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Infrared Spectra of the η^2 -M(NC)-CH₃, CH₃-MNC, and CH₂=M(H)NC Complexes Prepared by Reactions of Th and U Atoms with Acetonitrile

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Abstract

The η^2 -M(NC)-CH₃, CH₃-MNC, and CH₂=M(H)NC complexes are observed in the matrix IR spectra from reactions of laser ablated Th and U atoms with acetonitrile. These actinide products are in line with those from reactions of Group 4-6 metals with acetonitrile, and they are again the most stable steps in the previously proposed reaction path. The N-coordination and methylidyne products (M←NCCH₃ and HCM(H)₂NC) are not observed probably due to their high energies. The actinide methylenes show agostic distortion, and the nitrile π -complexes (η^2 -M(NC)-CH₃) reveal evidence of strong back-donations to the π^* -orbitals, and NBO analysis reveals single M-N and M-C bonds with full σ and π bonds in the N=C subunit. The unidentified N-coordinated-acetonitrile complexes show strong calculated interactions with the actinide

Table S1: Calculated Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km/mol) of $\text{Th} \leftarrow \text{NCCH}_3$ Isotopomers in the Ground $^3\text{A}_1$ State^a

Approximate Description	$\text{CH}_3\text{CN} \rightarrow \text{Th}$				$\text{CD}_3\text{CN} \rightarrow \text{Th}$				$^{13}\text{CH}_3^{13}\text{CN} \rightarrow \text{Th}$			
	Freq(cm^{-1}) ^b	IR int ^b	Freq(cm^{-1}) ^c	IR int ^c	Freq(cm^{-1}) ^b	IR int ^b	Freq(cm^{-1}) ^c	IR int ^c	Freq(cm^{-1}) ^b	IR int ^b	Freq(cm^{-1}) ^c	IR int ^c
A'' CH_3 as. str.	3068.3	2	3012.7	1	2266.4	1	2223.8	1	3057.9	2	3002.6	1
A' CH_3 as. str.	3060.0	16	3006.9	23	2262.0	18	2224.1	22	3050.4	14	2997.1	21
A' CH_3 s. str.	2957.5	83	2901.5	95	2128.6	28	2087.0	32	2952.9	86	2897.3	98
A' CH_3 bend	1464.9	33	1423.1	40	1357.6	39	1356.6	34	1461.7	35	1419.8	43
A'' CH_3 bend	1451.3	6	1400.3	6	1105.2	7	1073.9	8	1448.7	6	1397.8	6
A' CH_3 deform	1368.4	3	1350.4	18	1049.7	2	1012.7	3	1365.1	6	1349.9	20
A' CN str.	1334.6	48	1295.5	31	1023.8	27	985.2	39	1328.6	43	1286.2	27
A' CH_3 rock	1061.3	57	1018.5	73	904.4	98	872.0	117	1052.8	55	1010.3	70
A' C-C str.	940.6	28	928.5	40	856.8	3	840.3	5	928.1	27	916.1	39
A'' CH_3 rock	923.3	1	887.8	1	728.1	3	702.1	2	917.2	1	881.8	1
A' Th-N str.	621.9	63	599.8	63	559.9	34	539.3	32	621.9	63	599.8	64
A' CCN bend	378.5	4	366.3	4	364.9	6	353.1	5	374.2	5	362.3	4
A'' CCN bend	162.5	0	153.0	1	160.4	0	150.5	0	162.4	0	152.9	1
A' ThNC bend	135.2	14	127.2	14	124.7	12	117.4	12	133.4	14	125.6	14
A'' ThNC bend	79.1	3	84.4	4	58.4	3	62.6	4	79.1	3	84.4	4

^a Frequencies and intensities are computed with 6-311++G(3df, 3pd) for harmonic calculations, and the SDD pseudo potential and basis set are used for Th. Frequencies and intensities are in cm^{-1} and km/mol . ^b Computed with B3LYP. ^c Computed with BPW91. The symmetry notations are based on the C_s structure.

Table S2: Observed Matrix Infrared and Calculated Vibrational Frequencies of η^2 -Th(NC)-CH₃ Isotopomers in the Ground ¹A' State^a

Approximate Description	η^2 -Th(NC)-CH ₃					η^2 -Th(NC)-CD ₃					η^2 -Th(N ¹³ C)- ¹³ CH ₃				
	Obs ^b	Freq(cm ⁻¹) ^c	IR Int ^c	Fre(cm ⁻¹) ^d	IR Int ^d	Obs ^b	Freq(cm ⁻¹) ^c	IR Int ^c	Fre(cm ⁻¹) ^d	IR Int ^d	Obs ^b	Freq(cm ⁻¹) ^c	IR Int ^c	Fre(cm ⁻¹) ^d	IR Int ^d
A' CH ₃ as. str.		3086.4	20	3036.4	27		2288.7	10	2251.3	14		3075.1	20	3025.3	26
A'' CH ₃ as. str.		3073.7	6	3023.0	3		2272.3	3	2233.7	2		3063.1	6	3012.7	4
A' CH ₃ s. str.		3010.2	28	2953.5	30		2160.7	11	2119.8	11		3007.1	29	2950.4	31
A' CCN as. str.	1514.1	1577.5	28	1524.5	29	1505.7	1571.4	40	1517.6	43	1481.6	1541.6	23	1489.7	22
A'' CH ₃ bend	covered	1468.1	10	1418.7	10		1059.2	5	1023.0	5	covered	1465.8	10	1416.6	10
A' CH ₃ bend	1425.2	1459.1	23	1410.8	27	1128.4	1144.0	26	1111.6	26	covered	1455.4	27	1406.8	31
A' CH ₃ deform	1345.1	1382.9	10	1330.6	14	covered	1049.6	12	1014.8	15	covered	1372.3	10	1320.3	13
A' CH ₃ rock	1118.3	1143.5	40	1110.5	37	982.9	1002.9	21	969.6	15	1093.0	1116.6	39	1083.4	36
A'' CH ₃ rock		995.4	0	954.7	0		805.9	0	775.4	0		982.8	0	942.3	0
A' CCN s. str.		948.6	2	922.9	1	709.6	802.0	10	778.7	11		931.3	2	907.1	1
A' N-Th str.	604.8	610.6	109	597.4	105	572.5	575.6	110	565.4	105	601.2	607.0	113	594.4	108
A' C-Th str.		441.8	29	437.9	26		417.3	16	411.7	14		431.8	25	427.6	22
A'' CCNTh deform		295.4	1	284.7	1		265.4	0	255.0	1		286.9	1	276.6	1
A' CCTh bend		219.6	7	216.7	6		201.6	6	198.7	5		215.1	7	212.3	6
A'' CH ₃ tort		95.0	0	93.9	0		69.0	0	67.5	0		94.9	0	93.8	0

^aFrequencies and intensities are computed with 6-311++G(3df, 3pd) for harmonic calculations, and the SDD pseudo potential and basis set are used for Th. Frequencies and intensities are in cm⁻¹ and km/mol. ^bObserved in an argon matrix. ^cComputed with B3LYP. ^dBPW91. η^2 -Th(NC)-CH₃ has a C_s structure.

Table S3: Observed and Calculated Fundamental Frequencies of CH₃-ThNC Isotopomers in the Ground ¹A'' State^a

Approximate Description	CH ₃ -ThNC					CD ₃ -ThNC					¹³ CH ₃ -ThN ¹³ C				
	Obs ^b	Freq(cm ⁻¹) ^c	IR int ^c	Fre(cm ⁻¹) ^d	IR int ^d	Obs ^b	Freq(cm ⁻¹) ^c	IR int ^c	Fre(cm ⁻¹) ^d	IR int ^d	Obs ^b	Freq(cm ⁻¹) ^c	IR int ^c	Fre(cm ⁻¹) ^d	IR int ^d
A' CH ₃ as. str.		3128.2	1	3090.6	3		2307.4	3	2279.9	5		3118.2	1	3080.7	3
A'' CH ₃ as. str.		2929.1	2	2839.7	3		2162.3	1	2095.4	1		2919.2	2	2830.2	3
A' CH ₃ s. str.		2869.0	3	2772.8	8		2063.1	35	1995.1	18		2865.0	3	2768.9	8
A' NC str.	2034.6	2068.4	447	1978.2	363	2035.0	2068.9	412	1977.8	347	1989.3	2026.5	443	1938.1	359
A'' CH ₃ bend		1413.8	16	1364.9	21		1025.4	8	989.0	10		1410.6	16	1362.0	21
A' CH ₃ bend		1383.7	1	1326.3	4		1008.1	3	969.6	6		1380.4	1	1322.9	3
A' CH ₃ deform	1094.0	1155.0	44	1107.5	46	876.5	907.7	46	868.0	40		1145.1	40	1098.2	43
A' C-Th str.		538.0	41	546.1	38		465.3	22	471.9	20		525.8	39	533.6	37
A' N-Th str.		395.7	91	398.5	70		394.8	95	397.0	73		389.5	88	392.6	67
A'' CH ₃ rock		344.9	0	363.4	1		256.7	0	271.1	1		343.3	0	361.6	1
A' CH ₃ rock		283.0	2	264.2	1		228.3	0	212.6	0		279.3	2	260.9	1
A' ThNC ip bend		144.8	1	135.9	1		138.8	1	129.4	1		143.8	1	134.8	1
A'' ThNC oop bend		114.6	0	111.6	0		94.3	1	85.0	0		114.5	0	111.6	0
A'' CH ₃ tort		80.4	1	66.2	1		70.5	1	62.4	1		79.2	1	65.0	1
A' CThN bend		60.3	2	60.9	2		55.6	2	56.4	2		58.5	2	59.2	2

^a Frequencies and intensities are computed with 6-311++G(3df, 3pd) for harmonic calculations, and the SDD pseudo potential and basis set are used for Th. Frequencies and intensities are in cm⁻¹ and km/mol. ^b Observed in an argon matrix. ^c Computed with B3LYP. ^d Computed with BPW91. CH₃-ThNC has a C_s structure.

Table S4: Observed and Calculated Fundamental Frequencies of CH₂=Th(H)NC Isotopomers in the Ground ¹A State^a

Approximate Description	CH ₂ =Th(H)NC					CD ₂ =Th(D)NC					¹³ CH ₂ =Th(H)N ¹³ C				
	Obs ^b	Freq(cm ⁻¹) ^c	IR int ^c	Fre(cm ⁻¹) ^d	IR int ^d	Obs ^b	Fre(cm ⁻¹) ^c	IR int ^c	Fre(cm ⁻¹) ^d	IR int ^d	Obs ^b	Fre(cm ⁻¹) ^c	IR int ^c	Fre(cm ⁻¹) ^d	IR int ^d
CH ₂ as. str.		3147.8	1	3088.4	1		2325.3	2	2281.5	1		3137.4	1	3078.2	2
CH ₂ s. str.		2844.0	11	2747.3	6		2072.4	2	2002.2	5		2837.1	11	2740.7	7
NC str.	2030.4	2093.2	455	2012.5	401	2030.6	2093.2	460	2012.6	401	1983.8	2050.8	453	1971.7	399
Th-H str.	covered (1408)	1438.2	498	1417.7	436	1013.7	1026.6	187	1007.7	226	1408.1	1438.1	498	1417.6	436
CH ₂ scis.		1340.6	23	1308.3	27		1012.3	90	987.1	19		1333.8	23	1302.3	28
C-Th str.	682.7	684.7	137	689.7	131	618.7	622.1	103	629.0	100	661.9	664.1	132	668.7	125
Th-H ip bend	647.9	655.2	163	625.3	152	512.0	511.8	117	488.0	110	640.9	649.7	158	620.1	147
CH ₂ wag		495.4	76	516.4	33		382.7	128	397.7	51		492.7	76	512.8	33
CH ₂ rock		400.3	84	402.1	124		284.4	16	278.1	25		398.2	73	400.4	113
Th-N str.		371.1	106	376.8	92		362.7	41	376.1	90		367.8	112	374.4	100
CH ₂ twist		333.6	14	337.5	10		244.8	21	250.4	20		331.7	14	335.8	9
Th-H oop bend		253.7	39	228.4	19		194.2	12	177.9	4		253.5	39	228.0	19
CThN ip bend		122.9	16	114.4	11		113.4	12	103.6	8		121.7	15	113.4	11
ThNC oop bend		86.7	3	77.4	3		83.8	4	75.1	4		85.4	3	76.0	3
ThNC ip bend		66.0	10	64.4	12		63.2	10	61.8	11		64.1	10	62.6	12

^a Frequencies and intensities are computed with 6-311++G(3df, 3pd) for harmonic calculations, and the SDD pseudo potential and basis set are used for Th. Frequencies and intensities are in cm⁻¹ and km/mol. ^b Observed in an argon matrix. ^c Computed with B3LYP. ^d Computed with BPW91. CH₂=Th(H)NC has a planar C₁ structure.

Table S5: Calculated Fundamental Frequencies of HC=Th(H)₂NC Isotopomers in the Ground ³A₁ State^a

Approximate Description	HC=Th(H) ₂ NC		DC=Th(D) ₂ NC		H ¹³ C=Th(H) ₂ N ¹³ C	
	Freq(cm ⁻¹) ^b	IR int ^b	Freq(cm ⁻¹) ^c	IR int ^c	Freq(cm ⁻¹) ^b	IR int ^b
A' C-H str.	3121.1	8	2297.2	5	3111.4	8
A' N-C str.	2090.4	481	2090.3	484	2048.2	479
A' ThH ₂ s. str.	1424.1	283	1008.7	142	1424.0	283
A'' ThH ₂ as str.	1397.6	572	992.4	294	1397.6	572
A'' ThCH oop bend	693.1	14	543.6	9	687.0	14
A' ThH ₂ scis.	630.3	145	407.6	68	627.6	149
A' C-Th str.	486.8	35	507.8	26	474.7	41
A' ThCH ip bend	423.8	267	322.2	78	420.7	248
A' Th-NC str.	382.3	154	378.6	181	376.4	163
A' ThH ₂ wag	347.0	66	257.2	71	345.3	57
A'' ThH ₂ twist	322.1	4	232.2	1	322.0	4
A'' ThH ₂ rock	156.7	56	123.9	25	156.5	56
A' CThN bend	142.3	3	138.1	3	140.5	3
A'' ThNC oop bend	89.7	5	82.8	10	88.4	5
A' ThNC ip bend	73.8	3	71.1	3	71.5	3

^a Frequencies and intensities are computed with 6-311++G(3df, 3pd) for harmonic calculations, and the SDD pseudo potential and basis set are used for Th. Frequencies and intensities are in cm⁻¹ and km/mol. ^b Computed with B3LYP. Geometry optimization with BPW91 for HC=Th(H)₂NC did not converge. The symmetry notations are based on the C_s structure.

Table S6: Calculated Fundamental Frequencies of U←NCCH₃ Isotopomers in the Ground ⁵A₁ State^a

Approximate Description	U←NCCH ₃				U←NCCD ₃				U←N ¹³ C ¹³ CH ₃			
	Freq(cm ⁻¹) ^b	IR int ^b	Freq(cm ⁻¹) ^c	IR int ^c	Freq(cm ⁻¹) ^b	IR int ^b	Freq(cm ⁻¹) ^c	IR int ^c	Freq(cm ⁻¹) ^b	IR int ^b	Freq(cm ⁻¹) ^c	IR int ^c
A'' CH ₃ as. str.	3100.0	1	3039.3	1	2293.1	1	2247.4	1	3089.2	1	3028.7	1
A' CH ₃ as. str.	3083.9	9	3022.3	8	2279.2	9	2232.9	9	3074.3	7	3012.9	6
A' CH ₃ s. str.	2991.8	62	2929.4	80	2151.8	22	2107.0	31	2987.3	64	2925.0	82
A' CN str.	1867.4	15	1815.9	32	1865.8	17	1813.9	30	1866.9	15	1815.1	32
A' CH ₃ bend	1462.8	36	1416.7	35	1049.2	16	1016.0	17	1461.0	37	1415.1	36
A'' CH ₃ bend	1458.7	7	1409.4	8	1095.8	2	1065.0	4	1456.6	8	1407.5	8
A' CH ₃ deform	1381.0	2	1335.4	1	1051.6	3	1015.1	4	1371.6	2	1326.2	2
A' CH ₃ rock	1038.4	70	983.4	57	865.7	68	837.0	75	1030.3	68	975.7	54
A'' CH ₃ rock	1000.9	0	972.5	0	792.4	0	771.2	0	993.6	1	965.2	0
A' C-C str.	922.5	14	907.3	46	830.2	40	784.1	38	907.6	13	892.1	45
A' CCN bend	464.9	107	413.2	66	433.5	79	391.4	48	464.8	107	413.1	66
A' N-U str.	279.2	1	246.4	15	268.1	1	237.5	13	276.0	1	243.8	14
A'' CCN bend	183.2	0	151.5	0	176.9	0	144.5	0	183.3	0	151.5	0
A' UNC bend	99.7	7	102.4	9	93.3	6	95.9	8	98.8	7	101.5	9
A'' CH ₃ tort	92.6	4	84.1	3	76.6	3	75.0	3	92.5	4	83.9	3

^a Frequencies and intensities are computed with 6-311++G(3df, 3pd) for harmonic calculations, and the SDD pseudo potential and basis set are used for U. Frequencies and intensities are in cm⁻¹ and km/mol. ^b Computed with B3LYP. ^c Computed with BPW91. The symmetry notations are based on the C_s structure.

Table S7: Observed and Calculated Fundamental Frequencies of η^2 -U(NC)-CH₃ Isotopomers in the Ground ⁵A' State^a

Approximate Description	η^2 -U(NC)-CH ₃					η^2 -U(NC)-CD ₃					η^2 -U(N ¹³ C)- ¹³ CH ₃				
	Obs ^b	Freq ₁ (cm ⁻¹) ^c	IR int ^c	Fre(cm ⁻¹) ^d	IR int ^d	Obs ^b	Fre(cm ⁻¹) ^c	IR int ^c	Fre(cm ⁻¹) ^d	IR int ^d	Obs ^b	Fre(cm ⁻¹) ^c	IR int ^c	Fre(cm ⁻¹) ^d	IR int ^d
A' CH ₃ as. str.		3075.6	28	3025.6	28		2279.6	16	2242.5	16		3064.5	27	3014.6	27
A'' CH ₃ as. str.		3070.1	8	3016.7	7		2270.1	4	2229.6	3		3059.5	8	3006.3	7
A' CH ₃ s. str.		3001.7	63	2946.0	57		2154.8	24	2114.4	23		2998.5	65	2942.9	58.0
A' CN str.	1503.6	1560.0	29	1480.6	13	1496.8	1553.7	39	1470.8	27	covered	1524.4	25	1450.1	7
A'' CH ₃ bend	covered	1467.5	9	1419.9	9	1025.5	1059.2	5	1024.6	5	1439.7	1465.2	9	1417.7	9
A' CH ₃ bend	1421.5	1460.0	24	1410.7	29	covered	1119.8	43	1085.5	34	1415.7	1455.8	29	1402.6	35
A' CH ₃ deform	1342.3	1377.8	7	1328.2	6	1032.8	1050.5	12	1016.2	16	1331.4	1367.0	6	1317.9	6
A' CH ₃ rock	1091.2	1096.2	106	1072.0	63	955.4	957.9	102	941.4	55	1069	1074.5	95	1049.0	56
A'' CH ₃ rock		989.6	0	948.7	0		797.2	1	761.8	0		977.5	0	937.3	0
A' C-C str.		928.3	19	897.7	21		795.9	7	760.9	4		908.9	22	881.0	24
A' N-U str.	584.6	602.9	136	582.2	62	552.7	570.3	115	550.0	55	581.1	599.8	137	578.0	63
A' C-U str.		388.9	7	357.6	7		367.5	3	339.3	4		379.7	6	349.7	6
A'' CCN oop bend		281.3	1	233.4	2		253.7	1	208.4	1		273.1	1	226.6	1
A' CCU ip bend		222.5	12	218.4	11		205.2	11	200.9	10		218.0	12	213.9	11
A'' CH ₃ tort		86.3	0	69.6	0		62.2	1	51.0	0		86.2	0	69.6	0

^a Frequencies and intensities are computed with 6-311++G(3df, 3pd) for harmonic calculations, and the SDD pseudo potential and basis set are used for U. Frequencies and intensities are in cm⁻¹ and km/mol. ^b Observed in an argon matrix. ^c Computed with B3LYP. ^d Computed with BPW91. η^2 -U(NC)-CH₃ has a C_s structure.

Table S8: Observed and Calculated Fundamental Frequencies of CH₃-UNC Isotopomers in the Ground ⁵A'' State^a

Approximate Description	CH ₃ -UNC					CD ₃ -UNC					¹³ CH ₃ -UN ¹³ C				
	Obs ^b	Freq(cm ⁻¹) ^c	IR int ^c	Freq(cm ⁻¹) ^d	IR int ^d	Obs ^b	Freq(cm ⁻¹) ^c	IR int ^c	Freq(cm ⁻¹) ^d	IR int ^d	Obs ^b	Freq(cm ⁻¹) ^c	IR int ^c	Freq(cm ⁻¹) ^d	IR int ^d
A' CH ₃ as. str.		3054.3	7	3011.4	5		2255.7	3	2224.3	2		3044.0	8	3001.2	5
A'' CH ₃ as. str.		3015.8	14	2977.3	13		2227.8	6	2199.5	5		3005.5	15	2967.0	13
A' CH ₃ s. str.		2951.5	9	2903.1	13		2117.4	2	2082.0	1		2948.2	10	2900.0	7
A' NC str.	2029.7	2091.6	380	1991.8	245	2029.7	2091.6	380	1991.8	245	1988.6	2049.1	378	1951.0	244
A'' CH ₃ bend	covered	1422.3	10	1372.5	11		1032.4	6	996.4	7	covered	1419.1	10	1369.3	11
A' CH ₃ bend		1411.5	1	1361.5	1		1024.3	1	987.8	1		1408.4	1	1358.4	1
A' CH ₃ deform	1108.9	1150.5	18	1102.0	18	874.5	899.2	29	864.5	30	1099.2	1141.3	15	1092.9	16
A' C-U str.		438.9	40	433.6	45		390.7	30	386.1	32		428.4	36	422.4	43
A' CH ₃ rock		369.2	40	341.1	13		284.3	1	268.4	0		364.6	33	336.8	17
A' N-U str.		357.2	59	354.9	51		358.1	95	349.7	63		351.7	64	350.1	45
A'' CH ₃ rock		323.0	2	303.6	1		241.2	2	225.4	0		321.3	2	302.4	0
A' UNC ip bend		136.2	0	148.5	0		132.0	0	143.6	0		135.4	0	147.8	0
A'' UNC oop bend		112.5	0	114.0	0		111.4	0	108.8	1		111.7	0	113.3	0
A'' CH ₃ tort		102.0	0	58.7	1		73.6	1	44.2	1		101.8	0	58.3	0
A' CUN bend		58.7	4	63.1	4		53.5	4	58.0	4		57.0	4	61.2	3

^a Frequencies and intensities are computed with 6-311++G(3df, 3pd) for harmonic calculations, and the SDD pseudo potential and basis set are used for U. Frequencies and intensities are in cm⁻¹ and km/mol. ^b Observed in an argon matrix. ^c Computed with B3LYP. ^d Computed with BPW91. CH₃-UNC has a C_s structure.

Table S9: Observed and Calculated Fundamental Frequencies of CH₂=U(H)NC Isotopomers in the Ground ³A State^a

Approximate Description	CH ₂ =U(H)NC					CD ₂ =U(D)NC					¹³ CH ₂ =U(H)N ¹³ C				
	Obs ^b	Freq(cm ⁻¹) ^c	IR int ^c	Fre(cm ⁻¹) ^d	IR int ^d	Obs ^b	Fre(cm ⁻¹) ^c	IR int ^c	Fre(cm ⁻¹) ^d	IR int ^d	Obs ^b	Fre(cm ⁻¹) ^c	IR int ^c	Fre(cm ⁻¹) ^d	IR int ^d
CH ₂ as. str.		3146.4	1	3081.5	0		2324.2	1	2275.9	1		3136.0	1	3071.5	1
CH ₂ s. str.		2822.0	6	2629.8	1		2054.8	1	1915.1	0		2815.3	7	2623.6	1
NC str.	2014.7	2090.3	451	1995.7	338	2014.7	2090.3	453.5	1995.7	340	1973.5	2047.9	449	1955.0	337
U-H str.	1456.2*	1464.7	498	1508.7	400	1050.8*	1038.8	256	1069.8	203	1458.0*	1464.7	498	1508.8	400
CH ₂ scis.		1340.5	25	1338.5	21		1020.8	22	1005.8	18		1332.9	24	1332.7	21
CH ₂ wag		633.5	117	650.1	94		484.9	87	475.4	66		624.2	121	632.7	85
C-U str.		600.3	72	608.7	47		556.3	52	591.1	73		586.8	62	602.3	48
CH ₂ rock		507.9	73	599.0	94		393.0	84	464.7	36		504.5	74	594.1	95
U-H ip bend		396.0	101	428.0	84		278.6	24	300.3	35		394.2	90	427.3	81
U-N str.		366.3	101	392.0	99		362.5	74	374.2	87		362.7	108	390.3	95
U-H oop bend		322.5	19	351.8	12		237.4	22	268.4	10		321.0	17	348.2	15
CH ₂ twist		161.9	13	199.3	17		136.7	1	157.2	5		161.5	14	198.9	17
CUN ip bend		109.6	5	95.4	5		107.0	1	86.9	4		108.7	5	94.6	5
UNC oop bend		97.0	20	62.3	9		82.1	18	58.0	9		95.9	20	60.4	9
UNC ip bend		63.6	7	-90.8	7		59.7	7	-88.6	6		61.7	6	-91.1	7

^aFrequencies and intensities are computed with 6-311++G(3df, 3pd) for harmonic calculations, and the SDD pseudo potential and basis set are used for U. Frequencies and intensities are in cm⁻¹ and km/mol. ^bObserved in an argon matrix. ^cComputed with B3LYP.

^dComputed with BPW. *Tentative assignment. CH₂=U(H)NC has a planar C₁ structure.

Table S10: Calculated Fundamental Frequencies of HC≡U(H)₂NC Isotopomers in the Ground ¹A' State^a

Approximate Description	HC≡U(H) ₂ NC				DC≡U(D) ₂ NC				H ¹³ C≡U(H) ₂ N ¹³ C			
	Freq(cm ⁻¹) ^b	IR int ^b	Fre(cm ⁻¹) ^c	IR int ^c	Freq(cm ⁻¹) ^b	IR int ^b	Fre(cm ⁻¹) ^c	IR int ^c	Freq(cm ⁻¹) ^b	IR int ^b	Fre(cm ⁻¹) ^c	IR int ^c
A' C-H str.	3096.5	1	3018.0	0	2290.3	5	2232.4	3	30859	1	3007.8	0
A' N-C str.	2075.4	572	1989.1	495	2075.1	576	1988.9	499	2033.5	567	1949.0	490
A' UH ₂ s. str.	1575.8	492	1528.5	379	1115.6	249	1083.3	192	1573.8	492	1528.5	380
A'' UH ₂ as str.	1538.0	608	1511.0	478	1090.7	312	1071.8	246	1538.0	608	1511.0	478
A' C-U str.	776.1	44	760.1	48	742.2	46	727.1	50	749.8	39	734.4	44
A'' UCH oop bend	608.9	145	571.3	121	480.0	97	450.0	83	603.3	142	566.1	117
A' UH ₂ scis.	586.5	107	564.1	68	447.5	114	430.0	91	583.4	103	561.4	65
A' UCH ip bend	435.6	148	471.3	114	318.6	34	344.5	40	433.6	143	469.5	113
A' U-NC str.	402.1	180	389.8	157	387.1	116	381.8	88	398.2	186	384.2	160
A' UH ₂ wag	352.9	13	329.9	40	269.2	42	251.9	35	350.3	8	328.9	35
A'' UH ₂ twist	331.1	2	320.6	0	246.9	1	239.8	1	330.9	2	320.5	0
A' UNC ip bend	138.6	12	131.2	18	131.5	11	122.8	18	137.3	11	129.9	18
A'' UNC oop bend	108.1	41	164.1	54	74.7	37	125.7	24	107.8	46	163.7	55
A'' UH ₂ rock	99.2	28	90.5	5	99.5	0	83.8	8	98.2	23	89.2	5
A' CUN bend	73.2	4	65.2	5	68.9	4	61.4	5	70.9	4	63.1	5

^aFrequencies and intensities are computed with 6-311++G(3df, 3pd) for harmonic calculations, and the SDD pseudo potential and basis set are used for U. Frequencies and intensities are in cm⁻¹ and km/mol. ^bComputed with B3LYP. ^cComputed with BPW91. The symmetry notations are based on the C_s structure