Supplementary Materials

The Influence of Sulphur on Anharmonic Features of Vibrational Circular Dichroism, on Electronic Circular Dichroism and on Optical Rotatory Dispersion: A Study of (*R*)-2-Chloromethyl-Oxirane, (*R*)-2-Methyl-Oxirane, (*R*)-2-Chloromethyl-Thiirane, and (*R*)-2-Methyl-Thiirane

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1. NMR Spectra and Mass Spectrometry Results
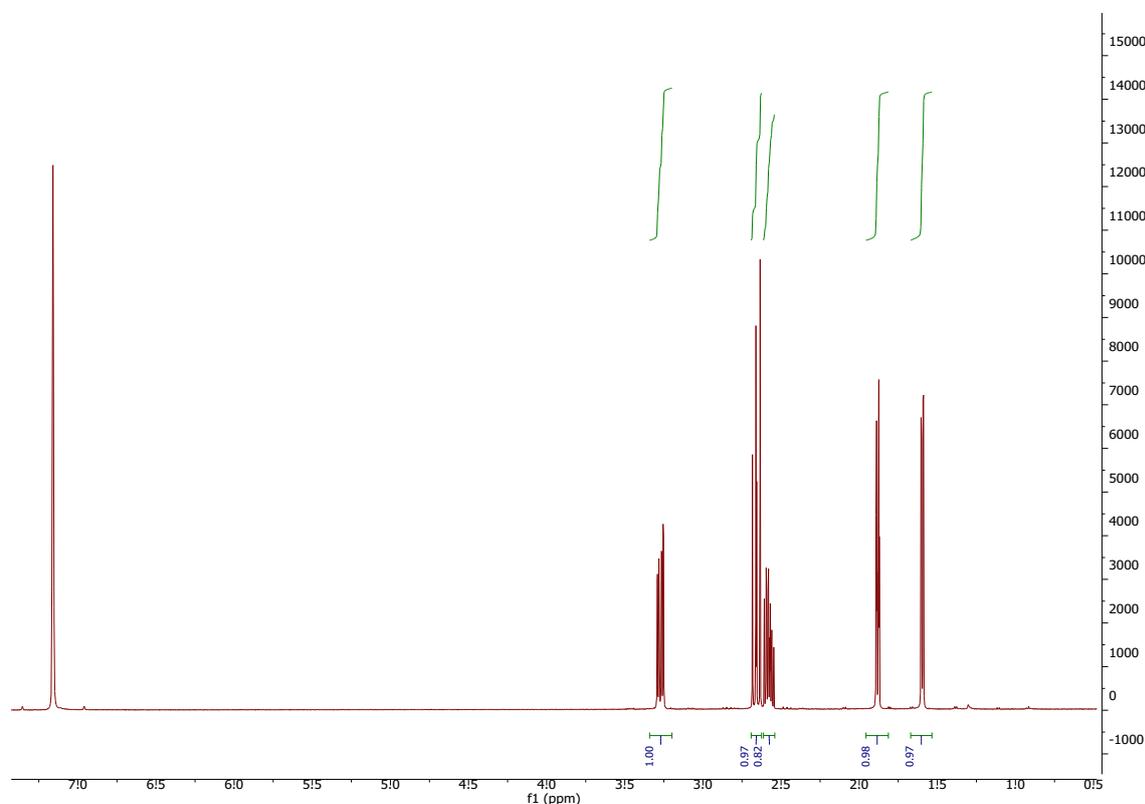
Figure S1. ^{1}H-NMR (C$_6$D$_6$, 400.13 MHz) spectrum of the synthetized (*R*)-2-(chloromethyl)thiirane.
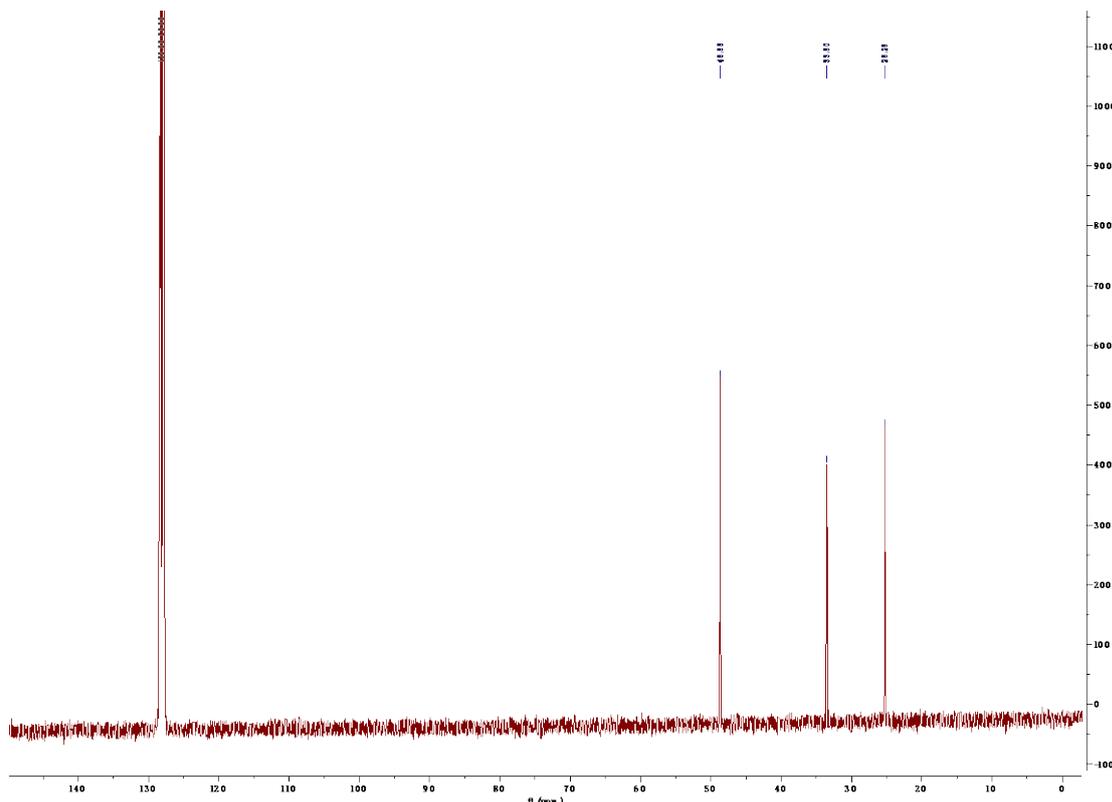
Figure S2. ^{13}C-NMR (C$_6$D$_6$, 100.61 MHz) spectrum of the synthetized (*R*)-2-(chloromethyl)thiirane.

1.1. Enantioselective GC and GC-MS of 2-(chloromethyl)thiirane

Since the circular dichroism measurements are affected by the enantiomeric purity, and because no data have been published on the enantiomeric purity of the 2-(chloromethyl)thiirane synthetized by this method, a direct analysis of the synthetized sample was performed by GC-FID (Gas Cromatography—Flame ionization detector) and GC-MS (Gas Cromatography—Mass spectrometry) using a chiral stationary phase. Among the available cyclodextrin derivatives, the 2-*O*-ethyl-3-*O*-methyl-6-*O-tert*-butyldimethylsilil-β-cyclodextrin was adopted as chiral selector for the analysis.

The results of the enantioselective gas chromatography (Es-GC) of the racemic 2-(chloromethyl)thiirane (synthetized from the racemic 2-(chloromethyl)oxirane (Sigma-Aldrich, 99% purity) according to the Scheme 1), and the synthetized *R*-enantiomer are reported in Figure S3. A two-component fit of the GC chromatogram with asymmetric Gaussian functions gave the following results: i) for the racemic sample, 51% and 49% for the S and R enantiomers, respectively; for the chiral sample, 4% and 96% for the S and R enantiomers, respectively. The enantiomer % abundance of the synthetized (*R*)-2-(chloromethyl)thiirane by ES-GC was 92%. Further technical details are given below.

GC-FID and GC-MS systems: Analyses were carried out on a Shimadzu GC-FID 2010 unit equipped with Shimadzu GC Solution 2.53U software and a Shimadzu GC 2010—Shimadzu QP2010-PLUS GC-MS system equipped with GCMS 2.51 software (Shimadzu, Milan, Italy).

Column: the column was coated with 2-*O*-ethyl-3-*O*-methyl-6-*O-tert*-butyldimethylsilil-β-cyclodextrin diluted at 30% in PS-086. Column characteristics were: length (l): 25 m, inner diameter (d_c) 0.25 mm, film thickness (d_f) 0.25 μm.

1.2. Analysis Methods

GC-FID conditions: temperatures: injector: 220 °C, detector: 230 °C, FID data acquisition rate: 50 Hz. Injection mode: split; split ratio: 1:20, injection volume: 1 μL. All analyses were carried out with hydrogen as carrier gas in constant linear velocity mode; initial flow rate: 1 mL/min. Temperature program: from 35 °C (kept for10 min) to 220 °C at 2 °C/min

GC-MS conditions: temperatures: injector: 220 °C, transfer line: 230 °C; ion source: 200 °C; carrier gas: He, flow control mode: constant linear velocity, initial flowrate: 1 mL/min. The MS operated in electron ionization mode (EI) at 70 eV, scan rate: 4.5 scan/sec, mass range: 35–350 m/z. For injection conditions and temperature program see GC-FID.
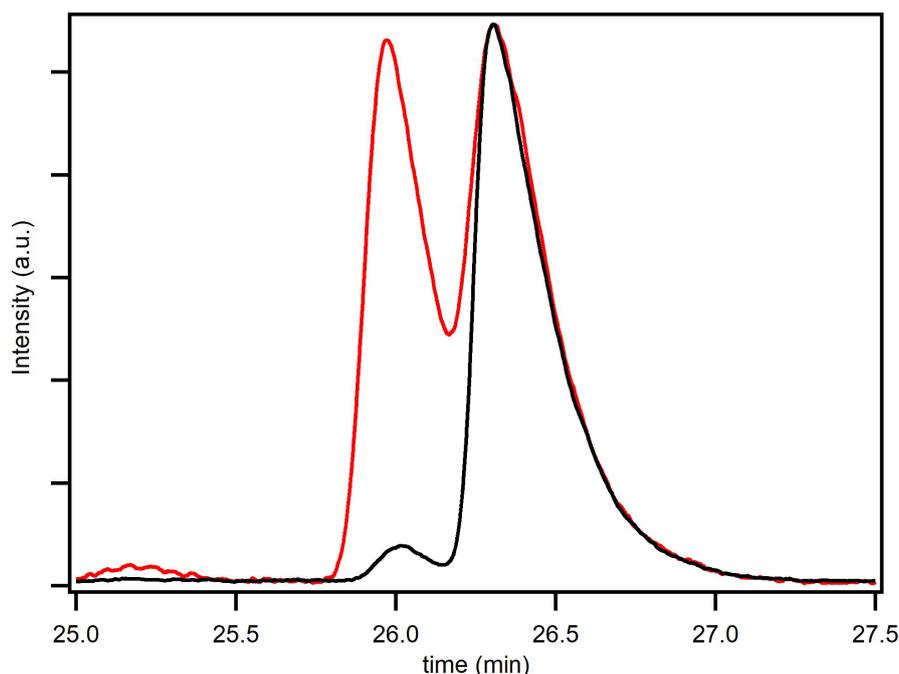
Figure S3. GC-FID chromatograms of 2-(chloromethyl)thiirane samples: (**a**) racemic sample (red curve); (**b**) synthetized (*R*)-2-(chloromethyl)thiirane (black curve). Both chromatograms were obtained with the same column and experimental conditions.

Table S1. In the top part of the table, energy, enthalpies and free-energy in Hartree units (and relative Boltzmann factors) computed at B3PW91/jun-cc-pVTZ level of theory for chloromethyl thiirane chloromethyl oxirane. In the bottom part, the Boltzmann populations factors taken from Palumbo et al. (https://doi.org/10.1016/j.saa.2020.119061 (accessed on 20 November 2025)) are reported.

	E	E. Pop.	H	H pop.	G.	G.pop
Chloromethyl Thiirane (Gas Phase)						
G I	−975.683429	0.083	−975.602325	0.095	−975.638688	0.087
Cis	−975.68167	0.013	−975.600587	0.015	−975.636782	0.012
G II	−975.68568	0.904	−975.604434	0.890	−975.640891	0.901
Chloromethyl Oxirane (Gas Phase)						
	E	E. Pop.	H	H pop.	G.	G.pop
G I	−652.702263	0.305	−652.619017	0.322	−652.654178	0.311
Cis	−652.701069	0.086	−652.617839	0.093	−652.652859	0.077
G II	−652.702916	0.609	−652.619579	0.585	−652.654815	0.612
Chloromethyl Thiirane (CCl₄ Solution)						
	E	E. Pop.	H	H pop.	G.	G.pop
G I	−975.685927	0.121	−975.604775	0.135	−975.641133	0.124
Cis	−975.684115	0.018	−975.603015	0.021	−975.63923	0.017
G II	−975.687775	0.861	−975.606503	0.844	−975.64296	0.859
Chloromethyl Oxirane (CCl₄ Solution)						
	E	E. Pop.	H	H pop.	G.	G.pop
G I	−652.705191	0.415	−652.621906	0.427	−652.65706	0.412
Cis	−652.703814	0.096	−652.620565	0.103	−652.655591	0.087
G II	−652.705346	0.489	−652.621998	0.470	−652.657243	0.501

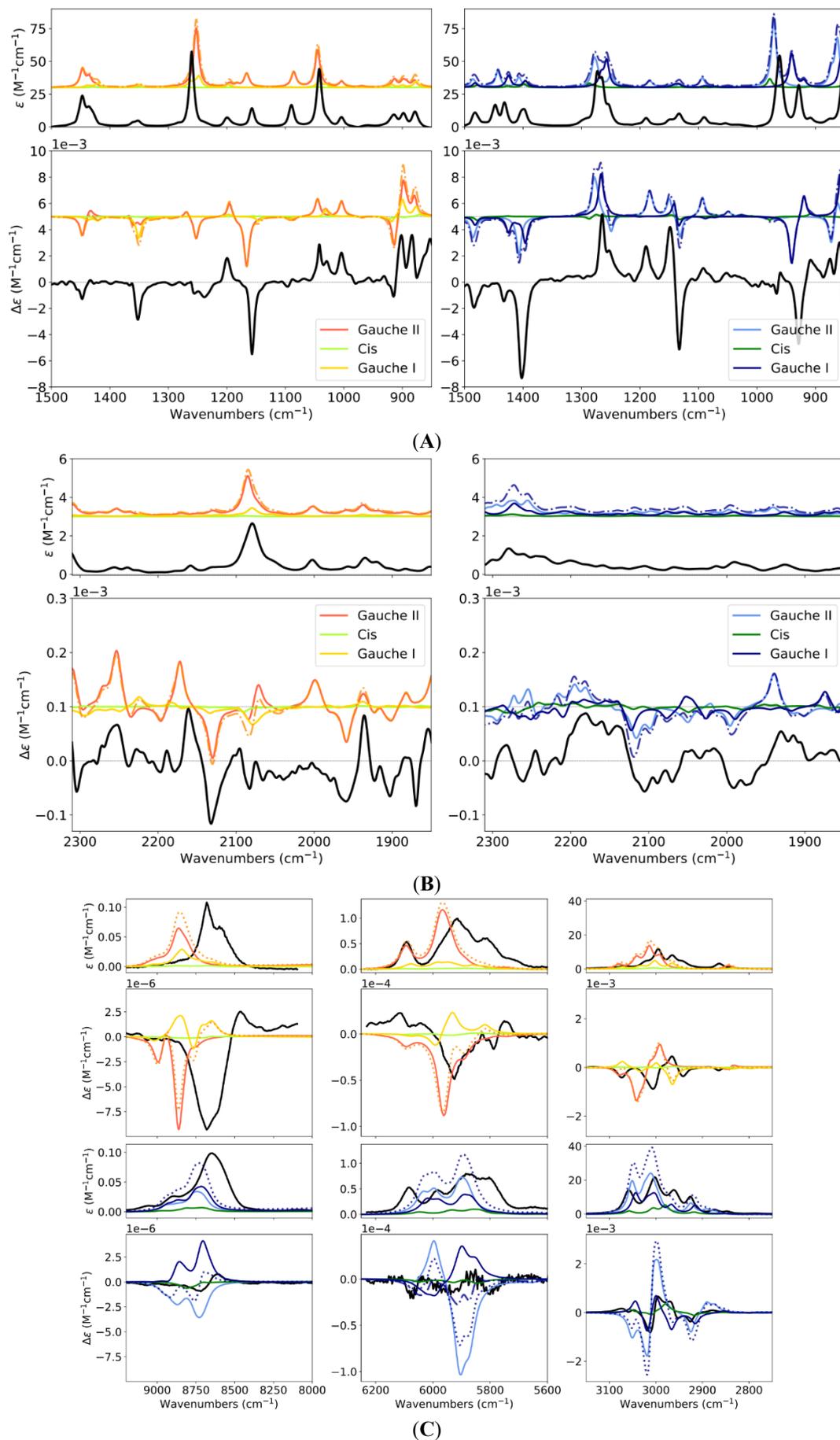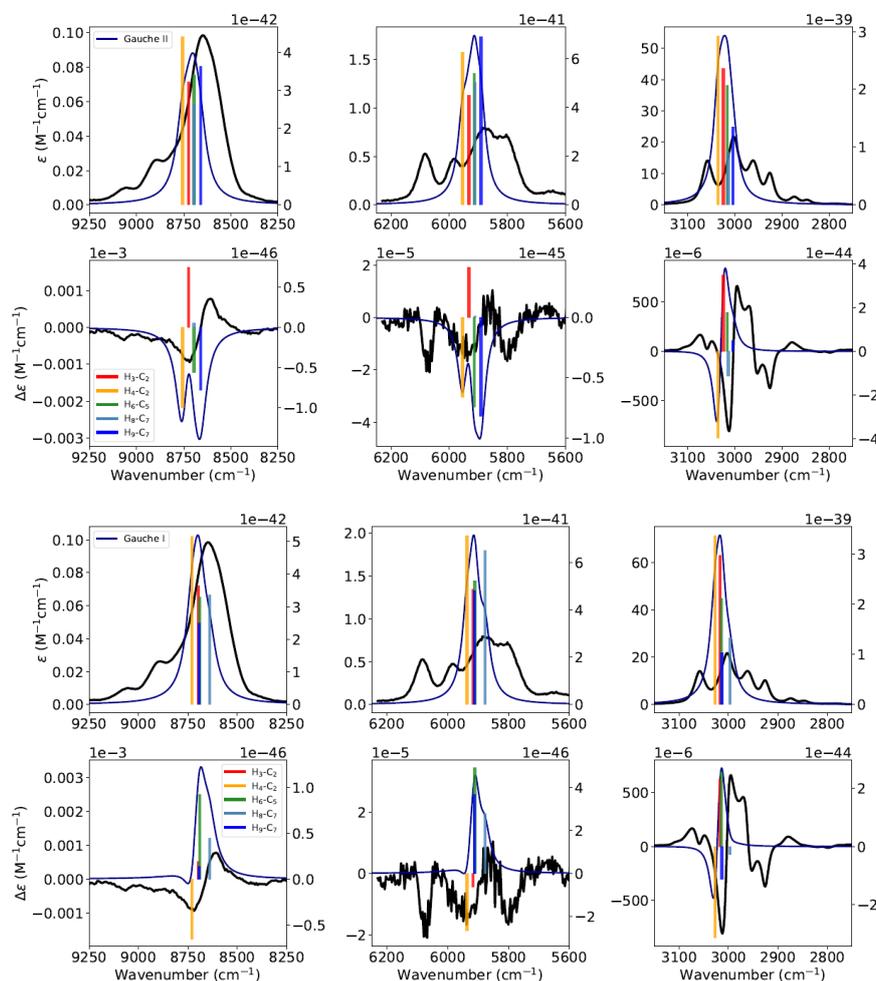|	Chloromethyl Thiirane			Chloromethyl Oxirane		
	Gas	CCl₄	Neat	Gas	CCl₄	Neat
G I	0.12	0.16	0.28	0.25	0.34	0.56
Cis	0.01	0.02	0.03	0.07	0.08	0.10
G II	0.87	0.82	0.68	0.68	0.58	0.34

**(A)**

(B)

(C)

Figure S4. (A). Fingerprint region between 850 and 1500 cm^{-1}. Comparison of experimental IR (top) and VCD spectra (bottom) with corresponding computed spectra for all conformers and Boltzmann average (dashed lines) of (*R*)-chloromethyl thiirane (left two panels) and (*R*)-chloromethyl oxirane (right two panels) based on GVPT2

approach. All experimental spectra are in black, computed spectra for (*R*)-chloromethyl thiirane have orange-hue, computed spectra for (*R*)-chloromethyl oxirane have blue-hue. Conformer spectra were multiplied by their Boltzmann factors in CCl₄. (**B**). Combination/overtone region between 1850 and 2350 cm⁻¹. Comparison of experimental IR (top) and VCD spectra (bottom) with corresponding computed spectra for all three conformers (solid lines) and for the Boltzmann averages (dashed-dotted lines) of (*R*)-chloromethyl thiirane (right two panels) and (*R*)-chloromethyl oxirane (left two panels) based on GVPT2 approach. All experimental spectra are in black, computed spectra for (*R*)-chloromethyl thiirane have orange-hue, computed spectra for (*R*)-chloromethyl oxirane have blue-hue. Conformer spectra are reported as already multiplied by their Boltzmann factors calculated for CCl₄ solution. (**C**). Comparison of experimental IR/NIR (1st and 3rd from top) and VCD spectra (2nd and 4th from top) with corresponding computed spectra for all three conformers (solid lines) and for the Boltzmann averages (dotted lines) for (*R*)-chloromethyl thiirane (top two panels) and (*R*)-chloromethyl oxirane (bottom two panels) for the fundamental (Δv = 1, right), first overtone (Δv = 2, center) and second overtone (Δv = 3, left) based on GVPT2 approach. All experimental spectra are in black, computed spectra for (*R*)-chloromethyl thiirane have orange-hue, computed spectra for (*R*)-chloromethyl oxirane have blue-hue. See Figure S4A for the definition of the color coding. Conformer spectra are reported as already multiplied by their Boltzmann factors for CCl₄ solution (Δv = 1) and for the neat, (Δv = 2 and Δv = 3), the factors being taken from Palumbo et al. (Spectrochim. Acta. A. Mol. Biomol. Spectrosc. 2021, 247, 119061). In the case of (*R*)-chloromethyl oxirane in the Δv = 2 region, also the computed Boltzmann average spectrum with weights for the CCl₄ solution is reported as dashed-dotted.

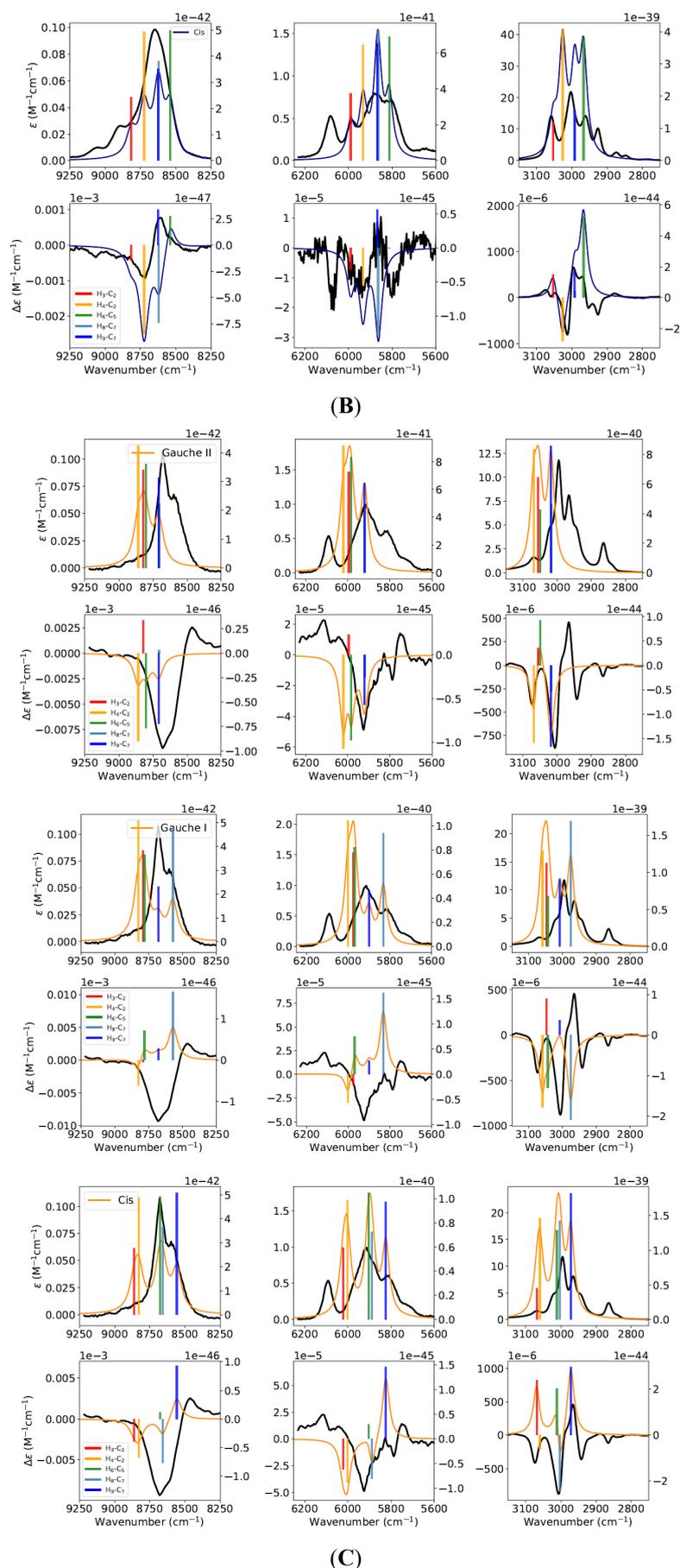
(A)

(B)

(C)
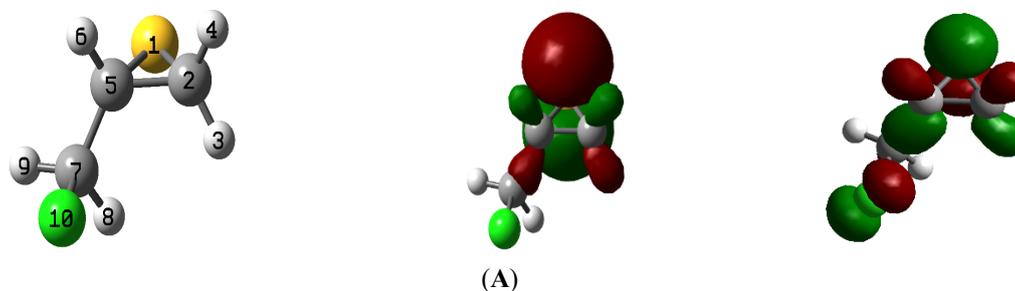
Figure S5. (A): Atom numbering used in calculation for (*R*)-2chloromethyl thiirane and (*R*)-2-chloromethyl oxirane. This figure may help the reader better understand the next local mode (lm) calculations; center: HOMO representation for (*R*)-2chloromethyl thiirane; right: HOMO representation for (*R*)-2chloromethyl oxirane. (The

same parameters for the orbital representation used in the two cases.). (**B**): (*R*)-2-chloromethyl-oxirane. Comparison of experimental (black) and computed (blue) absorption (top row) and VCD (bottom row) spectra. TOP: calculations for the major populated Gauche II conformer. MIDDLE: calculations for the second major populated Gauche I conformer. BOTTOM: calculations for the minor populated Cis conformer. We also give as bars the contributions of each local mode to the spectra. (For the nomenclature of local modes see Figure S5A above). (**C**): (*R*)-2-chloromethyl-thiirane. Comparison of experimental (black) and computed (blue) absorption (top row) and VCD (bottom row) spectra. TOP: calculations for the major populated Gauche II conformer. MIDDLE: calculations for the second major populated Gauche I conformer. BOTTOM: calculations for the minor populated Cis conformer. We also give as bars the contributions of each local mode to the spectra. (For the nomenclature of local modes see Figure S5A above).
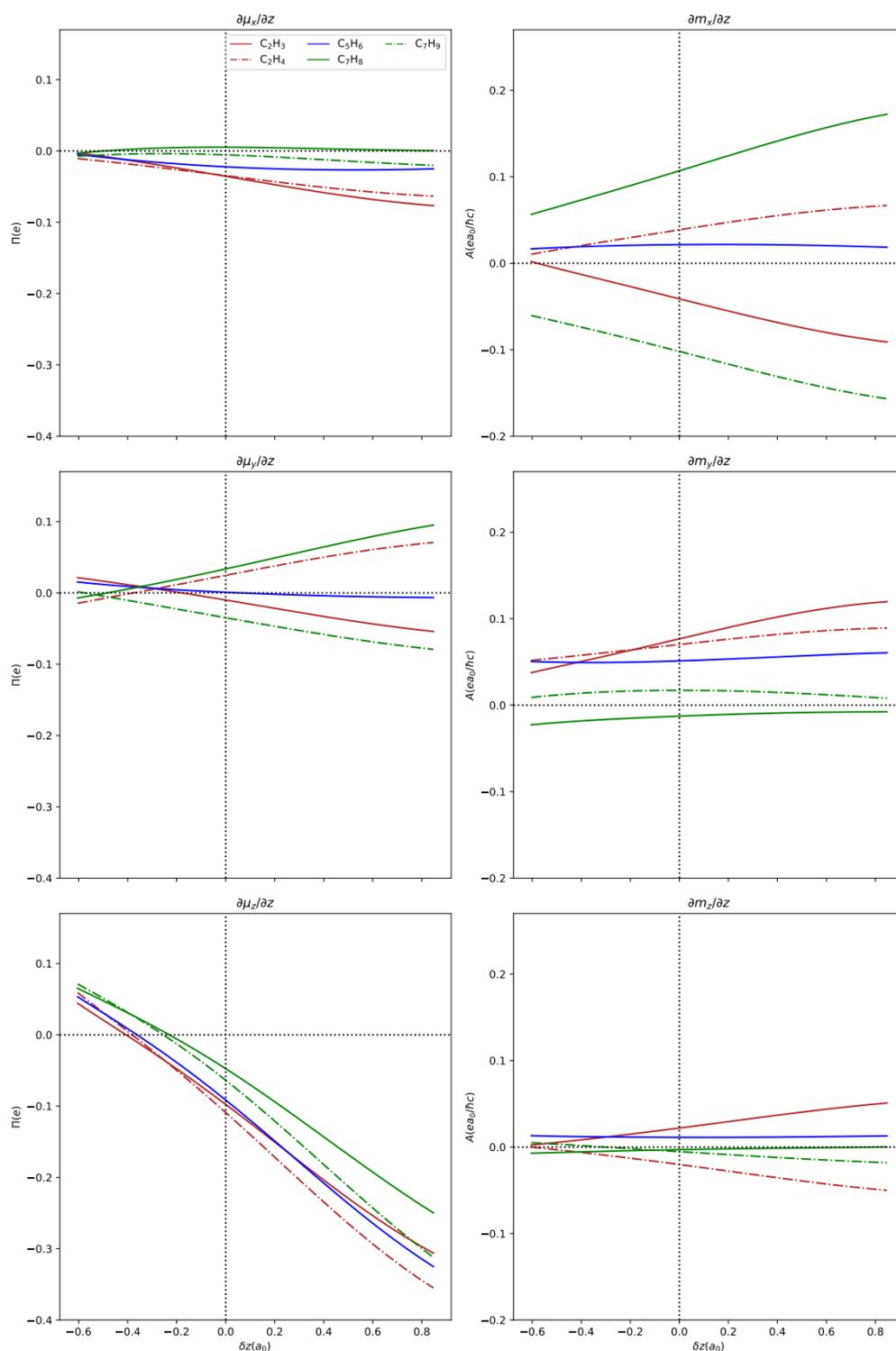
(A)
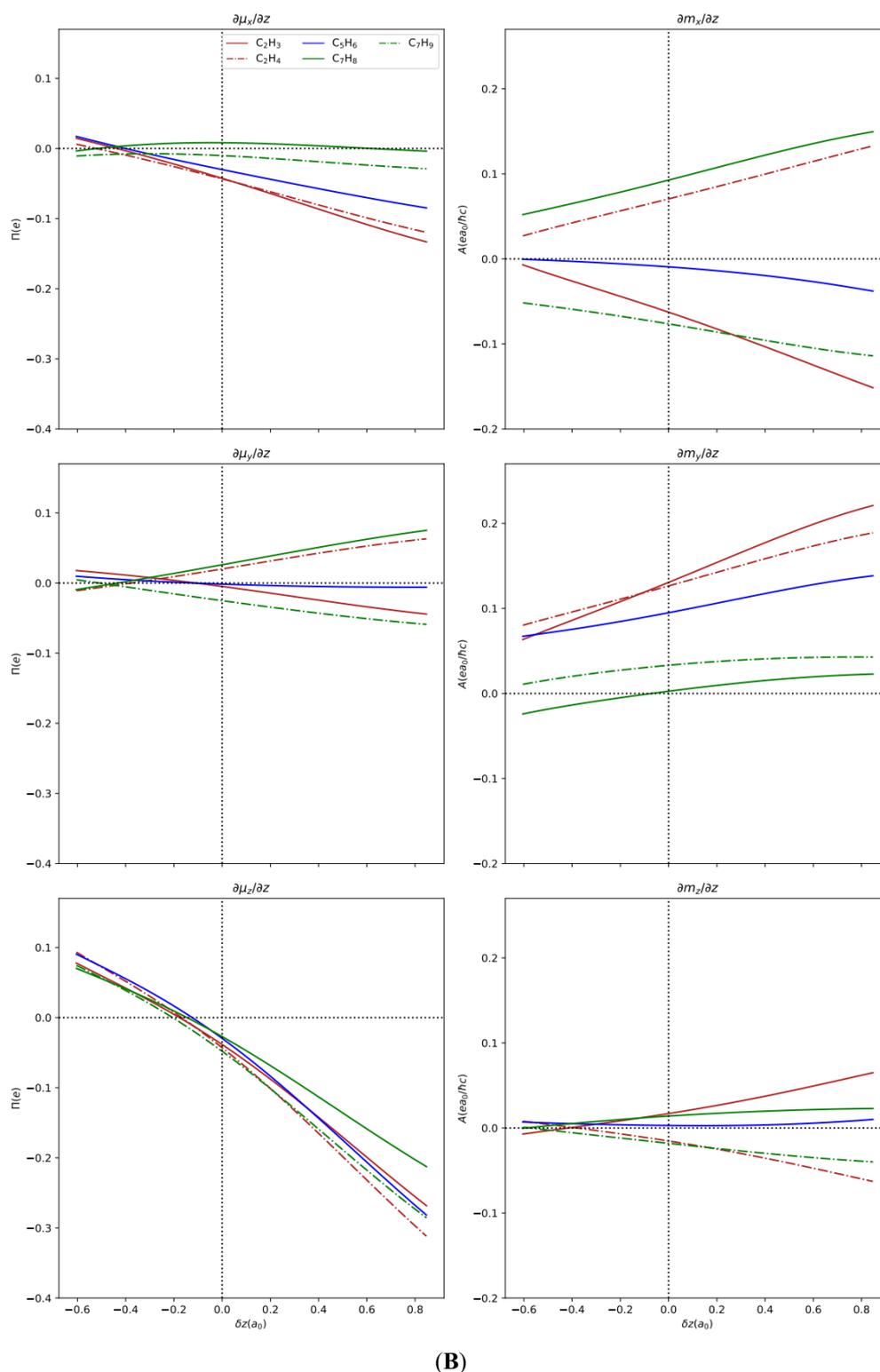
(B)

Figure S6. (**A**): (*S*)-2-chloromethyl-oxirane. Dependence of the longitudinal and transverse components of the APTs and AATs for the Hydrogen atoms with respect to the CH-bond length (z-direction) (see [12] for the definition of (x,y,z) axes for the CH-bonds). APTs are in atomic unit of charge *e* (electrons), AATs are in units of (ea$_0$)/($\hbar$c), where a$_0$ is the Bohr radius, and c the velocity of light. Displacements are in angstroms (Å). Green lines are used for CH$_2$Cl hydrogen atoms, red lines for CH$_2$ and the blue one for CH. (**B**): (*S*)-2-chloromethyl-thiirane. Dependence of the longitudinal and transverse components of the APTs and AATs for the Hydrogen atoms with respect to the CH-bond length (z-direction) (see [12] for the definition of (x,y,z) axes for the CH-bonds). APTs are in atomic unit of charge *e* (electrons), AATs are in units of (ea$_0$)/($\hbar$c), where a$_0$ is the Bohr radius, and c the velocity of light. Displacements are in angstroms (Å). Green lines are used for CH$_2$Cl hydrogen atoms, red lines for CH$_2$ and the blue one for CH.

Table S2. Comparison of the Calculated Bond Lengths (Å) and Interbond Angle CXC (X = O, S) (deg) for chloromethyl thiirane and chloromethyl oxirane at the B3PW91/jun-cc-pVTZ level of theory. The atom numbering is reported in Figure S5A.

|	Chloromethyl Thiirane			Chloromethyl Oxirane		
	G I	**Cis**	**G II**	**G I**	**Cis**	**G II**
R (1,2)	1.8136	1.8177	1.8177	1.4214	1.4280	1.4267
R (1,5)	1.8127	1.8122	1.8206	1.4191	1.4141	1.4228
R (2,3)	1.0838	1.0826	1.0833	1.0864	1.0840	1.0859
R (2,4)	1.0827	1.0825	1.0822	1.0856	1.0856	1.085
R (2,5)	1.4809	1.4753	1.4746	1.4632	1.4579	1.4575
R (5,6)	1.0840	1.0865	1.0836	1.0867	1.0904	1.0866
R (5,7)	1.4940	1.5039	1.4932	1.4912	1.5004	1.4961
R (7,8)	1.0900	1.0877	1.0871	1.0886	1.0891	1.0874
R (7,9)	1.0877	1.0903	1.0866	1.0875	1.0891	1.0880
R (7,10)	1.7930	1.7859	1.8053	1.7964	1.7868	1.7947
A (2,1,5)	48.2057	47.9629	47.8197	62.0098	61.7206	61.5269
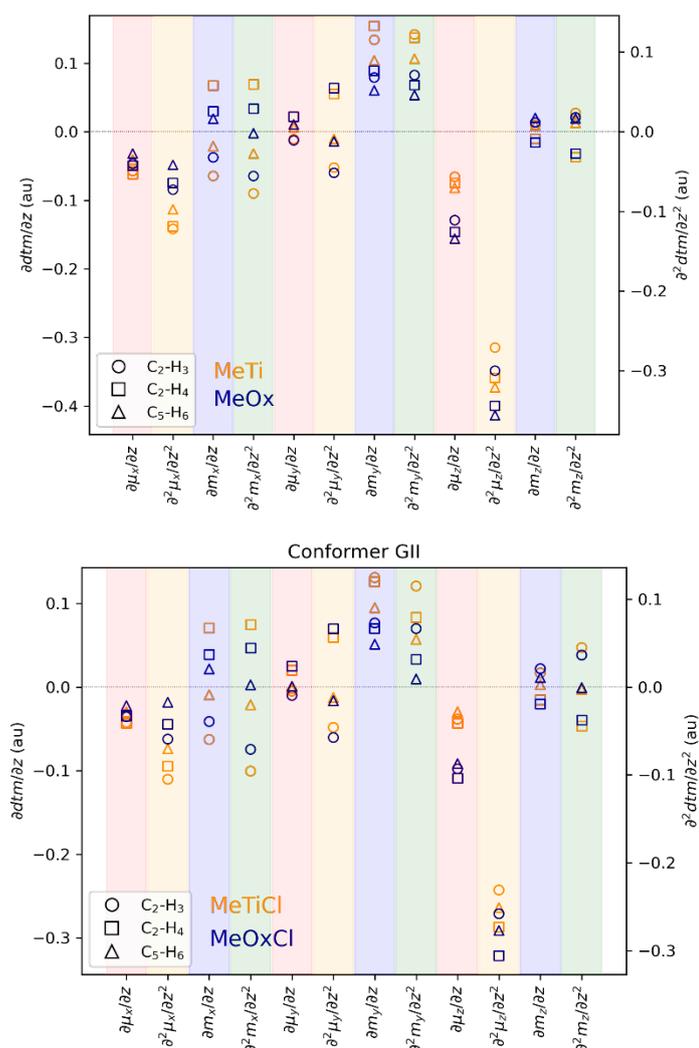
Figure S7. Graphical representation of three components of hydrogen APT and AAT and their first derivatives with respect to CH bond lengths at equilibrium of the three CH on the ring (z = 0, see ref in the captions of Figure S6). In the top panel, the values of (*R*)-methyloxirane (blue) and (*R*)-methylthiirane (orange) are reported. In the bottom panel, the values of (*S*)-2-chloromethyl-oxirane (blue) and (*S*)-2-chloromethyl-thiirane (orange) are reported. The *S* configuration is reported to allow a direct comparison with the non-chlorinated systems (see [12]).
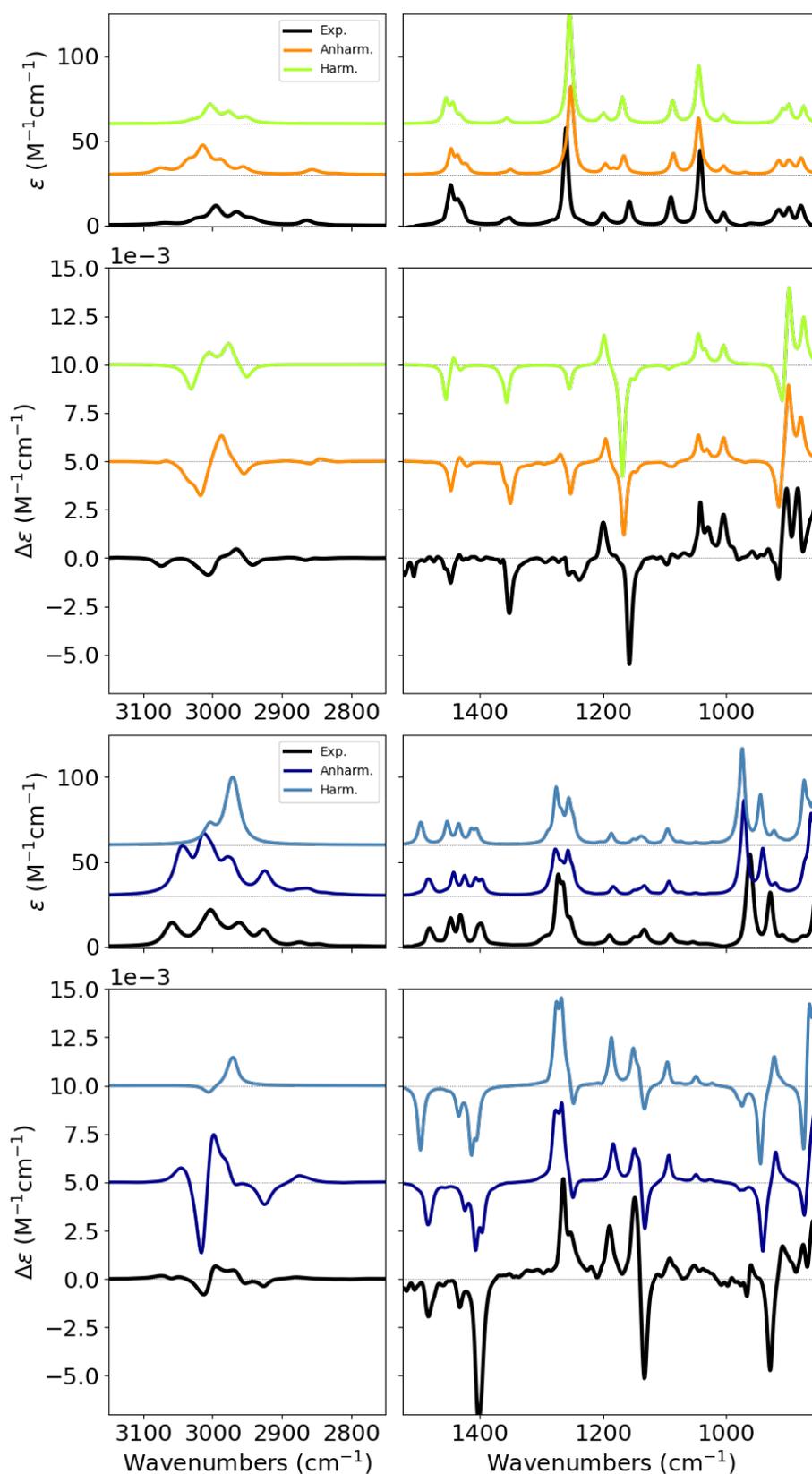
Figure S8. Fingerprint region between 850 and 1500 cm^{-1} and CH-stretching region. Comparison of experimental IR and VCD spectra with corresponding CCl$_4$ Boltzmann average computed spectra of (*R*)-chloromethyl thiirane (top two panels) and (*R*)-chloromethyl oxirane (bottom two panels) at the harmonic level and based on GVPT2 approach. Scaling factors of 0.98 and 0.96 were applied to computed harmonic frequencies in the fingerprint and CH-stretching regions respectively. All experimental spectra are in black, computed spectra for (*R*)-chloromethyl thiirane have orange-hue, computed spectra for (*R*)-chloromethyl oxirane have blue-hue.

Example of Gaussian16 input for a three quanta GVPT2 calculation.

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%nprocshared=24
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#P b3pw91 jun-cc-pvtz Opt=tight

opt

0 1
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     6                      0.362807     1.150545    -0.163711
     1                      0.083563     1.469638    -1.161076
     1                      0.840569     1.909998     0.442274
     6                     -0.501543     0.157586     0.514511
     1                     -0.578680     0.230654     1.593331
     6                     -1.746328    -0.297758    -0.174938
     1                     -2.569762     0.389473     0.019532
     1                     -1.586707    -0.389484    -1.246954
    17                     -2.281219    -1.903660     0.416627

---Link1---
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%nprocshared=24
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%chk=MethiCl_conf01_anh.chk
#P b3pw91 chkbas guess=read
  geom=check
  freq=(vcd,anharm,readanharm)

anharm DVPT2

0 1

pt2model=DVPT2
print=NMOrder=AscNoIrrep
---Link1---
%mem=24GB
%cpu=24
%oldchk=MethiCl_conf01_anh.chk
#P b3pw91 chkbas
  freq=(readfc,readanharm)
  geom=check guess=read

3quanta GVPT2 calc

0 1

pt2model=GVPT2
print=NMOrder=AscNoIrrep
Spectro=MaxQuanta=3
Resonances=(DFreq11=100,K11Min=10,K11MinI=0.3,DFreq12=200,K12Min=1.0,DFreq22=100,K22Min=10,
K13Min=1)
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