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Spatial localization in nuclear spin-induced circular dichroism - a quadratic response function analysis

Supplementary Information

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1 SOS-vs-B-term comparison

In order to gain insight into the local nature of NSCD, we first tried to decompose the NSCD signal using the sum-over-states (SOS) approach[1]. The SOS NSCD intensities were calculated according to Eq. 12 (last equality), scaled with the prefactor $\mathcal{L}$ defined as

$$\mathcal{L} = -\frac{1}{96\pi}\gamma_K I_K \frac{c_0 N_A e^3 \hbar \mu_0^2}{m_e a_0 E_H} \tag{1}$$

Where the SOS approach has been shown to be rather robust in previous cases[1], it does not perform equally well in the present case, as seen in Fig. S1. This is likely due to the fact that in the previously reported case the majority of the investigated NSCD intensity came from few states very close together. Therefore, the SOS was able to capture the main components with just a few states included. While in the present case we can see improvement with the number of states included, the convergence is rather slow due to the large number of small contributions making up the total intensity.

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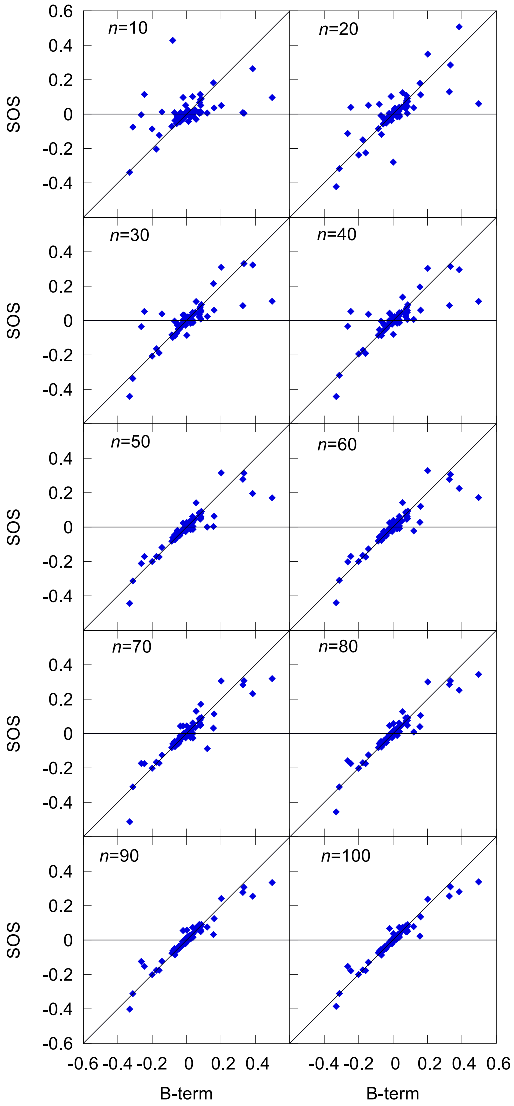
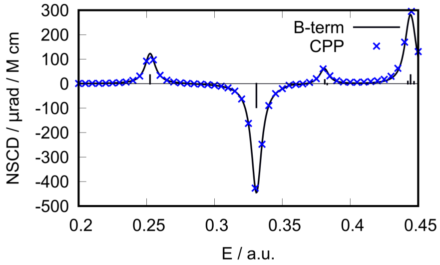
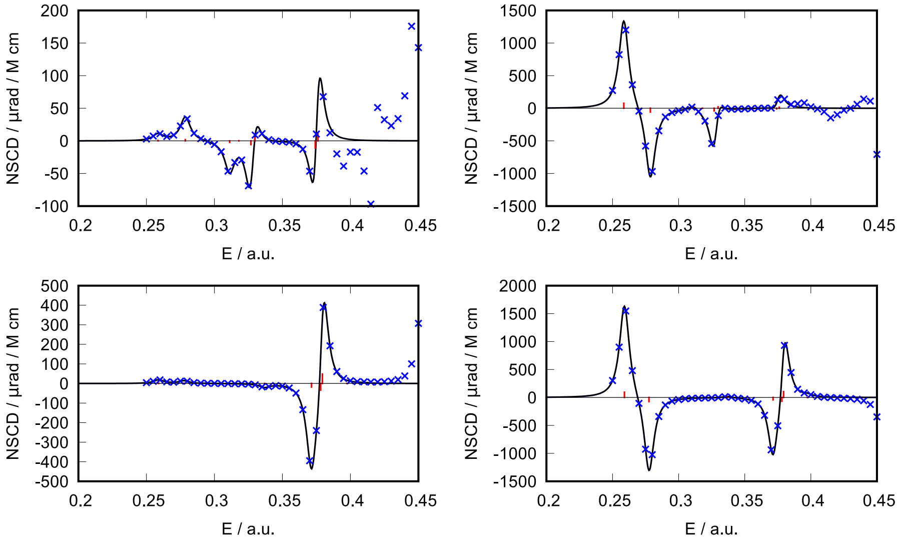


S 1: Comparison of results obtained by B-term calculations with those from the sum-over-states approach including 10 to 100 excited states in the summation. The solid line represents $y = x$ function, *i.e.* perfect correspondence.

2 Additional benchmark results



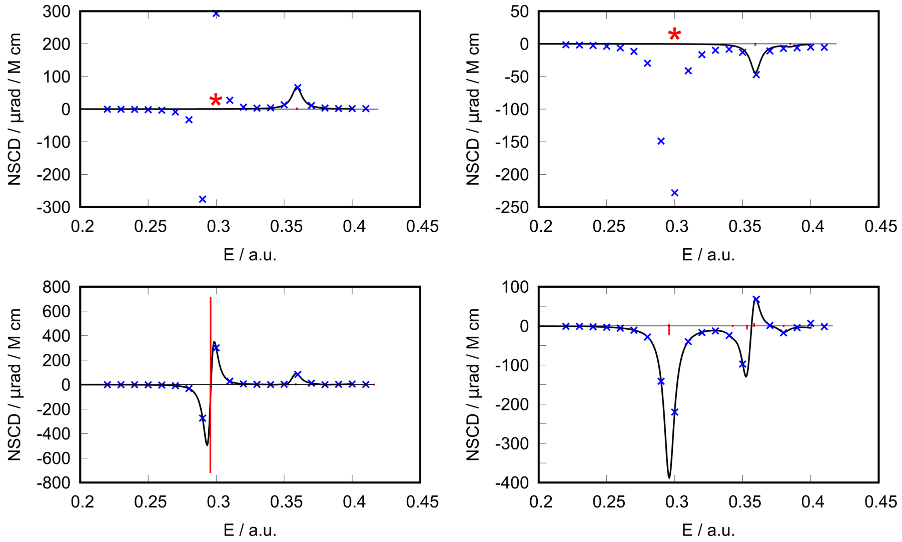
S 2: Benchmark results for water. Comparison of NSCD spectra obtained using the B-term approach (black solid line) and the CPP approach (blue crosses) at the B3LYP/aug-cc-pVTZ level. The NSCD sticks calculated via the B-term formalism have been broadened by a Lorentzian lineshape function of the same half-width $\gamma = 0.00456$ E_H as used in the CPP calculations.



S 3: Benchmark results for ethene, large basis sets. Comparison of NSCD signal of hydrogen (left) and carbon (right) atoms obtained via the CPP approach (blue crosses) with the spectrum produced via the new B-term formalism (black solid line) at the BHandHLYP/def-SVPDD-0 (top) and BHandHLYP/6-311++G** level. The NSCD values calculated by the B-term formalism have been broadened by the Lorentzian band of the same half-width $\gamma = 0.00456$ E_H as used in the CPP calculations.

2.1 Effect of degenerate states in molecules with high symmetry

Fig. S 4 shows the effect of the degeneracy of the electronic excited states in highly symmetric cases. When the B-term formalism is used for calculations on benzene in D_{6h} symmetry, the doubly degenerate state creates a numerical instability that prevents the evaluation of the NSCD intensity for that state. Other states appear unaffected by this. When the degeneracy is removed by breaking the high symmetry, the calculations clearly produce results identical with the CPP formalism.

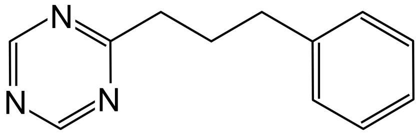


S 4: Benzene. Comparison of the NSCD signal of hydrogen (left) and carbon (right) calculated by the CPP approach (blue crosses) with the spectrum produced via the new B-term formalism (black solid line) at the HF/6-31G level. The top panels show the results of the calculations with the molecule in D_{6h} symmetry, whereas the spectra in the bottom panels correspond to a structure where one C-H bond has been elongated by 0.01 nm to break the degeneracy and yield C_{2v} symmetry. The red asterisk indicates the presence of a doubly degenerate electronic state.

3 PPT geometry

Table 1: Cartesian coordinates of PPT molecule in C_s symmetry

Atom	x	y	z
C	-0.7504207	-2.0263245	0
C	-2.0148422	-1.4359281	0
C	-3.1702935	-2.2165836	0
C	-3.0823579	-3.6027457	0
C	-1.8263693	-4.2061495	0
C	-0.6784219	-3.4246978	0
C	1.7270077	2.4912985	0
C	2.8557995	4.4447165	0
C	0.6225572	4.4576749	0
C	0.5394931	-1.2257598	0
C	0.3969865	0.2966098	0
C	1.7582875	0.9873725	0
N	2.9140872	3.1195059	0
N	0.5513173	3.1269858	0
N	1.7399669	5.1782664	0
H	-2.1119877	-0.3578935	0
H	-4.140983	-1.7342494	0
H	-3.9804541	-4.2088139	0
H	-1.7425805	-5.286788	0
H	0.2947248	-3.905433	0
H	3.7992924	4.9819482	0
H	-0.3179278	5.000306	0
H	1.1311304	-1.5289016	0.8722256
H	1.1311304	-1.5289016	-0.8722256
H	-0.1732681	0.6233573	-0.8728595
H	-0.1732681	0.6233573	0.8728595
H	2.3506969	0.6788855	0.8687956
H	2.3506969	0.6788855	-0.8687956



S 5: Sketch of the PPT molecule.

4 References

References

[1] P. Štěpánek, S. Coriani, D. Sundholm, V. A. Ovchinnikov and J. Vaara, *Scientific Reports*, 2017, **7**, art. no. 46617.