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Electronic Supplementary Information

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Weak interactions in ion-ligand complexes of $C_3H_3^+$ isomers: Competition between H-bound and C-bound structures in c-$C_3H_3^+$ · L and H_2CCCH^+ · L (L = Ne, Ar, N_2, CO_2, and O_2)

17 tables

Tables S1-S13 provide the input for the radial energy profiles which are displayed in Figures 2-5 of the paper. Intramolecular harmonic vibrational wavenumbers for Ne and Ar complexes of c-$C_3H_3^+$ and $H_2C_3H^+$ are listed in Tables S14-S17.

TABLE S1. CCSD(T*)-F12a relative energies for neon migration around rigid c-$C_3H_3^+$ perpendicular to molecular plane.[a]

θ_1 (°)	R^{opt} (Å)	E_{rel} (cm^{-1})
0	4.2368	-182.9
2.5	4.2351	-182.7
15	4.1703	-177.5
30	3.9621	-173.3
45	3.6303	-188.6
60	3.3431	-208.3
61	3.3311	-208.5
62	3.3201	-208.6
63	3.3101	-208.5
64	3.3010	-208.3
75	3.2471	-200.4
90	3.2353	-193.3
105	3.2471	-198.0
120	3.2968	-203.1
122	3.3066	-203.3
124	3.3169	-203.3
135	3.3815	-201.9
150	3.4713	-197.1
165	3.5366	-192.9
180	3.5600	-191.3

[a] Basis A: VQZ-F12(C,H), AV5Z (Ne). Equilibrium structure of c-$C_3H_3^+$: r_e(CH) = 1.07947 Å and R_e(CC) = 1.36253 Å.

TABLE S2. CCSD(T*)-F12a relative energies for in-plane neon migration around rigid c-$C_3H_3^+$.[a]

θ_2 (°)	R^{opt} (Å)	E_{rel} (cm^{-1})
0	4.2368	-182.9
2.5	4.2351	-182.7
7.5	4.2211	-181.1
15	4.1727	-176.6
22.5	4.0911	-172.0
30	3.9778	-170.0
32.5	3.9338	-170.3
37.5	3.8401	-172.7
45	3.7013	-180.0
52.5	3.5973	-187.9
57.5	3.5642	-190.9
60	3.5600	-191.3

[a] Basis A: VQZ-F12(C,H), AV5Z (Ne). Equilibrium structure of c-$C_3H_3^+$: r_e(CH) = 1.07947 Å and R_e(CC) = 1.36253 Å.

TABLE S3. CCSD(T*)-F12a relative energies for neon migration around rigid $H_2C_3H^+$ perpendicular to molecular plane.[a]

θ_1 (°)	R^{opt} (Å)	E_{rel} (cm^{-1})
0	4.6185	-206.5
15	4.5289	-194.5
30	4.2429	-181.1
45	3.7822	-193.0
60	3.4318	-194.4
75	3.3231	-167.5
90	3.2935	-160.0
105	3.3027	-182.5
120	3.3814	-226.0
127	3.5069	-238.8
128	3.5267	-239.3
129	3.5486	-239.5
130	3.5726	-239.4
131	3.5968	-239.0
135	3.7022	-234.8
150	4.1265	-205.6
165	4.4253	-187.0
180	4.5276	-181.7

[a] Basis: VQZ-F12(C,H), AV5Z (Ne). Equilibrium structure for $H_2C_3H^+$: $r_{1e}(CH_2)$ = 1.08721 Å, α_e(HCH) = 119.32°, R_{1e}(C-C) = 1.34894 Å, R_{2e}(C≡C) = 1.23044 Å, and r_{2e}(CH) = 1.07411 Å.

TABLE S4. CCSD(T*)-F12a relative energies for in-plane neon migration around rigid $H_2C_3H^+$.[a]

θ_1 (°)	R^{opt} (Å)	E_{rel} (cm^{-1})
0	4.6185	-206.5
2.5	4.6163	-206.0
15	4.5416	-189.5
30	4.3135	-160.2
45	3.9991	-139.4
60	3.7256	-126.1
75	3.4809	-132.8
90	3.2568	-179.7
105	3.3889	-206.2
120	3.8990	-181.5
135	4.3280	-175.3
150	4.5457	-169.6
165	4.5842	-171.2
177.5	4.5303	-181.2
180	4.5276	-181.7

[a] Basis: VQZ-F12(C,H), AV5Z (Ne). Equilibrium structure for $H_2C_3H^+$: $r_{1e}(CH_2)$ = 1.08721 Å, α_e(HCH) = 119.32°, R_{1e}(C-C) = 1.34894 Å, R_{2e}(C≡C) = 1.23044 Å, and r_{2e}(CH) = 1.07411 Å.

TABLE S5. CCSD(T*)-F12a relative energies for radial N_2 migration around rigid c-$C_3H_3^+$ perpendicular to molecular plane.[a]

θ_1 (°)	R^{opt} (Å)	E_{rel} (cm^{-1})	θ_1 (°)	R^{opt} (Å)	E_{rel} (cm^{-1})
0	4.6672	-1173.6	97.5	3.8418	-928.1
2.5	4.6664	-1170.5	105	3.8434	-945.3
7.5	4.6600	-1147.3	112.5	3.8537	-963.1
15	4.6349	-1083.4	115	3.8599	-967.7
22.5	4.5798	-1013.1	117.5	3.8677	-971.4
30	4.4836	-963.7	120	3.8770	-973.9
37.5	4.3426	-950.2	122.5	3.8879	-975.1
45	4.1694	-972.8	125	3.9002	-975.1
52.5	4.0037	-1009.7	127.5	3.9139	-973.8
57.5	3.9221	-1022.5	135	3.9613	-963.3
60	3.8929	-1022.1	142.5	4.0137	-946.1
62.5	3.8711	-1017.3	150	4.0652	-926.7
65	3.8560	-1008.6	157.5	4.1105	-908.8
67.5	3.8462	-997.2	165	4.1454	-894.9
75	3.8377	-958.4	172.5	4.1673	-886.2
82.5	3.8408	-929.9	177.5	4.1740	-883.6
90	3.8425	-920.5	180	4.1748	-883.1

[a] Basis: VTZ-F12 (C, H), AVQZ (N_2). Equilibrium structures: a) c-$C_3H_3^+$: r_e(CH) = 1.07973 Å and R_e(CC) = 1.36318 Å; b) N_2: R_e = 1.09938 Å.

TABLE S6. CCSD(T*)-F12a relative energies for in-plane N_2 migration around rigid c-$C_3H_3^+$ along a radial path.[a]

θ_2 (°)	R^{opt} (Å)	E_{rel} (cm^{-1})	θ_1 (°)	R^{opt} (Å)	E_{rel} (cm^{-1})
0	4.6672	-1173.6	62.5	4.1787	-882.7
2.5	4.6667	-1170.2	67.5	4.2088	-878.9
7.5	4.6620	-1144.3	75	4.2999	-873.0
15	4.6419	-1071.8	82.5	4.4164	-882.3
22.5	4.5978	-988.0	90	4.5220	-920.4
30	4.5220	-920.4	97.5	4.5978	-988.0
37.5	4.4164	-882.3	105	4.6419	-1071.8
45	4.2999	-873.0	112.5	4.6620	-1144.3
52.5	4.2088	-878.9	117.5	4.6667	-1170.2
57.5	4.1787	-882.7	120	4.6672	-1173.6
60	4.1748	-883.3			

[a] Basis: VTZ-F12 (C, H), AVQZ (N_2). Equilibrium structures: a) c-$C_3H_3^+$: r_e(CH) = 1.07973 Å and R_e(CC) = 1.36318 Å; b) N_2: R_e = 1.09938 Å.

TABLE S7. CCSD(T*)-F12a relative energies for radial N_2 migration around rigid $H_2C_3H^+$ perpendicular to molecular plane.[a]

θ_1 (°)	R^{opt} (Å)	E_{rel} (cm^{-1})	θ_1 (°)	R^{opt} (Å)	E_{rel} (cm^{-1})
0	5.0422	-1337.2	97.5	3.9094	-780.0
2.5	5.0414	-1331.3	105	3.8908	-860.6
7.5	5.0336	-1287.6	112.5	3.8663	-991.1
15	4.9986	-1172.8	120	3.8547	-1158.8
22.5	4.9167	-1055.1	125	3.8754	-1260.3
30	4.7666	-978.9	130	3.9435	-1313.3
37.5	4.5376	-963.3	135	4.0751	-1295.5
45	4.2538	-1002.6	140	4.2552	-1228.1
52.5	4.0176	-1032.6	150	4.6203	-1080.9
60	3.9150	-977.0	157.5	4.8369	-1009.5
67.5	3.8981	-876.0	165	4.9627	-963.0
75	3.9075	-792.9	172.5	5.0752	-947.5
82.5	3.9167	-748.5	177.5	5.1028	-942.2
90	3.9178	-744.2	180	5.1044	941.5

[a] Basis: VTZ-F12 ($H_2C_3H^+$), AVQZ (N_2). Equilibrium structures: a) $H_2C_3H^+$: r_{1e}(CH$_2$) = 1.08745 Å, α_e(HCH) = 119.33°, R_{1e}(C-C) = 1.34948 Å, R_{2e}(C≡C) = 1.23101 Å, and r_{2e}(CH) = 1.07430 Å; b) N_2: R_e = 1.09938 Å.

TABLE S8. CCSD(T*)-F12a relative energies for in-plane N_2 migration around rigid $H_2C_3H^+$ along a radial path.[a]

θ_1 (°)	R^{opt} (Å)	E_{rel} (cm^{-1})	θ_1 (°)	R^{opt} (Å)	E_{rel} (cm^{-1})
0	5.0422	-1337.2	105	3.9716	-936.3
2.5	5.0414	-1329.2	112.5	4.1875	-945.6
7.5	5.0381	-1275.6	115	4.2636	-951.3
15	5.0199	-1131.0	120	4.4081	-971.6
22.5	4.9715	-970.4	125	4.5373	-1001.6
30	4.8820	-836.9	127.5	4.5959	-1018.3
45	4.6081	-673.6	135	4.7512	-1062.0
52.5	4.4693	-626.2	142.5	4.8827	-1075.8
60	4.3470	-596.0	150	4.9916	-1050.7
62.5	4.3080	-590.8	157.5	5.0698	-1004.0
67.5	4.2289	-590.1	165	5.1076	-963.6
75	4.0998	-618.6	172.5	5.1097	-944.7
82.5	3.9634	-690.1	180	5.1044	-941.5
90	3.8574	-797.6			

[a] Basis: VTZ-F12 ($H_2C_3H^+$), AVQZ (N_2). Equilibrium structures: a) $H_2C_3H^+$: r_{1e} (CH_2) = 1.08745 Å, α_e (HCH) = 119.33°, R_{1e} (C-C) = 1.34948 Å, R_{2e} (C≡C) = 1.23101 Å, and r_{2e} (CH) = 1.07430 Å; b) N_2: R_e = 1.09938 Å.

TABLE S9. CCSD(T*)-F12a relative energies for radial CO_2 migration around rigid c-$C_3H_3^+$ perpendicular to molecular plane.[a]

θ_1 (°)	R^{opt} (Å)	E_{rel} (cm^{-1})	θ_1 (°)	R^{opt} (Å)	E_{rel} (cm^{-1})
0	5.0512	-1932.1	97.5	4.0979	-1800.5
2.5	5.0495	-1929.9	105	4.1084	-1818.0
7.5	5.0359	-1912.0	112.5	4.1306	-1831.9
15	4.9895	-1861.1	115	4.1409	-1834.0
22.5	4.9108	-1800.7	117.5	4.1528	-1834.4
30	4.7984	-1756.4	120	4.1660	-1833.1
37.5	4.6529	-1749.4	122.5	4.1806	-1830.0
45	4.4853	-1786.0	125	4.1964	-1825.2
52.5	4.3238	-1844.6	127.5	4.2133	-1818.7
57.5	4.2373	-1873.6	135	4.2681	-1791.8
60	4.2046	-1880.8	142.5	4.3249	-1758.6
62.5	4.1751	-1882.1	150	4.3784	-1725.1
65	4.1529	-1878.4	157.5	4.4241	-1696.0
67.5	4.1358	-1870.5	165	4.4588	-1674.1
75	4.1072	-1834.2	172.5	4.4804	-1660.6
82.5	4.0975	.1802.9	177.5	4.4870	-1656.6
90	4.0952	-1792.1	180	4.4878	-1656.1

[a] Basis: VTZ-F12 (C, H), AVQZ (CO_2). Equilibrium structures: a) c-$C_3H_3^+$: r_e(CH) = 1.07973 Å and R_e(CC) = 1.36318 Å; b) CO_2: R_e = 1.16209 Å.

TABLE S10. CCSD(T*)-F12a relative energies for in-plane CO_2 migration around rigid c-$C_3H_3^+$ along a radial path.[a]

θ_1 (°)	R^{opt} (Å)	E_{rel} (cm^{-1})
0	5.0512	-1932.1
2.5	5.0496	-1929.5
7.5	5.0370	-1908.8
15	4.9949	-1847.0
22.5	4.9250	-1768.6
30	4.8302	-1698.6
45	4.6027	-1644.9
60	4.4878	-1656.1
75	4.6027	-1644.9
90	4.8302	-1698.6
97.5	4.9250	-1768.6
105	4.9949	-1847.0
112.5	5.0370	-1908.8
117.5	5.0496	-1929.5
120	5.0512	-1932.1

[a] Basis: VTZ-F12 (C, H), AVQZ (CO_2). Equilibrium structures: a) c-$C_3H_3^+$: r_e(CH) = 1.07973 Å and R_e(CC) = 1.36318 Å; b) CO_2: R_e = 1.16209 Å.

TABLE S11. CCSD(T*)-F12a relative energies for radial CO_2 migration around rigid $H_2C_3H^+$ perpendicular to molecular plane.[a]

θ_1 (°)	R^{opt} (Å)	E_{rel} (cm^{-1})	θ_1 (°)	R^{opt} (Å)	E_{rel} (cm^{-1})
0	5.4385	-2134.5	97.5	4.1376	-1555.5
2.5	5.4364	-2129.7	105	4.1304	-1687.0
7.5	5.4176	-2095.5	112.5	4.1311	-1878.7
15	5.3521	-1997.0	120	4.1620	-2086.5
22.5	5.2417	-1877.6	125	4.2130	-2180.4
30	5.0797	-1783.6	130	4.3258	-2200.7
37.5	4.8610	-1749.5	135	4.4788	-2147.1
45	4.6016	-1781.7	142.5	4.7425	-2012.2
52.5	4.3698	-1817.0	150	4.9821	-1895.7
60	4.2364	-1766.2	157.5	5.1708	-1819.3
67.5	4.1830	-1649.3	165	5.3040	-1775.8
75	4.1638	-1542.8	172.5	5.3841	-1754.5
82.5	4.1541	-1486.3	177.5	5.4073	-1749.0
90	4.1459	-1489.6	180	5.4102	-1748.3

[a] Basis: VTZ-F12 (C, H), AVQZ (CO_2). Equilibrium structures: a) $H_2C_3H^+$: r_{1e} (CH_2) = 1.08745 Å, α_e (HCH) = 119.33°, R_{1e} (C-C) = 1.34948 Å, R_{2e} (C≡C) = 1.23101 Å, and r_{2e} (CH) = 1.07430 Å; b) CO_2: R_e = 1.16209 Å.

TABLE S12. CCSD(T*)-F12a relative energies for in-plane CO_2 migration around rigid $H_2C_3H^+$ along a radial path.[a]

θ_1 (°)	R^{opt} (Å)	E_{rel} (cm^{-1})	θ_1 (°)	R^{opt} (Å)	E_{rel} (cm^{-1})
0	5.4388	-2134.4	105	4.2968	-1708.0
2.5	5.4369	-2128.2	112.5	4.4939	-1740.5
15	5.3678	-1945.7	120	4.7159	-1770.2
22.5	5.2833	-1764.4	125	4.8572	-1793.9
30	5.1690	-1583.9	135	5.1050	-1825.9
45	4.8785	-1318.8	142.5	5.2519	-1819.9
52.5	4.7353	-1235.4	150	5.3582	-1791.0
60	4.6087	-1182.6	157.5	5.4187	-1757.1
67.5	4.4917	-1170.4	165	5.4347	-1738.5
75	4.3750	-1212.5	172.5	5.4216	-1741.6
82.5	4.2631	-1317.9	177.5	5.4119	-1747.4
90	4.1849	-1473.3	180	5.4105	-1748.3

[a] Basis: VTZ-F12 (C, H), AVQZ (CO_2). Equilibrium structures: a) $H_2C_3H^+$: r_{1e} (CH_2) = 1.08745 Å, α_e (HCH) = 119.33°, R_{1e} (C-C) = 1.34948 Å, R_{2e} (C≡C) = 1.23101 Å, and r_{2e} (CH) = 1.07430 Å; b) CO_2: R_e = 1.16209 Å.

TABLE S13. UCCSD(T*)-F12a relative energies for radial O_2 migration around rigid c-$C_3H_3^+$ perpendicular to molecular plane.[a]

θ_1 (°)	R^{opt} (Å)	E_{rel} (cm^{-1})	θ_1 (°)	R^{opt} (Å)	E_{rel} (cm^{-1})
0	4.7062	-635.9	97.5	3.6584	-726.8
2.5	4.7022	-635.8	105	3.6731	-732.8
7.5	4.6836	-635.5	112.5	3.6998	-737.0
15	4.6228	-635.5	115	3.7117	-737.4
22.5	4.5279	-635.7	117.5	3.7243	-737.3
30	4.4039	-639.0	120	3.7377	-736.5
37.5	4.2553	-651.0	122.5	3.7529	-735.1
45	4.0902	-675.9	125	3.7686	-733.1
52.5	3.9289	-709.5	127.5	3.7850	-730.7
57.5	3.8381	729.2	135	3.8315	-721.4
60	3.8001	-736.4	142.5	3.8894	-709.0
62.5	3.7676	-741.2	150	3.9379	-697.5
65	3.7406	-743.8	157.5	3.9790	-687.7
67.5	3.7186	-744.1	165	4.0101	-680.4
75	3.6763	-737.0	172.5	4.0291	-676.0
82.5	3.6586	-727.5	177.5	4.0349	-674.7
90	3.6560	-723.6	180	4.0356	-674.5

[a] Basis: VTZ-F12 (C, H), AVQZ (O_2). Equilibrium structures: a) c-$C_3H_3^+$: r_e(CH) = 1.07973 Å and R_e(CC) = 1.36318 Å; b) O_2: R_e = 1.20662 Å.

Table S14. CCSD(T*)-F12a intramolecular harmonic vibrational wavenumbers (in cm^{-1}) for different structures of c-$C_3H_3^+$ · Ne and for free c-$C_3H_3^+$.[a]

No. of vibration[b]	C_s Min 1	C_s Min 2	C_{2v} Min	c-$C_3H_3^+$
1	3304.1 (a')	3303.3 (a')	3303.0 (a_1)	3302.6 (a_1')
2	3258.4 (a'')	3257.2 (a'')	3257.0 (b_2)	3256.1 (e')
3	3257.2 (a')	3256.9 (a')	3256.1 (a_1)	3256.1 (e')
4	1642.8 (a')	1642.6 (a')	1642.5 (a_1)	1641.8 (a_1')
5	1319.3 (a')	1319.3 (a')	1319.3 (a_1)	1318.8 (e')
6	1319.1 (a'')	1319.0 (a'')	1318.4 (b_2)	1318.8 (e')
7	1049.8 (a'')	1049.6 (a'')	1050.9 (b_2)	1050.4 (a_2')
8	1016.1 (a')	1016.0 (a')	1019.5 (b_1)	1016.4 (e'')
9	1015.8 (a'')	1015.9 (a'')	1016.5 (a_2)	1016.4 (e'')
10	942.6 (a'')	942.4 (a'')	945.0 (b_2)	943.3 (e')
11	942.3 (a')	942.0 (a')	942.3 (a_1)	943.3(e')
12	760.3 (a')	759.0 (a')	761.8 (b_1)	761.2 (a_2'')

[a] Basis: (T, Q).

[b] Vibrations are ordered according to decreasing wavenumber.

Table S15. CCSD(T*)-F12a intramolecular harmonic vibrational wavenumbers (in cm^{-1}) for different structures of $H_2C_3H^+ \cdot Ne$ and for free $H_2C_3H^+$.[a]

No. of vibration[b]	C_s Min 1	C_s Min 2	C_s planar	C_{2v} Min	$H_2C_3H^+$
1	3358.3 (a')	3359.5 (a')	3358.0 (a')	3351.1 (a_1)	3357.6 (a_1)
2	3226.7 (a'')	3224.8 (a'')	3226.4 (a')	3225.0 (b_2)	3225.1 (b_2)
3	3116.8 (a')	3115.1 (a')	3116.4 (a')	3115.3 (a_1)	3115.3 (a_1)
4	2121.2 (a')	2120.2 (a')	2121.1 (a')	2120.0 (a_1)	2120.9 (a_1)
5	1479.1 (a')	1479.0 (a')	1477.6 (a')	1479.2 (a_1)	1478.9 (a_1)
6	1132.1 (a')	1133.1 (a')	1132.1 (a')	1133.1 (a_1)	1132.4 (a_1)
7	1117.6 (a')	1115.9 (a')	1118.1 (a'')	1116.4 (b_1)	1117.0 (b_1)
8	1036.4 (a'')	1036.4 (a'')	1036.7 (a')	1036.6 (b_2)	1038.4 (b_2)
9	875.2 (a')	876.8 (a')	875.8 (a'')	882.4 (b_1)	876.2 (b_1)
10	624.9 (a'')	624.7 (a'')	623.3 (a')	634.2 (b_2)	624.5 (b_2)
11	287.7 (a'')	287.9 (a'')	288.7 (a')	287.9 (b_2)	287.2 (b_2)
12	256.6 (a')	257.7 (a')	254.0 (a'')	255.5 (b_1)	254.0 (b_1)

[a] Basis: (T, Q).

[b] Vibrations are ordered according to decreasing wavenumber.

Table S16. CCSD(T*)-F12a intramolecular harmonic vibrational wavenumbers (in cm^{-1}) for different structures of c-$C_3H_3^+ \cdot Ar$.[a]

No. of vibration[b]	C_s Min 1	C_{2v} Min
1	3304.9 (a')	3297.4 (a_1)
2	3259.8 (a'')	3256.6 (b_2)
3	3257.1 (a')	3236.5 (a_1)
4	1642.0 (a')	1640.4 (a_1)
5	1318.6 (a')	1318.8 (a_1)
6	1317.9 (a'')	1316.0 (b_2)
7	1050.1 (a'')	1053.8 (b_2)
8	1014.6 (a')	1025.1 (b_1)
9	1011.9 (a'')	1016.2 (a_2)
10	943.4 (a'')	950.8 (b_2)
11	943.2 (a')	942.9 (a_1)
12	760.7 (a')	766.6 (b_1)

[a] Basis: (T, Q).

[b] Vibrations are ordered according to decreasing wavenumber.

Table S17. Intramolecular harmonic vibrational wavenumbers and shifts (in cm^{-1}) for C_s and C_{2v} structures of $H_2C_3H^+ \cdot Ar$.[a]

No. of vibration[b]	C_s Min 1	C_s Min 2	C_s planar	C_{2v} Min
1	3362.5 (a')	3363.7 (a')	3359.4 (a')	3314.2 (a_1)
2	3231.5 (a'')	3225.7 (a'')	3225.2 (a')	3225.5 (b_2)
3	3121.3 (a')	3116.3 (a')	3114.3 (a')	3116.3 (a_1)
4	2121.6 (a')	2117.3 (a')	2121.0 (a')	2116.4 (a_1)
5	1479.0 (a')	1478.8 (a')	1473.6 (a')	1479.8 (a_1)
6	1129.7 (a')	1134.8 (a')	1131.7 (a')	1134.0 (a_1)
7	1114.5 (a')	1111.9 (a')	1120.3 (a'')	1115.8 (b_1)
8	1036.8 (a'')	1036.0 (a'')	1036.3 (a')	1037.4 (b_2)
9	871.0 (a')	872.8 (a')	875.4 (a'')	897.8 (b_1)
10	627.6 (a'')	622.9 (a'')	621.6 (a')	658.7 (b_2)
11	290.9 (a'')	288.8 (a'')	287.3 (a')	289.2 (b_2)
12	270.6 (a')	269.1 (a')	253.8 (a'')	258.5 (b_1)

[a] Basis: (T, Q).

[b] Vibrations are ordered according to decreasing wavenumber.