SUPPLEMENTARY MATERIAL

Figure 1 shows a pictorial representation of the normal modes of vibration of nicotine in the *trans*-A conformation mentioned throughout the paper. Table 1 reports the optimized geometries of (S)-nicotine in the *trans*-A and *trans*-B conformations.

The conformer-specific VCD spectra are reported in figure 2. The spectra have been obtained by convoluting the calculated VCD intensities with non-normalized Gaussian functions with half-width at half-maximum arbitrarily chosen to be 10 cm^{-1}. Figure 2a shows the harmonic spectra, figure 2b the anharmonic spectra, and figure 2c shows the 4000-6500 cm^{-1} zone of the anharmonic spectra.

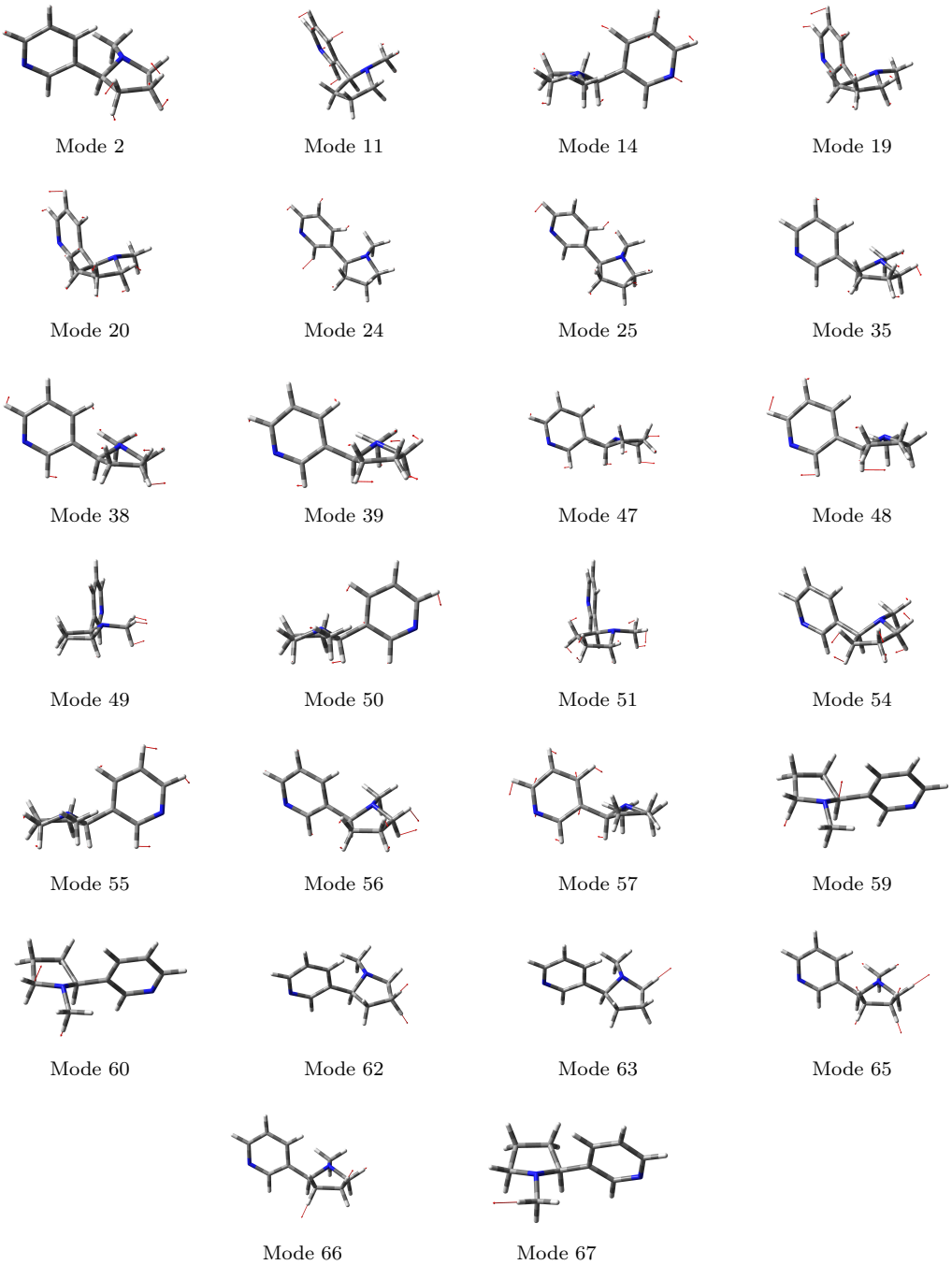

Figure 1: Normal modes of nicotine.

	***trans*-A**			***trans*-B**		
Atom	x	y	z	x	y	z
H	3.591655	-1.757083	-0.335913	-3.594438	-1.781862	0.239299
H	3.071343	-1.504433	1.330490	-3.003665	-1.470410	-1.394083
H	3.343318	0.527718	-0.913351	-3.353485	0.487001	0.910332
H	3.605631	0.788783	0.824762	-3.594630	0.795517	-0.823716
H	2.025697	2.799260	0.392802	-0.902529	-0.103406	1.601195
H	0.897383	-0.086589	-1.582551	-1.351578	-2.303175	0.909637
H	1.325041	-2.304674	-0.898968	-0.834802	-2.015986	-0.750905
H	0.866244	-1.999611	0.775876	-2.029749	2.802890	-0.331943
H	-0.514906	0.073868	1.942318	-0.356874	2.444812	0.132262
H	-1.323051	-0.282625	-2.258991	-1.671121	2.240530	1.322896
H	-4.514687	0.006935	0.343410	4.448067	0.049425	-0.673667
H	-2.995728	0.161948	2.316365	1.341982	-0.362056	2.277695
H	0.346979	2.443282	-0.052826	0.505215	0.152536	-1.902108
H	1.643359	2.270078	-1.267240	3.781516	-0.259776	1.711336
C	2.864695	-1.232017	0.290953	-2.844433	-1.232720	-0.337821
C	2.954491	0.290912	0.097658	-2.949675	0.281962	-0.102102
C	0.761423	-0.225462	-0.490116	-0.761398	-0.230512	0.507626
C	1.398382	-1.579369	-0.083068	-1.392648	-1.584448	0.085553
C	1.386816	2.134036	-0.197906	-1.397402	2.128124	0.254777
C	-0.718822	-0.126598	-0.194785	0.722127	-0.127078	0.224938
C	-3.434067	-0.028488	0.212656	3.396705	-0.003317	-0.394931
C	-1.208871	0.004192	1.108597	1.666781	-0.235789	1.246518
C	-1.661230	-0.192584	-1.226147	1.208810	0.048654	-1.078207
C	-2.583558	0.056444	1.316538	3.024555	-0.177594	0.936318
N	1.572706	0.759013	0.242681	-1.569722	0.761721	-0.216212
N	-2.990394	-0.150906	-1.045892	2.509088	0.112603	-1.395822

Table 1: B3LYP/aug-N07D optimized geometry of nicotine in chloroform in the *trans*-A and *trans*-B conformations. The cartesian coordinates for each atom are given in Ångstroms.

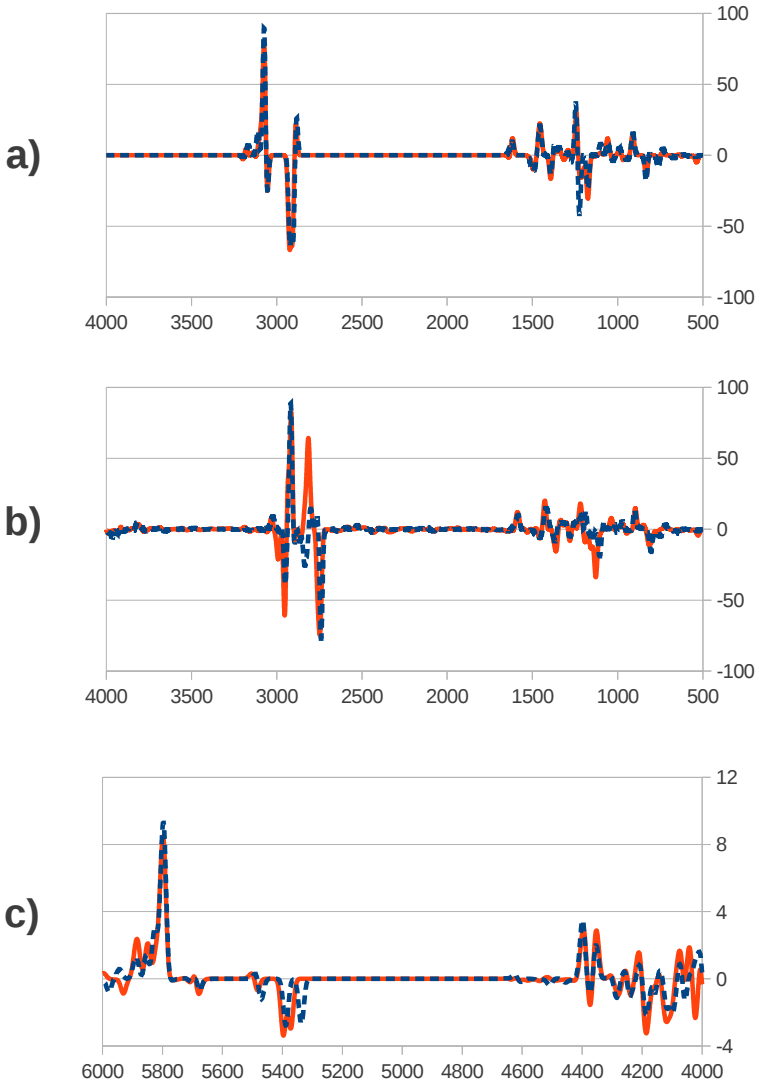

Figure 2: Calculated VCD spectra of for the two conformers of (S)-nicotine considered in the paper: the *trans*-A conformation (continuous orange line) and the *trans*-B conformation (dashed blue line). a) Harmonic spectrum. b) Anharmonic spectrum. c) Anharmonic spectrum, overtones region. Wavenumbers are reported in cm^{-1} and intensities in arbitrary units.