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



where the populations are determined by an unknown compartmental model, that depends upon the unknown kinetic parameters . In the target analysis constraints on the *SADS* are needed to estimate all parameters  and . 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  as a function of the detection wavelength constitutes a Damped Oscillation Associated Spectrum  with an accompanying phase characteristic . 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 [[1]](#endnote-1):



where  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 , and to estimate their parameters, the eigenfrequency  and damping rate , and the and . 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 .

## Materials and methods

### Modelling and parameter estimation

The population of the *l*-th compartment is . The concentrations of all compartments are collated in a vector:  which obeys the differential equation



where the transfer matrix *K* contains off-diagonal elements , 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 , with  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 ** for the location of the IRF maximum and Δ for the full width at half maximum (FWHM) of the IRF:



where . 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 theIRF parameters *μ* and Δ:



When the compartmental model consists of independently decaying species, with populations  (superscript D stands for decay) their spectra are termed  (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:



Here the matrix  contains in its *l*-th column the decay  and the matrix  contains in its columns the populations  of the general compartmental model.

The superposition model for the  is given by the matrix formula:



Here the matrices and 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  experiments can be analyzed simultaneously. For each additional data set  only one scaling parameter  and one time shift parameter  must be added:



The dimensions of the matrices are collated in Table 1.

|  |  |  |
| --- | --- | --- |
|  | Nrow | Ncol |
| TRS | nt | nλ |
|  | nt |  |
| SADS | nλ |  |
|  | nt |  |
| A | nλ |  |
|  | nt |  |
| B | nλ |  |

Table 1 Dimensions of the matrices

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





Note that we have chosen this approximate product expression in order to avoid the complications which arise from the convolution of with a sine or cosine function.

Using these two functions the matrices and  can be computed as a function of all . The intrinsically nonlinear parameters of this model are the vector θ (containing the microscopic decay rates and inputs to the compartments ), the IRF parameters (), scaling parameter  and time shift parameter  for each additional data set, and the -vectors . 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  at wavelength  is computed as:



The reconstruction of the phase  is more cumbersome. From  and  the phase  modulo  can be computed. Then undesired jumps between subsequent phases and  can be corrected by applying appropriate counterjumps of .

### 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 (typically between 4 and 40 DOAS, thus because of cos and sin between 8 and 80 “spectra”), number of electronically excited 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 ,  , , then the size of the matrix of conditionally linear parameters  , the size of the extended C matrix is , when you store all C matrices this amounts to . 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 then . 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  for every wavelength λ.



Figure S . 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 . (A,D) Cosine oscillations with frequencies  (in /cm) (where *n* is the DOAS number) and damping rates  (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.

1. 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* [↑](#endnote-ref-1)