# CAFE

CLS ANN FFCF Extractor

**MATLAB Library Documentation (v1.1)**

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## I. What is CAFE?

CAFE is a tool that takes an experimentally determined Center Line Slope (CLS) decay of 2D spectra and a corresponding linear FWHM and returns the underlying Frequency-Frequency Correlation Function (FFCF). In particular, it takes the parameters of a CLS decay fit to the form:

$$\mathrm{CLS}(T_w) = A_\infty + \sum_i A_i \exp\left(-T_w / \tau_i\right). \tag{1}$$

Here the A's are dimensionless amplitudes and τ's are time constants. CAFE returns the parameters for the FFCF, $C(t)$:

$$C(T_w) = \frac{\delta(T_w)}{T_2} + \Delta_\infty^2 + \sum_i \Delta_i^2 \exp\left(-T_w / \tau_i\right) \tag{2}$$

Where Δ's are frequency amplitudes, $T_2$ is the dephasing time, $\delta(t)$ is the Dirac delta function, and $\tau$'s are time constants that are identical to those in Eq. 1. $T_2$ can also be described as a homogeneous line width, $\Gamma = (\pi T_2)^{-1}$.

As the relationship between the CLS amplitudes and FFCF frequency amplitudes can be highly nonlinear and depends on both the values of the time constants and the width of the underlying peak, the FFCF parameters are calculated using a set of artificial neural networks (ANN). These networks were trained on a large set of parameters from simulated 2D spectra and can be thought of as functions that take combinations of the CLS parameters ($A$'s, $\tau$'s, and the linear FWHM) as inputs and returns an FFCF frequency amplitude, Δ. After all of the Δ's are determined in this way, the homogeneous component is calculated by inputting the known Δ's and τ's into the one-dimensional response function, and increasing the homogeneous component, Γ, until the simulated 1D spectrum has the correct FWHM. The complete algorithm typically takes not more than a few seconds to run. A complete description of the underlying algorithms can be found in the related publication.

# II. Installation Notes

The CAFE MATLAB library has been confirmed to run on MATLAB versions between 2014b and 2019b. The CAFE.m function uses supporting functions in the **CAFEfcn** folder. By default it is assumed that the CAFEfcn folder is sitting in the same directory as the CAFE.m file. If you wish to place these supporting folders in a different location, change the variable named "`suppfcndir`" in the CAFE.m file.

# III. How to use CAFE

## The Inputs

The CAFE.m function accepts the following arguments:

```
[FFCFpars, spec] = CAFE(CLSpars, fwhm, errprop,
                          {CLSError}, {fwhmerror})
```

All that is needed is the set of CLS fit parameters (`CLSpars`) and the FWHM (`fwhm`) of the linear spectra (e.g. from FTIR) in $cm^{-1}$. `CLSpars` is a column vector of CLS fit parameters in the order:

$[A_\infty, A_1, \tau_1, A_2, \tau_2, A_3, \tau_3]$.

The `CLSpars` vector can be truncated (e.g., if only two exponentials are fit a value for $A_3$ and $\tau_3$ does not need to be entered) but a value must always be entered for $A_\infty$. The $\tau$ parameters should be entered with units of ps.

CAFE offers multiple ways of propagating uncertainty to the resulting FFCF parameters which can be selected by changing the value of `errprop`:

1: ANN error only

2: Estimate from CLS parameter standard error

3: Calculate error from CLS parameter covariance matrix

If the user does not wish to propagate error, setting `errprop = 1` reports just the error from the ANN calculation itself. Setting `errprop = 2` estimates from the CLS parameter standard error, which makes mild assumptions about how the CLS parameters are correlated with each other to determine the FFCF Std. Errors. The CLS parameter standard errors should be input as a column vector in `CLSError` with the same ordering as the `CLSpars` vector. Additionally an error term can be optionally entered for the FWHM measurement as the `fwhmerror` term.

The most accurate method is using the covariance matrix (`errprop = 3`), which explicitly considers the covariance of the CLS fit parameters as determined from the fitting software. For example, in OriginPro, the covariance matrix can be found in the following options of the fit dialog (**Advanced->Quantities->Covariance matrix**) and appears in the fit output as follows:

Summary

| | y0 | | A1 | | t1 | | A | |
|---|---|---|---|---|---|---|---|---|
| | Value | Standard Error | Value | Standard Error | Value | Standard Error | Value | St |
| B | 5.51698E-4 | 0.00104 | 0.14923 | 0.04432 | 0.37188 | 0.12556 | 0.1288 | |

ANOVA

| | | DF | Sum of Squares | Mean Square | F Value | Prob>F |
|---|---|---|---|---|---|---|
| B | Regression | 4 | 0.05464 | 0.01366 | 2369.8149 | 6.16048E-47 |
| | Residual | 40 | 2.30567E-4 | 5.76418E-6 | | |
| | Uncorrected Total | 45 | 0.12932 | | | |
| | Corrected Total | 44 | 0.05487 | | | |

At the 0.05 level, the fitting function is significantly better than the function y=constant.

Covariance

B

| | y0 | A1 | t1 | A2 | t2 |
|---|---|---|---|---|---|
| y0 | 1.08138E-6 | 7.7888E-6 | -5.81916E-5 | 1.13088E-5 | -1.30738E-4 |
| A1 | 7.7888E-6 | 0.00196 | -0.00465 | 5.05347E-4 | -0.0035 |
| t1 | -5.81916E-5 | -0.00465 | 0.01576 | -0.00226 | 0.01813 |
| A2 | 1.13088E-5 | 5.05347E-4 | -0.00226 | 3.7601E-4 | -0.00321 |
| t2 | -1.30738E-4 | -0.0035 | 0.01813 | -0.00321 | 0.02968 |

The CLS parameter covariance matrix should be input as a matrix in `CLSError` with the same parameter ordering as the `CLSpars` vector. Again an error term can be optionally entered for the FWHM measurement as the `fwhmerror` term.

CAFE assumes that the CLS is a monotonically decreasing function that does not go below zero. Accordingly, all of the input parameters must be greater than or equal to zero. As the CLS is also normalized, the sum of the amplitudes cannot exceed one.

## “Calculated linewidth exceeds experimental FWHM”

Due to partial motional narrowing, not every CLS is possible for any given FWHM. This effect is illustrated in Fig. 6 of the associated publication. If CAFE determines the CLS is not possible for the given linewidth, it will return the error: “Calculated linewidth exceeds experimental FWHM.” This can be resolved manually by using CLS fit parameters with smaller amplitudes and/or longer time constants or increasing the input FWHM.

CAFE can attempt to use the covariance matrix of the CLS fit to automatically correct this error (v. 1.1 only). The covariance matrix encodes how every other fit parameter will vary under small perturbations of another fit parameter. The CAFE program will slowly increase the value of $\tau_1$ (generally the fastest way to approach a valid CLS for a given linewidth) while modifying the other CLS input variables accordingly. If a solution is found, the FFCF will be calculated using these new parameters. The new time constants can then be found in the output FFCF in the `parsnew` output variable.

It should be noted that such corrections will necessarily result in an FFCF with a homogeneous linewidth that is approximately zero, as that will be the closest valid CLS. As a result, the standard errors for $\Gamma$ and $T_2$ will likely be very large and ill-defined, as the error in the terms are clearly not symmetric when $\Gamma$ is near zero (since $\Gamma$ must be greater than zero). The standard errors for these terms should likely be discarded as poor approximations in these cases.

## The Outputs

Assuming no errors occur, the resulting FFCF parameters will be displayed formatted in the command line and returned in the `FFCFpars` element. `FFCFpars` has two columns, the first column is the output value and the second column is the standard error for the parameter. The output parameters are in the order:

$[\Delta_\infty, \Delta_1, \Delta_2, \Delta_3, \Gamma, T_2]$.

$\Delta$ and $\Gamma$ terms are in $cm^{-1}$ and $T_2$ is in ps.

Additionally, the calculated 1D spectrum for the FFCF is returned in the `spec` element. `spec` contains two columns, the first column is the frequency (in $cm^{-1}$) and the second column is the normalized spectrum.

The `parsnew` output variable contains the CLS input variables that were used in the calculation of the FFCF:

$[A_\infty, A_1, \tau_1, A_2, \tau_2, A_3, \tau_3]$.

These will be different from the original inputs if the error correction algorithm in the previous section is called.