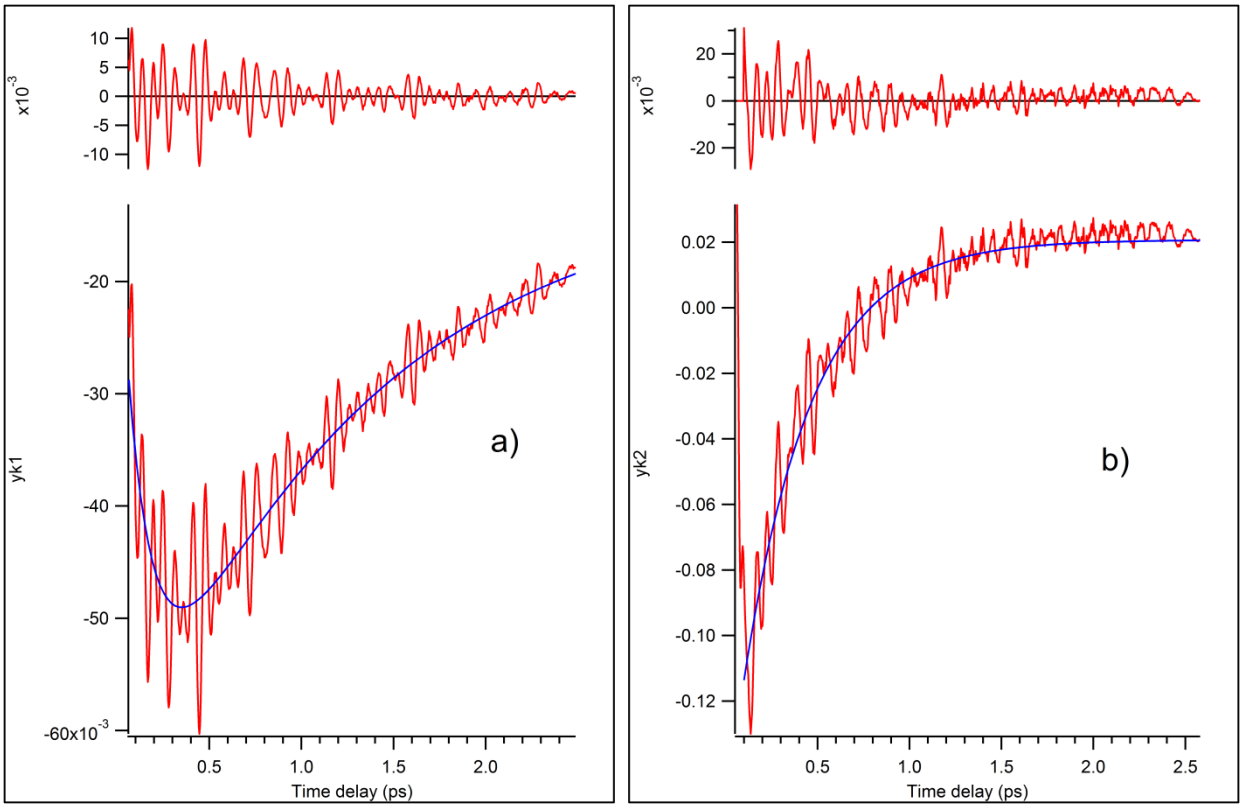


Figure SI 1.1 $CuCl_4^{2-}$ solution in 2 chlorobutane. Singular Value Decomposition of transient absorption matrix $\Delta A(\lambda,t)$ in the time window t=80 fs : 2.5 ps : $\Delta A(\lambda,t)= \mathbf{U}(\lambda)\,\mathbf{S}\,\mathbf{V}^T(t)$. First and second rows of **V**(t) matrix are shown.

Kinetic traces and residuals in the Figure SI 1.1 demonstrate complex oscillation. The spectrum of the oscillations was analyzed by FFT. Spectrum Power Density (SPD) is shown in the Figure SI 1.2.

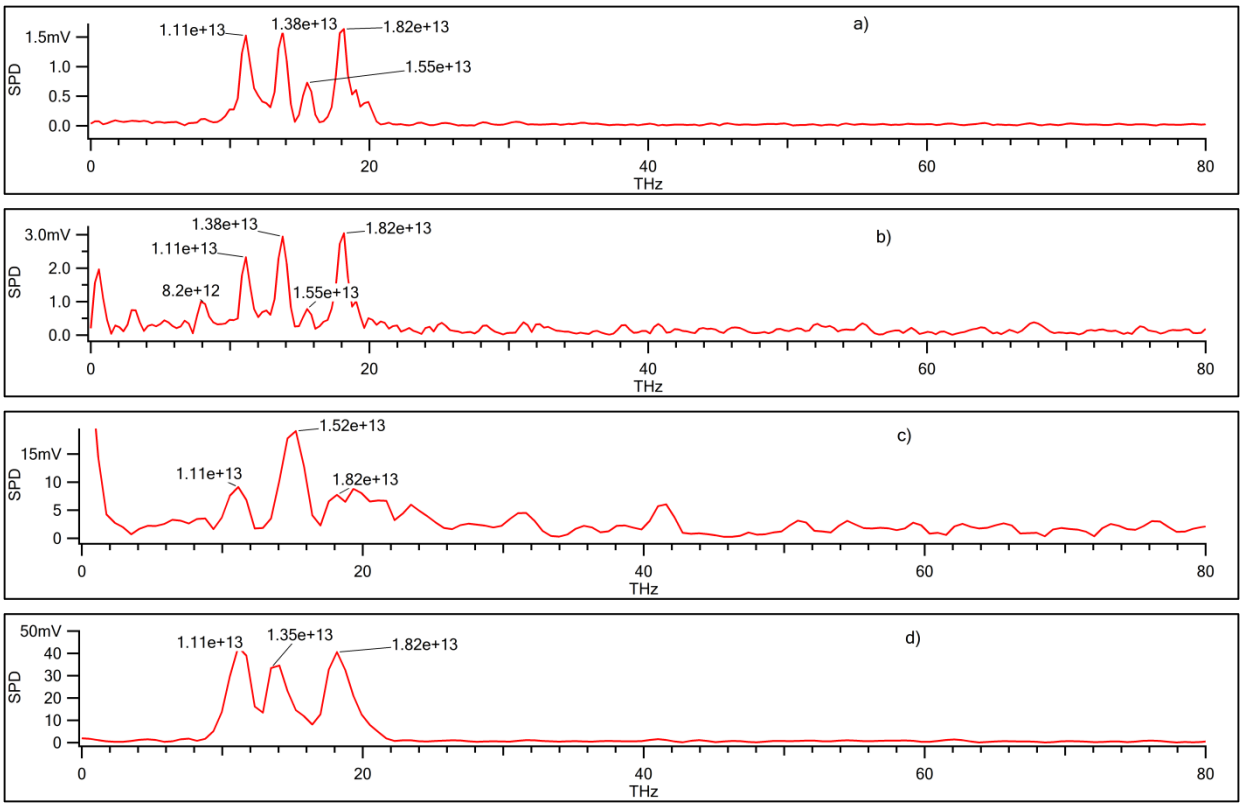


Figure SI 1.2 Spectrum of Power Density (SPD). a) and b) FFT of residuals for $CuCl_4^{2-}$ in 2 chlorobutane. c) and d) FFT of pure 2 chlorobutane kinetic traces.

To determine the spectrum of oscillations and damping parameters LPSVD (Linear Predictive Singular Value Decomposition) method was used. LPSVD is one of the most commonly used algorithm in biomedicine signal processing applications for parameter estimation of damped sinusoids. It is based on two major principles – singular value decomposition and estimation of linear prediction coefficients[SI 1, SI 2]. Algorithm uses a model to fitting data – this model attempts to approximate original noisy data and minimizes the difference between data and nonlinear model in least squares sense. The Lorentzian model was used:

$$A_{res} = \sum_{l-1}^{L} a_l e^{-i(2\pi\nu_l \cdot t + \phi_l)} \cdot e^{-\gamma_l \cdot t}$$

The enhancement of the resolution can be achieved by model (curve) fitting of the spectrum (3), which involves nonlinear least squares (LS) techniques. The linear LS procedure used is based on singular value decomposition (SVD) (5, 6). This enhances the numerical stability of the mathematical process. In addition, analysis of the singular values enables one to distinguish between signal and noise [SI 3].

Table SI 1.

Frequency and damping parameters of oscillations in kinetic traces.

Estimation parameters of oscillations using LP SVD								
ν (Hz)	$5.35\ 10^{12}$	$8.5\ 10^{12}$	$9.15\ 10^{12}$		$1.24\ 10^{13}$	$1.4\ 10^{13}$	$1.66\ 10^{13}$	$1.8\ 10^{13}$
ν(1/cm)	181	283	305		413	466	553	600
γ (1/ps)	$2.5\ 10^{12}$	$1.7\ 10^{12}$	$2.8\ 10^{12}$		$2\ 10^{12}$	$5.5\ 10^{11}$	$1.57\ 10^{12}$	$1.27\ 10^{12}$
τ_d (fs)	400	595	357		500	1820	637	787
Estimation parameters of oscillations using FFT								
ν (Hz)		$8.5\ 10^{12}$		$1.11\ 10^{13}$		1.3810^{13}	$1.54\ 10^{13}$	1.8210^{13}
ν(1/cm)		283		370		460	513	607
	Cu-Cl	Cu-Cl	2 ClBut	2 ClBut	2 ClBut	2 ClBut	2 ClBut	
	T_2	A_1						

ν(1/cm)	188	281	320	374	420	465	527	609

SI 2.

Singular Value Decomposition (SVD) is a matrix factorization method which can be used as a noise filtering or data reduction procedure [SI 4]. The SVD theorem stands that any (MxN) matrix ΔA(λ,t) , e.g. acquired by transient absorption spectroscopy, can be decomposed into the product of three matrices $\mathbf{\Delta A} = \mathbf{U}\,\mathbf{S}\,\mathbf{V}^T$. Matrices **U** and $\mathbf{V}^T$ are orthogonal, unitary and of dimension (MxM) and (NxN), respectively. (MxN) **S** matrix contains only diagonal elements defined as the singular values. They are sorted in decreasing order.

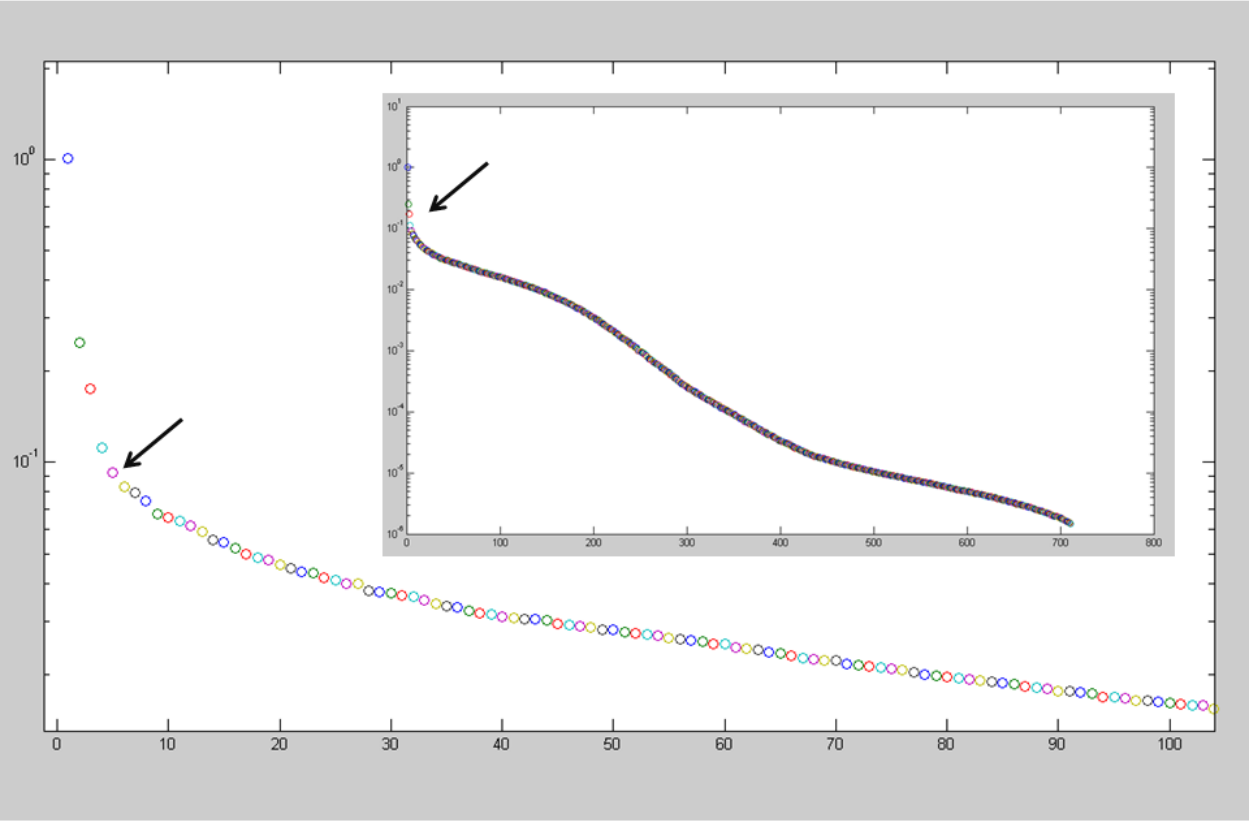


Figure SI 2.1 First 104 Singular Values (S) from the data SVD decomposition are shown in semilog scale. Insert demonstrates all diagonal values of S matrix. Arrow indicates a boarder of singular values that were attributed to nose.

Columns of **U** correspond to basis set of spectra (referred as singular spectra) and the columns of **V** to basis of transients (singular transients). Singular spectra and singular transients correspond to a linear combination of meaningful species associated data. First six singular spectra and singular spectra are shown in Figure SI 2.2 Discrimination between singular singular vectors carrying dynamical information on the system under study and those associated to noise can be made. The number of significant components is the number of singular values which sufficiently differs from the noise level. Qualitatively it can be seen from Figure SI 2.2 that singular spectra and transients corresponding to singular values higher 4 can be attributed to noise. Figure SI 2.1 depicts that boarder between meaningful singular values and noise is close to number 4 also. Four intermediates were suggested for kinetic scheme. It is in accord with results of decomposition of transient kinetics into multiexponential fit that given three rate constants.

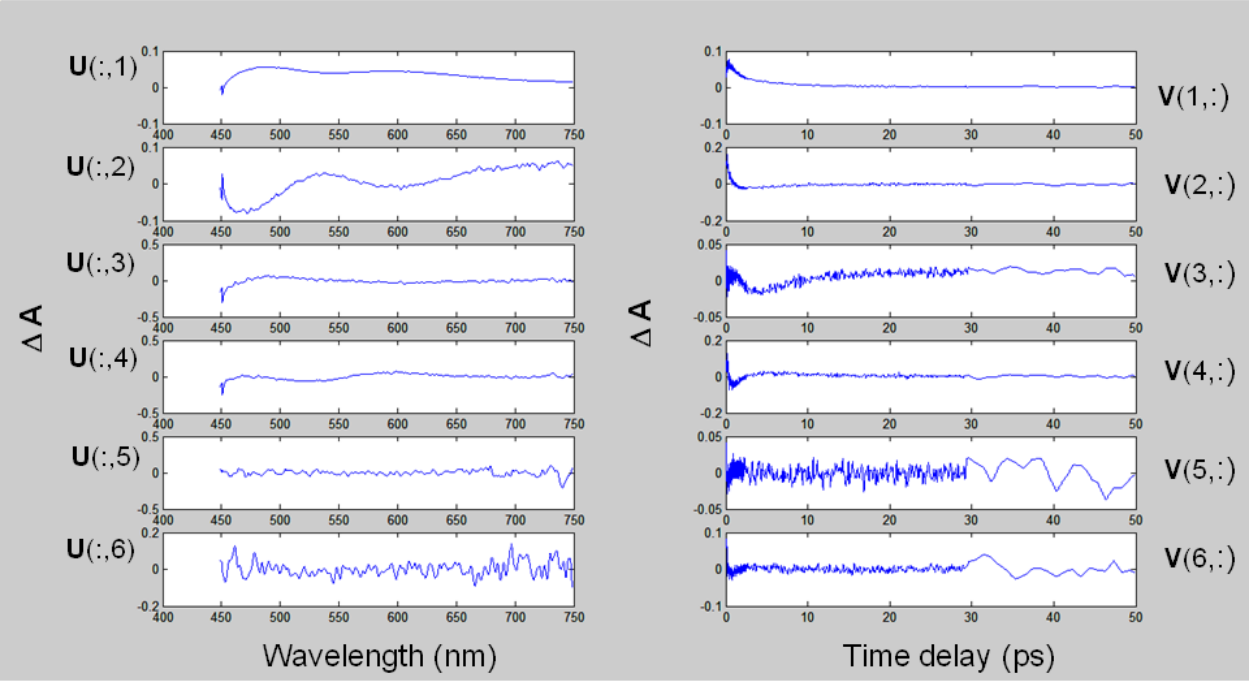


Figure SI 2.2 Six first singular spectra and singular transients corresponding to ΔA matrix decomposition. Left column is singular spectra **U**, right column is singular transients.

SI References

SI 1. Y.Lu, S.Joshi: *IEEE Trans. Biomed.* Eng., 1997, 44 (6), 512–528,

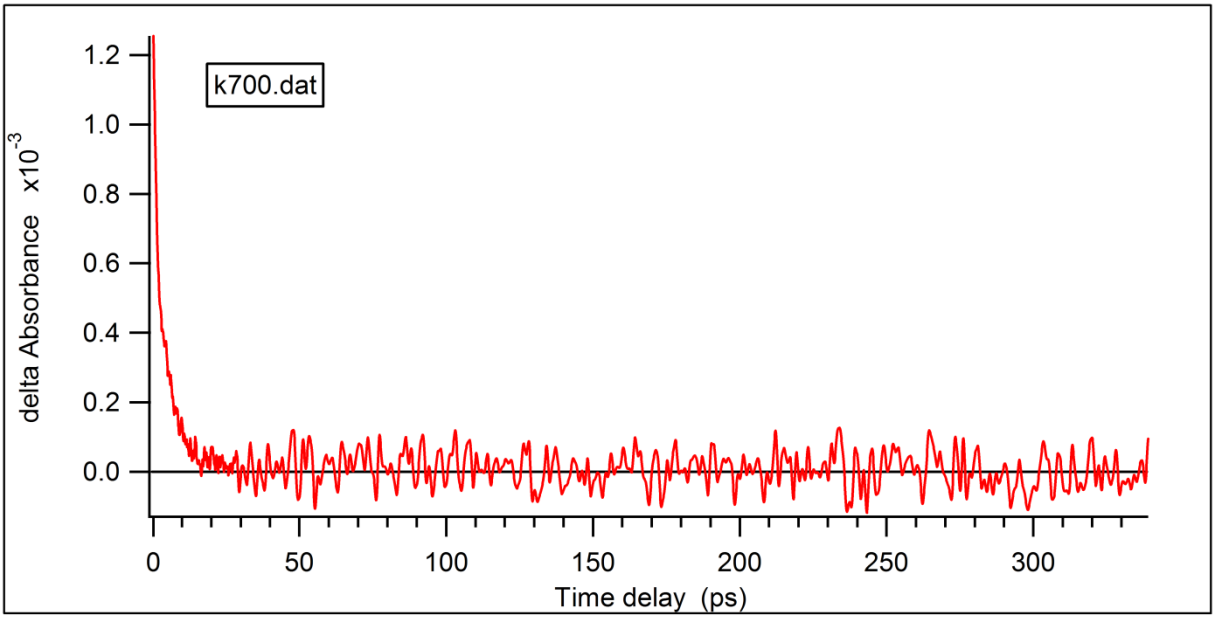
SI 2. J.H.Leclerc: *Journal of magnetic resonance*, 1991, 95,10-31,

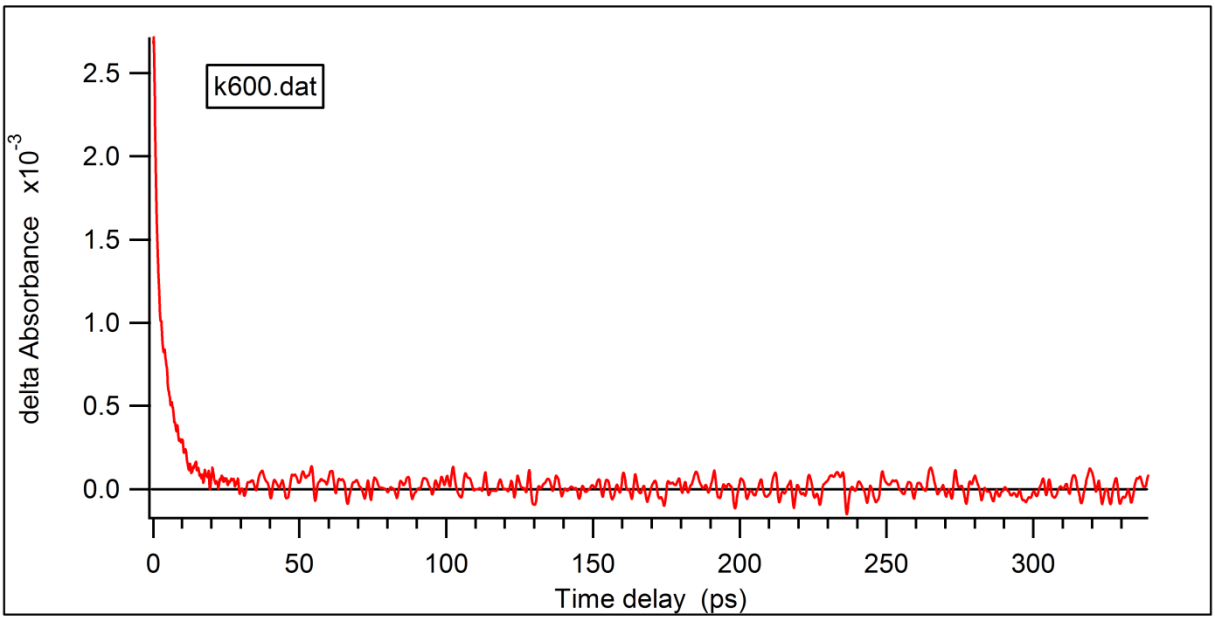
SI 3. H. Barkhuijesen, R.D. Beer, W. M. M. J. Bovée, BOVÉE, D. van Ormondt *Journal of magnetic resonance*, 1985, 61,465-48 1.

SI 4. S. A. Kovalenko, A. L. Dobryakov, J. Ruthmann and N. P. Ernsting, *Phys. Rev. A*, 1999, **59**, 2369-2384.

SI 3

Transient kinetics for delays up to 340 ps


k700.dat
delta Absorbance x10-3
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
50
100
150
200
250
300
Time delay (ps)


k600.dat
delta Absorbance x10-3
2.5
2.0
1.5
1.0
0.5
0.0
0
50
100
150
200
250
300
Time delay (ps)

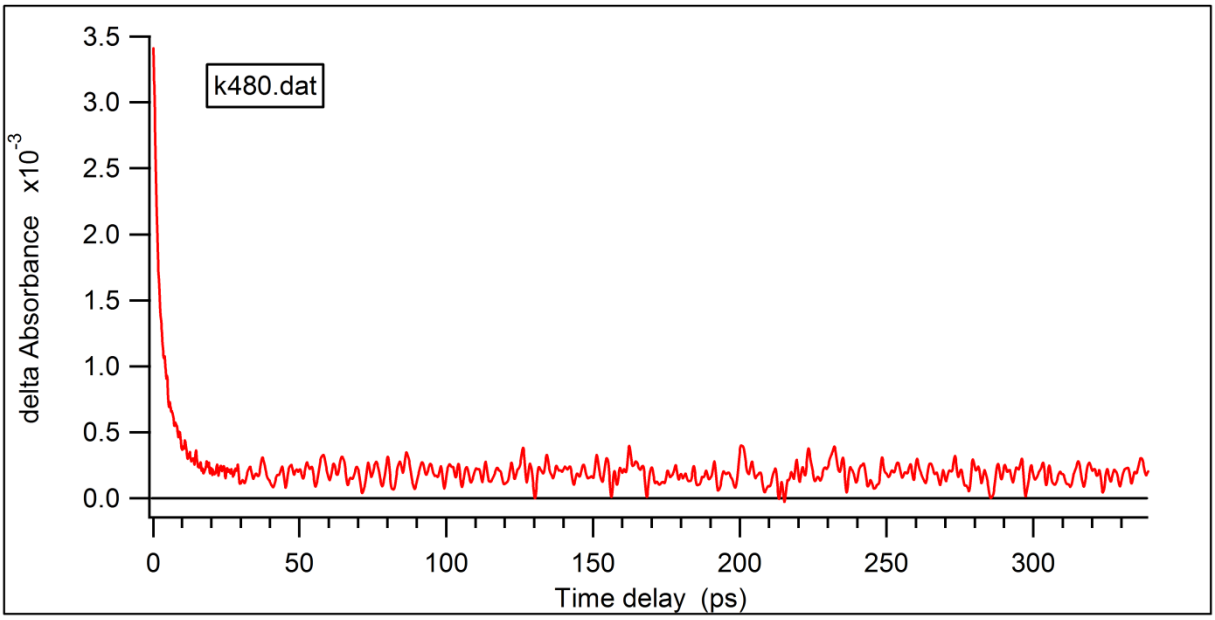

k480.dat
delta Absorbance x10-3
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
50
100
150
200
250
300
Time delay (ps)

Figure SI3.1

Kinetic traces for selected probe wavelengths (see legends to layout)

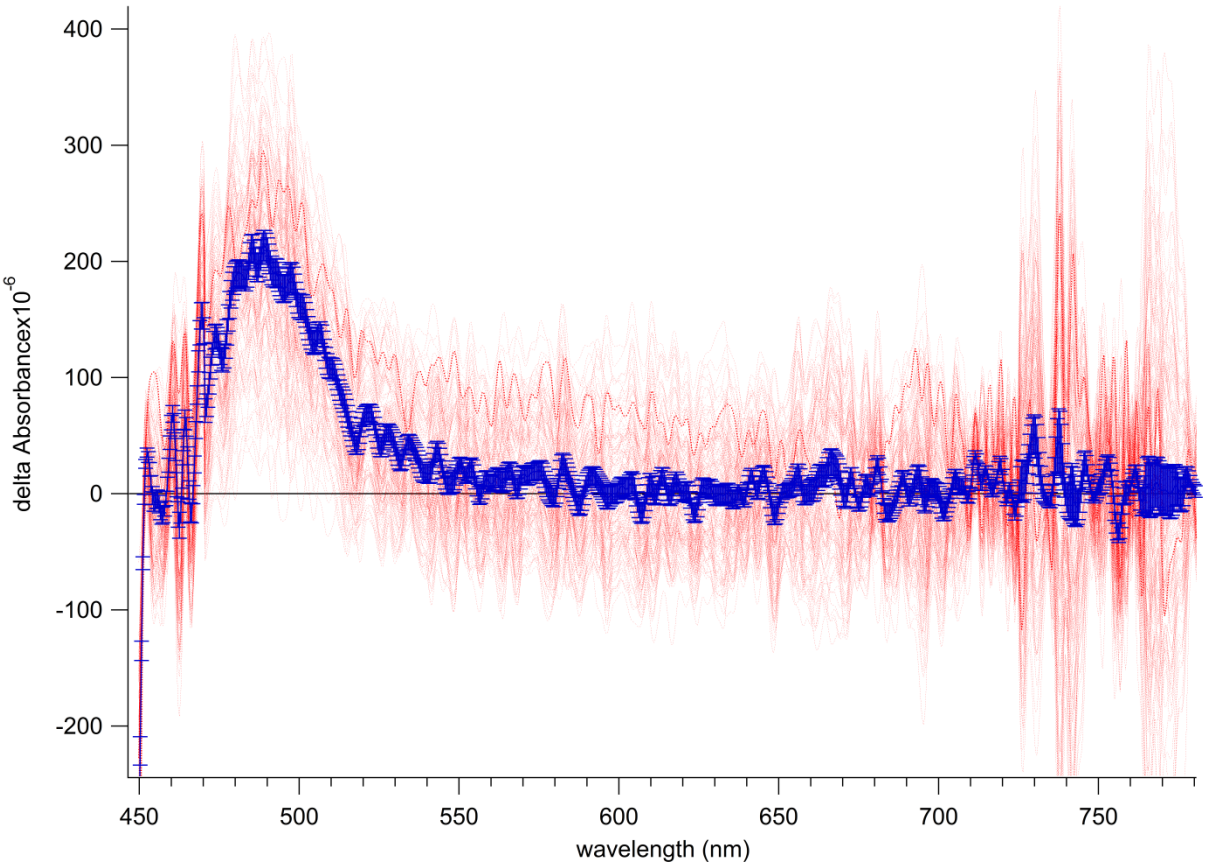


Figure SI3.2 Transient spectra for time delays between 200 ps and 340 ps with step delay of 1 ps (red). Average spectrum and error bars are shown by blue.

SI 4

a) **The duration of nonresonant fs coherent artefact for solvent 2-chlorobutane is close to 40 fs as it is shown in Figure SI 4.4. It is close to the time width of the fs pulse [**S. A. Kovalenko, A. L. Dobryakov, J. Ruthmann and N. P. Ernsting, *Phys. Rev. A*, 1999, **59**, 2369-2384.]

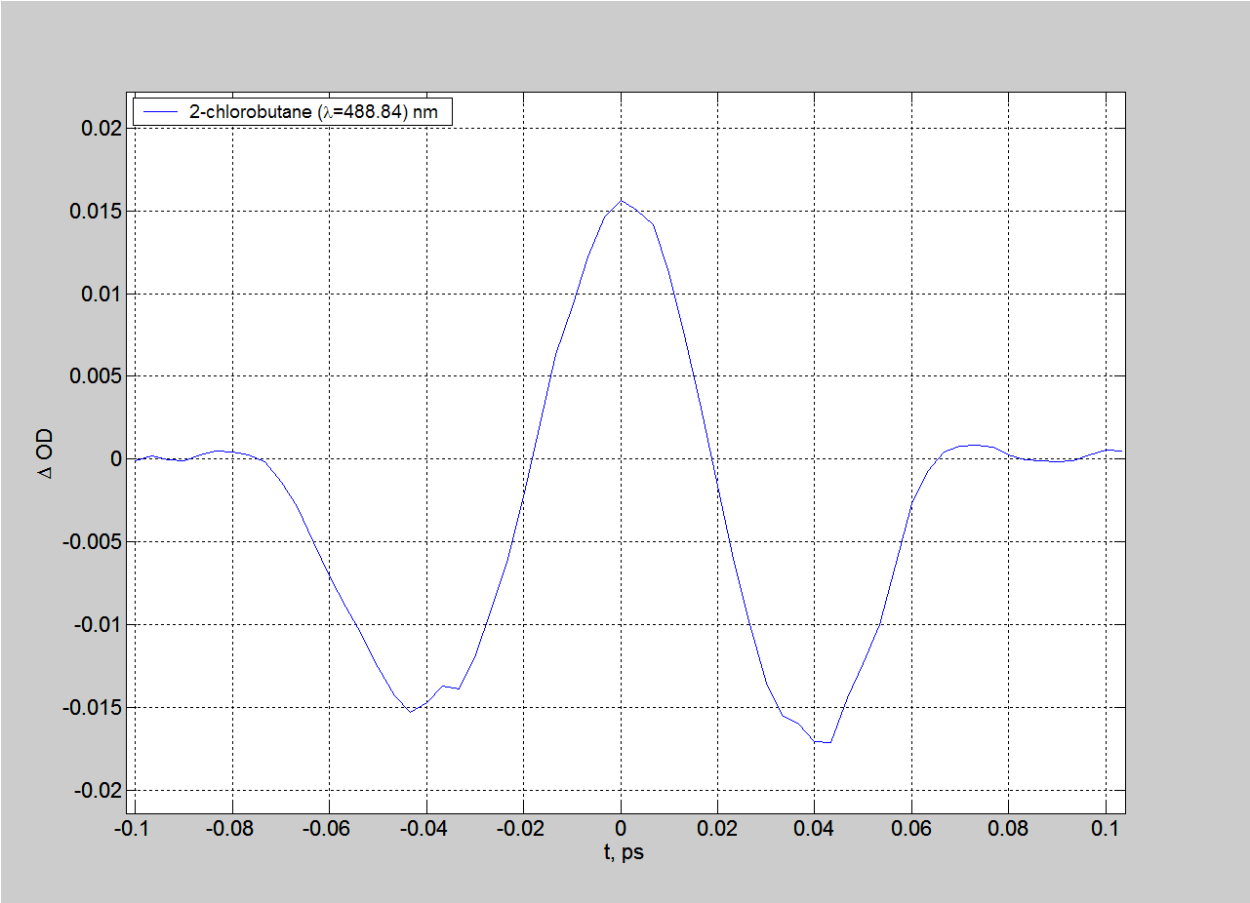


Figure SI 4.1 Femtosecond coherent artefact in pure 2-chlorobutane

b. Spectrum of the fs pump laser pulse is shown in Figure SI 4.2. For the Gauss pulse the relation is $\Delta\nu\Delta\tau$=0.441 valid. From the measurements of $\Delta\nu$ ~ 10^{13} Hz $\Delta\tau$ was estimated as 40 fs.

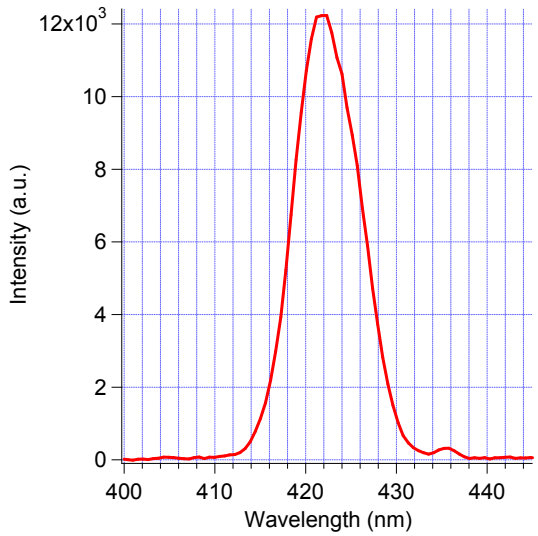


Figure SI 4.2 Spectrum of fs pump pulse.

SI 5. Cartesian coordinates of optimized structures. Calculations were performed using ORCA 2.9.1 software in the scope of DFT with B(38HF)P86 hybrid exchange-correlation functional.

$[N(CH_3)_4]_2CuCl_3$

29	-0.012351000	-1.486425000	-0.596424000
17	1.154466000	-2.090090000	1.256141000
17	-1.785209000	-2.712811000	-1.374126000
17	0.562016000	0.410596000	-1.768537000
7	-4.288613000	0.211893000	-0.698121000
7	4.326969000	0.080335000	-0.637766000
6	-4.096912000	-0.609570000	0.521898000
6	3.470467000	0.545555000	0.480475000
6	-2.993403000	0.827843000	-1.077841000
6	3.821751000	-1.224506000	-1.131532000
6	-5.286337000	1.270524000	-0.436279000
6	5.720654000	-0.071410000	-0.168543000
6	-4.758202000	-0.657538000	-1.803477000
6	4.271780000	1.070969000	-1.738026000
1	-6.233175000	0.805777000	-0.156629000
1	6.081074000	0.893637000	0.191347000
1	-5.416382000	1.866906000	-1.341180000
1	6.339988000	-0.415494000	-0.998994000
1	-4.926982000	1.902266000	0.378171000
1	5.741992000	-0.802799000	0.641651000
1	-2.265607000	0.035516000	-1.270018000
1	2.794633000	-1.083646000	-1.475192000
1	-2.653110000	1.460187000	-0.256101000
1	3.836700000	-1.941753000	-0.309479000
1	-3.138574000	1.430760000	-1.975936000
1	4.462961000	-1.560328000	-1.948658000
1	-3.354120000	-1.380988000	0.301361000
1	2.449883000	0.652454000	0.106267000
1	-5.051238000	-1.064488000	0.793014000

1	3.856540000	1.501508000	0.839700000
1	-3.749045000	0.038139000	1.328524000
1	3.489113000	-0.202238000	1.274569000
1	-5.709441000	-1.108440000	-1.515197000
1	4.642319000	2.028421000	-1.368150000
1	-4.003854000	-1.430320000	-1.973852000
1	3.232045000	1.164415000	-2.061419000
1	-4.888716000	-0.046942000	-2.698430000
1	4.896520000	0.719255000	-2.560791000

$[N(CH_3)_4]CuCl_3$

29	-0.311025000	-0.065134000	0.835219000
17	-1.600295000	-0.061706000	2.562149000
17	0.286877000	-2.109936000	0.361710000
17	0.669773000	1.268971000	-0.574755000
7	4.518373000	0.028382000	-0.789482000
6	4.266740000	0.634741000	0.539873000
6	3.658473000	-1.168833000	-0.953640000
6	5.941628000	-0.364493000	-0.893503000
6	4.196588000	1.015033000	-1.847895000
1	6.563400000	0.524633000	-0.777192000
1	6.113400000	-0.815064000	-1.872449000
1	6.167305000	-1.085738000	-0.106341000
1	2.611866000	-0.874925000	-0.846199000
1	3.920760000	-1.896900000	-0.184291000
1	3.832606000	-1.593115000	-1.944152000
1	3.218890000	0.937455000	0.590914000
1	4.914079000	1.504828000	0.658078000
1	4.486373000	-0.104754000	1.311765000
1	4.830390000	1.893242000	-1.715875000
1	3.144023000	1.290966000	-1.757636000
1	4.384502000	0.559745000	-2.821532000

$[N(CH_3)_4]_2CuCl_4$

29	-0.017588000	0.047050000	0.287221000
17	-1.490634000	1.312363000	1.482529000
17	1.008812000	-1.055811000	1.967473000
17	-0.307347000	-1.660005000	-1.179815000
17	0.712313000	1.624435000	-1.187485000
7	-4.365492000	-0.065388000	-0.895750000
7	4.372582000	0.047268000	-0.614083000
6	-3.809660000	-1.126106000	-0.020790000
6	3.901798000	0.828089000	0.555960000
6	-3.274074000	0.549985000	-1.690424000
6	3.418530000	-1.053313000	-0.895015000
6	-5.003066000	0.974821000	-0.055700000
6	5.708085000	-0.518927000	-0.324379000
6	-5.368712000	-0.654885000	-1.808443000
6	4.450969000	0.937866000	-1.794931000
1	-5.801581000	0.515089000	0.529120000
1	6.402282000	0.297392000	-0.117485000
1	-5.412588000	1.750297000	-0.705046000
1	6.047648000	-1.088060000	-1.191422000
1	-4.244905000	1.398767000	0.606881000
1	5.630963000	-1.173928000	0.545199000
1	-2.783814000	-0.226846000	-2.278833000
1	2.444641000	-0.625252000	-1.139515000
1	-2.552763000	0.999109000	-1.004283000
1	3.328105000	-1.678980000	-0.005765000
1	-3.705054000	1.312132000	-2.342162000
1	3.796491000	-1.635907000	-1.737483000
1	-3.304375000	-1.867891000	-0.640942000
1	2.927040000	1.257895000	0.315953000

1	-4.629577000	-1.584878000	0.534830000
1	4.626332000	1.617659000	0.762399000
1	-3.092423000	-0.668432000	0.664697000
1	3.808163000	0.158890000	1.412098000
1	-6.168779000	-1.101632000	-1.215945000
1	5.154977000	1.744087000	-1.582946000
1	-4.884144000	-1.420244000	-2.417152000
1	3.455639000	1.344828000	-1.987091000
1	-5.772064000	0.131578000	-2.448781000
1	4.793267000	0.356882000	-2.653074000