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

## Infrared Spectra of CH<sub>3</sub>-MH, CH<sub>3</sub>-M, and CH<sub>3</sub>-MH<sup>-</sup> Prepared via Methane Activation by

## Laser-Ablated Au, Ag, and Cu Atoms

by

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Approximate		СӉ	3-AuH	_			C	<sub>3</sub> -AuH				<sup>13</sup> C	:H <sub>3</sub> -AuF	<b>–</b>	
Description	Obs <sup>b</sup>	B3LYP <sup>c</sup>	$Int^{c}$	BPW91 <sup>d</sup>	Int <sup>d</sup>	Obs <sup>b</sup>	ВЗLYP°	int <sup>c</sup>	BPW91 <sup>d</sup>	Int <sup>d</sup>	Obs <sup>b</sup>	B3LYP <sup>c</sup>	int <sup>c</sup>	BPW91 <sup>d</sup>	Int <sup>d</sup>
A" CH <sub>3</sub> as. str.		3194.2	~	3135.9	-		2372.0	0	2327.9	0		3181.8	-	3123.8	-
A' CH <sub>3</sub> as. str.		3157.5	e	3098.2	с		2339.5	~	2294.5	<del>~</del>		3146.4	ო	3087.4	ო
A' CH <sub>3</sub> s. str.		3040.1	<del>.                                    </del>	2978.8	<del>.                                    </del>		2168.9	2	2125.9	÷		3037.6	-	2976.3	-
A' Au-H str.	1853.5	1918.4	10	1917.5	7		1360.8	9	1360.1	4		1918.3	10	1917.4	7
A' CH <sub>3</sub> scis.		1446.4	2	1401.0	2		1054.4	~	1020.8	÷		1442.6	2	1397.4	7
A" CH <sub>3</sub> scis.		1410.8	б	1361.8	e		1031.0	2	995.1	7		1406.7	e	1357.9	с
A' CH <sub>3</sub> 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 <sub>3</sub> rock		698.5	22	693.2	18		520.8	7	518.4	0		695.2	22	690.4	18
A" CH <sub>3</sub> rock		692.8	1	682.2	10		507.9	9	500.8	5		690.4	1	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	-	301.3	0		391.3	6	411.3	-
A" CH <sub>3</sub> tort		182.0	ი	198.8	5		129.3	4	141.2	б		182.0	6	198.8	£
<sup>a</sup> Frequencies and	d intensiti	es are in	ı cm	<sup>-1</sup> and k	m/mo	.1. <sup>b</sup> Obs	erved in	an ai	rgon mati	rix. °	Compute	ed with ]	B3LY	P/6-311-	++G(3.

Table S1: Observed and Calculated Fundamental Frequencies of CH<sub>3</sub>-AuH isotopomers in the Ground <sup>2</sup>A' State (C<sub>s</sub> structure)<sup>a</sup>

Approximate		CH	l <sub>3</sub> -Au				CI	D <sub>3</sub> -Au				1 <sup>3</sup> C	CH <sub>3</sub> -Au		
Description	Obs <sup>b</sup>	B3LΥP°	Int <sup>c</sup>	BPW91 <sup>d</sup>	Int <sup>d</sup>	Obs <sup>b</sup>	$B3LYP^{c}$	int <sup>c</sup>	BPW91 <sup>d</sup>	Int <sup>d</sup>	Obs <sup>b</sup>	$B3LYP^{c}$	int <sup>c</sup>	BPW91 <sup>d</sup>	Int <sup>d</sup>
E CH <sub>3</sub> 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 <sub>1</sub> CH <sub>3</sub> str.		3054.4	1	2991.7	6		2179.4	7	2134.7	9		3052.4	7	2989.8	6
E CH <sub>3</sub> 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 <sub>3</sub> 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	90.6	799.9	29 x 2	784.1	25 x 2
A <sub>1</sub> C-Au str.		527.1	0	538.4	<del>.</del>		484.2	0	493.3	0		510.9	0	521.9	<del>.                                    </del>
<sup>a</sup> Frequencies and i	ntensities ¿	are in cm	<sup>-1</sup> and	ł km/mo	I. <sup>b</sup> Obs	served in	an argoi	n matr	ix. ° Com	puted v	with B3I	YP/6-31	1++G(	3df, 3pd)/	SDD.

Table S2: Observed and Calculated Fundamental Frequencies of CH<sub>3</sub>-Au in the Ground <sup>1</sup>A<sub>1</sub> State (C<sub>3v</sub> structure)<sup>a</sup>

Computed with BPW91/6-311++G(3df, 3pd)/SDD. CH<sub>3</sub>-Au has a C<sub>3</sub>v structure.

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Approximate		CH <sub>3</sub> -AuH	1			CE	) <sub>3</sub> -AuD <sup>-</sup>				<sup>13</sup> C	H <sub>3</sub> -AuH	1	
Description	Obs <sup>b</sup>	B3LYP <sup>c</sup> Int <sup>c</sup>	MP2	int	Obs <sup>b</sup>	взгүр	int <sup>c</sup>	MP2	int	Obs <sup>b</sup>	Β3LΥΡ <sup>c</sup>	int <sup>c</sup>	MP2	int
E CH <sub>3</sub> str.		3009.9 77 x 2	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 <sub>1</sub> CH <sub>3</sub> str.		2951.4 165	2999.4	139		2113.3	72	2149.1	60		2948.8	167	2996.6	140
A <sub>1</sub> 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 <sub>3</sub> 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	9
E CH <sub>3</sub> rock	726.6	722.2 23 x 2	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	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 <sub>1</sub> C-Au str.		453.7 50	483.9	42		413.5	39	438.2	31		440.2	47	469.8	39
<sup>a</sup> Frequencies and	intensities	are in $\mathrm{cm}^{-1}$ and	km/mol.	<sup>b</sup> Observ	ved in an	argon ma	trix. ° (	Computed	I with B3	3LYP/6-	.311++G(	3df, 3p	d)/SDD.	q

Approximate		CH	3-Agh	-			B	3-AgH				<sup>13</sup> C	H <sub>3</sub> -AgF	<b>–</b>	
Description	Obs <sup>b</sup>	взгүр	Int <sup>c</sup>	BPW91 <sup>d</sup>	Int <sup>d</sup>	Obs <sup>b</sup>	ВЗLYP°	int <sup>c</sup>	BPW91 <sup>d</sup>	Int <sup>d</sup>	Obs <sup>b</sup>	$B3LYP^{c}$	int <sup>c</sup>	BPW91 <sup>d</sup>	Int <sup>d</sup>
A" CH <sub>3</sub> as. str.		3214.3	0	3150.4	-		2388.4	0	2339.5	0		3201.7	0	3138.2	-
A' CH <sub>3</sub> as. str.		3185.6	<del>.                                    </del>	3120.5	7		2364.3	0	2314.3	-		3173.6	-	3109.0	5
A' CH <sub>3</sub> s. str.		3059.4	-	2996.2	7		2177.5	2	2134.3	2		3057.7	<del>.                                    </del>	2994.4	7
A' Ag-H str.		1622.3	17	1644.6	13		1152.7	6	1168.6	7		1622.2	17	1644.6	13
A' CH <sub>3</sub> scis.		1436.4	~	1398.5	<del>.                                    </del>		1049.7	-	1017.3	-		1432.2	<del>.                                    </del>	1389.6	-
A" CH <sub>3</sub> scis.		1412.1	с	1366.7	e		1033.6	2	999.7	2		1407.8	2	1362.6	7
A' CH <sub>3</sub> deform		985.2	101	980.6	60		745.5	70	746.9	39		980.1	98	975.2	58
A" CH <sub>3</sub> rock		590.4	4	595.7	15		430.9	œ	440.4	19		588.7	4	593.8	15
A' CH <sub>3</sub> rock		580.0	36	592.0	36		429.4	19	436.1	80		577.7	36	589.5	36
A' CAgH bend		347.0	ω	376.6	<del>.                                    </del>		319.4	с	349.6	<del></del>		339.6	15	366.5	с
A' C-Ag str.		307.5	109	343.4	68		223.5	57	245.4	33		304.7	101	342.5	66
A" CH <sub>3</sub> tort		84.2	38	77.2	29		59.9	19	55.0	15		84.2	38	77.3	29
<sup>a</sup> Frequencies and inte	insities a	re in cm	-1 and	d km/mol.	<sup>b</sup> Not c	bserved	in an arg(	n me	utrix. ° Cor	nputed	with B3	LYP/6-31	[]++G	(3df, 3pd	IOS/(

Table S4: Calculated Fundamental Frequencies of CH<sub>3</sub>-AgH isotopomers in the Ground <sup>2</sup>A' State (C<sub>s</sub> structure)<sup>a</sup>

Approximate		Ч С	H <sub>3</sub> -Ag				U	D <sub>3</sub> -Ag				<sup>13</sup> C	CH <sub>3</sub> -Ag		
Description	Obs <sup>b</sup>	Β3LΥΡ°	Int <sup>c</sup>	BPW91	<sup>1</sup> Int <sup>d</sup>	Obs <sup>b</sup>	Β3LΥΡ°	int <sup>c</sup>	BPW91 <sup>d</sup>	Int <sup>d</sup>	Obs <sup>b</sup>	B3LYP <sup>c</sup>	int <sup>c</sup>	BPW91 <sup>d</sup>	Int <sup>d</sup>
E CH <sub>3</sub> 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 <sub>1</sub> CH <sub>3</sub> str.		3059.7	23	3001.9	16		2182.9	13	2141.8	10		3057.7	22	3000.0	16
E CH <sub>3</sub> 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 10	069.3	1090.6	69	1059.5	56
E CH <sub>3</sub> 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 6	63.6	690.7	51 x 2	682.2	44 x 2
A <sub>1</sub> C-Ag str.		445.2	7	450.2	<del>.</del>		410.4	ы	414.4	5		432.5	7	437.3	<del>~</del>
<sup>a</sup> Frequencies and	intensities	are in cm	n <sup>-1</sup> and	l km/mc	ol. <sup>b</sup> Ol	bserved ir	n an argo	n matr	rix. ° Com	puted w	ith B3L	JYP/6-31	1++G(	3df, 3pd)/	SDD.
Computed with BP	W91/6-311	++G(3df,	3pd)/S	DD. CF	I <sub>3</sub> -Ag I	ias a C <sub>3v</sub> s	tructure.								

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Approximate		J	CH <sub>3</sub> -AgF	<b>'</b>			O	:D <sub>3</sub> -AgH	L			13(	CH₃-Ag⊢	<u>_</u>	
Description	Obs <sup>b</sup>	Β3LΥΡ°	Int <sup>c</sup>	BPW91 <sup>d</sup>	Int <sup>d</sup>	Obs <sup>b</sup>	Β3LΥΡ <sup>c</sup>	int <sup>c</sup>	BPW91 <sup>d</sup>	Int <sup>d</sup>	Obs <sup>b</sup>	Β3LΥΡ <sup>c</sup>	int <sup>c</sup>	BPW91 <sup>d</sup>	Int <sup>d</sup>
E CH <sub>3</sub> 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 <sub>1</sub> CH <sub>3</sub> str.		2953.7	165	2897.8	175		2114.5	71	2074.9	76		2951.1	167	2895.2	177
A <sub>1</sub> 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 <sub>3</sub> 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
A1 CH3 deform		1095.3	4	1062.3	2		846.3	13	821.8	6		1087.7	с	1054.9	<del></del>
E CH <sub>3</sub> 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 <sub>1</sub> 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
<sup>a</sup> Frequencies and	intensit	ties are in	n cm <sup>-1</sup>	and km/m	ol. <sup>b</sup> Ot	served i	n an arg	on mat	trix. ° Co	mputed	with B3	LYP/6-3	11++G(	(3df, 3pc	I)/SDD.

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Computed with BPW91/6-311++G(3df,3pd)/SDD. CH<sub>3</sub>-AgH<sup>-</sup> has a C<sub>3v</sub> structure.

Approximate		CH	3-CuH	_			CD <sub>3</sub>	-CuH				<sup>13</sup> C	H3-Cut	Ŧ	
Description	Obs <sup>b</sup>	Β3LΥΡ°	: Int <sup>c</sup>	BPW91 <sup>d</sup>	Int <sup>d</sup>	Obs <sup>b</sup>	Β3LΥΡ <sup>c</sup>	int <sup>c</sup>	BPW91 <sup>d</sup>	Int <sup>d</sup>	Obs <sup>b</sup>	Β3LΥΡ <sup>c</sup>	int <sup>c</sup>	BPW91 <sup>d</sup>	Int <sup>d</sup>
A" CH <sub>3</sub> as. str.		3165.0	ю	3113.8	2		2347.7	0	2309.5	0		3153.0	с	3102.1	2
A' CH <sub>3</sub> as. str.		3133.1	5	3080.5	4		2320.0	2	2280.5	<del>.                                    </del>		3122.2	9	3069.8	4
A' CH <sub>3</sub> s. str.		3024.5	5	2966.1	ю		2159.1	4	2117.3	2		3022.1	4	2963.7	с
A' Cu-H str.	1718.8	1707.5	33	1704.1	18	1243.7	1216.9	18	1214.6	6	1717.7	1707.5	33	1704.1	17
A' CH <sub>3</sub> scis.		1439.4	<del>.                                    </del>	1392.0	÷		1048.4	~	1013.8	<del>.                                    </del>		1435.7	<del></del>	1388.5	-
A" CH <sub>3</sub> scis.		1411.4	2	1359.2	ю		1029.7	2	992.1	2		1407.5	2	1355.5	7
A' CH <sub>3</sub> 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 <sub>3</sub> rock	covered	623.2	53	605.4	48		473.0	27	464.5	22	covered	620.0	53	602.1	48
A" CH <sub>3</sub> rock		599.8	21	581.0	19		443.6	12	429.6	1		597.4	20	578.7	18
A' CCuH bend		463.0	~	471.2	<del></del>		425.3	2	426.0	4		450.8	<del>.                                    </del>	459.1	-
A' C-Cu str.		382.2	70	364.1	50		272.8	36	259.9	25		382.2	70	364.1	50
A" CH <sub>3</sub> tort		150.4	47	95.6	37		107.6	25	68.8	19		150.4	47	95.6	37
<sup>a</sup> Frequencies and in	tensities ar	e in cm <sup>-1</sup>	and l	km/mol. <sup>b</sup>	Obser	ved in an a	urgon matr	ix. °C	Computed	with <b>F</b>	317P/6-	·311++G(	3df, 3p	od). <sup>d</sup> Com	puted

Table S7: Observed and Calculated Fundamental Frequencies of CH<sub>3</sub>-CuH isotopomers in the Ground <sup>2</sup>A' State (C<sub>s</sub> structure)<sup>a</sup>

with BPW91/6-311++G(3df,3pd). CH<sub>3</sub>-CuH has a  $C_s$  structure.

Annroximate		5 5	l₃-Cu				O	D <sub>3</sub> -Cu				<sup>13</sup> C	:H <sub>3</sub> -Cu		
Description	Obs <sup>b</sup>	B3LYP°	Int <sup>c</sup>	BPW91 <sup>d</sup>	Int <sup>d</sup>	Obs <sup>b</sup>	Β3LΥΡ°	int <sup>c</sup>	BPW91 <sup>d</sup>	Int <sup>d</sup>	Obs <sup>b</sup>	Β3LΥΡ <sup>c</sup>	int <sup>c</sup>	BPW91 <sup>d</sup>	Int <sup>d</sup>
E CH <sub>3</sub> 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 <sub>1</sub> CH <sub>3</sub> str.		3032.9	24	2974.3	18		2166.5	13	2124.2	10		3030.7	23	2972.2	17
E CH <sub>3</sub> 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 <sub>3</sub> 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 <sub>1</sub> C-Au str.		525.7	4	541.0	ო		480.1	5	491.2	4		512.4	б	527.5	7
<sup>a</sup> Frequencies and in	tensities ar	e in cm <sup>-1</sup>	and kı	m/mol. <sup>b</sup> ,	Observ	ved in an a	rgon mat	rix. °C	Computed	with B	3LYP/6-	311++G(3	df, 3p	d).	
<sup>d</sup> Computed with BF	W91/6-31	1++G(3d	f,3pd).	. CH <sub>3</sub> -Cu	has a	C <sub>3v</sub> structi	tre. The	four lo	west frequ	lencies	compute	ed with			

MP2/6-311++G(3df,3pd) are 1453 cm<sup>-1</sup>(0.3x2km/mol), 1150(63), 679(67), 564 (15).

Table S8: Observed and Calculated Fundamental Frequencies of CH<sub>3</sub>-Cu in the Ground <sup>1</sup>A<sub>1</sub> State (C<sub>3v</sub> structure)<sup>a</sup>

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Approximate		Ю	3-CuH⁻				C	3-CuH <sup>-</sup>				<sup>13</sup> CF	H <sub>3</sub> -CuH		
Description	Obs <sup>b</sup>	$B3LYP^{c}$	Int <sup>c</sup>	BPW91 <sup>d</sup>	Int <sup>d</sup>	Obs <sup>b</sup>	Β3LΥΡ <sup>c</sup>	int <sup>c</sup>	BPW91 <sup>d</sup>	Int <sup>d</sup>	Obs <sup>b</sup>	$B3LYP^{c}$	int <sup>c</sup>	BPW91 <sup>d</sup>	Int <sup>d</sup>
E CH <sub>3</sub> 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 <sub>1</sub> CH <sub>3</sub> str.		2927.7	163	2867.8	187		2097.2	71	2054.4	83		2924.9	166	2865.1	189
A <sub>1</sub> 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 <sub>3</sub> 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
A1 CH3 deform		1107.4	12	1071.7	9		860.0	21	834.4	14		1099.4	10	1063.8	5
E CH <sub>3</sub> 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 <sub>1</sub> 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
<sup>a</sup> Frequencies and i	intensities a	are in cm	-1 and 1	km/mol.	<sup>b</sup> Observ	'ed in an a	rgon mat	rix. °C	omputed	l with B	3LYP/6-	311++G(3	3df, 3p	d). <sup>d</sup> Co	mputed

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with BPW91/6-311+++G(3df,3pd). CH<sub>3</sub>-CuH<sup>-</sup> has a C<sub>3v</sub> structure.

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Compound	σ occ <sup>b</sup>	a* occ <sup>b</sup>	%C°	%M°	q(C) <sup>d</sup>	d(M) <sup>d</sup>	EBO <sup>e</sup>	
CH <sub>3</sub> -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 <sub>3</sub> -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 <sub>3</sub> -AuH <sup>-</sup>	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 <sub>3</sub> -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 <sub>3</sub> -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	
CH₃-AgH <sup>−</sup>	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 <sub>3</sub> -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 <sub>3</sub> -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 <sub>3</sub> -CuH <sup>-</sup>	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	
<sup>a</sup> Computed with J	B3LYP/6-3	11++G(3df, 3p	d). The SDD core potentials	s and bases are used for Au and Ag	g, whereas a	all electron	n basis	
for Cu. <sup>b</sup> Occupati	ion number.	<sup>c</sup> Contribution	to the bonding orbital in %	o. <sup>d</sup> Natural charge. Additional cha	arges for CI	H <sub>3</sub> -AuH <sup>-</sup> ir	nclude q(H) = .	-0.413
and $q(3H = 3 \times 0)$ .	167). <sup>e</sup> Effe	ective bond ord	er [( $\sigma \operatorname{occ} - \sigma^* \operatorname{occ})/2$ ].					



**Figure S1.** Infrared spectra in the 1950-1750, 1400-900, and 800-500 cm<sup>-1</sup> 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 **i**<sup>-</sup> 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<sup>-1</sup> 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 **i**<sup>-</sup> 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<sup>-1</sup> 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 **i**<sup>-</sup> stand for product absorption groups while P, c, and w stand for the precursor, common, and water residue absorptions.