Infrared Spectroscopy Characterization of the Chemistry of C_4 Hydrocarbons on Pt(111) Single-Crystal Surfaces

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Supporting Information

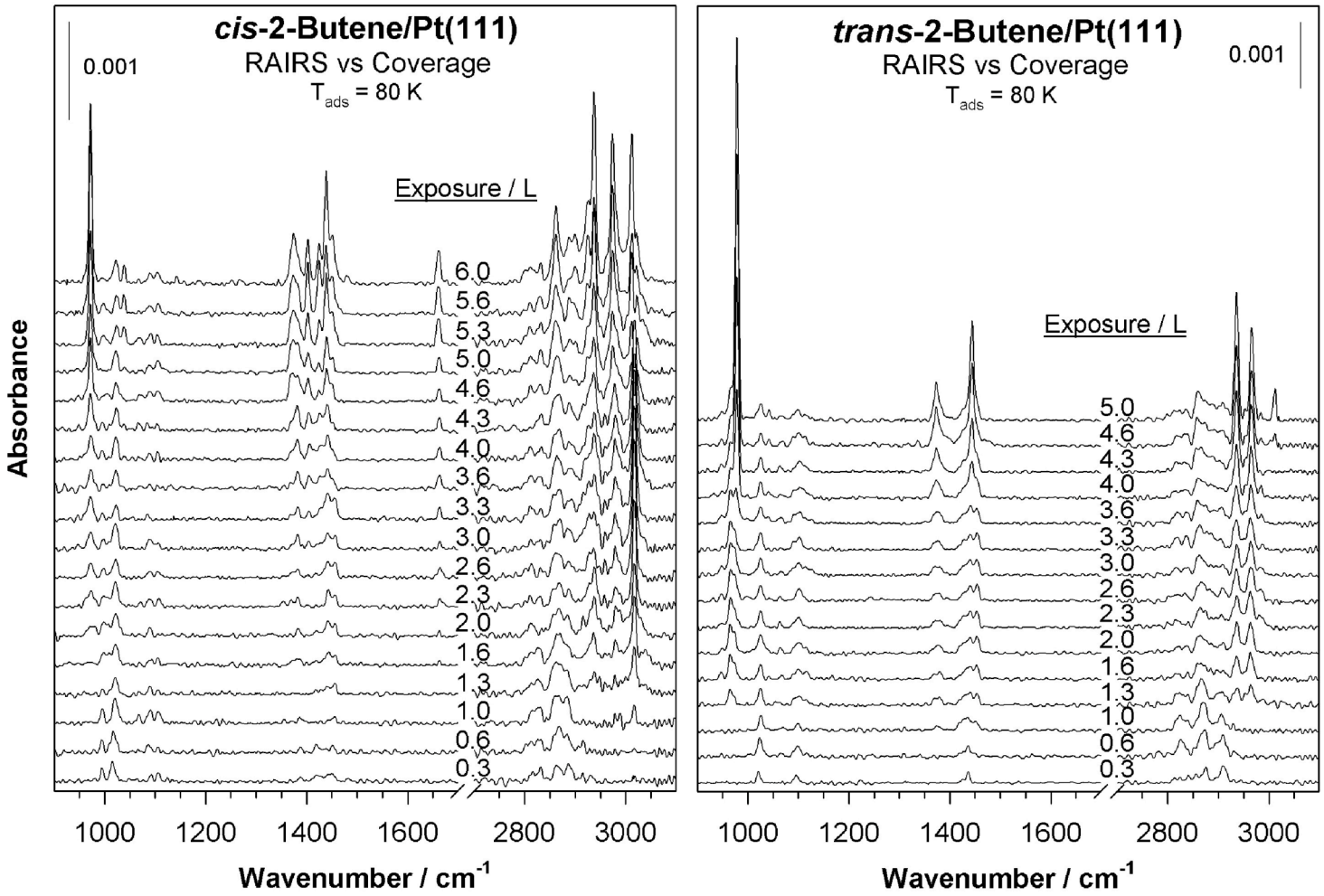

Figure 1. Reflection-absorption infrared spectroscopy (RAIRS) traces for the uptake of cis-2-butene (left) and trans-2-butene (right) on Pt(111) at 80 K. A clear change is seen in both cases at exposures around 1 L, signifying the transition from di-σ to π bonding commonly seen during the adsorption of alkenes on transition metals.

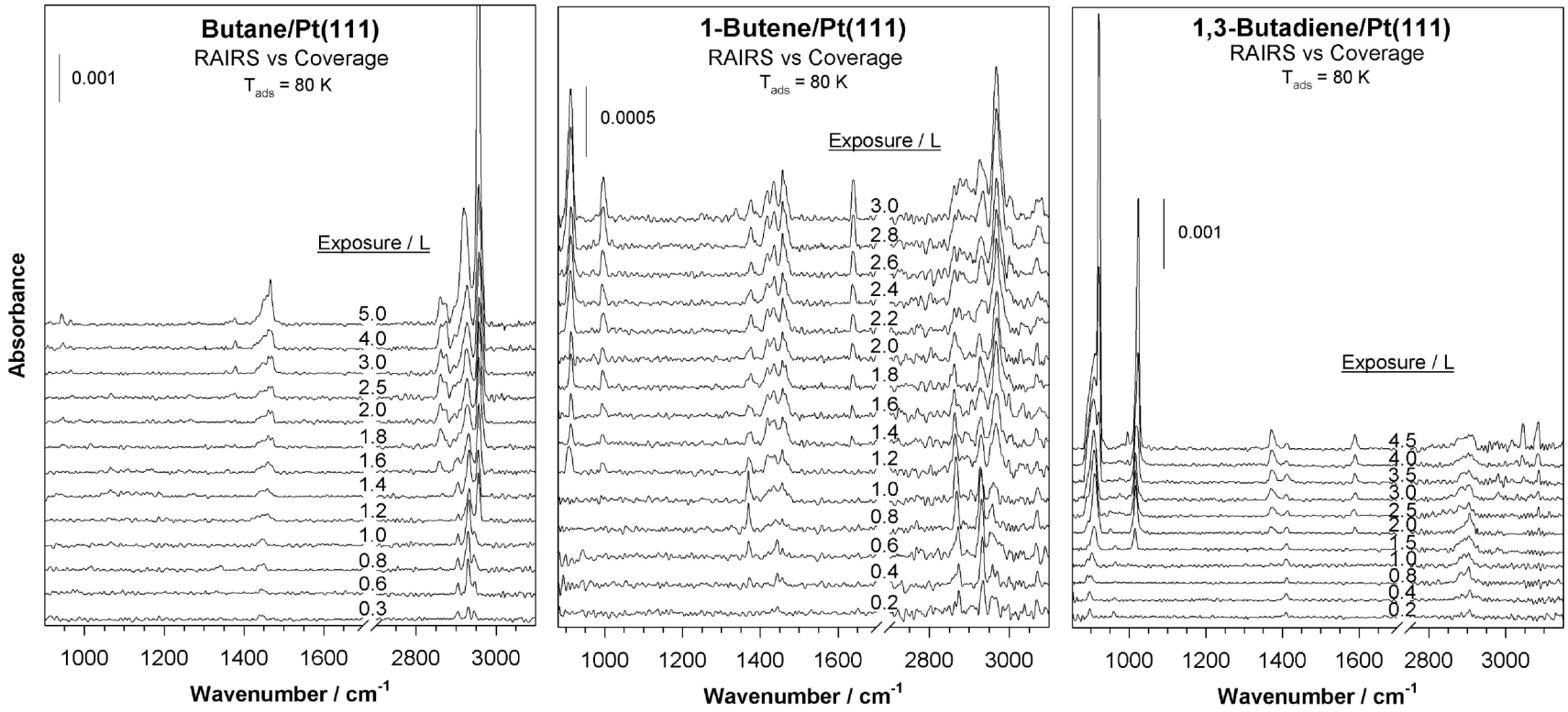

Figure 2. RAIRS traces for the uptake of butane (left), 1-butene (center), and 1,3-butadiene (right) on Pt(111) at 80 K. Definite adsorption geometries are identified in all these cases for the adsorbed monolayer by the relative intensities of the bands due to vibrational modes of different symmetries.

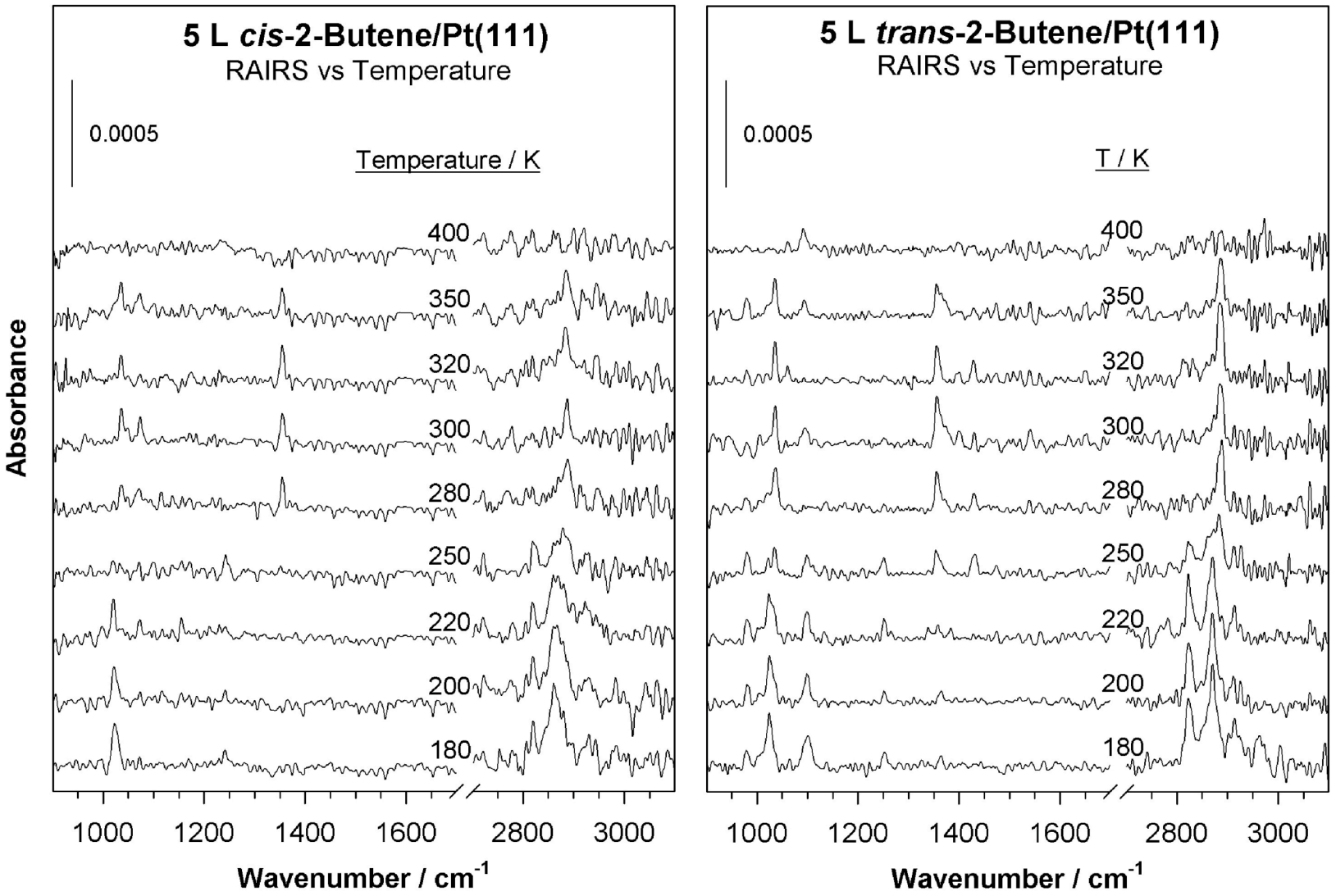

Figure 3. RAIRS traces from 5.0 L of cis-2-butene (left) and trans-2-butene (right) on Pt(111) as a function of annealing temperature.

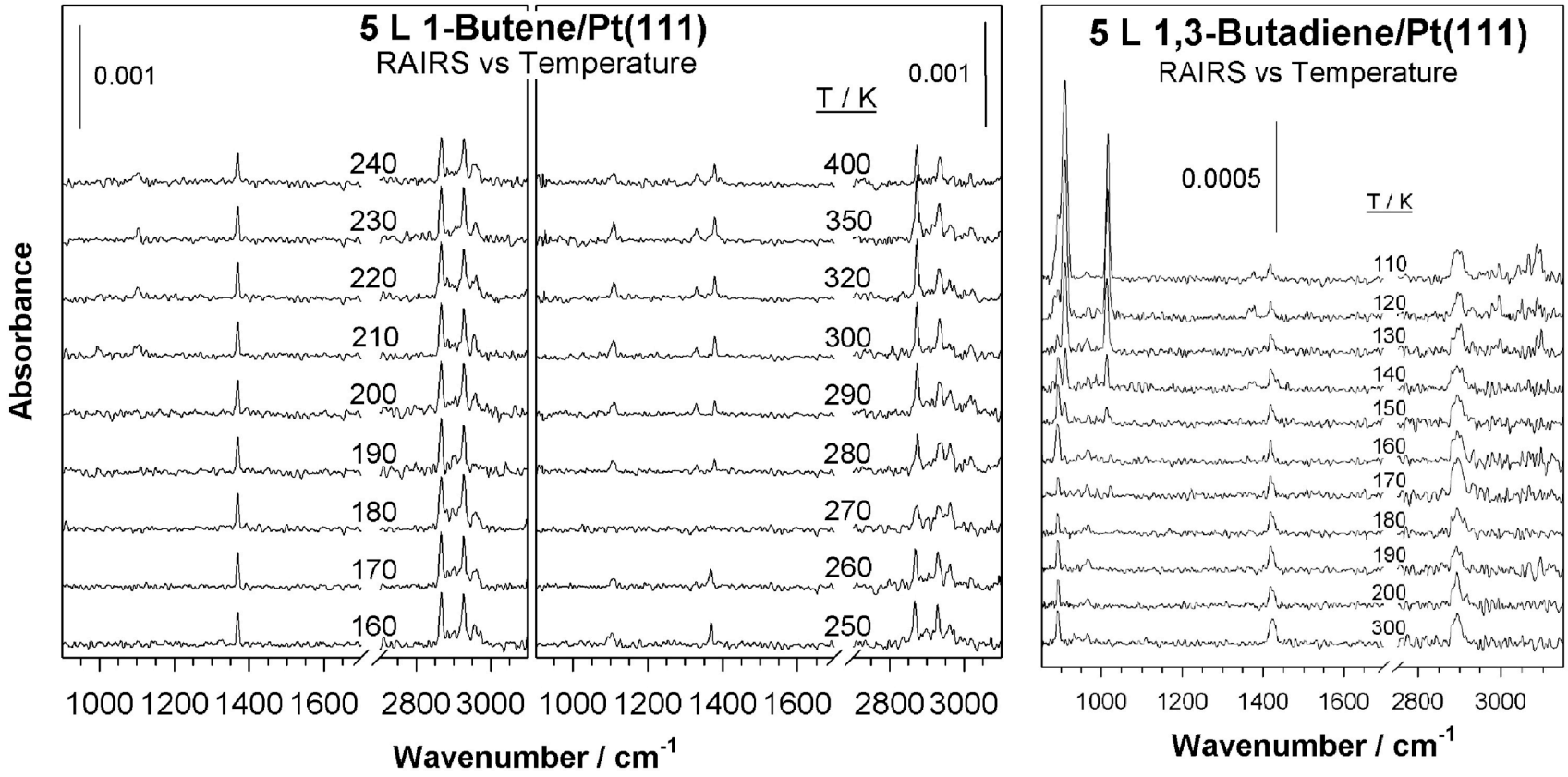

Figure 4. RAIRS traces from 5.0 L of 1-butene (left) and 1,3-butadiene on Pt(111) as a function of annealing temperature.

Table 1. Vibrational assignment of the features seen in the RAIRS spectra of cis-2-, trans-2-, and 1-butenes adsorbed on Pt(111) at 80 K. Two coverage regimes are reported, one for exposures below 1.0 L, which corresponds to di-σ bonding, and another at close to monolayer saturation, where π surface species form on the surface.[a]

	cis-2-Butene[1-4]		trans-2-Butene[1-5]		1-Butene[3,5,6]	
Mode[b]	Low Coverage	High Coverage	Low Coverage	High Coverage	Low Coverage	High Coverage
$\omega(=CH_2)_{oop}$						913 (vs)
$\omega(C–H)_{oop}$		972 (vs)		966 (sh), 976 (vs)		995 (m)
$\rho(CH_3)$	995 (m), 1016 (m)	1022 (w), 1039 (m)	1022 (m)	1026 (m), 1041 (w)		
$\nu(C–C)$	1093 (w), 1106 (w)	1090 (w), 1104 (w)	1097 (m)	1068 (w), 1099 (w)		
$\delta_s(CH_3)$	1372 (m)	1374 (s)		1373 (m)	1369 (s)	1376 (m)
$\delta(C–H)_{ip}$	1405 (m), 1425 (w)	1403 (s), 1425 (w)				1418 (m)
$\gamma(=CH_2)$					1444 (m)	1436 (m)
$\delta_{as}(CH_3)$	1442 (m) 1454 (m)	1439 (vs), 1450 (s)	1436 (m)	1444 (s), 1453 (sh)	1457 (w)	1458 (s)
$\nu(C=C)$		1661 (s)				1639 (m)
$\nu_s(CH_3)$	2868 (m), 2884 (m)	2868 (s), 2888 (m)	2870 (m)	2859 (m)	2872 (s)	2874 (m)
$\nu_{as}(CH_2)_{et}$					2931 (s)	2930 (s)
$\nu_{as}(CH_3)$		2937 (vs), 2974 (vs)		2937 (vs), 2966 (vs)	2958 (m)	2967 (vs)
$\nu(=C–H)$	2910 (w)	2926 (sh)	2910 (m)		2958 (m)	2967 (vs)
$\nu(=C–H)$		3011 (vs), 3021 (sh)	3019 (m)	3012 (s)		
$\nu_{as}(=CH_2)$					3070 (m)	3070 (w)

Footnotes

[a] Frequencies in cm^{-1}. Relative intensities in parenthesis: w = weak, m = medium, s = strong, vs = very strong, sh = shoulder.

[b] ν = stretching, δ = deformation, γ = scissoring, ρ = rocking, ω = wagging; s = symmetric, as = asymmetric, ip = in plane, oop = out of plane, et = ethyl group.

References

(1) Manzanares I, C.; Blunt, V. M.; Peng, J. *J. Phys. Chem.* **1993**, *97*, 3994.

(2) McKean, D. C.; Mackenzie, M. W.; Morrisson, A. R.; Lavalley, J. C.; Janin, A.; Fawcett, V.; Edwards, H. G. M. *Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy* **1985**, *41A*, 435.

(3) Barnes, A. J.; Howells, J. D. R. *Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics* **1973**, *69*, 532.

(4) Avery, N. R.; Sheppard, N. *Proc. R. Soc. London A* **1986**, *405*, 27.

(5) Anson, C. E.; Sheppard, N.; Bender, B. R.; Norton, J. R. *J. Am. Chem. Soc.* **1999**, *121*, 529.

(6) Durig, J. R.; Compton, D. A. C. *J. Phys. Chem.* **1980**, *84*, 773.