Supplementary Information

Anionic states of C_6Cl_6 probed in electron transfer experiments

S. Kumar[1], T. Kilich[2], M. Łabuda[2], G. García[3], and P. Limão-Vieira[1,a)]

[1] Atomic and Molecular Collisions Laboratory, CEFITEC, Department of Physics, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal

[2] Department of Theoretical Physics and Quantum Information, Gdańsk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland

[3] Instituto de Física Fundamental, Consejo Superior de Investigaciones Científicas (CSIC), Serrano 113-bis, 28006 Madrid, Spain

Hexachlorobenzene molecule was considered in the D_{2h} symmetry for benchmarking the calculations and choice of the molecular framework. Then, the geometry of the ground S_0 $^1A'$ singlet state of C_6Cl_6 was considered to be of C_{2v} symmetry and has been optimized by means of Møller-Plesset perturbation theory (MP2) calculations with the balanced polarized triple-zeta def2-TZVP basis set[1] which has been shown to be computationally efficient and provides accurate structures and transition energies. All calculations have been performed using the ORCA and MOLPRO packages of *ab initio* programmes.[2,3] The energy of the optimized molecule is E_{MP2} = -2986.35880 a.u. The HOMO is located at $20b_1$ with an energy E_{HOMO} = -9.68 eV and the LUMO at $22a_1$ with an energy E_{LUMO} = 1.83 eV. The LUMO-HOMO energy difference is 11.51 eV.

Figure caption

FIG. S1. Selection of the molecular orbitals for K + C_6Cl_6 (K: magenta, C: grey, Cl: green) at CAS(13,16). See also Table S1.

FIG. S2. Selection of the molecular orbitals for C_6Cl_6 (C: grey, Cl: green) at CAS(12,12). See also Table S2.

FIG. S3. $C_6Cl_6^-$ molecular orbitals: the highest doubly occupied (68-69), singly occupied (70, SOMO) as well as the lowest unoccupied (71-73) (RKS, B3LYP+D3) (C: grey, Cl: green).

FIG. S4. TOF mass spectrum of Cl_2^- anion at 100 eV collision energy and fitted with functions to reproduce its isotope contributions at 70 u (100%), 72 u (~65%) and 74 u (~15%).

Table caption

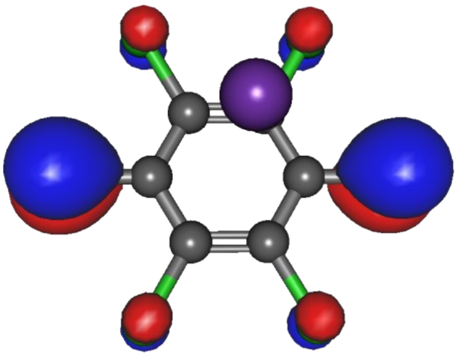
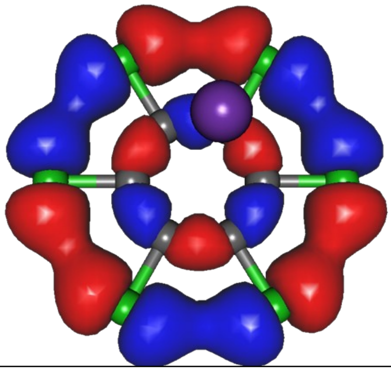
Table S1. Character and energy of calculated molecular orbitals for K + C_6Cl_6 with an active space CAS(13,16) at the MP2/def2-TZVP level of theory in C_{2v} symmetry.

Table S2. Character and energy of calculated molecular orbitals for C_6Cl_6 with an active space CAS(12,12) at the MP2/def2-TZVP level of theory in C_{2v} symmetry.

Table S3. Adiabatic and vertical ionisation energies, adiabatic and vertical electron affinities and vertical detachment energy (VDE) for C_6Cl_6 geometry optimized at RKS/B3LYP+D3/aug-cc-pVTZ level.

Table S4. Calculated energies (in a.u.) of the neutral, anion and cation of C_6Cl_6 at geometries of neutral and ionized system using RKS/B3LYP+D3/aug-cc-pVTZ for RHF-SCF, RMP2, and RKS methods.

FIG. S1. Selection of the molecular orbitals for K + C_6Cl_6 (K: magenta, C: grey, Cl: green) at CAS(13,16). See also Table S1.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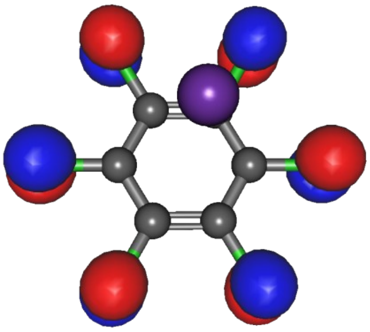	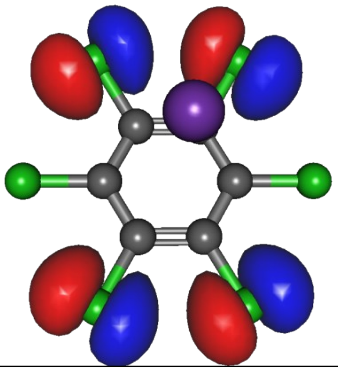
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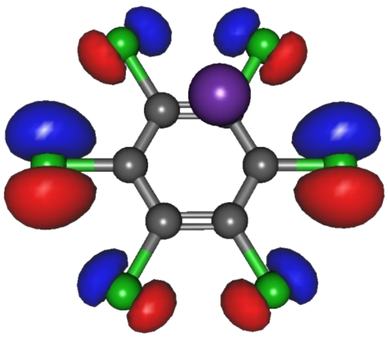	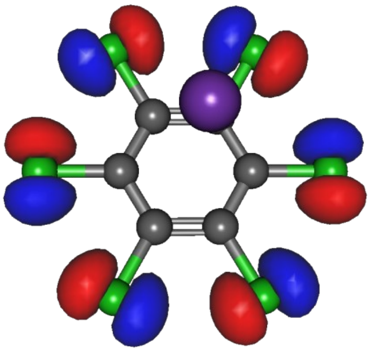
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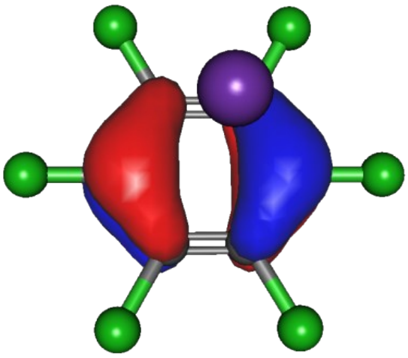
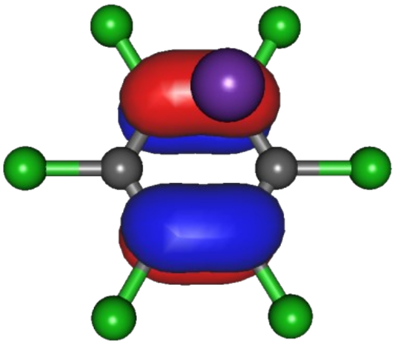
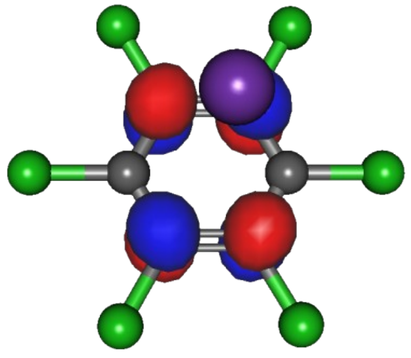
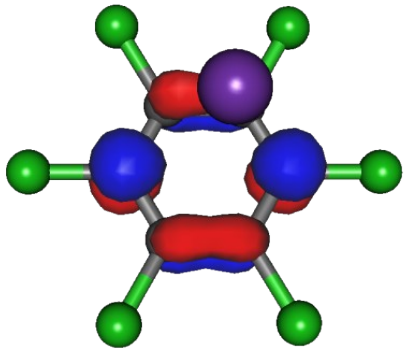
	
HOMO-1, π_{CCl}	HOMO, π_{CC}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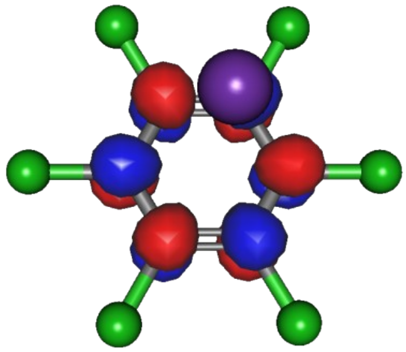	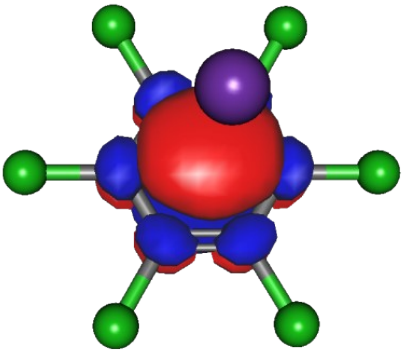
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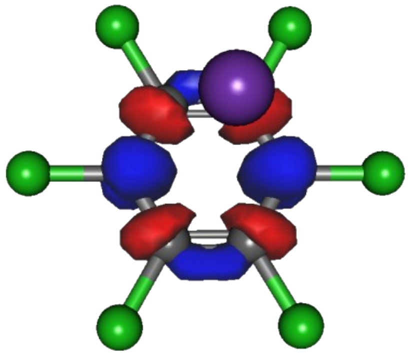	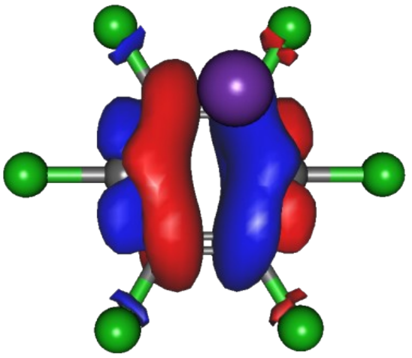
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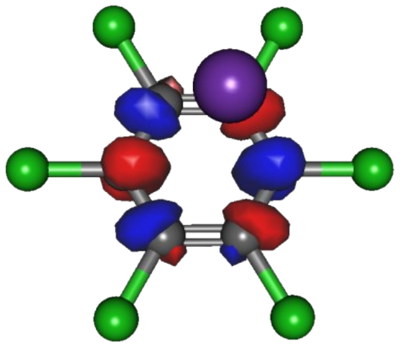
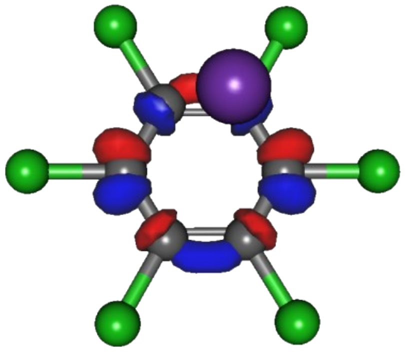
	
LUMO+6, σ_{CC}^*	LUMO+7, σ_{CC}^*

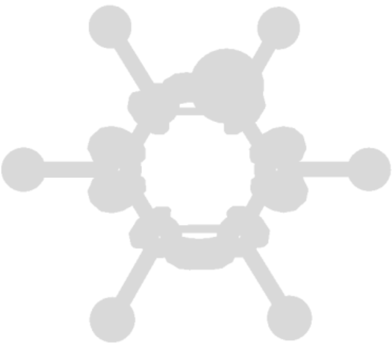
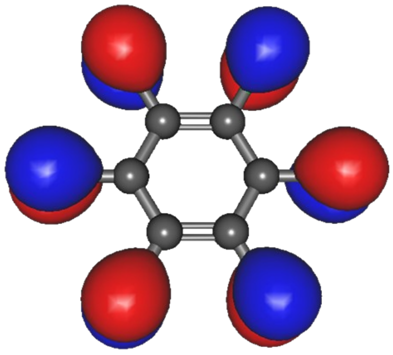
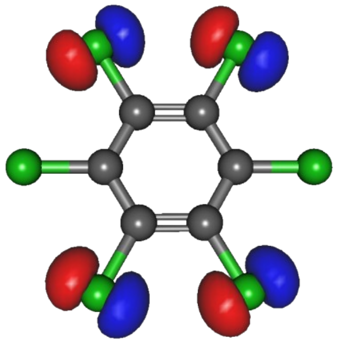
	
LUMO+8, σ_{CC}^*	

FIG. S2. Selection of the molecular orbitals for C_6Cl_6 (C: grey, Cl: green) at CAS(12,12). See also Table S2.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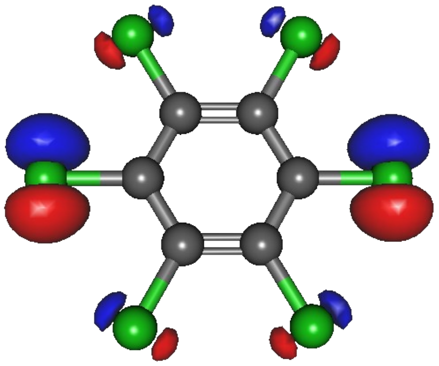	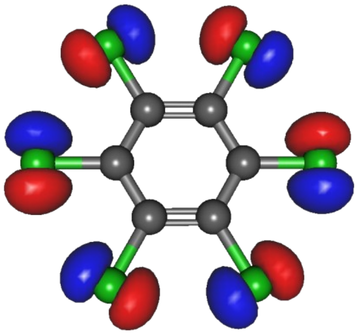
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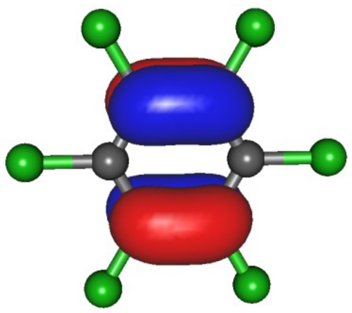
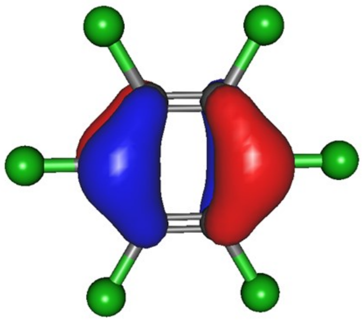
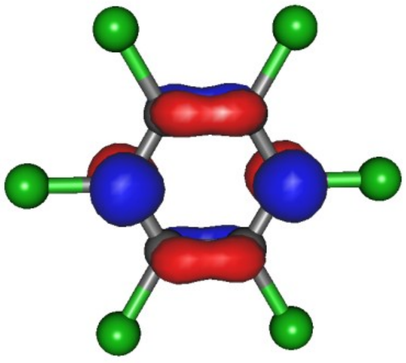
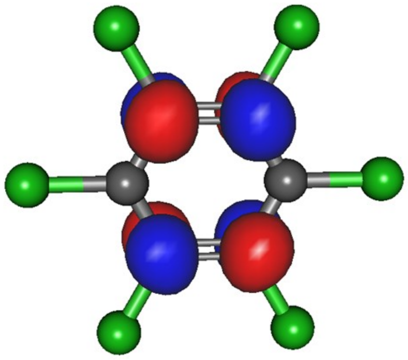
	
HOMO-1, π_{CC}	HOMO, π_{CCl}
	
LUMO, $\pi_{CC}^*/\sigma_{CC}^* + \sigma_{CCl}^*$	LUMO+1, π_{CC}^*

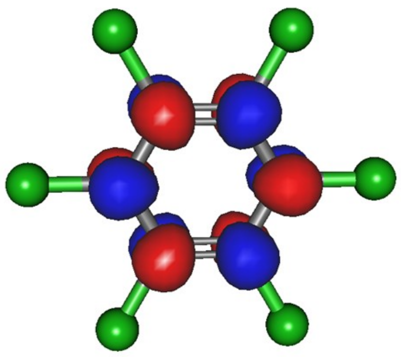
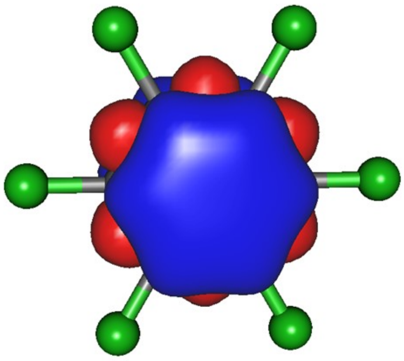
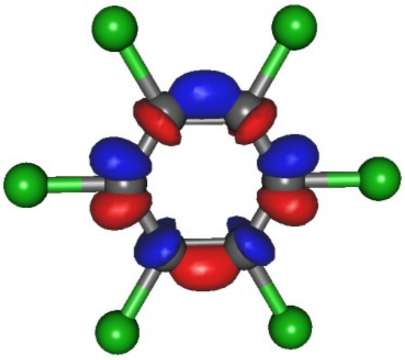
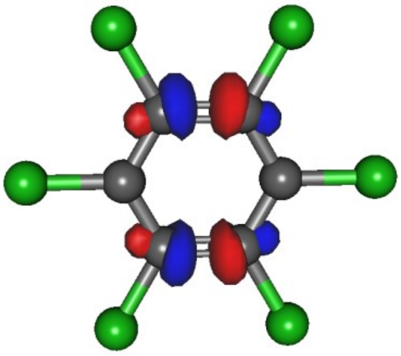
	
LUMO+2, π_{CC}*	LUMO+3, σ_{CC}*
	
LUMO+4, σ_{CC}*	LUMO+5, π_{CC}* + σ_{CC}*

FIG. S3. $C_6Cl_6^-$ molecular orbitals: the highest doubly occupied (68-69), singly occupied (70, SOMO) as well as the lowest unoccupied (71-73) (RKS, B3LYP+D3) (C: grey, Cl: green).

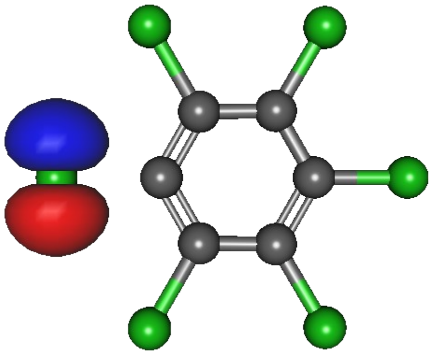
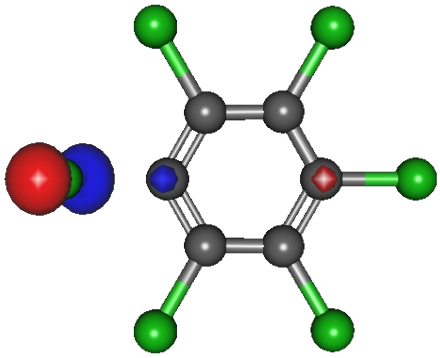
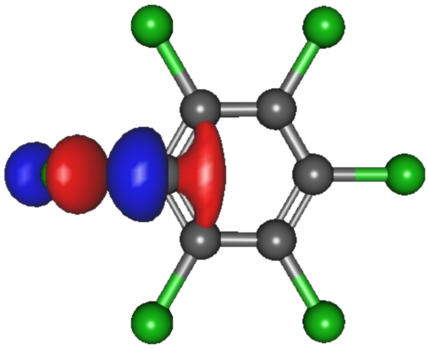
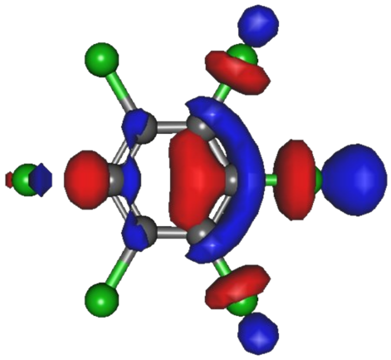
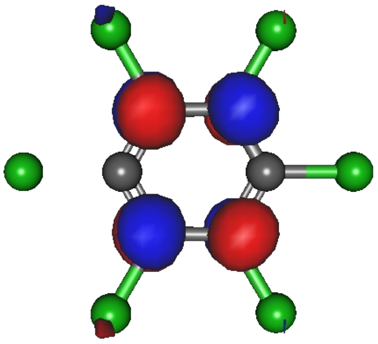
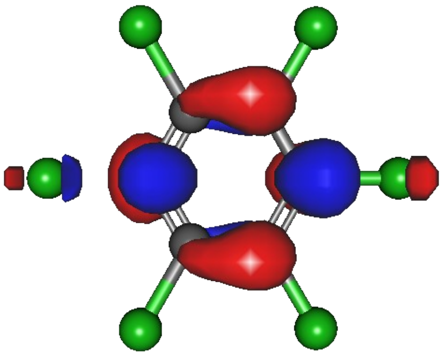
	
68, π (-3.366 eV)	69, π (-3.148 eV)
	
70, SOMO, π_{CCl} (-1.096 eV)	71, σ_{CCl}* (1.918 eV)
	
72, π* (2.174 eV)	73, σ_{CCl}* (2.435 eV)

FIG. S4. TOF mass spectrum of Cl_2^- anion at 100 eV collision energy and fitted with functions to reproduce its isotope contributions at 70 u (100%), 72 u (~65%) and 74 u (~15%).

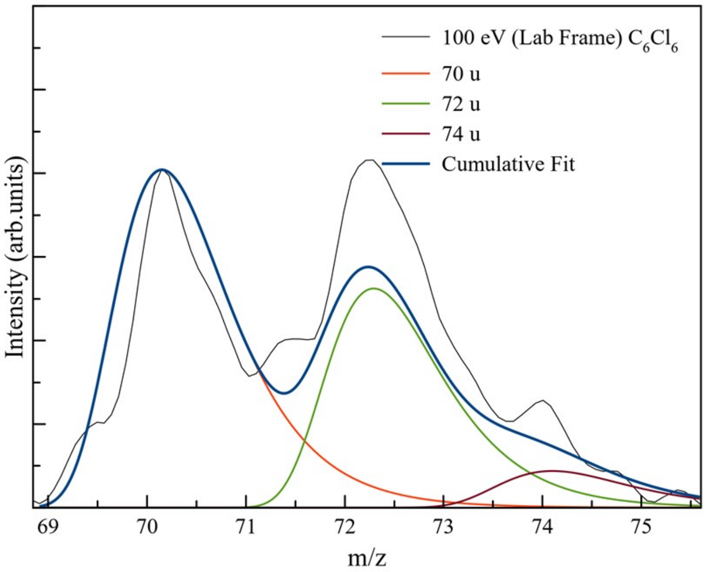


Table S1. Character and energy of calculated molecular orbitals for K + C_6Cl_6 with an active space CAS(13,16) at the MP2/def2-TZVP level of theory in C_{2v} symmetry.

Character	Energy (a.u.)	Energy (eV)
HOMO-2	-0.4420	-12.027
HOMO-1	-0.3903	-10.621
HOMO	-0.3884	-10.569
SOMO	-0.0604	-1.644
LUMO	0.1061	2.887
LUMO+1	0.1138	3.097
LUMO+2	0.3617	9.842
LUMO+3	0.5812	15.815
LUMO+4	0.5946	16.180
LUMO+5	0.6113	16.634
LUMO+6	0.6537	17.788
LUMO+7	0.6746	18.357
LUMO+8	0.9701	26.398

Table S2. Character and energy of calculated molecular orbitals for C_6Cl_6 with an active space CAS(12,12) at the MP2/def2-TZVP level of theory in C_{2v} symmetry.

Character	Energy (a.u)	Energy (eV)
HOMO-4	-0.4734	-12.882
HOMO-3	-0.4734	-12.882
HOMO-2	-0.4404	-11.984
HOMO-1	-0.3860	-10.504
HOMO	-0.3848	-10.471
LUMO	0.1059	2.882
LUMO+1	0.1090	2.966
LUMO+2	0.3571	9.717
LUMO+3	0.6252	17.013
LUMO+4	0.6310	17.170
LUMO+5	0.6428	17.491

Table S3. Adiabatic and vertical ionisation energies, adiabatic and vertical electron affinities and vertical detachment energy (VDE) for C_6Cl_6 geometry optimized at RKS/B3LYP+D3/aug-cc-pVTZ level.

Method	**Ionisation energy (eV)**		**Electron affinity (eV)**			**Vertical detachment energy (eV)**
	adiabatic	vertical	adiabatic	vertical	exp.	
RKS, B3LYP+D3[4]	-	9.00 9.19[5]	0.95	0.38	0.91[6] 0.98[7]	2.70
RKS, B3LYP	-	9.0	0.94	0.38		2.70
RMP2	-	9.45	0.50	0.01		2.56
RHF-SCF	-	8.93	-0.07	-1.16		2.19

Table S4. Calculated energies (in a.u.) of the neutral, anion and cation of C_6Cl_6 at geometries of neutral and ionized system using RKS/B3LYP+D3/aug-cc-pVTZ for RHF-SCF, RMP2, and RKS methods.

System	**C_6Cl_6**		**$C_6Cl_6^+$**		**$C_6Cl_6^-$**	
Geometry	neutral	anion	neutral	cation	neutral	anion
RHF-SCF	-2984.346506	-2984.263442	-2984.018226	-2984.027835	-2984.304053	-2984.344016
RMP2	-2986.464580	-2986.388667	-2986.117420	-2986.126892	-2986.464917	-2986.482805
RKS. B3LYP	-2989.562438	-2989.497801	-2989.231727	-2989.237619	-2989.576324	-2989.597158
RKS, B3LYP+D3	-2989.566924	-2989.502321	-2989.236213	-2989.242182	-2989.580810	-2989.601678

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