# Calculating Vibrational Spectra from Molecular Dynamics

## A     Simulating a Trajectory with Wannier Centers

To calculate IR spectra from Molecular Dynamics, it is necessary to have dipole information for the molecules available in the simulated trajectory. This is, in principle, also possible from classical MD, but might give poor results. The best way is to perform an *ab initio* Molecular Dynamics simulation of the system of interest, and localize the molecular orbitals to obtain Wannier centers.

In the following, an example CP2k input file is given to simulate a trajectory suitable for IR spectra calculation. Please note that it is sufficient to perform the Wannier localization every 2.5 fs, which is every 5$^{\text{th}}$ time step for a step length of 0.5 fs, like usual in AIMD.

```
&GLOBAL
  PROJECT Methanol
  RUN_TYPE MD
  PRINT_LEVEL LOW
&END GLOBAL

&FORCE_EVAL
  &DFT
    BASIS_SET_FILE_NAME BASIS_MOLOPT
    POTENTIAL_FILE_NAME POTENTIAL
    &MGRID
      CUTOFF 280
      REL_CUTOFF 40
      NGRIDS 5
    &END
    &SCF
      SCF_GUESS ATOMIC
      MAX_SCF 200
      &OT
        MINIMIZER DIIS
        PRECONDITIONER FULL_SINGLE_INVERSE
      &END
      &PRINT
        &RESTART
          &EACH
            MD 0
          &END
        &END
      &END
    &END
    &LOCALIZE
      METHOD CRAZY
      MAX_ITER 2000
      &PRINT
        &WANNIER_CENTERS
          IONS+CENTERS
```

```
                    FILENAME =methanol_wannier.xyz
                  &EACH
                    MD 5
                  &END
              &END
          &END
      &END
      &XC
        &XC_FUNCTIONAL BLYP
        &END
        &XC_GRID
          XC_DERIV NN10_SMOOTH
          XC_SMOOTH_RHO NN10
        &END
        &VDW_POTENTIAL
          DISPERSION_FUNCTIONAL PAIR_POTENTIAL
          &PAIR_POTENTIAL
            TYPE DFTD3
            PARAMETER_FILE_NAME dftd3.dat
            REFERENCE_FUNCTIONAL BLYP
          &END
        &END
      &END
    &END

  &SUBSYS
    &CELL
      ABC 10.0 10.0 10.0
    &END
    &COORD
      H        0.84754        0.03474        1.03453
      C        0.35048        0.00675        0.06084
      H        0.63507        0.89276       -0.52006
      H        0.66294       -0.89338       -0.48283
      O       -1.01083       -0.00823        0.36439
      H       -1.48520       -0.03263       -0.45685
    &END
    &KIND H
      BASIS_SET DZVP-MOLOPT-SR-GTH
      POTENTIAL GTH-BLYP-q1
    &END
    &KIND O
      BASIS_SET DZVP-MOLOPT-SR-GTH
      POTENTIAL GTH-BLYP-q6
    &END
    &KIND C
      BASIS_SET DZVP-MOLOPT-SR-GTH
      POTENTIAL GTH-BLYP-q4
    &END
  &END
&END

&MOTION
  &MD
    ENSEMBLE NVT
    STEPS 60000
    TIMESTEP 0.5
    &THERMOSTAT
      TYPE NOSE
      &NOSE
        TIMECON 100
```

```
        &END
      &END
      TEMPERATURE 400
    &END
    &PRINT
      &RESTART
        &EACH
          MD 1
        &END
      &END
    &END
```

This input file simulates a single methanole molecule in a periodic cell of 10 x 10 x 10 Angstrom. Of course, also bulk phase systems can be simulated with the input file given above. The Wannier centers are written each $5^{th}$ time step, together with the atomic positions. This is the input we used for the simulation of the systems published in our recent article [2]. For more details, refer to the CP2k manual.

**How many time steps do I have to simulate for a good spectrum?**

This depends on the system size. For an isolated molecule (e.g. methanol, like in the example above), around 40000 to 60000 simulation steps (*this means: 8000 to 12000 steps with Wannier centers written to trajectory*) should be sufficient. For bulk-phase systems, less is ok, depending on the number of molecules. **In general, longer simulations will yield better spectra.**

## B    Computing IR spectra with TRAVIS

The trajectory `methanol_wannier.xyz` is then opened with TRAVIS [1]:

```
travis -p methanol_wannier.xyz
```

In the following, some of the options for calculating spectra will be discussed. TRAVIS is an interactive program, it asks the user questions to answer. No input file needs to be prepared before. In general, if a question is not mentioned here, and you are not sure what you should answer, **please take the default values** (by just pressing RETURN). The default values are reasonable and will give good results.

```
Enter length of cell vector in pm:
```

Please enter the size of the simulation cell for periodic simulations. For non-periodic simulations, enter any value that is larger than the largest system extent in space.

```
Which functions to compute (comma separated)?
```

Here you should tell TRAVIS to compute an IR spectrum. Enter "ir".

```
Enter the length of one trajectory time step in fs: [0.5]
```

TRAVIS needs to know how long the trajectory time step is. If you used the settings from the CP2k input file above, the time step is 2.5 fs (every $5^{th}$ of 0.5 fs). Enter "2.5".

```
Compute IR spectrum of whole system (y/n)? [yes]
```

If you decide to answer with yes, TRAVIS will calculate an IR spectrum of the whole system, including all molecules.

```
Compute also IR spectra for certain molecule types (y/n)? [no]
```

This enables to calculate additional IR spectra from only one molecule kind (e.g. in a mixture). This could be useful e.g. to assign bands to molecule types, or exclude the spectrum of the solvent.

```
Which atom label do the wannier centers have (C, H, N, O, X)? [X]
```

The label of the Wannier centers in the trajectory. In CP2k simulations, this is always "X".

```
Enter the negative charge of the wannier centers (without sign): [2.0]
```

The (negative) charge of the Wannier centers. In closed-shell DFT, each Wannier center represents one electron pair, therefore keep the default value 2.

```
Enter core charge (mind pseudopotentials!) for atom type *:
```

Enter the core charge of the elements in your simulation. If you used pseudopotentials, you have to enter the number of explicitly calculated electrons here. The default values for the most common elements (C, H, N, O, ...) represent the right values for CP2k simulations.

```
Please enter dipole reference point for C6H11N2: [#1]
```

For charged molecules, there is no unique definition of a dipole vector. Therefore, you need to enter a reference point here. But the dipole vector is derived later, so the reference point is not important for spectra. Just keep the default value.

```
Enter the resolution (=depth) of the dipole ACF (in time steps):
```

This is the most important quantity to influence the spectrum: The depth of the autocorrelation function. If you calculated Wannier centers in every $5^{th}$ time step (like in the example above), a value of 1024 or 2048 should be fine. If you calculated Wannier centers in each step, try 4096. You can, of course, try different values, and take the spectrum with the best quality. Higher values will increase the spectral resolution, but also the noise level.

```
Calculate spectrum up to which wave number (cm^-1)?
```

The upper bound of the frequency interval shown in the spectrum. The default value should be ok, unless you expect very high wave numbers to appear for some reason.

```
Convert intensity axis of spectrum to decibel (y/n)? [no]
```

This will use a logarithmic intensity axis for the spectrum (unit decibel). Please note that the spectrum will not have a base line then. Should only be used if required for some reason.

As already noted, please choose the default value for all questions not listed above.

If everything worked, you should find a file with the name "`spectrum_*.csv`" after TRAVIS has finished. This file contains the spectrum. Please use the first column as X axis and the second column as Y axis.

## C    Computing Raman spectra with TRAVIS

The calculation of Raman spectra is a two-step procedure. As starting point, the Wannier center trajectory used for IR spectra is needed. In a first run, TRAVIS creates CP2k input files in which the Wannier centers are recalculated with an external electric field. This allows TRAVIS to obtain polarizabilities which are required for Raman spectra in a second run.

Many TRAVIS options for Raman spectra are analogous to IR spectra. Only the differences will be explained in this section.

```
Which functions to compute (comma separated)?
```

You should choose "raman" here.

```
Do you wish to create new CP2k input files (y) or process existing results (n)?
```

If you are in the first run and want to create the CP2k input for the recalculation of Wannier centers with an external field, enter "y". If you are in the second run and want to process the CP2k results, enter "n".

In the first run, the following questions appear:

```
Use orientational averaging? [no]
```

During one recalculation of the Wannier centers, the electric field vector has a fixed orientation such that only a certain part of the polarizability tensor can be obtained. In principle, it is better to average over all possible orientations, but this requires three calculations, one for each independent direction of three-dimensional space, and therefore triples the computational demands. If you have a flexible system where the molecules steadily change their orientation with respect to the simulation box, it is usually a good start to omit the averaging and perform the calculation only for one field direction.

```
Field strength in atomic units [5.0e-4]
```

This option allows to change the strength of the external electric field. It should not be to small to avoid numerical problems, but it should also not be too large to stay in the linear range of polarization. The default value usually works fine.

```
Calculate polarizability for every n-th timestep [1]
```

This allows to skip some steps of the original trajectory, if you e. g. calculated Wannier centers in every step of the AIMD simulation but want to save computer time and recalculate with an external field only every $5^{th}$ step.

In the second run, all options are the same as for the IR spectra. If TRAVIS successfully finishes, you will find the results in the directory you specified to collect the Raman data. There will be three "`spectrum_*.csv`" files containing the Raman scattering intensities for different polarization directions of the scattered light and a "`depol_ratio*.csv`" file containing the depolarization ratio. Please note that the values of the depolarization ratio are only meaningful in frequency ranges with significant Raman scattering intensity.

# Bibliography

**[1]** M. Brehm and B. Kirchner: "TRAVIS - A free Analyzer and Visualizer for Monte Carlo and Molecular Dynamics Trajectories", *J. Chem. Inf. Model.* **2011**, *51 (8)*, pp 2007–2023.

**[2]** M. Thomas, M. Brehm, R. Fligg, P. Vöhringer, B. Kirchner: "Computing vibrational spectra from ab initio molecular dynamics", *Phys. Chem. Chem. Phys.* **2013**, *15*, pp 6608-6622.