Electronic Supporting Information - Variation of the Optical Properties with Size and Composition of Small, Isolated $Cd_xSe_y^+$ Clusters

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(Dated: September 1, 2020)

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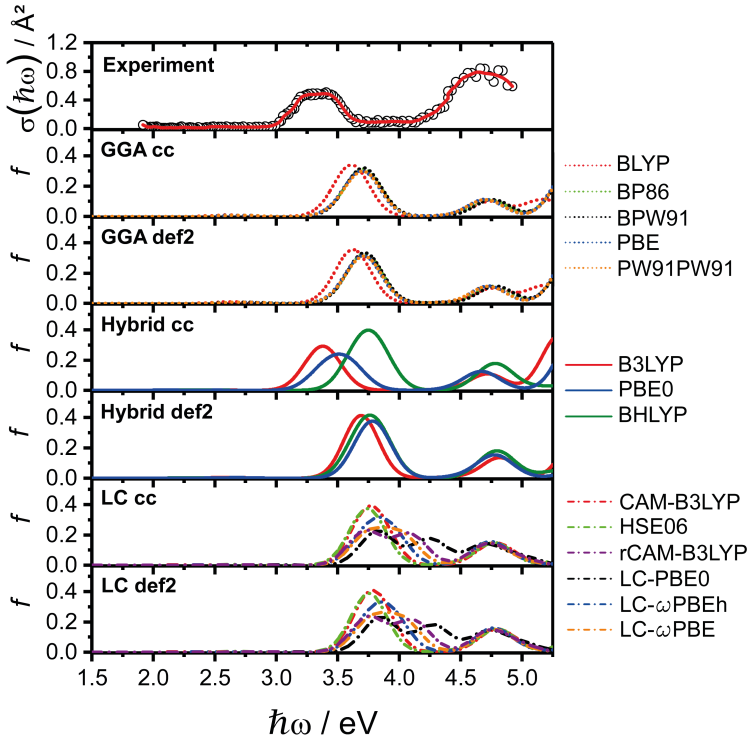

Figure S1. Benchmark of xc functional/basis combinations in comparison with experimental data of $Cd_2Se_2^+$. The basis set cc-pVTZ-PP (labeled by cc) and def2-tzvpp (labeled by def2) were used with different xc functionals as shown by the legend to calculate the optical absorption spectra by TDDFT calculations. The spectra are generated by Gaussian convolution of line spectra using a full width at half maximum of 0.30 eV. The benchmark shows that only PBE0/cc-pVTZ-PP and B3LYP/cc-pVTZ-PP are able to predict the position of the absorption maxima with a good accuracy.

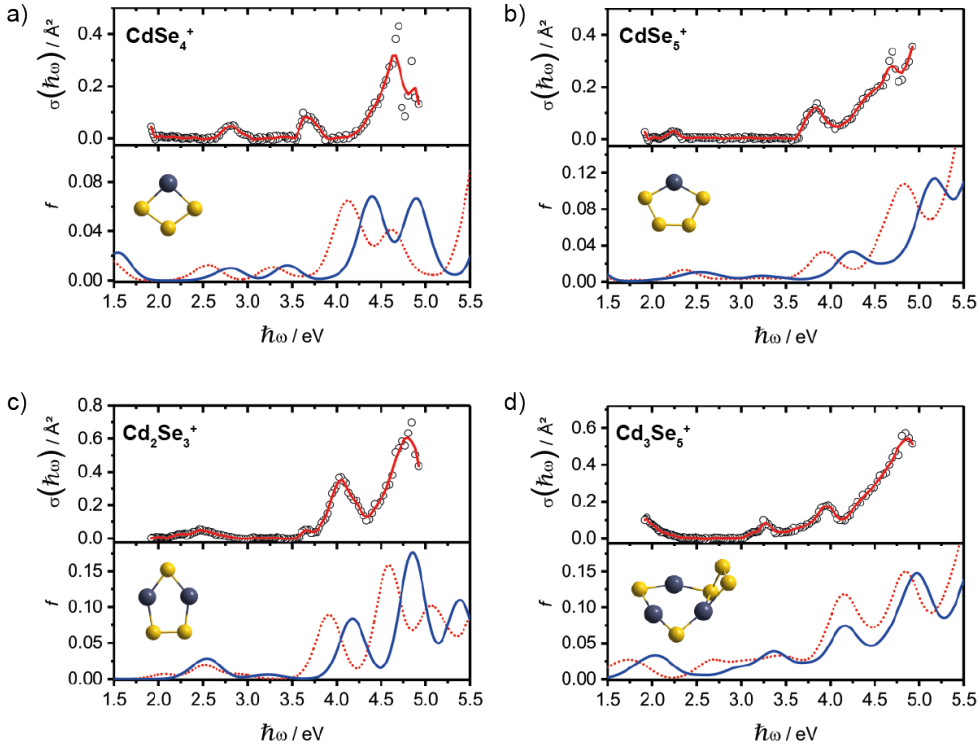

Figure S2. Comparison of the selected not previously shown experimental absorption spectra of a) $CdSe_4^+$, b) $CdSe_5^+$, c) $Cd_2Se_3^+$ and d) $Cd_3Se_5^+$ in comparison with TDDFT predictions by PBE0/cc-pVTZ-PP (solid blue solid line) and B3LYP/cc-PVTZ-PP (dotted red line). All calculations show a good match with the experimental results, which again justifies the choice of B3LYP/cc-PVTZ-PP and PBE0/cc-pVTZ-PP being a good description for the optical properties of $Cd_xSe_y^+$ clusters.

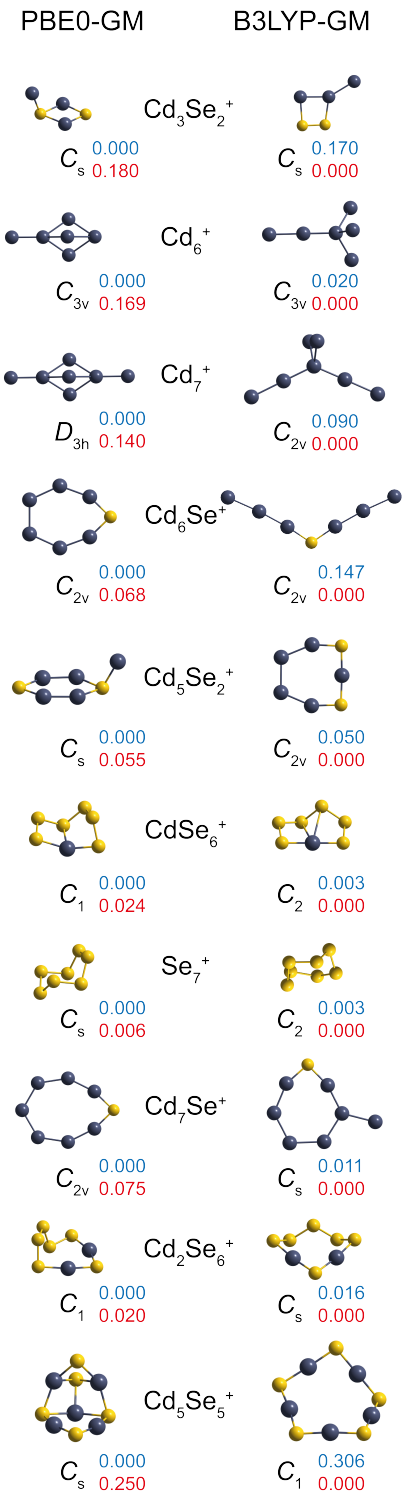

Figure S3. $Cd_xSe_y^+$ clusters with different global minimum (GM) structures regarding both level of theories (Cd: dark atoms, Se: light atoms). Each structure is labelled by its point group symmetry and the relative energy differences in eV at the PBE0 (blue) and at the B3LYP (red) level of theory.

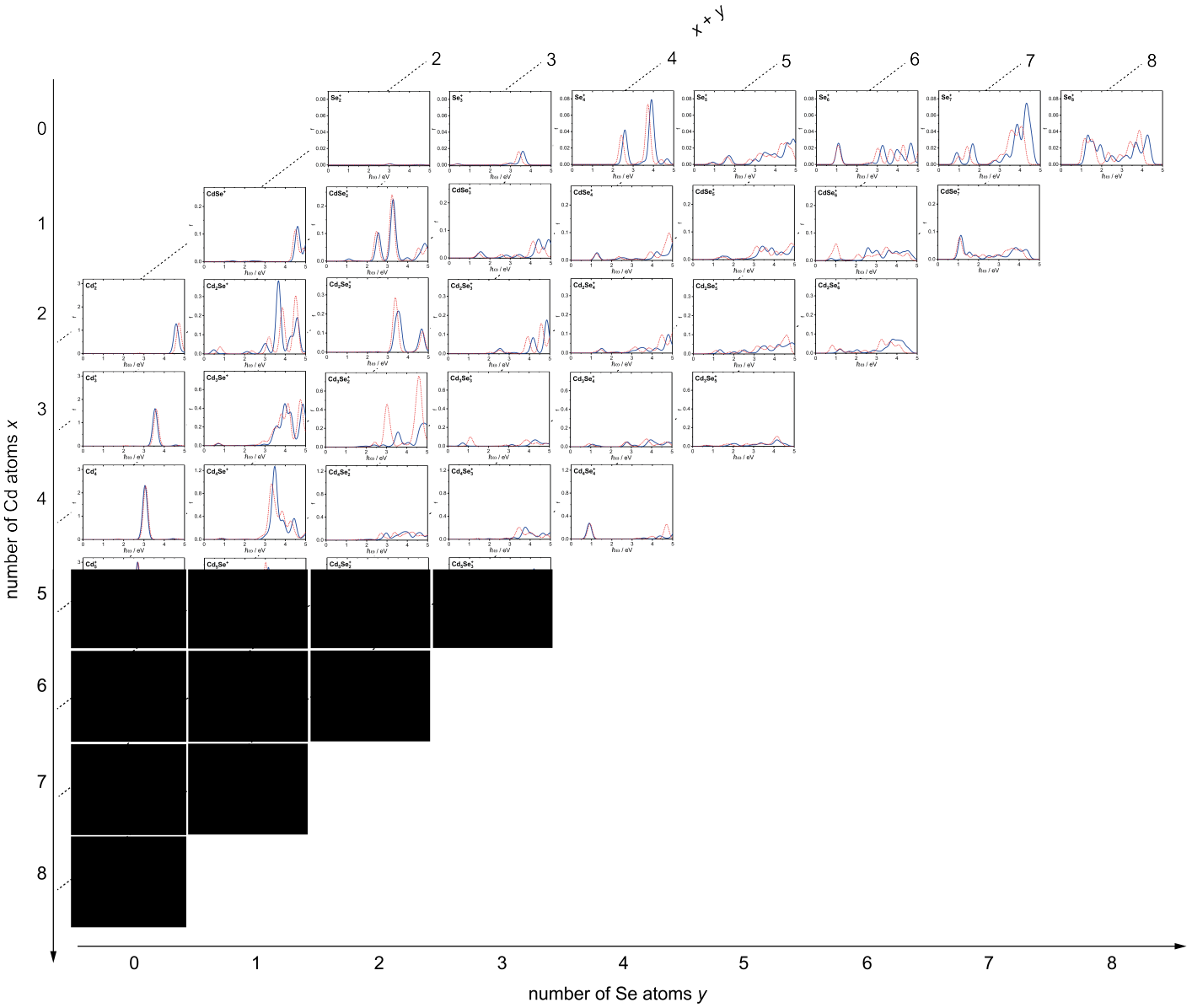

Figure S4. Optical absorption spectra obtained by PBE0 (solid blue line) and B3LYP (dotted red line) TDDFT calculations of the lowest energy structures of $Cd_xSe_y^+$ clusters (with $2 \leq x + y \leq 8$). The spectra are generated by Gaussian convolution of line spectra using a full width at half-maximum of 0.30 eV. In horizontal direction the number of Selenium atoms increases, while in vertical direction the amount of Cadmium atoms for a fixed number of atom increases. The spectra are shown in the range of 0.0 eV to 5.0 eV

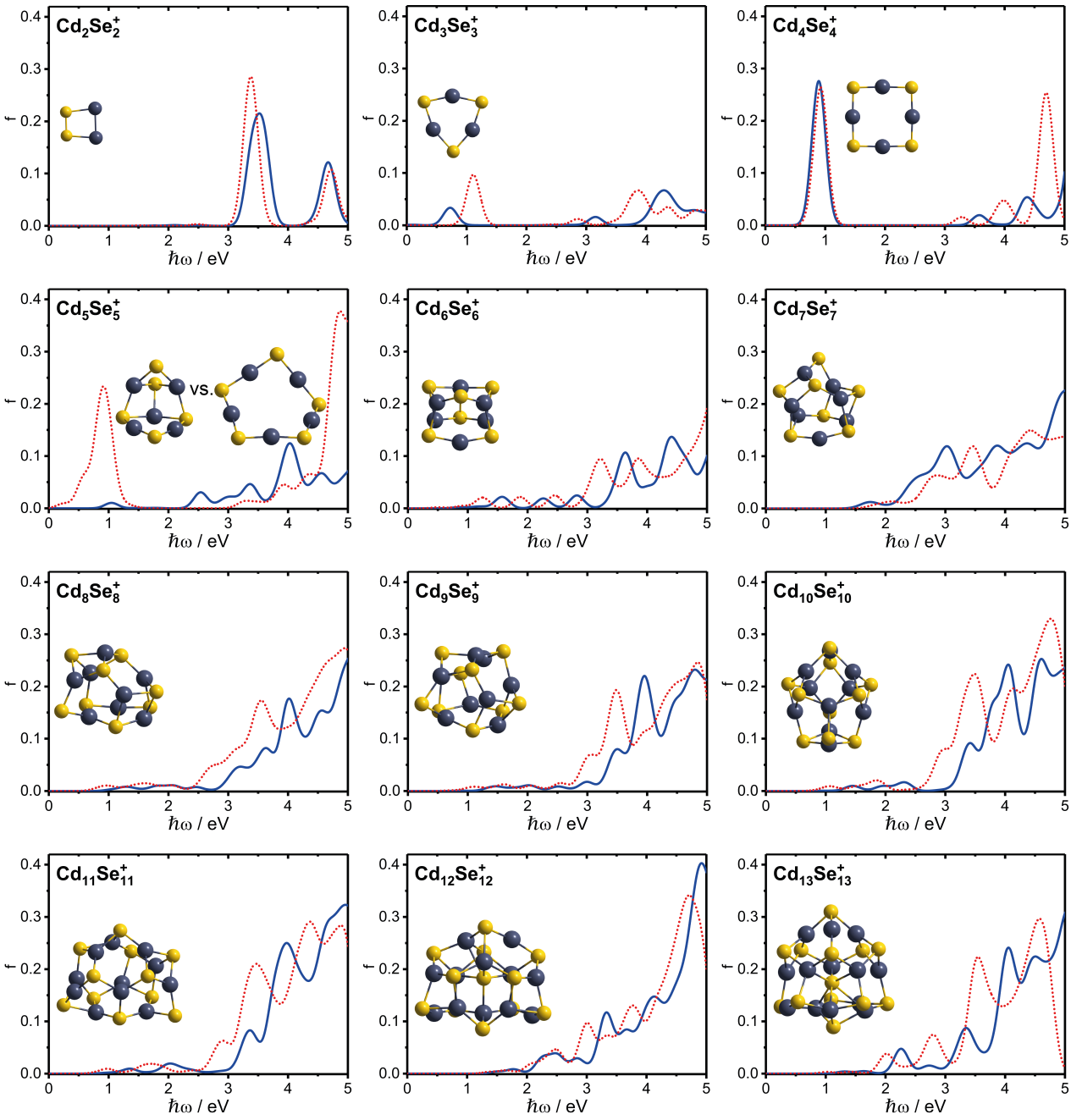

Figure S5. Optical absorption spectra obtained by PBE0 (solid blue line) and B3LYP (dotted red line) TDDFT calculations of the lowest energy structures of stoichiometric $Cd_xSe_y^+$ clusters (with $4 \leq x + y \leq 26$). The spectra are generated by Gaussian convolution of line spectra using a full width at half-maximum of 0.30 eV.

TABLE S1. Optoelectronic properties for the lowest energy structures of $Cd_xSe_y^+$ clusters with respect to PBE0 and B3LYP calcuations. For each species, the values of the HOMO-LUMO gap (E_{HL}), optical gap E_g and first electronic excitation $E_{g,1}$ are shown in eV.

	PBE0			B3LYP		
Cluster	E_{HL} / eV	E_g / eV	$E_{g,1}$ / eV	E_{HL} / eV	E_g / eV	$E_{g,1}$ / eV
Cd_2^+	4.12	2.82	2.82	3.51	2.79	2.79
$CdSe^+$	2.53	1.41	0.18	1.90	1.15	0.08
Se_2^+	2.02	3.05	0.06	1.56	2.97	0.02
Cd_3^+	3.46	2.11	2.11	2.91	2.11	2.11
Cd_2Se^+	1.49	0.48	0.48	1.45	0.79	0.79
$CdSe_2^+$	2.66	1.10	1.10	2.01	2.46	0.86
Se_3^+	1.84	0.41	0.41	1.43	0.37	0.37
Cd_4^+	2.90	1.71	1.71	2.49	1.74	1.74
Cd_3Se^+	1.49	0.72	0.72	1.28	0.70	0.70
$Cd_2Se_2^+$	3.15	2.53	1.74	2.61	2.48	1.53
$CdSe_3^+$	2.72	1.55	1.41	2.14	1.44	1.12
Se_4^+	1.84	2.59	0.21	1.54	2.42	0.26
Cd_5^+	2.45	1.45	1.45	2.18	1.50	1.50
Cd_4Se^+	1.55	0.90	0.90	1.34	0.81	0.81
$Cd_3Se_2^+$	2.62	1.61	1.61	2.31	2.42	1.23
$Cd_2Se_3^+$	2.27	2.40	1.45	1.83	2.06	1.19
$CdSe_4^+$	2.36	1.28	1.28	2.00	1.25	1.25
Se_5^+	2.23	0.92	0.92	1.80	0.80	0.80
Cd_6^+	2.71	1.79	1.69	2.37	1.60	1.60
Cd_5Se^+	0.85	0.50	0.50	0.82	0.59	0.59
$Cd_4Se_2^+$	2.75	1.67	1.67	2.14	1.39	1.39
$Cd_3Se_3^+$	0.84	0.09	0.09	0.47	1.12	0.79
$Cd_2Se_4^+$	2.25	1.44	1.44	1.85	1.23	1.23
$CdSe_5^+$	2.14	1.43	1.05	1.73	1.26	0.86
Se_6^+	2.20	1.09	1.09	1.89	1.07	1.07
Cd_7^+	2.42	1.59	1.49	2.21	1.66	1.49
Cd_6Se^+	2.26	1.36	1.36	0.70	0.87	0.87
$Cd_5Se_2^+$	2.50	1.84	1.84	1.64	1.51	0.86
$Cd_4Se_3^+$	2.25	1.97	1.59	1.56	1.42	1.05
$Cd_3Se_4^+$	1.70	1.09	1.09	1.31	0.90	0.90
$Cd_2Se_5^+$	1.67	0.84	0.84	1.28	0.93	0.63
$CdSe_6^+$	1.60	0.77	0.77	1.14	0.78	0.78
Se_7^+	1.91	0.86	0.86	1.44	0.94	0.62
Cd_8^+	2.14	1.24	1.24	2.10	1.67	1.38
Cd_7Se^+	2.02	1.17	1.17	1.62	1.15	1.15
$Cd_6Se_2^+$	2.52	1.85	1.85	2.11	1.61	1.61
$Cd_5Se_3^+$	2.84	2.12	2.12	2.11	1.92	1.65
$Cd_4Se_4^+$	1.07	0.89	0.89	0.90	0.92	0.92
$Cd_3Se_5^+$	1.46	0.75	0.75	1.12	0.62	0.62
$Cd_2Se_6^+$	1.79	1.01	1.01	1.28	0.73	0.73
$CdSe_7^+$	1.69	1.11	1.11	1.37	1.07	1.07
Se_8^+	2.17	1.28	1.28	1.72	1.11	1.11
$Cd_5Se_5^+$	2.37	1.05	1.05	0.49	0.25	0.25
$Cd_6Se_6^+$	1.54	0.84	0.84	1.05	0.51	0.51
Cd_7Se_7	2.05	1.03	1.03	1.51	0.83	0.83
$Cd_8Se_8^+$	1.91	1.05	1.04	1.39	0.85	0.76
$Cd_9Se_9^+$	1.93	1.36	0.88	1.40	0.71	0.71
$Cd_{10}Se_{10}^+$	2.19	1.42	0.97	1.63	1.05	0.81
$Cd_{11}Se_{11}^+$	2.05	0.94	0.94	1.51	0.78	0.78
$Cd_{12}Se_{12}^+$	2.59	1.48	1.48	2.23	1.37	1.37
$Cd_{13}Se_{13}^+$	2.43	1.27	1.27	1.96	0.99	0.99