Grubb, M. P., Orr-Ewing, A. J., & Ashfold, M. N. R. (2014). KOALA: A program for the processing and decomposition of transient spectra. *Review of Scientific Instruments*, 85(6), [064104].
<https://doi.org/10.1063/1.4884516>

Peer reviewed version

Link to published version (if available):
[10.1063/1.4884516](https://doi.org/10.1063/1.4884516)

[Link to publication record in Explore Bristol Research](#)
PDF-document

Copyright (2014) American Institute of Physics. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics.
The following article appeared in Rev. Sci. Instrum. 85, 064104 (2014) and may be found at
<http://dx.doi.org/10.1063/1.4884516>

University of Bristol - Explore Bristol Research

General rights

This document is made available in accordance with publisher policies. Please cite only the published version using the reference above. Full terms of use are available:
<http://www.bristol.ac.uk/red/research-policy/pure/user-guides/ebr-terms/>

KOALA: A program for the processing and decomposition of transient spectra

Michael P. Grubb^a, Andrew J. Orr-Ewing, Michael N. R. Ashfold

School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK

Extracting meaningful kinetic traces from time-resolved absorption spectra is a non-trivial task, particularly for solution phase spectra where solvent interactions can substantially broaden and shift the transition frequencies. Typically, each spectrum is composed of signal from a number of molecular species (e.g. excited states, intermediate complexes, product species) with overlapping spectral features. Additionally, the profiles of these spectral features may evolve in time (i.e. signal non-linearity), further complicating the decomposition process. Here we present a new program for decomposing mixed transient spectra into their individual component spectra and extracting the corresponding kinetic traces: KOALA (Kinetics Observed After Light Absorption). The software combines spectral target analysis with brute-force linear least squares fitting, which is computationally efficient because of the small non-linear parameter space of most spectral features. Within, we demonstrate the application of KOALA to two sets of experimental transient absorption spectra with multiple mixed spectral components. Although designed for decomposing solution-phase transient absorption data, KOALA may in principle be applied to any time-evolving spectra with multiple components.

I. INTRODUCTION

A transient absorption experiment captures the time-resolved dynamics of a chemical process from the time-evolution of its absorption spectrum. Generally, a pump laser pulse will be used to initiate the reaction (by breaking a chemical bond or electronically exciting a molecule), and a second broadband probe laser pulse is then used to measure a change in the absorption spectrum of the system after an adjustable pump-probe time delay.^{1,2} A typical transient absorption dataset might contain between 30-500 absorption spectra at different pump-probe time-delays, and each spectrum may contain features from multiple chemical species: ground and excited state reactants, reaction intermediates, solvent complexes, product species and isomers, etc. The absorption signals from these different species will often be heavily overlapped, and must first be separated from the combined total spectrum before the full story of the chemical process can be discerned.

^{a)} Author to whom correspondence should be addressed. Electronic mail: michael.grubb@bristol.ac.uk

Separating mixed spectral signals is a general concern in the fields of physical and analytical chemistry,³ and the problem is approached by two broad methodological categories: target analysis and blind source separation. Target analysis describes techniques in which a spectral and/or kinetic model is assumed and utilized to constrain the decomposition,^{4,5} while blind source separation aims to separate the spectral signal based only on its time-variation in order to determine the most strongly contributing components. Blind source separation is useful when no prior information is known about the component spectra or reaction kinetics, and includes methods such as Principal Component Analysis, Independent Component Analysis,⁶ and Multivariate Curve Resolution.⁷ The drawback of blind source separation methods is that the underdetermined nature of the decomposition problem often returns solutions that are mathematically or statistically optimal but ultimately unphysical,⁸ although this is less true for advanced methods like Multivariate Curve Resolution.⁹ Additionally, all blind source separation techniques have difficulty modeling non-linearity in the signal such as the broadening or shifting of the component spectra in time.

Spectral target analysis is a particularly suitable and easily implemented technique for the decomposition of transient absorption spectra. For instance, the absorption spectrum of a stable chemical species can be measured in isolation and used as a basis function for modeling its contribution to the transient spectrum. The other components can often be well-modeled using simple Gaussian or Lorentzian profiles, which can be given floating width and position parameters in order to capture the time-dependent shifts due to vibrational cooling or other solvent interactions. Target analysis does require some manual oversight by the analyst, however, in order to ensure that the parameters of the spectral model are sufficiently constrained to avoid over-fitting and to obtain physically reasonable spectral profiles and kinetic traces. Data analysis software that can facilitate the convenient testing of various spectral models and constraints, and provide simultaneous feedback of the resulting kinetic traces, is therefore desirable.

Here, we present the KOALA (Kinetics Observed After Light Absorption) software to allow the pre-processing, decomposition, and subsequent kinetic trace analysis of transient absorption data-sets. KOALA uses an inelegant brute-force linear least squares algorithm to allow non-linear fitting of the spectra, which can counter-intuitively result in a faster computation of the best global fit than standard non-linear optimization methods due to the relatively small non-linear parameter space. This approach allows the decomposition to be computed efficiently and simultaneously with pre-processing and kinetic analysis, such that different spectral models can be easily tested. All of these features are incorporated into an intuitive graphical user interface for additional ease of use and to provide real-time feedback during analysis.

II. SPECTRUM PRE-PROCESSING

Transient pump-probe absorption spectra are subject to several unwanted but systematic experimental effects that must be corrected for before the spectra may be analyzed. The KOALA program incorporates three main procedures for correcting these unwanted effects: negative-time subtraction, re-baselining, and chirp correction. These procedures will be briefly reviewed here.

Figure 1: Transient vibrational spectrum of a solution of ICN in 5% methanol / 95% dichloromethane, after 266 nm photolysis of the I-CN bond. Before analysis is possible, the raw spectra (a) are first negative-time corrected to remove imprinted structure from the probe spectrum (b) and then re-baselined to correct for transient lensing effects (c).

A. Negative-time subtraction

A negative-time transient spectrum (i.e. a spectrum where the probe pulse arrives before the pump pulse) should theoretically result in a flat zero-value baseline. In reality, slight non-linearity in the photon detection efficiency of the detector can distort this baseline and imprint the wavelength distribution of the probe light onto the transient absorption spectrum. Therefore, it is common practice to subtract a negative time spectrum from each time-resolved spectrum in the dataset in order to correct for this distortion.¹ For spectra collected from experiments where the repetition rate of the laser is faster than the flow rate of the sample solution, negative-time subtraction has the added benefit of correcting for the presence of long lived product signal generated from previous pump/probe laser shots. Figure 1 displays a set of transient vibrational absorption spectra before (a) and after (b) subtracting the negative time spectrum, correcting some of the imprinted frequency oscillations caused by etaloning effects in the difference frequency generation crystal responsible for generating the infrared probe pulse.

B. Re-baselining

As observed in Figure 1, transient spectra are often subject to large time-dependent baseline offsets. The offsets are due to pump-induced transient lensing effects.^{10, 11} Absorption of the Gaussian-profiled pump laser causes a spatial gradient in either the energetic state population or structure of the solvent, which leads to a corresponding refractive index gradient in the sample. The end result is a slight deflection and focusing of the probe beam as it propagates through the liquid sample, altering the coupling of the probe into the detector and leading to the observed baseline shifts. Although transient lensing can be reduced by using low sample concentrations, reduced pump power, and focusing the probe beam into the sample more tightly than the pump beam, it cannot generally be eliminated and thus must be corrected for by re-baselining. KOALA allows up to five user-defined signal-free baseline regions to be selected and fit with a quadratic, linear, or unit function which is then subtracted from the experimental spectrum. Unfortunately, re-baselining can only be reliably performed when signal-free regions of the spectrum can be confidently identified. Figure 1 (c) demonstrates the result of applying a linear baseline correction to the negative-time subtracted spectra shown in Figure 1 (b).

Figure 2: Raw (a) and chirp-corrected (b) transient electronic spectra of a 30 mM solution of catechol in dichloromethane after 266 nm excitation. The dashed horizontal line in (a) defines the time zero threshold absorbance, and the inset plot shows the wavelength dependence of time zero with the best fit function to Equation (1). The plot indicates a positive chirp, characterized by a GDD of $80 \text{ fs}^2/\text{rad}$, and a TOD of $-86 \text{ fs}^3/\text{rad}^2$.

C. Chirp correction

Although not typically an issue for infrared probe wavelengths, the ultraviolet-visible super-continuum generated for transient electronic absorption experiments can be subject to substantial spectral chirp. The effect of this on the transient spectrum is that each frequency detected on a broadband detector will have a unique “time zero”, when the pump and probe laser pulses are overlapped in time. Although it is possible to reduce the chirp experimentally,¹² the effect can be corrected for during spectral pre-processing if enough early-time spectra are collected.^{1, 13} The chirp-correcting procedure incorporated in the KOALA program is outline below and demonstrated in Figure 2:

1. First, the unique time zero for each wavelength, t_0 , is defined as the moment when the absorbance reaches a user-set threshold.

2. Time zero is plotted as a function of wavelength, and fit with the Equation (1) to determine the absolute phase (ABP), the group delay dispersion (GDD), and the third order dispersion (TOD).^{14, 15}

$$t_0(\lambda) = ABP + GDD \left(\frac{2\pi c}{\lambda} \right) + \frac{1}{2} TOD \left(\frac{2\pi c}{\lambda} \right)^2 \quad (1)$$

3. The absorbance values of each wavelength of each spectrum at a particular time delay are re-assigned to a modified time delay based Equation (1). As only a discrete number of time delays can be obtained experimentally, most of the new absorbance values are obtained by linear interpolation of the available spectra. Small experimental time-steps, at least at early times where the spectra may be rapidly evolving, are therefore desirable for obtaining accurate interpolated absorbance values.

Because each chirp-corrected spectrum includes signal contributions from many experimental spectra, it should be mentioned that an abnormal signal level in one experimental spectrum will propagate into all of the chirp-corrected spectra. This effect is responsible for the sharp spikes at the blue end of the spectrum in Figure 2, and can be minimized by acquiring more spectra at early time delays. Regardless, as long as the artifact spikes are significantly narrower than the underlying spectral features, the ultimate effect on the extracted kinetic traces will be minimal.

III. DECOMPOSITION OF SPECTRAL COMPONENTS

A. Linear least squares decomposition

The spectral decomposition in KOALA is based on Linear Least Squares regression using a particular spectral model as the basis set. Each experimental transient spectrum, $[A]_\lambda$, can be decomposed as the sum of n component spectra, $[C]_{n,\lambda}$, each weighted by a weighting factor, $[I]_n$, related to the concentration of that component.

$$[A]_\lambda = [C]_{n,\lambda} [I]_n + [\epsilon]_\lambda \quad (2)$$

In Eqn. (1), $[\epsilon]_\lambda$ is the residual signal not captured by the spectral model. The best fit decomposition is obtained when the residual is minimized, which occurs when $[\epsilon]_\lambda$ is orthogonal to $[C]_{n,\lambda}$ and thus $[C]_{c,\lambda}^T [\epsilon]_\lambda = 0$. Substituting this expression into Equation (2) and solving for $[I]_n$ results in the equation for the best-fit component weights:

$$[I]_n = ([C]_{n,\lambda}^T [C]_{n,\lambda})^{-1} [C]_{n,\lambda}^T [A]_\lambda \quad (3)$$

Plotting $[I]_n$ as a function of time gives the kinetic trace of the components, which is the main result of the decomposition analysis. The decomposed spectrum can be recovered by substituting the weighting factors obtained from Equation (3) into Equation (2).

B. Non-linear decomposition by brute force linear least squares

A limitation of pure linear least squares decomposition is that the individual spectral components must evolve linearly in time. That is, only their weighting factor, and not their spectral profile, is allowed to change. In reality this is often not the case, as particular spectral features may shift or narrow in time as they structurally relax or their solvation environment is altered. When the shapes of the spectral components change in time, the spectral decomposition can no longer be solved analytically, and iterative non-linear optimization methods must be employed. Non-linear least squares algorithms, such as the popular Levenberg-Marquardt method, find minima on multi-parameter surfaces by using an estimated Hessian matrix to intelligently guide their search over the parameter space.^{16, 17} When the parameter space is small and sufficiently discretized, however, it is faster to simply perform an analytical least squares calculation for each possible non-linear parameter value and choose the value which returns the best fit to the data. Most UV-VIS array detectors are typically composed of about 1000 pixels, and infrared array detectors contain no more than a few hundred. Non-linear evolution of the spectral components is generally subtle, and a spectral feature might only shift by 10-20 pixels. Therefore, two-parameter functions such as a Gaussian spectral feature with floating width and shift parameters will only realistically require a few hundred least squares calculations, which most modern computers can perform in a less than ten milliseconds. For basis functions requiring more than two floating parameters, a brute force linear least squares fit quickly becomes impractical. Brute force linear least squares also becomes impractical if multiple overlapping components are fit with floating parameters, although we recommend against constructing such models as the decomposition will most likely suffer from over-fitting and the resulting kinetic traces will become nonphysical. The KOALA fitting algorithm therefore optimizes each nonlinear spectral component independently, for the purposes of computational efficiency.

C. Choosing spectral component basis functions

First, any stable species in the sample should be modeled using its static absorption spectrum, when it is available. Bleaches in the transient spectrum, arising from molecules initially present in the system that are destroyed by the pump laser, can usually be modeled in this manner. This approach is convenient since transient bleaches are often overlapped by positive signal from an excited or intermediate state, which can be decomposed much more easily if the bleach profile is

already known. When another isolated bleach feature from the same molecule is present in the spectrum, the decomposition becomes even easier as the timescale of the bleach recovery is also well-defined.

After all the stable species have been accounted for, the spectrum of remaining features can be modeled using logical functions. In transient infrared spectra, most features can be modeled as simple Gaussian or Lorentzian functions. Transient UV-VIS spectra do not always assume such pleasing functional forms, and require a more elaborate effort from the analyzer. One try, if the profile of the transient spectrum appears to settle to a final form at late time-delays, is to use the late time spectrum as the basis function representing the chemical product. KOALA also allows the construction of basis functions of arbitrary form from the sum of multiple Gaussian functions, if there is experimental or theoretical justification for the use of a particular spectral profile. When all else fails, some kinetic information can be extracted by simply forgoing decomposition and integrating the total transient signal over different wavelength ranges, and looking for differences in the time constants of the kinetic traces. All of these modeling methods have been implemented in KOALA in a convenient and accessible manner.

After all of the desired spectral features have been modeled with linear functions, various non-linear parameters can be floated. Although allowing all of the non-linear parameters to float will always result in a fit with a smaller residual, this will not necessarily result in the most physically correct model. Shifting or narrowing in the spectrum is the result of a kinetic process, and thus a floated position or width parameter should evolve with an exponential time constant. If a particular floated parameter varies chaotically in time, the model is simply fitting noise and the parameter should remain fixed. Care should be taken to constrain the limiting parameter values such that spectral features other than the one intended are not accidentally fit by stray basis functions.

Figure 3: Decomposed transient vibrational spectrum of a solution of ICN in 5% methanol / 95% dichloromethane, 180 ps after 266 nm photolysis of the I-CN bond.

D. Example analysis of transient absorption datasets

Figure 3 shows the transient vibrational absorption spectrum of a solution of ICN in 5% methanol / 95% dichloromethane, 180 ps after 266 nm photolysis of the I-CN bond (from the dataset displayed in Figure 1). The resulting $\cdot\text{CN}$ radicals can then either promptly recombine to reform ICN or the INC isomer, or react with hydrogen atoms on either of the solvent molecules to form HCN. The transient vibrational spectrum from 2000-2200 cm^{-1} is crowded with a number of spectral features that can be assigned as follows: an ICN bleach (2164 cm^{-1}), an INC feature (2065 cm^{-1}), a feature due to an intermediate complex of CN with the solvent (2043 cm^{-1}),¹⁸ an HCN product feature (2085 cm^{-1}) that is formed vibrationally hot and relaxes in time (as evidenced by the blue shifting of the spectral feature in time), a broad methanol bleach (2044 cm^{-1}) that grows as it is consumed by reactions with the $\cdot\text{CN}$ radical, and two sharper bleaches (2053, 2126 cm^{-1}) from dichloromethane also due to consumption by reactions with the $\cdot\text{CN}$ radical. A detailed interpretation and assignment of bands in the spectrum are discussed in detail elsewhere,¹⁹ but here we simply note that many of the features are partially, or wholly, overlapped and must be properly decomposed in order to extract their kinetic traces.

Following the procedure outlined in the preceding section, we first import static infrared spectra of neat dichloromethane and methanol to be used as basis functions representing their corresponding molecular species. Although the HCN product is stable and could also be modeled using its static absorption spectrum, we observe that it displays some time-dependent

shifting (due to being formed vibrationally hot)²⁰ and thus choose instead to model the HCN feature with a Gaussian function with a variable peak center. The neighboring INC feature does not display a noticeable time-dependent shift, and thus we choose a linearly weighted Gaussian function to represent the INC component.

The spectrum around 2040 cm^{-1} is composed of absorption features from three different molecules: methanol, dichloromethane, and the CN-solvent complex (CN*). The dichloromethane contribution here has already been independently determined by the isolated dichloromethane bleach feature at 2126 cm^{-1} , but the relative weightings of the methanol and CN* contributions are ambiguous as many combinations of weighting factors will lead to an acceptable fit. Therefore, we must apply some additional constraints to our model. One method is to remove the methanol contribution from the least squares fit, which we can do if we know both its spectral profile (which we do from the FTIR spectrum) and its kinetic behavior. First, we can see from the early time spectra in Figure 1 that no methanol bleach is initially present, so we can assume this feature starts off with a contribution of zero. From our late time spectrum we can see that the CN* intermediate complex has been consumed within the time window of the experiment, and thus the signal in that region of the spectrum arises from only the methanol bleach. Therefore, we know the bleach grows in from zero to its late time limit, and the only thing we do not know is the timescale of this growth.

The time evolution of the methanol bleach can be estimated a number of ways. From our reactive model, we could assume the growth should match the timescale of the HCN feature growth (as both features arise due to the same reactive step), which is a roughly exponential growth with a time constant of $\sim 150\text{ ps}$. We could also integrate the spectral signal on the red edge of the methanol bleach, which is broad and probably has only a small contribution from the CN-complex feature in this region. The low wavenumber side of the bleach shows exponential depletion with a time constant of $\sim 300\text{ ps}$. Therefore, we fix the methanol bleach to grow in with an exponential time constant between 150-300 ps, and fit the CN-complex to the remaining signal. We find by trial that choosing any time constant between 150-300 ps makes very little difference to the resulting kinetic traces of the remaining features.

Figure 4: Decomposed transient electronic absorption spectrum of a 30mM catechol solution in dichloromethane, 70 fs after pumping with a 266 nm laser pulse. Two features are present: a broad flat feature attributed to the excited state absorption of catechol (red), and a short lived (<250 fs) feature around 360 nm due to two photon absorption when the pump and probe lasers are temporally overlapped (blue).

Transient electronic spectra can be difficult to decompose, as the spectral profiles of the components can assume a variety of forms. The transient electronic spectra of catechol shown in Figure 2 are comprised of two components: a broad catechol excited state absorption (ESA) that spans the detected wavelength range, and a short lived two-photon absorption (TPA) feature at 340 nm present only when the pump and probe pulses are temporally overlapped.²¹ We use a late time transient spectrum as a basis function to model the excited state feature, as the spectral profile of the excited state does not noticeably change during the time window of the experiment, and a Gaussian function to model the two-photon signal at early times. The Gaussian function only roughly fits the experimental data, but as evidenced in Figure 5, is sufficient to produce reasonable kinetic traces.

IV. KINETIC TRACE ANALYSIS

The kinetic traces of the modeled components are generated from the weighting factors computed by the least squares regression during the decomposition step. Each basis function is area-normalized before decomposition, so that the weighting factor obtained from the least squares regression is always proportional to the concentration of the modeled component, regardless of changes in basis function width over time.

The KOALA program can be set to fit the kinetic traces with mono or bi-exponential functions to estimate the time constants of the chemical reactions involved in the measured system, although a simultaneous fit of all the kinetic traces to the integrated rate equations describing a particular chemical model is a more rigorous approach (and is implemented in a separate software package).²² The kinetic traces do, however, provide useful feedback for spectral pre-processing and decomposition. For instance, it must be ensured that the re-baselining process does not artificially create time-evolving signal where there should be none. Additionally, when spectral components are overlapping, the expected late-time evolution of the system can be used as a constraint on the shapes and positions of the basis functions when this information is ambiguous. For example, if a reagent or transient intermediate is completely consumed during the measured timescale, the basis functions can be optimized under the condition that their late-time signal asymptotically approaches zero.

Figure 5: Kinetic traces obtained from the decomposition of Figure 1, fit with bi-exponential functions (left), and Figure 2, fit with exponentially modified Gaussian functions and assuming an instrument response function of 100 fs (right).

Kinetic traces can also be fit with mono or bi-exponential functions that have been convolved with a Gaussian instrument response function of a particular full-width-half-maximum, defined by the temporal width of the experimental laser pulses.²³ This convolution results in the following bi-exponentially modified Gaussian function (without the second term for a mono-exponentially modified Gaussian function):

$$[I]_n(t) = Y - \frac{Y}{2} \operatorname{Erfc} \left[\frac{-t}{\sqrt{2}\sigma} \right] + \frac{A}{2} \exp(0.5\lambda_1(-2t + \lambda_1\sigma^2)) \operatorname{Erfc} \left[\frac{-t + \lambda_1\sigma^2}{\sqrt{2}\sigma} \right] + \frac{B}{2} \exp(0.5\lambda_2(-2t + \lambda_2\sigma^2)) \operatorname{Erfc} \left[\frac{-t + \lambda_2\sigma^2}{\sqrt{2}\sigma} \right] \quad (4)$$

where t is the pump-probe delay time, λ_n represents the exponential decay rates ($1/\lambda$ = the time constant of the reaction), Y represents the asymptotic limit of the weighting factor at infinite time, and σ is related to the full-width-half-maximum (FWHM) of the Gaussian instrument response function by $\text{FWHM} = 2\sqrt{2\ln 2}\sigma$.

Figure 5 shows the resulting kinetic traces obtained from decomposition of the example datasets in the previous section. The traces exhibit satisfactory exponential time evolution consistent with the expected kinetics, despite the absence of kinetic constraints (apart from the methanol trace, as discussed in the previous section) being applied during the spectral decomposition. An animation (generated using KOALA) of the time-evolving decomposed transient spectrum and corresponding kinetic traces from Figure 5 can be found in the supplemental material.²⁴

V. CONCLUSION

We have detailed the methodology of KOALA, new data analysis software for pre-processing, decomposing, and extracting kinetic traces from time-resolved spectra. The simultaneous computation and visualization of these processes allows real-time feedback during the testing of spectral models.²⁵ KOALA uses a constrained brute-force linear least squares technique to allow for non-linear evolution of the component spectra during decomposition in a computationally efficient manner, and includes tools for importing or creating spectral model functions. The software is written in LABVIEW, and the source code is freely available, along with a stand-alone executable file.²⁶

ACKNOWLEDGMENTS

We would like to thank the ERC for the award of Advanced Grant 290966 CAPRI. M.P.G is supported by a Marie Curie International Incoming Fellowship (PIIF-GA-2012-326988). M.P.G. thanks Dr. Ben Truscott for help in the derivation of Equation 4, and Dr. Tom Zhang (Montana State University) for helpful discussion regarding chirp correction. We thank Dr. Gareth Roberts, Hugo Marroux, Greg Dunning, Joel Luke, and Jack Warren for their feedback and testing the KOALA program.

REFERENCES

- ¹U. Megerle, I. Pugliesi, C. Schriever, C. F. Sailer and E. Riedle, *Appl. Phys. B* **96**, 215 (2009).
- ²G. M. Greetham, P. Burgos, Q. A. Cao, I. P. Clark, P. S. Codd, R. C. Farrow, M. W. George, M. Kogimtzis, P. Matousek, A. W. Parker, M. R. Pollard, D. A. Robinson, Z. J. Xin and M. Towrie, *Appl. Spectrosc.* **64**, 1311 (2010).
- ³S. Wold and M. Sjostrom, *Chemometrics and Intelligent Laboratory Systems* **44**, 3 (1998).

- ⁴I. H. M. van Stokkum, D. S. Larsen and R. van Grondelle, *Biochimica Et Biophysica Acta-Bioenergetics* **1657**, 82 (2004).
- ⁵J. M. Beechem, M. Ameloot and L. Brand, *Analytical Instrumentation* **14**, 379 (1985).
- ⁶C. J. Rowlands and S. R. Elliott, *Journal of Raman Spectroscopy* **42**, 1761 (2011).
- ⁷C. Ruckebusch and L. Blanchet, *Anal. Chim. Acta* **765**, 28 (2013).
- ⁸M. Defernez and E. K. Kemsley, *Trac-Trends in Analytical Chemistry* **16**, 216 (1997).
- ⁹C. Ruckebusch, S. Aloise, L. Blanchet, J. P. Huvenne and G. Buntinx, *Chemometrics and Intelligent Laboratory Systems* **91**, 17 (2008).
- ¹⁰M. Terazima, *Chem. Phys. Lett.* **230**, 87 (1994).
- ¹¹M. Kopczynski, T. Lenzer, K. Oum, J. Seehusen, M. T. Seidel and V. G. Ushakov, *PCCP* **7**, 2793 (2005).
- ¹²C. H. B. Cruz, P. C. Becker, R. L. Fork and C. V. Shank, *Opt. Lett.* **13**, 123 (1988).
- ¹³C. G. Elles, C. A. Rivera, Y. Zhang, P. A. Pieniazek and S. E. Bradforth, *J. Chem. Phys.* **130**, 084501 (2009).
- ¹⁴I. Walmsley, L. Waxer and C. Dorrer, *Rev. Sci. Instrum.* **72**, 1 (2001).
- ¹⁵R. Trebino, *Frequency-Resolved Optical Gating: The Measurement of Ultrashort Laser Pulses* (Kluwer Academic Publishers, 2002).
- ¹⁶D. W. Marquardt, *J. Soc. Ind. Appl. Math.* **11**, 431 (1963).
- ¹⁷S. Roweis, (<http://www.cs.toronto.edu/roweis/notes/lm.pdf>).
- ¹⁸A. C. Crowther, S. L. Carrier, T. J. Preston and F. F. Crim, *J. Phys. Chem. A* **112**, 12081 (2008).
- ¹⁹R. A. Rose, S. J. Greaves, T. A. A. Oliver, I. P. Clark, G. M. Greetham, A. W. Parker, M. Towrie and A. J. Orr-Ewing, *J. Chem. Phys.* **134**, 244503 (2011).
- ²⁰S. J. Greaves, R. A. Rose, T. A. A. Oliver, D. R. Glowacki, M. N. R. Ashfold, J. N. Harvey, I. P. Clark, G. M. Greetham, A. W. Parker, M. Towrie and A. J. Orr-Ewing, *Science* **331**, 1423 (2011).
- ²¹M. Lorenc, M. Ziolk, R. Naskrecki, J. Karolczak, J. Kubicki and A. Maciejewski, *Appl. Phys. B* **74**, 19 (2002).
- ²²M.P. Grubb, AKITA software package (2014, unpublished)
- ²³R. Spesyvtsev, PhD Thesis, University College London, 2013.
- ²⁴See supplemental material at [URL will be inserted by AIP] for the animation of the time-evolving decomposed spectrum
- ²⁵See supplemental material at [URL will be inserted by AIP] for a screenshot of KOALA's graphical interface.
- ²⁶The source code and .exe file can be downloaded from www.bristoldynamics.com/resources, free of charge