Supporting Information

A New Way to Predict the Efficiency of Optical Limiters without Providing an Experiment: Processing of TDDFT Calculations for the Case of Pure Two-Photon Absorption

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1. Mathematical investigations

1.1. Absorption Curves

Below is a nonlinear function to approximate the relationship between absorption coefficient and incident impact:

\[ k(x) = \frac{c}{b \left(1 + \frac{(\ln(x) - a)^2}{b^2}\right)^{-1}} \]  

(1)

In our simulations, the incident impact is the power of external electric fields that are applied to the molecules on calculating the TDDFT transitions. Function (1) is the modified Cauchy distribution. All three parameters – \(a, b, c\) are responsible for stretching the curve along the X; Y axes. They have no physical meaning in terms of describing nonlinear absorption but are necessary for fitting the FF-TDDFT simulation data. In contrast to the polynomial function describing nonlinear absorption as

\[ k(x) = \alpha + \beta x + \gamma x^2, \]  

(2)

where \(\alpha, \beta\) and \(\gamma\) are linear and nonlinear two- and three-photon absorption coefficients, respectively, the modified Cauchy distribution (1) allows obtaining smoother curves with a higher \(R^2\) factor and calculating more parameters of the optical limiting efficiency (Table 1 in the main text). Expression (1) can be reduced to (2) by expanding into a Taylor series. In this work, we restrict ourselves to a pure two-photon absorption model (\(\gamma = 0\) in Eqn. 2). However, it is important to find the point in the vicinity of which to carry out this decomposition.

Function (1) consists of a large number of twists that can be found by differential methods (Fig. S1).

\[ \frac{dk}{dt} = \frac{2bc(a - t)}{(b^2 + (a - t)^2)^2} = k \cdot \frac{2(a - t)}{b^2 + (a - t)^2}, \]  

(3)

where \(t = \ln(x)\).
Figure S1. Modified Cauchy function and its derivatives in logarithmic coordinates: (a, b) fitting of absorption points (TDDFT calculations) and tangents to the points \(x_{NL1}\) and \(x_{NL2}\); (c, d) the view of the 1\(^{st}\) and 2\(^{nd}\) derivatives with localization of characteristic points: \(x_D\) – absorption saturation, \(x_{NL1}\) and \(x_{NL2}\) – points at which twists of the Cauchy function are observed on increasing nonlinearity.

Solution of \(\frac{dk}{dt} = 0\) gives the absorption saturation position – \(x_D\).

However, function (3) itself has an extremum, which is calculated from the equality to zero of the second derivative:

\[
\frac{1d^2k}{k dt^2} = \frac{-2b^2 + 6(a-t)^2}{(b^2 + (a-t)^2)^2}
\]  

(4)

to give the point
\[ x_{NL1} = \exp \left( a - \frac{b}{\sqrt[3]{3}} \right). \] (5)

We have chosen only the first solution because the second one is out of range and has no physical meaning. Similarly, we find the position of the point \( x_{NL2} \) from the equality to zero of the third derivative:

\[ x_{NL2} = \exp (a - b) \] (6)

In the vicinity of these points, we are reducing function (1) to the linear two-photon absorption model:

\[
k_{(x_{NL1})} = \left( -\frac{3(\sqrt[3]{3} - 2b)c}{8b^2} \right) + \frac{3\sqrt[3]{3} \exp(-a + b/\sqrt[3]{3})c}{8b^2} x \] (7)

\[
k_{(x_{NL2})} = \frac{(-1 + b)c}{2b^2} + \frac{\exp(-a + b)c}{2b^2} x \] (8)

Both tangents are shown in Fig. S1.

As we can see, the tangent to \( x_{NL2} \) better repeats the movement of the absorption points at the start of the increase in the electric field strength. Therefore, we use expression (8) as a result of reducing nonlinear function (1) to a two-photon absorption model. Also, note that the second derivative (Figure S1-d) provides more information than the first derivative. A further increase in the degree of differentiation tends \( x_{NL} \) to zero, and the slope of the tangent no longer fairly describes the absorption in the framework of the two-photon model.

**1.2. Limiter Curves**

The output performance of the optical limiter is the product of the power or energy of the input radiation and the transmission. For the two-photon absorption model, the output flux is described by the expression:

\[ y = x \cdot \exp \left( - (\alpha + \beta x) \cdot d \right) \] (9)

In logarithmic coordinates \( x = \exp (t) \):

\[ y = \exp \left[ t - d(\alpha + e^t\beta) \right] \] (10)

Derivatives for \( t \):

- 1\textsuperscript{st} derivative:

\[
\frac{1 dy}{y dt} = 1 - e^t\beta d \] (11)

- 2\textsuperscript{nd} derivative:
\[
\frac{1 d^2 y}{y dt^2} = 1 - 3e^t \beta d + e^{2t} \beta^2 d^2
\]  
(12)

- 3\textsuperscript{rd} derivative:

\[
\frac{1 d^3 y}{y dt^3} = 1 - 7e^t \beta d + 6e^{2t} \beta^2 d^2 - e^{3t} \beta^3 d^3
\]  
(13)

etc.

Position of extrema of functions \(d^n y/dt^n\) \((n > 1)\) are found numerically. Below are the results for the linear scale \((x)\):

Extremum of the 1\textsuperscript{st} derivative:

\[
0.38197 \frac{\beta d}{\beta d}
\]

Extrema of the 2\textsuperscript{nd} derivative:

\[
0.165757 \ 1.34338 \ 4.49086 \ \frac{\beta d}{\beta d} \ \frac{\beta d}{\beta d}
\]

Extrema of the 3\textsuperscript{rd} derivative:

\[
0.0760038 \ 0.762169 \ 2.65169 \ 6.51013 \ \frac{\beta d}{\beta d} \ \frac{\beta d}{\beta d}
\]

Extrema of the 4\textsuperscript{th} derivative:

\[
0.0359045 \ 0.453251 \ 1.70387 \ 4.18079 \ 8.62619 \ \frac{\beta d}{\beta d} \ \frac{\beta d}{\beta d} \ \frac{\beta d}{\beta d} \ \frac{\beta d}{\beta d}
\]

In general terms, the position of the extrema can be written as \(m/\beta d\), where \(m\) – is a real number. We consider only the first solution for each series since the others are of no practical importance. With increasing order of differentiation, \(m \to 0\).

For a real optical limiter with a smooth increase in nonlinearity, the optical limiting threshold, \(x_0\), can be evaluated based on the theory of errors. The difference between functions \(y\) and \(y_T = x e^{-\alpha d}\) in the vicinity of certain point \(x = m/\beta d\), which we call the nonlinear deviation threshold with an error \(\xi\), is taken equal to or less than this error, then:

\[
\Delta f = |y_T - y| = \left| e^{-(m + \alpha d)}(-1 + e^m)\frac{m}{\beta d}\right| \leq \xi
\]  
(14)

This equation cannot be solved analytically for \(m\). Let’s move on to the relative error:

\[
\frac{\Delta f}{y_T} = 1 - e^{-m}, \ \frac{\Delta f}{y} = -1 + e^m
\]

\[
1 - e^{-m} < \delta < -1 + e^m
\]  
(15)
A sequential enumeration of the values of the position of the first extremum on the differential curves gives:

**Table S1.** Iterative procedure to search deviation from linearity.

| Iteration | Derivative | \( m \) | Range \( \delta \) |
|-----------|------------|--------|----------------|
| 1         | 1\(^\text{st}\) | 0.38197 | 0.317;0.465 |
| 2         | 2\(^\text{nd}\) | 0.165757 | 0.153;0.180 |
| 3         | 3\(^\text{rd}\) | 0.0760038 | 0.073;0.079\(^1\) |
| 4         | 4\(^\text{th}\) | 0.0359045 | 0.035;0.036 |

\(^1\) \( \delta \approx m \) – this means that at the 3\(^\text{rd}\) iteration we may stop.

The higher the order of differentiation, the smaller the error in the deviation of linear and nonlinear functions. At the same time, the limiting threshold also tends to zero. Let’s stop on the third derivative and assume that the accuracy of ca. 4\% will be quite enough for us. We will keep this value constant to find the limiting threshold \( x_0 \) for all dyes presented in our investigation.

**Statement.** The only extremum of the limiter function (9) is the point at which all processes of deviation from linearity are finished.

**Evidence.** Let’s expand function (9) in a Taylor series in the vicinity of some point \( x_1 \) in powers of \( n = 1 \):

\[
y_\text{tan}(x_1) = e^{-d(\alpha + x_1\beta)} x_1^2 \beta d - e^{-d(\alpha + x_1\beta)} (-1 + x_1\beta d) \cdot x = A - B \cdot x
\]

The tangent must run parallel to the abscissa axis; \( B=0 \), therefore:

\[
x_1 = \frac{1}{\beta d}
\]

The same result is obtained when solving the differential equation

\[
\frac{1}{y} \frac{dy}{dx} = 0
\]

The statement is valid for the pure two-photon absorption model: \( k = \alpha + \beta x \).

At the intersection of \( y_\text{tan}(x_1) \) and \( y_{T,0} \) we find the threshold for turning on the ideal limiter (Fig. 3b in the main text):

\[
x_L = \frac{1}{\epsilon \beta d} \approx 0.367879
\]

The area between the two routes – the ideal and the “real” limiters shown in Fig. 3b (yellow shape) can be associated with the speed at which the limiter is turned on. Find the area of the shape:

\[
S = \int_0^{x_L} e^{-\alpha x} dx + \frac{e^{-(1+\alpha d)}}{\beta d} \int_{x_L}^{x_1} dx - \int_0^{x_1} e^{-\alpha x} x dx = - \frac{e^{-(2-a d)}(1 - 6 \epsilon + 2 \epsilon^2)}{2 \beta^2 d^2}
\]
\[ \frac{0.26579 e^{-(2 + \alpha d)}}{\beta^2 d^2} \]  \hfill (18)

The smaller this area, the faster the limiter "turns on":  

\[ r = \sqrt{1/S} \approx 1.93968 \sqrt{e^{2 + \alpha d} \beta d} \left[ \frac{\text{cm}^2}{\text{W}} \right] \]  \hfill (19)

As we can see, the speed of the limiter activation, as well as the limiting thresholds, depends on the nonlinearity of the medium. But not only. Equation (19) also contains the linear absorption coefficient \( \alpha \). Therefore, the higher the concentration of the dye and the thicker the layer, the faster the limiter turns on. However, with an increase in \( \alpha d \), the limiter goes to a blacking-out, since the linear section will be followed by a sharp drop in transmission (Fig. 3a in the main text). Nevertheless, as follows from equation (19), nonlinearity is in priority. Therefore, it is necessary to create materials with high polarization and intramolecular separation of electron density.