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PERSPECTIVE

Electronic spectroscopy of transient species in solid neon: the indene-motif polycyclic hydrocarbon cation family $C_9H_y^+$ (y = 7–9) and their neutrals†

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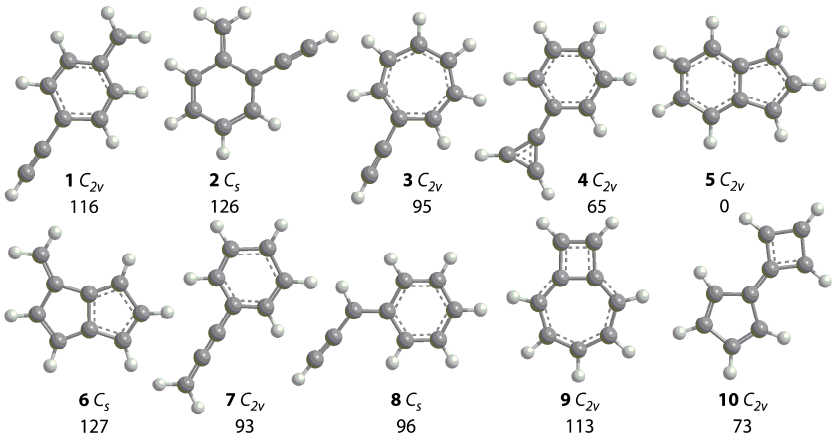

Fig. S1 Scheme and group symmetry of some considered $C_9H_7^+$ (m/z = 115) cations. The indicated relative ground-state energy (kJ mol^{-1}, corrected for zero-point vibrations) of the isomers was calculated with DFT at the B3LYP/6-31G(d,p) level. As seen, no structure is within 50 kJ mol^{-1} of the most stable 1-indenylium, "**5**".

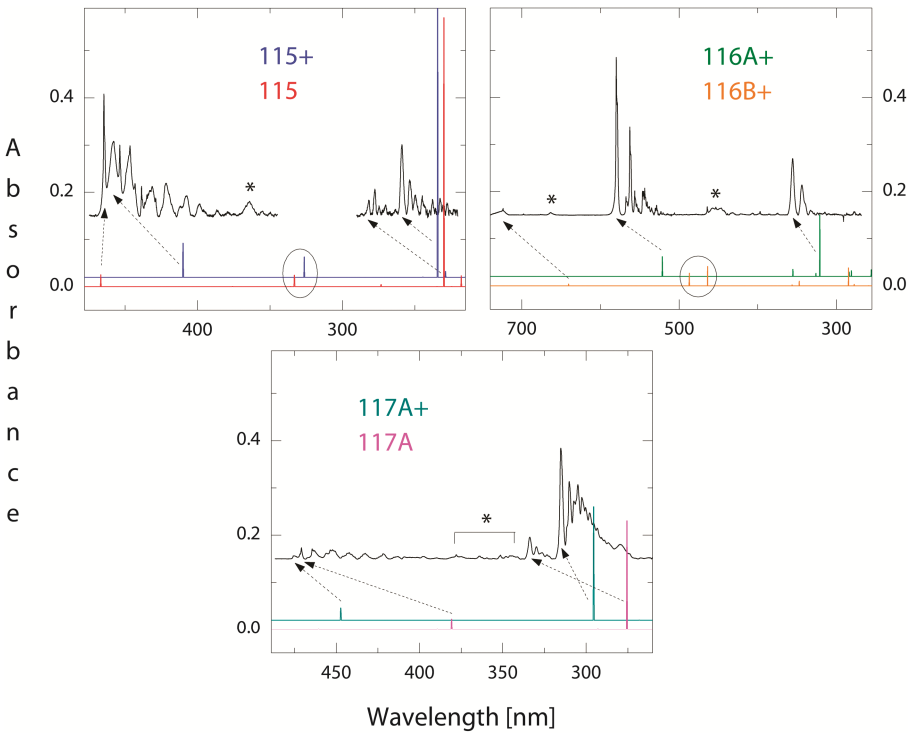

Fig. S2 Electronic absorption spectra of $C_9H_y^+$ cations and C_9H_y neutrals (y = 7–9) observed in 6 K neon matrices (black; see Figures 3–5) are compared with TD DFT calculations at the (u)BLYP/cc-pVDZ level shown in colored stick diagrams. Features marked by asterisks or circles are not or only tentatively assigned (Table 6).

Table S1 Ground-state totally symmetric (a' in C_s or a_1 in C_{2v}) vibrational fundamentals (cm^{-1}, unscaled) of $C_9H_y^+$ cations and C_9H_y neutrals (y = 7–10) calculated with DFT at the (u)BLYP/cc-pVDZ level of theory

Nr.	Cations						Neutrals					
	$C_9H_7^+$	$C_9H_8^{\bullet+}$		$C_9H_9^+$		$C_9H_{10}^{\bullet+}$	$C_9H_7^{\bullet}$	C_9H_8		$C_9H_9^{\bullet}$		C_9H_{10}
	115+	**116A+**	**116B+**	**117A+**	**117B+**	**118+**	**115**	**116A**	**116B**	**117A**	**117B**	**118**
1	3186	3159	3153	3140	3136	3137	3158	3143	3143	3124	3129	3110
2	3148	3144	3142	3129	3126	3124	3131	3119	3114	3116	3114	3083
3	3143	3143	3128	3125	3117	3053	3119	3115	3092	3103	3088	3015
4	3125	3134	2932	3117	2870	2976	3093	3102	2925	3089	2866	2989
5	1618	3130	1517	3114	1551	2968	1571	3090	1524	3083	1571	2959
6	1490	3121	1465	2966	1432	2861	1441	3084	1490	2955	1458	2919
7	1442	2949	1399	2931	1349	1503	1427	2937	1398	2911	1385	1571
8	1372	1600	1349	1595	1269	1437	1340	1595	1335	1558	1338	1458
9	1180	1497	1292	1536	1201	1411	1185	1579	1316	1534	1258	1433
10	1159	1457	1214	1492	1185	1349	1138	1547	1205	1452	1190	1411
11	1055	1415	1156	1443	1147	1326	1041	1442	1134	1420	1138	1339
12	981	1390	992	1398	1008	1253	1003	1437	961	1413	1015	1257
13	843	1379	925	1369	899	1194	844	1368	913	1393	903	1201
14	725	1346	819	1361	809	1150	731	1357	813	1370	791	1181
15	527	1326	715	1316	710	1119	534	1308	708	1313	691	1139
16		1274	529	1279	523	970		1265	532	1261	519	1023
17		1228		1275		962		1202		1258		1014
18		1196		1225		929		1186		1204		917
19		1142		1173		878		1143		1158		888
20		1134		1171		791		1135		1144		839
21		1096		1147		748		1091		1127		743
22		1049		1096		708		1044		1076		729
23		981		996		611		1011		1003		603
24		921		989		510		927		985		507
25		840		903		392		844		892		416
26		802		848		215		817		847		251
27		711		797		118		721		782		144
28		576		703				585		690		
29		508		574				527		573		
30		380		521				376		521		
31				376						373		

Table S2 Excited-state symmetries, vertical excitation energies ΔE < 5.8 eV (or maximum eight) and transition oscillator strengths f calculated for $C_9H_y^+$ cationic and C_9H_y neutral (y = 7–10) isomers with TD DFT at the (u)BLYP/cc-pVDZ level,[a] and comparison with experimental data

Cations				Neutrals			
Exc. St.	ΔE /eV	f	Expt.[b] /eV	Exc. St.	ΔE /eV	f	Expt.[b] /eV
$C_9H_7^+$ **115+**, $\tilde{X}\,^1A_1$, planar C_{2v}				$C_9H_7^\bullet$ **115**, $\tilde{X}\,^2A_2$, planar C_{2v}			
$^1B_1$	1.03	0.0002		$^2B_1$	1.31	0.0001	
$^1A_1$	3.02	0.072	2.71	$^2A_1$	2.66	0.025	2.67
$^1B_1$	3.80	0.043	(3.40)	$^2B_1$	3.30	0.0005	
$^1B_2$	3.83	0.0001		$^2A_1$	3.69	0.0003	
$^1B_2$	5.07	0.0006		$^2B_1$	3.72	0.024	(*)
$^1A_1$	5.29	0.58	4.79	$^2B_2$	4.48	0.0001	
$^1B_1$	5.42	0.012		$^2B_1$	4.53	0.0043	4.40
$^1B_2$	5.76	0.0003		$^2B_1$	4.82	0.0001	
$C_9H_8^{\bullet+}$ **116A+**, $\tilde{X}\,^2A''$, C_s (0)				C_9H_8 **116A**, $\tilde{X}\,^1A'$, C_s (0)			
$^2A'$	0.95	0.0001		$^1A'$	4.37	0.0090	
$^2A'$	2.38	0.042	2.14	$^1A'$	4.63	0.14	
$^2A'$	3.49	0.015		$^1A'$	5.16	0.14	
$^2A'$	3.80	0.0066		$^1A'$	5.58	0.0004	
$^2A'$	3.86	0.13	3.49				
$^2A'$	4.37	0.0091					
$^2A'$	4.41	0.012					
$^2A'$	4.85	0.014					
$C_9H_8^{\bullet+}$ **116B+**, $\tilde{X}\,^2A_2$, C_{2v} (9)				C_9H_8 **116B**, $\tilde{X}\,^1A_1$, C_{2v} (81)			
$^2B_2$	1.94	0.0036	1.71	$^1B_1$	2.71	0.046	(2.72)
$^2A_1$	2.55	0.027	(*)	$^1B_1$	4.26	0.0053	
$^2B_2$	2.67	0.041	(*)	$^1A_1$	4.31	0.012	
$^2B_2$	3.48	0.0019		$^1B_2$	5.28	0.0003	
$^2A_1$	3.57	0.0096		$^1B_1$	5.32	0.0006	
$^2A_1$	4.35	0.038					
$^2B_2$	4.47	0.0027					
$^2B_1$	4.79	0.0002					

Table S2 (*Continued*)

Cations				Neutrals			
Exc. St.	ΔE /eV	f	Expt.[b] /eV	Exc. St.	ΔE /eV	f	Expt.[b] /eV
$C_9H_9^+$ **117A+**, $\tilde{X}\,^1A'$, C_s (0)				$C_9H_9^\bullet$ **117A**, $\tilde{X}\,^2A''$, C_s (0)			
$^1A'$	2.77	0.026	2.61	$^2A'$	2.69	0.0010	
$^1A'$	4.20	0.24	3.93	$^2A'$	3.18	0.0011	
$^1A''$	4.23	0.0001		$^2A'$	3.26	0.022	2.63
$^1A''$	4.62	0.0003		$^2A'$	4.23	0.0014	
$^1A''$	5.12	0.0001		$^2A'$	4.50	0.23	3.71
$^1A''$	5.32	0.0027		$^2A''$	4.92	0.0003	
$^1A'$	5.37	0.070		$^2A'$	5.28	0.0007	
$^1A'$	5.60	0.12		$^2A''$	5.36	0.0001	
$C_9H_9^+$ **117B+**, $\tilde{X}\,^1A_1$, C_{2v} (106)				$C_9H_9^\bullet$ **117B**, $\tilde{X}\,^2B_1$, C_{2v} (46)			
$^1B_2$	0.81	0.0005		$^2A_1$	3.09	0.0014	
$^1A_1$	1.22	0.025		$^2B_2$	3.28	0.0029	
$^1B_1$	2.82	0.0003		$^2A_1$	3.49	0.0001	
$^1A_1$	3.51	0.0026		$^2B_2$	3.65	0.0003	
$^1B_1$	4.46	0.0009		$^2A_1$	5.02	0.010	
$^1A_1$	5.04	0.0009		$^2B_1$	5.07	0.0031	
$^1B_1$	5.22	0.0007		$^2B_1$	5.30	0.0022	
$^1B_2$	5.67	0.0001		$^2B_1$	5.60	0.0020	
$C_9H_{10}^{\bullet+}$ **118+**, $\tilde{X}\,^2A'$, C_s				C_9H_{10} **118**, $\tilde{X}\,^1A'$, C_s			
$^2A''$	0.77	0.0005		$^1A'$	4.91	0.019	
$^2A'$	2.22	0.049		$^1A''$	5.62	0.010	
$^2A'$	2.46	0.019					
$^2A''$	2.55	0.0005					
$^2A'$	2.75	0.0071					
$^2A'$	3.32	0.0004					
$^2A''$	4.08	0.018					
$^2A'$	4.24	0.0006					

[a] Wherever applicable, relative ground-state energy (kJ mol^{-1}, zero-point vibrational correction included) with respect to the more stable isomer is given in parentheses. [b] Origin band position of transitions observed in neon matrices of this study. Tentatively assigned or predicted but missing (asterisk) features are in parentheses.