Quantum Chemistry EI Mass Spectrometry Database for Exposome Research

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Aim

Evaluate the accuracy of in-silico generation of spectra for chemicals with experimental high-resolution electron ionization mass spectra (HR-[EI+]-MS) available in the RECETOX Exposome library[1] to assess potential of spectral predictions for chemicals with no reference spectra.

Method

Used the Quantum Chemical Electron Ionization Mass Spectrometry package (QCxMS v5.1.3)[2] (**Figure 1**) for spectra prediction at the semiempirical quantum mechanical and density functional theory (DFT) levels & evaluated accuracy against experimental spectra of coumarin & estragole.

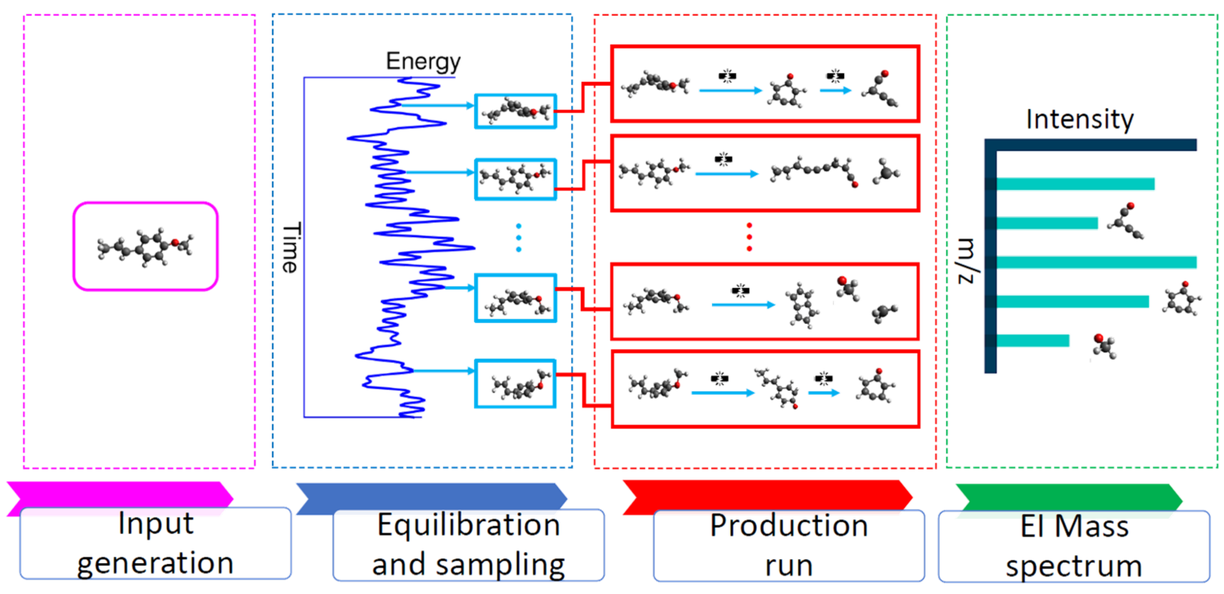
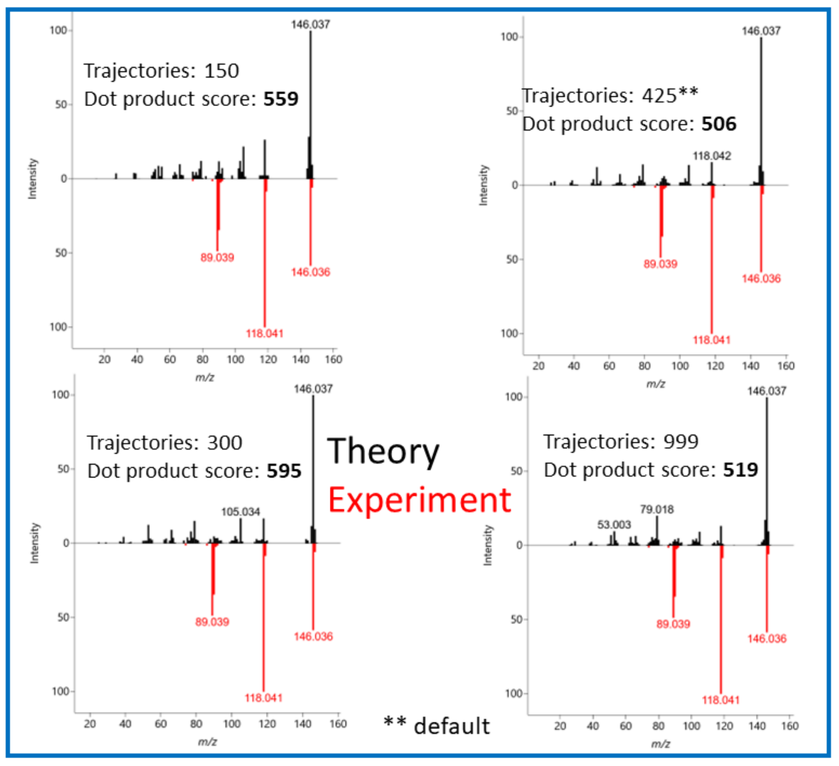


Figure 1. *Diagram of the QCxMS workflow & parameters applied.*

- Equilibration: GFN2-xTB[3] semiempirical method (extended tight binding).
- Production run: GFN2-xTB[3] or DFT PBE0-D3/SV(p)[4,5] level.
- DFT calculations with ORCA[6].
- Ground state sampling:
  - Temperature 500 K
  - MD trajectory 20 ps
  - Timestep 0.5 fs
- Production run:
  - Temperature 500 K
  - MD trajectory 20 ps
  - Timestep 0.5 fs
  - Impact excess energy 0.6 eV/atom
  - Electron ionization 70 eV

Results



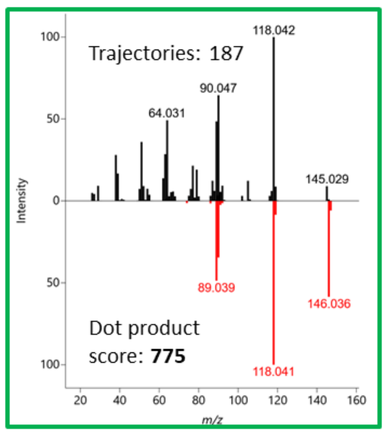
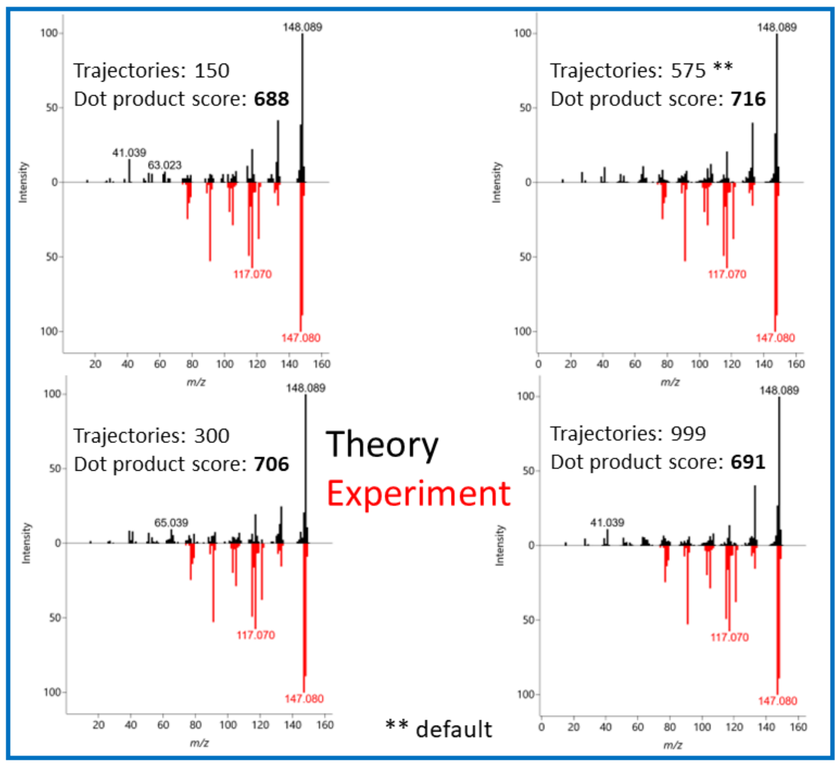


Figure 2. *Predicted spectra (black) compared to experimental spectra (red) for coumarin via semiempirical (blue box) and DFT (green box).*



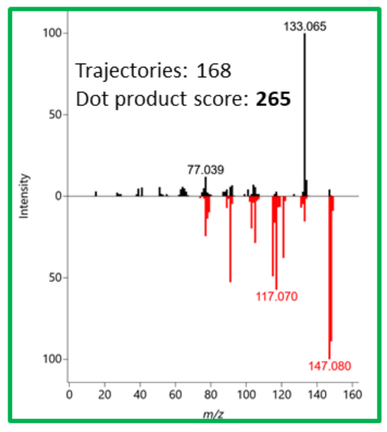


Figure 3. *Predicted spectra (black) compared to experimental spectra (red) for estragole via semiempirical (blue box) and DFT (green box).*

Discussion & Conclusions

- Effect of number of trajectories on spectra evaluated only using the semiempirical method.
- Default number of trajectories (25x#of atoms) gives acceptable score.
- Number of trajectories has low impact on spectra for both molecules.
- Spectra predicted at semiempirical level are sufficient for identification if reverse score match > 500.
- Computation times using semiempirical method are dramatically lower than DFT (using one core -> mins/hours vs weeks, respectively).
- DFT gives highest match score for coumarin (**Figure 2**) but lowest for estragole (**Figure 3**). Low number of trajectories reached for estragole likely reason of low match score.
- Semiempirical method more accurately predicts the highest m/z peak than DFT for these two molecules.
- Generation of in-silico spectral library by semiempirical methods is potentially feasible.

Future work

- Assessment of semiempirical method's performance of molecules classified by common features.

Acknowledgements

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References

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