Electronic Supplementary Information to Anharmonic Vibrational Spectra from Double Incremental Potential Energy and Dipole Surfaces

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Convergence of the spectra and surface-originated errors with chain length

As mentioned in the main text, one important technical parameter in band-Lanczos driven damped response calculations of spectra is the so-called chain length. It determines the dimension of the included vibrational space and thereby affects the quality of the resulting spectra. The exact convergence with chain length can of course differ for different PES representations. Table S-I shows the ΔS values for the spectra with the largest and second largest applied chain length for all molecules and surface representations. They are labelled by ΔS_{b-X}^{a-X} , where a and b are the chain lengths, X specifies the chosen surface representation and "b-X" labels the surfaces used for the reference spectrum. Additionally, the ΔS values for the different fragmented surface representations with respect to the non-fragmented (2M) ones are listed for both chain lengths individually.

For the two small molecules, we observe ΔS values for the different chain lengths that are all below 0.004. The obtained ΔS values for the spectra from the different DIF and DIFACT schemes with respect to those using the non-fragmented 2M PES and dipole surfaces are about two orders of magnitude larger. In these cases, the ΔS values can be assumed to be dominated by the differences in the chosen surface representation.

For the oligo-phenyl examples, however, the ΔS values for different the chain lengths are of the same order as the ones for the different property surfaces. This holds particularly true for the spectra with high fragmentation level. In these cases, the error in the spectrum caused by the DIF and DIFACT approximations cannot clearly be distinguished from the error due to a reduced chain length. This complicates the convergence considerations for the spectrum with respect to fragmentation level. Still, in particular for the tetra-phenyl, the DIF and DIFACT errors are rather stable for the different chain lengths, so that these can be used as indicators for the convergence of the fragmented schemes. Finally, we note that the errors for the spectra of oligo-phenyls due to the chain lengths and the fragmented surface generation are clearly below what can be expected from other error sources.

Molecule	a	b	Х	ΔS_{b-X}^{a-X}	ΔS_{a-2M}^{a-X}	ΔS_{b-2M}^{b-X}
Tetra-phenyl	2500	3000	2M (HF-3c)	0.0225		
			DIF-2M2F (HF-3c)	0.0212	0.0669	0.0634
			DIFACT-2M2F (HF-3c)	0.0159	0.0672	0.0656
			DIF-2M3F (HF-3c)	0.0220	0.0335	0.0300
			DIFACT-2M3F (HF-3c)	0.0161	0.0463	0.0523
Hexa-phenyl	2000	2200	2M (HF-3c)	0.0493		
			DIF-2M2F (HF-3c)	0.0280	0.1234	0.1053
			DIFACT-2M2F (HF-3c)	0.0622	0.1004	0.1110
			DIF-2M3F (HF-3c)	0.0641	0.0598	0.0559
			DIFACT-2M3F (HF-3c)	0.0508	0.0366	0.0596
			DIF-2M4F (HF-3c)	0.0560	0.0184	0.0293
			DIFACT-2M4F (HF-3c)	0.0559	0.0182	0.0371
5-methylfurfural	2500	3000	2M (RI-MP2/cc-pVTZ)	0.0033		
			DIF-2M (RI-MP2/cc-pVTZ)	0.0030	0.1578	0.1574
			DIFACT-2M (RI-MP2/cc-pVTZ)	0.0023	0.1632	0.1627
Dicyclopropyl ketone	2500	3000	2M (RI-MP2/cc-pVTZ)	0.0013		
			DIF-2M (RI-MP2/cc-pVTZ)	0.0020	0.6874	0.6874
			DIFACT-2M (RI-MP2/cc-pVTZ)	0.0017	0.6848	0.6848

TABLE S-I: ΔS values for spectra calculated with different chain lengths (a and b) and property surface representations (X) for all molecules considered in this study for VCC[2].

Supplementary information for 5-methylfurfural and dicyclopropyl ketone

TABLE S-II: Types of FALCON coordinates for 5-methylfurfural for the fragmentation A: aldehyde, B: furan ring, C: methyl: INTRA denotes internal coordinates within one of the fragments and IC labels inter-connecting modes. The latter are further classified using the nomenclature explained in the main text. The quasi-harmonic frequencies (ω), which are given for each FALCON mode, are obtained from the respective diagonal element of the Hessian matrix (RI-MP2/cc-pVTZ) in these FALCON coordinates.

Mode nr.	ω / cm ⁻¹	IC/INTRA	IC type
1	118.89	IC	$(AB) \leftrightarrow (C)$
2	208.23	IC	$(AB) \leftrightarrow (C)$
3	228.33	\mathbf{IC}	$(A) \leftrightarrow (B) \leftrightarrow [C]$
4	273.85	IC	$(A) \leftrightarrow (B) \leftrightarrow [C]$
5	286.49	IC	$(A) \leftrightarrow (B) \leftrightarrow [C]$
6	301.08	\mathbf{IC}	$(AB) \leftrightarrow (C)$
7	611.59	IC	$(A) \leftrightarrow (B) \leftrightarrow [C]$
8	644.80	INTRA	
9	701.14	INTRA	
10	818.91	INTRA	
11	839.73	IC	$(AB) \leftrightarrow (C)$
12	881.83	INTRA	
13	932.45	IC	$(A) \leftrightarrow (B) \leftrightarrow [C]$
14	945.08	INTRA	
15	957.65	INTRA	
16	1003.05	IC	$(A) \leftrightarrow (B) \leftrightarrow [C]$
17	1042.03	INTRA	
18	1047.25	IC	$(AB) \leftrightarrow (C)$
19	1065.82	IC	$(AB) \leftrightarrow (C)$
20	1184.54	INTRA	
21	1260.91	INTRA	
22	1279.39	INTRA	
23	1392.65	INTRA	
24	1406.09	INTRA	
25	1414.66	INTRA	
26	1471.58	INTRA	
27	1486.98	INTRA	
28	1517.18	INTRA	
29	1589.39	INTRA	
30	1730.78	INTRA	
31	2984.81	INTRA	
32	3079.49	INTRA	
33	3155.93	INTRA	
34	3188.29	INTRA	
35	3289.47	INTRA	
36	3304.42	INTRA	

TABLE S-III: Types of FALCON coordinates for dicyclopropyl ketone for the fragmentation A,C: cyclopropyl, B: C=O. INTRA denotes internal coordinates within one of the fragments and IC labels inter-connecting modes. The latter are further classified using the nomenclature explained in the main text. The quasi-harmonic frequencies (ω), which are given for each FALCON mode, are obtained from the respective diagonal element of the Hessian matrix (RI-MP2/cc-pVTZ) in these FALCON coordinates.

Mode nr	$m \omega / cm^{-1}$	IC/INTRA	IC type
1	51.96	IC	$(A) \leftrightarrow (B) \leftrightarrow (C)$
2	74.47	IC	$(A) \leftrightarrow (B) \leftrightarrow (C)$
3	196.46	IC	$(A) \leftrightarrow (B) \leftrightarrow (C)$
4	261.23	IC	$(A) \leftrightarrow (B) \leftrightarrow (C)$
5	305.29	IC	$(A) \leftrightarrow (B) \leftrightarrow (C)$
6	318.98	IC	$(A) \leftrightarrow (B) \leftrightarrow (C)$
7	391.43	IC	$(A) \leftrightarrow (B) \leftrightarrow (C)$
8	713.30	IC	$(A) \leftrightarrow (B) \leftrightarrow (C)$
9	800.22	INTRA	
10	800.23	INTRA	
11	806.87	IC	$(A) \leftrightarrow (B) \leftrightarrow (C)$
12	842.22	INTRA	
13	842.23	INTRA	
14	882.91	INTRA	
15	882.91	INTRA	
16	930.94	INTRA	
17	930.95	INTRA	
18	935.23	IC	$(A) \leftrightarrow (B) \leftrightarrow (C)$
19	1050.26	INTRA	
20	1050.27	INTRA	
21	1070.90	INTRA	
22	1070.93	INTRA	
23	1087.81	INTRA	
24	1087.85	INTRA	
25	1125.80	INTRA	
26	1125.80	INTRA	
27	1196.80	IC	$(A) \leftrightarrow (B) \leftrightarrow (C)$
28	1218.02	INTRA	
29	1218.03	INTRA	
30	1234.25	INTRA	
31	1234.26	INTRA	
32	1369.94	INTRA	
33	1369.97	INTRA	
34	1464.02	INTRA	
35	1464.03	INTRA	
36	1501.62	INTRA	
37	1501.63	INTRA	
38	1714.06	INTRA	
39	3186.32	INTRA	
40	3186.32	INTRA	
41	3188.86	INTRA	
42	3188.87	INTRA	
43	3236.60	INTRA	
44	3236.62	IN TKA	
45 46	3286.90	INTRA INTED A	
40 47	3∠00.93 2000 ⊑2	IN 1 KA INTD A	
41 18	3299.33 300 55	IN I KA INTD A	
40	ə∠99.əə	INIKA	

TABLE S-IV: Zero-point energies (ZPEs), root mean square deviations and maximum absolute deviations of the difference in VSCF state energies for fundamental states from the ZPE (Δ E) for 5-methylfurfural for different 2F2M HF-3c PES calculations. The deviations for inter-connecting (IC) modes and intra-fragment (INTRA) modes are given combined and separately. All energies are given in cm⁻¹.

	2M	DIF-2F2M	DIFACT-2F2M		
ZPE	26937.40	26945.14	26940.85		
Δ ZPE to					
2M		7.74	3.45		
DIF-2F2M			-4.29		
Root mean square deviation	on of ΔE	to			
2M		2.49	5.46		
2M only IC		1.79	8.61		
2M only INTRA		2.77	2.76		
DIF-2F2M			4.45		
DIF-2F2M only IC			7.65		
DIF-2F2M only INTRA			0.63		
Maximum absolute deviation of ΔE from					
2M only IC		4.05	24.10		
2M only INTRA		7.32	7.40		
DIF-2F2M only IC			22.75		
DIF-2F2M only INTRA			2.16		

TABLE S-V: Zero-point energies (ZPEs), root mean square deviations and maximum absolute deviations of the difference in VSCF state energies for fundamental states from the ZPE (Δ E) for 5-methylfurfural for different 2F3M HF-3c PES calculations. The deviations for inter-connecting (IC) modes and intra-fragment (INTRA) modes are given combined and separately. All energies are given in cm⁻¹.

	3M	DIF-2F3M	DIFACT-2F3M		
ZPE	26947.81	26955.66	26953.91		
Δ ZPE to					
3M		7.85	6.10		
DIF-2F3M			-1.75		
Root mean square deviation	on of ΔE	to			
3M		2.45	4.21		
3M only IC		1.73	6.31		
3M only INTRA		2.74	2.60		
DIF-2F3M			3.21		
DIF-2F3M only IC			5.53		
DIF-2F3M only INTRA			0.45		
Maximum absolute deviation of ΔE from					
3M only IC		3.75	18.84		
3M only INTRA		7.29	7.25		
DIF-2F3M only IC			17.61		
DIF-2F3M only INTRA			1.90		

TABLE S-VI: Zero-point energies (ZPEs), root mean square deviations and maximum absolute deviations of the difference in VSCF state energies for fundamental states from the ZPE (Δ E) for 5-methylfurfural for different 2F2M RI-MP2/cc-pVTZ PES calculations. The deviations for inter-connecting (IC) modes and intra-fragment (INTRA) modes are given combined and separately. All energies are given in cm⁻¹.

	2M	DIF-2F2M	DIFACT-2F2M			
ZPE	23706.25	23693.53	23690.06			
Δ ZPE to						
2M		-12.73	-16.20			
DIF-2F2M			-3.47			
Root mean square deviation	on of ΔE	to				
2M		2.51	4.06			
2M only IC		2.47	5.75			
2M only INTRA		2.53	2.86			
DIF-2F2M			2.16			
DIF-2F2M only IC			3.61			
DIF-2F2M only INTRA			0.69			
Maximum absolute deviation of ΔE from						
2M only IC		5.01	13.05			
2M only INTRA		6.73	7.47			
DIF-2F2M only IC			9.62			
DIF-2F2M only INTRA			2.05			