Supporting Information

Scaling of the Permanent Electric Dipole Moment in Isolated Silicon Clusters with Near-Spherical Shape

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1. Mass Spectrum

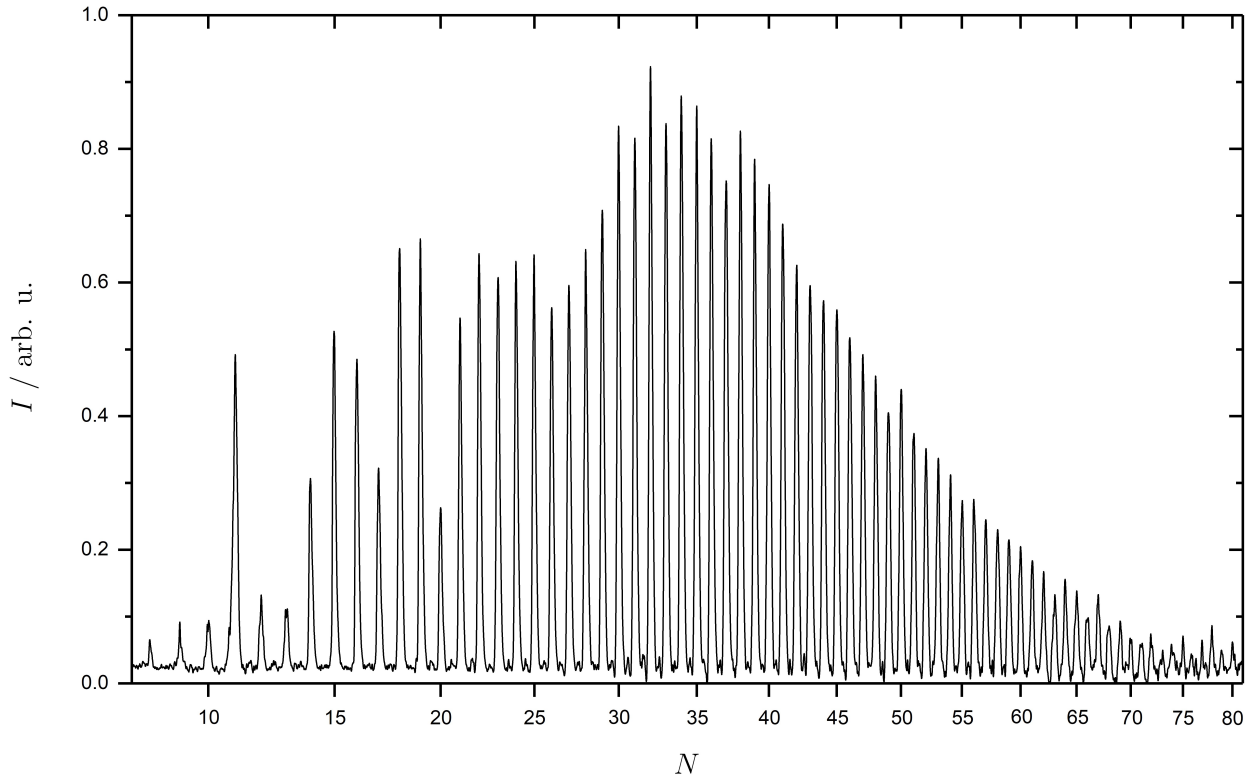

Figure S1. Time-of-flight mass spectrum of Si_N clusters generated by laser vaporization of a silicon target rod at $T_{\mathrm{nozzle}} = 16$ K and subsequent photoionization by an F_2 excimer laser (7.89 eV). The mass spectrum corresponds to an electric deflection measurement with $U = 11$ kV.

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2. Electric Beam Deflection Measurements

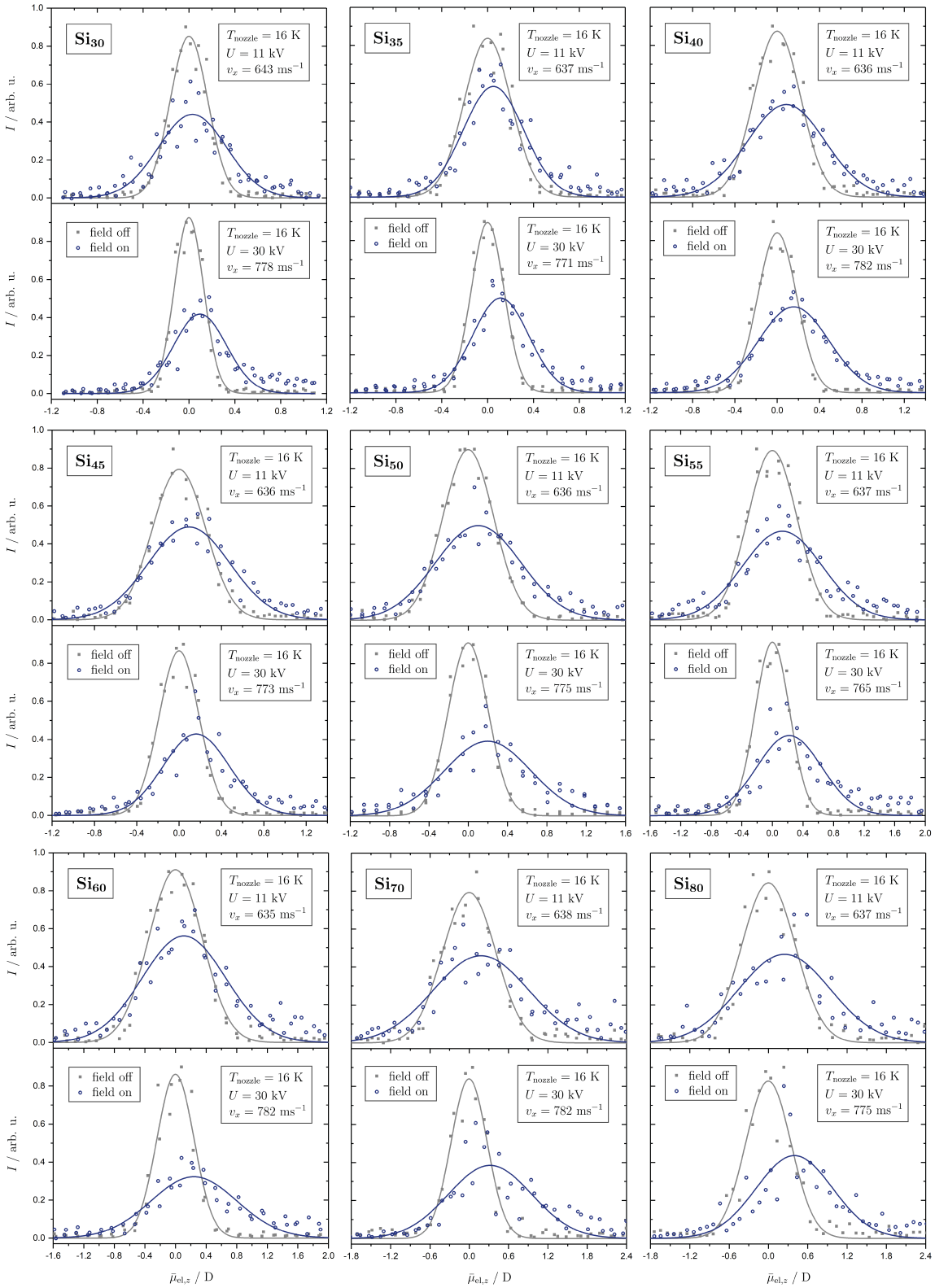

Figure S2. Electric beam deflection profiles of Si_N with $N = 30, 35, 40, 45, 50, 55, 60, 70$ and 80 at $T_{nozzle} = 16$ K and deflection voltages of $U = 11$ kV (top) and 30 kV (bottom). The measured intensity I is given as a function of the projection of the observed electric dipole moment on the field direction averaged over the length of the deflection unit and all quantum states $\bar{\mu}_{el,z}$. The gray squares represent the cluster intensity without applied field whereas blue open circles represent the intensity with applied field. Gaussians are fitted to the experimental data without applied field (gray line) and to the data with applied field (blue line). The velocities of the clusters in beam direction v_x are given as well.

Table S1. Experimental electric permanent dipole moments and polarizabilities per atom μ/N and α_{eff}/N of Si_N clusters with $N = 30, 35, 40, 45, 50, 55, 60, 70$ and 80 shown together with experimental uncertainties.

	Experiment (11 kV)		**Experiment** (30 kV)	
N	$\frac{\mu}{N}$ / 10^{-2} D	$\frac{\alpha_{\text{eff}}}{N}$ / Å^3	$\frac{\mu}{N}$ / 10^{-2} D	$\frac{\alpha_{\text{eff}}}{N}$ / Å^3
30	2.41 ± 0.18	4.15 ± 2.03	1.91 ± 0.12	4.84 ± 0.50
35	1.40 ± 0.16	5.87 ± 1.39	1.67 ± 0.08	4.86 ± 0.35
40	2.12 ± 0.13	8.77 ± 1.48	2.07 ± 0.09	5.84 ± 0.41
45	1.92 ± 0.14	8.55 ± 1.52	1.65 ± 0.11	5.40 ± 0.45
50	2.09 ± 0.14	8.35 ± 1.53	2.25 ± 0.11	5.89 ± 0.51
55	2.16 ± 0.15	9.70 ± 1.63	1.92 ± 0.13	5.99 ± 0.56
60	2.06 ± 0.16	7.46 ± 1.68	2.44 ± 0.16	5.94 ± 0.73
70	2.35 ± 0.20	9.98 ± 2.31	2.34 ± 0.18	6.67 ± 0.82
80	1.95 ± 0.23	12.53 ± 2.48	1.61 ± 0.19	7.38 ± 0.78

3. Computed Dielectric Properties of Si_{30}

To get a feeling for the uncertainties of the DFT-predicted dielectric properties comprising the permanent dipole moment μ and the polarizability α_{el}, a series of hybrid functionals is employed, namely the PBE0[1], B3LYP[2], B3P86[3], M06[4], TPSSh[5–7], HSE06[8,9], CAM-B3LYP[10], LC-ωPBEh[11,12] and the double-hybrid B2PLYP.[13,14] The calculations comprise a geometry optimization as well as a subsequent frequency analysis and the computation of dielectric properties using Gaussian16[15] and Orca v5.0.3[16–18] and the results are summarized in Tab. S2. The optimized geometries all mimic the same structural isomer, but small changes in bond lengths and angles can be observed being, *inter alia*, reflected in large dipole moment and vibrational frequency deviations compared to the chosen PBE0 result. Due to an overall good performance in the description of pure tetrel clusters in the past, the PBE0 functional is employed for all further calculations.[19–24]

Table S2. Computed electric permanent dipole moments and polarizabilities μ and α_{el} together with the computed lowest vibrational frequencies $\tilde{\nu}_{\text{min}}$ for the Si_{30} cluster. A series of hybrid functionals is compared all employing the cc-pVTZ basis set.[25]

	μ / D	$\frac{\mu}{N}$ / 10^{-2} D	α_{el} / Å^3	$\frac{\alpha_{\text{el}}}{N}$ / Å^3	$\tilde{\nu}_{\text{min}}$ / cm^{-1}
PBE0	**1.14**	**3.80**	**130.32**	**4.34**	**38.79**
B3LYP	0.72	2.41	135.39	4.51	53.84
B3P86	0.96	3.21	132.08	4.40	21.70
M06	1.16	3.86	132.65	4.42	58.28
TPSSh	1.54	5.12	131.53	4.38	40.77
HSE06	1.07	3.55	131.41	4.38	30.67
CAM-B3LYP	2.49	8.30	128.71	4.29	46.46
LC-ωPBEh	1.14	3.78	123.14	4.10	58.94
B2PLYP	1.12	3.73	136.29	4.54	29.33

4. Cartesian Coordinates and Mulliken Partial Charges

Table S3. Cartesian coordinates and Mulliken partial charges δq for the Si_{30} and Si_{35} clusters optimized and computed at the PBE0/cc-pVTZ level of theory.

	Si_{30}				**Si_{35}**			
Si	x	y	z	δq	x	y	z	δq
1	2.863 824	1.980 894	1.535 121	0.093	−2.103 777	-1.365338	2.410 320	0.031
2	1.059 321	−3.218 005	−0.727 860	0.079	3.690 445	-0.066920	2.609 629	−0.036
3	−3.131 029	0.097 092	1.957 971	0.092	−2.222 422	2.315990	1.321 001	0.116
4	−0.705 504	1.310 417	−3.090 951	0.029	−0.540 547	-3.007734	−1.701 585	0.054
5	−1.850 102	−2.740 785	0.209 044	0.061	2.877 817	-3.411155	0.310 922	0.016
6	0.651 384	3.114 938	−0.941 488	0.092	−0.552 297	-0.077798	3.736 415	0.060
7	2.242 033	1.600 377	−1.636 982	0.026	−3.247 984	-2.272280	−0.200 464	0.126
8	−0.985 990	−3.061 397	2.416 836	0.015	−2.797 598	-0.645219	−1.804 704	0.034
9	−3.289 692	0.171 235	−1.446 032	0.105	−2.054 247	2.406724	−1.873 534	0.046
10	3.341 239	−0.922 285	0.077 248	0.001	1.262 889	3.379696	2.337 340	0.019
11	3.092 466	−1.764 935	2.268 536	0.004	4.364 027	-0.094322	−1.519 487	0.068
12	−2.485 314	2.065 211	−0.444 730	0.037	1.539 247	3.131094	−1.676 593	0.062
13	−0.795 468	−1.546 672	−1.937 359	−0.048	2.634 102	-1.077906	−3.027 125	0.032
14	0.051 731	0.741 336	3.996 842	−0.014	0.527 557	0.023772	−3.074 197	0.041
15	−0.744 826	2.120 572	2.241 179	0.057	1.455 868	-0.854967	2.786 679	0.043
16	1.418 389	−0.873 361	−2.461 638	0.036	−1.032 756	-3.144899	1.372 148	0.094
17	−2.247 080	−0.432 542	−3.467 034	−0.012	−4.166 368	1.253930	−1.842 485	−0.027
18	−3.039 416	2.491 820	1.807 973	−0.036	3.513 608	2.155349	−0.768 763	0.031
19	3.019 182	−2.378 410	−1.727 355	0.003	0.346 746	3.708996	0.184 179	0.095
20	1.866 801	0.199 992	2.604 522	0.033	2.617 648	1.652285	1.393 963	0.043
21	−0.971 187	−3.926 796	−1.660 840	−0.010	−2.037 447	-4.325663	−0.394 139	−0.038
22	1.536 084	0.975 343	−3.810 111	0.027	−3.691 604	0.759525	0.473 935	0.088
23	−1.276 930	−0.802 006	2.901 291	0.039	3.562 770	-1.160433	0.520 747	0.086
24	1.028 129	3.418 365	1.337 136	0.088	−4.383 695	-1.244177	1.659 027	−0.026
25	−3.873 020	−1.402 590	0.229 580	0.034	−1.922 587	4.078932	−0.192 443	0.001
26	1.079 382	−2.621 673	1.550 285	0.008	−0.805 464	2.270841	3.223 062	0.045
27	4.189 755	1.254 544	−0.334 641	−0.011	−1.235 430	-1.492533	−3.348 994	−0.013
28	−1.341 217	3.314 547	−2.098 698	−0.017	1.189 911	-3.080263	2.033 582	0.098
29	−1.466 925	−0.247 007	0.185 156	−0.415	−0.039 847	2.351570	−3.314 714	0.065
30	0.763 978	1.081 784	0.466 997	−0.395	1.728 386	-2.852287	−1.684 400	0.058
31					−1.434 842	-0.352652	0.300 275	−0.329
32					−0.118 723	1.381640	−0.999 039	−0.281
33					0.794 690	-1.584246	0.182 404	−0.246
34					1.999 873	0.215287	−0.917 955	−0.210
35					0.282 053	1.025161	1.484 993	−0.246

Table S4. Cartesian coordinates and Mulliken partial charges δq for the Si_{40} and Si_{45} clusters optimized and computed at the PBE0/cc-pVTZ level of theory.

	Si_{40}				**Si_{45}**			
Si	x	y	z	δq	x	y	z	δq
1	−3.189 538	1.483 332	−3.347 302	−0.036	2.073 077	3.004023	1.597 080	0.057
2	−1.841 434	−0.511 798	−3.267 542	0.050	−2.222 592	3.466688	1.905 582	0.064
3	0.606 851	3.257 451	−1.725 014	0.064	−0.927 329	3.375803	−0.218 445	0.077
4	3.251 304	2.176 799	−0.714 677	0.071	1.179 492	4.489593	−0.040 350	−0.039
5	1.935 243	0.528 451	−2.947 714	0.022	4.353 735	2.217202	1.116 198	0.066
6	−4.382 260	1.893 752	0.590 430	0.037	3.846 440	-0.000640	1.767 624	0.083
7	−2.484 414	3.177 774	0.146 421	0.091	4.353 693	-2.218090	1.114 767	0.066
8	0.909 190	4.539 425	0.335 481	0.048	4.392 321	2.244623	−1.454 181	0.060
9	0.516 543	−0.674 789	1.813 928	−0.185	3.731 514	0.000539	−2.090 229	0.060
10	0.384 910	−1.025 173	−3.921 766	0.055	4.392 136	-2.244015	−1.455 618	0.060
11	−3.579 030	−1.395 200	0.892 134	0.060	−1.374 395	1.890722	−3.079 756	0.078
12	−1.015 105	−1.520 483	3.632 993	0.060	0.942 716	2.155338	−3.683 190	0.054
13	−0.255 127	0.009 460	−1.550 517	−0.208	2.077 769	3.036259	−1.720 897	0.101
14	2.583 912	2.835 333	−2.961 996	−0.043	−2.518 882	3.669080	−1.990 439	−0.060
15	2.278 509	−0.082 218	−0.605 548	−0.179	1.179 181	-4.489527	−0.043 178	−0.039
16	−3.916 416	0.489 993	−1.284 903	0.051	2.073 051	-3.005210	1.595 231	0.057
17	−2.130 080	0.773 835	0.468 892	−0.321	−0.927 596	-3.375560	−0.220 496	0.077
18	−1.873 260	−2.652 863	1.768 908	0.087	2.077 528	-3.035257	−1.722 812	0.102
19	0.872 750	2.033 881	0.292 642	−0.217	1.217 968	-2.211444	3.727 735	0.070
20	−1.571 176	2.425 800	−1.886 238	0.072	2.070 136	-0.001181	3.305 161	0.051
21	3.610 445	−3.420 411	0.732 269	−0.019	−1.138 458	-1.795368	3.237 268	0.046
22	1.473 819	1.761 218	2.612 793	0.073	−2.222 912	-3.467775	1.903 407	0.064
23	2.756 841	3.386 962	1.275 332	0.021	−2.310 737	-0.001336	4.361 504	−0.060
24	−1.101 918	−4.017 028	−1.588 749	0.062	−1.138 347	1.793328	3.238 431	0.046
25	3.634 428	−1.045 548	1.120 954	0.059	1.218 113	2.208914	3.729 150	0.070
26	0.699 301	−2.679 122	−2.293 242	0.088	−4.198 560	-2.081795	1.359 934	0.035
27	−0.628 857	−4.401 813	0.828 596	0.054	−3.449 563	-0.000626	2.276 149	0.074
28	4.754 942	0.345 544	−0.485 406	0.031	−4.198 287	2.081120	1.361 211	0.035
29	−4.751 303	−1.739 578	−1.092 711	−0.017	−3.615 113	-1.847508	−0.940 175	0.096
30	2.734 555	−2.487 418	−1.220 001	0.076	0.942 486	-2.152937	−3.684 465	0.054
31	−0.720 438	3.436 387	1.588 991	0.052	−1.374 589	-1.888613	−3.080 980	0.078
32	2.621 703	−0.252 111	3.115 688	0.044	−2.519 070	-3.667637	−1.992 753	−0.060
33	−0.432 586	2.600 047	3.794 158	−0.032	1.699 282	0.000994	−3.173 137	0.062
34	−1.474 990	0.676 977	2.868 455	0.011	−2.578 395	0.001400	−4.052 465	0.036
35	−3.812 709	0.407 459	2.372 155	0.056	−4.327 114	0.000844	−2.276 870	0.058
36	−2.552 411	−2.170 048	−1.796 022	0.069	−3.614 979	1.848296	−0.939 058	0.096
37	1.348 842	−3.162 209	1.366 318	0.052	2.509 609	1.181005	−0.151 829	−0.285
38	−0.371 455	−1.981 217	−0.113 576	−0.381	−1.982 030	0.000613	−1.570 505	−0.284
39	1.267 542	−2.207 026	3.576 066	0.054	−1.882 106	-1.309399	0.807 246	−0.261
40	3.842 879	−0.813 823	−2.390 677	0.066	0.526 151	-1.156607	1.591 371	−0.004
41					2.509 578	-1.181023	−0.152 526	−0.285
42					0.255 160	-1.295543	−1.330 826	−0.195
43					−1.881 744	1.309011	0.808 020	−0.261
44					0.255 358	1.296388	−1.330 140	−0.195
45					0.526 305	1.155308	1.592 252	−0.004

Table S5. Cartesian coordinates and Mulliken partial charges δq for the Si_{50} and Si_{55} clusters optimized and computed at the PBE0/cc-pVTZ level of theory.

	Si_{50}				**Si_{55}**			
Si	x	y	z	δq	x	y	z	δq
1	3.839 489	−3.144 161	1.727 683	−0.048	−3.056 836	3.940318	−1.723 646	0.056
2	0.738 124	−1.317 824	1.289 172	−0.087	−4.397 158	-1.051557	−0.354 154	−0.014
3	2.281 098	−1.309 736	−1.005 712	−0.168	−2.276 429	2.524065	−3.593 556	0.044
4	4.276 463	0.675 735	2.965 635	0.055	−1.810 602	1.798155	−1.311 199	−0.134
5	−2.371 929	3.680 388	2.906 017	−0.012	1.643 436	3.597969	1.139 223	0.052
6	1.022 371	−1.156 156	4.503 349	0.026	0.897 169	4.268152	−2.617 824	−0.039
7	−3.456 120	1.969 291	1.655 383	0.065	2.822 196	-0.021107	−3.120 226	0.044
8	1.881 579	−3.398 101	0.371 769	0.051	1.146 314	0.623059	−4.738 815	0.007
9	−0.146 053	−4.688 084	0.345 814	0.038	0.223 278	0.230257	−1.573 486	−0.193
10	−0.810 508	−2.271 125	−0.451 852	−0.138	−2.993 734	0.404150	1.044 196	−0.049
11	−2.878 918	3.557 833	−2.088 435	0.043	−0.809 825	4.263484	−0.943 781	0.044
12	1.634 823	1.995 308	−0.016 391	−0.212	0.096 522	2.110570	−3.157 388	0.027
13	−4.509 472	0.128 042	2.737 979	0.052	4.637 618	2.726968	−0.920 161	0.067
14	5.439 289	0.664 038	0.759 596	0.026	0.575 340	-0.805652	0.572 213	0.077
15	−0.271 059	0.911 318	1.051 313	−0.120	−1.080 609	-0.371933	2.170 843	−0.221
16	4.373 228	−1.868 156	−2.240 065	0.048	2.850 918	-2.289850	−2.401 796	0.053
17	−1.960 816	−0.142 234	−3.500 263	0.051	−2.077 064	-0.747471	−1.392 276	−0.131
18	−3.935 493	−1.428 066	−2.985 615	0.033	2.369 046	3.312535	−1.053 542	0.050
19	2.432 900	2.094 623	2.606 664	0.103	−0.633 151	-2.702550	−0.612 244	−0.357
20	−1.134 442	2.010 787	−1.068 754	−0.281	2.346 415	0.412617	1.600 384	−0.110
21	−0.867 018	−1.851 983	3.082 279	0.048	−5.503 210	0.730725	−1.555 024	−0.033
22	0.819 791	3.470 168	−1.952 051	0.068	−2.527 837	-3.786618	0.599 590	0.054
23	−1.768 072	−3.325 168	1.501 723	0.068	2.973 930	0.893993	−0.867 207	−0.238
24	3.328 136	0.284 846	−2.566 640	0.050	−0.295 426	2.356977	0.521 843	−0.208
25	2.750 823	−1.341 671	2.842 108	0.049	−3.518 203	0.576378	−2.891 506	0.072
26	−2.273 414	−0.280 388	1.753 674	−0.306	4.494 652	1.565695	1.193 047	0.045
27	2.892 715	3.966 598	−0.777 257	0.071	4.666 985	-3.102137	−1.082 476	0.050
28	−1.008 326	4.502 843	−0.835 050	0.069	2.817 263	-1.632322	−0.111 121	−0.204
29	0.221 878	−0.253 006	−1.818 054	−0.170	−1.440 698	-1.902734	4.068 869	0.070
30	4.570 463	−1.508 724	0.121 791	0.091	−0.366 159	4.853718	1.323 136	0.041
31	2.606 811	−3.551 777	−1.995 589	0.052	−3.834 575	0.663518	3.263 008	0.050
32	3.927 795	1.739 282	−0.832 134	0.077	6.003 015	-0.230620	1.552 910	−0.056
33	1.772 793	4.003 889	1.425 572	0.038	1.619 867	1.195815	3.737 546	0.004
34	1.334 590	0.909 798	−3.592 008	0.009	−1.622 679	3.073811	2.309 051	0.051
35	2.962 048	0.184 525	0.956 028	−0.218	0.675 631	-2.923269	−2.676 837	0.088
36	−1.026 954	−4.233 140	−1.909 551	0.055	0.668 809	-2.181117	3.054 420	0.059
37	−4.881 502	−0.130 710	−1.132 785	0.085	−2.244 155	0.208117	5.122 431	0.005
38	−4.008 569	−3.651 328	0.665 320	−0.039	−2.846 898	-2.346854	2.330 906	0.070
39	0.650 315	0.935 981	3.456 388	0.061	−4.030 937	2.183695	−0.313 077	0.042
40	−1.526 243	2.142 348	−3.467 061	0.058	−0.207 289	-1.011674	−3.641 539	0.055
41	−3.601 987	1.807 387	−0.658 499	0.086	4.956 111	0.788747	−2.368 105	0.040
42	0.557 181	3.011 573	−4.276 722	−0.025	−2.608 132	-3.136594	−2.281 793	0.083
43	−2.660 183	−0.427 587	4.241 729	0.029	1.165 211	-3.466383	1.151 113	0.077
44	0.094 931	−1.019 097	−4.298 639	0.064	−0.721 311	1.385841	3.699 388	0.046
45	−1.556 225	1.592 355	3.617 093	0.149	−0.747 884	-4.736510	−2.222 696	0.057
46	−2.428 125	−0.466 750	−1.097 401	−0.274	3.556 840	-3.588719	1.169 328	0.049
47	0.559 334	−2.658 223	−2.712 643	0.067	−4.407 815	-3.439169	−0.836 574	−0.026
48	−2.985 293	−3.008 895	−1.420 203	0.062	−2.526 362	-1.383081	−3.835 527	0.071
49	−4.285 942	−1.300 151	0.859 105	0.046	3.964 577	-1.380349	2.105 261	0.040
50	−0.616 307	3.493 283	1.256 190	0.052	5.117 151	-0.764960	−0.575 578	0.090
51					2.468 435	-0.988139	3.899 435	0.049
52					−3.928 614	2.692714	2.049 352	0.023
53					−4.824 944	-1.102107	2.072 958	0.043
54					−0.534 752	-5.043596	0.248 122	0.037
55					3.116 558	2.755025	2.774 580	0.034

Table S6. Cartesian coordinates and Mulliken partial charges δq for the Si_{60} and Si_{70} clusters optimized and computed at the PBE0/cc-pVTZ level of theory.

	Si_{60}				**Si_{70}**			
Si	x	y	z	δq	x	y	z	δq
1	−0.885 438	−1.737 749	−1.448 508	−0.268	−0.001 084	6.052921	−1.112 895	−0.021
2	0.752 243	1.932 539	−1.764 414	−0.213	−0.712 083	4.801173	0.771 012	0.003
3	1.931 594	−0.300 929	−2.194 488	−0.319	0.826 025	4.066648	2.478 454	0.097
4	−1.221 596	0.496 194	−2.065 631	0.103	−0.268 672	2.543405	3.783 064	0.075
5	−0.114 224	−1.596 632	0.732 745	0.153	0.486 745	1.056797	5.522 967	−0.015
6	−2.140 039	0.105 258	2.347 314	−0.333	−0.630 681	-0.689212	4.328 650	−0.058
7	2.149 719	−2.153 886	0.989 249	−0.303	0.303 680	-2.673786	3.537 961	0.140
8	2.622 524	1.249 826	0.380 169	−0.177	−0.892 868	-4.056607	1.999 887	0.020
9	−0.618 212	2.346 932	1.513 466	−0.103	0.663 303	-5.648209	1.083 926	−0.020
10	0.703 920	0.461 825	1.440 975	0.114	−0.025 552	-5.046366	−1.088 273	0.065
11	−3.067 194	−1.359 400	−0.407 540	−0.106	1.382 547	-4.415726	−2.892 805	0.112
12	−2.435 615	0.981 306	0.022 246	−0.165	0.072 753	-2.654677	−3.639 941	0.061
13	4.216 332	−3.124 700	0.400 608	0.088	0.846 841	-0.757719	−4.918 968	0.076
14	2.646 714	−4.480 496	1.577 158	0.078	−0.662 289	1.059942	−4.391 208	0.050
15	5.559 109	−1.726 458	1.805 994	−0.030	−0.064 777	3.338695	−4.093 010	0.002
16	4.983 890	0.341 427	0.783 812	0.023	−1.179 273	4.205042	−2.131 778	−0.030
17	4.294 951	0.965 120	−1.378 053	0.046	1.905 432	4.631794	−1.162 817	0.113
18	4.192 706	3.029 309	−2.568 973	−0.027	1.904 045	3.073820	−2.926 938	0.014
19	2.419 946	3.549 331	−1.032 809	0.008	3.774 924	1.814830	−3.563 056	0.110
20	0.866 457	5.391 825	−1.391 738	−0.024	2.927 379	-0.373009	−3.867 425	0.026
21	3.585 316	−1.265 800	3.073 194	0.034	4.457 142	-2.043717	−3.402 373	−0.033
22	−1.246 827	−3.182 530	2.105 345	0.007	3.243 482	-3.346301	−1.853 537	−0.009
23	−0.214 558	−3.001 906	4.246 120	−0.038	4.411 853	-4.331218	−0.057 544	−0.025
24	1.997 724	−2.924 832	3.284 149	0.052	2.441 865	-4.071564	1.231 436	−0.035
25	−0.671 465	−0.685 096	4.111 188	0.069	2.519 888	-3.354798	3.540 584	0.063
26	2.410 409	1.894 132	−3.663 262	0.080	3.453 435	-1.204908	3.245 079	0.011
27	−0.647 496	3.888 514	−2.397 971	−0.015	2.390 269	0.697034	4.175 945	0.084
28	0.297 024	2.754 339	−4.235 959	0.079	3.445 696	2.290773	2.994 946	0.132
29	−2.967 957	3.971 431	−1.925 769	−0.028	3.117 776	4.573170	2.604 337	−0.007
30	−3.458 176	1.693 104	−2.218 070	0.040	3.456 785	3.907964	0.350 434	0.017
31	−3.095 578	0.287 248	−4.094 301	0.058	5.587 899	2.913508	0.028 989	−0.027
32	−0.763 813	0.647 803	−4.396 473	0.027	5.000 983	1.319632	−1.560 959	0.044
33	−3.276 690	−1.772 624	−2.981 695	0.067	5.517 765	-0.918011	−1.630 064	0.057
34	2.799 017	−0.272 318	−4.579 840	0.065	5.139 878	-2.107166	0.332 947	0.030
35	4.228 836	−0.968 310	−2.805 268	0.080	5.620 401	-0.890984	2.316 068	0.016
36	3.116 943	−2.636 352	−1.597 284	0.055	4.794 467	1.163649	1.437 621	0.010
37	0.671 461	−1.159 753	−4.076 563	0.113	−2.833 308	4.801699	1.739 855	0.009
38	−2.469 904	−3.985 941	−3.441 937	−0.013	−2.449 791	2.782874	2.928 162	0.070
39	−0.165 773	−3.155 103	−3.150 007	−0.002	−3.799 695	0.948936	3.353 656	0.039
40	1.707 937	−4.361 591	−2.278 864	−0.009	−2.967 686	-0.836221	4.551 392	0.015
41	−2.418 511	−3.911 346	−1.023 562	0.062	−3.504 498	-2.260714	2.770 982	0.039
42	−1.170 882	−5.025 108	0.609 520	−0.003	−3.146 286	-4.582869	2.504 615	−0.016
43	0.951 285	−4.379 024	−0.064 851	−0.003	−3.640 262	-3.992068	0.293 766	0.060
44	−4.446 991	−3.262 728	0.095 010	0.078	−2.260 635	-4.612695	−1.520 423	0.116
45	−0.384 246	4.772 359	0.512 576	0.060	−2.189 023	-2.733809	−2.990 604	0.005
46	−2.474 669	3.607 117	0.383 428	−0.007	−3.981 133	-1.703633	−4.180 978	−0.025
47	−4.031 422	3.557 842	2.232 626	−0.027	−2.853 568	0.401256	−4.046 199	0.070
48	−4.384 762	1.302 259	1.538 949	0.098	−3.936 518	1.994340	−2.701 425	0.034
49	−4.858 766	0.582 346	−0.671 266	0.095	−3.541 981	4.244439	−2.291 067	−0.005
50	−5.192 350	−1.663 173	−1.545 654	0.047	−3.948 352	3.772577	−0.044 361	0.071
51	4.030 109	1.747 803	2.305 128	0.056	−4.975 331	1.735849	0.285 715	0.028
52	3.078 793	3.609 039	1.269 444	0.059	−5.849 489	0.756178	2.231 493	−0.001
53	−0.028 087	3.016 034	4.054 543	0.055	−5.128 641	-1.327958	1.432 513	0.060
54	0.941 192	4.039 288	2.208 277	0.016	−5.526 070	-2.777137	−0.341 389	−0.010
55	−2.247 007	2.415 354	3.378 507	0.047	−4.678 714	-1.211470	−1.908 105	−0.041
56	1.043 839	0.886 973	3.760 844	−0.035	−5.713 422	0.901109	−1.764 939	0.000
57	3.355 740	0.703 852	4.358 024	−0.037	1.068 861	-2.516861	−1.211 988	−0.162
58	−3.367 051	−2.153 952	1.932 582	0.084	3.556 628	-0.315759	0.075 803	−0.238
59	−4.369 297	−0.451 224	3.199 184	0.044	−2.257 148	-0.825313	1.214 191	−0.235
60	−2.721 136	0.471 235	4.748 375	0.048	−2.426 095	-1.188732	−1.180 064	0.009
61					−1.034 744	-2.925524	−0.079 830	−0.185
62					1.920 139	-1.775655	1.485 479	−0.052
63					2.428 138	0.876978	−1.689 357	−0.042
64					−2.547 492	1.545083	0.877 966	−0.253
65					−0.911 822	2.407577	−0.599 332	−0.050
66					1.418 660	2.374521	−0.183 927	−0.195
67					1.183 344	1.493762	2.026 628	−0.340
68					−0.059 589	-0.548188	1.998 984	0.167
69					−1.343 747	0.651016	−2.043 528	−0.127
70					0.673 292	-0.480410	−2.464 395	0.036

Table S7. Cartesian coordinates and Mulliken partial charges δq for the Si_{80} cluster optimized and computed at the PBE0/cc-pVTZ level of theory.

Si_{80}									
Si	x	y	z	δq	Si	x	y	z	δq
1	5.874 190	−0.849 970	−2.417 883	0.040	41	−1.326 637	5.103 481	−0.793 771	0.083
2	4.448 778	−1.095 447	−4.424 884	0.029	42	0.314 006	6.398 709	0.339 628	−0.009
3	3.100 042	0.832 353	−4.030 454	0.146	43	1.886 547	5.065 608	−0.719 822	0.066
4	0.739 126	0.646 498	−4.132 392	−0.042	44	−2.387 441	−4.037 922	3.938 105	−0.003
5	−0.912 143	2.077 180	−5.048 036	−0.010	45	−0.013 463	−4.074 333	3.623 326	0.061
6	−2.579 426	0.878 881	−3.832 647	−0.040	46	1.359 694	−4.865 769	1.944 420	0.086
7	−4.626 954	1.874 122	−3.267 929	0.082	47	3.683 420	−4.889 401	1.671 650	−0.012
8	−5.594 007	0.082 357	−2.002 264	0.016	48	3.385 830	−3.993 986	−0.580 505	0.022
9	−6.325 822	0.413 434	0.242 468	0.092	49	2.952 752	−4.893 659	−2.810 359	−0.017
10	−5.213 748	−1.212 118	1.573 043	0.047	50	2.676 833	−2.604 502	−3.572 913	−0.006
11	−4.628 333	−0.702 660	3.771 966	−0.030	51	0.516 414	−1.723 499	−4.048 540	0.028
12	−2.415 335	−1.653 990	3.942 599	−0.111	52	−1.298 040	−2.926 366	−5.106 202	−0.027
13	−0.778 607	−0.802 790	5.455 596	−0.003	53	−2.822 258	−1.477 971	−3.918 685	0.103
14	0.906 923	−2.111 719	4.547 983	0.053	54	−4.612 866	−1.950 740	−2.556 713	0.068
15	3.233 431	−1.607 341	4.539 750	0.093	55	−5.256 784	−4.015 507	−1.630 072	−0.024
16	3.971 925	−2.659 544	2.522 986	−0.007	56	−4.807 810	−3.289 900	0.639 702	0.089
17	5.983 369	−1.902 271	1.449 658	0.079	57	−2.964 380	−4.250 427	1.706 436	−0.013
18	5.061 200	−2.323 140	−0.714 393	0.088	58	−2.237 409	−5.846 341	0.230 275	−0.002
19	5.334 895	1.144 088	−1.126 835	0.068	59	0.022 127	−5.398 405	0.071 569	0.041
20	5.774 238	0.447 874	1.115 743	0.051	60	0.711 370	−4.866 064	−2.029 166	0.054
21	4.527 253	1.736 121	2.582 462	0.055	61	−1.322 723	−4.255 492	−3.128 094	0.054
22	2.902 854	0.706 772	3.938 160	0.032	62	−2.990 027	−4.696 120	−1.644 815	0.031
23	1.611 092	2.363 155	5.012 317	−0.018	63	0.584 132	0.826 434	−1.748 491	0.111
24	−0.398 900	1.257 982	4.342 519	−0.118	64	−2.454 587	1.697 929	−1.610 355	−0.116
25	−2.419 776	2.615 471	4.122 815	0.085	65	−2.026 931	−2.264 407	−1.771 683	−0.218
26	−4.293 493	1.558 328	3.229 428	0.037	66	−2.977 870	−1.754 933	0.281 556	−0.048
27	−4.959 143	2.231 379	1.054 814	0.040	67	−3.897 749	0.341 656	−0.315 313	−0.125
28	−5.180 504	4.327 392	−0.021 744	−0.027	68	0.148 115	−1.464 432	−1.732 125	−0.068
29	−3.848 155	3.633 718	−1.921 716	−0.008	69	1.247 194	−3.011 806	−0.395 138	−0.096
30	−2.461 735	5.389 397	−2.869 525	−0.033	70	0.481 766	−2.472 802	1.804 849	−0.045
31	−0.769 519	3.822 780	−3.479 972	0.052	71	2.127 085	−0.907 896	2.367 189	−0.202
32	1.494 927	4.115 594	−2.743 765	0.135	72	−0.550 634	0.923 571	2.007 024	0.089
33	3.499 999	2.827 780	−2.951 021	−0.001	73	−1.435 637	−1.221 038	1.881 845	−0.044
34	5.544 102	3.477 383	−1.793 164	−0.027	74	3.826 673	−0.812 083	0.706 324	−0.029
35	3.981 875	4.191 480	−0.059 295	−0.002	75	2.985 282	2.325 141	0.940 671	−0.079
36	4.197 886	4.110 904	2.349 541	0.055	76	0.677 087	2.616 743	1.054 507	−0.092
37	2.007 207	3.733 195	3.117 982	0.042	77	−0.134 126	2.993 142	−1.125 833	−0.255
38	0.224 311	4.769 912	2.062 402	0.006	78	−2.455 972	2.237 322	1.686 599	−0.184
39	−1.973 660	4.518 019	2.887 724	0.071	79	2.874 343	1.157 513	−1.344 731	−0.106
40	−2.976 677	4.396 734	0.764 774	0.042	80	3.448 986	−0.980 741	−2.101 164	−0.224

5. Lowest Vibrational Modes

It is crucial for the interpretation of the experimental data to get a feeling for the thermal excitation of the clusters for both measurements. A good indicator for this is the cluster velocity [26] which is different for both measurements shown in the paper. Another indicator are the vibrational nodes given by quantum chemical calculations. To give the readers a better understanding of the thermal excitation, the lowest vibrational modes are shown for the calculated clusters except for Si_{70} and Si_{80}, since frequency analyses of such large clusters are very expensive in regards to the computational resources and time consuming. Please note, that without a frequency analysis it cannot be clearly determined, if the shown geometric structures is only a local minimum on the potential curve, i.e. the cluster has imaginary vibrational modes. However, although the geometric structure can be slightly different in the local minimum, the general (near-)spherical shape of the cluster still remains. Therefore, the qualitative statement and discussion in the paper is still valid.

Table S8. Lowest vibrational modes for the discussed Si_N clusters with $N = 30 - 60$ computed at the PBE0/cc-pVTZ level of theory.

Si	$\widetilde{\nu}_{\mathrm{min}}$ / cm^{-1}
30	38.79
35	75.11
40	44.31
45	90.73
50	60.45
55	70.66
60	47.93
70	–
80	–

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