# ThermoTraj - Manual

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**Laurens Peters and Johannes Dietschreit**

**University of Munich (LMU)**

## 1 Theory

ThermoTraj calculates thermodynamics properties as a frequency ($\nu$) integral over the weighted density of states function ($D$), using the following integrations:

$$A_{\text{vib}} = \beta^{-1} \int_0^\infty d\nu D(\nu) W_{\text{A}}(\nu) \tag{1}$$

$$E_{\text{vib}} = \beta^{-1} \int_0^\infty d\nu D(\nu) W_{\text{E}}(\nu) \tag{2}$$

$$S_{\text{vib}} = T\beta^{-1} \int_0^\infty d\nu D(\nu) W_{\text{S}}(\nu) \tag{3}$$

$\beta$ is equal to $1/(k_{\text{B}}T)$ with $k_{\text{B}}$ being the Boltzmann constant and $T$ the absolute temperature. The weighting functions ($W_{\text{A}}$, $W_{\text{E}}$, and $W_{\text{S}}$) for the classic (CL) and the quantum (QM) harmonic oscillator are defined as follows:

$$W_{\text{A}}^{\text{CL}}(\nu) = \ln[\beta h\nu] \tag{4}$$

$$W_{\text{A}}^{\text{QM}}(\nu) = \ln\left[\frac{1-\exp(-\beta h\nu)}{\exp(-\frac{1}{2}\beta h\nu)}\right] \tag{5}$$

$$W_{\text{E}}^{\text{CL}}(\nu) = 1 \tag{6}$$

$$W_{\text{E}}^{\text{QM}}(\nu) = \frac{\beta h\nu}{2} + \frac{\beta h\nu}{\exp(\beta h\nu)-1} \tag{7}$$

$$W_{\text{S}}^{\text{CL}}(\nu) = 1 - \ln[\beta h\nu] \tag{8}$$

$$W_{\text{S}}^{\text{QM}}(\nu) = \frac{\beta h\nu}{\exp(\beta h\nu)-1} - \ln[1-\exp(-\beta h\nu)] \tag{9}$$

$h$ is the Planck constant.

## 2 Usage

Please use ThermoTraj as follows:

```
python ThermoTraj.py [options] [educt power spectra-files] [product power
                     spectra-files] > output
```

using the output of SpecTraj as input:

| Wavenumber [cm$^{-1}$] | Re($D/\beta$) | Im($D/\beta$) | Abs($D/\beta$) | Re($D^2/\beta^2$) |
|---|---|---|---|---|
| $\vdots$ | $\vdots$ | $\vdots$ | $\vdots$ | $\vdots$ |

The following options are supported:

| *Option* | *Type* | *Explanation* | *Default* |
|---|---|---|---|
| `-t --temperature` | double | Temperature | 298.15 |
| `-s --start-wavenumber` | double | Wavenumber at which the integration starts | 0 |
| `-m --max-wavenumber` | double | Wavenumber until which $D$ is integrated | max |
| `-n --ndegfree` | double | Set number of degrees of freedom to $i$; Set to 0 to perform no rescaling | 0 |
| `-e --neducts` | integer | Number of educt spectra | 1 |
| `-p --products` | integer | Number of product spectra | 1 |
| `-b --corr-baseline` | string | Correct spectrum for a baseline so that $\lim_{\nu\to\infty} D(\nu) = 0$: `true` or `false` | `false` |
| `-i --integration-method` | string | Applied integration method: `simps` or `trapz` | `simps` |

The program returns $A_{\mathrm{vib}}^{\mathrm{CL}}$, $A_{\mathrm{vib}}^{\mathrm{QM}}$, $E_{\mathrm{vib}}^{\mathrm{CL}}$, $E_{\mathrm{vib}}^{\mathrm{QM}}$, $S_{\mathrm{vib}}^{\mathrm{CL}}$, $S_{\mathrm{vib}}^{\mathrm{QM}}$, and the determined number of degrees of freedom $N_{\mathrm{F}} = \int_0^\infty d\nu D(\nu)$. The $dA$-values are calculated via $A^{\mathrm{QM}} - A^{\mathrm{CL}}$.

# 3 Examples

1. Calculate thermodynamics for an isomerization ($a \to b$):

   ```
   python ThermoTraj.py -e 1 -p 1 spec_a.dat spec_b.dat
   ```

2. Calculate thermodynamics for an reaction ($a + b \to c$):

   ```
   python ThermoTraj.py -e 2 -p 1 spec_a.dat spec_b.dat spec_c.dat
   ```

3. Calculate thermodynamics for an reaction ($a \to b + c$):

   ```
   python ThermoTraj.py -e 1 -p 2 spec_a.dat spec_b.dat spec_c.dat
   ```

4. Perform the integration for only one spectrum with $N_{\mathrm{F}} = 10$ and baseline correction:

   ```
   python ThermoTraj.py -e 0 -p 1 -n 10 -b true spec_a.dat
   ```