Appendix A

A.1. Main IR peaks (in cm^{-1}) for CH_3CCD and CD_3CCH on Pt(111): 2x2 unit cell

vibrational	CH_3CCD		vibrational	CD_3CCH	
mode	ω_i	I_i[a]	mode	ω_i	I_i[a]
CD st	2246	0.6	CH st	3048	1.2
CH_3 as st	3028	0.7	CD_3 as st	2241	0.5
CH_3 as-s st	3011	2.1	CD_3 as-s st	2228	1.1
CH_3 s st	2943	7.2	CD_3 s st	2113	2.8
CH_3 as-s df + C^1–C^2 st	1432	0.7	C^1–C^2 st	1361	0.8
CH_3 as df	1407	2.0	CD_3 as df	1011	1.3
C^1-C^2 st – CH_3 as-s df	1346	0.1	CD_3 as-s df	1023	0.0
CH_3 s df	1330	1.6	CD_3 s df[b]	1066	1.4

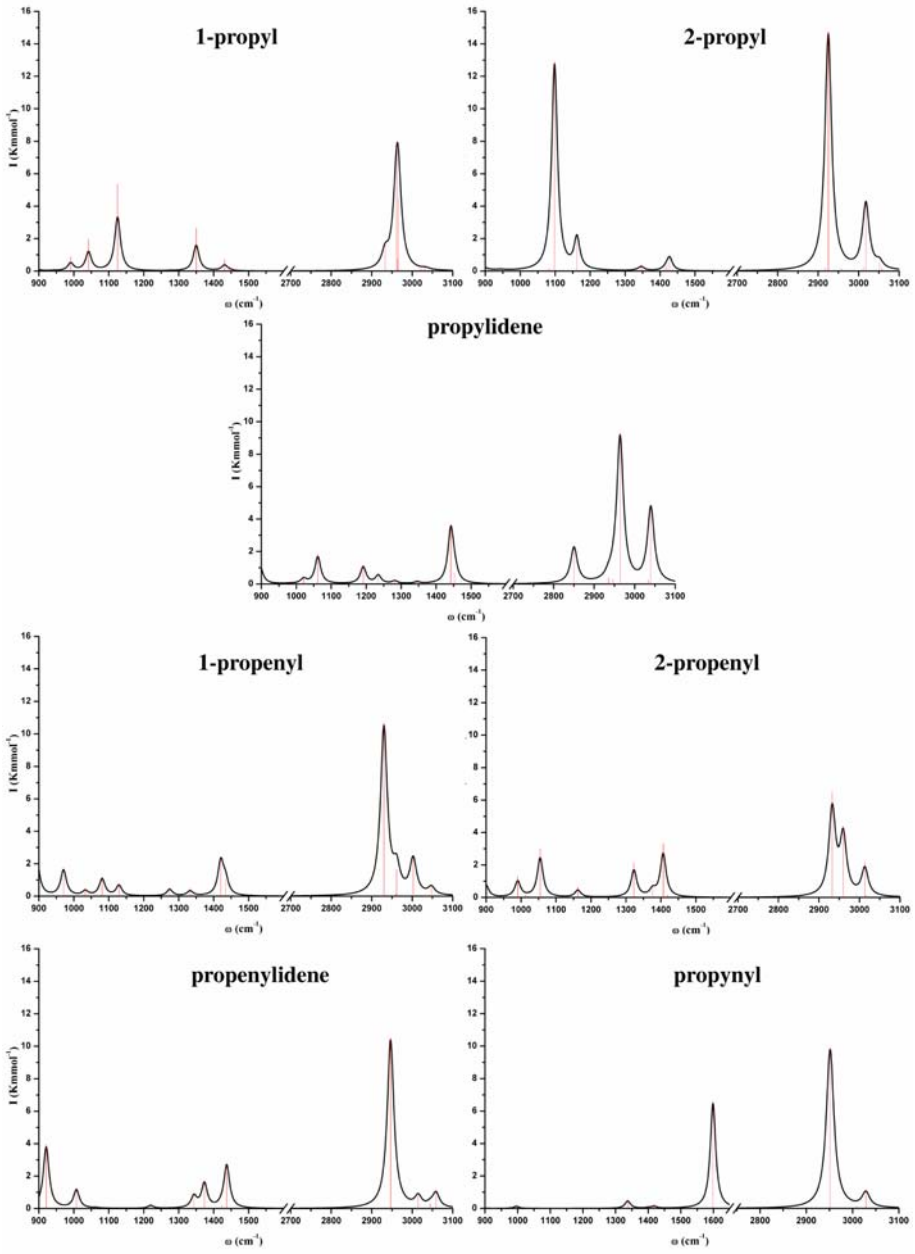
Key: as, asymmetric; s, symmetric; st, stretching; df, deformation; ro, rocking; b, bending.
[a]Intensities in $Kmmol^{-1}$. [b]tnis mode mixes with the CH bi and C^2–C^3 st modes.

A.2. Main IR peaks (in cm^{-1}) for CH_3CCD and CD_3CCH on Pd(111): 2x2 unit cell

vibrational	CH_3CCD		vibrational	CD_3CCH	
mode	ω_i	I_i[a]	mode	ω_i	I_i[a]
CD st	2246	0.3	CH st	3045	0.7
CH_3 as st	3016	0.7	CD_3 as st	2231	0.4
CH_3 as-s st	3004	2.7	CD_3 as-s st	2223	1.5
CH_3 s st	2935	9.1	CD_3 s st	2106	3.7
CH_3 as-s df + C^1–C^2 st	1436	0.7	C^1–C^2 st	1410	0.1
CH_3 as df	1403	1.0	CD_3 as df	1010	1.2
C^1-C^2 st – CH_3 as-s df	1385	0.4	CD_3 as-s df	1025	0.1
CH_3 s df	1327	0.8	CD_3 s df	1061	1.3

Key: as, asymmetric; s, symmetric; st, stretching; df, deformation; ro, rocking; b, bending.
[a]Intensities in $Kmmol^{-1}$.

A.3. Simulated vibrational spectra for the possible C_3H_x (x= 3–7) intermediates on Pt(111): 2x2 unit cell



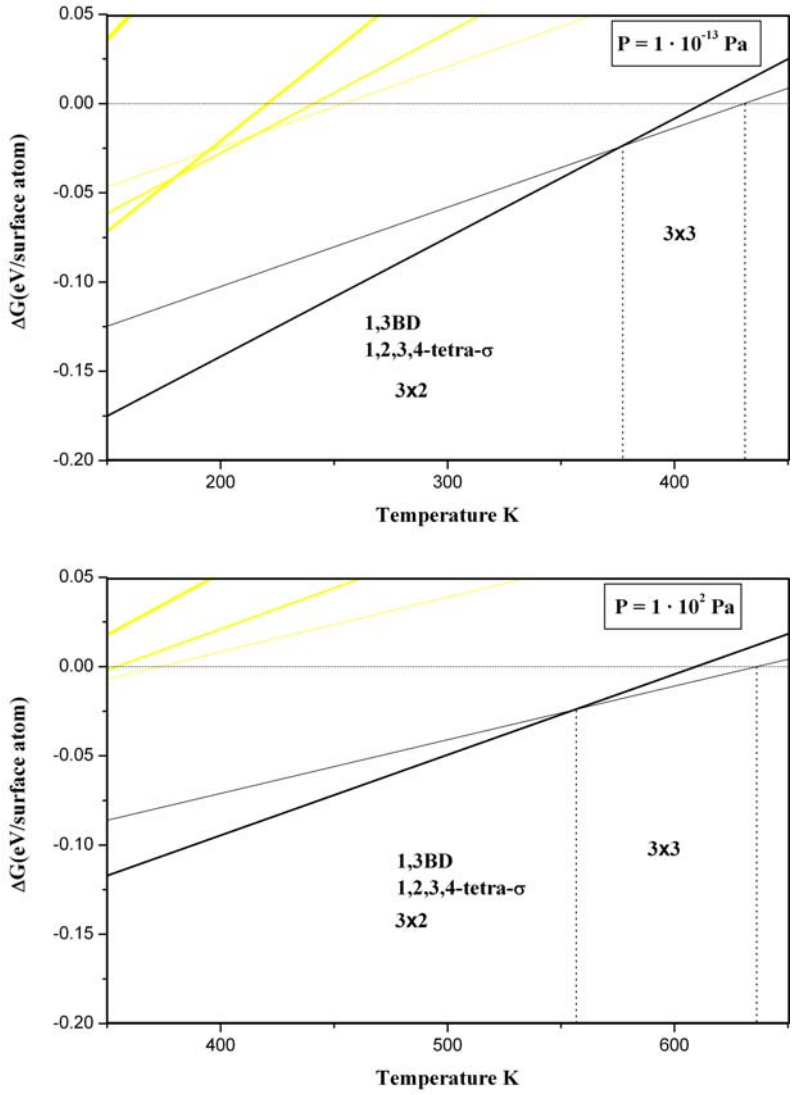
A.4 Vibrational frequencies (in cm^{-1}) for the gas phase 1,3-butadiene molecule

Exp.[a]	Computed	Assignment
3100	3217	CH_2 as st
3100	3179	CH_2 as st
3055	3122	CH st
3013	3049	CH_2 s st
3010	3035	CH_2 s st
3013	3007	CH st
1644	1647	C=C s st
1597	1600	C=C as st
1441	1428	CH_2 s sci
1381	1372	CH_2 as sci
1291	1286	CH bi
1295	1272	CH bi
1203	1196	C-C st
1014	1029	CH bo
965	970	CH bo
990	968	CH_2 as ro
908	905	CH_2 as wag
908	901	CH_2 s wag
888	877	CH_2 s ro
752	762	CH_2 as twi
525	535	CH_2 s twi
512	502	C=C-C bi
291	270	C=C-C bo
163	184	C-C to

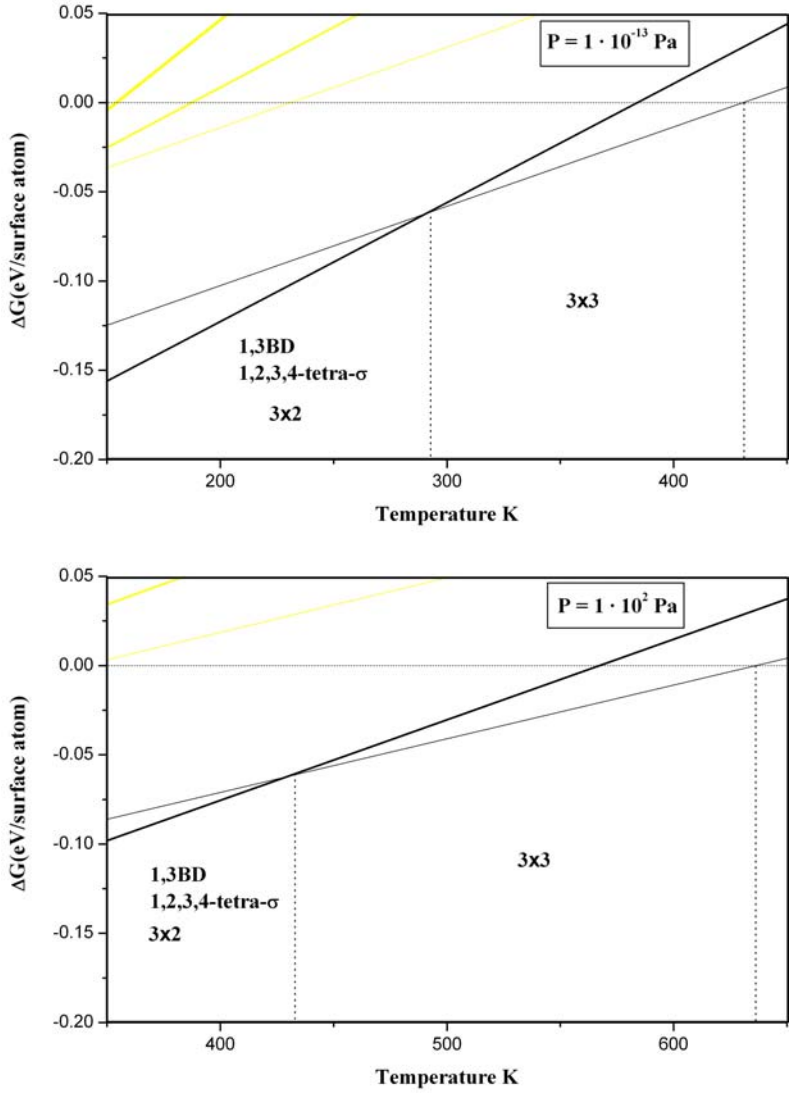
Key: as, asymmetric; s, symmetric; st, stretching; sci, scissoring; bi, bending in plane; bo, bending out of plane; ro, rocking; wag, wagging; twi, twisting.
[a] values from G.R. De Maré *et al. J. Chys. Chem* A 148 (1988) 13.

A.5. Temperature-pressure phase diagrams for 1,3 butadiene and 1-butene on Pt(111) and Pd(1111)

A.5.1. Pt(111)



A.5.2. Pd(111)



1,3BD (1,3-buradiene, black) and 1B (1-butene, yellow) on Pt(111) (A.5.1) and Pd(111) (A.5.2). Here, we depicted only the most stable adsorption modes (1,2,3,4-tetra-σ for 13BD and di-σ for 1B). The thicker the line the higher the coverage.

A.6. Co-adsorption of hydrogen and C_4H_x species (x= 6,7) on Pt(111) and Pd(111)

species	H position[a]	ΔE(kJmol^{-1})[b]
	Pt(111)	
13BD	1	30
	2	16
	3	32
	4	17
1B4R	1	11
	2	24
	3	26
2B1R	1	21
	2	8
	3	20
	Pd(111)	
13BD	1	25
	2	18
	3	54
	4	17
1B4R	1	11
	2	29
	3	22
2B1R	1	19
	2	30
	3	17

[a] H position from Figure 5.9 (Chapter 5). [b]Energy difference between the co-adsorbed system (C_4H_x and H adsorbed on the same unit cell) and the two species at infinite distance. On co-adsorption the system is destabilised.