Electronic Supplementary Information

Infrared spectra of the 2-chloroethyl radical in solid *para*-hydrogen†

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† Electronic Supplementary Information (ESI) Available: B3LYP/aug-cc-pVDZ vibrational frequencies of the Cl + C_2H_4 addition and abstraction products (Table S1), MP2/aug-cc-pVDZ vibrational frequencies of the Cl_2-C_2H_4 complex and its isotopomers (Table S2), comparison of observed and calculated line positions and intensities of the Cl_2-C_2H_4 complex and its isotopomers (Table S3), MP2/aug-cc-pVDZ vibrational frequencies of 1,2-dichloroethane and its isotopomers (Table S4), comparison of observed and calculated line positions and intensities of 1,2-dichloroethane and its isotopomers (Table S5), MP2/aug-cc-pVDZ vibrational frequencies of ethylchloride, CD_2HCD_2Cl isotopomers and C_2H_5 (Table S6), comparison of observed and calculated line positions and intensities of ethyl chloride and its isotopomers (Table S7), B3LYP/aug-cc-pVDZ structures of the Cl + C_2H_4 addition and abstraction products (Fig. S1), MP2/aug-cc-pVDZ structure of the Cl_2-C_2H_4 complex (Fig. S2), IR spectrum of 1,2-dichloroethane in p-H_2 (Fig. S3), structures of gauche and trans $C_2H_2D_2Cl_2$ (Fig. S4), MP2/aug-cc-pVDZ transition state structure for the reaction of the 2-chloroethyl radical with H_2 (Fig. S5), experimental IR difference spectra of a Cl_2/C_2D_4/p-H_2 matrix after 2 hours of irradiation at 365 nm followed by 2 hours of IR irradiation (Fig. S6), structures of the isotopomers of CD_2HCD_2Cl (Fig. S7), and a discussion of the results of the secondary IR irradiation experiments of Cl_2/C_2D_4/p-H_2 matrices.

Table S1. Unscaled B3LYP/aug-cc-pVDZ calculated harmonic vibrational frequencies (cm^{-1}) and intensities (km/mol) of several of the possible products of the addition and abstraction reaction between atomic chlorine and ethylene.[a]

species	frequency (intensity)
$\bullet CHClCH_3$	147 (1.7), 296 (20.2), 365 (11.3), 719 (29.1), 981 (0.4), 1024 (18.5), 1114 (4.6), 1284 (41.3), 1382 (6.6), 1427 (8.4), 1449 (2.9), 2976 (22.0), 3053 (13.5), 3105 (11.6), 3223 (4.8)
$\bullet CH_2CH_2Cl$	238 (0.8), 297 (14.4), 490 (43.9), 694 (67.4), 781 (1.1), 1038 (0.5), 1105 (10.6), 1200 (9.2), 1237 (0.4), 1446 (4.7), 1481 (0.4), 3107 (9.5), 3156 (2.9), 3179 (1.1), 3271 (3.9)
$\bullet C_2H_3$	704 (20.8), 796 (20.9), 932 (71.1), 1041 (8.7), 1377 (8.9), 1648 (2.0), 3053 (4.3), 3157 (3.2), 3242 (0.4)
P_{vdw}	25 (3.3), 83 (3.1), 99 (4.8), 282 (10.9), 364 (13.2), 707 (20.4), 812 (29.2), 950 (81.0), 1043 (8.6), 1379 (10.6), 1641 (3.7), 2757 (480.7), 3056 (1.3), 3159 (1.0), 3241 (1.2)

[a] The 1-chloroethyl radical is listed as $\bullet CHClCH_3$ and the 2-chloroethyl radical is listed as $\bullet CH_2CH_2Cl$.

Table S2. Unscaled MP2/aug-cc-pVDZ calculated harmonic vibrational frequencies (cm^{-1}) and intensities (km/mol) of the Cl_2-C_2H_4, Cl_2-C_2D_4, and Cl_2-*trans*-$C_2H_2D_2$ complexes.

species	frequency (intensity)
Cl_2-C_2H_4	78 (0.1), 82 (0.1), 101 (10.6), 121 (0.4), 195 (0.3), 482 (42.1), 823 (0.0), 954 (0.0), 990 (137.4), 1044 (0.0), 1228 (0.0), 1367 (3.5), 1467 (8.0), 1652 (10.9), 3176 (4.5), 3191 (0.5), 3274 (0.0), 3301 (6.7)
Cl_2-C_2D_4	72 (0.0), 76 (0.0), 96 (9.5), 113 (0.5), 147 (0.3), 482 (44.0), 591 (0.0), 738 (0.0), 749 (86.8), 784 (0.0), 998 (0.0), 999 (0.4), 1088 (4.0), 1530 (11.8), 2293 (2.1), 2358 (2.7), 2442 (0.0), 2459 (4.1)
Cl_2-*t*-$C_2H_2D_2$	74 (0.1), 81 (0.1), 98 (10.0), 116 (0.4), 169 (0.3), 482 (43.1), 671 (0.0), 744 (47.2), 874 (0.0), 1005 (1.1), 1017 (64.0), 1303 (1.4), 1316 (6.0), 1586 (11.8), 2370 (3.0), 2397 (1.4), 3235 (0.2), 3244 (5.7)

Table S3. Observed experimental peak positions (cm^{-1}) of the Cl_2-C_2H_4, Cl_2-C_2D_4, and Cl_2-*trans*-$C_2H_2D_2$ complexes in *p*-H_2 , N_2, and Ar matrices and the corresponding scaled harmonic vibrational frequencies (cm^{-1}) calculated at the MP2/aug-cc-pVDZ level.

Mode Description[a]	pH_2	N_2[b]	Ar[c]	MP2[d]
	Cl_2-C_2H_4			
C=C stretch	1619.9	1619	1619	1616
	1619.2			
	1617.8			
IP antisymmetric CH_2 scissor	1440.9	1440		1435
IP symmetric CH_2 scissor	1340.7	1340		1337
OOP symmetric CH_2 wag	963.5	959		968
	960.1	954		
^{35}Cl–^{35}Cl stretch	531.7	527	526	471
^{35}Cl–^{37}Cl stretch	524.5	520		466
^{37}Cl–^{37}Cl stretch	517.3	513		459
	Cl_2-C_2D_4			
C=C stretch	1512.1	1511		1496
	1511.1			
IP antisymmetric CD_2 scissor	1075.6	1076		1064
OOP symmetric CH_2 wag	727.2	733		733
^{35}Cl–^{35}Cl stretch	530.7	526		471
^{35}Cl–^{37}Cl stretch	523.4	519		466
^{37}Cl–^{37}Cl stretch		512		459
	Cl_2-*trans*-$C_2H_2D_2$			
C=C stretch	1565.1			1551
	1564.3			
	1563.2			
IP antisymmetric CH bend	1296.3			1287
OOP symmetric CH wag	990.3			995
OOP symmetric CD wag	726.5			728
^{35}Cl–^{35}Cl stretch	531.2			471
^{35}Cl–^{37}Cl stretch	524.0			466

[a] IP indicates in-plane and OOP indicates out-of-plane. [b] L. Fredin and B. Nelander, *J. Mol. Struct.*, 1973, **16**, 205-216. [c] S. Holroyd, A. J. Barnes, S. Suzuki and W. J. Orville-Thomas, *J. Raman Spectrosc.*, 1982, **12**, 162-164. [d] The MP2/aug-cc-pVDZ calculated frequencies have been scaled by 0.978.

Table S4. Unscaled MP2/aug-cc-pVDZ calculated harmonic vibrational frequencies (cm^{-1}) and intensities (km/mol) of gauche and trans 1,2-dichloroethane ($C_2H_4Cl_2$) and its isotopomers $C_2D_4Cl_2$ and $C_2H_2D_2Cl_2$.[a]

species	frequency (intensity)
	$C_2H_4Cl_2$
gauche	116 (0.8), 264 (0.8), 414 (7.1), 683 (15.7), 705 (21.4), 900 (16.5), 964 (9.0), 1071 (1.5), 1161 (0.7), 1229 (0.4), 1309 (34.4), 1336 (16.2), 1455 (11.1), 1460 (0.3), 3106 (3.7), 3111 (22.3), 3181 (0.5), 3192 (2.4)
trans	120 (6.6), 216 (8.8), 305 (0.0), 747 (86.5), 778 (1.6), 786 (0.0), 1015 (0.0), 1097 (0.0), 1143 (1.3), 1247 (32.0), 1288 (0.0), 1331 (0.0), 1478 (6.5), 1480 (0.0), 3121 (0.0), 3128 (13.9), 3191 (0.0), 3211 (1.3)
	$C_2D_4Cl_2$
gauche	110 (0.8), 228 (0.4), 364 (4.9), 632 (11.8), 635 (10.7), 761 (9.0), 777 (4.4), 831 (0.4), 835 (0.2), 952 (1.2), 1030 (43.8), 1062 (9.5), 1069 (7.0), 1189 (14.5), 2254 (3.6), 2265 (13.2), 2364 (0.3), 2370 (1.2)
trans	110 (5.6), 203 (7.8), 301 (0.0), 572 (0.3), 718 (61.7), 724 (0.0), 781 (0.0), 824 (0.4), 923 (0.0), 951 (50.1), 985 (0.0), 1058 (0.0), 1089 (3.0), 1196 (0.0), 2269 (10.1), 2272 (0.0), 2374 (0.0), 2386 (1.2)
	$C_2H_2D_2Cl_2$
gauche A	112 (0.8), 243 (0.6), 371 (5.2), 665 (16.5), 677 (15.5), 802 (0.8), 829 (6.0), 888 (19.6), 946 (0.9), 1096 (12.9), 1245 (10.7), 1278 (25.6), 1302 (11.2), 1318 (0.2), 2319 (4.8), 2322 (4.2), 3134 (0.5), 3142 (15.9)
gauche B/D	113 (0.8), 242 (0.6), 387 (5.8), 640 (11.2), 676 (16.4), 787 (6.6), 811 (2.6), 906 (14.2), 976 (16.1), 1086 (6.5), 1254 (10.9), 1271 (17.6), 1313 (11.5), 1316 (6.6), 2301 (4.7), 2321 (5.4), 3137 (7.3), 3162 (6.1)
gauche C	113 (0.8), 242 (0.5), 403 (6.5), 636 (10.6), 657 (12.5), 768 (7.3), 832 (1.4), 885 (12.0), 971 (26.8), 1131 (3.5), 1215 (17.3), 1294 (1.8), 1296 (13.6), 1342 (14.1), 2297 (0.9), 2307 (10.3), 3155 (5.3), 3168 (5.2)
trans A/D	114 (6.1), 209 (8.2), 303 (0.0), 642 (1.3), 730 (66.2), 737 (0.0), 875 (0.0), 882 (27.3), 951 (0.0), 1138 (0.0), 1201 (21.6), 1275 (0.0), 1317 (5.5), 1357 (0.0), 2324 (0.0), 2329 (6.3), 3163 (0.0), 3177 (6.9)
trans B/C	114 (6.1), 209 (8.3), 303 (0.0), 633 (0.5), 726 (63.4), 741 (0.0), 848 (24.9), 909 (0.4), 998 (9.8), 1077 (0.0), 1240 (17.7), 1266 (0.6), 1327 (0.3), 1340 (4.5), 2324 (5.4), 2330 (0.5), 3167 (6.3), 3174 (0.7)

[a] For the isotopomers of $C_2H_2D_2Cl_2$, the labels for the species refer to the structures displayed in Figure S3.

Table S5. Comparison of observed experimental band positions (cm^{-1}) and relative intensities assigned to the gauche and trans isomers of 1,2-dichloroethane ($C_2H_4Cl_2$) and its isotopomers $C_2D_4Cl_2$ and $C_2H_2D_2Cl_2$ in *p*-H_2 with the scaled harmonic vibrational frequencies and relative intensities calculated at the MP2/aug-cc-pVDZ level.[a]

Species/Mode Description	ν_{expt}	I_{expt}[b]	ν_{MP2}[c]	I_{MP2}[d]
	$C_2H_4Cl_2$			
trans CH_2 stretch	3031.3	3.4	3047	1.5
gauche CH_2 stretch	3001.0	30.2	3029	7.0
trans CH_2 stretch	2979.6	12.5	2968	16.1
gauche CH_2 stretch	2961.2	62.0	2952	64.8
gauche CH_2 stretch	2954.7	8.1	2948	10.8
trans CH_2 scissor	1456.7	11.4	1445	7.5
gauche CH_2 scissor	1434.6	42.8	1423	32.2
gauche CCl stretch, comb bands	1364.7, 1356.7	24.3	1357	
gauche CH_2 wag	1314.4	32.4	1307	47.1
gauche CH_2 wag	1290.9	100.0	1280	100.0
trans CH_2 wag	1232.0	30.8	1219	37.0
gauche CH_2 rock	949.8	39.7	943	26.2
gauche CH_2 rock	889.1, 887.3, 887.0	67.4	880	48.0
trans CH_2 rock	772.0	4.4	761	1.8
trans CCl stretch	727.8, 725.0, 722.4	100.0	730	100.0
gauche CCl stretch	691.5, 689.6	61.0	694	62.2
gauche CCl stretch	669.2, 666.4, 664.2	56.0	668	45.6
	$C_2D_4Cl_2$			
trans CD_2 stretch	2184.9	12.8	2153	16.3
gauche CD_2 stretch	2174.8, 2174.0	38.4	2149	30.1
gauche CD_2 scissor	1152.9	48.1	1163	33.1
trans CD_2 scissor	1081.1	6.6	1065	4.8
gauche CD_2 wag	1049.0	23.5	1039	21.7
gauche CD_2 wag	1019.6	100.0	1007	100.0
trans CD_2 wag	940.4	87.8	930	81.1
trans CCl stretch	702.8, 699.7, 697.3	100.0	702	100.0
	$C_2H_2D_2Cl_2$			
trans B/C CHD scissor	1327.0	7.9	1311	7.1
trans A/D CHD scissor	1302.3	14.2	1288	8.3
gauche	1255.1			
gauche	1249.8			
gauche	1232.9			
trans B/C CH wag	1221.0	19.8	1213	27.9
trans A/D CH wag	1187.9	27.1	1175	32.6
gauche	1067.1			

gauche	1054.2			
gauche	966.0			
gauche	958.4			
gauche	892.8			
gauche	876.1			
trans A/D CD wag	870.6	34.6	863	41.2
trans B/C CD wag	841.7	38.2	829	39.3
trans A/D+B/C CCl stretch	713.0, 710.1, 707.3	100.0	714/710	100.0

[a] For the isotopomers of $C_2H_2D_2Cl_2$, the labels for the species refer to the structures displayed in Figure S3. [b] Intensities are normalized to the most intense peaks. Experimental IR intensities are estimated by integrating the areas of the corresponding peaks. For $C_2H_2D_2Cl_2$, the most intense peaks at 713.0, 710.1, and 707.3 cm-1 correspond to a sum of intensity for the trans A/D and trans B/C isotopomers. The ratio of trans A/D to trans B/C determined to be 1.3±0.2:1 and based on this, an integrated area for each isotopomer was estimated. These were then used to normalize the peak areas for the trans A/D and trans B/C isotopomers. [c] The MP2/aug-cc-pVDZ calculated frequencies have been scaled by 0.978 and 0.949 for frequencies below and above 2000 cm^{-1}, respectively. [d] MP2/aug-cc-pVDZ predicted intensities are normalized to the most intense vibrational frequency. For $C_2H_4Cl_2$, the intensity of the 1280 cm^{-1} frequency of the gauche conformer is 34.4 km mol^{-1} and the intensity of the 730 cm^{-1} frequency of the trans conformer is 86.5 km mol^{-1}. For $C_2D_4Cl_2$, the intensity of the 1007 cm^{-1} frequency of the gauche conformer is 43.8 km mol^{-1} and the intensity of the 702 cm^{-1} frequency of the trans conformer is 61.7 km mol^{-1}. For $C_2H_2D_2Cl_2$, the intensity of the 714 cm^{-1} frequency of the trans A/D conformer is 66.2 km mol^{-1} and the intensity of the 710 cm^{-1} frequency of the trans B/C conformer is 63.4 km mol^{-1}.

Table S6. Unscaled MP2/aug-cc-pVDZ calculated harmonic vibrational frequencies (cm^{-1}) and intensities (km/mol) of ethyl chloride (C_2H_5Cl), the isotopomers of CD_2HCD_2Cl and C_2H_5.[a]

species	frequency (intensity)
C_2H_5Cl	267 (0.1), 336 (2.3), 690 (23.8), 785 (2.1), 995 (17.9), 1079 (0.0), 1101 (0.5), 1271 (0.2), 1311 (32.5), 1397 (6.0), 1475 (8.0), 1481 (0.9), 1489 (2.0), 3069 (14.8), 3119 (15.8), 3162 (17.2), 3173 (2.2), 3195 (14.4)
CD_2HCD_2Cl	
VII	213 (0.1), 305 (2.0), 580 (0.6), 669 (20.6), 814 (0.0), 847 (0.8), 916 (0.2), 984 (0.0), 1051 (32.2), 1086 (3.5), 1167 (15.7), 1298 (1.3), 1300 (7.5), 2258 (6.6), 2268 (10.4), 2354 (2.3), 2373 (6.8), 3120 (18.2)
VIII/IX	209 (0.2), 311 (2.0), 605 (1.1), 636 (13.4), 792 (7.8), 815 (0.0), 945 (0.5), 1024 (11.9), 1041 (19.2), 1070 (9.9), 1166 (7.3), 1302 (8.7), 1320 (2.5), 2245 (5.8), 2269 (12.9), 2345 (5.6), 2370 (4.0), 3150 (10.2)
C_2H_5	136 (0.0), 467 (54.3), 808 (1.2), 974 (0.6), 1088 (0.02), 1194 (1.8), 1387 (0.6), 1466 (4.9), 1475 (4.8), 1493 (0.9), 3026 (22.7), 3113 (18.2), 3160 (17.8), 3206 (13.7), 3321 (10.6)

[a] For the isotopomers of CD_2HCD_2Cl, the roman numerals refer to the structures displayed in Figure S7.

Table S7. Comparison of observed experimental peak positions (cm^{-1}) and relative intensities assigned to the ethylchloride (C_2H_5Cl) and its CD_2HCD_2Cl isotopomers in *p*-H_2 with the scaled harmonic vibrational frequencies and relative intensities calculated at the MP2/aug-cc-pVDZ level.[a]

Mode Description	ν_{expt}	I_{expt}[b]	ν_{MP2}[c]	I_{MP2}[d]
	C_2H_5Cl			
CH_3 degenerate stretch	2938.1	34.3	2960	48.6
CH_3 degenerate deformation	1464.0	11.3	1456	6.2
CH_3 symmetric deformation	1382.6	24.1	1366	18.5
CH_2 wag	1287.4	100.0	1282	100.0
CC stretch/CH_3 rock	1073.0	2.2	1077	1.5
CH_3 rock/CC stretch	972.0	63.4	973	55.1
CH_2 rock	785.0	13.3	768	6.2
CCl stretch	672.5	58.2	675	73.2
	CD_2HCD_2Cl			
gauche CHD scissor	1304.2	17.0	1291	13.0
staggered CH wag	1286.4	17.1	1271	23.3
gauche CH wag	1285.5	55.7	1273	45.3
gauche CC stretch	1136.9	30.4	1140	38.0
staggered CC stretch	1136.1	53.2	1141	48.8
gauche α,β-CD_2 scissor	1059.5	25.7	1046	51.6
staggered α-CD_2 wag/β-CD_2 scissor	1035.8	100.0	1028	100.0
gauche α-CD_2 wag/β-CD_2 scissor	1027.3	100.0	1018	100.0
gauche α-CD wag/β-CD_2 wag	1014.4	52.2	1001	62.0
gauche α-CD_2 wag/β-CD wag	780.9	24.9	752	40.6
staggered CCl stretch	652.8	44.4	654	64.0
gauche CCl stretch	624.5	31.2	622	69.8

[a] For the isotopomers of C_2D_4HCl, the labels for the species refer to the structures displayed in Figure S7. [b] Intensities are normalized to the most intense peak for each isotopomer. Experimental IR intensities are estimated by integrating the areas of the corresponding peaks. For C_2D_4HCl, the peaks assigned to the staggered isotopomer are normalized to the peak at 1035.8 cm^{-1} and the peaks assigned to the gauche isotopomer are normalized to the peak at 1027.3 cm^{-1}. The experimental relative intensity of the 1027.3 to the 1035.8 cm^{-1} line is (1.17 ± 0.04) :1. [c] The MP2/aug-cc-pVDZ calculated frequencies have been scaled by 0.978 and 0.949 for frequencies below and above 2000 cm^{-1}, respectively. [d] Intensities are normalized to the most intense predicted vibrational mode for each isotopomer. The MP2/aug-cc-pVDZ predicted intensity for the 1282 cm^{-1} mode of C_2H_5Cl is 32.5 km mol^{-1}, for the 1028 cm^{-1} mode of staggered CD_2HCD_2Cl is 32.2 km mol^{-1} and for the 1018 cm^{-1} mode of gauche CD_2HCD_2Cl is 19.2 km mol^{-1}.

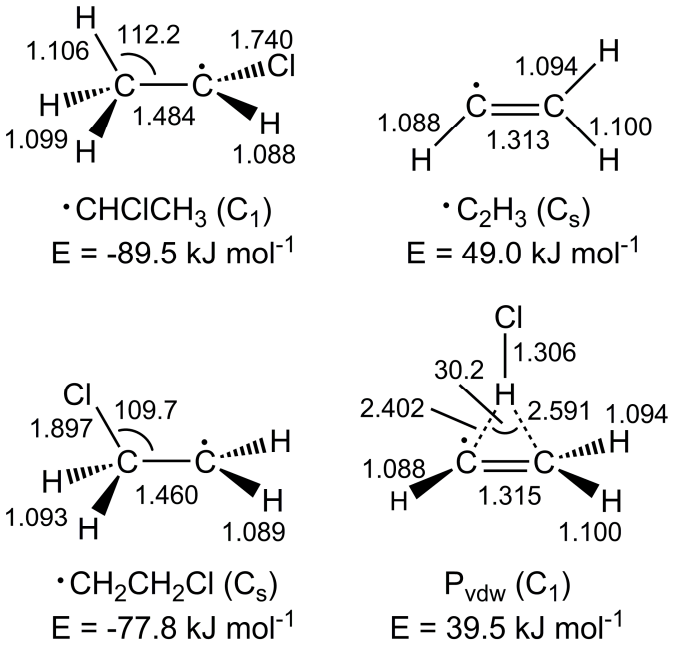

Fig. S1. Optimized geometries and energies (relative to the Cl + C_2H_4 reactants) at the B3LYP/aug-cc-pVDZ level for the intermediates and products of the addition and abstraction reaction between atomic chlorine and ethylene. For •C_2H_3, the relative energy includes the energy of HCl optimized at the same level of theory. The bond lengths are in angstroms and the bond angles are in degrees. The symmetry of each species is listed in parenthesis. The 1-chloroethyl radical is listed as •$CHClCH_3$ and the 2-chloroethyl radical is listed as •CH_2CH_2Cl.

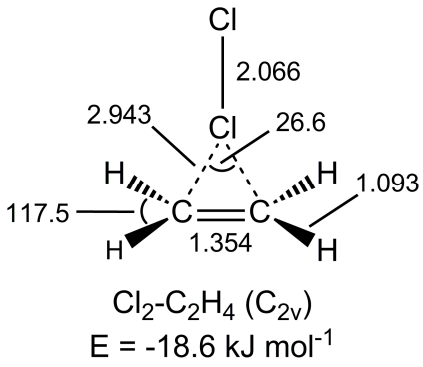

Fig. S2. Optimized geometry and energy (relative to the Cl_2 + C_2H_4 reactants) at the MP2/aug-cc-pVDZ level for the Cl_2-C_2H_4 complex. The bond lengths are in angstroms and the bond angles are in degrees. The symmetry of the complex is listed in parenthesis.

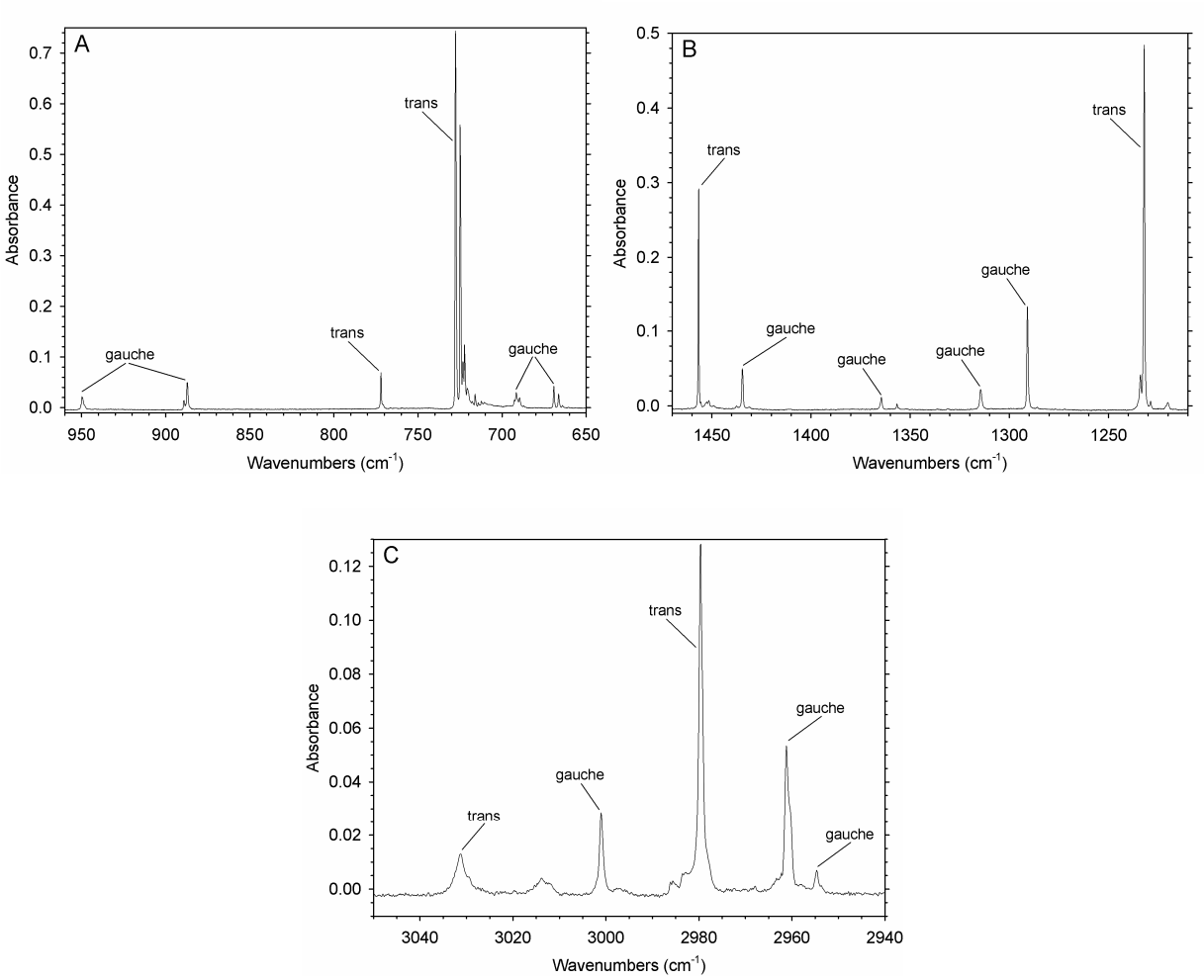

Fig. S3. Experimental IR spectrum of a 1 hour deposited 1:1000 1,2-dichloroethane/*p*-H_2 matrix at 3.2 K in the (A) 960 – 650 cm^{-1} region, (B) 1470 – 1210 cm^{-1} region and (C) 3050 – 2940 cm^{-1} region. The peaks assigned to gauche and trans isomers of 1,2-dichloroethane are labeled as gauche and trans, respectively.

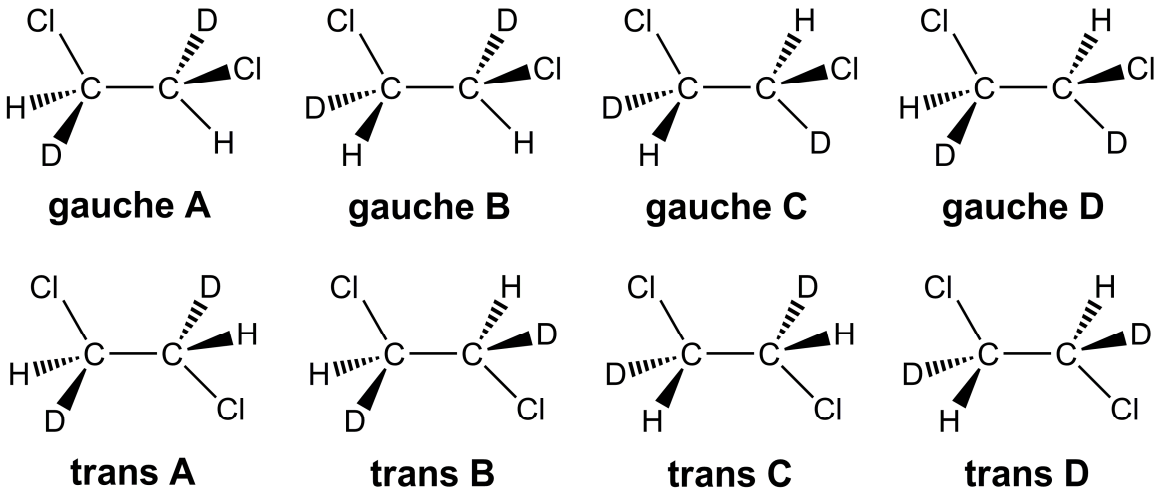

Fig. S4. Structures of the eight isotopomers of gauche and trans $C_2H_2D_2Cl_2$.

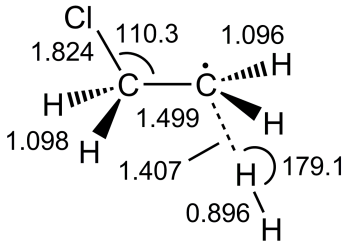

Fig. S5. Optimized geometry at the MP2/aug-cc-pVDZ level of the transition state of the reaction between molecular hydrogen and the 2-chloroethyl radical (reaction 3 in paper). The bond lengths are in angstroms and the bond angles are in degrees.

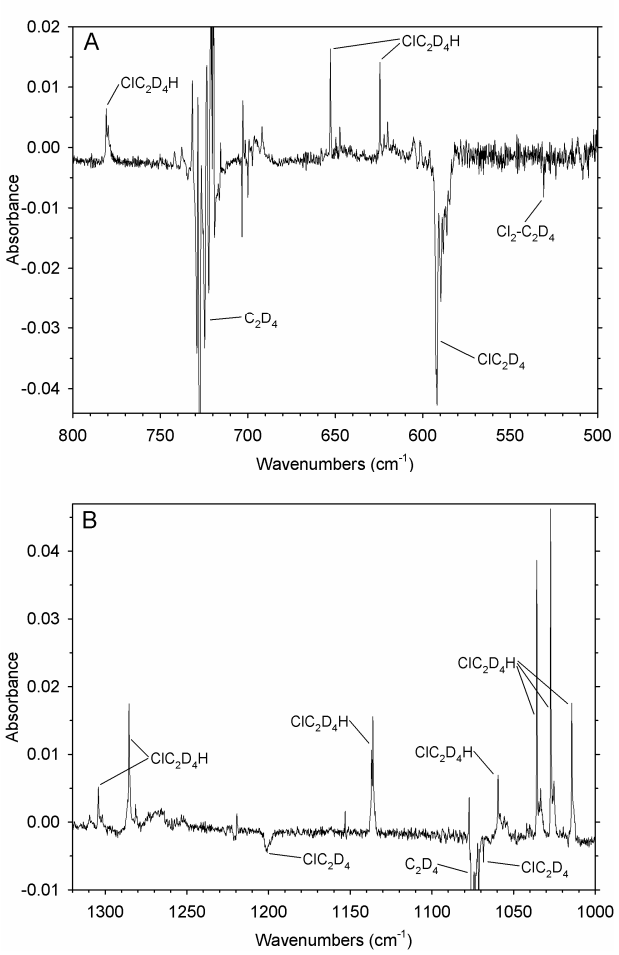

Fig. S6. Experimental IR difference spectra of a 8 hour co-deposited $Cl_2/C_2D_4/p\text{-}H_2$ (1:1:2000) matrix after 2 hours of irradiation at 365 nm at 3.2 K followed by 2 hours of IR irradiation (3876 – 4975 cm^{-1}) at 3.2 K in the (A) 800 – 500 cm^{-1} and (B) 1320 – 1000 cm^{-1} regions. The lines assigned to the 2-chloroethyl radical and ethyl chloride are labeled as ClC_2D_4 and C_2D_4HCl, respectively.

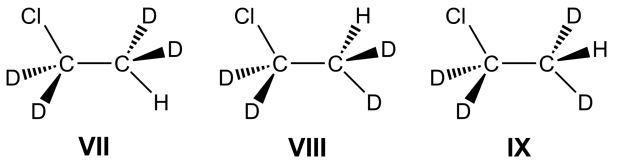

Fig. S7. Structures of the three isotopomers of CD_2HCD_2Cl with the H atom attached to the carbon without chlorine.

IR irradiation of $Cl_2/C_2D_4/p$-H_2 matrices. In the $Cl_2/C_2D_4/p$-H_2 experiment, the matrix was irradiated with 365 nm radiation for two hours followed by IR irradiation for two hours and several new lines appeared in the spectrum. Similar to the $Cl_2/C_2H_4/p$-H_2 infrared experiment, the most intense lines observed are due to the formation of HCl at 2894.1 and 2892.2 cm^{-1} and HCl-C_2D_4 at 2770.0 and 2767.9 cm^{-1}. Given that ethyl chloride was formed in the $Cl_2/C_2H_4/p$-H_2 IR irradiation experiment, it is reasonable to assume that the mixed hydrogen-deuterium isotopomer of ethyl chloride (CD_2HCD_2Cl) would also be formed in the $Cl_2/C_2D_4/p$-H_2 experiments according to reactions 4 and 5.

$$\bullet CD_2CD_2Cl + H \rightarrow CD_2HCD_2Cl \quad (4)$$

$$\bullet CD_2CD_2Cl + H_2(v = 1) \rightarrow CD_2HCD_2Cl + H \quad (5)$$

The spectral region that was found to be most informative regarding the identification of the products formed with IR irradiation in this experiment is below 1400 cm^{-1} and a representative portion of the IR difference spectrum in this region obtained by the subtraction of the 365 nm irradiated $Cl_2/C_2D_4/p$-H_2 spectrum from the spectrum after infrared irradiation is presented in Figure S6.

For the mixed hydrogen-deuterium isotopomer of ethyl chloride, CD_2HCD_2Cl, in which the H atom is attached to the carbon without chlorine, there are three conformational isomers, one staggered (VII in Figure S7) and two *gauche* isomers (VIII and IX in Figure S7), and the IR spectra for all three isomers was calculated at the MP2/aug-cc-pVDZ level (Table S6). In terms of energies, these isomers are all within 0.1 kJ/mol of each other. The IR spectra of the two *gauche* isomers are equivalent and therefore only two distinct IR spectra are expected, one for the staggered and the other for the *gauche* isomers. When the positions of the new lines observed in Figure S6 are compared with the unscaled MP2/aug-cc-pVDZ predicted vibrational

frequencies (Table S6) of staggered and *gauche* CD_2HCD_2Cl, the lines at 1286.4, 1136.1, 1035.8 and 652.8 cm^{-1} are assigned to staggered CD_2HCD_2Cl and the lines at 1304.2, 1285.5, 1136.9, 1059.5, 1027.3, 1014.4, 780.9, and 624.5 cm^{-1} are assigned to *gauche* CD_2HCD_2Cl. A table showing a direct comparison of the experimentally observed and the scaled MP2/aug-cc-pVDZ predicted vibrational frequencies and relative intensities is given in Table S7. Using the experimental intensities of several of the staggered and *gauche* lines of CD_2HCD_2Cl and the intensities for the corresponding theoretical vibrational frequencies, it is estimated that the concentration ratio of the *gauche* to staggered CD_2HCD_2Cl isotopomer is (1.6±0.4):1.