

On the Use of Density Functional based Tight Binding Methods in Vibrational Circular Dichroism

T.Q. Teodoro,^{†,‡} M.A.J. Koenis,[¶] R. Rüger,[§] S.E. Galembeck,[†] W.J. Buma,[¶] V.P.
Nicu,^{||} and L. Visscher^{*,‡}

[†]*Departamento de Química, FFCLRP, Universidade de São Paulo, Av. Bandeirantes 3900,
Ribeirão Preto, 14040-901 São Paulo, Brazil*

[‡]*Amsterdam Center for Multiscale Modeling, Faculty of Science, Vrije Universiteit
Amsterdam, de Boelelaan 1083, 1081 HV Amsterdam, The Netherlands*

[¶]*Van't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904,
1098 XH Amsterdam, The Netherlands*

[§]*Software for Chemistry & Materials BV, De Boelelaan 1083, 1081 HV Amsterdam, The
Netherlands*

^{||}*Lucian Blaga University of Sibiu, Department of Environmental Science, Physics,
Physical Education and Sport, Ioan Ratiu Street, Nr. 7-9, 550012 Sibiu, Romania*

E-mail: l.visscher@vu.nl

Table 1: Harmonic vibrational frequencies ν_n (in cm^{-1}), dipole strengths \mathcal{D}_n (in $10^{-39}\text{esu}^2\text{cm}^2$) and rotational strengths \mathcal{R}_n^{01} (in $10^{-44}\text{esu}^2\text{cm}^2$) of the n^{th} normal modes of (S,S)-[2,3- $^2\text{H}_2$]oxirane (gas phase) calculated by several methods, and experimental data.

n	DFTB1						DFTB2						DFTB3						BP86				Exp. ^a			
	QUASINANO2015			mio-1-1			QUASINANO2015			mio-1-1			3ob-3-1			3ob-freq-1-2			TZP				ν_n	\mathcal{D}_n	\mathcal{R}_n	
	ν_n	\mathcal{D}_n	\mathcal{R}_n	ν_n	\mathcal{D}_n	\mathcal{R}_n	ν_n	\mathcal{D}_n	\mathcal{R}_n^{01}	\mathcal{R}_n	ν_n	\mathcal{D}_n	\mathcal{R}_n	ν_n	\mathcal{D}_n	\mathcal{R}_n	ν_n	\mathcal{D}_n	\mathcal{R}_n^{01}	\mathcal{R}_n	ν_n	\mathcal{D}_n				\mathcal{R}_n
1	699	4.1	-0.6	643	0.7	1.5	717	3.8	3.6	0.4	660	1.6	0.9	652	1.9	0.9	646	1.7	1.0	643	0.1	-0.9	-0.4	673		
2	826	6.4	1.5	737	64.8	11.8	811	0.1	0.6	0.0	733	0.9	-0.1	728	1.0	-0.7	704	1.3	-1.2	733	10.0	14.4	7.5	754		
3	925	23.2	-20.0	758	39.0	-15.8	964	4.1	6.3	-0.3	839	1.1	-1.4	836	1.2	1.7	824	0.7	1.7	794	5.5	6.7	3.6	817		
4	953	29.3	-55.4	806	150.4	-63.6	968	1.4	2.1	-11.2	879	1.4	5.4	880	1.9	2.8	871	1.8	2.7	866	12.6	-27.2	10.8	885		5
5	986	7.3	44.6	862	8.6	73.4	1031	1.1	1.4	9.6	896	3.3	-9.1	901	3.8	-8.9	875	2.8	-7.4	890	0.8	-14.7	-3.7	914	0.6	-6.2
6	1034	71.2	87.0	904	6.5	79.7	1096	3.8	5.2	17.8	971	11.2	15.7	967	10.5	18.5	938	9.8	17.9	938	7.2	6.7	-27.3	961	5.4	-29
7	1205	25.2	-36.5	1066	14.1	-43.3	1201	5.4	6.7	0.5	1070	3.0	-1.4	1074	5.8	-2.7	1051	11.5	-14.8	1079	0.4	23.2	7.1	1106	0.9	11.1
8	1205	15.5	-6.9	1073	3.4	-33.5	1253	15.2	13.3	-6.8	1083	7.0	-11.3	1082	9.5	-11.9	1065	3.6	-0.5	1089	0.0	-1.0	-1.7	1112		-4.9
9	1365	0.2	-5.1	1211	0.0	4.1	1387	0.0	0.0	-1.9	1232	0.7	6.7	1220	0.7	5.9	1191	0.8	5.9	1216	2.4	-3.2	11.5	1235	3.0	24.1
10	1438	13.6	-23.5	1239	6.9	-16.2	1454	9.8	8.2	-16.4	1272	5.9	-5.8	1272	5.9	-8.1	1263	5.8	-7.4	1314	0.0	-0.3	-0.6	1339	0.2	-2.5
11	1620	13.7	15.3	1508	3.8	1.8	1649	6.9	8.4	8.2	1491	0.7	0.6	1419	2.4	2.7	1398	2.3	2.7	1378	1.5	-2.8	-8.6	1397	1.2	-15
12	2681	7.8	-14.5	2238	10.8	-47	2625	7.2	13.3	-13.4	2162	11.4	-13.7	2162	12.5	-16.3	2159	1.9	18.4	2236	4.6	-21.1	-20.2	2240	2.7	-10.4
13	2691	2.5	15.9	2263	1.6	55.5	2636	1.8	3.4	14.3	2180	1.4	14.5	2174	3.1	17.2	2166	12.2	-17.6	2246	1.3	23.4	16.4	2254	0.6	12.1
14	3653	1.8	-18.3	3061	0.9	-61.8	3581	1.6	3.2	-20.0	2953	1.2	-22.3	2947	3.7	-24.4	2926	1.7	-28.6	3050	1.1	-31.7	-31.7	3015		-8.9
15	3662	8.0	17.9	3065	11.4	69.2	3587	8.8	16.6	19.8	2962	15.5	22.1	2964	16.4	24.3	2967	16.7	28.4	3056	5.5	32.1	41.6	3028	5.3	11.4
MAE ^d	214	14.1	31.7	47	5.6	48.4	215	4.0	5.9	14.0	42	4.2	12.9	39	5.3	14.3	47	4.6	15.0	22	0.8	16.6	8.8			
MAE ^e	228	12.6	27.6	30	18.4	34.9	229	5.0	5.8	12.9	44	4.3	10.7	38	5.0	10.5	41	4.8	9.8							

^a) Experimental data from Ref. 1.

^b) Results obtained by integrating over the deformation density rather than through the point charges model.

^c) Results obtained with the APT model.²

^d) Mean absolute error of the respective columns (with the respective units) with respect to the available experimental data (after reordering of the modes according to Table 1 in the main text).

^e) Mean absolute error of the respective columns (with the respective units) with respect to the BP86/TZP data (after reordering of the modes according to Table 1 in the main text).

References

- (1) Freedman, T. B.; Spencer, K. M.; Ragunathan, N.; Nafie, L. A.; Moore, J. A.; Schwab, J. M. Vibrational circular dichroism of (S,S)-[2,3- $^2\text{H}_2$]oxirane in the gas phase and in solution. *Can. J. Chem.* **1991**, *69*, 1619–1629.
- (2) Freedman, T. B.; Nafie, L. A. Vibrational optical activity calculations using infrared and Raman atomic polar tensors. *J. Chem. Phys.* **1983**, *78*, 27–31.
- (3) Jr., G. L. C.; Boyd, A. W.; Myers, R. J.; Gwinn, W. D.; Van, W. I. L. The Microwave Spectra, Structure, and Dipole Moments of Ethylene Oxide and Ethylene Sulfide. *J. Chem. Phys.* **1951**, *19*, 676–685.

Table 2: Dipole strengths \mathcal{D}_n (in $10^{-39}\text{esu}^2\text{cm}^2$) and rotational strengths \mathcal{R}_n (in $10^{-44}\text{esu}^2\text{cm}^2$) of (*S,S*)-[2,3- $^2\text{H}_2$]oxirane (gas phase) calculated by combining the transformation matrices \mathbf{S}^n in Eqn. 5 (in the main text) at several levels (shown in the header) with APTs and AATs calculated at the BP86/TZP level.^{a,b,c}

n^d	DFTB				DFTB2				DFTB3				BP86	
	qnano15		mio11		qnano15		mio11		3ob31		3obf12		TZP	
	\mathcal{D}_n	\mathcal{R}_n	\mathcal{D}_n	\mathcal{R}_n	\mathcal{D}_n	\mathcal{R}_n	\mathcal{D}_n	\mathcal{R}_n	\mathcal{D}_n	\mathcal{R}_n	\mathcal{D}_n	\mathcal{R}_n	\mathcal{D}_n	\mathcal{R}_n
1	0.0	-0.2	0.0	-1.2	0.0	(0.1)	0.0	-0.5	0.0	-0.8	0.0	-0.9	0.1	-0.4
2	9.8	5.8	19.6	4.6	9.8	5.1	9.2	6.9	9.8	8.7	10.8	10.4	10.0	7.5
3	3.3	3.9	5.3	4.3	3.3	0.5	4.7	3.8	5.9	3.4	6.0	3.4	5.5	3.6
4	7.0	17.6	6.5	0.2	7.0	13.4	5.6	14.0	4.2	11.0	2.5	8.8	12.6	10.8
5	2.0	-5.2	1.0	-4.7	2.0	-1.8	1.5	-4.8	0.6	-3.5	0.5	-3.7	0.8	-3.7
6	10.6	-31.6	0.0	-1.0	10.6	-38.6	16.7	-35.8	5.6	-38.8	16.1	-42.2	7.2	-27.3
7	0.5	8.5	0.5	8.3	0.5	8.4	0.5	8.7	0.8	8.8	0.5	8.5	0.4	7.1
8	0.1	-2.2	1.2	-10.0	0.1	-6.3	0.5	-6.7	1.1	-9.3	2.4	-13.2	0.0	-1.7
9	1.0	8.9	0.0	2.0	1.0	10.9	0.1	4.0	0.5	6.9	0.7	7.4	2.4	11.5
10	0.0	-0.8	0.0	-0.5	0.0	-0.9	0.1	-0.9	0.1	-0.9	0.1	-1.0	0.0	-0.6
11	1.7	-5.6	0.5	-2.1	1.7	-5.4	1.0	-3.4	1.5	-5.3	1.5	-5.5	1.5	-8.6
12	3.8	-21.1	4.4	-20.8	3.8	-20.6	4.6	-19.7	4.4	-16.4	4.6	-19.2	4.6	-20.2
13	1.0	17.4	1.4	16.5	1.0	17.4	1.3	16.2	1.5	13.3	1.3	15.7	1.3	16.4
14	1.0	-33.3	1.1	-33.3	1.0	-32.3	1.1	-31.8	1.6	-23.9	1.1	-30.9	1.1	-31.7
15	4.5	42.3	5.4	41.9	4.5	41.8	5.6	40.7	5.1	32.5	5.6	40.4	5.5	41.6
MAE ^e	1.1	1.8	1.9	4.7	1.1	2.5	1.5	2.6	1.0	3.9	1.7	3.2		

^a) Figures in bold indicate normal modes with overlaps ≥ 0.99 with BP86/TZP modes (Table 1 in the main text).

^b) Figures in parentheses refer to rotational strengths with opposite signs with respect to those calculated by BP86/TZP.

^c) Nomenclature of DFTB parametrizations is abbreviated.

^d) The order of the normal modes (n) follows the energy of the BP86/TZP normal modes and was adjusted for other levels in accordance with the matches shown in Table 1 in the main text.

^e) Mean absolute error of the respective columns (with the respective units) with respect to the BP86/TZP data.

Table 3: Norm of the electric dipole moment^{a)} and norm of the electric dipole moment derivatives upon displacing the atoms of ethylene oxide^{b)} in the x, y, z directions (both properties displayed in atomic units, a.u.) as calculated at several levels.^{c)}

	DFTB1		DFTB2			DFTB3		BP86	
	qnano15	mio11	qnano15	qnano15 ^{d)}	mio11	3ob31	3obf12	TZP	
$ \vec{\mu}_e $	1.358	1.930	0.723	0.800	0.888	0.928	0.945	0.760	
C	Δx	0.738	0.745	0.461	0.449	0.383	0.418	0.398	0.232
	Δy	1.082	1.099	0.533	0.422	0.484	0.557	0.465	0.361
	Δz	0.596	0.661	0.467	0.505	0.542	0.648	0.526	0.316
O	Δx	0.829	1.035	0.323	0.225	0.269	0.292	0.276	0.346
	Δy	1.842	2.124	0.791	0.707	0.786	0.865	0.761	0.864
	Δz	0.684	0.838	0.373	0.375	0.396	0.521	0.395	0.326
H	Δx	0.167	0.129	0.158	0.183	0.150	0.163	0.157	0.082
	Δy	0.080	0.015	0.073	0.062	0.073	0.072	0.069	0.068
	Δz	0.136	0.135	0.151	0.175	0.192	0.221	0.183	0.124

^{a)}Experimental value: 0.74 au (1.88 D).³

^{b)}The calculations were performed with the C-C bond and C₂ axis oriented, respectively, along the x -axis and the y -axis of the Cartesian coordinate system.

^{c)}Nomenclature of DFTB parametrizations is abbreviated.

^{d)}Results obtained by integrating over the deformation density rather than through the point charges model.