Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for the paper entitled:

How Does Theory Compare to Experiment for Oscillator Strengths in Electronic Spectra? Proposing Range-Separated Hybrids with Reliable Accountability

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This file includes 16 tables (Tables S1-S16) and 1 figure (Figure S1).

Table S1. The computed oscillator strengths using the proposed approximations within the framework of OT-RSHs-PCM based on different DFAs, BLYP, PBE, and TPSS, for all the molecules with the "very high" confidence level on their experimental oscillator strengths.

Molecule	$\alpha = 0.0$, $\beta = 1.0$			$\alpha = 0.05$, $\beta = 0.95$		
	BLYP	PBE	TPSS	BLYP	PBE	TPSS
I	1.026	0.985	1.011	1.040	0.997	1.022
II	0.480	0.484	0.497	0.490	0.494	0.506
III	0.269	0.271	0.276	0.277	0.280	0.284
IV	0.071	0.072	0.075	0.078	0.079	0.082
V	0.054	0.056	0.059	0.060	0.062	0.065
VI	0.083	0.084	0.089	0.091	0.092	0.097
VII	0.392	0.397	0.411	0.409	0.415	0.426
VIII	0.437	0.439	0.453	0.458	0.459	0.473
IX	0.777	0.781	0.805	0.803	0.807	0.829
X	0.737	0.742	0.763	0.759	0.764	0.785
XI	0.264	0.267	0.283	0.279	0.282	0.296
XII	0.102	0.100	0.106	0.108	0.106	0.111
XIII	0.075	0.073	0.077	0.080	0.078	0.082
XIV	0.118	0.115	0.119	0.124	0.122	0.125

Molecule	$\alpha = 0.10$, $\beta = 0.90$			$\alpha = 0.15$, $\beta = 0.85$		
	BLYP	PBE	TPSS	BLYP	PBE	TPSS
I	1.054	1.009	1.032	1.014	1.020	1.042
II	0.496	0.504	0.516	0.507	0.514	0.526
III	0.284	0.287	0.290	0.287	0.290	0.293
IV	0.086	0.087	0.090	0.093	0.094	0.097
V	0.066	0.068	0.072	0.073	0.075	0.079
VI	0.099	0.100	0.105	0.107	0.108	0.113
VII	0.424	0.430	0.440	0.436	0.443	0.451
VIII	0.478	0.480	0.493	0.498	0.499	0.512
IX	0.828	0.834	0.852	0.847	0.852	0.870
X	0.780	0.786	0.805	0.800	0.806	0.823
XI	0.291	0.294	0.306	0.302	0.305	0.316
XII	0.114	0.111	0.116	0.119	0.117	0.121
XIII	0.085	0.083	0.087	0.090	0.087	0.088
XIV	0.130	0.128	0.131	0.136	0.134	0.137

Table S2. The excitation energies, oscillator strengths, D and M_{AC} indexes, as well as the character of the excited states computed using the PBE-based OT-RSH-PCM ($\alpha = 0.0, \beta = 1.0$). The values of $\Delta\mathbf{r}$ index (Å) are also shown in parenthesis (see the main text).

Molecule	E (eV)	f	D(Å)	M_{AC}(eV)	Character
I	4.40	0.985	0.38	-33.33	L
II	4.15	0.379	0.68	-14.40	L
III	4.42	0.255	2.23	0.72	CT (real)
IV	3.50	0.072	1.59	-4.63	L
V	3.47	0.055	1.57	-4.75	L
VI	3.24	0.084	1.29	-7.12	L
VII	4.22	0.381	2.40 (1.67)	-1.05	L
VIII	3.14	0.433	3.17 (2.51)	-0.77	CT (real)
IX	3.89	0.758	2.08 (1.26)	-2.56	L
X	3.86	0.647	2.25 (1.57)	-1.86	L
XI	4.01	0.266	0.62	-18.81	L
XII	5.39	0.099	0.16	-84.18	L
XIII	4.72	0.070	0.98	-7.01	L
XIV	4.62	0.115	0.74	-11.91	L

Table S3. The excitation energies, oscillator strengths, D and M_{AC} indexes, as well as the character of the excited states computed using the PBE-based OT-RSH-PCM ($\alpha = 0.05, \beta = 0.95$). The values of $\Delta\mathbf{r}$ index (Å) are also shown in parenthesis (see the main text).

Molecule	E (eV)	f	D(Å)	M_{AC}(eV)	Character
I	4.44	0.997	0.38	-33.55	L
II	4.18	0.412	0.69	-14.21	L
III	4.48	0.262	2.18	0.66	CT (real)
IV	3.61	0.079	1.52	-4.90	L
V	3.57	0.061	1.51	-5.00	L
VI	3.33	0.092	1.25	-7.45	L
VII	4.31	0.403	2.25 (1.65)	-1.44	L
VIII	3.21	0.454	3.08 (2.53)	-0.93	CT (real)
IX	3.96	0.757	1.94 (1.35)	-3.06	L
X	3.90	0.407	2.53 (1.93)	-1.18	L
XI	4.06	0.281	0.53	-22.78	L
XII	5.42	0.105	0.15	-89.43	L
XIII	4.79	0.075	0.91	-8.09	L
XIV	4.69	0.122	0.67	-13.87	L

Table S4. The excitation energies, oscillator strengths, D and M_{AC} indexes, as well as the character of the excited states computed using the PBE-based OT-RSH-PCM ($\alpha = 0.10, \beta = 0.90$). The values of $\Delta\mathbf{r}$ index (Å) are also shown in parenthesis (see the main text).

Molecule	E (eV)	f	D(Å)	M_{AC}(eV)	Character
I	4.48	1.009	0.38	-33.58	L
II	4.22	0.437	0.69	-14.26	L
III	4.53	0.267	2.15	0.58	CT (real)
IV	3.71	0.086	1.46	-5.30	L
V	3.68	0.068	1.45	-5.37	L
VI	3.42	0.100	1.19	-7.97	L
VII	4.41	0.422	2.11 (1.63)	-1.86	L
VIII	3.28	0.474	2.98 (2.53)	-1.13	CT (real)
IX	4.04	0.539	2.09 (1.94)	-1.76	L
X	3.98	0.691	1.99 (1.37)	-2.84	L
XI	4.11	0.293	0.48	-25.69	L
XII	5.45	0.110	0.15	-92.64	L
XIII	4.86	0.080	0.84	-9.36	L
XIV	4.76	0.128	0.63	-15.45	L

Table S5. The excitation energies, oscillator strengths, D and M_{AC} indexes, as well as the character of the excited states computed using the PBE-based OT-RSH-PCM ($\alpha = 0.15, \beta = 0.85$). The values of $\Delta\mathbf{r}$ index (Å) are also shown in parenthesis (see the main text).

Molecule	E (eV)	f	D(Å)	M_{AC}(eV)	Character
I	4.52	1.020	0.38	-33.10	L
II	4.25	0.458	0.69	-14.22	L
III	4.55	0.270	2.15	0.31	CT (real)
IV	3.82	0.094	1.39	-5.76	L
V	3.78	0.075	1.38	-5.88	L
VI	3.50	0.108	1.13	-8.61	L
VII	4.49	0.438	1.96 (1.60)	-2.36	L
VIII	3.36	0.495	2.85 (2.55)	-1.38	CT (real)
IX	4.07	0.706	1.79 (1.37)	-3.06	L
X	4.06	0.761	1.76 (1.28)	-3.20	L
XI	4.15	0.304	0.43	-29.34	L
XII	5.47	0.116	0.13	-103.34	L
XIII	4.93	0.084	0.79	-10.71	L
XIV	4.84	0.134	0.58	-17.25	L

Table S6. The computed oscillator strengths using the PBE-based OT-RSH-PCM ($\alpha = 0.0, \beta = 1.0$) with different basis sets for all the molecules with the "very high" confidence level on their experimental oscillator strengths. Also given as the boldface in the last rows are the corresponding statistical metrics.

Molecule	6-31+G(d)	6-311++G(d,p)	6-311++G(2df,2p)	TZVP
I	0.985	1.020	1.018	0.980
II	0.484	0.476	0.470	0.475
III	0.271	0.269	0.269	0.262
IV	0.072	0.072	0.070	0.073
V	0.056	0.055	0.053	0.056
VI	0.084	0.083	0.080	0.083
VII	0.397	0.389	0.381	0.382
VIII	0.439	0.434	0.432	0.447
IX	0.781	0.775	0.774	0.798
X	0.742	0.736	0.737	0.759
XI	0.267	0.263	0.258	0.260
XII	0.100	0.102	0.100	0.105
XIII	0.073	0.072	0.072	0.077
XIV	0.115	0.116	0.119	0.123
MSD	**0.071**	**0.070**	**0.068**	**0.071**
MAD	**0.073**	**0.073**	**0.072**	**0.074**
RMSD	**0.106**	**0.109**	**0.108**	**0.108**

Table S7. The computed oscillator strengths using the PBE-based OT-RSH-PCM ($\alpha = 0.0, \beta = 1.0$) with different geometries optimized at different basis sets for all the molecules with the "very high" confidence level on their experimental oscillator strengths. Also given as the boldface in the last rows are the corresponding statistical metrics.

Molecule	6-31+G(d)	6-311++G(d,p)	6-311++G(2df,2p)	TZVP
I	0.985	0.988	0.990	0.989
II	0.484	0.490	0.493	0.494
III	0.271	0.265	0.267	0.264
IV	0.072	0.074	0.075	0.074
V	0.056	0.056	0.057	0.057
VI	0.084	0.085	0.085	0.085
VII	0.397	0.395	0.396	0.396
VIII	0.439	0.429	0.432	0.427
IX	0.781	0.777	0.780	0.778
X	0.742	0.738	0.740	0.738
XI	0.267	0.286	0.272	0.287
XII	0.100	0.101	0.101	0.101
XIII	0.073	0.073	0.073	0.073
XIV	0.115	0.116	0.117	0.116
MSD	**0.071**	**0.071**	**0.071**	**0.071**
MAD	**0.073**	**0.074**	**0.074**	**0.074**
RMSD	**0.106**	**0.106**	**0.107**	**0.107**

Table S8. Assessment of the integration grid dependence of the best proposed approximation in the calculations of the oscillator strengths for all the molecules with the "very high" confidence level on their experimental oscillator strengths.

Molecule	*FineGrid*	*UltraFineGrid*	*SuperFineGrid*
I	0.9851	0.9851	0.9851
II	0.4843	0.4843	0.4843
III	0.2714	0.2713	0.2713
IV	0.0723	0.0723	0.0723
V	0.0555	0.0555	0.0555
VI	0.0839	0.0839	0.0839
VII	0.3970	0.3970	0.3970
VIII	0.4387	0.4387	0.4387
IX	0.7812	0.7812	0.7812
X	0.7417	0.7418	0.7418
XI	0.2668	0.2668	0.2668
XII	0.0999	0.0999	0.0999
XIII	0.0729	0.0729	0.0729
XIV	0.1153	0.1153	0.1153
MSD	**0.071**	**0.071**	**0.071**
MAD	**0.073**	**0.073**	**0.073**
RMSD	**0.106**	**0.106**	**0.106**

Table S9. Optimally tuned values of the range-separation parameter ($Bohr^{-1}$) for the molecules with the "high" confidence level on their experimental oscillator strengths using the combination $\alpha = 0.0, \beta = 1.0$.

Molecule	μ
XV	0.1294
XVI	0.0294
XVII	0.0443
XVIII	0.0355
XIX	0.0440
XX	0.0471
XXI	0.0423
XXII	0.0993
XXIII	0.0320

Table S10. The computed values of the oscillator strengths for the molecules with the "high" confidence level on their experimental oscillator strengths using the best proposed approximation.

Molecule	Band	f
XV	1	0.026
XVI	1	0.602
XVII	1	0.326
XVIII	1	0.506
XIX	2	0.258
XX	2	0.279
XXI	1	0.089
	2	0.228
XXII	1	0.443
XXIII	1	0.101

Table S11. The excitation energies, oscillator strengths, *D* and M_{AC} indexes, as well as the character of the excited states computed using the PBE-based OT-RSH ($\alpha = 0.0, \beta = 1.0$). For those cases where *D* is equal to zero, the values of the integral revealing the degree of hole and electron overlap are also shown in parenthesis (see the main text). Also given in the table are the values of the range-separation parameter μ (Bohr^{-1}) and the CC2 oscillator strengths (f^{CC2}) used as reference.

Molecule	μ	f^{CC2}	f	E (eV)	D(Å)	M_{AC}(eV)	Character
A	0.234	0.547	0.482	5.29	0.00 (0.86)	-75500.46	L
B	0.238	0.499	0.480	3.08	0.32	-38.85	L
C	0.251	0.337	0.334	4.33	0.83	-8.88	L
D	0.218	0.891	0.948	3.97	1.01	-6.80	L
E	0.242	0.266	0.196	3.94	0.21	-59.08	L
F	0.239	0.239	0.231	4.06	0.50	-21.17	L
G	0.201	1.313	1.264	3.45	1.65	-2.09	L
H	0.202	0.247	0.232	2.35	1.02	-8.55	L
I	0.209	0.038	0.046	3.55	0.78	-11.32	L
J	0.211	0.381	0.397	3.09	0.00 (0.91)	-794914.44	L
K	0.182	1.792	1.278	2.33	0.00 (0.72)	-71828.52	L
L	0.262	0.062	0.066	3.99	1.43	-1.75	L
M	0.197	0.960	0.996	3.45	4.51	3.03	CT (real)
N	0.180	0.504	0.461	3.57	0.30	-41.18	L
O	0.180	1.683	1.523	3.32	0.00 (0.81)	-5222.37	L
P	0.245	0.498	0.435	3.00	3.31	2.01	CT (real)
Q	0.231	0.431	0.393	3.41	1.03	-6.80	L
R	0.159	1.248	1.116	2.24	0.00 (0.85)	-3280.11	L
S	0.212	0.965	0.805	3.01	0.67	-15.16	L
T	0.180	0.235	0.218	2.57	0.00 (0.78)	-76318.92	L
U	0.188	1.351	1.306	3.83	0.06	-231.06	L
V	0.219	1.145	1.039	3.77	0.00 (0.79)	-7456.19	L
W	0.213	0.326	0.339	3.59	0.96	-8.05	L
X	0.215	0.454	0.393	3.59	2.11	0.21	CT (real)
Y	0.163	0.789	0.719	2.07	0.34	-38.39	L
Z	0.207	0.857	0.729	2.66	0.54	-20.75	L
AA	0.183	2.214	2.036	3.35	0.00 (0.84)	-61544.42	L
BB	0.198	0.743	0.728	2.64	0.00 (0.88)	-239905.37	L
CC	0.171	0.798	0.763	2.53	0.80	-12.70	L
DD	0.182	2.222	1.941	3.17	0.49	-23.60	L
EE	0.207	0.338	0.310	2.49	0.00 (0.70)	-670202.44	L
FF	0.219	0.680	0.653	3.91	1.14	-5.14	L
GG	0.203	0.326	0.309	4.06	0.55	-18.26	L
HH	0.213	0.402	0.410	3.14	0.05	-277.41	L
II	0.194	0.859	0.683	2.90	1.30	-5.06	L
JJ	0.192	0.234	0.154	3.20	1.19	-5.35	L
KK	0.234	0.890	0.897	4.11	1.00	-6.75	L
LL	0.211	0.057	0.061	2.95	1.93	-0.80	L
MM	0.180	0.067	0.068	2.97	1.82	-1.38	L
NN	0.157	0.440	0.421	2.05	0.00 (0.87)	-668470.15	L

Table S12. The excitation energies, oscillator strengths, *D* and M_{AC} indexes, as well as the character of the excited states computed using the standard LC-PBE with the default parameters. For those cases where *D* is equal to zero, the values of the integral revealing the degree of hole and electron overlap are also shown in parenthesis (see the main text). Also given in the table are the values of the CC2 oscillator strengths (f^{CC2}) used as reference.

Molecule	f^{CC2}	f	E (eV)	D(Å)	M_{AC}(eV)	Character
A	0.547	0.412	5.57	0.00 (0.89)	-91972.63	L
B	0.499	0.564	3.07	0.26	-47.57	L
C	0.337	0.399	4.69	0.64	-12.50	L
D	0.891	0.998	4.38	0.59	-15.22	L
E	0.266	0.261	4.42	0.18	-70.35	L
F	0.239	0.272	4.47	0.32	-35.71	L
G	1.313	1.366	3.91	1.02	-5.60	L
H	0.247	0.310	2.80	0.86	-9.61	L
I	0.038	0.065	4.07	0.54	-17.59	L
J	0.381	0.539	3.49	0.00 (0.91)	-591919.75	L
K	1.792	1.580	2.53	0.00 (0.76)	-94730.32	L
L	0.062	0.089	4.50	1.07	-3.69	L
M	0.960	1.337	4.15	2.53	2.83	CT (real)
N	0.504	0.557	4.10	0.18	-72.29	L
O	1.683	1.550	3.78	0.00 (0.83)	-6050.83	L
P	0.498	0.455	3.49	3.18	2.99	CT (real)
Q	0.431	0.514	3.78	0.72	-11.31	L
R	1.248	1.230	2.62	0.00 (0.85)	-4409.48	L
S	0.965	1.002	3.27	0.49	-21.68	L
T	0.235	0.357	3.06	0.00 (0.83)	-62851.61	L
U	1.351	1.322	4.28	0.03	-433.48	L
V	1.145	1.040	4.06	0.00 (0.81)	-8024.59	L
W	0.326	0.497	4.16	0.37	-29.90	L
X	0.454	0.505	4.11	1.41	-1.29	L
Y	0.789	0.869	2.07	0.23	-56.84	L
Z	0.857	0.941	2.85	0.53	-20.06	L
AA	2.214	2.078	3.87	0.00 (0.85)	-81723.13	L
BB	0.743	0.911	3.09	0.00 (0.88)	-199299.01	L
CC	0.798	0.921	3.01	0.29	-41.57	L
DD	2.222	2.380	3.85	0.32	-36.84	L
EE	0.338	0.395	2.99	0.00 (0.71)	-653187.67	L
FF	0.680	0.654	4.27	0.74	-10.14	L
GG	0.326	0.406	4.56	0.24	-49.90	L
HH	0.402	0.520	3.57	0.06	-255.35	L
II	0.859	0.933	3.42	1.23	-3.90	L
JJ	0.234	0.404	3.72	0.39	-27.88	L
KK	0.890	1.008	4.49	0.59	-15.35	L
LL	0.057	0.113	3.70	1.69	-0.19	L
MM	0.067	0.149	3.85	1.51	-0.95	L
NN	0.440	0.506	1.81	0.00 (0.88)	-393301.15	L

Table S13. The experimental excitation energies for the considered compounds used as reference, as well as the corresponding computed data using the PBE-based OT-RSH-PCM ($\alpha = 0.0, \beta = 1.0$) and its standard version within the frameworks of LR-PCM (eq), LR-PCM (non-eq), SS-PCM (eq), and SS-PCM (non-eq). Also given as the boldface in the last rows are the related statistical metrics. All values are in eV.

		LR-PCM (non-eq)		LR-PCM (eq)		SS-PCM (non-eq)		SS-PCM (eq)	
Molecule	Exp.	PBE-based OT-RSH-PCM ($\alpha = 0.0, \beta = 1.0$)	LC-PBE	PBE-based OT-RSH-PCM ($\alpha = 0.0, \beta = 1.0$)	LC-PBE	PBE-based OT-RSH-PCM ($\alpha = 0.0, \beta = 1.0$)	LC-PBE	PBE-based OT-RSH-PCM ($\alpha = 0.0, \beta = 1.0$)	LC-PBE
I	3.99	4.40	4.67	4.16	4.42	4.56	4.84	4.55	4.82
II	4.06	4.15	4.47	4.15	4.48	4.22	4.62	4.22	4.62
III	4.92	4.42	5.33	4.42	5.33	4.41	5.34	4.41	5.33
IV	3.78	3.50	4.55	3.45	4.46	3.48	4.57	3.41	4.52
V	3.78	3.47	4.52	3.41	4.42	3.44	4.53	3.37	4.48
VI	3.36	3.24	4.14	3.17	4.01	3.25	4.17	3.21	4.11
VII	4.35	4.22	5.10	4.07	4.94	4.24	5.14	4.16	5.06
VIII	3.23	3.14	4.06	2.95	3.85	3.20	4.07	3.14	4.13
IX	4.37	3.89	4.63	3.64	4.39	3.98	4.74	3.67	4.69
X	4.31	3.86	4.67	3.65	4.47	3.92	4.78	3.59	4.74
XI	3.96	4.01	4.44	3.81	4.20	4.10	4.56	4.09	4.53
XII	4.85	5.39	5.54	5.30	5.42	5.42	5.59	5.41	5.58
XIII	4.53	4.72	5.33	4.72	5.33	4.72	5.36	4.72	5.36
XIV	4.46	4.62	5.25	4.62	5.25	4.63	5.28	4.63	5.28
MSD		**-0.07**	**0.62**	**-0.18**	**0.50**	**-0.03**	**0.69**	**-0.10**	**0.66**
MAD		**0.27**	**0.62**	**0.33**	**0.50**	**0.28**	**0.69**	**0.35**	**0.66**
RMSD		**0.32**	**0.65**	**0.38**	**0.55**	**0.33**	**0.71**	**0.41**	**0.68**

Table S14. The numerical results of the oscillator strengths computed using the standard LC functionals for the molecules with the "very high" confidence level on their experimental oscillator strengths.

Molecule	Standard LC functionals		
	LC-BLYP	LC-PBE	LC-TPSS
I	1.060	1.065	1.070
II	0.618	0.621	0.626
III	0.324	0.327	0.323
IV	0.162	0.162	0.000
V	0.148	0.149	0.149
VI	0.185	0.184	0.185
VII	0.477	0.492	0.485
VIII	0.620	0.632	0.632
IX	0.890	0.903	0.902
X	0.834	0.848	0.848
XI	0.360	0.366	0.367
XII	0.141	0.139	0.141
XIII	0.117	0.116	0.117
XIV	0.164	0.164	0.165

Table S15. The numerical results of the oscillator strengths computed using the RSH and SX functionals for the molecules with the "very high" confidence level on their experimental oscillator strengths.

Molecule	RSHs and SX			
	CAM-B3LYP	M11	ωB97XD	MN12-SX
I	1.043	1.024	1.042	0.922
II	0.562	0.565	0.564	0.530
III	0.324	0.340	0.327	0.289
IV	0.137	0.155	0.137	0.112
V	0.117	0.137	0.117	0.088
VI	0.153	0.170	0.153	0.123
VII	0.477	0.495	0.480	0.411
VIII	0.574	0.602	0.577	0.517
IX	0.899	0.899	0.906	0.841
X	0.845	0.845	0.855	0.794
XI	0.338	0.332	0.345	0.275
XII	0.133	0.136	0.131	0.137
XIII	0.105	0.112	0.104	0.086
XIV	0.154	0.163	0.153	0.144

Table S16. The numerical results of the oscillator strengths computed using the hybrid functionals for the molecules with the "very high" confidence level on their experimental oscillator strengths.

Molecule	Hybrids		
	B3LYP	M06-2X	PBE0
I	1.025	1.030	1.039
II	0.517	0.555	0.533
III	0.290	0.336	0.302
IV	0.100	0.140	0.110
V	0.081	0.122	0.090
VI	0.115	0.156	0.125
VII	0.448	0.487	0.462
VIII	0.517	0.586	0.536
IX	0.864	0.896	0.883
X	0.816	0.843	0.835
XI	0.312	0.333	0.324
XII	0.123	0.136	0.127
XIII	0.090	0.112	0.094
XIV	0.138	0.159	0.144

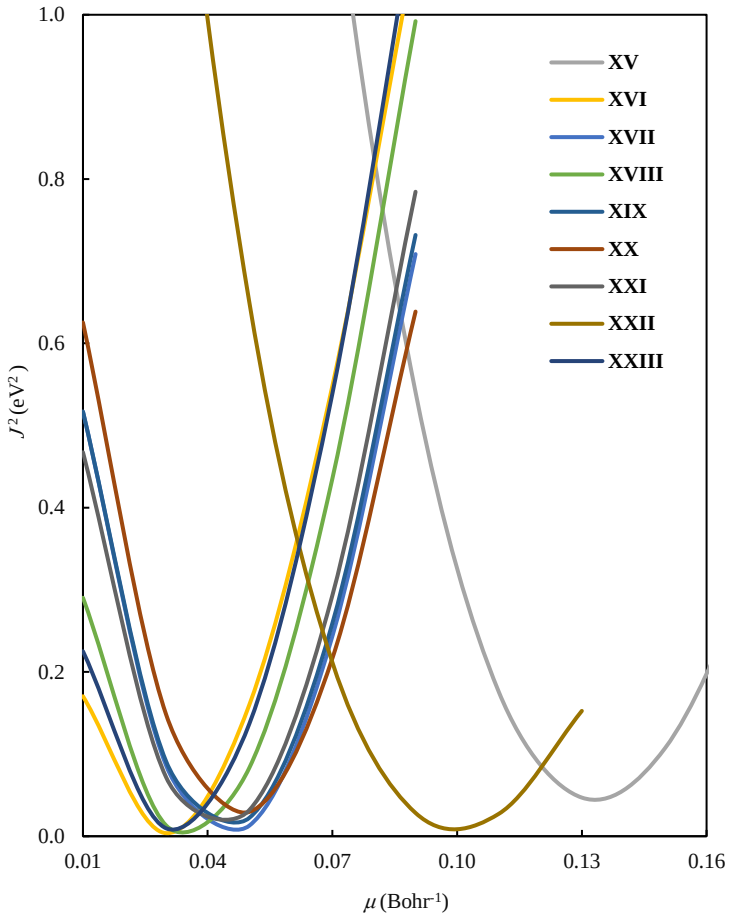

Figure S1. Plot of the target function J^2 as a function of the range-separation parameter μ for the molecules with the "high" confidence level on their experimental oscillator strengths using the combination $\alpha = 0.0, \beta = 1.0$.