Supporting Information

On the Origin of the Shift Between Vertical Excitation and Band Maximum in Molecular Photoabsorption

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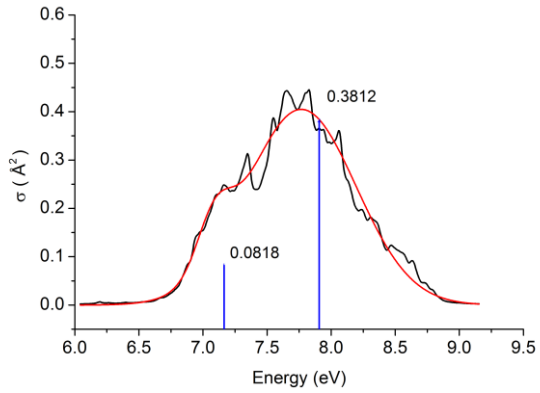
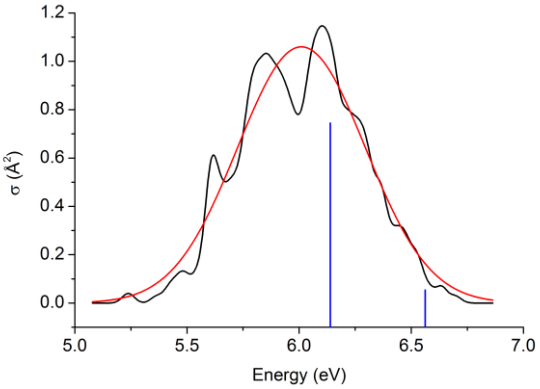
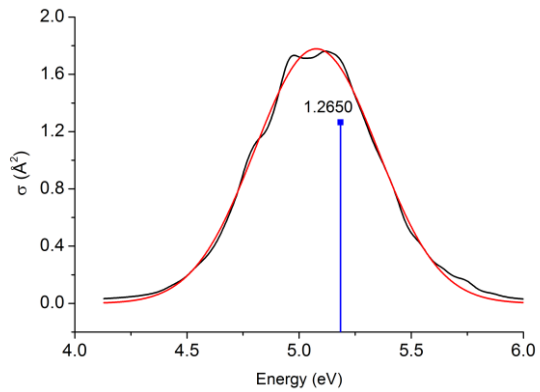
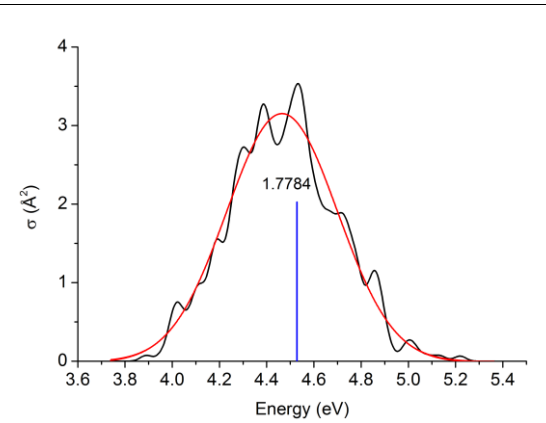
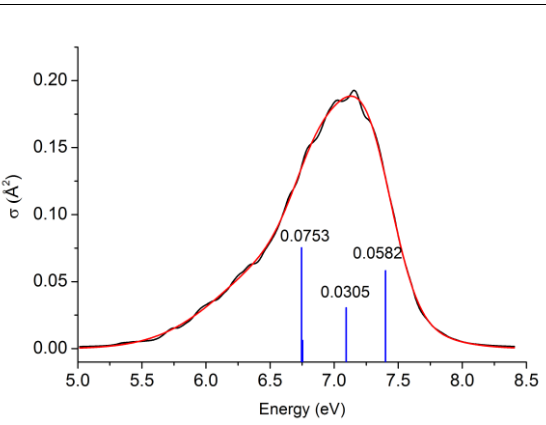
Nuclear ensemble spectrum simulation and vertical excitations

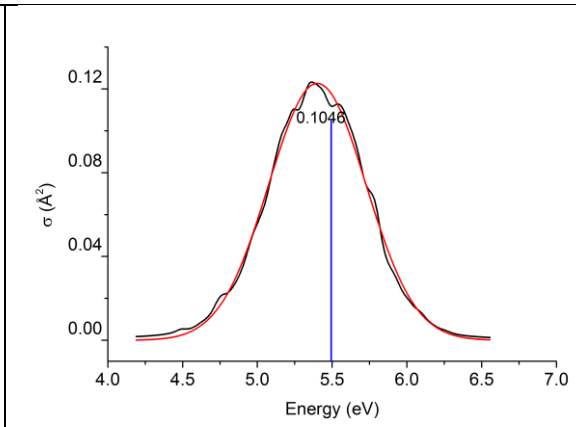
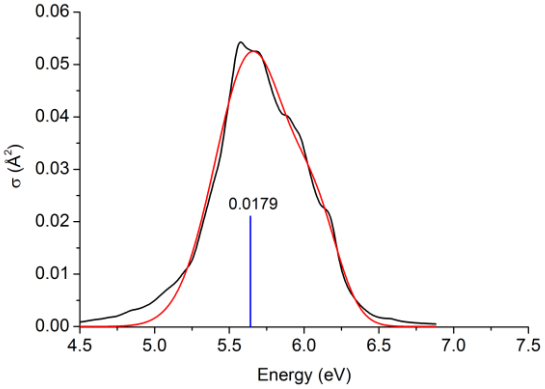
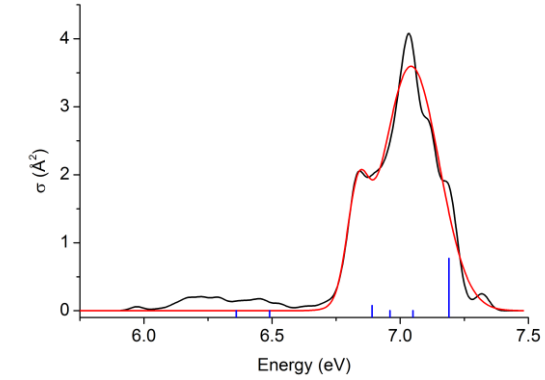
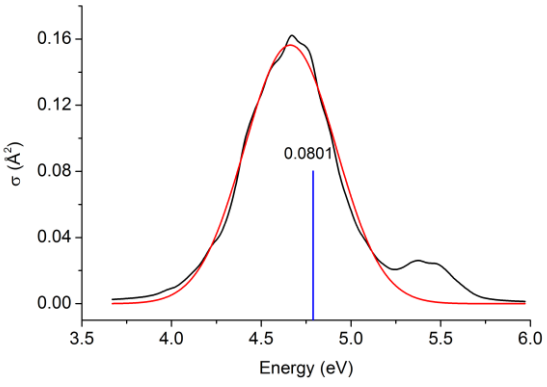
The nuclear ensemble spectrum for each of the molecules in the Mülheim molecular dataset was computed for N_f states. The spectrum was then fitted with the equation

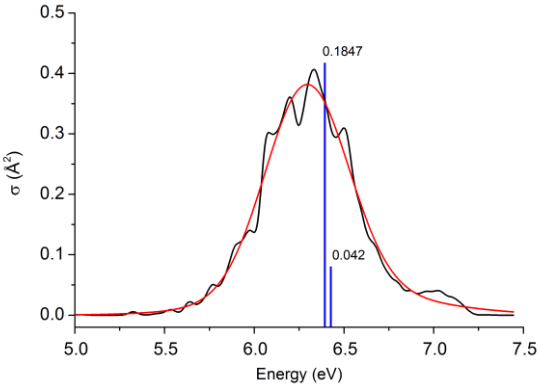
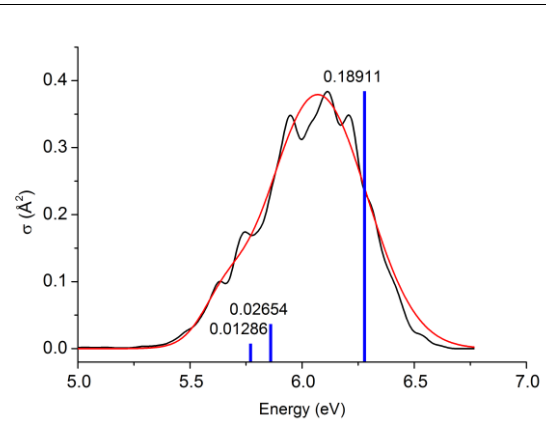
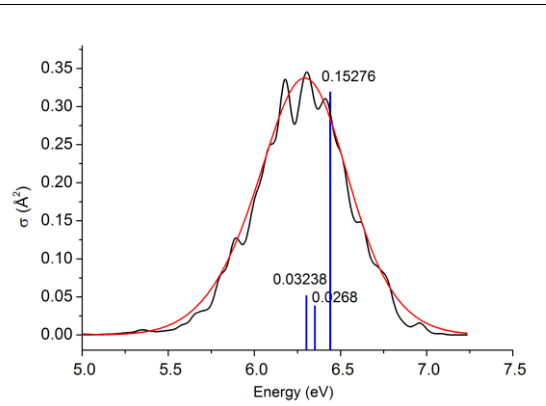
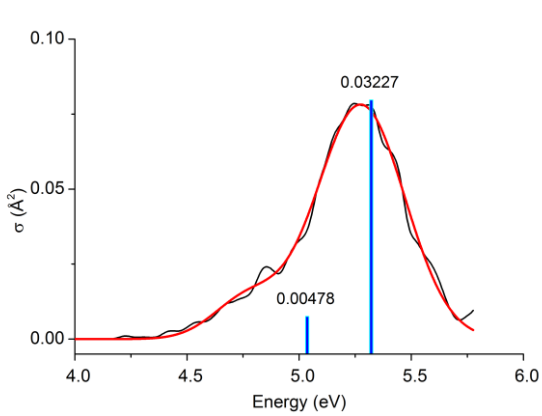
$$\sigma_A(E) = 0.619 \sum_{i=1}^{N} \frac{f_i}{\Gamma_i} e^{-\left(E - E_i^v + \delta_i\right)^2 / \Gamma_i^2},$$

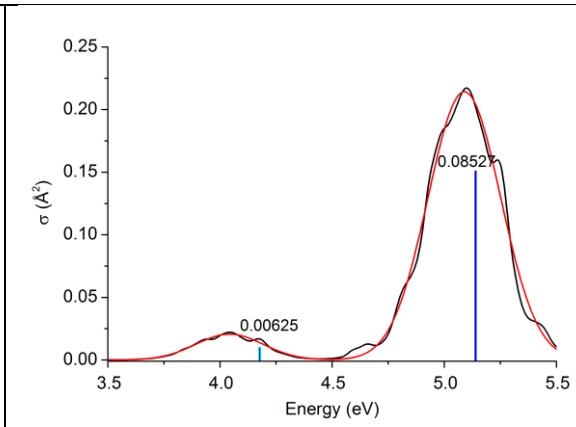
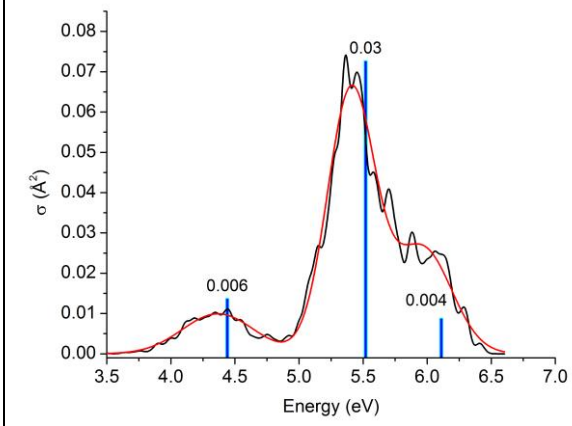
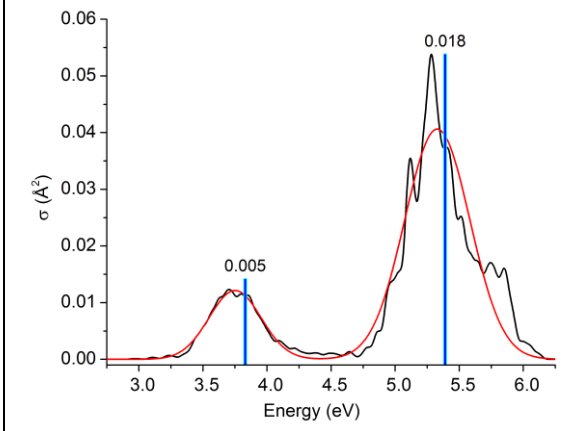
where E_i^v, f_i, δ_i, and Γ_i are, respectively, the vertical excitation, oscillator strength, shift, and width of sub-band *i*. In this equation, energies *E* in eV yield absorption cross sections in Å^2.molecule^{-1}. The number *N* of sub-bands was determined by the number of vertical excitations with the largest oscillator strengths lying within the spectral region to be fitted. In the fitting process, E_i^v (eV) and f_i were kept fixed. Γ_i (eV) and δ_i (eV) are the results of the fitting. For some of the molecules, f_i was further released to improve the fitting, producing f_i^{fit}. One band with spectral band maximum E^{max} (eV) may be composed of one or more sub-bands.

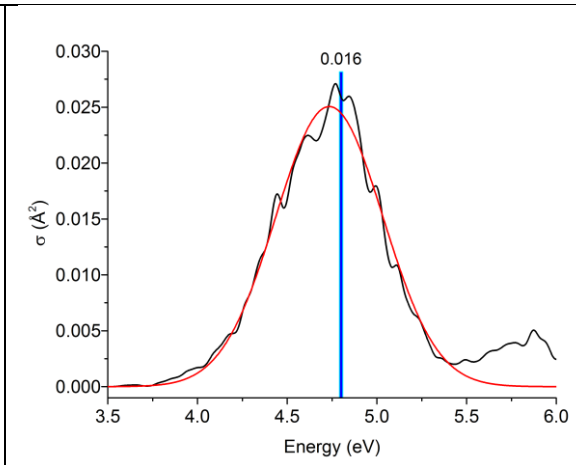
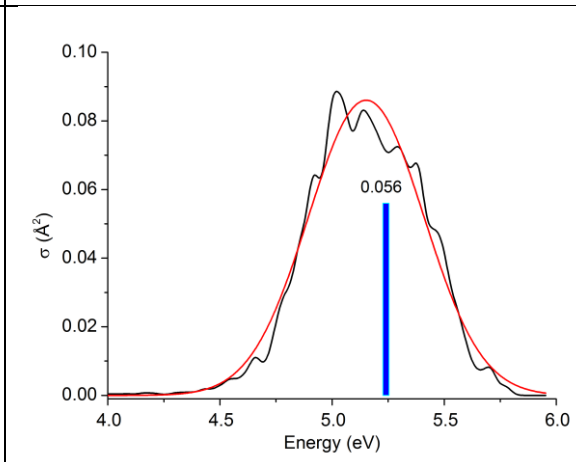
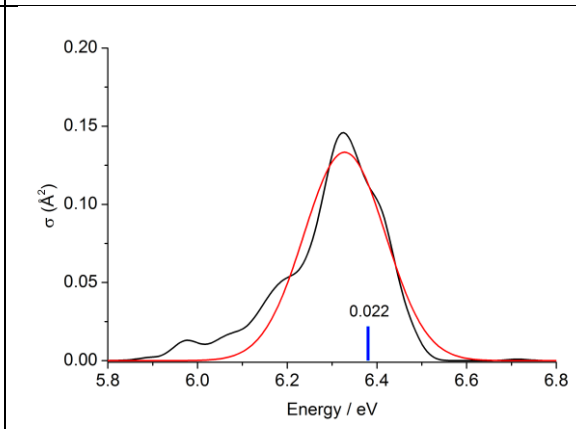
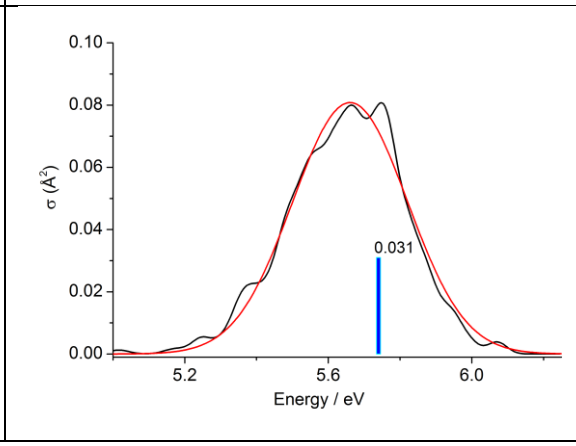
Mol. (N_f)	Spectrum convolution	E_i^v	f_i	δ_i	Γ_i	f_i^{fit}	E^{max}
1		7.16	0.082	0.07	0.192	0.032	
(6)		7.91	0.381	0.14	0.605	0.395	7.77

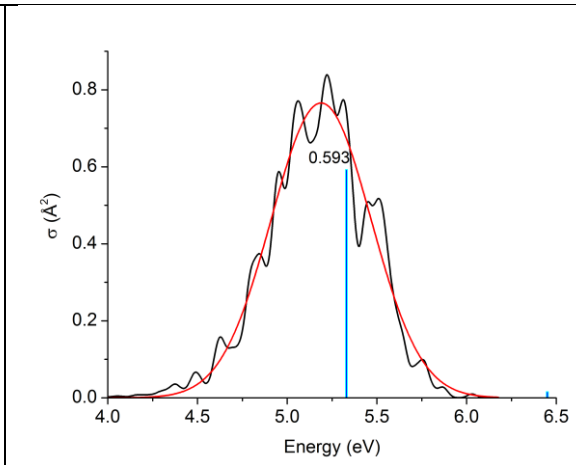
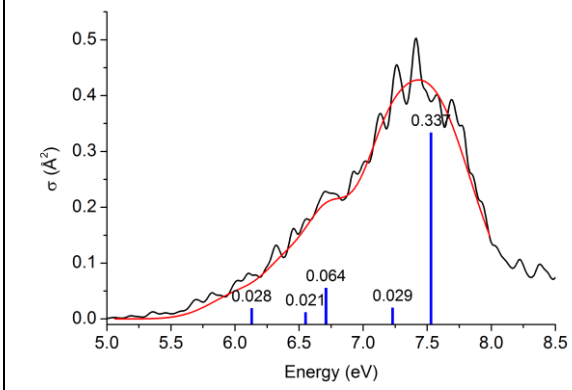
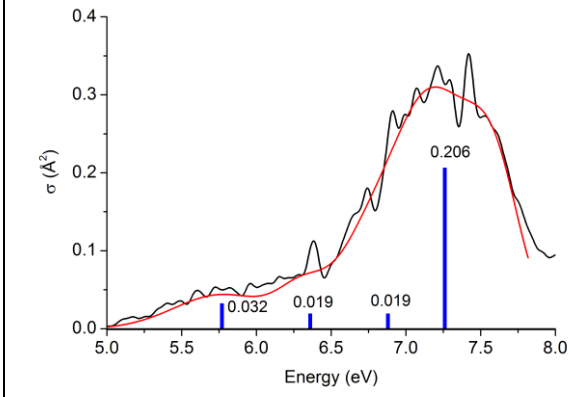
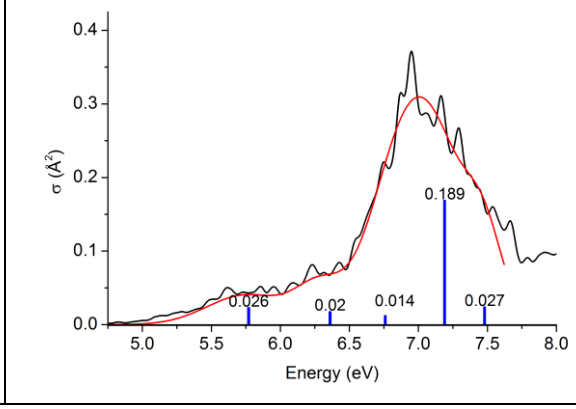
2 (6)		6.14	0.745	0.13	0.403	0.690	6.01
3 (6)		5.18	1.265	0.10	0.400	1.110	5.08
4 (6)		4.53	1.778	0.06	0.329	1.681	4.47
5 (6)		6.75 7.09 7.40	0.075 0.031 0.058	0.02 0.19 0.14	0.771 0.294 0.287	0.094 0.034 0.052	7.12

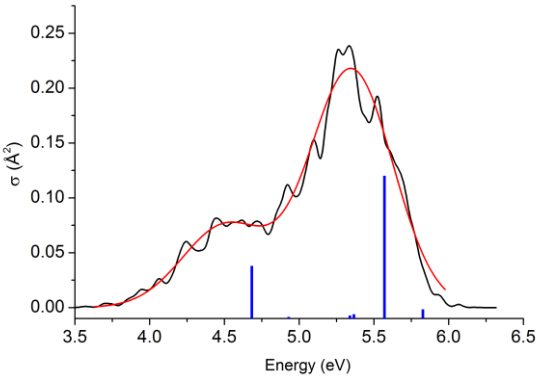
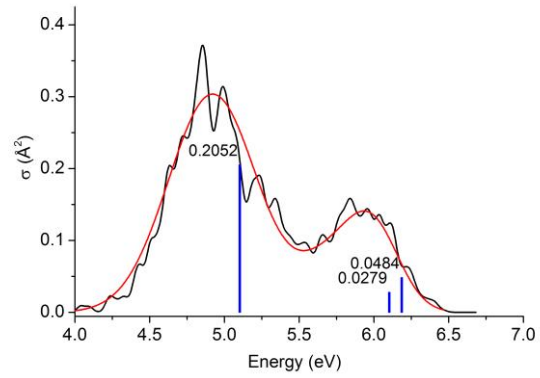
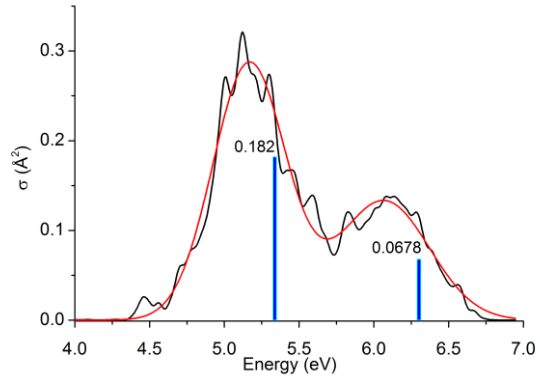
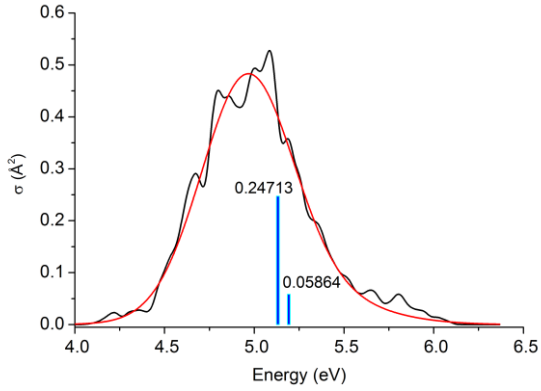
6 (6)		5.49	0.105	0.09	0.460	0.091	5.40
7 (6)		5.64 6.09	0.018 0.018	0.07 0.18	0.296 0.356	0.018 0.017	5.67
8 (10)		6.89 7.19	0.078 0.77	0.06 0.15	0.059 0.155	0.1353 0.898	7.03
9 (6)		4.79	0.08	0.13	0.360	0.091	4.66

10 (6)		6.39 6.43	0.185 0.042	0.10 0.00	0.328 0.749	0.185 0.042	6.29
11 (6)		5.77 5.86 6.28	0.013 0.027 0.189	0.15 0.21 0.21	0.4 0.134 0.309	0.000 0.010 0.189	6.07
12 (6)		6.30 6.35 6.44	0.032 0.027 0.153	0.03 0.00 0.14	0.032 0.027 0.153	0.277 0.271 0.455	6.28
13 (6)		5.04 5.32	0.005 0.032	0.27 0.05	0.216 0.278	0.005 0.035	5.27

14 (6)		4.18 5.14	0.006 0.085	0.14 0.05	0.213 0.229	0.007 0.079	4.04 5.09
15 (6)		4.44 5.52 6.11	0.006 0.030 0.004	0.07 0.11 0.15	0.395 0.262 0.323	0.006 0.028 0.017	4.37 5.43
16 (6)		3.83 5.39	0.005 0.018	0.08 0.06	0.286 0.359	0.006 0.024	3.75 5.33

17 (6)		4.80	0.016	0.006	0.422	0.017	4.74
18 (6)		5.24	0.056	0.09	0.364	0.051	5.15
19 (6)		6.38	0.022	0.05	0.128	0.028	6.33
20 (6)		5.74	0.031	0.08	0.226	0.0295	5.66

21 (6)		5.33	0.593	0.14	0.393	0.486	5.18
22 (15)		6.13 6.55 6.71 7.23 7.53	0.028 0.021 0.064 0.029 0.337	0.05 0.17 0.01 0.10 0.05	0.349 0.215 0.251 0.241 0.500	0.028 0.021 0.064 0.029 0.337	7.43
23 (15)		5.77 6.36 6.88 7.26 7.60	0.032 0.019 0.019 0.206 0.056	0.00 0.03 0.19 0.09 0.00	0.452 0.239 0.241 0.421 0.240	0.032 0.019 0.019 0.206 0.056	7.17
24 (15)		5.77 6.36 6.76 7.19 7.48	0.026 0.020 0.014 0.189 0.027	0.02 0.08 0.00 0.16 0.00	0.399 0.247 0.259 0.394 0.192	0.026 0.020 0.014 0.189 0.027	6.88

25 (6)		4.68 5.57	0.05 0.137	0.08 0.18	0.412 0.391	0.050 0.137	5.35
26 (6)		5.10 6.10 6.19	0.205 0.028 0.048	0.18 0.41 0.20	0.418 0.275 0.254	0.205 0.028 0.048	4.93
27 (6)		5.34 6.30	0.182 0.068	0.17 0.23	0.344 0.430	0.159 0.093	5.16
28 (6)		5.13 5.19	0.247 0.059	0.17 0.00	0.357 0.569	0.247 0.059	4.98

Cartesian coordinates

All coordinates in Angstrom.

```
6
Molecule 1
H      0.0000000    0.9232467    1.2293590
H      0.0000000   -0.9232467    1.2293590
H     -0.0000000    0.9232467   -1.2293590
H     -0.0000000   -0.9232467   -1.2293590
C     -0.0000000    0.0000000    0.6675732
C      0.0000000   -0.0000000   -0.6675732
```

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10
Molecule 2
H      1.0716094   -2.5511276   -0.0000003
H     -1.0716095    2.5511281   -0.0000001
H      2.0952751   -1.0081485    0.0000003
H     -2.0952755    1.0081484    0.0000001
H     -0.9688536   -1.2159346   -0.0000002
H      0.9688540    1.2159347   -0.0000001
C      0.0006529    0.7263744   -0.0000001
C     -0.0006547   -0.7263736    0.0000013
C      1.1170725   -1.4719244   -0.0000006
C     -1.1170706    1.4719231   -0.0000004
```

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14
Molecule 3
H     -0.9525277    1.2011149    0.0000004
H      0.9525267   -1.2011153   -0.0000004
H      2.1466767    0.9483596   -0.0000005
H     -2.1466844   -0.9483538    0.0000000
H      2.1222281    3.3884926    0.0000003
H     -2.1222352   -3.3884984   -0.0000006
H      0.2712134    3.3813557    0.0000005
H     -0.2712065   -3.3813613    0.0000003
C     -0.0010365    0.6767206   -0.0000004
C      0.0010410   -0.6767142    0.0000006
C      1.2008285    1.4800638    0.0000011
C     -1.2008236   -1.4801147   -0.0000014
C      1.2002189    2.8258219   -0.0000013
C     -1.2002195   -2.8257713    0.0000013
```

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18
Molecule 4
H      0.9663455    1.2176794    0.0000016
H     -0.9663493   -1.2176814    0.0000018
H     -2.0920308    0.9800199   -0.0000005
H      2.0920347   -0.9800197   -0.0000015
H     -0.1468336    3.4046013   -0.0000002
H      0.1468219   -3.4046052   -0.0000009
H     -2.1821816    4.7530984    0.0000016
H      2.1821827   -4.7531093    0.0000030
H     -3.2133565    3.2150322   -0.0000006
H      3.2133672   -3.2150287   -0.0000012
C      0.0009424    0.7185001    0.0000046
C     -0.0009259   -0.7185050    0.0000030
C      1.1249822   -1.4757392   -0.0000036
C     -1.1250038    1.4757540   -0.0000015
C      1.1175711   -2.9192987   -0.0000039
C     -1.1175144    2.9192693   -0.0000005
C      2.2328780   -3.6739928    0.0000012
C     -2.2329297    3.6740255   -0.0000023
```

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7
Molecule 5
H      0.9127303   -0.0000001    1.4510015
H     -0.9127304    0.0000000    1.4510016
H     -0.0000003   -1.5803835   -1.0358614
H      0.0000002    1.5803835   -1.0358616
C      0.0000001   -0.0000000    0.8638999
C      0.0000008   -0.6512093   -0.4980231
C     -0.0000006    0.6512094   -0.4980231
```

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11
Molecule 6
H     -0.8772743    0.0000001    1.8689369
H      0.8772739   -0.0000003    1.8689366
H      0.0000001    2.2059727    0.6101774
H      0.0000003   -2.2059725    0.6101774
H      0.0000001    1.3477836   -1.8794144
H     -0.0000001   -1.3477836   -1.8794142
C     -0.0000003    0.0000001    1.2141704
C     -0.0000005   -1.1763050    0.2869545
C      0.0000010    1.1763049    0.2869540
C      0.0000011   -0.7309867   -0.9928428
C     -0.0000013    0.7309867   -0.9928422
```

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15
Molecule 7
H      0.9024903    0.0000001    1.9591074
H     -0.9024910   -0.0000001    1.9591075
H     -0.0000002    2.1509860    0.6161901
H     -0.0000001   -2.1509860    0.6161901
H      1.9193699    1.3357038   -1.0212815
H     -1.9193688   -1.3357025   -1.0212802
H     -1.9193689    1.3357027   -1.0212803
H      1.9193700   -1.3357040   -1.0212816
C      0.0000004    0.0000000    1.3474477
C      0.0000004    1.1201914    0.2735412
C      0.0000006   -1.1201914    0.2735412
```

```
12
Molecule 8
H     -0.0000000    2.4750393   -0.0000003
H      0.0000000   -2.4750393    0.0000004
H      2.1434469    1.2375192    0.0000002
H     -2.1434469   -1.2375192   -0.0000003
H     -2.1434469    1.2375193    0.0000002
H      2.1434469   -1.2375193   -0.0000002
C      0.0000000    1.3936079    0.0000009
C     -0.0000000   -1.3936079   -0.0000011
C      1.2068995    0.6968038   -0.0000009
C     -1.2068995   -0.6968038    0.0000010
C     -1.2068995    0.6968039   -0.0000009
```

C 1.2343141 0.6721548 -0.5155031 C -1.2343154 -0.6721611 -0.5155044 C -1.2343151 0.6721610 -0.5155042 C 1.2343139 -0.6721547 -0.5155029	C 1.2068995 -0.6968039 0.0000009 *optimized at RI-MP2/cc-pVTZ level
18 Molecule 9 H 1.2387361 2.4852891 -0.0000002 H -1.2387361 -2.4852892 0.0000003 H -1.2387361 2.4852891 -0.0000003 H 1.2387362 -2.4852893 0.0000003 H 3.3702322 1.2425151 0.0000001 H -3.3702322 -1.2425151 0.0000002 H -3.3702322 1.2425151 -0.0000001 H 3.3702322 -1.2425150 -0.0000003 C 0.0000000 0.7154392 -0.0000013 C -0.0000000 -0.7154393 0.0000016 C 1.2395355 1.4017778 0.0000008 C -1.2395355 -1.4017777 -0.0000004 C -1.2395354 1.4017778 0.0000011 C 1.2395354 -1.4017777 -0.0000014 C 2.4302135 0.7063576 -0.0000007 C -2.4302135 -0.7063576 -0.0000009 C -2.4302136 0.7063576 0.0000001 C 2.4302135 -0.7063576 0.0000010	9 Molecule 10 H -0.0000016 2.0473103 0.8448067 H 0.0000022 -2.0473087 0.8448472 H -0.0000109 1.3707890 -1.8152153 H 0.0000108 -1.3708283 -1.8152150 C 0.0000081 1.0946836 0.3475987 C -0.0000085 -1.0946645 0.3475732 C 0.0000040 0.7144683 -0.9628240 C -0.0000037 -0.7144847 -0.9627598 O -0.0000004 0.0000072 1.1668186
10 Molecule 11 H -0.0000005 2.1083509 0.7688032 H -0.0000004 -2.1083512 0.7688032 H 0.0000004 1.3576204 -1.8447764 H 0.0000004 -1.3576204 -1.8447765 H 0.0000017 0.0000001 2.1246750 C 0.0000020 1.1246561 0.3336327 C 0.0000019 -1.1246564 0.3336323 C -0.0000006 0.7100398 -0.9849131 C -0.0000009 -0.7100398 -0.9849128 N -0.0000038 0.0000004 1.1198566	9 Molecule 12 H -0.0000004 2.1139070 0.7122962 H 0.0000002 1.2013347 -1.8988291 H 0.0000004 -2.0977404 0.6631097 H -0.0000007 -0.0101215 2.1118901 C 0.0000008 1.1192313 0.3047695 C -0.0000011 0.6359040 -0.9834410 C -0.0000018 -1.0904628 0.2837659 N 0.0000008 -0.7421553 -0.9927654 N 0.0000018 -0.0005283 1.1056377
11 Molecule 13 H -0.0000001 2.0559118 1.3028845 H -0.0000000 -2.0559118 1.3028846 H -0.0000000 2.1518767 -1.1812720 H 0.0000001 -2.1518767 -1.1812720 H -0.0000001 -0.0000000 -2.4677547 C 0.0000007 1.1428147 0.7195745 C -0.0000001 -1.1428147 0.7195745 C -0.0000006 1.1971585 -0.6736021 C -0.0000003 -1.1971585 -0.6736021 C 0.0000006 0.0000000 -1.3861630 N -0.0000001 0.0000000 1.4258934	10 Molecule 14 H -0.0000006 2.0636968 1.2508116 H 0.0000003 -2.0636965 1.2508115 H 0.0000006 2.0636960 -1.2508112 H -0.0000003 -2.0636968 -1.2508118 C -0.0000017 1.1328034 0.6970646 C 0.0000018 -1.1328076 0.6970604 C 0.0000017 1.1328058 -0.6970641 C -0.0000018 -1.1328050 -0.6970608 N 0.0000002 0.0000035 1.4170793 N -0.0000002 0.0000004 -1.4170794
10 Molecule 15 H -0.0000003 2.1487345 1.1194143 H 0.0000003 -2.1487345 1.1194143 H 0.0000001 0.0000000 -2.3909966 H -0.0000000 0.0000000 2.4340434 C -0.0000017 1.1849441 0.6244814 C -0.0000002 -1.1849442 0.6244814 C 0.0000015 0.0000000 -1.3081913 C 0.0000018 0.0000000 1.3536021 N 0.0000005 1.2047540 -0.7183218 N -0.0000020 -1.2047541 -0.7183218	10 Molecule 16 H 0.0000000 2.4009899 -0.1465016 H -0.0000000 -2.4009899 -0.1465016 H -0.0000000 1.2683224 2.0975182 H 0.0000000 -1.2683224 2.0975182 C -0.0000001 1.3220461 -0.0625706 C 0.0000001 -1.3220461 -0.0625706 C -0.0000012 0.6922491 1.1826742 C 0.0000012 -0.6922491 1.1826742 N 0.0000013 0.6725719 -1.2368636 N -0.0000013 -0.6725719 -1.2368636

9 Molecule 17 H 0.0000000 0.0000000 2.3777587 H 0.0000000 -2.0592001 -1.1888797 H 0.0000000 2.0592002 -1.1888797 C -0.0000002 0.0000000 1.2949728 C -0.0000002 1.1214797 -0.6474859 C -0.0000002 -1.1214797 -0.6474860 N 0.0000002 -0.0000001 -1.3812197 N 0.0000002 1.1961723 0.6906109 N 0.0000002 -1.1961723 0.6906108	8 Molecule 18 H -0.0000001 0.0000000 -2.3443429 H -0.0000000 0.0000000 2.3443429 C -0.0000012 -0.0000002 1.2633169 C -0.0000011 -0.0000002 -1.2633169 N 0.0000016 1.2038705 0.6690823 N -0.0000003 -1.2038703 0.6690824 N -0.0000004 1.2038704 -0.6690823 N 0.0000015 -1.2038703 -0.6690824
4 Molecule 19 H -0.0000000 0.9345111 -0.5851088 H -0.0000000 -0.9345111 -0.5851089 C 0.0000000 -0.0000000 -0.0011336 O -0.0000000 0.0000001 1.2162993	10 Molecule 20 H 0.2672357 2.1177411 -0.0811858 H -0.2706580 -2.1191451 0.0050999 H -0.7931082 1.3992524 -1.3165325 H 0.8095583 -1.4556420 -1.2434852 H -0.9237166 -1.2343667 -1.3998431 H 0.9426138 1.1750095 -1.4369899 C -0.0010054 0.0018813 0.0955916 C 0.1165675 1.2610620 -0.7306552 C -0.1086545 -1.2912054 -0.6780215 O -0.0085518 0.0277723 1.3207213
12 Molecule 21 H 0.0000494 2.1750309 1.2559309 H -0.0000624 -2.1750410 1.2559394 H -0.0000456 2.1749964 -1.2559163 H 0.0000663 -2.1750070 -1.2559245 C 0.0000074 -0.0000012 1.4399660 C -0.0000098 -0.0000015 -1.4400032 C 0.0000311 1.2623586 0.6743512 C -0.0000265 -1.2623498 0.6743014 C -0.0000163 1.2623125 -0.6743359 C 0.0000208 -1.2623029 -0.6742857 O 0.0000182 0.0000024 2.6774407 O -0.0000328 0.0000025 -2.6774640 *optimized at RI-MP2/cc-pVTZ level	6 Molecule 22 H -0.9181389 -0.6047967 0.0000001 H 1.0604197 -1.7752852 -0.0000009 H 2.0213846 -0.3257870 -0.0000003 C 0.0026261 -0.0007044 0.0000001 O -0.0004313 1.2227863 -0.0000004 N 1.1211160 -0.7739624 0.0000015
9 Molecule 23 C -1.4535385 -0.1460459 -0.0137572 C 0.0435384 0.0674388 -0.0036137 N 0.7882631 -1.0802540 -0.0300894 O 0.5565716 1.1831450 -0.0251860 H 0.3737140 -1.9782431 0.1354097 H 1.7877234 -0.9870211 0.0305193 H -1.9256843 0.6889138 0.4937899 H -1.7498349 -1.0804199 0.4595219 H -1.7987483 -0.1584021 -1.0468075	12 Molecule 24 C -2.5156437 0.0291523 0.0032803 C -1.2688900 -0.8368858 -0.0195522 C 0.0003103 -0.0033223 -0.0583083 N 1.1564389 -0.7346161 -0.1367601 O 0.0050363 1.2233025 0.0142435 H 1.1301933 -1.7058354 -0.3903800 H 2.0111614 -0.2257292 -0.2875381 H -1.2218126 -1.4778825 0.8636852 H -1.2715911 -1.5046319 -0.8844989 H -3.4116558 -0.5879151 0.0446155 H -2.5641817 0.6559302 -0.8843390 H -2.5040564 0.6898574 0.8666003
13 Molecule 25 H -2.1065431 -1.4317395 0.0000015 H -0.1704627 -2.7983215 0.0000006 H 2.0671476 -1.6557616 0.0000002 H 3.1646905 0.5575736 -0.0000023 H 2.2294828 2.0273267 -0.0000011	15 Molecule 26 H 0.2122931 -2.6709033 0.0000020 H 2.0472045 0.9214924 0.0000007 H -1.9374296 -1.7007677 0.0000012 H -3.3538478 0.3072525 -0.0000000 H -2.6130697 1.6606002 0.8746831

C -0.0614403 -1.7230070 0.0000026 C 1.1458836 -1.0955859 -0.0000016 C 1.1088609 0.3366400 -0.0000024 C -1.2231779 0.4320932 0.0000003 O -2.3114325 0.9979696 -0.0000012 N -0.0008648 1.0579731 0.0000036 N -1.1988996 -0.9901176 -0.0000044 N 2.2778551 1.0234108 0.0000042	H -2.6130698 1.6605993 -0.8746830 C 1.3549915 -0.9933332 -0.0000021 C -0.0035506 1.1206863 -0.0000020 C -1.2135013 0.3088024 -0.0000005 C -1.0817869 -1.0395569 0.0000025 C -2.5279876 1.0167456 0.0000005 O 2.4400423 -1.5594333 0.0000027 O 0.0215293 2.3508550 0.0000011 N 0.1432358 -1.6653702 -0.0000068 N 1.1906971 0.3811858 0.0000007 *optimized at RI-MP2/cc-pVTZ level
12 Molecule 27 H -2.0190306 -1.5179910 -0.0000013 H -0.0217045 1.9899598 -0.0000013 H 2.1741287 -1.6030759 0.0000000 H -0.0257062 -2.7824323 -0.0000006 C -1.2377676 0.3594731 -0.0000017 C 1.2809741 0.3891476 0.0000018 C 1.2433659 -1.0615108 0.0000021 C 0.0530383 -1.7049613 -0.0000019 O -2.3080074 0.9510125 0.0000010 O 2.2875846 1.0917236 -0.0000021 N -1.1387795 -1.0271625 0.0000021 N -0.0006569 0.9775873 0.0000018	15 Molecule 28 H 0.9724910 -3.0652695 0.0000008 H 2.1282579 2.0673034 0.0000015 H 3.3043287 0.7723159 0.0000012 H -3.0452884 -0.3331035 -0.0000011 H -2.7089700 2.1952694 0.0000005 C 0.6633946 -2.0276064 0.0000010 C 1.3584129 0.1743808 -0.0000031 C 0.0029969 0.5485451 0.0000008 C -0.9220597 -0.4996009 -0.0000030 C -1.9040277 1.4786901 -0.0000019 N -0.6610026 -1.8148417 0.0000022 N 1.6729121 -1.1327488 -0.0000016 N -2.1481429 0.1262956 0.0000020 N -0.6168560 1.7850284 0.0000020 N 2.3516071 1.0887607 -0.0000013 *optimized at RI-MP2/cc-pVTZ level