Electronic Supplementary Information

for

Spectroscopy and Photochemistry of Copper Nitrate Clusters

Tobias F. Pascher, Milan Ončák, Christian van der Linde and Martin K. Beyer**

Institut für Ionen und Angewandte Physik, Universität Innsbruck, Technikerstraße 25, 6020 Innsbruck, Austria

Corresponding Author

*E-mail: Milan.Oncak@uibk.ac.at, Martin.Beyer@uibk.ac.at

Complete Partial Cross Sections

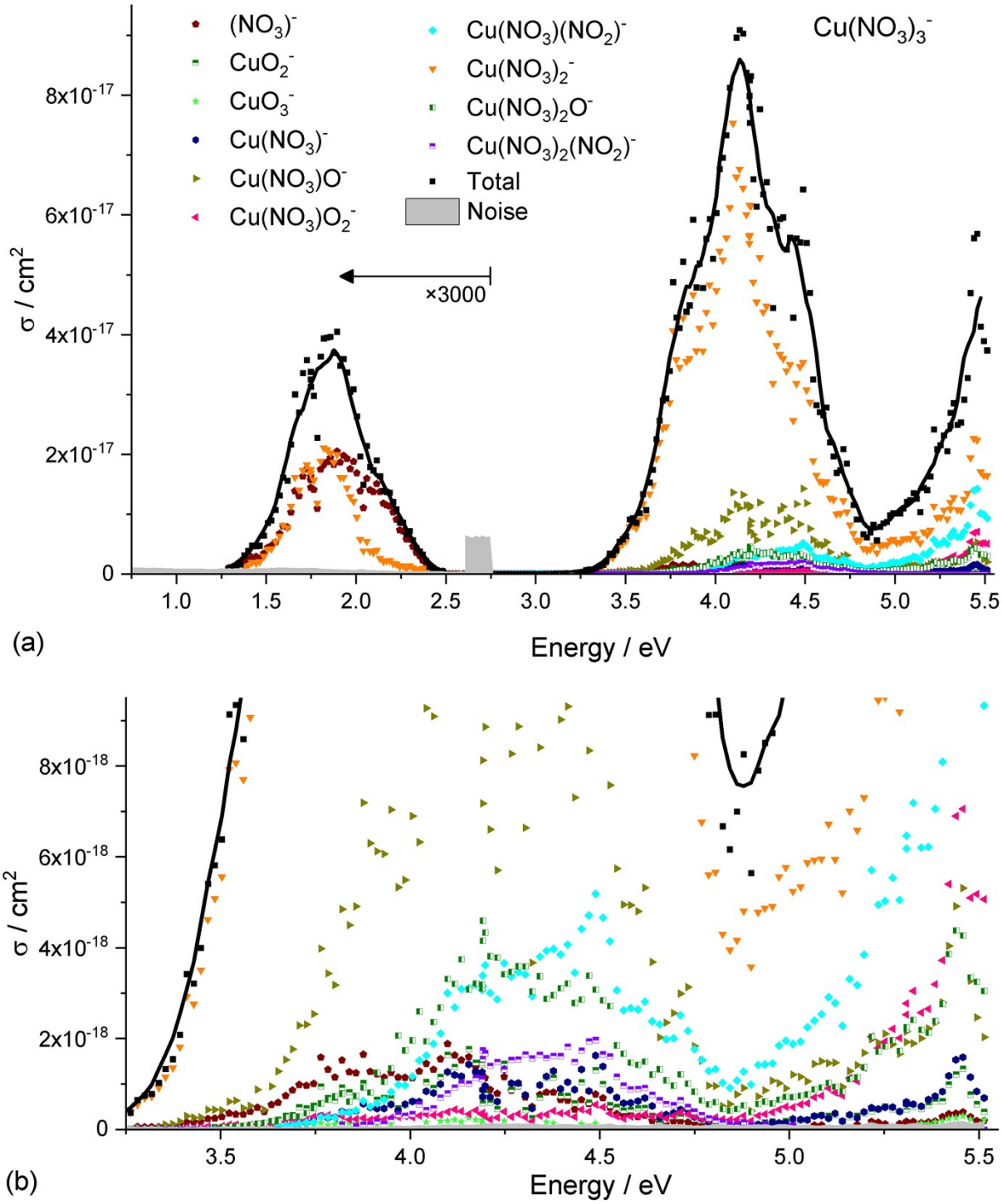

FIGURE S1. The partial cross sections of the detected fragments from $Cu(II)(NO_3)_3^-$ in addition to the total dissociation cross section using a running average over eight points with values below 2.75 eV multiplied by 30 in a) and the UV absorption enlarged in b).

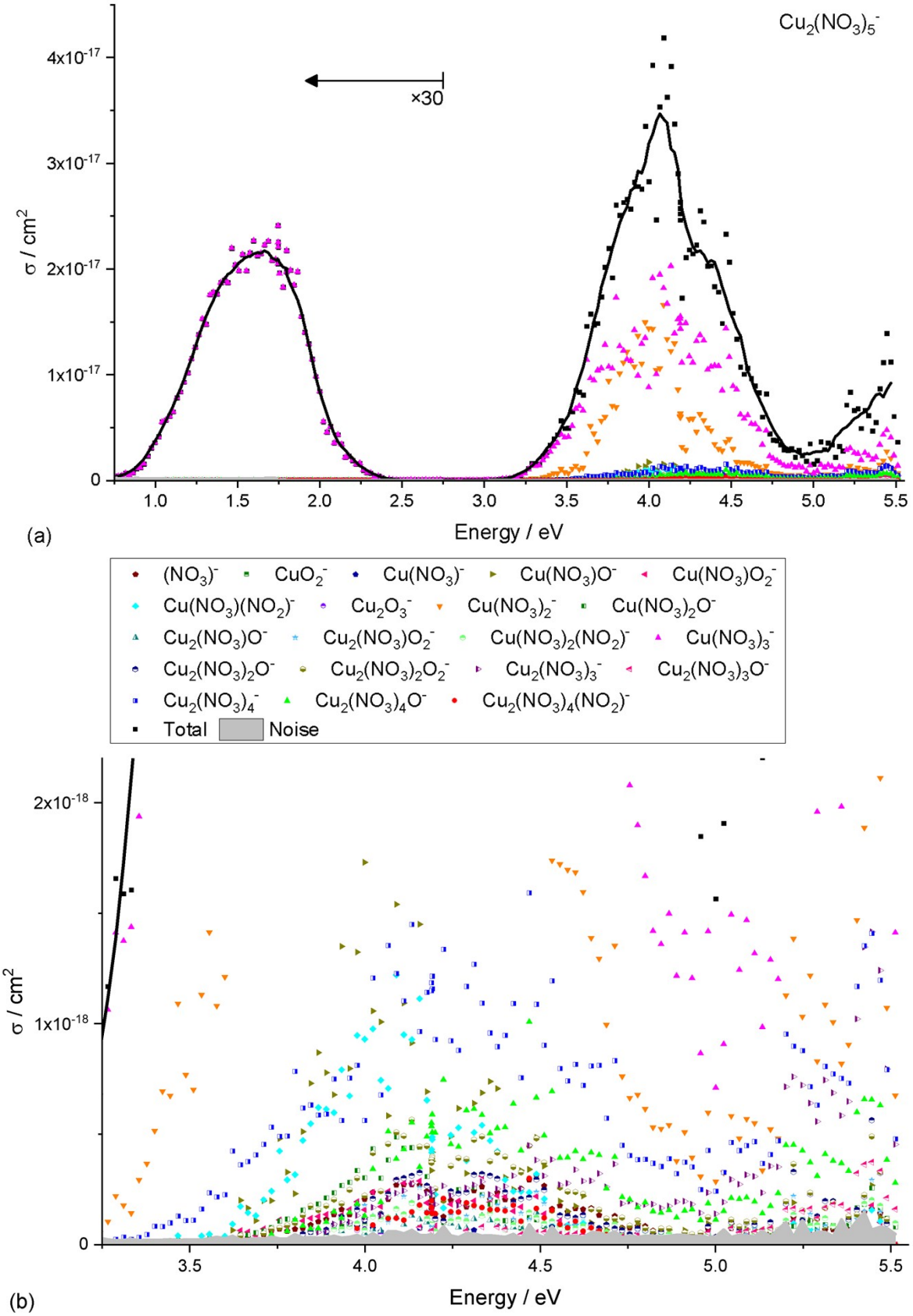

FIGURE S2. The partial cross sections of the detected fragments from $Cu(II)_2(NO_3)_5^-$ in addition to the total dissociation cross section using a running average over eight points with values below 2.75 eV multiplied by 30 in a) and the UV absorption enlarged in b).

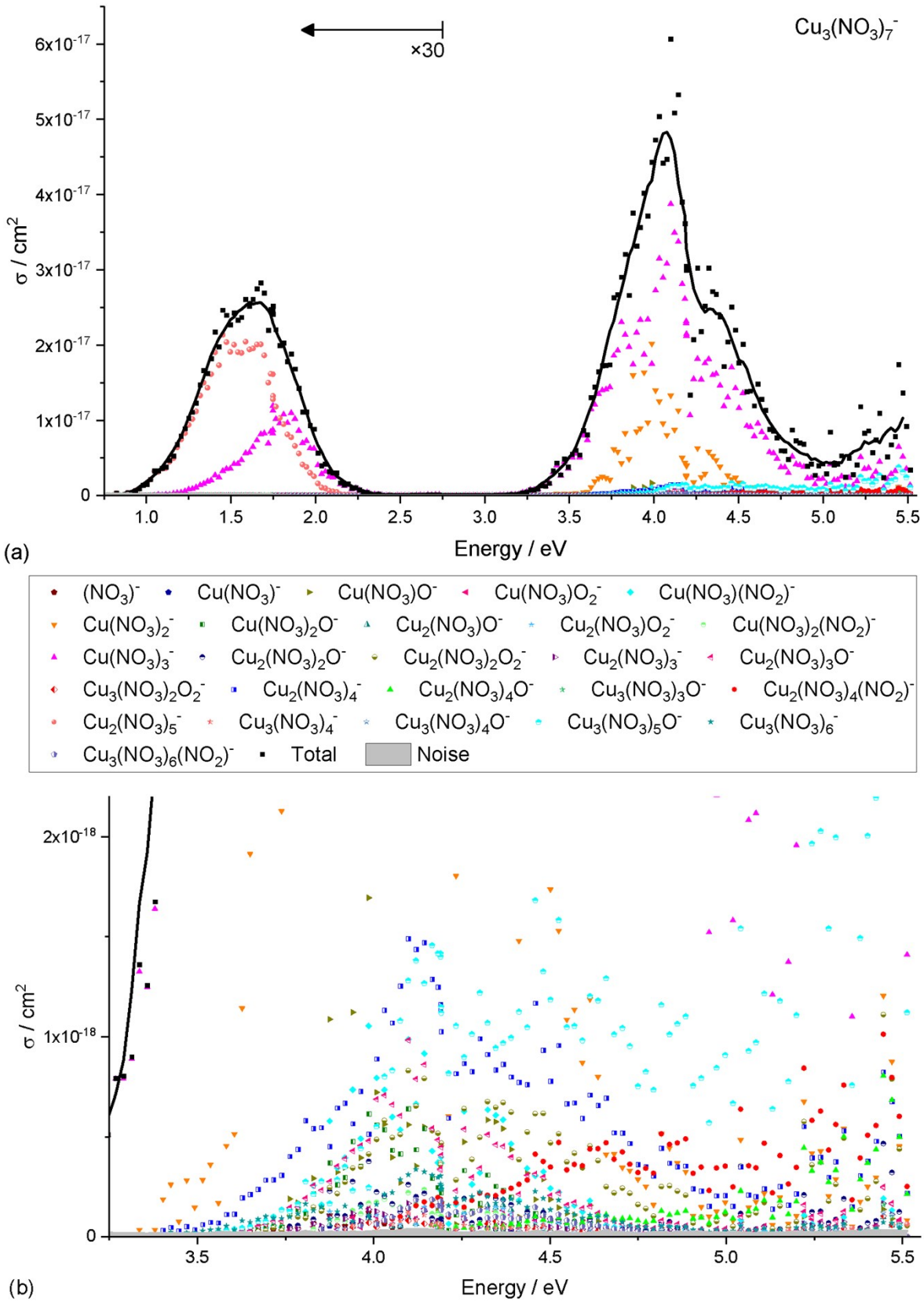

FIGURE S3. The partial cross sections of the detected fragments from $Cu(II)_3(NO_3)_7^-$ in addition to the total dissociation cross section using a running average over eight points with values below 2.75 eV multiplied by 30 in a) and the UV absorption enlarged in b).

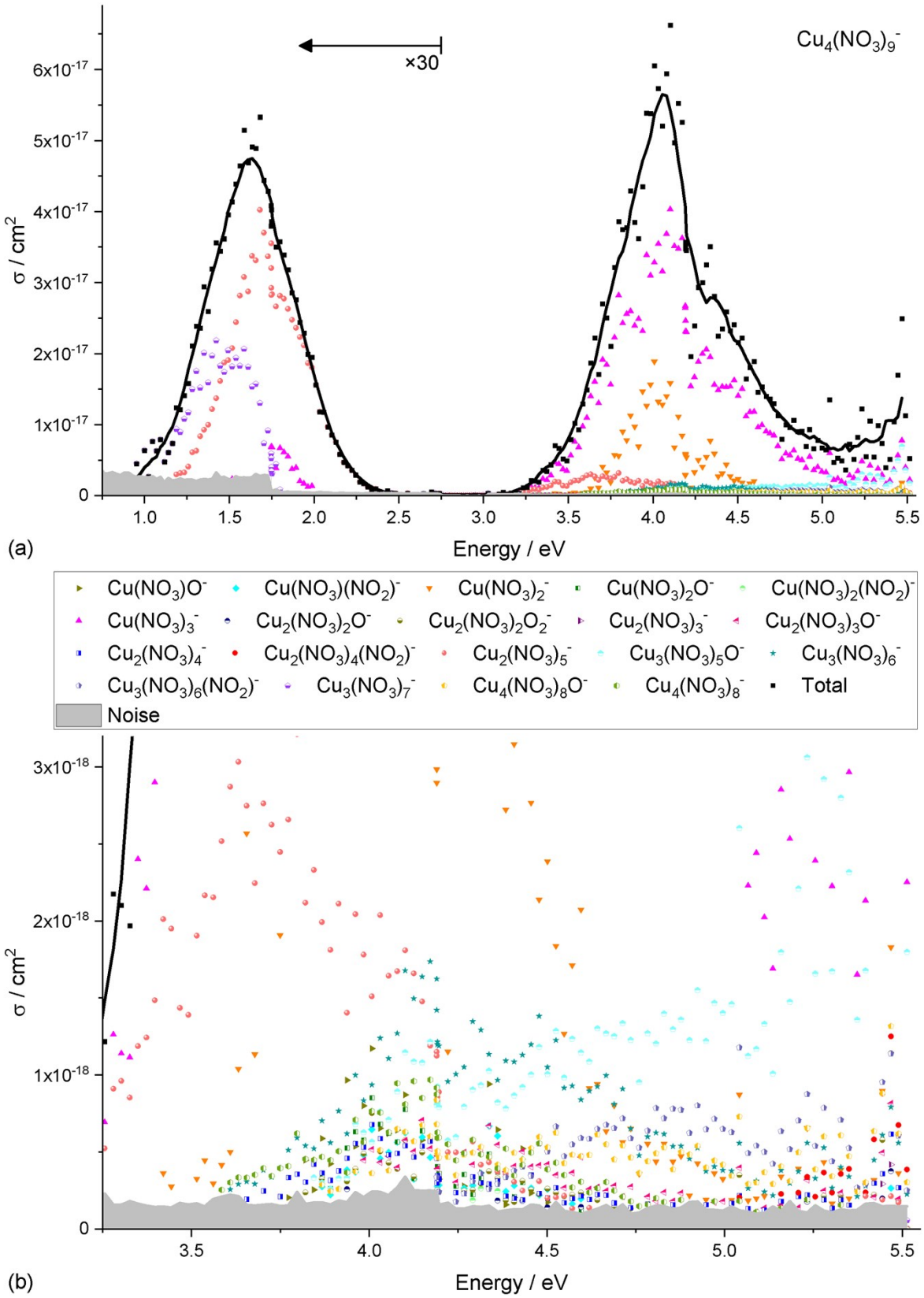

FIGURE S4. The partial cross sections of the detected fragments from $Cu(II)_4(NO_3)_9^-$ in addition to the total dissociation cross section using a running average over eight points with values below 2.75 eV multiplied by 30 in a) and the UV absorption enlarged in b).

TABLE S1. Benchmarking of the calculated transition energies E (in eV) and the corresponding oscillator strengths f in $Cu(NO_3)_3$- with the TD-DFT functional TD-BMK against the EOM-CCSD method across multiple basis sets.

BMK						EOM-CCSD			
6-31+g*		aug-cc-pVDZ		aug-cc-pVTZ		6-31+g*		aug-cc-pVDZ	
E	f	E	f	E	f	E	f	E	f
1.08	0.0007	1.13	0.0006	1.17	0.0006	1.36	0.0000	1.49	0.0002
1.30	0.0001	1.32	0.0001	1.33	0.0001	1.44	0.0013	1.54	0.0011
1.47	0.0000	1.49	0.0001	1.52	0.0001	1.78	0.0001	1.88	0.0002
1.47	0.0001	1.50	0.0001	1.54	0.0001	1.78	0.0002	1.89	0.0001
4.02	0.0002	4.02	0.0001	4.08	0.0001	4.28	0.0001	4.30	0.0001
4.02	0.0000	4.02	0.0000	4.08	0.0000	4.28	0.0000	4.30	0.0000
4.11	0.0000	4.11	0.0000	4.16	0.0000	4.33	0.0000	4.37	0.0000
4.27	0.0000	4.27	0.0000	4.28	0.0000	4.54	0.0004	4.56	0.0003
4.27	0.0000	4.27	0.0000	4.29	0.0000	4.55	0.0001	4.57	0.0001
4.43	0.0001	4.43	0.0000	4.44	0.0000	4.76	0.0000	4.79	0.0000
4.45	0.0025	4.45	0.0006	4.50	0.0007	4.76	0.0000	4.79	0.0000
4.46	0.0007	4.46	0.0003	4.51	0.0003	4.85	0.0010	4.87	0.0007
4.68	0.0355	4.70	0.0009	4.74	0.0010	4.90	0.0000	4.94	0.0000
4.72	0.0207	4.90	0.0520	4.93	0.0536	5.16	0.0837	5.24	0.0797
4.83	0.0414	4.93	0.0002	4.98	0.0003	5.36	0.0471	5.41	0.0008
4.94	0.0000	5.03	0.0368	5.07	0.0375	5.41	0.0001	5.45	0.0433
5.04	0.0028	5.10	0.0005	5.15	0.0005	5.53	0.0023	5.55	0.0009
5.12	0.0004	5.11	0.0027	5.15	0.0025	5.58	0.0012	5.57	0.0022
5.13	0.0001	5.29	0.0036	5.32	0.0037	5.60	0.0008	5.66	0.0038
5.47	0.0000	5.48	0.0000	5.51	0.0000	5.86	0.0539	5.91	0.0454
5.47	0.0000	5.48	0.0000	5.51	0.0000	5.90	0.0000	5.92	0.0000
5.50	0.0007	5.51	0.0001	5.53	0.0001	5.90	0.0000	5.92	0.0008
5.50	0.0009	5.72	0.0008	5.76	0.0008	5.92	0.0029	5.95	0.0072
5.60	0.0696	5.79	0.0662	5.80	0.0659	6.03	0.0027	6.11	0.0012
5.74	0.0002	5.88	0.0014	5.91	0.0013	6.09	0.0003	6.11	0.0000
5.85	0.0014	5.89	0.0001	5.92	0.0001	6.09	0.0000	6.12	0.0022
5.87	0.0001	5.89	0.0000	5.92	0.0000				
5.88	0.0001	5.94	0.0014	5.98	0.0008				
5.90	0.0001	5.96	0.0002	6.02	0.0009				
5.94	0.0010	6.09	0.0003	6.11	0.0002				
5.99	0.0008	6.11	0.0021	6.19	0.0021				
6.11	0.0024	6.21	0.0015	6.23	0.0018				

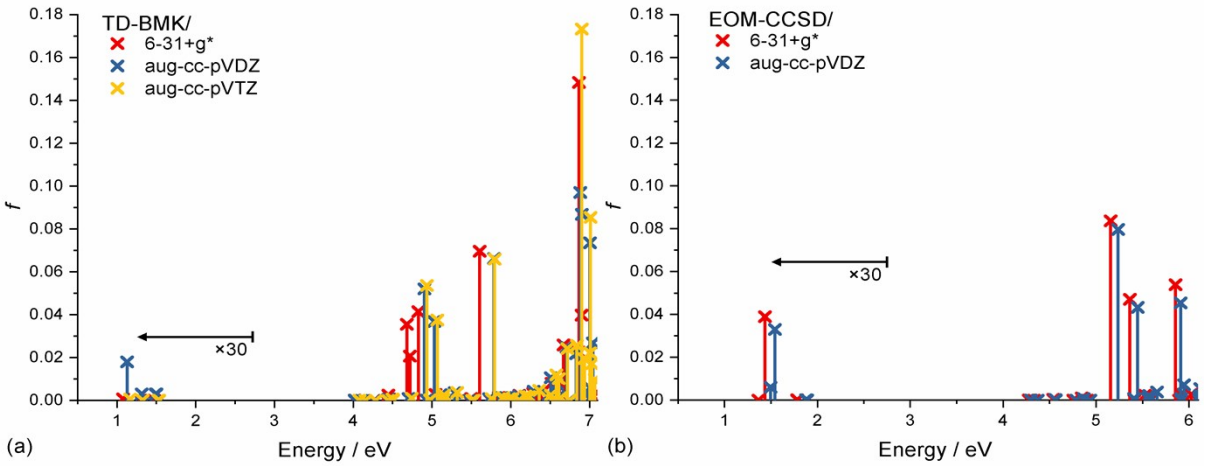

Figure S5. Benchmarking of the calculated transition energies and the corresponding oscillator strengths *f* in $Cu(NO_3)_3^-$ with a) the TD-DFT functional TD-BMK and b) the EOM-CCSD method across multiple basis sets. The section below 2.75 eV has been scaled for better visibility.

The optimized structure and zero-point corrected energy of the calculated ions and molecules on the B3LYP/def2TZVP level of theory in Å at the lowest possible spin multiplicity *M* (unless otherwise noted).

Cu(NO3)(NO2)-
E= -2126.330248
O -0.641665 -1.418385 -0.000000
N 0.258551 -2.362802 -0.000000
O -0.136907 -3.525827 -0.000000
Cu -0.000000 0.377506 0.000000
O 0.656576 2.162872 0.000000
N -0.204521 3.125046 0.000000
O -1.379423 2.793771 0.000000
O 1.454144 -2.047853 -0.000000

Cu(NO3)O2-
E= -2071.507362
O -0.877491 -1.035118 -0.000000
Cu -0.000000 0.651378 0.000000
O 0.755429 2.356692 0.000000
N -0.133681 -2.107580 -0.000000
O 1.095367 -1.983669 0.000000
O -0.707014 -3.194559 -0.000000
O -0.149320 3.339541 -0.000000

Cu(NO3)O-
E= -1996.295308
O 0.000000 -1.062551 0.000000
N 1.304009 -1.144274 -0.000000
O 1.797126 -2.271560 0.000000
Cu -0.853732 0.642340 0.000000
O -1.816860 2.115531 -0.000000
O 1.973505 -0.108662 -0.000000

Cu(NO3)2
E= -2201.420214
Cu 0.000168 -0.000269 -0.000090
N -2.384770 0.000113 0.000164
O -3.571672 0.001022 -0.000040
O -1.664121 -1.073208 0.000443
O -1.662625 1.072594 -0.000251
O 1.662763 -1.072769 -0.000491
N 2.384855 0.000100 0.000141
O 1.663424 1.073302 0.000203
O 3.571548 -0.000153 0.000197

Cu(NO3)2-
E= -2201.553981
cu -0.000000 0.000000 0.000453
o -0.590106 1.802345 0.000421
o 0.590106 -1.802345 0.000421
N 0.349082 2.711802 -0.000242
o -0.000000 3.887593 -0.000570
O 1.529842 2.346244 -0.000461
N -0.349082 -2.711802 -0.000242
o -0.000000 -3.887593 -0.000570
O -1.529842 -2.346244 -0.000461

Cu(NO3)2(NO2)-
E= -2406.743626
O -3.286704 -1.609084 -0.035420
N -2.217721 -1.045549 -0.043310
O -1.245742 -1.399630 -0.780919
Cu -0.080171 0.189503 0.022697
O 1.647252 -1.330102 1.023000
N 2.274400 -0.969448 0.011038
O 3.400167 -1.344672 -0.265581
O -1.974960 -0.027961 0.703241
O 0.379052 1.910082 0.924303
N 0.066526 2.858536 0.130362
O -0.409224 2.514038 -0.944029
O 1.672974 -0.137715 -0.792698

Cu(NO3)2O- *M*=3
E= -2276.711734
O -3.303791 -1.227627 0.045511
N -2.241054 -0.648604 -0.020064
O -1.203816 -1.155139 -0.546913
Cu -0.101475 0.627925 -0.105159
O 1.652964 -0.811983 1.158289
N 2.269159 -0.605583 0.101132
O 3.386744 -1.042677 -0.133547
O -2.083525 0.538513 0.442269
O 0.211508 2.399448 0.152642
O 1.683170 0.120651 -0.807985

Cu(NO3)3 *M*=3
E= -2481.766397
Cu -0.000037 -0.000266 0.000034
N 0.088594 2.439632 -0.000003
O 0.131767 3.626305 -0.000042
O -0.495966 1.745511 -0.911309
O 0.621229 1.704932 0.911320
O -1.264263 -1.302601 -0.911331
N -2.157499 -1.142919 0.000029
O -3.206949 -1.698583 0.000130
O -1.787325 -0.314370 0.911226
O 1.166522 -1.390791 0.911369
N 2.068925 -1.296338 -0.000063
O 1.759755 -0.443170 -0.911285
O 3.075345 -1.926597 -0.000171

Cu(NO3)3-
E=-2481.964553
Cu 0.000000 0.000000 0.110006
N 0.000000 0.000000 2.560382
O 0.000000 0.000000 3.766082
O 1.011326 0.358009 1.863722
O -1.011326 -0.358009 1.863722
O 1.287818 0.723546 -1.188068
N 0.966087 1.981067 -1.318862
O 1.617477 2.678408 -2.075080
O 0.000000 2.388230 -0.649164
O -1.287818 -0.723546 -1.188068
N -0.966087 -1.981067 -1.318862
O -0.000000 -2.388230 -0.649164
O -1.617477 -2.678408 -2.075080

Cu2(NO3)4-
E= -4403.011750
O 0.935826 -1.610942 2.072772
N 0.213370 -0.976339 1.340511
O -1.034373 -0.879285 1.552762
Cu -1.945300 0.187181 0.109984
O -2.492794 1.797846 -1.051471
N -2.300561 2.585131 -0.062821
O -2.481585 3.769885 -0.111649
O 0.655728 -0.359478 0.303370
Cu 2.523917 -0.469756 -0.118067
O 4.462393 1.328270 0.083530
N 5.024096 0.374683 -0.472618
O 4.307725 -0.697191 -0.720916
O -1.892741 1.982808 0.999853
O -2.258017 -1.320279 -1.083267
N -3.479022 -1.678696 -0.775054
O -4.036421 -1.010406 0.118638
O -3.986764 -2.611002 -1.356529
O 6.197889 0.367427 -0.804058

Cu2(NO3)4(NO2)-

E= -4608.196465
O 1.117497 -1.700326 -0.688555
N -0.094247 -1.488652 -0.578282
O -0.368873 -0.319194 -0.170689
Cu 2.268896 -0.094076 -0.197525
Cu -2.279195 0.176501 0.006360
O -3.468184 -1.841396 0.451535
N -3.583577 -1.876152 -0.790914
O -4.168474 -2.736720 -1.406354
O -1.985378 1.513117 1.470966
N -3.145694 2.045874 1.302647
O -3.819265 1.509845 0.357335
O -3.018871 -0.890402 -1.442756
O 2.269624 0.806481 -1.978995
N 2.836300 1.873574 -1.524903
O 3.079793 1.831807 -0.275421
O 2.575423 -0.643834 1.643447
N 3.737018 -1.242588 1.569245
O 4.257253 -1.288401 0.436129
O 4.230177 -1.706093 2.572424
O 3.102892 2.810731 -2.227551
O -3.547359 2.957545 1.970888

Cu2(NO3)4O- *M*=4
E= -4478.188844
Cu -1.477430 0.463809 -0.344739
Cu 1.477408 -0.463994 -0.344737
O 2.976511 0.550870 -1.369027
N 3.866055 0.005219 -0.630689
O 3.391732 -0.813412 0.234059
O 5.042684 0.233103 -0.739518
O 0.763101 -2.090473 0.503484
N -0.361261 -2.178786 1.143428
O -0.598669 -3.214212 1.732571
O -1.152313 -1.212142 1.143251
O -2.977146 -0.549667 -1.369561
N -3.866346 -0.004478 -0.630469
O -5.043068 -0.231958 -0.739223
O -3.391602 0.813227 0.234892
O -0.763017 2.089790 0.504569
N 0.361585 2.178273 1.143932
O 1.152475 1.211461 1.144009
O 0.599427 3.213966 1.732451
O -0.000064 -0.000081 -1.410534

Cu2(NO3)5-
E= -4683.415102
N 0.014922 0.046730 -1.483941
O 0.839512 0.166938 -2.367859
O 0.362923 0.018566 -0.251608
Cu 2.386069 0.150611 -0.111781
O -1.218703 -0.057466 -1.734168
Cu -2.343708 -0.276218 -0.067975
O -2.198547 -2.263514 0.113107
O -2.799072 1.605980 0.113236
N -3.951916 1.667160 -0.503848
O -4.533600 2.724967 -0.572581
O -4.369601 0.593141 -0.985349
N -2.740344 -2.255941 1.281905
O -2.936526 -3.255156 1.915217
O -3.046512 -1.084807 1.692169
O 2.783579 -1.803164 -0.240935
O 2.477809 2.085601 0.053033
N 4.039154 -1.601647 -0.449708
O 4.823657 -2.496020 -0.604985
O 4.359290 -0.365739 -0.474336
N 2.608153 2.230267 1.347887
O 2.724135 3.338025 1.815157
O 2.604373 1.172226 2.013259

(NO3)-
E=-280.470791
N 0.000000 0.000000 0.000000
O 0.000000 1.256426 -0.000000
O 1.088097 -0.628213 -0.000000
O -1.088097 -0.628213 -0.000000

NO3
E=-280.335255
N 0.000000 0.000000 0.000000
O 0.000000 1.230539 -0.000000
O 1.065678 -0.615269 -0.000000
O -1.065678 -0.615269 -0.000000

O *M*=3
E= -75.096275
O 0.000000 0.000000 0.000000

NO2
E= -205.158340
N 0.000000 -0.000000 0.320860
O 0.000000 -1.097677 -0.140376
O 0.000000 1.097677 -0.140376

N2O5
E= -485.518864
N 1.270142 0.009048 0.080105
O 2.169098 0.621143 -0.389169
O -0.000062 0.817237 -0.000027
O 1.196575 -1.037700 0.631050
N -1.270081 0.009107 -0.080147
O -2.169000 0.621192 0.389192
O -1.196665 -1.037757 -0.631009