Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information for:

Matrix-isolation and theoretical study of the HXeCCXeH···HCCH and HXeCC···HCCH complexes

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Table S1. Calculated interaction energies (in kJ mol^{-1}) of the HXeCCXeH···HCCH complex.[a]

	Structure 1	Structure 2
	M06-2X /aug-cc-pVTZ-PP	
E_{int}	–19.9	
$E_{int,\ ZPVE}$	–16.6	[b]
$E_{int,\ ZPVE,\ BSSE}$	–15.9	
	CCSD/cc-pVTZ-PP	
E_{int}	–17.7	–2.1
$E_{int,\ ZPVE}$	–15.2	–2.1
$E_{int,\ ZPVE,\ BSSE}$	–12.0	–1.7

[a]E_{int} – interaction energy, $E_{int,\ ZPVE}$ – interaction energy after ZPVE correction, $E_{int,\ ZPVE,\ BSSE}$ – interaction energy after ZPVE and BSSE corrections. [b]Not an energy minimum at this level.

Table S2. Calculated bond lengths (in pm) in acetylene and HXeCCXeH monomers and the HXeCCXeH···HCCH complex calculated at the M06-2X and CCSD levels of theory.[a]

Bond	M06-2X/aug-cc-pVTZ-PP	CCSD/cc-pVTZ-PP
	HCCH	
CH	106.3	106.2
CC	119.4	120.3
	HXeCCXeH	
HXe	176.3	177.5
XeC	232.6	232.1
CC	122.4	123.1
	HXeCCXeH···HCCH (structure 1)	
HXe	175.8	176.7
XeC	233.6	233.3
CC	122.6	123.2
CXe_T	234.9	233.9
XeH_T	174.9	176.3
$HC_{Ac\text{-}Int}$	107.2	107.0
CC_{Ac}	119.6	120.5
CH_{Ac}	106.3	106.2
	HXeCCXeH···HCCH (structure 2)	
HXe_{Int}		178.5
XeC		230.5
CC		123.0
CXe	[b]	232.7
XeH		176.9
$HC_{Ac\text{-}Int}$		106.3
CC_{Ac}		120.3
CH_{Ac}		106.2

[a] T – atoms located on the side to which the acetylene molecule is tilted; Ac – atoms of acetylene; Int – atoms directly involved in the interaction. [b]Not an energy minimum at this level.

Table S3. Calculated wavenumbers (ω, in cm^{-1}) and infrared intensities (I, in km mol^{-1}) of acetylene and HXeCCXeH monomers and the HXeCCXeH···HCCH and HXeCCXeH···$(HCCH)_2$ complexes.[a]

	M06-2X		**CCSD**		**Assig.**
	ω	I	ω	I	
HCCH					
	3535.5	0	3535.6	0	Sym. CH stretch
	3422.3	93	3430.4	85	Asym. CH stretch
	2102.7	0	2047.4	0	CC stretch
	790.5	96	767.3	91	Sym. CCH bend
	790.5	96	767.3	91	
	707.9	0	621.5	0	Asym. CCH bend
	707.9	0	621.5	0	
HXeCCXeH					
	2115.6	0	2079.6	0	CC stretch
	1718.1	0	1636.1	0	Sym. HXe stretch
	1655.9	4600	1559.8	4800	Asym. HXe stretch
	651.9	15	674.0	27	Sym. HXeC bend
	651.9	15	674.0	27	
	651.6	0	671.0	0	Asym. HXeC bend
	651.6	0	671.0	0	
	412.7	1031	424.5	916	Asym. XeC stretch
	134.0	0	142.4	0	Asym. XeCC bend
	134.0	0	142.4	0	
	125.7	0	128.4	0	Sym. XeC stretch
	28.4	11	56.0	10	Sym. XeCC bend
	28.4	11	56.0	10	

	M06-2X		CCSD		Assig.
	ω	*I*	*ω*	*I*	
HXeCCXeH···HCCH structure 1					
	3500.9	2	3506.5	0	Sym. CH stretch
	3332.8	313	3357.1	288	Asym. CH stretch
	2103.3	0	2071.4	0	CC stretch (Ng)
	2084.6	14	2033.3	11	CC stretch (Ac)
	1738.4	77	1660.6	27	Sym. HXe stretch
	1676.4	4228	1586.5	4629	Asym. HXe stretch
	878.5	73	848.7	57	Sym. CCH bend
	844.6	53	822.7	58	
	727.3	18	672.4	25	Sym. HXeC bend
	718.5	18	672.2	19	
	668.5	6	670.6	0	Asym. HXeC bend
	666.0	8	669.6	0	
	652.3	6	652.9	12	Asym. CCH bend
	650.5	4	636.2	13	
	405.9	974	416.4	894	Asym. XeC stretch
	189.0	2	178.1	1	Asym. XeCC bend
	153.0	2	150.2	0	
	141.5	0	132.3	4	Ac-HNgY
	122.1	3	125.2	1	Sym. XeC stretch
	108.2	9	111.8	10	Ac- HNgY
	96.3	0	104.8	0	Ac- HNgY
	51.5	6	52.4	10	Sym. XeCC bend
	30.6	12	39.5	0	

	M06-2X		CCSD		Assig.
	ω	*I*	*ω*	*I*	
	26.1	0	11.3	0	Ac- HNgY
[b] **HXeCCXeH···HCCH structure 2**					
	-	-	3529.6	9	Sym. CH stretch
	-	-	3422.3	220	Asym. CH stretch
	-	-	2082.3	0	CC stretch (HNgY)
	-	-	2045.6	4	CC stretch (Ac)
	-	-	1638.0	159	Sym. HXe stretch
	-	-	1550.8	5260	Asym. HXe stretch
	-	-	775.8	84	Sym. CCH bend
	-	-	775.8	84	
	-	-	673.1	22	Sym. HXeC bend
	-	-	673.1	22	
	-	-	667.9	7	Asym. HXeC bend
	-	-	667.9	7	
	-	-	620.9	1	Asym. CCH bend
	-	-	620.9	1	
	-	-	424.7	1014	Asym. XeC stretch
	-	-	145.3	0	Asym. XeCC bend
	-	-	145.3	0	
	-	-	129.5	0	Sym. XeC stretch
	-	-	57.8	9	Sym. XeCC bend
	-	-	57.8	9	
	-	-	41.8	0	Ac-HNgY
	-	-	41.8	0	Ac-HNgY

	M06-2X		CCSD		Assig.
	ω	*I*	*ω*	*I*	
	-	-	28.9	0	Ac-HNgY
	-	-	3.0	0	Ac-HNgY
	-	-	3.0	0	Ac-HNgY
HXeCCXeH···$(HCCH)_2$ structure 1					
	3499.9	0	-	-	-
	3499.7	3	-	-	-
	3336.8	0	-	-	-
	3333.0	653	-	-	-
	2093.1	0	-	-	-
	2085.3	0	-	-	-
	2084.4	29	-	-	-
	1754.4	0	-	-	-
	1698.6	3989	-	-	Asym. HXe stretch
	871.0	0	-	-	-
	869.1	150	-	-	-
	848.9	0	-	-	-
	848.4	108	-	-	-
	729.5	0	-	-	-
	729.4	33	-	-	-
	726.1	35	-	-	-
	726.1	0	-	-	-
	662.1	0	-	-	-
	660.3	13	-	-	-
	649.6	0	-	-	-

	M06-2X		CCSD		Assig.
	ω	*I*	*ω*	*I*	
	649.2	6	-	-	-
	397.9	920	-	-	-
	205.4	0	-	-	-
	174.5	16	-	-	-
	149.7	0	-	-	-
	146.9	0	-	-	-
	124.2	11	-	-	-
	115.4	0	-	-	-
	105.3	0	-	-	-
	98.1	0	-	-	-
	77.6	0	-	-	-
	51.4	6	-	-	-
	37.1	12	-	-	-
	33.4	0	-	-	-
	23.3	0	-	-	-
	9.0	0	-	-	-
HXeCCXeH···$(HCCH)_2$ structure 2					
	3500.9	3	-	-	-
	3500.7	0	-	-	-
	3339.1	117	-	-	-
	3335.3	511	-	-	-
	2099.3	0	-	-	-
	2085.9	4	-	-	-
	2084.8	23	-	-	-

	M06-2X		CCSD		Assig.
	ω	*I*	*ω*	*I*	
	1748.6	114	-	-	-
	1686.5	3895	-	-	Asym. HXe stretch
	846.0	110	-	-	-
	845.5	0	-	-	-
	843.7	45	-	-	-
	842.7	130	-	-	-
	726.1	4	-	-	-
	726.1	33	-	-	-
	726.0	19	-	-	-
	725.8	0	-	-	-
	650.2	5	-	-	-
	648.9	5	-	-	-
	646.0	2	-	-	-
	644.2	10	-	-	-
	398.2	921	-	-	-
	208.9	12	-	-	-
	145.1	0	-	-	-
	137.2	1	-	-	-
	133.0	6	-	-	-
	118.9	0	-	-	-
	101.9	8	-	-	-
	101.9	0	-	-	-
	94.2	0	-	-	-
	74.9	0	-	-	-
	45.6	5	-	-	-

	M06-2X		CCSD		Assig.
	ω	*I*	*ω*	*I*	
	30.9	12	-	-	-
	27.8	0	-	-	-
	10.9	1	-	-	-
	7.3	0	-	-	-
HXeCCXeH···$(HCCH)_2$ structure 3					
	3501.3	3	-	-	-
	3501.0	0	-	-	-
	3339.4	255	-	-	-
	3335.7	341	-	-	-
	2094.7	0	-	-	-
	2086.2	9	-	-	-
	2085.0	15	-	-	-
	1759.1	189	-	-	-
	1693.9	3831	-	-	Asym. HXe stretch
	875.0	72	-	-	-
	872.9	75	-	-	-
	840.2	71	-	-	-
	835.9	39	-	-	-
	728.8	29	-	-	-
	728.7	5	-	-	-
	717.9	21	-	-	-
	717.4	12	-	-	-
	667.4	5	-	-	-
	657.1	3	-	-	-

	M06-2X		CCSD		Assig.
	ω	*I*	*ω*	*I*	
	650.2	5	-	-	-
	645.0	7	-	-	-
	398.0	919	-	-	-
	190.1	5	-	-	-
	181.7	1	-	-	-
	151.9	1	-	-	-
	146.8	0	-	-	-
	118.4	2	-	-	-
	108.8	10	-	-	-
	108.2	3	-	-	-
	84.7	3	-	-	-
	82.8	1	-	-	-
	48.7	8	-	-	-
	44.7	6	-	-	-
	27.1	0	-	-	-
	18.1	1	-	-	-
	5.0	0	-	-	-

[a] Ac – acetylene; HNgY – noble-gas hydride. The basis sets are aug-cc-pVTZ-PP for M06-2X and cc-pVTZ-PP for CCSD. [b]Not an energy minimum at the M06-2X level.

Table S4. Calculated interaction energies (in kJ mol^{-1}) of the HXeCC···HCCH complex.[a]

	Structure 1	Structure 2
	M06-2X /aug-cc-pVTZ-PP	
E_{int}	–19.0	
$E_{int,\ ZPVE}$	–16.0	[b]
$E_{int,\ ZPVE,\ BSSE}$	–15.3	
	CCSD/cc-pVTZ-PP	
E_{int}	–16.7	–4.7
$E_{int,\ ZPVE}$	–14.3	–3.9
$E_{int,\ ZPVE,\ BSSE}$	–11.8	–3.2

[a]E_{int} – interaction energy, $E_{int,\ ZPVE}$ – interaction energy after ZPVE correction, $E_{int,\ ZPVE,\ BSSE}$ – interaction energy after ZPVE and BSSE corrections. [b]Not an energy minimum at this level.

Table S5. Calculated bond lenghts (in pm) of acetylene and HXeCC monomers and the HXeCC···HCCH complex at the M06-2X and CCSD levels of theory.[a]

Bond	M06-2X/aug-cc-pVTZ-PP	CCSD/cc-pVTZ-PP
	HCCH	
CH	106.3	106.2
CC	119.4	120.3
	HXeCC	
HXe	172.5	170.6
XeC	236.4	235.0
CC	122.0	123.2
	HXeCC···HCCH (structure 1)	
HXe	171.2	169.5
XeC	239.1	237.8
CC	122.2	123.4
$HC_{Ac\text{-}Int}$	107.0	106.7
CC_{Ac}	119.6	120.5
CH_{Ac}	106.3	106.2
	HXeCC···HCCH (structure 2)	
HXe_{Int}	[b]	169.8
XeC		237.4
CC		123.4
HC_{Ac}		106.3
CC_{Ac}		120.4
CH_{Ac}		106.3

[a] Ac – atoms of acetylene; Int – atoms directly involved in the interaction. [b]Not an energy minimum at this level.

Table S6. Calculated wavenumbers (ω, in cm^{-1}) and infrared intensities (I, in km mol^{-1}) of acetylene and HXeCC monomers and the HXeCC···HCCH and HXeCC···$(HCCH)_2$ complexes.[a]

	M06-2X		**CCSD**		**Assig.**
	ω	I	ω	I	
HCCH					
	3535.5	0	3535.6	0	Sym. CH stretch
	3422.3	93	3430.4	85	Asym. CH stretch
	2102.7	0	2047.4	0	CC stretch
	790.5	96	767.3	91	Sym. CCH bend
	790.5	96	767.3	91	
	707.9	0	621.5	0	Asym. CCH bend
	707.9	0	621.5	0	
HXeCC					
	2074.9	17	2010.0	22	CC stretch
	1751.3	999	1911.9	771	HXe stretch
	629.1	0	656.1	0	HXeC bend
	629.1	0	656.1	0	
	303.6	172	306.4	202	XeC stretch
	67.2	4	102.6	5	XeCC bend
	67.2	4	102.6	5	
HXeCC···HCCH structure 1					
	3504.6	4	3511.9	3	Sym. CH stretch
	3358.9	197	3384.1	167	Asym. CH stretch
	2087.7	5	2037.4	4	CC stretch (Ac)
	2057.8	25	2003.2	1	CC stretch (HNgY)

	M06-2X		CCSD		Assig.
	ω	*I*	*ω*	*I*	
	1788.7	844	1958.3	643	HXe stretch
	831.7	58	814.5	101	Sym. CCH bend
	829.0	111	803.8	65	
	722.9	7	646.1	4	Asym. CCH bend + HXeC bend
	720.4	15	643.0	0	HXeC bend
	672.2	1	641.4	1	Asym. CCH bend + HXeC bend
	654.5	0	633.2	8	Asym. CCH bend
	291.3	155	293.5	178	XeC stretch
	157.5	7	140.0	7	XeCC bend
	100.2	2	111.4	2	
	96.0	3	101.6	5	Ac-HNgY
	86.3	2	83.9	0	Ac-HNgY
	80.0	1	81.7	2	Ac-HNgY
	45.6	2	36.2	3	Ac-HNgY
HXeCC···HCCH structure 2					
	-	-	3530.3	1	Sym. CH stretch
	-	-	3424.7	89	Asym. CH stretch
	-	-	2045.3	3	CC stretch (Ac)
	-	-	2004.2	8	CC stretch (HNgY)
	-	-	1953.6	459	HXe stretch
	-	-	774.5	134	Sym. CCH bend
	b	-	768.4	86	
	-	-	659.2	0	HXeC bend

	M06-2X		CCSD		Assig.
	ω	*I*	*ω*	*I*	
	-	-	654.7	0	
	-	-	628.0	0	Asym. CCH bend
	-	-	622.5	0	
	-	-	297.1	212	XeC stretch
	-	-	94.9	5	XeCC bend
	-	-	94.4	6	
	-	-	55.4	0	Ac-HNgY
	-	-	37.7	2	Ac-HNgY
	-	-	7.4	5	Ac-HNgY
	-	-	6.1	5	Ac-HNgY
HXeCC···$(HCCH)_2$ structure 1					
	3505.1	9	-	-	-
	3504.8	0	-	-	-
	3364.0	143	-	-	-
	3361.4	236	-	-	-
	2089.7	3	-	-	-
	2088.6	7	-	-	-
	2040.0	33	-	-	-
	1874.7	704	-	-	HXe stretch
	842.1	84	-	-	-
	838.1	136	-	-	-
	831.0	96	-	-	-
	827.6	19	-	-	-

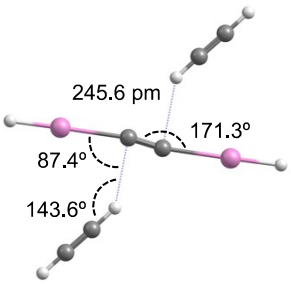
	M06-2X		CCSD		Assig.
	ω	*I*	*ω*	*I*	
	726.8	12	-	-	-
	726.3	5	-	-	-
	721.8	20	-	-	-
	721.4	7	-	-	-
	623.5	3	-	-	-
	589.5	1	-	-	-
	282.6	137	-	-	-
	165.6	8	-	-	-
	147.1	2	-	-	-
	100.9	3	-	-	-
	98.7	3	-	-	-
	88.4	1	-	-	-
	82.3	1	-	-	-
	76.2	0	-	-	-
	74.5	1	-	-	-
	46.5	4	-	-	-
	44.5	2	-	-	-
	5.5	0	-	-	-
HXeCC···$(HCCH)_2$ structure 2					
	3511.0	1	-	-	-
	3496.0	5	-	-	-
	3385.4	170	-	-	-
	3338.2	234	-	-	-

	M06-2X		**CCSD**		**Assig.**
	ω	*I*	*ω*	*I*	
	2092.8	2	-	-	-
	2084.3	7	-	-	-
	2044.1	34	-	-	-
	1828.7	766	-	-	HXe stretch
	848.2	90	-	-	-
	837.2	77	-	-	-
	825.0	69	-	-	-
	803.6	86	-	-	-
	730.5	19	-	-	-
	723.8	9	-	-	-
	719.3	10	-	-	-
	714.5	5	-	-	-
	641.2	2	-	-	-
	623.7	2	-	-	-
	285.7	153	-	-	-
	154.6	5	-	-	-
	129.4	3	-	-	-
	104.0	3	-	-	-
	102.4	0	-	-	-
	94.5	3	-	-	-
	90.1	2	-	-	-
	86.5	3	-	-	-
	61.3	0	-	-	-
	51.6	1	-	-	-

	M06-2X		CCSD		Assig.
	ω	*I*	*ω*	*I*	
	38.1	2	-	-	-
	24.2	2	-	-	-

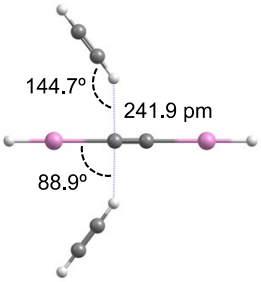
[a] Ac – acetylene; HNgY – noble-gas hydride. The basis sets are aug-cc-pVTZ-PP for M06-2X and cc-pVTZ-PP for CCSD. [b]Not an energy minimum at the M06-2X level.

a)



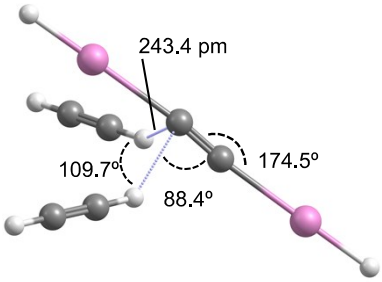
E_{int} = -40.2 kJ mol^{-1}
$E_{int, ZPVE}$ = -34.1 kJ mol^{-1}
$E_{int, ZPVE, BSSE}$ = -32.7 kJ mol^{-1}
Symm. = C_{2h}

b)



E_{int} = -38.7 kJ mol^{-1}
$E_{int, ZPVE}$ = -33.8 kJ mol^{-1}
$E_{int, ZPVE, BSSE}$ = -32.5 kJ mol^{-1}
Symm. = C_{2v}

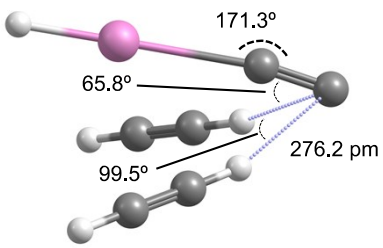
c)



E_{int} = -39.2 kJ mol^{-1}
$E_{int, ZPVE}$ = -33.4 kJ mol^{-1}
$E_{int, ZPVE, BSSE}$ = -32.0 kJ mol^{-1}
Symm. = C_s

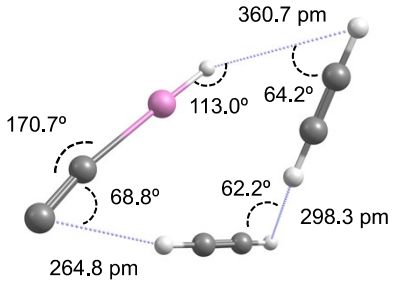
Figure S1. Optimized structures of the HXeCCXeH···$(HCCH)_2$ complex calculated at the M06-2X/aug-cc-pVTZ-PP level: structure 1 (a), structure 2 (b) and structure 3 (c).

a)



E_{int} = -37.7 kJ mol^{-1}
$E_{int, ZPVE}$ = -32.6 kJ mol^{-1}
$E_{int, ZPVE, BSSE}$ = -31.3 kJ mol^{-1}
Symm. = C_s

b)



E_{int} = -34.2 kJ mol^{-1}
$E_{int, ZPVE}$ = -29.2 kJ mol^{-1}
$E_{int, ZPVE, BSSE}$ = -28.0 kJ mol^{-1}
Symm. = C_1

Figure S2. Optimized structure of the HXeCC···$(HCCH)_2$ complex calculated at the M06-2X/aug-cc-pVTZ-PP level: structure 1 (a) and structure 2 (b).

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