Supporting Information

Fourier Transform Microwave Spectrum of Propene-3-d_1 (CH_2=$CHCH_2D$), Quadrupole Coupling Constants of Deuterium and a Semiexperimental Equilibrium Structure of Propene

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Appendix I. Median absolute deviation and iteratively reweighted least squares

To minimize the influence of outliers the median absolute deviation (MAD) is used to estimate the standard deviation

The definition of the MAD is

MAD = median$|r_i$ – median$(r_i)|$

where r_i are the residuals. The derived residual standard deviation, called in this case scale estimate, is

s = MAD/0.6745.

Then, the scaled residuals are calculated as $u_i = |r_i|/s$

and, the weights are calculated by applying the biweight function

$$w_i = \left[1 - \left(u_i/4.685\right)^2\right]^2 \quad \text{if } u_i \le 4.685$$

otherwise $w_i = 0$.

Appendix II. Kraitchman's equations

To calculate a Cartesian coordinate for a non-planar molecule, Kraitchman's equations are

$$|x| = \left[\frac{\Delta P_x}{\mu}\left(1 + \frac{\Delta P_y}{I_x - I_y}\right)\left(1 + \frac{\Delta P_z}{I_x - I_z}\right)\right]^{1/2}$$

where y and z are obtained by cyclic permutation and μ is the reduced mass defined as

$$\mu = \frac{M\Delta m}{M + \Delta m}$$

M is the total mass of the parent molecule, and Δm is the change of mass upon isotopic substitution. P_x is defined as $P_x = (I_y + I_z - I_z)/2$

In Kraitchman's equation for $|x|$, the leading term is ΔP_x. When it is small, the equation is ill-conditioned, and there is an amplification of errors.

The difficulty is to estimate the error on ΔP_x because it is known that, for the semiexperimental equilibrium rotational constants, the systematic errors, which are a few per cent of the rovibrational corrections, are much larger than the random errors.[39] However, it is possible to make a reasonable estimate using the standard deviations of least-squares fit. Using only the accurate rotational constants of set I, from the semiexperimental fit, we obtain (in MHz)

$s(A) \approx 0.2$; $s(B) \approx s(C) \approx 0.1$

Using $\left[s\left(P_g\right)\right]^2 = \left[s\left(I_a\right)^2 + s\left(I_b\right)^2 + s\left(I_c\right)^2\right] \Big/ 4$

it gives $s(\Delta P_g) \approx 0.00075$ uÅ^2 $\forall g$

and

$$s(g) \approx \frac{s(\Delta P_g)}{2\mu\sqrt{\Delta P_g}}$$

Application: b coordinate of the out-of-plane H atom

The accurate value (fit with predicates) is $b(H_a)$ = -0.1296(5) Å

The Kraitchman value is $b(H_a)$ = -0.1259 Å, i.e. a rather large difference of 0.0037 Å. If we now add 0.00075 to ΔP_b whose original value is 0.0159, we obtain $b(H_a)$ = -0.1288 Å, quite close to the correct value.

This treatment can be generalized to the other coordinates.

Figure S1a. Gas-phase IR spectrum of propene-3-d_1 from 4000-2000 cm^{-1} at 51 torr and 0.5 cm^{-1} resolution. Spectrometer not purged.

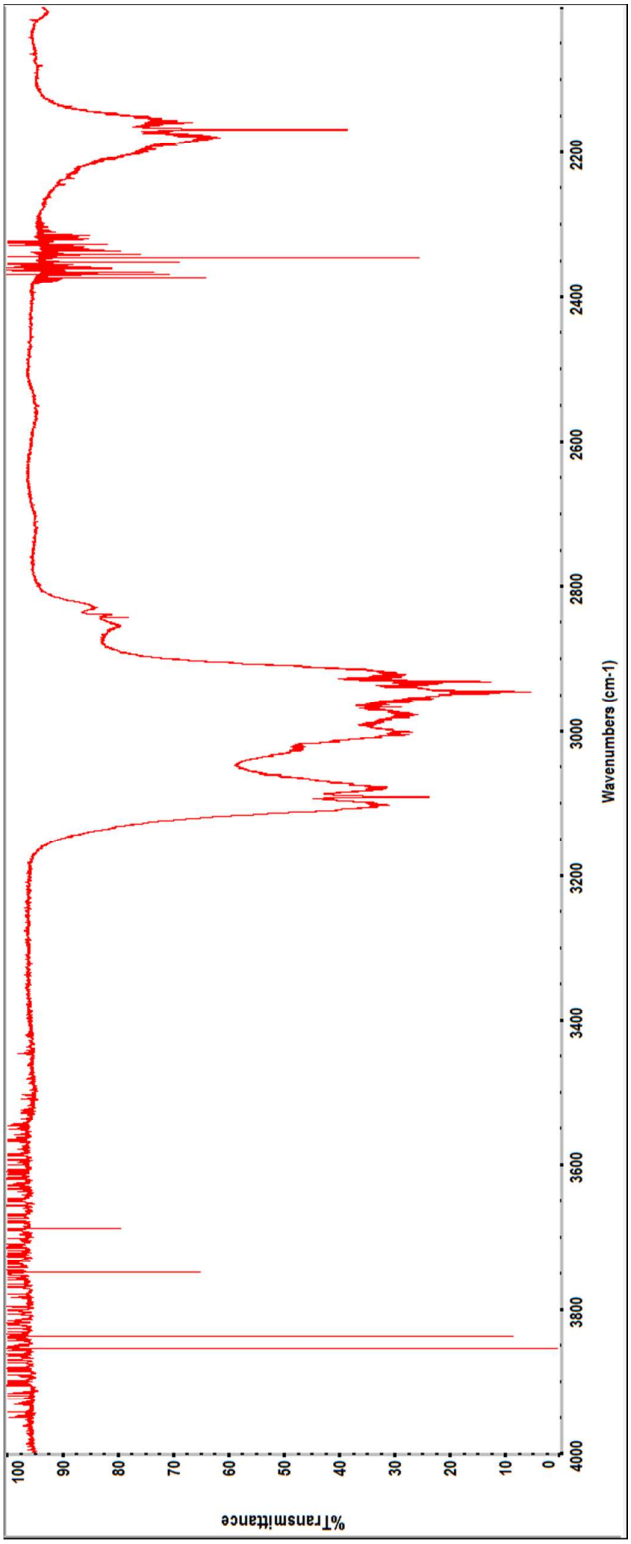

Figure S1b. Gas-phase IR spectrum of propene-3-d_1 from 2000-400 cm^{-1} at 51 torr and 0.5 cm^{-1} resolution. Spectrometer not purged.

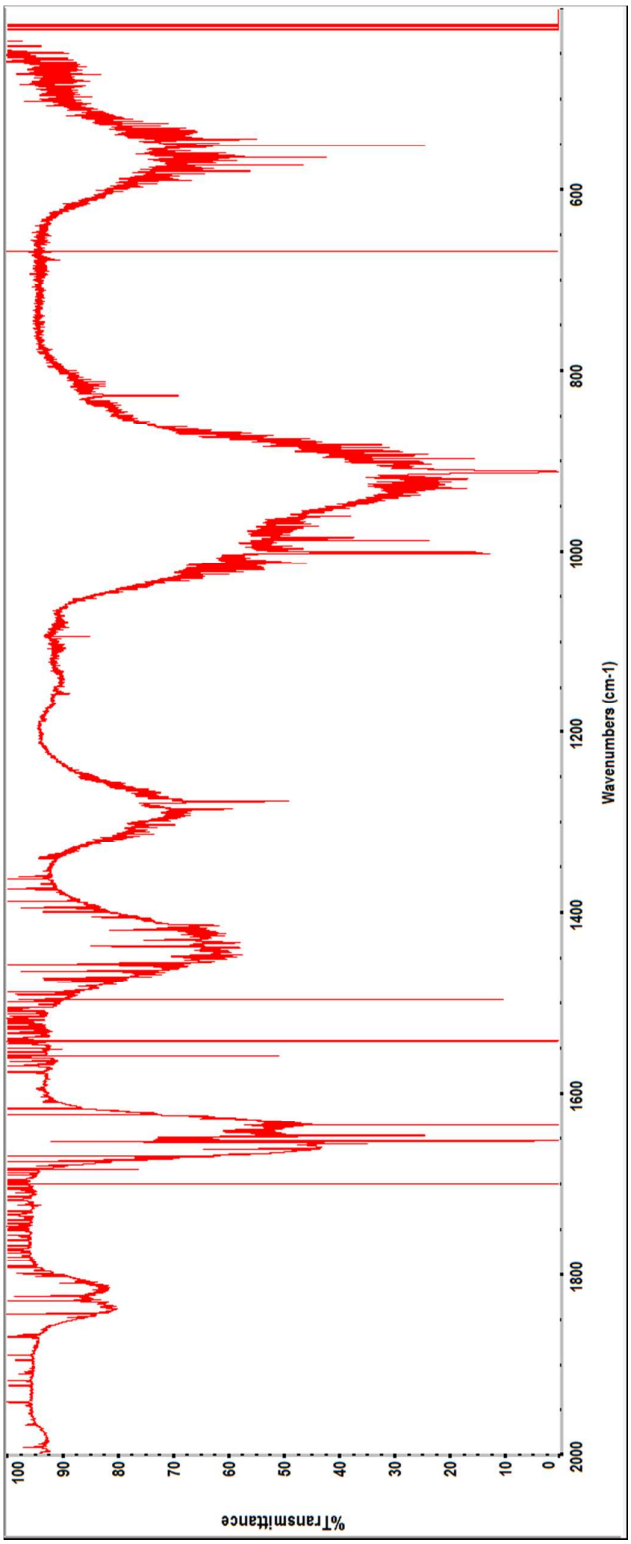

Table S1. Structure of the transition state of propene corresponding to the maximum of the barrier to internal rotation (distances in Å, angles in degrees).

Parameter	CCSD(T)/cc-pwCV(Q,T)Z		
	Transition state	Min. *E* form	r_e [a]
C2-C3	1.5053	1.4957	1.4954
C1=C2	1.3323	1.3319	1.3317
C1C2C3	124.19	124.50	124.48
C3Hs	1.0884	1.0897	1.0888
C2C3Hs	111.48	111.08	111.03
C1C2C3Hs	180	0	
C3Ha	1.0906	1.0917	1.0907
C2C3Ha	111.12	110.97	110.97
C1C2C3Ha	59.85	120.61	120.58
C2H	1.0845	1.0856	1.0845
C3C2H	117.26	116.62	116.66
C1Ht	1.0812	1.0813	1.0804
C2C1Ht	121.35	121.47	121.46
C1Hc	1.0838	1.0834	1.0825
C2C1Hc	121.43	121.17	121.15

[a] Equilibrium structure for the minimum energy form with a C–H bond eclipsing the C=C bond; see Fig. 1

Table S2. Experimental and ab initio quartic (kHz) and sextic (Hz) centrifugal distortion constants for CH_2=$CHCH_3$.

Method	Experimental		B3LYP	MP2	CCSD(T)
Basis set	Ref. [a]	This work	cc-pVTZ	cc-pVTZ	cc-pV(Q,T)Z
Δ_J /кHz	6.27432(71)	6.27503(78)	6.24	6.36	6.386
Δ_K /кHz	-27.4490(39)	-27.4377(43)	-30.8	-32.794	-31.490
Δ_{JK} /кHz	455.051(57)	455.058(66)	475	466.448	463.411
δ_J /кHz	1.22517(17)	1.22455(18)	1.2	1.2553	1.2497
δ_K /кHz	-29.07270(76)	-29.015(14)	-21.8	-20.6	-21.965
Φ_J /Hz	0.00580(56)	0.00600(63)	0.00556	0.0058	0.00668
Φ_{JK} /Hz	-0.480(16)	-0.27(fixed)	-0.258	-0.238	-0.270
Φ_{KJ} /Hz	-4.302(51)	-4.961(15)	-3.71	-3.874	-4.177
Φ_K /Hz	20.03(64)	20.86(74)	18	17.973	18.149
φ_J /Hz	0.00280(17)	0.00208(18)	0.00361	0.0034	0.00295
φ_{JK} /Hz	0	-0.039(17)	0.189	0.158	0.075
φ_K /Hz	-15.31(64)	-7.06(19)	1.91	1.792	-8.666

[a] From Ref. 4.

Table S3. Harmonic frequencies ω_i and anharmonic frequencies ν_i for CH_2=$CHCH_3$ (in cm^{-1})

Mode	Description	exp.[a]		B3LYP/VTZ			MP2/VTZ			MP2/AVTZ			CCSD(T)/CV(Q,T)Z			
				harm	anharm	e-c	harm	anharm	e-c	harm	anharm	e-c	harm	anharm	e-c	Int.[b]
$\nu_1(a')$	CH_2 asym stretch	3091.62	s	3209.4	3071.3	20.3	3277.8	3139.3	-47.7	3270.2	3131.8	-40.1	3235.7	3089.7	1.9	13.45
$\nu_2(a')$	CH stretch	3015		3129.2	2998.8	16.2	3191.6	3062.0	-47.0	3183.2	3053.6	-38.6	3153.4	2993.4	21.6	11.37
$\nu_3(a')$	CH_2 sym stretch	2991.03	w	3122.5	2994.6	-3.6	3177.7	3031.5	-40.5	3169.9	3023.7	-32.7	3141.8	2951.9	39.1	14.77
$\nu_4(a')$	CH_3 asym stretch	2973		3091.1	2951.5	21.5	3164.0	3017.0	-44.0	3157	3010.1	-37.1	3119.8	2975.9	-2.9	9.39
$\nu_5(a')$	CH_3 sym stretch	2931.46	s	3014.3	2930.7	0.8	3068.5	2971.4	-40.0	3062.3	2965.3	-33.8	3033.7	2942.8	-11.3	20.32
$\nu_6(a')$	C=C stretch	1653.18	m	1712.7	1671	-17.8	1707.1	1662.0	-8.9	1699.5	1654.4	-1.3	1702.5	1658.5	-5.3	10.46
$\nu_7(a')$	CH_3 asym def	1451.04	w	1495.2	1453.8	-2.8	1509.8	1467.6	-16.6	1513.1	1470.9	-19.8	1503.4	1460.2	-9.1	13.63
$\nu_8(a')$	CH_2 scissor	1420		1453.1	1417.6	2.4	1461.4	1423.4	-3.4	1457.7	1419.7	0.3	1456.9	1419.4	0.6	1.21
$\nu_9(a')$	CH_3 sym def	1377.94	m	1411.1	1378.8	-0.9	1410.2	1377.8	0.1	1413	1380.6	-2.7	1413.2	1380.0	-2.0	1.78
$\nu_{10}(a')$	CCH bend	1297.86	vw	1332.3	1303.6	-5.7	1327.7	1300.1	-2.2	1324.3	1296.7	1.1	1325.6	1297.6	0.3	0.11
$\nu_{11}(a')$	C-C stretch	1170.04	vw	1193.3	1161.9	8.1	1197.7	1174.2	-4.2	1196.9	1173.5	-3.5	1196.9	1172.0	-2.0	0.17
$\nu_{12}(a')$	CH_2 rock	935		950.8	940.8	-5.8	946.8	935.7	-0.7	945.7	934.5	0.5	946.2	936.3	-1.3	3.07
$\nu_{13}(a')$	CH_3 rock	919		924.6	909.4	9.6	943.0	928.2	-9.2	940.5	925.7	-6.7	935.7	920.0	-1.0	2.09
$\nu_{14}(a')$	CCC def	426.02	m	426.3	429.7	-3.7	422.2	424.6	1.4	420.4	422.9	3.2	423.1	426.1	0.0	0.87
$\nu_{15}(a'')$	CH_3 asym stretch	2954.30	s	3055.3	2916.9	37.4	3142.4	3004.6	-50.3	3136.2	2998.4	-44.1	3095.7	2950.1	4.2	15.95
$\nu_{16}(a'')$	CH_3 anti ip bend	1442.71	s	1480.3	1434.8	7.9	1496.2	1448.6	-5.9	1499.6	1452.0	-9.3	1490.3	1420.7	22.0	6.51
$\nu_{17}(a'')$	CH_3 rock+CH oop bend	1045.04	w	1074.8	1049.8	-4.8	1073.7	1047.9	-2.9	1073.7	1047.9	-2.9	1071.2	1046.2	-1.2	2.53
$\nu_{18}(a'')$	CH_2 twist+CH oop bend	991.05	s	1030.2	1006.1	-15.1	1034.6	1010.4	-19.3	1027.6	1003.4	-12.3	1018.8	994.0	-3.0	13.06
$\nu_{19}(a'')$	CH_2 wag	912.62	s	947.6	929.2	-16.6	939.2	921.7	-9.1	933.9	916.4	-3.8	931.4	918.0	-5.3	40.91
$\nu_{20}(a'')$	oop CH bend+...	576.27	s	592.5	584.5	-8.2	591.7	581.9	-5.6	568.3	558.5	17.8	586.7	577.2	-0.9	11.32
$\nu_{21}(a'')$	CH_3 torsion	188		205.7	192	-4	206.2	193.1	-5.1	207.9	194.8	-6.8	202.9	189.2	-1.2	0.39
MAD[c]						5.5			7.7			7.2			1.8	

[a] From Ref. 33.

[b] Intensities computed at the harmonic level with the CCSD(T)/CV(Q,T)Z model.

[c] Median absolute deviation.

Table S4. Experimental [a] and ab initio vibration-rotation interaction constants (MHz) for the *B* and *C* rotational constants of the torsional mode (ν_{21}) of three isotopologues of propene.

Method		Exp. [a]	MP2	B3LYP	CCSD(T)
Basis set			cc-pVTZ	cc-pVTZ	cc-pV(Q,T)Z
CH_2=$CHCH_3$	*b*	11.3	9.9	12.0	10.9
	c	-4.8	-3.6	-2.2	-3.2
CHD_t=$CHCH_3$	*b*	9.6	8.1	–.–	9.0
	c	-4.0	-3.2	–.–	-2.8
CH_2=$CDCH_3$	*b*	11.2	9.5	–.–	–.–
	c	-2.5	-1.9	–.–	–.–

[a] From Ref. 31.

Table S5. Rovibrational contributions (MHz) for CH_2=$CHCH_3$ and CHD_t=$CHCH_3$.

	Method	$A_e - A_0$	$B_e - B_0$	$C_e - C_0$
CH_2=$CHCH_3$ [a]	MP2/cc-pVTZ	389.12	77.21	72.10
	CCSD(T)/cc-pV(Q,T)Z	405.80	79.76	73.80
	difference	16.69	2.55	1.71
CHD_t=$CHCH_3$	MP2/cc-pVTZ	392.15	68.70	64.46
	CCSD(T)/cc-pV(Q,T)Z	408.82	71.18	66.21
	difference	16.67	2.48	1.75

[a] The B3LYP/cc-pVTZ values are: 384.30, 74.74, and 69.58 MHz.

Table S6. Semiexperimental rotational constants [a] and residuals of the fits (in MHz).

p	*g*	B_g(se)	0[b]	14[b]
Set I				
CH_2=CHCH_3	*a*	46671.412	-0.406	-0.387
$^{13}CH_2$=CHCH_3	*a*	46458.245	0.072	0.038
CH_2=^{13}CHCH_3	*a*	45831.489	0.006	0.064
CH_2=CH^{13}CH_3	*a*	46542.569	0.123	0.089
CH_2=CHCH_2D-s	*a*	40922.049	-0.015	-0.013
CH_2=CHCH_2D-a	*a*	43749.605	11.627	11.324
CH_2=CHCH_3	*b*	9382.674	0.101	0.103
$^{13}CH_2$=CHCH_3	*b*	9122.971	-0.030	-0.029
CH_2=^{13}CHCH_3	*b*	9380.626	-0.067	-0.061
CH_2=CH^{13}CH_3	*b*	9122.240	-0.005	-0.001
CH_2=CHCH_2D-s	*b*	9142.101	-0.007	-0.001
CH_2=CHCH_2D-a	*b*	8730.092	-0.004	0.002
CH_2=CHCH_3	*c*	8206.276	0.095	0.096
$^{13}CH_2$=CHCH_3	*c*	8000.607	-0.009	-0.009
CH_2=^{13}CHCH_3	*c*	8178.340	-0.041	-0.036
CH_2=CH^{13}CH_3	*c*	8002.533	0.003	0.005
CH_2=CHCH_2D-s	*c*	7832.646	0.152	0.156
CH_2=CHCH_2D-a	*c*	7784.712	-0.114	-0.121
Set II				
c-CHD=CHCH_3	*b*	9108.730	-0.182	-0.202
t-CHD=CHCH_3	*b*	8616.900	0.160	0.162
CH2=CDCH_3	*b*	9378.570	-0.388	-0.426
CH2=CDCH_2D-s	*b*	9133.490	-0.120	-0.173
CH2=CDCH_2D-a	*b*	8725.940	0.877	0.840
c-CHD=CHCH_2D-s	*b*	8888.310	-0.190	-0.207
c-CHD=CHCH_2D-a	*b*	8475.550	0.835	0.813
t-CHD=CDCH_3	*b*	8614.920	-0.017	-0.041
CH_2=CHCHD_2-sa	*b*	8538.500	-0.150	-0.135
CH_2=CHCHD_2-aa	*b*	8177.240	0.495	0.500
CD_2=CHCH_3	*b*	8409.460	-0.107	-0.120
t-CHD=CHCH_2D-s	*b*	8390.830	-0.174	-0.173
t-CHD=CHCH_2D-a	*b*	8039.860	0.078	0.086
c-CHD=CDCH_3	*b*	9108.540	0.105	0.071
c-CHD=CHCH_3	*c*	7794.950	-0.136	-0.125
t-CHD=CHCH_3	*c*	7606.620	0.095	0.086
CH2=CDCH_3	*c*	7906.370	-0.210	-0.202
CH2=CDCH_2D-s	*c*	7547.910	0.066	0.071
CH2=CDCH_2D-a	*c*	7514.290	0.165	0.159
c-CHD=CHCH_2D-s	*c*	7457.680	0.039	0.051
c-CHD=CHCH_2D-a	*c*	7401.480	0.193	0.192
t-CHD=CDCH_3	*c*	7351.620	0.000	0.006
CH_2=CHCHD_2-sa	*c*	7457.230	-0.230	-0.238
CH_2=CHCHD_2-aa	*c*	7431.300	-0.121	-0.134
CD_2=CHCH_3	*c*	7263.060	-0.054	-0.055
t-CHD=CHCH_2D-s	*c*	7269.800	0.075	0.067

t-CHD=CHCH$_2$D-a	*c*	7223.720	-0.102	-0.119
c-CHD=CDCH$_3$	*c*	7514.520	0.042	0.064

[a] c = cis to methyl, t = trans to methyl., s = in-plane H, a = out-of-plane H.
[b] Number of predicates in the fit.

Table S7. Comparison of Cartesian coordinates for propene (in Å).

Sub[a]	z	ΔP_z	Kraitchman	p_0 [b]	p_{14} [c]
^{13}C1	*a*	1.53338	-1.25017(30)	-1.24983(11)	-1.249826(89)
	b	0.04975	0.2293(17)	0.22940(12)	0.229369(98)
	c	-0.00007	0.000(26)		
^{13}C2	*a*	0.01184	-0.1097(34)	-0.10473(29)	-0.10481(20)
	b	0.19853	-0.45016(85)	-0.450167(52)	-0.450178(46)
	c	-0.00008	0.000(26)		
^{13}C3	*a*	1.53785	1.25227(30)	1.251984(95)	1.251989(76)
	b	0.03008	0.1783(22)	0.17836(15)	0.17832(12)
	c	-0.00010	0.000(26)		
D_s	*a*	1.41687	1.17931(31)	1.17927(18)	1.17928(15)
	b	1.52081	1.26425(31)	1.26456(11)	1.264554(91)
	c	0.00053	-0.026(14)		
D_a	*a*	3.31905	1.82455(20)	1.823746(86)	1.823753(79)
	b	0.01592	-0.1259(29)	-0.12998(58)	-0.12962(48)
	c	0.70725	0.87653(46)	0.877874(39)	0.877875(35)
D_g [d]	*a*	0.01982		-0.1414(19)	-0.1406(13)
	b	2.31623		-1.53446(24)	-1.53455(19)
	c	0.00375			
D_c [d]	*a*	1.62016		-1.25868(26)	-1.25862(22)
	b	1.62956		1.31171(32)	1.31179(27)
	c	-0.00024			
D_t [d]	*a*	4.77821		-2.20535(11)	-2.20535(10)
	b	0.07673		-0.27685(66)	-0.27665(55)
	c	0.00855			

[a] Atom substituted.
[b] Fit without predicate.
[c] Fit with 14 predicates, see text.
[d] As the *A* rotational constant is not known, the substitution coordinates are not expected to be reliable.