Supplementary data

Comparison of various Franck-Condon and vibronic coupling approaches for simulating electronic spectra: The case of the lowest photoelectron band of ethylene

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Table 1: Quadratic coupling constants E^{ij}_{ab} (eV) for the lowest ionized state a=b=1. The numbers in parenthesis corresponds to the normal modes i and j.

.0034(1, 1)	.0836(7, 7)	.0081(1, 2)
.0204(2, 2)	.0522(8, 8)	.0038(1, 3)
.0159(3, 3)	.0075(9, 9)	.0115(2, 3)
.0413(4, 4)	.0089(10,10)	.0093(5, 6)
.0078(5, 5)	.0046(11,11)	.0036(9,10)
.0040(6, 6)	.0071(12,12)	.0072(11,12)

Table 2: Cubic coupling constants E^{iii}_{ab} (eV) for the lowest two ionized states. The number in parenthesis corresponds to the normal mode i.

	b=1	b=2
a=1	-.1173(1)	.0205(4)
	.0383(2)	
	.0162(3)	
a=2	.0205(4)	-.1178(1)
		.0377(2)
		.0072(3)

Table 3: Quartic coupling constants E_{ab}^{iiii} (eV) for the lowest ionized state a=b=1. The numbers in parenthesis corresponds to the normal mode i.

.0308(1)	.0354(5)	.0345(9)
.0083(2)	.0062(6)	.0406(10)
.0038(3)	.0183(7)	.0316(11)
.0109(4)	.0238(8)	.0032(12)

CAPTIONS FOR FIGURES

FIG. 1. Spectrum calculated using the vertical FC approach where the full *ab initio* one-dimensional potential energy surfaces are used for the symmetric modes and the torsion mode.

FIG. 2. Spectrum calculated using the symmetry constrained adiabatic FC approach with a one-dimensional scan of the torsion potential centered at the symmetry constrained optimized geometry.

FIG. 3. The FC and vibronic spectra calculated for models with only the torsion normal mode, the rest of the normal modes being fixed at three different symmetric geometries: (a, top panel) Ground state equilibrium geometry. (b, middle panel) Mid point between the ground state geometry and the symmetry constrained optimized geometry of the lowest ionized state. (c, bottom panel) Symmetry constrained optimized geometry of the lowest ionized state. The potential energy surfaces corresponding to these different geometries are shown in the bottom panel of Figure 6. In each case, the FC and vibronic spectra are identical within the accuracy of the plot.

FIG. 4. Spectrum calculated using the vibronic approach with the torsion normal mode excluded from the vibronic model.

FIG. 5. Spectrum calculated using the symmetry constrained adiabatic vibronic model with the torsion normal mode excluded from the vibronic model.

FIG. 6. Spectrum calculated using the vibronic model with only linear coupling constants.

FIG. 7. Spectrum calculated using a vibronic model with linear coupling constants for all normal modes except torsion for which up to quartic coupling constants are included.

Figure 1:

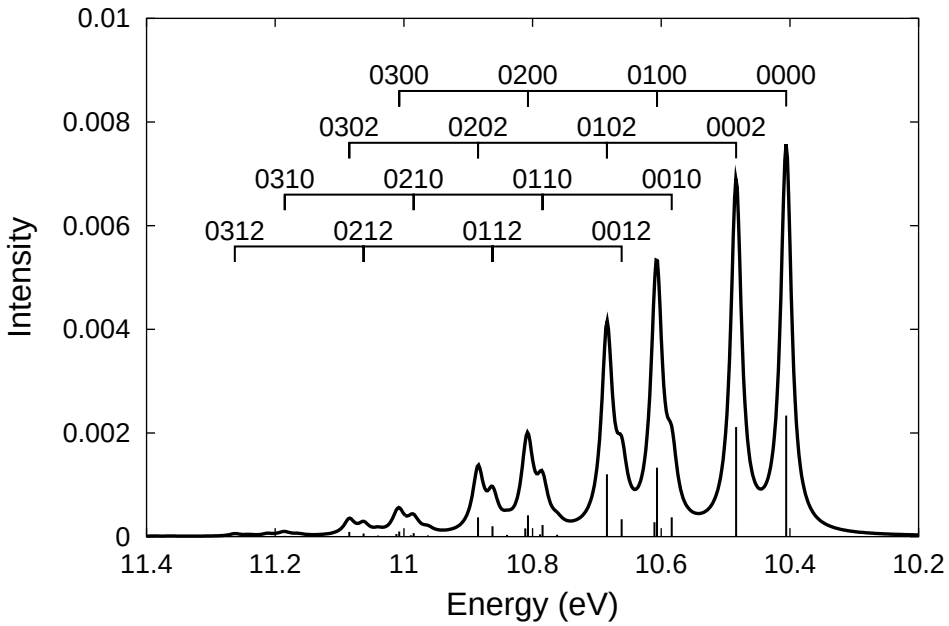

0.01
0.008
0.006
0.004
0.002
0
Intensity
11.4
11.2
11
10.8
10.6
10.4
10.2
Energy (eV)
0300
0200
0100
0000
0302
0202
0102
0002
0310
0210
0110
0010
0312
0212
0112
0012

Figure 2:

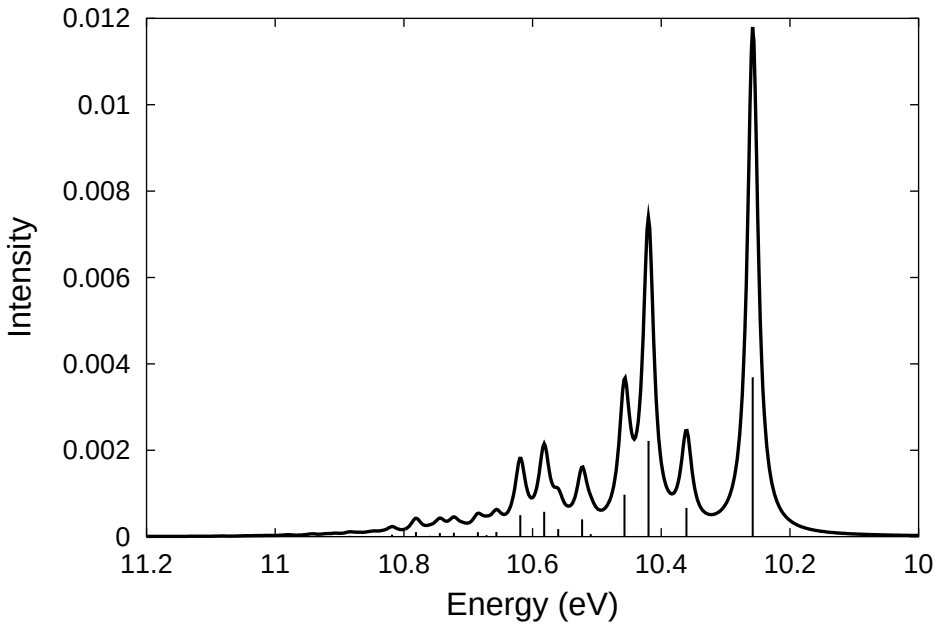

0.012
0.01
0.008
0.006
0.004
0.002
0
Intensity
11.2
11
10.8
10.6
10.4
10.2
10
Energy (eV)

Figure 3:

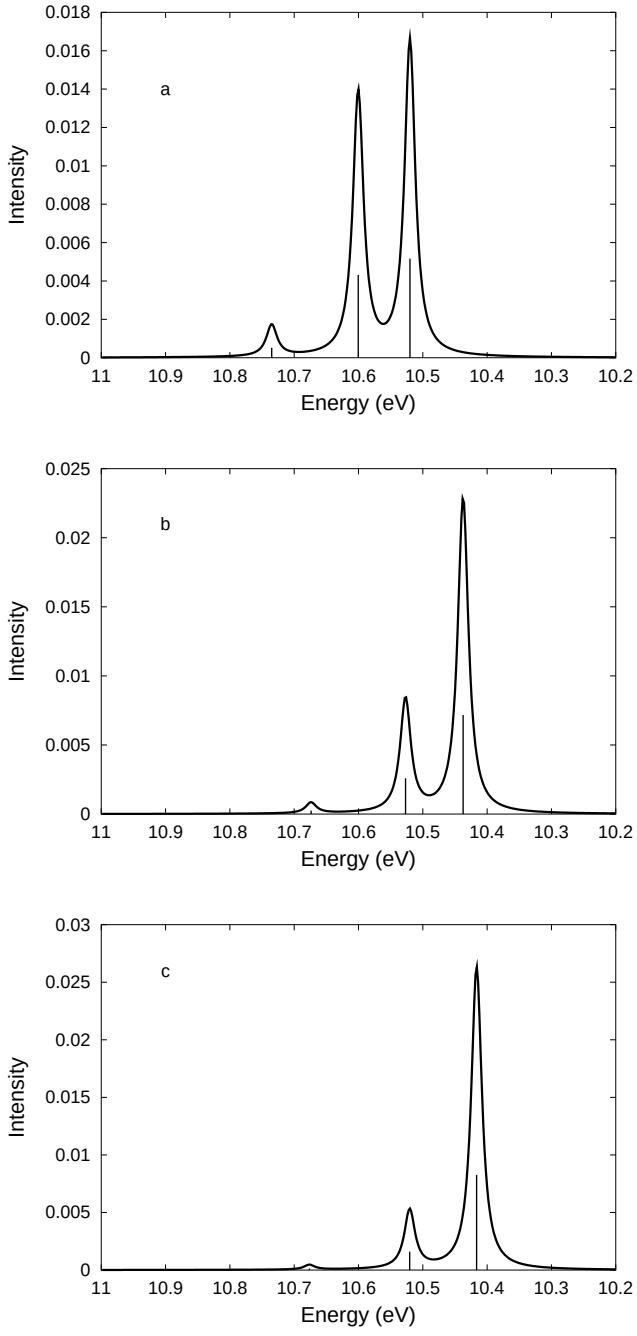

a
Intensity
Energy (eV)
b
Intensity
Energy (eV)
c
Intensity
Energy (eV)

Figure 4:

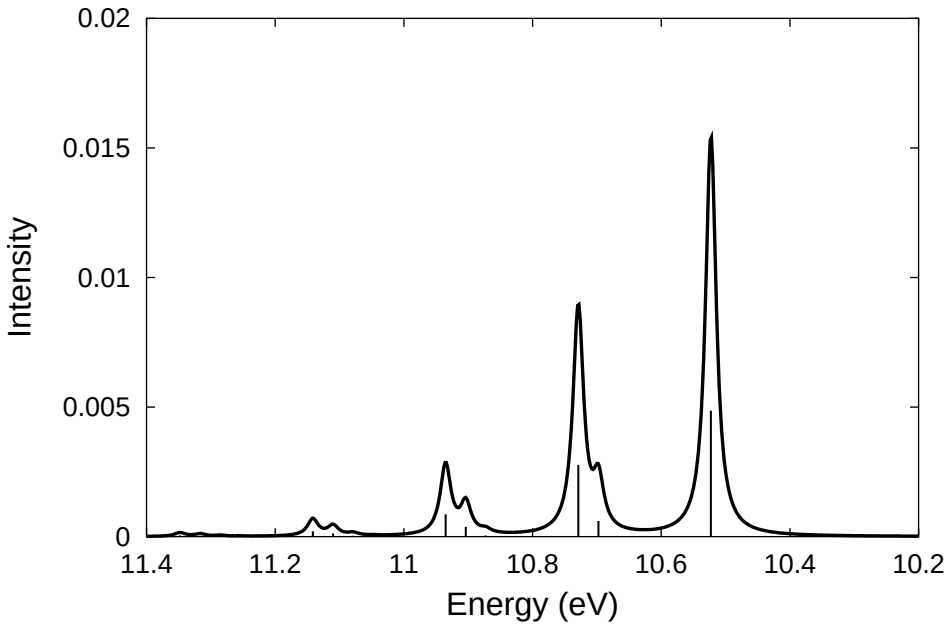

0.02
0.015
0.01
0.005
0
Intensity
11.4
11.2
11
10.8
10.6
10.4
10.2
Energy (eV)

Figure 5:

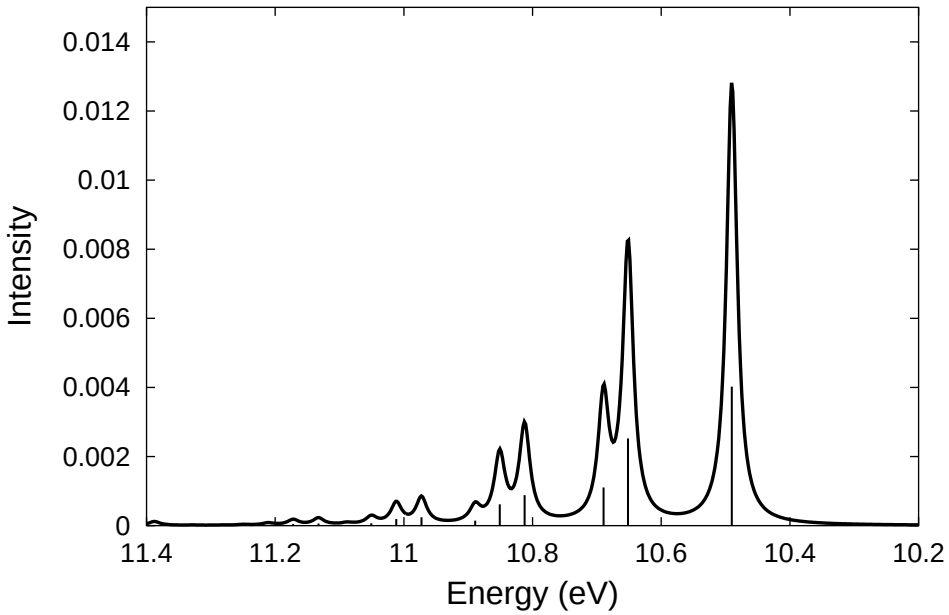

0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
Intensity
11.4
11.2
11
10.8
10.6
10.4
10.2
Energy (eV)

Figure 6:

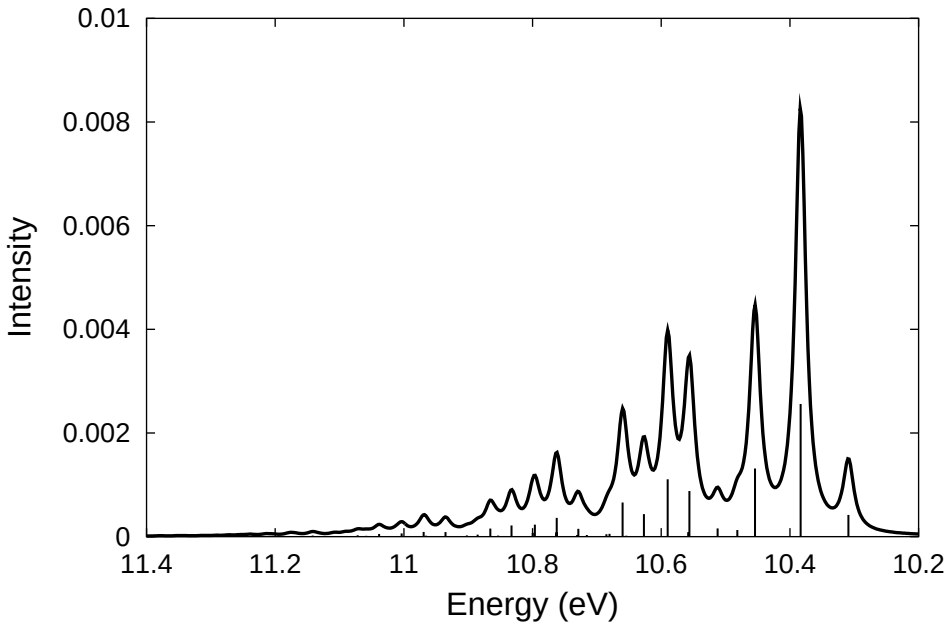
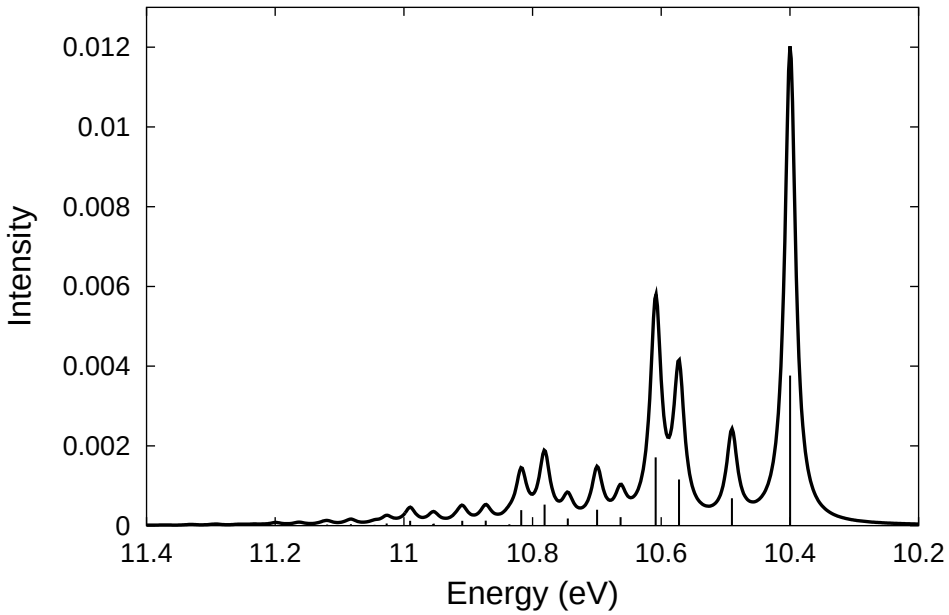

0.01
0.008
0.006
0.004
0.002
0
Intensity
11.4
11.2
11
10.8
10.6
10.4
10.2
Energy (eV)

Figure 7:


0.012
0.01
0.008
0.006
0.004
0.002
0
Intensity
11.4
11.2
11
10.8
10.6
10.4
10.2
Energy (eV)