Electronic Supplementary Information for DT-ART-12-2010-001827

Infrared Spectra of CH_3-MH, CH_3-M, and CH_3-MH^- Prepared via Methane Activation by Laser-Ablated Au, Ag, and Cu Atoms

by

Han-Gook Cho and Lester Andrews*

*lsa@virginia.edu

Table S1: Observed and Calculated Fundamental Frequencies of CH_3-AuH isotopomers in the Ground ^{2}A' State (C_s structure)[a]

Approximate Description	CH_3-AuH					CD_3-AuH					$^{13}CH_3$-AuH				
	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.		3194.2	1	3135.9	1		2372.0	0	2327.9	0		3181.8	1	3123.8	1
A' CH_3 as. str.		3157.5	3	3098.2	3		2339.5	1	2294.5	1		3146.4	3	3087.4	3
A' CH_3 s. str.		3040.1	1	2978.8	1		2168.9	2	2125.9	1		3037.6	1	2976.3	1
A' Au-H str.	1853.5	1918.4	10	1917.5	7		1360.8	6	1360.1	4		1918.3	10	1917.4	7
A' CH_3 scis.		1446.4	2	1401.0	2		1054.4	1	1020.8	1		1442.6	2	1397.4	2
A" CH_3 scis.		1410.8	3	1361.8	3		1031.0	2	995.1	2		1406.7	3	1357.9	3
A' CH_3 deform	1044.9	1089.7	45	1063.4	26	790.3	825.1	30	808.5	17	1040.2	1084.2	44	1057.8	26
A' CH_3 rock		698.5	22	693.2	18		520.8	11	518.4	9		695.2	22	690.4	18
A" CH_3 rock		692.8	11	682.2	10		507.9	6	500.8	5		690.4	11	679.8	10
A' CAuH bend		419.9	18	424.5	5		295.6	16	394.0	0		418.6	24	424.6	17
A' C-Au str.		402.8	15	424.6	12		378.6	1	301.3	9		391.3	9	411.3	1
A" CH_3 tort		182.0	9	198.8	5		129.3	4	141.2	3		182.0	9	198.8	5

[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. CH_3-AuH has a C_s structure.

Table S2: Observed and Calculated Fundamental Frequencies of CH_3-Au in the Ground $^1A_1$ State (C_{3v} structure)[a]

Approximate Description	CH_3-Au					CD_3-Au					$^{13}CH_3$-Au				
	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]
E CH_3 str.		3161.0	1 x 2	3102.5	1 X 2		2345.2	0 x 2	2301.3	0 x 2		3149.1	1 x 2	3090.8	1 x 2
A_1 CH_3 str.		3054.4	11	2991.7	9		2179.4	7	2134.7	6		3052.4	11	2989.8	9
E CH_3 scis.		1450.9	1 x 2	1403.0	1 x 2		1055.7	1 x 2	1020.9	1 x 2		1447.3	1 x 2	1399.6	1 x 2
A_1 CH_3 deform	1181.7	1199.5	55	1164.2	45	920.5	922.2	33	897.3	28	1173.3	1192.2	54	1157.1	44
E CH_3 rock	794.5	803.4	29 x 2	788.5	25 x 2	584.0	594.0	16 x 2	582.7	13 x 2	790.6	799.9	29 x 2	784.1	25 x 2
A_1 C-Au str.		527.1	0	538.4	1		484.2	0	493.3	0		510.9	0	521.9	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. CH_3-Au has a C_{3v} structure.

Table S3: Observed and Calculated Fundamental Frequencies of CH_3-AuH^- isotopomers in the Ground $^1A_1$ State (C_{3v} structure)[a]

Approximate Description	CH_3-AuH^-					CD_3-AuD^-					$^{13}CH_3$-AuH^-				
	Obs[b]	B3LYP[c]	Int[c]	MP2	int	Obs[b]	B3LYP[c]	int[c]	MP2	int	Obs[b]	B3LYP[c]	int[c]	MP2	int
E CH_3 str.		3009.9	77 x 2	3079.0	56 x 2		2221.5	36 x 2	2276.5	26 x 2		2993.5	78 x 2	3068.3	57 x 2
A_1 CH_3 str.		2951.4	165	2999.4	139		2113.3	72	2149.1	60		2948.8	167	2996.6	140
A_1 Au-H str.	1868.7	1843.7	683	1992.2	459	1341.5	1307.1	336	1412.9	222	1868.7	1848.7	684	1992.0	461
E CH_3 scis.		1455.5	0 x 2	1457.5	0 x 2		1056.6	0 x 2	1056.5	0 x 2		1452.4	0 x 2	1454.4	0 x 2
A_1 CH_3 deform		1145.2	1	1153.4	7	858	884.4	10	895.6	20		1137.4	0	1145.2	6
E CH_3 rock	726.6	722.2	23 x 2	756.3	19 x 2	553.4	544.4	13 x 2	571.4	10 x 2	722.8	717.5	22 x 2	751.8	18 x 2
E CAuH bend		491.1	11 x 2	481.8	7 x 2		349.0	5 x 2	342.6	3 x 2		491.0	11 x 2	481.7	7 x 2
A_1 C-Au str.		453.7	50	483.9	42		413.5	39	438.2	31		440.2	47	469.8	39

[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 MP2/6-311++G(3df,3pd)/SDD. CH_3-AuH^- has a C_{3v} structure with MP2, but a near C_{3v} structure with B3LYP and BPW91.

Table S4: Calculated Fundamental Frequencies of CH_3-AgH isotopomers in the Ground $^2A'$ State (C_s structure)[a]

Approximate Description	CH_3-AgH					CD_3-AgH					$^{13}CH_3$-AgH				
	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.		3214.3	0	3150.4	1		2388.4	0	2339.5	0		3201.7	0	3138.2	1
A' CH_3 as. str.		3185.6	1	3120.5	2		2364.3	0	2314.3	1		3173.6	1	3109.0	2
A' CH_3 s. str.		3059.4	1	2996.2	2		2177.5	2	2134.3	2		3057.7	1	2994.4	2
A' Ag-H str.		1622.3	17	1644.6	13		1152.7	9	1168.6	7		1622.2	17	1644.6	13
A' CH_3 scis.		1436.4	1	1398.5	1		1049.7	1	1017.3	1		1432.2	1	1389.6	1
A" CH_3 scis.		1412.1	3	1366.7	3		1033.6	2	999.7	2		1407.8	2	1362.6	2
A' CH_3 deform		985.2	101	980.6	60		745.5	70	746.9	39		980.1	98	975.2	58
A" CH_3 rock		590.4	14	595.7	15		430.9	8	440.4	19		588.7	14	593.8	15
A' CH_3 rock		580.0	36	592.0	36		429.4	19	436.1	8		577.7	36	589.5	36
A' CAgH bend		347.0	8	376.6	1		319.4	3	349.6	1		339.6	15	366.5	3
A' C-Ag str.		307.5	109	343.4	68		223.5	57	245.4	33		304.7	101	342.5	66
A" CH_3 tort		84.2	38	77.2	29		59.9	19	55.0	15		84.2	38	77.3	29

[a] Frequencies and intensities are in cm^{-1} and km/mol. [b] Not 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. CH_3-AgH is not identified while it has a C_s structure.

Table S5: Observed and Calculated Fundamental Frequencies of CH_3-Ag in the Ground $^1A_1$ State (C_{3v} structure)[a]

Approximate Description	CH_3-Ag					CD_3-Ag					$^{13}CH_3$-Ag				
	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]
E CH_3 str.		3166.0	3 x 2	3113.0	3 x 2		2348.1	0 x 2	2308.4	0 x 2		3154.1	3 x 2	3101.4	3 x 2
A_1 CH_3 str.		3059.7	23	3001.9	16		2182.9	13	2141.8	10		3057.7	22	3000.0	16
E CH_3 scis.		1448.6	0 x 2	1402.0	0 x 2		1054.5	1 x 2	1020.5	1 x 2		1445.0	0 x 2	1398.5	0 x 2
A_1 CH_3 deform	1076.4	1097.7	69	1066.4	56	824.1	845.4	35	822.4	28	1069.3	1090.6	69	1059.5	56
E CH_3 rock	666.1	693.6	52 x 2	685.1	45 x 2	499.1	512.7	31 x 2	506.8	26 x 2	663.6	690.7	51 x 2	682.2	44 x 2
A_1 C-Ag str.		445.2	2	450.2	1		410.4	3	414.4	2		432.5	2	437.3	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. CH_3-Ag has a C_{3v} structure.

Table S6: Observed and Calculated Fundamental Frequencies of CH_3-AgH^- isotopomers in the Ground $^1A_1$ State (C_{3v} structure)[a]

Approximate Description	CH_3-AgH^-					CD_3-AgH^-					$^{13}CH_3$-AgH^-				
	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]
E CH_3 str.		3010.6	77 x 2	2962.2	74 x 2		2226.2	33 x 2	2189.8	32 x 2		3000.1	78 x 2	2951.9	75 x 2
A_1 CH_3 str.		2953.7	165	2897.8	175		2114.5	71	2074.9	76		2951.1	167	2895.2	177
A_1 Ag-H str.	1562.0	1554.5	615	1575.5	587	1124.2	1103.9	308	1118.8	293	1562.0	1554.5	615	1575.5	588
E CH_3 scis.		1452.8	0 x 2	1407.9	0 x 2		1055.2	0 x 2	1022.1	0 x 2		1449.5	0 x 2	1404.8	0 x 2
A_1 CH_3 deform		1095.3	4	1062.3	2		846.3	13	821.8	9		1087.7	3	1054.9	1
E CH_3 rock		622.9	75 x 2	619.3	61 x 2		471.0	42 x 2	469.1	33 x 2		619.3	74 x 2	615.7	60 x 2
A_1 C-Ag str.		417.5	38	422.7	36		382.3	28	386.6	26		415.7	51	411.0	33
E CAgH bend		415.7	51 x 2	415.4	37 x 2		296.1	24 x 2	295.9	17 x 2		405.8	35 x 2	415.4	37 x 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. CH_3-AgH^- has a C_{3v} structure.

Table S7: Observed and Calculated Fundamental Frequencies of CH_3-CuH isotopomers in the Ground ^{2}A' State (C_s structure)[a]

Approximate Description	CH_3-CuH					CD_3-CuH					$^{13}CH_3$-CuH				
	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.		3165.0	3	3113.8	2		2347.7	0	2309.5	0		3153.0	3	3102.1	2
A' CH_3 as. str.		3133.1	5	3080.5	4		2320.0	2	2280.5	1		3122.2	6	3069.8	4
A' CH_3 s. str.		3024.5	5	2966.1	3		2159.1	4	2117.3	2		3022.1	4	2963.7	3
A' Cu-H str.	1718.8	1707.5	33	1704.1	18	1243.7	1216.9	18	1214.6	9	1717.7	1707.5	33	1704.1	17
A' CH_3 scis.		1439.4	1	1392.0	1		1048.4	1	1013.8	1		1435.7	1	1388.5	1
A" CH_3 scis.		1411.4	2	1359.2	3		1029.7	2	992.1	2		1407.5	2	1355.5	2
A' CH_3 deform	1012.1	1050.3	68	1017.9	38	786.0	810.8	40	790.9	21	1003.6	1043.5	67	1010.9	37
A' CH_3 rock	covered	623.2	53	605.4	48		473.0	27	464.5	22	covered	620.0	53	602.1	48
A" CH_3 rock		599.8	21	581.0	19		443.6	12	429.6	11		597.4	20	578.7	18
A' CCuH bend		463.0	1	471.2	1		425.3	2	426.0	4		450.8	1	459.1	1
A' C-Cu str.		382.2	70	364.1	50		272.8	36	259.9	25		382.2	70	364.1	50
A" CH_3 tort		150.4	47	95.6	37		107.6	25	68.8	19		150.4	47	95.6	37

[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). [d] Computed with BPW91/6-311++G(3df,3pd). CH_3-CuH has a C_s structure.

Table S8: Observed and Calculated Fundamental Frequencies of CH_3-Cu in the Ground $^1A_1$ State (C_{3v} structure)[a]

Approximate Description	CH_3-Cu					CD_3-Cu					$^{13}CH_3$-Cu				
	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]
E CH_3 str.		3128.1	5 x 2	3076.4	4 x 2		2317.6	1 x 2	2279.1	1 x 2		3116.7	5 x 2	3065.1	4 x 2
A_1 CH_3 str.		3032.9	24	2974.3	18		2166.5	13	2124.2	10		3030.7	23	2972.2	17
E CH_3 scis.		1444.1	0 x 2	1394.5	0 x 2		1049.5	1 x 2	1013.3	1 x 2		1440.7	0 x 2	1391.2	0 x 2
A_1 CH_3 deform	1203.0	1120.9	42	1082.7	38	920.0	876.3	19	851.6	17	1195.1	1003.6	43	1074.4	38
E CH_3 rock	648.3	662.7	52 x 2	650.0	46 x 2	494.2	494.0	32 x 2	484.9	28 x 2	645	659.5	51 x 2	646.8	45 x 2
A_1 C-Au str.		525.7	4	541.0	3		480.1	5	491.2	4		512.4	3	527.5	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).

[d] Computed with BPW91/6-311++G(3df,3pd). CH_3-Cu has a C_{3v} structure. The four lowest frequencies computed with MP2/6-311++G(3df,3pd) are 1453 cm^{-1}(0.3x2km/mol), 1150(63), 679(67), 564 (15).

Table S9: Observed and Calculated Fundamental Frequencies of CH_3-CuH^- isotopomers in the Ground $^1A_1$ State (C_{3v} structure)[a]

Approximate Description	CH_3-CuH^-					CD_3-CuH^-					$^{13}CH_3$-CuH^-				
	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]
E CH_3 str.		2975.9	89 x 2	2924.1	84 x 2		2198.8	39 x 2	2160.0	37 x 2		2965.7	90 x 2	2914.1	85 x 2
A_1 CH_3 str.		2927.7	163	2867.8	187		2097.2	71	2054.4	83		2924.9	166	2865.1	189
A_1 Cu-H str.	1612.9	1606.1	529	1629.7	493	1165.0	1143.9	264	1160.6	245	1612.9	1606.1	530	1629.7	493
E CH_3 scis.		1446.3	0 x 2	1399.2	0 x 2		1049.8	0 x 2	1015.2	0 x 2		1443.0	0 x 2	1396.1	0 x 2
A_1 CH_3 deform		1107.4	12	1071.7	6		860.0	21	834.4	14		1099.4	10	1063.8	5
E CH_3 rock		612.8	85 x 2	609.6	63 x 2		468.2	45 x 2	466.4	33 x 2		609.2	85 x 2	605.9	63 x 2
A_1 C-Cu str.		462.1	23	473.2	20		423.2	15	432.2	12		450.4	22	461.2	18
E CCuH bend		406.9	48 x 2	401.4	33 x 2		291.0	22 x 2	287.1	15 x 2		406.8	48 x 2	401.4	33 x 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). [d] Computed with BPW91/6-311++G(3df,3pd). CH_3-CuH^- has a C_{3v} structure.

Table S10: Natural Occupation Numbers and Effective Bond Orders of the C-M bond for Group 11 Metal Complexes[a]

Compound	σ occ[b]	σ* occ[b]	%C[c]	%M[c]	q(C)[d]	q(M)[d]	EBO[e]
CH_3-AuH	1.92706	0.09588	58.96, s(14.1), p(85.8)	41.04, s(41.8), p(24.1), d(34.0)	-0.625	0.031	0.916
CH_3-Au	1.99837	0.00891	56.46, s(14.5), p(85.4)	43.54, s(80.4), p(0.1), d(19.5)	-0.750	0.159	0.995
CH_3-AuH^-	1.89010	0.15201	82.06, s(24.8), p(75.2)	17.94, s(42.3), p(47.0), d(10.4)	-1.108	0.019	0.869
CH_3-AgH	1.89331	0.09731	58.88, s(12.5), p(87.5)	41.12, s(44.6), p(24.6), d(30.8)	-0.749	0.411	0.898
CH_3-Ag	1.99826	0.00502	66.91, s(13.5), p(86.5)	33.09, s(93.1), p(0.1), d(6.8)	-0.923	0.351	0.997
CH_3-AgH^-	1.92383	0.10141	85.02, s(24.9), p(75.1)	14.98, s(47.3), p(47.1), d(5.6)	-1.167	0.202	0.911
CH_3-CuH	1.93819	0.06763	65.55, s(16.2), p(83.7)	34.45, s(45.5), p(24.0), d(30.5)	-0.667	0.148	0.935
CH_3-Cu	1.99881	0.00292	70.32, s(15.9), p(84.1)	29.68, s(91.2), p(0.2), d(8.6)	-1.010	0.420	0.998
CH_3-CuH^-	1.94457	0.07638	85.97, s(28.1), p(71.9)	14.03, s(49.2), p(45.2), d(5.5)	-1.204	0.250	0.934

[a] Computed with B3LYP/6-311++G(3df, 3pd). The SDD core potentials and bases are used for Au and Ag, whereas all electron basis for Cu. [b] Occupation number. [c] Contribution to the bonding orbital in %. [d] Natural charge. Additional charges for CH_3-AuH^- include q(H) = -0.413 and q(3H = 3 x 0.167). [e] Effective bond order [(σ occ – σ* occ)/2].

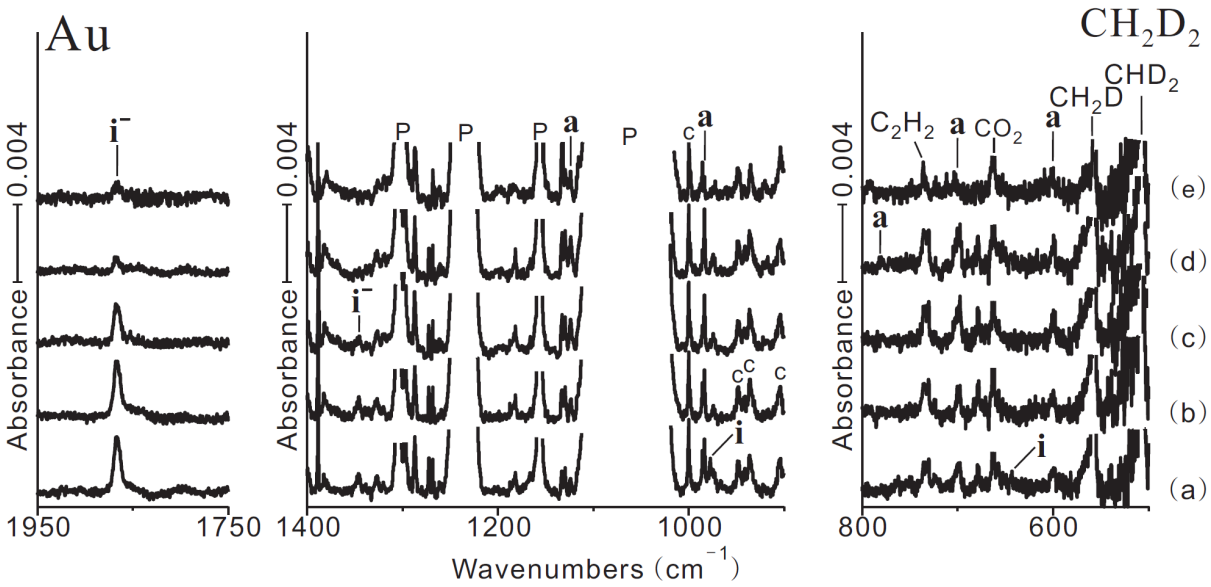

Figure S1. Infrared spectra in the 1950-1750, 1400-900, and 800-500 cm^{-1} regions for the reaction products of the laser-ablated gold with CH_2D_2 in excess argon at 8 K. (a) Au and CH_2D_2 (2.0 % in argon) co-deposited for 1 h, (b)-(d) as (a) after visible, uv, and full arc irradiation, and (e) as (d) after annealing to 26 K. **a**, **i**, and $\mathbf{i}^-$ stand for product absorption groups while P and c stand for the precursor and common absorptions.

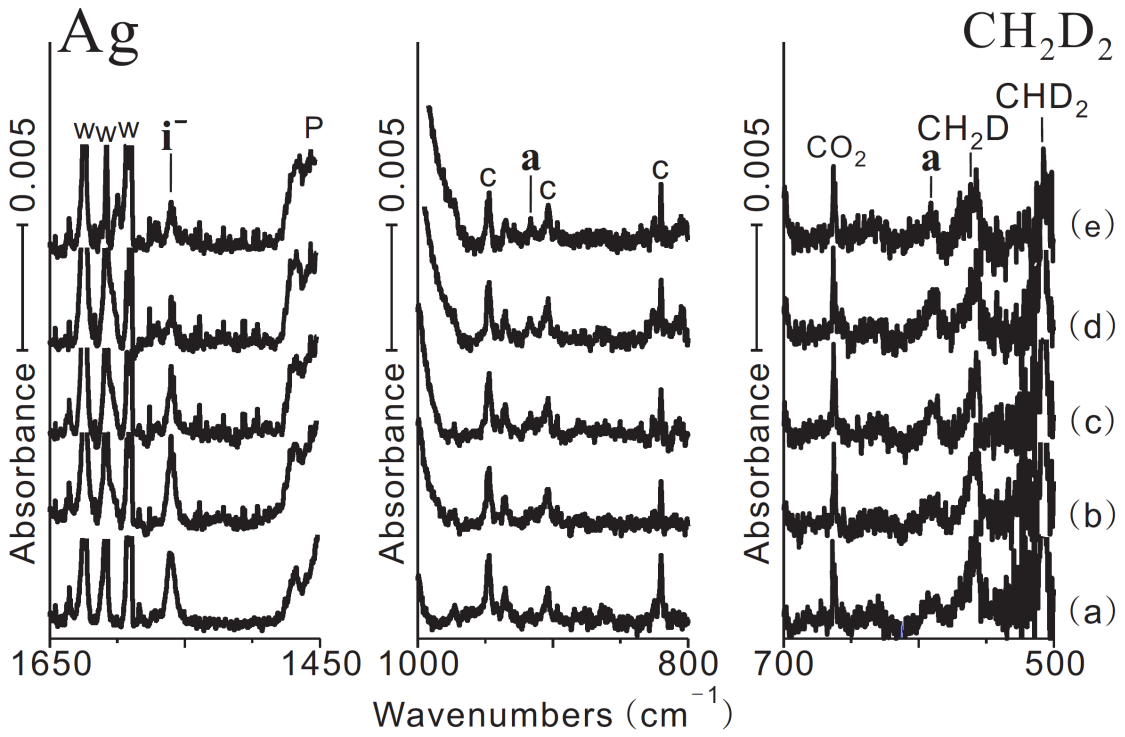

Figure S2. Infrared spectra in the 1650-1450, 1000-800, and 700-500 cm^{-1} regions for the reaction products of the laser-ablated silver with CH_2D_2 in excess argon at 8 K. (a) Ag and CH_2D_2 (2.0 % in argon) co-deposited for 1 h, (b)-(d) as (a) after visible, uv, and full arc irradiation, and (e) as (d) after annealing to 26 K. **a** and $\mathbf{i}^-$ stand for product absorption groups while P, c, and w stand for the precursor, common, and water residue absorptions.

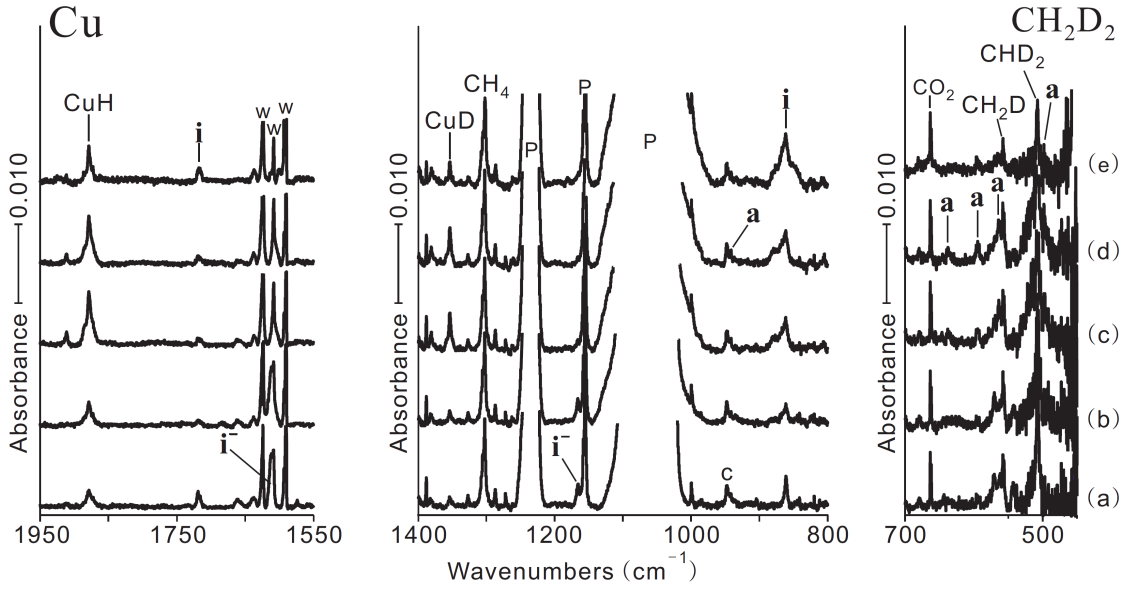

Figure S3. Infrared spectra in the 1950-1550, 1400-800, and 700-500 cm^{-1} regions for the reaction products of the laser-ablated copper with CH_2D_2 in excess argon at 8 K. (a) Cu and CH_2D_2 (2.0 % in argon) co-deposited for 1 h, (b)-(d) as (a) after visible, uv, and full arc irradiation, and (e) as (d) after annealing to 26 K. **a**, **i**, and $\mathbf{i}^-$ stand for product absorption groups while P, c, and w stand for the precursor, common, and water residue absorptions.