# Intelligently optimized global analysis of time resolved spectra with particle swarm optimization

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Time-resolved spectroscopy, especially transient absorption spectroscopy (TAS), provides valuable insights to excited state dynamics. Analyzing TAS data involves fitting complex kinetic traces at various probe wavelengths using different rate equations. Conventional TAS global fitting methods require domain experts to establish physically valid models and provide good initial guesses to generate converged solutions. This poses challenges for non-experts who seek to utilize TAS, thus limiting its broader application and impact. To address this problem, we propose an intelligent optimization framework based on the particle swarm optimization (PSO) algorithm. In the proposed method, the PSO algorithm acts as the global fitting method to find the optimal values of the target variables or unknown parameters in the kinetics models. The target solution is optimized by iteratively updating candidate solutions with respect to an objective feedback signal. We demonstrated the effectiveness of the proposed PSO-based global fitting method with both synthetic and experimental datasets. The results show that our proposed method can successfully find the optimal target values in the global fitting process automatically, thus eliminating the iterative manual labor traditionally required. The proposed intelligent optimization framework provides a novel approach for automatic global fitting of TAS data, which significantly enhances the accessibility and utilization of the TAS methodology.

## 1. Introduction

Time-resolved spectroscopy is a powerful experimental technique to investigate the dynamics of excited states or transient species. It has been extensively applied in various fields, such as photochemistry, photobiology, photophysics, and materials science [1-8]. Among various time-resolved spectroscopic techniques, the transient absorption spectroscopy (TAS), also known as the pump-probe spectroscopy, undoubtedly stands out as one of the most widely used techniques. TAS provides insight into kinetic processes involving both bright (emissive) and dark (non-emissive) excited states. It has emerged as a prominent technique for studying electron and energy transfer dynamics in complex systems. Especially in recent years, the popularity and accessibility of TAS has continued to increase due to the availability of commercial TAS setups and lower-cost ultrafast lasers. However, the increasing complexity of data analysis and modeling requirements has become a challenge. TAS experiments produce two-dimensional (2D) data matrices containing spectral and temporal information, as well as a significant level of noise. Analyzing the TAS data often requires fitting the complex kinetics at various probe wavelengths using different rate equations. Global fitting over the entire 2D data matrix is often necessary to account for strong spectral overlap of various excited states or transient species and to discern key features of the involved ultrafast processes [9,10].

In the conventional global fitting process, for example least square method (LSM), the initial values of the variable for the fitting problem are usually required to be set by users for the optimization algorithm to find the optimal values within the search space. However, choosing a good set of initial values for the unknown parameters is quite challenging and there is no such a standard approach to set it in the existing literature. A common method is to fit individual kinetic traces at various characteristic wavelengths to obtain a basic idea on the possible model and approximate time constants involved. This requires expertise that users need to develop over time by trial-and-error. Without this expertise, users must manually try many potential initial values through repeated trials to achieve a converged fitting result. This is time-consuming, inefficient and error-prone. Even users with rich experiences in setting those initial values need to run multiple trials manually. Therefore, most TAS users prefer to choose single wavelength fitting over global fitting as an "easier" or quicker approach, on the expense of ignoring the valuable insights that global fitting could bring. However, if global fitting were made more accessible through automating the initialization step, many users with limited experience in the field could achieve more insightful analyses by applying this technique.

To solve the problem, in this work, we proposed an intelligent optimization framework to enable the automatic global fitting of TAS data based on particle swarm optimization (PSO) algorithm. PSO algorithm was originally proposed by Kennedy and Eberhart [3]. It is inspired by the social behavior of birds flocking or fish schooling. As a population-based intelligent computational method, it globally optimizes problems by iteratively updating candidate solutions with respect to an objective feedback signal. PSO is an efficient heuristic optimization method that is computationally simple and easy to implement, making it widely used in various applications, such as geotechnical engineering [11], power generation and controlling [12], healthcare

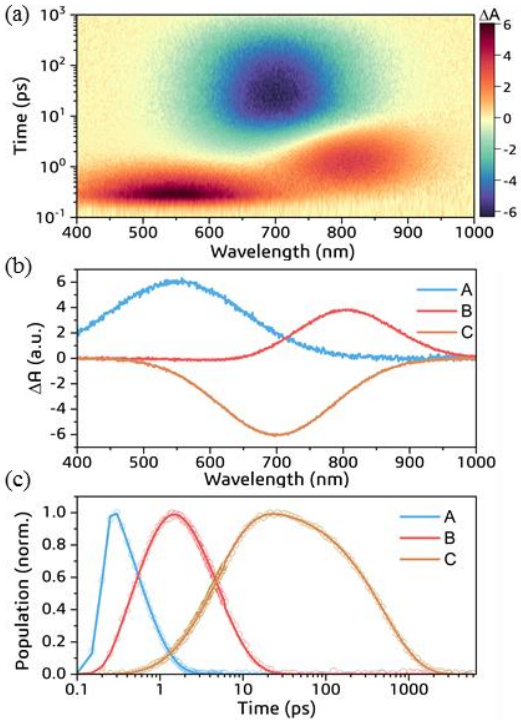


FIG. 1. (a) Synthetic TAS data based on a sequential three species model. Species-associated (b) spectra and (c) kinetics reconstructed from global fitting.

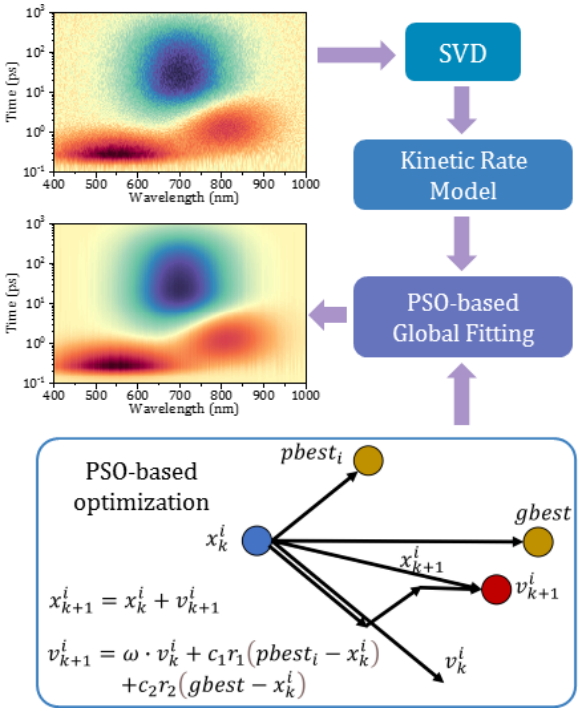


FIG. 2. The overall workflow of the proposed PSO-based optimization.

[13], traffic monitoring and scheduling [14], environmental engineering [15], and optical engineering [16,17]. PSO maintains a swarm of candidate solutions and iteratively morphs this swarm toward optimality [18]. Unlike conventional approaches requiring precise initial guesses for model parameters, our PSO-based framework globally optimizes TAS fits without demanding expert judgment or nuanced trial-and-error. PSO and related metaheuristic algorithms are well-suited to navigate the complex parameter spaces of TAS models and unearthing optimal solutions even from random starts.

## 2. Results and Discussion

For the global fitting analysis of the time-resolved spectra, there are mainly two types of methods: global lifetime analysis (GLA) and global target analysis (GTA) [9,10]. GLA is a relatively simple and fast method for assessing the number and values of the lifetime constants involved and generates the decay-associated spectra (DAS). GTA, on the other hand, offers a more physically significant kinetic model that provides species-associated spectra (SAS) to explain the underlying mechanism and reveal ultrafast processes in complex systems. In this work, we used GTA for global fitting analysis, but it should be noted that our proposed optimization mechanism based on PSO can be readily applied to GLA and to replace other fitting methods which require providing initial variable values. Analysis of the TAS datasets were performed using singular value decomposition (SVD) followed by global fitting to a specific kinetic rate model. To illustrate the GTA method, we take the commonly used sequential three species model as an example, as shown in Fig. 1. We assume that there is a series of states evolving with following sequence:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C} \xrightarrow{k_3} \mathrm{GS}$$

where the excited state/species A first converts to intermediate state/species B, then B converts to the final product of state/species C, and finally C relaxes back to ground state (GS). To do GTA global fitting analysis, we first conducted SVD to deconvolute the two-dimensional spectra to produce an orthonormal set of basis spectra which describes the wavelength dependence of the species, and a corresponding set of orthogonal vectors which describes the time dependent amplitude of the basis spectra [19]. During the global fitting process, a species-associated kinetic model (Eqs 1-3) was fit to a linear combination of the time-dependent amplitude vectors and the same linear combination of basis spectra was used to construct the spectra for the species [20]. The rate equations of this model are described as follows:

$$\frac{dN_1}{dt} = -k_1 N_1 \quad (1)$$

$$\frac{dN_2}{dt} = k_1 N_1 - k_2 N_2 \quad (2)$$

$$\frac{dN_3}{dt} = k_2 N_2 - k_3 N_3 \quad (3)$$

where $N_1$ is the population of initially generated excited state or species A, $N_2$ is the population of intermediate state or species B, $N_3$ is population of final product of state or species C, $k_1$ is the rate constant for the process converting A to B, $k_2$ is the rate constant for the process converting B to C, and $k_3$ is the rate constant of C relaxation back to ground state (GS). In Eqs. (1-3), the

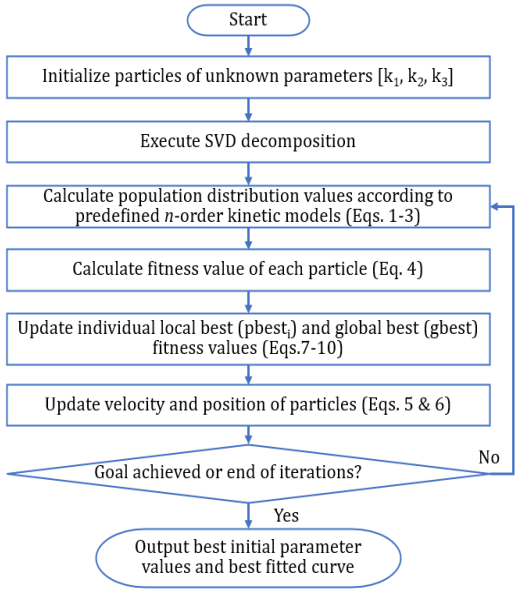


FIG. 3. The detailed steps of PSO-based global fitting method to automatically adjust the initial parameters for global fitting using LSM.

unknown rate parameters [$k_1$, $k_2$, $k_3$] are to be extracted after the global fitting. The objective of fitting is to minimize the error between the fitted results and the input data. After SVD and global fitting, a well-fitted procedure can provide valuable information: (1) Spectra corresponding to the excited state/species A, intermediate state/species B, and final product state/species C (Fig. 1b), allowing for the identification of unique spectral signatures for each species involved in the reaction, even with strong spectral overlap; (2) Kinetic traces showing how the concentrations of A, B, and C change over time (Fig. 1(c)), providing insights into the lifetimes of each species, their sequence of appearance and disappearance, and interconversion mechanisms. Manually setting initial values for the unknown parameters in the global fitting process using the LSM algorithm is time-consuming, inefficient and prone to error. To overcome these limitations, we applied the PSO optimization algorithm to find the optimal value of the unknown parameters in the kinetic models automatically. For time-resolved spectra with three state/species sequential mechanism, the vector [$k_1$, $k_2$, $k_3$] formed by the unknown parameters is considered as the particle. Each particle represents a candidate solution in a multidimensional search space and has a position and a velocity. The velocity and position of particles are influenced by their own best position and the best position of the entire swarm, allowing particles to communicate and move towards optimal regions in the search space. PSO iteratively updates the velocity and position of particles in a population according to the fitness function until the optimal solution is found or a predefined stopping criterion is met. In this work, the fitness value of the PSO optimization is determined by calculating the root mean square error (RMSE) between the input data as shown in Fig. 1(a) and the fitted values based on kinetic model. The RMSE is given as:

$$fitness = \sqrt{\sum_{i=1}^{N} \frac{(\hat{y}_i - y_i)^2}{N}} \quad (4)$$

where $y_i$ represents the original data points in transient absorption spectra, $\hat{y}_i$ represents the estimated TA data value which is obtained by multiplying matrix of species-associated spectra data (Fig. 1(b)) and the fitted matrix in population distribution data based on kinetics Eq. 1-3 and $N$ is the total number of data points.

The overall workflow of the proposed PSO-based global fitting method is depicted in Fig. 2. As indicated in Fig. 2, the original spectral data is fed into the SVD decomposition block to generate a brief idea on the number of feature spectra and kinetics. The time-dependent population kinetics of each state can be then estimated according to the predefined kinetics equations (Eqs. 1-3). The PSO optimization algorithm finds the best values of unknown parameters with the objective of minimizing the error between the original input value and its estimated value within the search space. After the fitting process, we can fix the parameters of the kinetics models [$k_1$, $k_2$, $k_3$] and finally obtain the best fitted transient absorption spectra data. Fig. 3 shows the workflow of the optimization process. The detailed steps for the PSO-based fitting process are given as follows:

**Step 1**: Initialize the position and velocity of each particle (e.g. [$k_1$, $k_2$, $k_3$], a vector formed by unknown parameters in kinetics models).

**Step 2**: Execute SVD decomposition for the input data.

**Step 3**: Calculate population distribution values according to predefined *n*-order kinetic models (Eqs. 1-3).

**Step 4**: Calculate the fitness value of each particle in the population for the current step.

**Step 5:** Update individual local and global best fitness values (Eqs. 7-10 in Supporting Information).

**Step 6**: Update the velocity and position of each particle according to the current local and global best fitness values (Eqs. 5-6 in Supporting Information).

**Step 7**: Check whether the goal of optimization (reach predefined error) is achieved or the maximum number of iterations is reached. If not, then go back to **Step 3** and repeat the process.

During the PSO optimization process, users need to specify certain control parameters such as inertia weight ($w$), acceleration coefficient ($c_1$, $c_2$), and lower/upper bounds of the search space for each unknown parameter ($L_b$, $U_b$). The first two parameters can be easily set with default values in the PSO algorithm implemented in Matlab or Python. Typically, users only need to specify the fitness function of the PSO optimization process and the population size of the swarm particles. In this study, we set the population size to 50. For all other control parameters, we utilized the default values in the PSO algorithm in Matlab. However, in certain scenarios where the kinetics models are more complex or the signal-to-noise ratio is high, users have the flexibility to

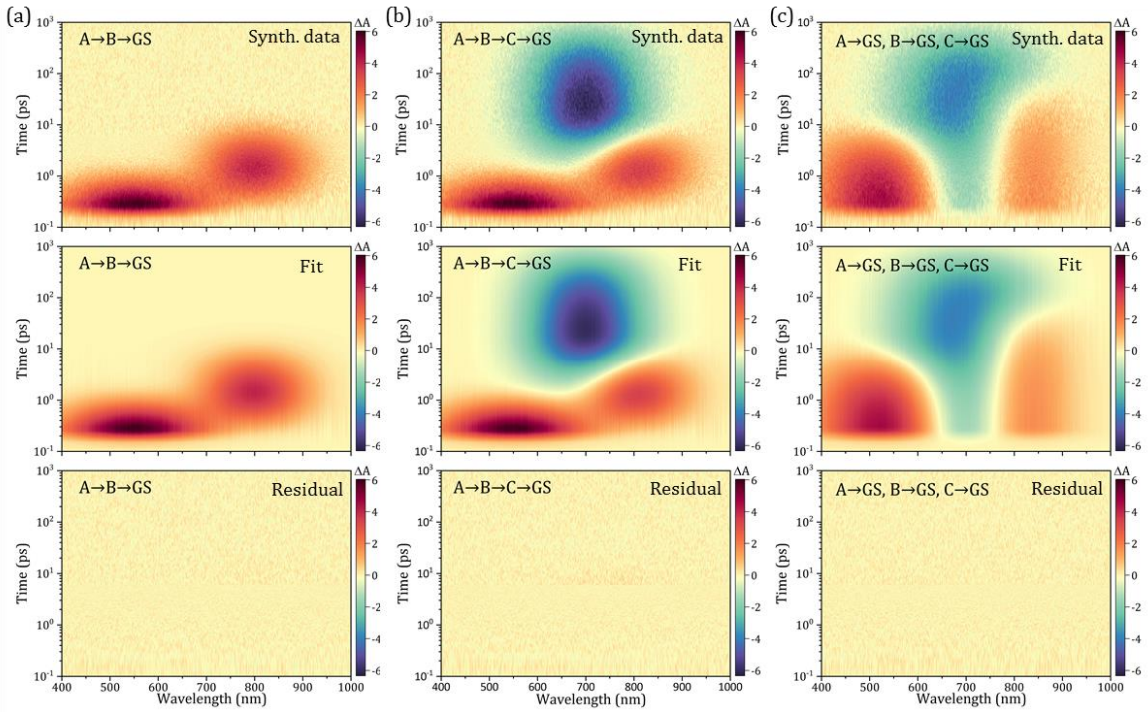


FIG. 4. Synthetic TA data (upper panel), global fitting (middle panel), and RMS (bottom panel) of (a) two species model: A→B→GS; (b) sequential three species model: A→B→C→GS; (c) parallel three species model: A→GS, B→GS, C→GS.

adjust the lower and upper bounds of the search space within a reasonably large range. In the default settings of the PSO algorithm in Matlab, the initial positions and velocities were randomly assigned for both experiments.

The detailed steps of a standard PSO optimization algorithm to search the optimal value is provided in Supporting Information. With this proposed PSO-based optimization algorithm, the optimal values for the unknown parameters can be found automatically with fast speed, which eliminates the need for manual trial-and-error searching. This approach allows non-professionals in the target domain to perform curve fitting without prior domain knowledge, thus lowering the professional requirements for personnel performing curve fitting. The traditional global fitting approach requires users to manually attempt various potential initial values through repeated trials in order to achieve a converged fitting. This process is inherently unstable and does not guarantee successful convergence. It heavily relies on the expertise and familiarity of the user with the system under study. In this work, we have addressed this issue by eliminating the need for an initial guess in the fitting process, thus mitigating this instability.

To demonstrate the accuracy and robustness of the proposed PSO-based global fitting method, we evaluated its performance using both synthetic and experimental TAS data sets. The synthetic TAS data sets were generated based on three different sets of kinetic models: 1) two state/species sequential, 2) three state/species sequential, and 3) three state/species parallel models. For the two-state/species sequential mechanism, two kinetic rate equations (Eqs. 1-2) were used for fitting, and the particle in PSO optimization was represented as [$k_1$, $k_2$]. For the three-state/species sequential mechanism, three kinetic models (Eqs. 1-3) were used for fitting, and the particle in PSO optimization was represented as [$k_1$, $k_2$, $k_3$]. For the parallel models, three kinetic models (Eq. 1) with different rate $k_i$ were involved in parallel style, and the particle in PSO optimization was represented as [$k_1$, $k_2$, $k_3$]. In all cases, significant white noises were added to the synthetic TAS data to simulate the experimental signal-to-noise level, as shown in the upper panel of Fig. 4. The original synthetic datasets were provided in the Supporting Information. After performing PSO-based global fitting with these three types of kinetics mechanisms, their average residual and RMSE values were calculated and presented in Table 1. The average residual is defined as $AR = (1/N)\sum_{i=1}^{i=N}(\hat{y}_i - y)$, where N is the number of fitting points, $\hat{y}_i$ is the fitted value of the spectra data, and $y$ is the synthetic/measured data. According to the results in Table 1, we can see that the average residual and RMSE values are very small and the kinetic models are very well-fitted. This indicates that the proposed PSO-based method can successfully find the best parameters for the kinetic models in the global fitting process. The corresponding fitting results and residuals are presented in the middle and bottom panels of Fig. 4.

Furthermore, we also applied the PSO-based global fitting to our previous experimental TAS data measured from various materials using higher-order kinetic models, such as perovskites and two-dimensional transition metal dichalcogenides (TMD). For the

perovskite ($CH_3NH_3SnI_3$) experiment, the 120 fs, 1 kHz output of a commercial Ti:sapphire oscillator/amplifier (Tsunami/Spitfire, Spectra-Physics) was split to seed and pump a laboratory-constructed optical parametric amplifier used to generate the 650 nm excitation ("pump") beam, and to generate a femtosecond continuum probe, by using either a sapphire crystal for the visible range or a proprietary crystal for the NIR spectral region (Ultrafast Systems, LLC). Transient spectra were collected by using customized commercial detectors (Helios, Ultrafast Systems, LLC) [21]. For the monolayer TMD ($WS_2$), The TA spectra were collected using an amplified Ti:sapphire laser system (Solstice Ace, Spectra Physics) with an output of 800 nm at 1 kHz repetition rate, a 35 fs pulse width and a power of 5.6W. 20% of the output 800 nm (1.12 W) was delivered to an optical parametric amplifier (TOPAS-prime, Newport) to generate the tunable pump pulses. A small portion of 800 nm fundamental beams (500 nJ per pulse) was focused onto a 3 mm sapphire plate to produce the white-light continuum (WLC) probe pulses. A computer-controlled, piezodriven high-precision translation stage (Physik Instrumente) incorporating a long travel range motorized stage (Newport) was placed in the pump beam arm to generate a time delay between pump and probe pulses with 1 fs time delay precision and an 8 ns time window [22]. Fig. 5 illustrates the proficiency of the proposed approach in achieving commendable fittings across the experimental datasets. These results demonstrate that our proposed PSO-based global fitting methodology is capable of achieving good global fittings by extracting the key kinetic features of complex TAS data accurately, even in the presence of strong spectral overlap and significant noise level.

Table 1. The performance of the PSO-based global fitting for three kinetics mechanisms.

| Dataset | Average Residual | RMSE |
|---|---|---|
| 1 | -2.1401E-4 | 0.2873 |
| 2 | 8.1044E-4 | 0.2866 |
| 3 | 4.858910E-4 | 0.2866 |

Furthermore, we have compared the fitting results obtained using the PSO-based GTA method and those achieved using the conventional GTA method with various initial guesses. As an illustrative example, the comparison is conducted on simulated dataset 2. First, we employed the conventional GTA with "good" initial guesses ($k_1$=0.1, $k_2$=1, $k_3$=100, $t_0$=1.5), which converged within a few seconds, yielding the fitting results presented in table S1 in the Supporting Information ($t_0$ represents the time zero shift). Subsequently, we deliberately selected "bad" (suboptimal) initial guess values ($k_1$= 100, $k_2$=10, $k_3$=1, $t_0$=1.5), which impeded the convergence of the fitting process, resulting in the inability to obtain any meaningful results. Then we implemented our proposed PSO-based GTA without any initial guess inputs, we achieved fitting results of the same accuracy to those attained by the conventional GTA with the "good" initial inputs provided by an expert. Therefore, we can discern that the advantage of the PSO-based GTA method in our study does not lie solely in improving the fitting accuracy, but rather in eliminating the need for manual attempts to attain convergent fitting results. This particular advantage is highly beneficial for non-experts in the field of ultrafast spectroscopy or when investigating unfamiliar systems.

## 3. Conclusion

In conclusion, we proposed an optimization framework for global fitting of transient absorption spectroscopic data based on PSO optimization algorithm. Our proposed approach can automatically and intelligently find the unknown parameters in the complex variable space for TAS kinetic models. The accuracy and robustness of our global fitting methodology is demonstrated on multiple complex TAS datasets. Automating process of searching for the best parameter values of kinetics models through PSO can drastically boost efficiency and quality of TAS global fitting for users by focusing their effort on interpreting results rather than tuning inputs through guesswork. Our proposed PSO-based global fitting methodology can be readily applied to fit other time-resolved spectroscopic data as well, such as time-resolved fluorescence (TRF), indicating its versatility and widespread applicability for the analysis of diverse time resolved spectral data. It is noteworthy that in this study, the PSO optimization algorithm was used only to automatically search for the best parameters of kinetic models for the global fitting of TAS dataset. However, prior to the optimization procedure, the detailed kinetic models for a particular type of material still needs to be predefined, which requires a certain level of expertise from domain experts. In our future work, we will explore the solution to further automate this process even without determining the order or the types of the kinetics models for various materials using deep learning techniques.

## Declaration of Competing Interest

The authors have no conflicts to disclose.


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## Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/

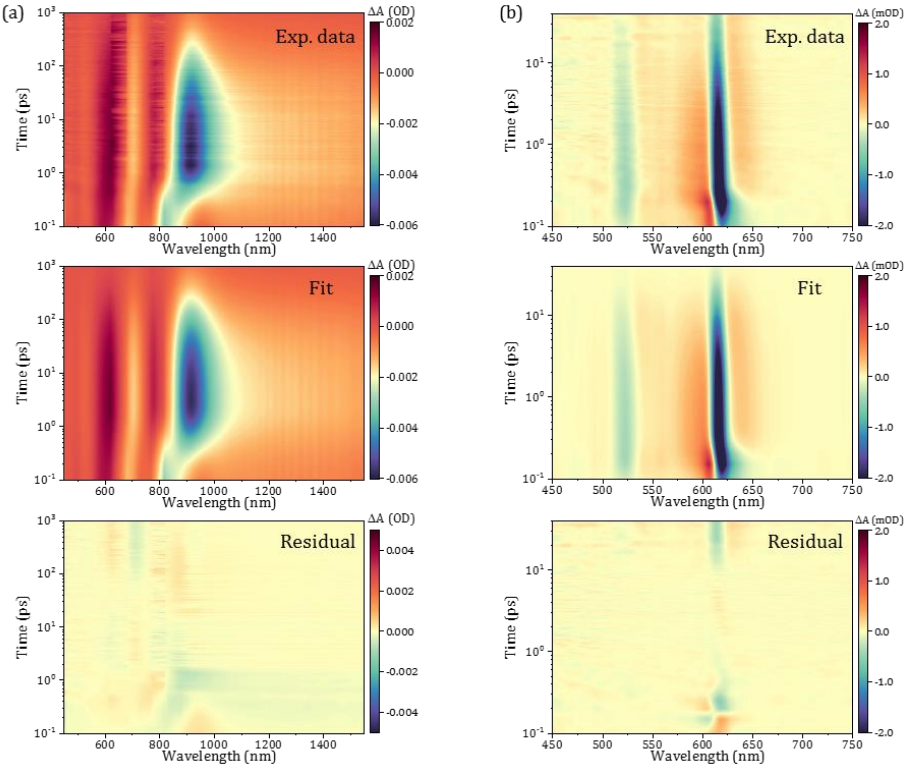


FIG. 5. Experimental TA data (upper panel), PSO based global fitting result (middle panel), and RMS (bottom panel) of $MASnI_3$ perovskite film excited under 650 nm from Ref. [21] (a) and oleic acid treated monolayer $WS_2$ excited under 630 nm from Ref. [22] (b).

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# Supplementary Material

### 1. PSO Optimization

The PSO optimization method involves the following steps:

**Step 1 (Initialization)**: Initialize a population of particles randomly within the search space. Each particle is associated with a local best position ( $pbest_i$ ) and a fitness value ($pbest_{i_{value}}$), which are initialized with the current position and fitness value of n particles.

**Step 2 (Update Velocity)**: Update the velocity of each particle based on its current velocity, global best position, and local best position. The velocity of the ith particle in the next step is calculated using equation:

$$v_{k+1}^i = \omega \cdot v_k^i + c_1 r_1 \left(pbest_i - x_k^i\right) + c_2 r_2 \left(gbest - x_k^i\right) \quad (5)$$

where $v_k^i$ is the velocity of the ith particle at step $k$; $w$ is the inertia weight, which controls the influence of the velocity in the previous step on the velocity in next step; $c_1$ and $c_2$ are the acceleration coefficients, which define the influence of local best position and global best position, respectively; $r_1$ and $r_2$ are the random numbers between zero and one; $pbest_i$ is the local best position of the ith particle; $x_k^i$ is the current position of the ith particle at step $k$; $gbest$ is the global best position of the particles.

**Step 3 (Update Position)**: Update the position of each particle based on its velocity in next step using equation:

$$x_{k+1}^i = x_k^i + v_{k+1}^i \quad (6)$$

**Step 4 (Evaluate Fitness Function):** Calculate the fitness value of each particle based on its new position. The fitness value of the ith particle is given by $f(x_{k+1}^i)$, where $x_{k+1}^i$ is the new position of the ith particle.

**Step 4.1 (Update Local Best)**: Update the local best position and fitness value of each particle based on its new position and fitness value. If the fitness value of the ith particle at (k+1)th step is better than its local best fitness value ($pbest_{value}$), then update the local best position and its fitness value as follows:

$$pbest_i = x_{k+1}^i \quad (7)$$
$$pbest_{value} = f(x_{k+1}^i) \quad (8)$$

**Step 4.2 (Update Global Best)**: If the fitness value of the ith particle at step k+1 is better than the global best fitness value ($gbest_{value}$), then update the global best position and its fitness value as follows:

$$gbest = pbest_i \quad (9)$$
$$gbest_{value} = f(gbest) \quad (10)$$

**Step 5 (Termination)**: If the termination criterion (e.g., the maximum number of iterations or a predefined change in fitness value) has been satisfied, stop the iteration. Otherwise, go back to step 2 and repeat the process until the termination criterion is met.

By iteratively following these steps, PSO can eventually find the optimal solution to the optimization problem.

Table S1. Comparison between the fitting results of the PSO-based GTA method and the conventional(Conv) GTA method with various initial guesses.

| (ps) | Para for synthetic data | PSO-based GTA without initial guesses | Conv GTA with best initial guesses ($k_1$= 0.1, $k_2$=1, $k_3$=100, $t_0$=1.5) | Conv GTA with bad initial guesses ($k_1$=100, $k_2$=10, $k_3$=1, $t_0$=1.5) |
|---|---|---|---|---|
| $k_1$ | 0.5 | 0.502±0.002 | 0.502±0.002 | Fitting does not converge |
| $k_2$ | 5 | 5.03±0.02 | 5.03±0.02 | |
| $k_3$ | 500 | 532±4 | 532±4 | |
| $t_0$ | 0.2 | 0.2239±0.0003 | 0.2239±0.0003 | |