Supplementary Information for jp-2012-05117d:

Infrared Spectra of CH_3-MH through Methane Activation by Laser-Ablated Sn, Pb, Sb, and Bi Atoms

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Table S1: Observed and Calculated Fundamental Frequencies of CH_3-SnH isotopomers in the Ground ^{1}A' state[a]

Approximate Description	CH_3-SnH					CD_3-SnH					$^{13}CH_3$-SnH				
	Obs[b]	B3LYP[c]	Int[c]	BPW91[d]	Int[d]	Obs[b]	B3LYP[c]	int[c]	BPW91[d]	Int[d]	Obs[b]	B3LYP[c]	int[c]	BPW91[d]	Int[d]
A' CH_3 as. str.		3124.6	14	3081.0	13		2314.5	5	2282.2	5		3113.3	14	3069.8	13
A" CH_3 as. str.		2085.6	21	3041.4	17		2280.6	11	2247.5	9		3074.9	21	3030.8	17
A' CH_3 s. str.		3018.4	17	2967.5	13		2162.3	6	2125.4	4		3015.4	18	2964.6	14
A' Sn-H str.	1627.3	1626.6	535	1577.4	482	1169.4	1155.5	271	1120.6	244	1627.3	1626.6	535	1577.4	482
A" CH_3 bend		1454.0	7	1405.8	7		1055.7	4	1020.9	4		1450.7	7	1402.6	7
A' CH_3 bend		1447.2	3	1400.6	3		1047.6	3	1013.6	3		1444.4	3	1397.9	3
A' CH_3 deform		1195.7	3	1145.1	2		917.9	8	878.7	7		1188.0	2	1137.9	2
A' CH_3 rock	775.7	793.8	48	764.3	39	582.5	599.0	24	577.0	20	770.0	789.0	48	759.6	40
A" CH_3 rock		563.0	3	543.9	2		418.0	2	403.7	1		560.5	3	541.5	1
A' CSnH bend		516.8	25	499.0	22		366.9	11	354.1	9		516.8	25	499.0	22
A' C-Sn str.		445.3	46	436.1	42		409.7	40	401.5	38		432.6	43	423.6	40
A" CH_3 tort		142.4	2	129.5	2		101.3	1	92.0	1		142.4	2	129.4	2

[a] Frequencies and intensities are in cm^{-1} and km/mol. [b] Observed in an argon matrix. [c] Computed with B3LYP/6-311++G(3df, 3pd)/SDD. [d] Computed with BPW91/6-311++G(3df,3pd)/SDD.

Table S2: Calculated Fundamental Frequencies of CH_2=SnH_2 isotopomers in the Ground $^1A_1$ state[a]

Approximate Description	CH_2=SnH_2				CD_2=SnD_2				$^{13}CH_2$=SnH_2			
	B3LYP[b]	Int[b]	BPW91[c]	Int[c]	B3LYP[b]	Int[b]	BPW91[c]	Int[c]	B3LYP[b]	Int[b]	BPW91[c]	Int[c]
B_2 CH_2 str.	3268.1	0	3214.0	0	2433.3	1	2393.4	1	3254.6	0	3200.7	0
A_1 CH_2 str.	3159.9	1	3100.9	1	2287.4	0	2243.8	0	3154.5	2	3095.7	1
B_2 SnH_2 str.	1930.4	173	1871.2	159	1372.8	90	1330.7	82	1930.4	173	1871.2	159
A_1 SnH_2 str.	1925.1	57	1857.5	52	1365.1	30	1317.3	28	1925.0	57	1857.5	52
A_1 CH_2 scis.	1372.9	0	1321.7	0	1038.6	1	999.4	0	1366.9	0	1315.9	0
B_2 CH_2 rock	758.3	62	736.7	54	582.0	42	565.0	37	753.0	60	731.6	53
A_1 C-Sn str.	738.6	7	711.5	5	666.7	4	644.7	3	726.8	23	698.6	18
A_1 SnH_2 scis.	698.3	64	671.7	58	506.2	34	485.5	31	688.5	45	663.7	45
B_1 CH_2 wag	691.8	21	655.4	21	520.2	16	492.0	16	688.4	23	652.3	21
A_2 CH_2 twist	648.0	0	629.3	0	458.4	0	445.1	0	648.0	0	629.3	0
B_2 SnH_2 rock	387.9	34	371.9	28	278.0	17	266.6	14	387.7	34	371.7	28
B_1 SnH_2 wag	225.3	21	172.6	16	169.5	13	129.7	10	224.3	21	171.9	16

[a] Frequencies and intensities are in cm^{-1} and km/mol. [b] Computed with B3LYP/6-311++G(3df, 3pd)/SDD. [c] Computed with BPW91/6-311++G(3df,3pd)/SDD. CH_2=SnH_2 is not identified in the product spectra while it has a C_{2v} structure.

Table S3: Observed and Calculated Fundamental Frequencies of CH_3-PbH isotopomers in the Ground ^{1}A' state[a]

Approximate Description	CH_3-PbH					CD_3-PbH					$^{13}CH_3$-PbH				
	Obs[b]	B3LYP[c]	Int[c]	BPW91[d]	Int[d]	Obs[b]	B3LYP[c]	int[c]	BPW91[d]	Int[d]	Obs[b]	B3LYP[c]	int[c]	BPW91[d]	Int[d]
A' CH_3 as. str.		3126.9	16	3083.2	15		2316.9	6	2284.4	6		3115.5	17	3071.9	15
A" CH_3 as. str.		3095.7	24	3050.4	20		2289.0	12	2255.1	10		3084.8	24	3039.7	20
A' CH_3 s. str.		3024.4	25	2972.9	19		2165.1	9	2128.0	7		3021.6	25	2970.1	19
A' Pb-H str.	1505.0	1547.4	600	1512.5	530	1079.6	1097.3	302	1072.5	267	1505.1	1547.4	600	1512.5	530
A" CH_3 bend		1453.9	5	1406.4	5		1056.4	3	1021.9	3		1450.5	5	1403.1	5
A' CH_3 bend		1449.5	3	1403.5	3		1050.3	2	1016.7	2		1446.5	3	1400.7	3
A' CH_3 deform		1175.8	2	1128.3	2		899.4	2	862.5	1		1168.6	3	1121.4	3
A' CH_3 rock		766.3	29	740.6	24		575.9	15	556.9	12		761.8	29	736.2	24
A" CH_3 rock		575.9	0	559.7	0		426.6	0	414.6	0		573.4	0	557.2	0
A' CPbH bend		495.3	24	480.0	21		374.3	39	368.2	36		495.3	24	480.0	20
A' C-Pb str.		406.9	42	399.9	38		351.0	9	340.1	7		394.5	39	387.7	36
A" CH_3 tort		108.8	6	103.3	6		77.2	3	73.3	3		108.8	6	103.3	6

[a] Frequencies and intensities are in cm^{-1} and km/mol. [b] Observed in an argon matrix. [c] Computed with B3LYP/6-311++G(3df, 3pd)/SDD. [d] Computed with BPW91/6-311++G(3df,3pd)/SDD.

Table S4: Calculated Fundamental Frequencies of CH_2=PbH_2 isotopomers in the Ground ^{1}A' state[a]

Approximate Description	CH_2=PbH_2				CD_2=PbD_2				$^{13}CH_2$=PbH_2			
	B3LYP[b]	Int[b]	BPW91[c]	Int[c]	B3LYP[b]	Int[b]	BPW91[c]	Int[c]	B3LYP[b]	Int[b]	BPW91[c]	Int[c]
A" CH_2 str.	3255.6	0	3194.2	0	2424.1	1	2378.2	0	3242.1	0	3181.0	0
A' CH_2 str.	3143.6	4	3079.0	4	2273.9	1	2226.6	1	3138.4	4	3073.9	4
A" PbH_2 str.	1859.2	212	1794.1	197	1319.0	107	1272.8	100	1859.1	212	1794.0	197
A' PbH_2 str.	1839.8	80	1763.0	80	1304.1	42	1249.9	41	1839.7	80	1762.9	80
A' CH_2 scis.	1378.9	2	1331.6	3	1031.8	0	995.8	1	1373.6	2	1326.5	3
A" CH_2 rock	805.3	48	780.7	42	605.6	33	586.1	29	801.1	46	776.8	41
A' PbH_2 scis.	745.7	63	719.3	62	540.2	46	523.4	45	742.0	67	715.8	65
A' C-Pb str.	653.4	41	628.3	35	611.1	5	586.2	4	636.4	43	612.1	37
A" CH_2 twist	618.3	3	596.6	3	441.1	1	426.0	1	617.7	3	595.9	3
A' CH_2 wag	612.0	35	580.7	36	444.8	27	423.6	27	609.1	28	577.6	30
A" PbH_2 rock	359.9	35	343.0	28	257.9	18	245.8	15	359.6	35	342.7	28
A' PbH_2 wag	252.1	45	274.9	35	189.1	27	205.1	20	250.7	45	273.5	35

[a] Frequencies and intensities are in cm^{-1} and km/mol. [b] Computed with B3LYP/6-311++G(3df, 3pd)/SDD. [c] Computed with BPW91/6-311++G(3df,3pd)/SDD. CH_2=PbH_2 is not identified in the product spectra while it has a C_s structure.

Table S5: Observed and Calculated Fundamental Frequencies of CH_3-SbH isotopomers in the Ground ^{2}A" state[a]

Approximate Description	CH_3-SbH					CD_3-SbD					$^{13}CH_3$-SbH				
	Obs[b]	B3LYP[c]	Int[c]	BPW91[d]	Int[d]	Obs[b]	B3LYP[c]	int[c]	BPW91[d]	Int[d]	Obs[b]	B3LYP[c]	int[c]	BPW91[d]	Int[d]
A' CH_3 as. str.		3140.5	7	3095.0	6		2327.6	3	2293.9	2		3128.9	7	3084.1	6
A" CH_3 as. str.		3130.8	7	3084.6	5		2319.0	3	2284.4	2		3119.4	7	3073.3	5
A' CH_3 s. str.		3047.8	15	2995.6	12		2181.1	6	2143.5	5		3045.1	15	2993.0	12
A' Sb-H str.	1842.0	1924.2	244	1870.1	212	1323.1	1366.7	123	1328.4	108	1842.0	1924.2	244	1870.1	212
A' CH_3 bend		1463.5	4	1417.8	4		1059.7	3	1026.4	3		1460.7	4	1415.0	4
A" CH_3 bend	1413.9	1462.7	4	1416.3	4		1060.6	2	1027.0	2	1410.3	1459.5	4	1413.3	4
A' CH_3 deform	1199.4	1239.3	2	1190.9	2		947.9	0	910.6	0	1192.9	1231.9	3	1183.9	3
A' CH_3 rock	828.2	862.2	31	833.3	27	627.7	649.6	17	628.0	14	817.1	857.1	31	828.4	27
A" CH_3 rock		719.7	1	698.8	2		535.1	0	519.5	1		716.4	1	695.5	2
A' CSbH bend	555.8	568.7	7	551.7	5		401.5	8	389.4	6		568.3	8	551.3	6
A' C-Sb str.	505.2	488.1	21	479.7	20	470.6	453.6	13	446.0	13	488.4	474.2	19	466.0	18
A" CH_3 tort		154.4	1	144.6	1		109.5	0	102.5	0		154.4	1	144.6	1

[a] Frequencies and intensities are in cm^{-1} and km/mol. [b] Observed in an argon matrix. [c] Computed with B3LYP/6-311++G(3df, 3pd)/SDD. [d] Computed with BPW91/6-311++G(3df,3pd)/SDD.

Table S6: Calculated Fundamental Frequencies of CH_2-SbH_2 isotopomers in the Ground ^{2}A' state[a]

Approximate Description	CH_2-SbH_2				CD_2-SbD_2				$^{13}CH_2$-SbH_2			
	B3LYP[b]	Int[b]	BPW91[c]	Int[c]	B3LYP[b]	Int[b]	BPW91[c]	Int[c]	B3LYP[b]	Int[b]	BPW91[c]	Int[c]
A" CH_2 str.	3243.8	1	3193.3	1	2415.4	0	2378.0	0	3230.4	1	3180.0	1
A' CH_2 str.	3130.2	10	3076.3	10	2263.0	5	2223.4	5	3125.1	10	3071.3	10
A" SbH_2 str.	1942.1	209	1887.7	178	1379.9	106	1341.2	91	1942.1	209	1887.7	178
A' SbH_2 str.	1933.1	173	1871.5	153	1372.5	89	1328.9	78	1933.1	173	1871.5	153
A' CH_2 scis.	1366.9	9	1320.3	10	1019.8	2	984.9	3	1361.5	10	1315.2	10
A' SbH_2 scis.	834.6	41	797.5	34	595.7	22	570.4	18	834.5	41	797.3	34
A" CH_2 rock	801.0	13	777.2	11	605.4	7	587.5	6	796.4	13	772.7	11
A' CH_2 wag	643.0	24	617.6	18	518.0	1	505.9	1	638.8	25	612.9	19
A" CH_2 twist	541.0	1	526.4	1	383.4	1	372.9	0	540.9	1	526.3	0
A' C-Sb str.	534.6	27	521.3	25	463.1	35	444.3	30	520.0	25	507.5	23
A' SbH_2 wag	438.4	28	425.2	27	329.1	13	318.4	13	435.9	28	422.8	27
A" SbH_2 rock	106.6	0	119.1	0	75.5	0	84.3	0	106.6	0	119.1	0

[a] Frequencies and intensities are in cm^{-1} and km/mol. [b] Computed with B3LYP/6-311++G(3df, 3pd)/SDD. [c] Computed with BPW91/6-311++G(3df,3pd)/SDD. CH_2-SbH_2 is not identified in the product spectra while it has a C_s structure.

Table S7: Observed and Calculated Fundamental Frequencies of CH_3-BiH isotopomers in the Ground ^{2}A" state[a]

Approximate Description	CH_3-BiH					CD_3-BiD					$^{13}CH_3$-BiH				
	Obs[b]	B3LYP[c]	Int[c]	BPW91[d]	Int[d]	Obs[b]	B3LYP[c]	int[c]	BPW91[d]	Int[d]	Obs[b]	B3LYP[c]	int[c]	BPW91[d]	Int[d]
A' CH_3 as. str.		3147.7	7	3102.3	6		2333.7	3	2299.7	2		3136.0	7	3090.8	6
A" CH_3 as. str.		3144.4	6	3097.9	5		2330.1	2	2295.3	2		3132.8	6	3086.5	5
A' CH_3 s. str.		3052.0	18	2999.9	14		2182.5	8	2145.0	6		3049.6	18	2997.5	14
A' Bi-H str.	1664.0	1814.2	332	1772.8	282	1194.1	1286.5	167	1257.1	142	1664.0	1814.2	332	1772.8	282
A' CH_3 bend		1459.0	4	1413.7	4		1058.0	3	1024.9	3		1456.0	3	1410.7	3
A" CH_3 bend		1455.9	3	1410.0	3		1057.1	2	1023.7	2		1452.6	3	1406.8	3
A' CH_3 deform	1150.5	1202.9	8	1155.6	7		922.9	1	886.4	1	1144.1	1195.4	9	1148.5	8
A' CH_3 rock	796.6	810.6	20	784.9	17	594.5	608.0	11	588.9	9		806.1	20	780.5	17
A" CH_3 rock		692.8	4	673.4	4		513.0	2	498.7	2		689.8	4	670.5	4
A' CBiH bend		516.8	7	501.6	5		364.5	8	353.6	7		516.4	8	501.1	6
A' C-Bi str.	448.7	460.1	25	451.9	23		424.5	16	417.4	14	426.2	446.4	22	438.5	21
A" CH_3 tort		130.3	4	124.4	4		92.3	2	88.1	2		130.3	4	124.4	4

[a] Frequencies and intensities are in cm^{-1} and km/mol. [b] Observed in an argon matrix. [c] Computed with B3LYP/6-311++G(3df, 3pd)/SDD. [d] Computed with BPW91/6-311++G(3df,3pd)/SDD.

Table S8: Calculated Fundamental Frequencies of CH_2-BiH_2 isotopomers in the Ground ^{2}A' state[a]

Approximate Description	CH_2-BiH_2				CD_2-BiD_2				$^{13}CH_2$-BiH_2			
	B3LYP[c]	Int[c]	BPW91[d]	Int[d]	B3LYP[c]	int[c]	BPW91[d]	Int[d]	B3LYP[c]	int[c]	BPW91[d]	Int[d]
A" CH_2 str.	3245.2	2	3196.9	2	2417.4	0	2381.8	0	3231.6	2	3183.4	2
A' CH_2 str.	3123.1	14	3071.0	13	2256.4	6	2218.1	6	3118.2	14	3066.2	13
A" BiH_2 str.	1813.6	309	1769.1	260	1286.2	156	1254.6	131	1813.6	309	1769.1	260
A' BiH_2 str.	1801.2	283	1753.3	243	1277.0	143	1243.1	123	1801.2	283	1753.3	243
A' CH_2 scis.	1347.3	31	1301.8	30	1006.8	9	972.6	9	1341.7	32	1296.4	30
A' BiH_2 scis.	754.9	28	723.0	22	537.4	15	515.7	12	754.8	28	722.8	21
A" CH_2 rock	742.7	8	722.7	7	560.2	5	545.1	4	738.4	8	718.5	7
A' CH_2 wag	579.8	24	557.3	16	426.1	31	408.2	26	576.9	26	554.1	19
A' C-Bi str.	507.1	35	495.3	32	476.6	12	466.5	9	492.0	32	480.9	27
A" CH_2 twist	496.1	0	484.1	0	351.2	0	342.7	0	496.0	0	484.1	0
A' BiH_2 wag	399.5	36	388.0	36	300.6	19	291.7	19	397.0	35	385.6	35
A" BiH_2 rock	30.7	1	58.2	0	21.7	0	41.2	0	30.7	1	58.2	0

[a] Frequencies and intensities are in cm^{-1} and km/mol. [b] Computed with B3LYP/6-311++G(3df, 3pd)/SDD. [c] Computed with BPW91/6-311++G(3df,3pd)/SDD. CH_2-BiH_2 is not identified in the product spectra while it has a C_s structure.

Table S10: Natural Occupation Numbers and Effective C-M Bond Orders for Sn, Pb, Sb, and Bi Insertion and Methylidene Complexes and Metal Contribution to the C-M and M-H bonds[a]

Compound	σ occ[b]	σ* occ[b]	EBO(C-M)[c]	q(C)[d]	q(M)[d]	C-M (%M)[e]	M-H (%M)[e]
CH_3-SnH	1.927	0.096	0.916	-1.174	0.958	22.43, s(8.3), p(91.7)	29.05, s(8.0), p(92.0)
CH_2=SnH_2	3.975	0.027	1.974	-1.083	1.182	34.62, s(0.0), p(100.0) 30.77, s(39.2), p(60.8)	37.16, s(30.5), p(69.5) 37.16, s(30.5), p(69.5)
CH_3-PbH	1.995	0.002	0.997	-1.127	0.931	23.63, s(6.2), p(93.8)	29.25, s(6.2), p(93.7)
CH_2=PbH_2	3.929	0.686	1.930	-0.961	1.020	33.77, s(1.2), p(98.8) 35.79, s(39.9), p(60.1)	38.75, s(29.6), p(70.4) 38.75, s(29.6), p(70.4)
CH_3-SbH	1.995	0.002	0.997	-1.023	0.621	30.82, s(8.7), p(91.3)	38.3, s(8.9), p(91.1)
CH_2-SbH_2	1.993	0.005	0.994	-0.736	0.756	33.21, s(11.2), p(88.8)	40.75, s(10.4), p(89.6) 40.75, s(10.4), p(89.6)
CH_3-BiH	1.996	0.001	0.998	-1.001	0.636	30.94, s(6.2), p(93.8)	37.37, s(6.5), p(93.5)
CH_2-BiH_2	1.994	0.004	0.995	-0.701	0.781	32.52, s(7.5), p(92.5)	39.70, s(7.1), p(92.9) 39.70, s(7.1), p(92.9)

[a] Computed with B3LYP/6-311++G(3df, 3pd). The SDD core potentials and bases are used for Sn, Pb, Sb, and Bi. [b] Occupation number. [c] Effective bond order [(σ occ – σ* occ)/2]. [d] Natural charge. [e] Metal contribution to the bonding orbital in %.

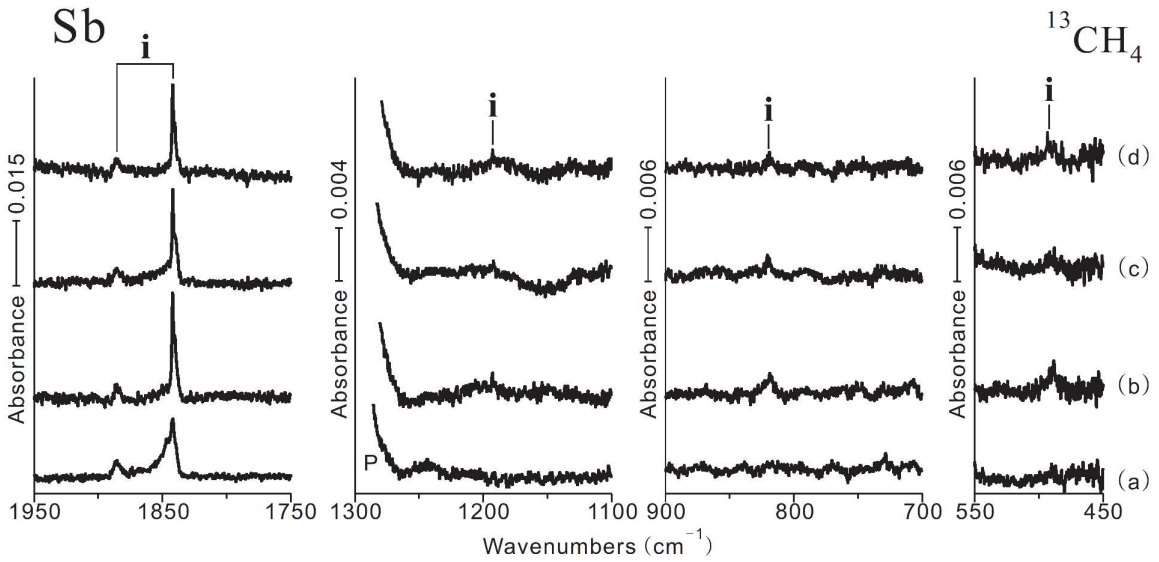

Figure S1. Infrared spectra in the product absorption regions from reaction of the laser-ablated antimony atom with $^{13}CH_4$ in excess argon at 4 K. (a) Sb and $^{13}CH_4$ (1.0% in argon) co-deposited for 1 hr, (b) as (a) after annealing to 30 K, (c) as (b) after full arc ($\lambda > 220$ nm) irradiation, and (d) as (c) after annealing to 35 K. The product absorptions are marked with "**i**" while P designates the precursor absorption in the $^{13}CH_4$ matrix spectra.

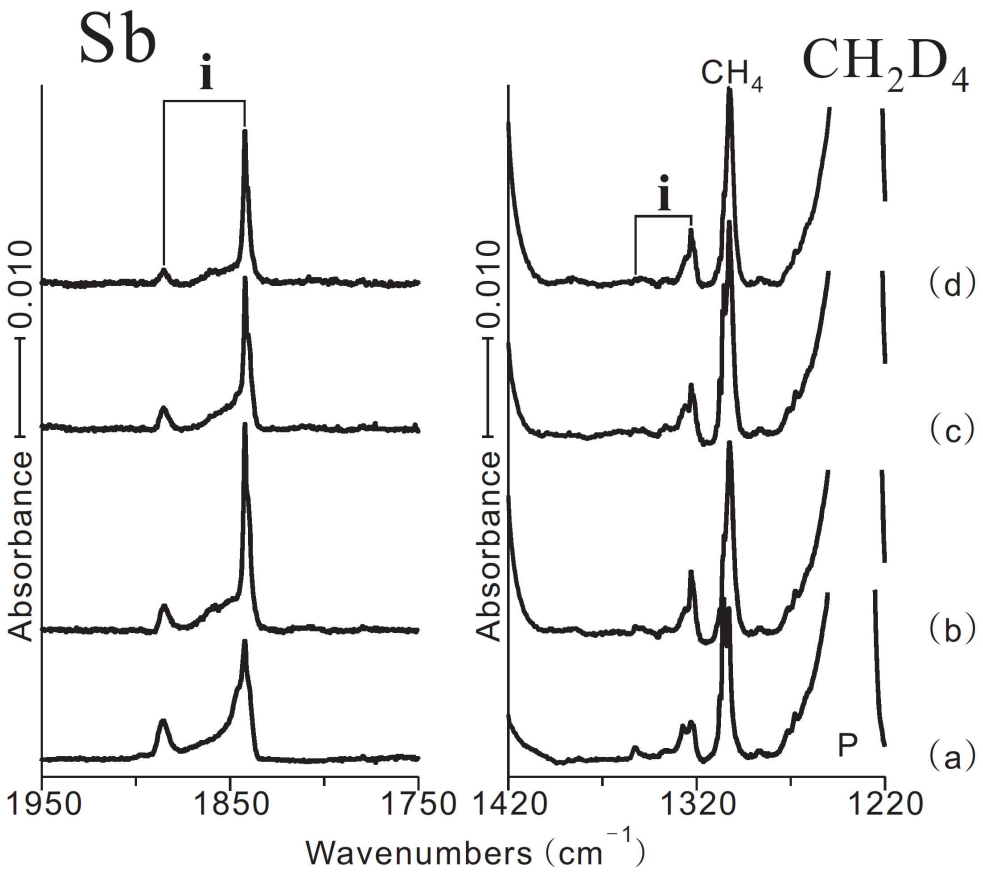

Figure S2. Infrared spectra in the product absorption regions from reaction of the laser-ablated antimony atom with CH_2D_2 in excess argon at 4 K. (a) Sb and CH_2D_2 (3.0% in argon) co-deposited for 1 hr, (b) as (a) after annealing to 30 K, (c) as (b) after full arc ($\lambda > 220$ nm) irradiation, and (d) as (c) after annealing to 35 K. The product absorptions are marked with "**i**" while P designates the precursor absorption in the CH_4 matrix spectra.