

Electronic Supplementary Information for PCCP

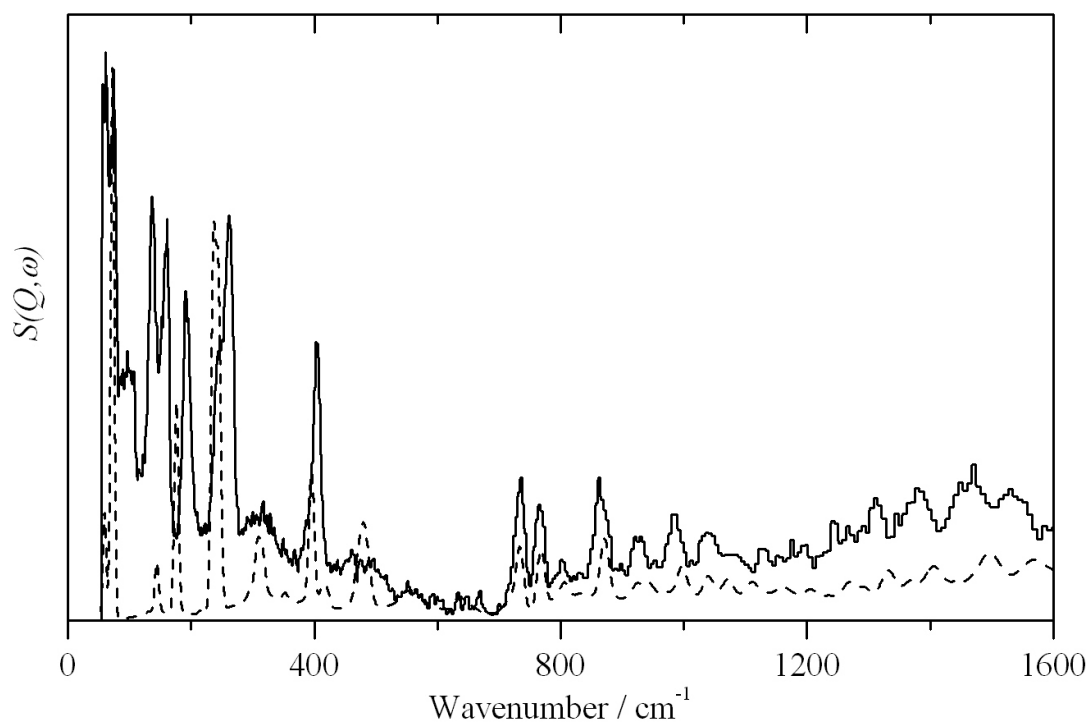


Figure S1. Comparison of the inelastic neutron scattering spectrum of pentane (solid line) with that calculated by DFT (B3LYP/6-31G*(d,p)) (dashed line).

Tables.

Table S1: Comparison of observed and calculated positions and intensities of *cis*-1,3-pentadiene

Observed			DFT			Assignment
Position / cm ⁻¹	Infrared intensity	Raman intensity	Position / cm ⁻¹	Infrared intensity / km mol ⁻¹	Raman intensity / Å ⁴ amu ⁻¹	
A'' modes						
			118	0.9	0.4	Methyl torsion
140		vw	144	0.1	2.0	=C-C= torsion
353	vw	vw	361	0.5	2.1	Out-of-plane skeletal deformation
621	s	w	643	32.5	1.7	<i>cis</i> -CH=CH wag
777	s	w	802	7.4	1.3	<i>cis</i> -CH=CH wag
905	vs	w	933	54.6	8.1	CH ₂ wag
			992	1.1	4.5	=CH out-of-plane deformation
997	s		1038	15.8	0.1	=CH out-of-plane deformation
1035	w	w	1059	1.7	3.9	Methyl rock
1452	w	m	1482	7.7	6.9	Asymmetric methyl deformation
2949	w	vw	3052	18.3	126.1	Methyl C-H stretch
A' modes						
214	vw	vw	217	1.7	0.2	In-plane skeletal deformation d
385	m	m	390	4.3	7.8	In-plane skeletal deformation
612		w	618	5.0	4.1	In-plane skeletal deformation
884	w	m	891	4.0	3.3	=CH ₂ rock

954	w		964	12.6	1.5	C-CH ₃ stretch
1127	w	w	1063	0.1	1.9	Methyl rock
1166	w	m	1188	1.5	18.3	=CH-CH= stretch
1251	w	s	1289	2.4	91.9	-CH= bend
1297	w	s	1323	0.8	33.0	-CH= bend
1358	w	w	1394	1.9	3.0	=CH-CH= stretch
1390	m	m	1417	3.3	25.9	Symmetric methyl deformation
1437	m	w	1469	15.8	6.8	=CH ₂ scissors
			1491	8.6	67.1	Asymmetric methyl deformation
1603	s	m	1651	6.3	18.0	C=C asymmetric stretch
1655	m	vs	1705	13.6	468.3	C=C symmetric stretch
2928	m	m	3015	29.6	290.3	Symmetric methyl C-H stretch
2970	vw	w	3107	5.7	60.7	Asymmetric methyl C-H stretch
2990		w	3124	4.6	38.6	Symmetric =C-H stretch
3010		s	3130	8.4	67.5	Symmetric =CH ₂ stretch
3033	s		3143	16.7	224.8	Symmetric -CH= stretch
3068	w		3152	28.1	19.8	Asymmetric -CH= stretch
3097	m	m	3219	15.0	89.6	Asymmetric =CH ₂ stretch

Table S2: Comparison of observed and calculated positions and intensities of *trans*-1,3-pentadiene

Observed			DFT			Assignment
Position / cm^{-1}	Infrared intensity	Raman intensity	Position / cm^{-1}	Infrared intensity / km mol^{-1}	Raman intensity / $\text{\AA}^4 \text{amu}^{-1}$	
A'' modes						
150		vw	136	1.6	0.4	Out-of-plane skeletal deformation
205	vw	w	208	0.2	0.8	Methyl torsion
250	m	w	259	2.2	0.2	Out-of-plane skeletal deformation
698	w		647	3.4	0.1	Out-of-plane skeletal deformation
			847	8.0	7.0	=CH out-of-plane deformation
899	s	w	926	41.7	11.0	CH ₂ wag
948	m	vvw	978	15.6	0.5	=CH out-of-plane deformation
1003	vs		1041	47.8	1.2	=CH out-of-plane deformation
1043	vw	w	1063	0.5	3.1	Methyl rock
1435	w	vw	1478	8.3	8.5	Asymmetric methyl deformation
2946	w	w	3050	19.5	137.3	Methyl C-H stretch
A' modes						
383	vw	vw	198	1.8	1.0	In-plane skeletal deformation
454	w	vw	454	0.5	1.2	In-plane skeletal deformation

483	vw	s	483	0.1	13.4	In-plane skeletal deformation
630	w		908	7.1	1.2	=CH ₂ rock
977	w	vw	990	10.8	1.1	
1082		w	1097	0.1	0.6	C-CH ₃ stretch
1170		w	1207	1.7	77.0	=CH-CH= stretch
1180		m	1298	1.6	0.2	-CH= bend
1280	w	s	1318	1.0	87.1	-CH= bend
1306	m		1335	3.1	0.8	-CH= bend
1376	m	w	1412	2.8	38.9	Symmetric methyl deformation
1420	m	w	1451	5.0	17.3	=CH ₂ scissors
1449	m	w	1491	11.3	56.3	Asymmetric methyl deformation
1608	m		1660	10.0	43.7	C=C asymmetric stretch
1660	m	vs	1711	21.3	521.1	C=C symmetric stretch
2931	m	w	3009	36.4	356.1	Symmetric methyl C-H stretch
2973	m	vw	3091	10.1	95.1	Asymmetric methyl C-H stretch
2980	w		3116	1.5	137.9	Symmetric =C-H stretch
2997		s	3121	9.8	13.4	Symmetric =CH ₂ stretch
3018	s	vw	3130	47.8	10.6	Symmetric -CH= stretch
3050	w		3134	5.9	156.8	Asymmetric -CH= stretch
3098	m	w	3219	14.3	93.3	Asymmetric =CH ₂ stretch

