

Supporting Information:

The important role of non-covalent interactions for the vibrational circular dichroism of lactic acid in aqueous solution

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Background moment screening in solution

To cope with the sampling problem in disordered phase, the scaling of moments has been introduced.^{S1} The first solvation shell usually remains unaffected by moment scaling, yet superfluous dipole correlations between different solvent molecules as well as local dipole correlations may still enter the IR and VCD spectra. Thermodynamic convergence thereof requires large amounts of AIMD computation time. Similar to the experiment, having traces of solvent peaks in the spectra need not be a problem, unless solvent signals overlap with the regions of interest. It may nevertheless be desirable to filter out unnecessary contributions to IR absorption and VCD stemming from solvent molecules. As this likens to measuring a baseline spectrum in experiment, the approach can be considered as virtual "background correction".

The classical TCF that is used to compute the rotational strength in its velocity form is:

$$C_{\text{cl}}(t) = \langle \dot{\mathbf{j}}(0) \mathbf{m}(t) \rangle, \quad (1)$$

with $\dot{\mathbf{j}}$, the time derivative of the electric dipole moment, and \mathbf{m} , the magnetic dipole moment. C_{cl} can be written in terms of molecular mo-

ments, $\mathbf{j} = \sum_i \mathbf{j}_i$ and $\mathbf{m} = \sum_i \mathbf{m}_i$:^{S1}

$$C_{\text{cl}}(t) = \sum_i \sum_j \langle \dot{\mathbf{j}}_i(0) \mathbf{m}_j(t) \rangle, \quad (2)$$

where the magnetic moments are defined with respect to a common origin taking account of gauge transport.^{S1-S3} The double sum runs over molecular indices i and j , which includes all solvent molecules. If the molecular index of the solute is denoted with subscript m and the lower sum over solvent molecules $\sum_{i \neq m}$ summarised in subscript s , the expression for C_{cl} becomes:

$$\begin{aligned} C_{\text{cl}}(t) = & \langle \dot{\mathbf{j}}_m(0) \mathbf{m}_m(t) \rangle \\ & + \langle \dot{\mathbf{j}}_m(0) \mathbf{m}_s(t) \rangle + \langle \dot{\mathbf{j}}_s(0) \mathbf{m}_m(t) \rangle \\ & + \langle \dot{\mathbf{j}}_s(0) \mathbf{m}_s(t) \rangle. \end{aligned} \quad (3)$$

The first term (mm) contains only *local* contributions stemming from the molecule itself, while the mixed terms (ms) sum up all *non-local* correlations between solvent and solute. The last term (ss) contains only (local and non-local) contributions within the solvent molecules and can be considered as "noise" or *background* signal. With this, a background-corrected TCF, C'_{cl} , is defined:

$$\begin{aligned} C'_{\text{cl}}(t) &= C_{\text{cl}}(t) - \langle \dot{\mathbf{j}}_s(0) \mathbf{m}_s(t) \rangle \\ &= C_{\text{cl}}(t) - C_{\text{cl}}^{\text{BG}}(t). \end{aligned} \quad (4)$$

The background correction has been implemented in the *ChirPy* code.^{S4}

In particular in water where solvent molecules possess large dipole moments, the removal of background signal is almost inevitable when supramolecular correlations are to be studied with AIMD.

References

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- (S4) Jähnigen, S. ChirPy – A Python Package for Analysing Supramolecular and Electronic Structure, Chirality and Dynamics (Version 0.21.5). Zenodo, 2021; <http://doi.org/10.5281/zenodo.4775330>.