In target analysis, the inverse problem is to determine the number of electronically excited states (N_{states}) present in the system, and to estimate their spectral properties $SADS_l(\lambda)$ (Species Associated Difference Spectra) and their populations $c_l^S(t)$ (superscript S stands for species). The time resolved spectra $TRS(t,\lambda)$ are described by a parameterized superposition model:

$$TRS(t,\lambda) = \sum_{l=1}^{Nstates} c_l^S(t,\theta) SADS_l(\lambda)$$

where the populations are determined by an unknown compartmental model, that depends upon the unknown kinetic parameters θ. In the target analysis constraints on the *SADS* are needed to estimate all parameters θ and $SADS_l(\lambda)$. We here describe the evolution of the vibrationally excited state wavepackets created by the short laser pulse with a superposition of damped oscillations. The amplitude of a damped oscillation $\cos(\omega_n t)\exp(-\gamma_n t)$ as a function of the detection wavelength constitutes a Damped Oscillation Associated Spectrum $DOAS_n(\lambda)$ with an accompanying phase characteristic $\varphi_n(\lambda)$. When the vibrational evolution can be considered independently from the electronic evolution (Born-Oppenheimer approximation), we arrive at a superposition of the electronic and vibrational contributions to the $TRS(t,\lambda)$ [i]:

$$TRS(t,\lambda) = \sum_{l=1}^{Nstates} c_l^S(t',\theta) SADS_l(\lambda) + \sum_{n=1}^{Nosc} DOAS_n(\lambda)\cos(\omega_n t' - \varphi_n(\lambda))\exp(-\gamma_n t')$$

where t' indicates that the actual model function still has to take into account the IRF (*vide infra*). Thus the inverse problem is now extended: to determine additionally the number of vibrationally excited states N_{osc}, and to estimate their parameters, the eigenfrequency ω_n and damping rate γ_n, and the $DOAS_n(\lambda)$ and $\varphi_n(\lambda)$. Note that it is now the system that reveals its eigenfrequencies from the complete data set. The amount of vibrationally excited states that can reliably be resolved will critically depend upon the signal to noise ratio of the measurements $TRS(t,\lambda)$.

Materials and methods

Modelling and parameter estimation

The population of the *l*-th compartment is $c_l^S(t)$. The concentrations of all compartments are collated in a vector:

$c^S(t) = \left[c_1^S(t) \quad c_2^S(t) \quad \ldots \quad c_{n_{comp}}^S(t) \right]^T$ which obeys the differential equation

$$\frac{d}{dt} c^S(t) = K c^S(t) + j(t)$$

where the transfer matrix *K* contains off-diagonal elements k_{pq}, representing the microscopic rate constant from compartment *q* to compartment *p.* The diagonal elements contain the total decay rates of each compartment. The input to the compartments is $j(t) = IRF(t)\left[x_1 \ldots \quad x_{n_{comp}} \right]^T$, with x_l the absorption of the *l*-th compartment.

The impulse response of the system, which is a sum of exponential decays, has to be convolved with the IRF. Typically, a Gaussian shaped IRF is adequate, with parameters μ for the location of the IRF maximum and Δ for the full width at half maximum (FWHM) of the IRF:

$$IRF(t) = \frac{1}{\tilde{\Delta}\sqrt{2\pi}} \exp(-\log(2)(2(t-\mu)/\Delta)^2)$$

where $\tilde{\Delta} = \Delta/(2\sqrt{2\log(2)})$. The convolution (indicated by an *) of this IRF with an exponential decay (with decay rate *k*) yields an analytical expression which facilitates the estimation of the decay rate *k* and the IRF parameters μ and Δ:

$$c^D(t,k,\mu,\Delta) = \exp(-kt) * IRF(t) = \frac{1}{2}\exp(-kt)\exp(k(\mu + \frac{k\tilde{\Delta}^2}{2}))\{1 + erf(\frac{t-(\mu + k\tilde{\Delta}^2))}{\sqrt{2}\tilde{\Delta}}\}$$

When the compartmental model consists of independently decaying species, with populations $c_l^D(t,k_l,\mu,\Delta)$ (superscript D stands for decay) their spectra are termed $DADS_l(\lambda)$ (Decay Associated Difference Spectra). The solution of the general compartmental model described by the *K* matrix consists of exponential decays with decay rates equal to the eigenvalues of the *K* matrix. The interrelation between the DADS and SADS is expressed in the following matrix equation:

$$C^D(\theta,\mu,\Delta)\cdot DADS^T = C^S(\theta,\mu,\Delta)\cdot SADS^T$$

Here the matrix $C^D(\theta,\mu,\Delta)$ contains in its *l*-th column the decay $c_l^D(t,k_l,\mu,\Delta)$ and the matrix $C^S(\theta,\mu,\Delta)$ contains in its columns the populations $c_l^S(t)$ of the general compartmental model.

The superposition model for the $TRS(t,\lambda)$ is given by the matrix formula:

$$TRS = C^S(\theta,\mu,\Delta)\cdot SADS^T + \mathrm{Cos}(\omega,\gamma,\mu,\Delta)\cdot A^T + \mathrm{Sin}(\omega,\gamma,\mu,\Delta)\cdot B^T$$

Here the matrices $\mathrm{Cos}(\omega,\gamma,\mu,\Delta)$ and $\mathrm{Sin}(\omega,\gamma,\mu,\Delta)$ contain the damped oscillations, which will be detailed below, and the matrices *A* and *B* comprise their amplitudes.

To improve the precision of the estimated parameters, the experiment can be repeated, and the set of $N_{\exp}$ experiments can be analyzed simultaneously. For each additional data set TRS_e only one scaling parameter α_e and one time shift parameter μ_e must be added:

$$TRS_e = \alpha_e(C^S(\theta,\mu_e,\Delta)\cdot SADS^T + \mathrm{Cos}(\omega,\gamma,\mu_e,\Delta)\cdot A^T + \mathrm{Sin}(\omega,\gamma,\mu_e,\Delta)\cdot B^T)$$

The dimensions of the matrices are collated in Table 1.

	Nrow	Ncol
TRS	nt	nλ
$C^S(\theta,\mu,\Delta)$	nt	N_{states}
SADS	nλ	N_{states}
$\mathrm{Cos}(\omega,\gamma,\mu,\Delta)$	nt	N_{osc}
A	nλ	N_{osc}
$\mathrm{Sin}(\omega,\gamma,\mu,\Delta)$	nt	N_{osc}
B	nλ	N_{osc}

Table 1 Dimensions of the matrices

Assuming wavelength independence of the eigenfrequency ω_n and of the damping rate γ_n is necessary to limit the amount of free parameters. The model function for the *n*-th damped oscillation is given by

$$\cos(\omega_n(t-\mu))\cdot c^D(t,\gamma_n,\mu,\Delta)$$

$$\sin(\omega_n(t-\mu))\cdot c^D(t,\gamma_n,\mu,\Delta)$$

Note that we have chosen this approximate product expression in order to avoid the complications which arise from the convolution of $c^D(t,\gamma_n,\mu,\Delta)$ with a sine or cosine function.

Using these two functions the matrices $\mathrm{Cos}(\omega,\gamma,\mu,\Delta)$ and $\mathrm{Sin}(\omega,\gamma,\mu,\Delta)$ can be computed as a function of all ω_n,γ_n. The intrinsically nonlinear parameters of this model are the vector θ (containing the microscopic decay rates and inputs to the compartments x_l), the IRF parameters (μ,Δ), scaling parameter α_e and time shift parameter μ_e for each additional data set, and the N_{osc}-vectors ω,γ. The conditionally linear parameters are the matrices *SADS, A* and *B*. Typically, there are nλ times more conditionally linear parameters than intrinsically nonlinear parameters, see Table 1. The variable projection algorithm [53, 55-57] which minimizes the nonlinear least squares criterion as a function of the intrinsically nonlinear parameters only, and implicitly solves for the conditionally linear parameters, makes the parameter estimation feasible.

The DOAS and phases cannot be fitted directly, but must be computed from the estimated cosine and sine amplitude matrices *A* and *B*. The *n*-th $DOAS_n$ at wavelength λ_j is computed as:

$$DOAS_{jn}=\sqrt{A_{jn}^2+B_{jn}^2}$$

The reconstruction of the phase φ_n is more cumbersome. From A_{jn} and B_{jn} the phase φ_{jn} modulo 2π can be computed. Then undesired 2π jumps between subsequent phases φ_{jn} and $\varphi_{j+1,n}$ can be corrected by applying appropriate counterjumps of 2π.

Back of the envelope calculation of storage when all is kept in memory

Let us assume a typical computation with number of vibrationally excited states N_{osc} (typically between 4 and 40 DOAS, thus because of cos and sin between 8 and 80 "spectra"), number of electronically excited states (N_{states}) (typically between 4 and 80), number of time points nt (typically between 40 and 16000), number of wavelengths nλ (typically between 40 and 4000). Assume $nspec=2*N_{osc}+N_{states}=100=10^2$, $n\lambda=10^3$, $nt=10^3$, then the size of the matrix of conditionally linear parameters $CLP=n\lambda\times nspec=10^5$, the size of the extended C matrix is $C=nt\times nspec=10^5$, when you store all C matrices this amounts to $nt\times nspec\times n\lambda=10^8$. In principle you also need the weighted C matrix for the weighted VARPRO. With double precision (8 bytes) the maximal C matrix would be about 1 GB. For the finite difference gradient you need to recompute the matrix of residuals for every nonlinear parameter that is optimized, assume $nparm=100=10^2$ then $nt\times nparm\times n\lambda=10^8$. Thus also the maximal gradient matrix would be about 1 GB. Thus in worst case you will not be able to store the complete gradient matrix of C, and that is why you must store it only for a single wavelength, and recompute $C_j(\theta+\Delta\theta_j)$ for every wavelength λ.

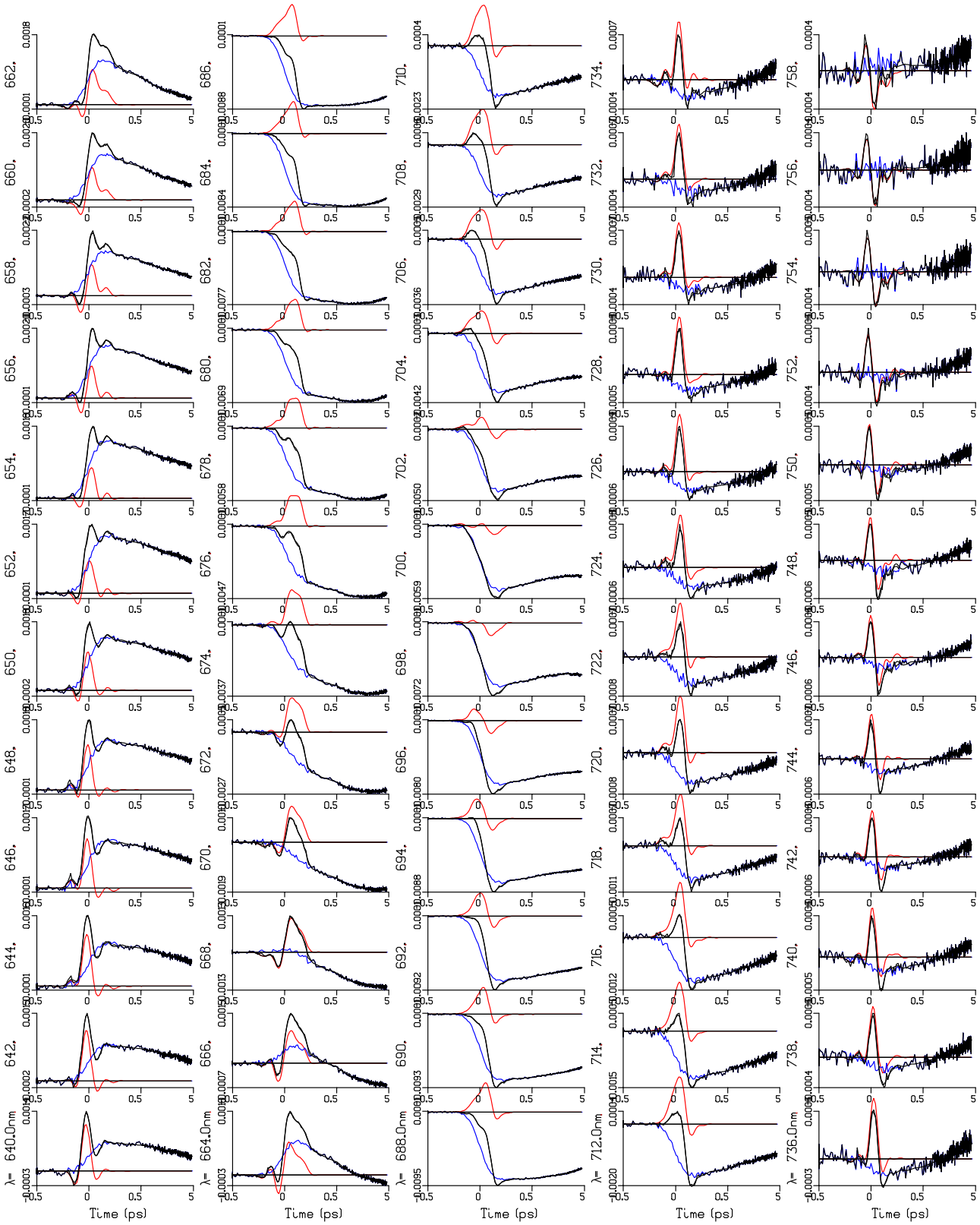

Figure S 1. Preprocessing of the WT data with 700 nm excitation. Key: original data (black), part of the data described by the four DOAS (red), preprocessed data where the part of the data described by the DOAS has been subtracted (blue). Note that the time axis is linear until 0.5 ps and logarithmic thereafter.

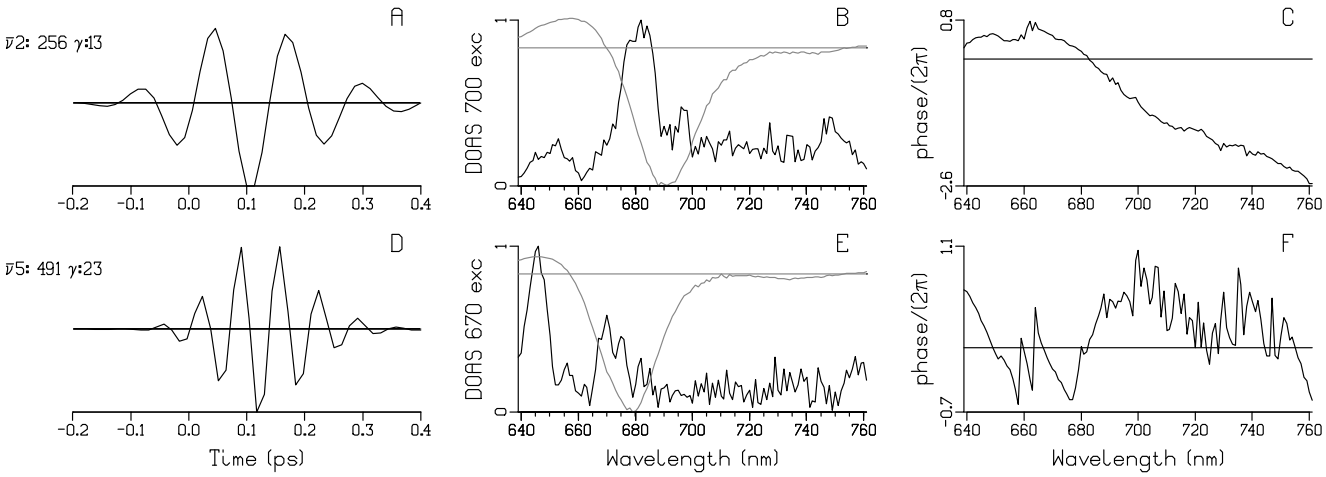

Figure 1. (A,D) Cosine oscillations with frequencies $\bar{\nu}n$ (in /cm) (where *n* is the DOAS number) and damping rates γ (in 1/ps) written in the legend at the left. (B,E) Estimated DOAS (black) and first EADS (grey). (C) Estimated phase profiles of the DOAS. Panels A-C depict the most slowly decaying damped oscillation with 700 nm excitation, whereas panels D-F refer to 670 nm excitation.

[i] After the submission of our manuscript we learned that an alternative approach to globally fit damped oscillations was developed independently and simultaneously by S. Schott, L. Ress, J. Hrušák, P. Nuernberger, and T. Brixner (submitted) *Identification of photofragmentation patterns in trihalide anions by global analysis of vibrational wavepacket dynamics in broadband transient absorption data*