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

Supplementary Information

Probing the structure of giant fullerenes by high resolution trapped ion mobility spectrometry

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Abstract

We present high-resolution trapped ion mobility spectrometry (TIMS) measurements for fullerene ions in molecular nitrogen. Three different charge states were studied (monocations, monoanions and dianions) with fullerenes ranging in size from C_{60} to C_{150}. Ions were prepared by either electrospray ionization (ESI, for mono- and dianions) or by atmospheric pressure chemical ionization (APCI, for monocations) of a preformed fullerene soot extract solution. We demonstrate that TIMS allows to identify (and separate) constituent isomers in favorable cases. Using DFT calculations based on known condensed phase structures and trajectory method (TM) calculations we can reproduce the experimental $^{TIMS}CCS_{N2}$ for fullerenes up to C_{108} to within 0.5%. Using candidate structures based on quantum chemical predictions, we have also obtained structural information for fullerenes C_{110}-C_{150} - a size range not previously accessed in condensed phase studies. We find that soluble fullerenes in this size have near-spherical rather than tubular structures. While the TM programs presently available for CCS modelling do a remarkably good job at describing the ion mobility of high (and even giant) fullerenes we observe a slight but systematic size-dependent deviation between $^{TIMS}CCS_{N2}$ values and our best computational fits which may reflect systematic bonding changes as the cage size increases.

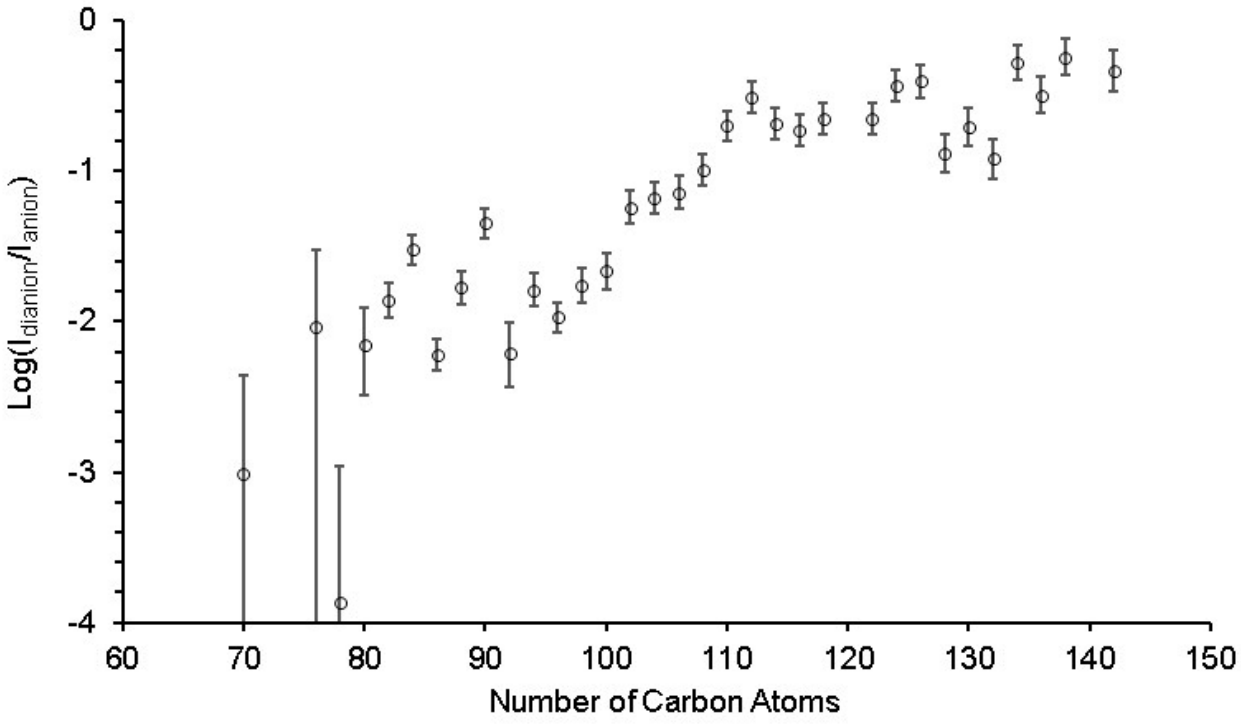

Figure SI 1: Ratio of fullerene dianion and monoanion signal intensities as function of the carbon atom count. Note the logarithmic scale: the relative dianion intensity increases dramatically with size by more than two orders of magnitude from C_{70} to C_{140}.

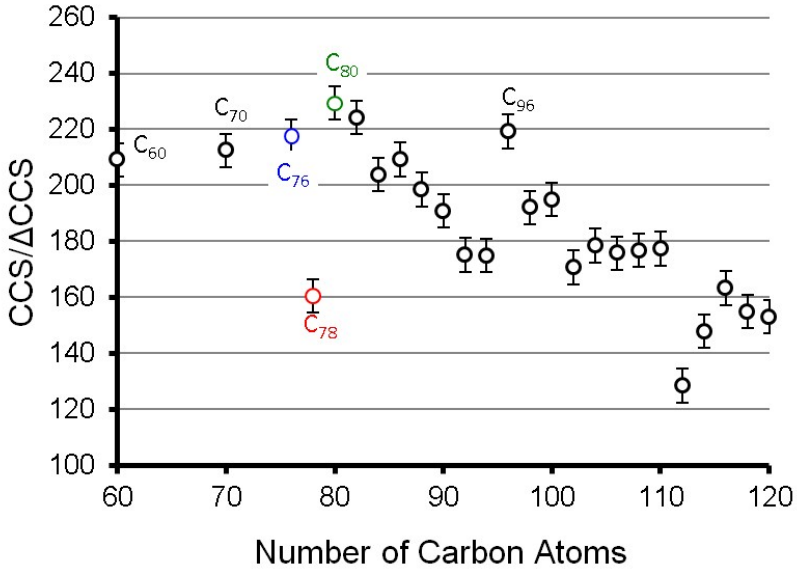

Figure S2: TIMS peak widths (measured as CCS/ΔCCS based on a Gaussian fit) for fullerene monoanions as obtained in a typical run. Scan parameters: ramp duration 500 ms, width 0.05 ($1/K_0$).

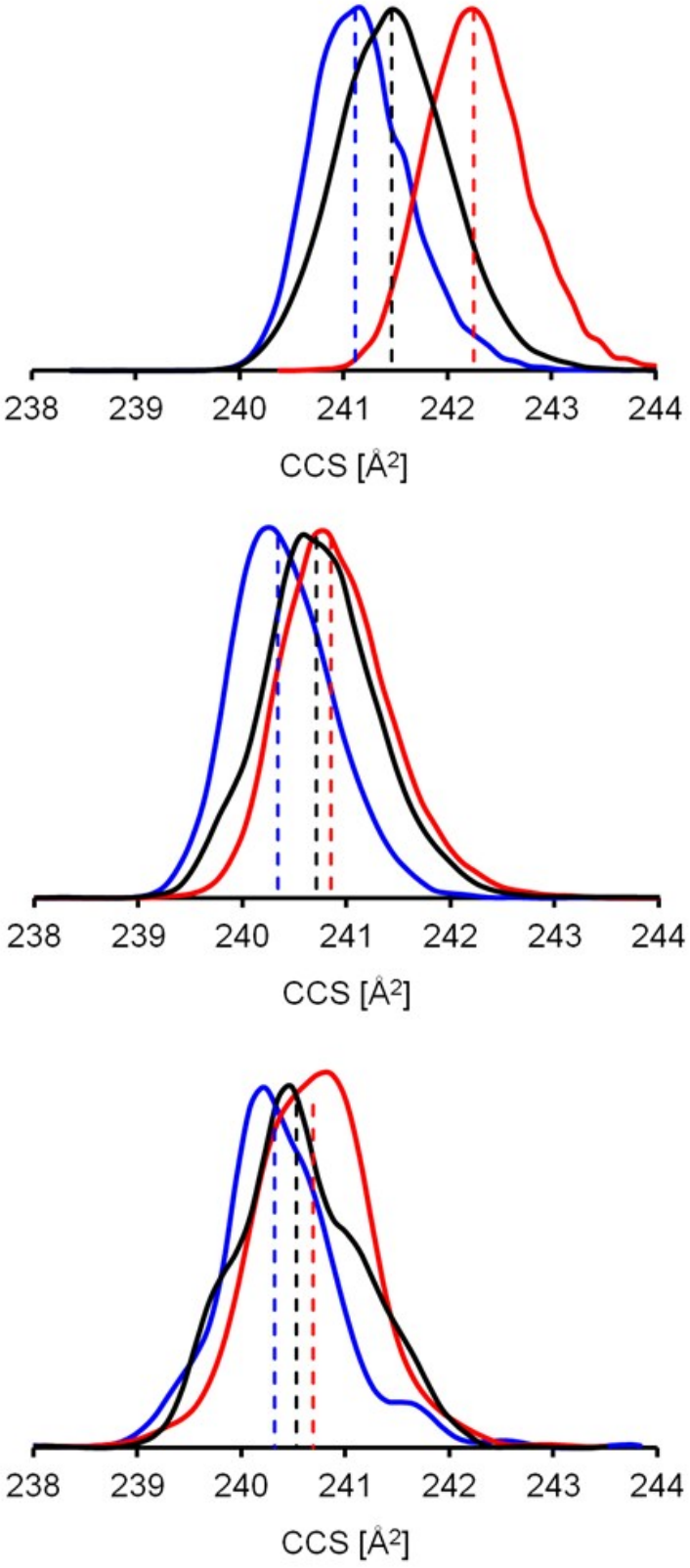

Figure S3: Typical mobilograms of HPLC selected C_{78}-isomers (D_3 red and C_{2v} blue) and the isomer mixture present in our soot extract (black), recorded on three different days.

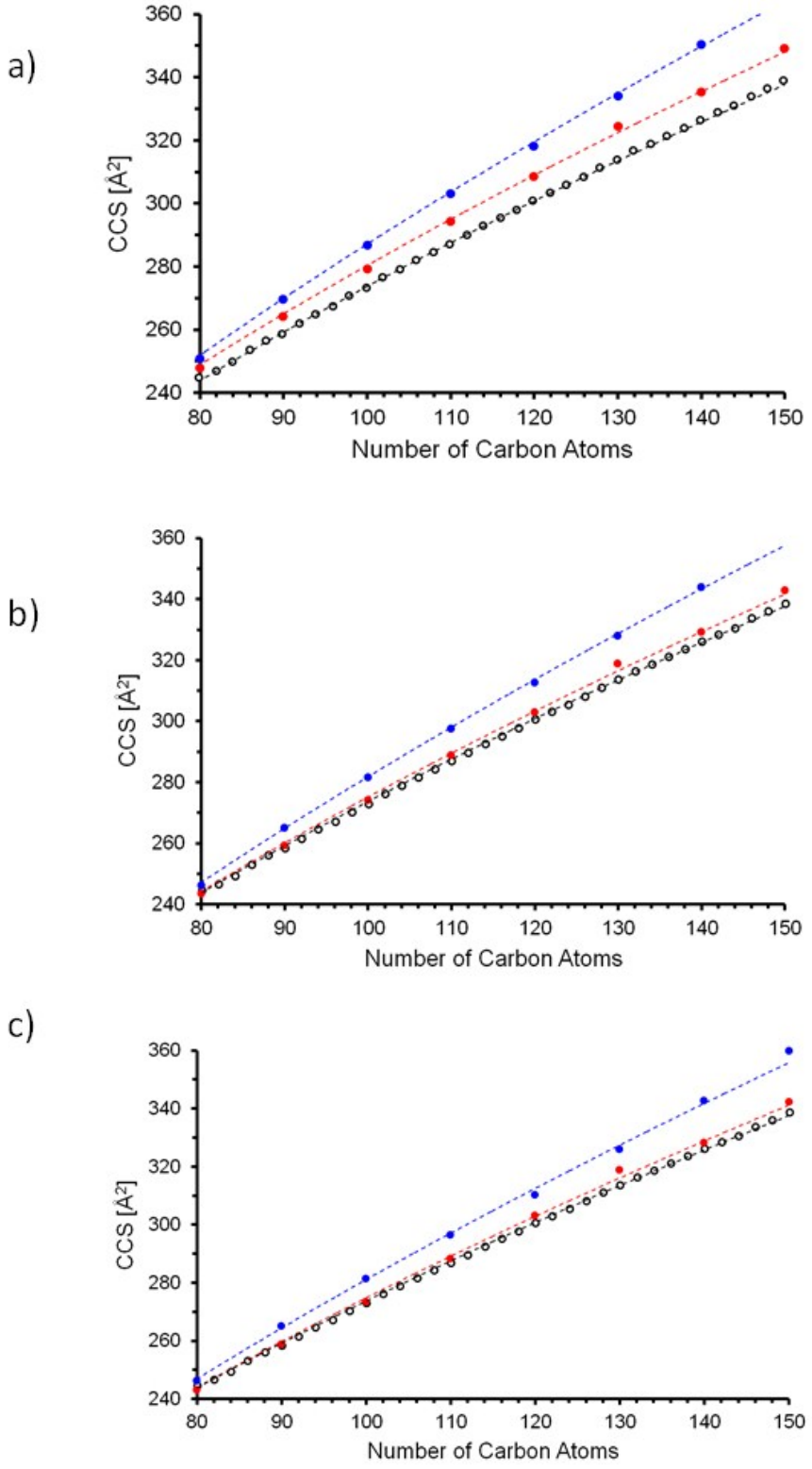

Figure S4: Comparison of calculated and measured CCS values for fullerene (mono)anions. Open circles correspond to the experimental $^{TIMS}CCS_{N2}$ data. CCS values calculated for tubular model structures are shown as solid blue circles. Spherical model structures are represented as red circles. The dotted lines are fits to the respective data sets and serve as a guide to the eye only. a) using method 1(cf. table 2), b) method 5 (=method 1 with a scaling factor of 0.9815), c) method 4

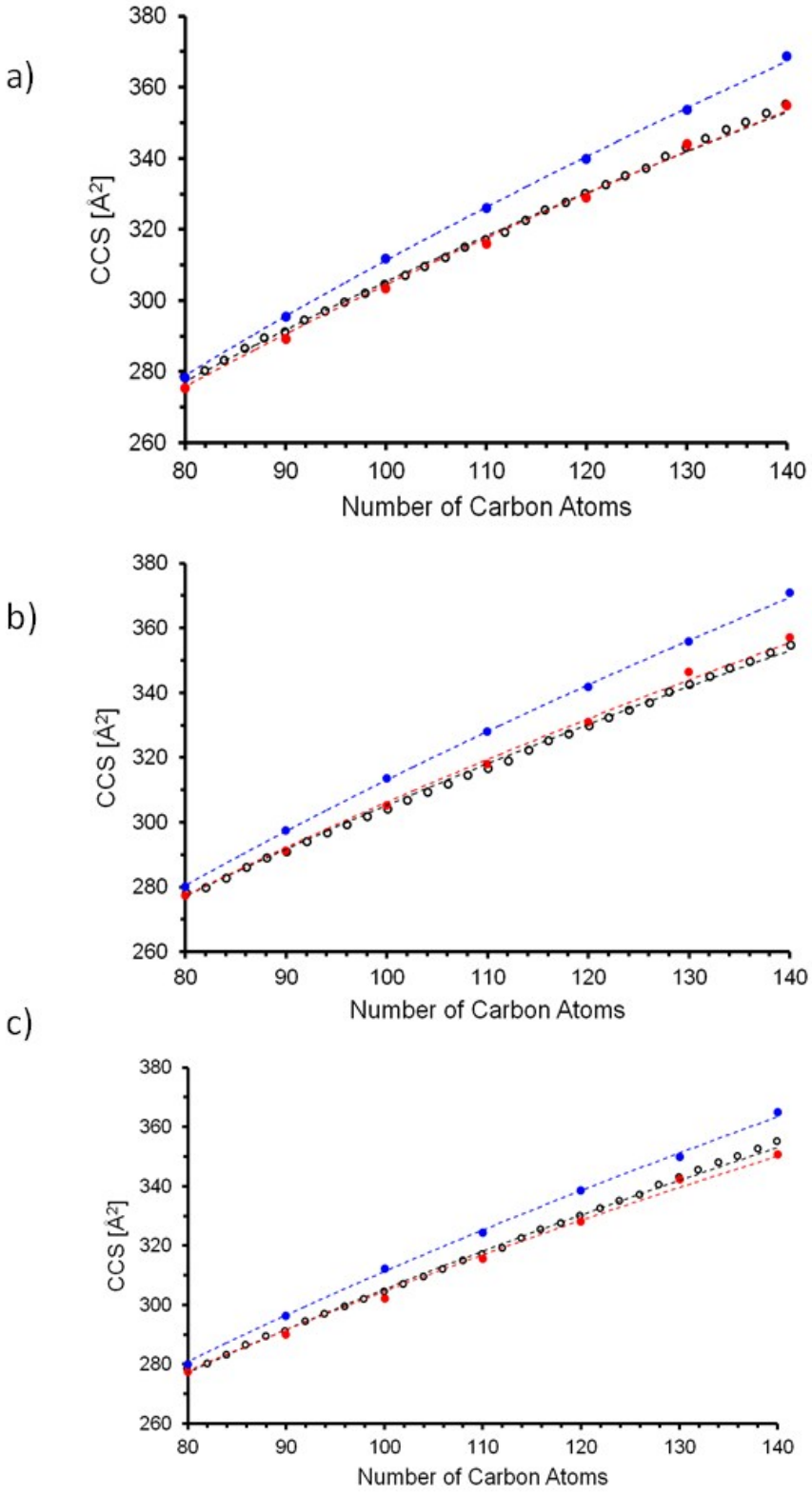

Figure S5: Comparison of calculated and measured CCS values for fullerene dianions. Open circles correspond to the experimental $^{TIMS}CCS_{N2}$ data. CCS values calculated for tubular model structures are shown as solid blue circles. Spherical model structures are represented as red circles. The dotted lines are fits to the respective data sets and serve as a guide to the eye only. a) using method 1(cf. table 2), b) method 5 (=method 1 with a scaling factor of 1.0057, c) method 4

"tubes"					"spheres"			
$C_{80}(1)$	1.000	1.000	0.747		$C_{80}(7)$	1.000	0.999	0.988
$C_{90}(1)$	1.000	1.000	0.651		$C_{90}(45)$	1.000	0.909	0.887
$C_{100}(1)$	1.000	1.000	0.566		$C_{100}(449)$	1.000	0.929	0.899
$C_{110}(1)$	1.000	1.000	0.499		$C_{110}(2331)$	1.000	0.978	0.948
$C_{120}(1)$	1.000	1.000	0.442		$C_{120}(10774)$	1.000	0.967	0.967
$C_{130}(1)$	1.000	1.000	0.391		$C_{130}(39175)$	1.000	0.977	0.964
$C_{140}(1)$	1.000	1.000	0.350		$C_{140}(121354)$	1.000	1.000	0.999
$C_{150}(1)$	1.000	1.000	0.314		$C_{150}(335569)$	1.000	0.997	0.934

Table S1: Geometry parameters (main axes of inertia tensor, normalized to its largest component, based on the optimized anion geometry) of the most spherical and most tube-like fullerenes as discussed in the main text.

	Method 1		Method 2		Method 3		Method 4		Method 5		Method 6		Method 7		Method 8		
	IMoS, Mullik. w/o ion quad. α_{N2}=1.74 Å^3 ρ=3.5 Å, ε=4.65 meV		IMoS, Mullik. w/o ion quad. α_{N2}=0 Å^3 ρ=3.5 Å, ε=4.65 meV		IMoS, Mullik. with ion quad. α_{N2}=1.74 Å^3 ρ=3.22 Å, ε=3.57 meV		IMoS, Mullik. with ion quad. α_{N2}=2.00 Å^3 ρ=3.145 Å, ε=3.57 meV		method 1 with charge-dependent scaling factors: anions: 0.9815, cations: 0.9743, dianions: 1.0057		same as method 1, except NBO charges instead of Mulliken		Collidoscope with default parameters, i.e. ρ=3.797 Å ε=3.17 meV		Mobcal with default parameters, i.e. ρ=3.581 Å ε=4.23 meV		exp
	CCS [Å^2]	X [%]	CCS [Å^2]	χ [%]	CCS [Å^2]	χ [%]	CCS [Å^2]	X [%]	CCS [Å^2]	χ [%]	CCS [Å^2]	χ [%]	CCS [Å^2]	χ [%]	CCS [Å^2]	χ [%]	$^{TIMS}CCS_{N2}$ [Å^2]
C_{60}^-	214.8	1.4	203.9	-3.7	216.1	2.0	210.9	-0.4	210.8	-0.5	214.8	1.4	208.5	-1.6	210.6	-0.6	211.8
C_{70}^-	232.0	1.9	222.3	-2.4	233.0	2.3	227.0	-0.3	227.7	0.0	232.0	1.9	228.9	0.5	227.4	-0.1	227.7
C_{76}^-	242.3	1.8	233.5	-1.9	244.0	2.5	237.9	-0.1	237.8	-0.1	242.5	1.9	239.6	0.7	238.0	0.0	238.1
C_{84}^-	254.1	1.9	245.7	-1.5	255.4	2.4	249.1	-0.1	249.4	0.0	254.2	1.9	253.5	1.7	249.0	-0.2	249.4
C_{96}^-	273.9	2.5	266.5	-0.2	274.7	2.8	267.5	0.1	268.8	0.6	274.1	2.6	272.5	2.0	268.8	0.6	267.2
C_{70}^{2-}	261.8	-0.5	222.5	-15.4	265.3	0.9	265.0	0.7	263.3	0.1	261.9	-0.5	259.8	-1.2	256.0	-2.7	263.1
C_{76}^{2-}	270.7	-0.7	233.6	-14.3	274.8	0.8	273.9	0.5	272.3	-0.1	271.4	-0.4	268.1	-1.7	264.8	-2.9	272.6
C_{84}^{2-}	281.0	-0.6	245.8	-13.1	284.4	0.6	282.8	0.0	282.6	-0.1	281.2	-0.6	276.3	-2.3	273.9	-3.2	282.8
C_{96}^{2-}	297.9	-0.5	266.6	-10.9	300.3	0.4	297.4	-0.6	299.6	0.1	298.4	-0.3	297.2	-0.7	291.0	-2.7	299.3
C_{60}^+	214.6	2.2	203.8	-2.9	215.3	2.5	210.1	0.1	209.1	-0.4	214.6	2.2	208.5	-0.7	213.4	1.6	210.0
C_{70}^+	231.9	2.4	222.1	-2.0	233.1	2.9	227.0	0.2	226.0	-0.3	231.9	2.3	228.9	1.0	230.6	1.7	226.6
C_{76}^+	242.4	2.6	233.3	-1.2	243.5	3.1	237.4	0.5	236.2	0.0	242.1	2.5	239.8	1.5	241.5	2.2	236.2
C_{84}^+	254.2	2.6	245.6	-0.9	254.5	2.7	248.3	0.2	247.7	-0.1	254.0	2.5	253.8	2.4	251.7	1.6	247.9
C_{96}^+	274.4	3.2	266.3	0.1	275.1	3.4	267.9	0.7	267.4	0.5	273.8	2.9	273.5	2.8	272.4	2.4	266.0
$\Sigma\chi^2$	53.8		772.8		74.6		2.2		1.2		51.6		37.5		52.7		

Table S2: Comparison of experimental and calculated CCS (for C_{60}, C_{70}, C_{76}(1) (D_2), C_{84}(23) (D_2) and C_{96}(183) (D_2) derived monoanions. This table is an extension of table 2 in the main text: Besides the methods 1-5 discussed therein it contains CCS calculations based on charges determined with the "natural bond analysis" scheme (method 6), as well as calculations with the Collidoscope and Mobcal packages (method 7 and 8).

C60+	x	y	z	Mulliken-charges	NBO-charges	ESP-charges
C	-1.24215	-1.23E-05	3.36689	0.0142	0.0136	0.0169
C	-0.384313	-1.18036	3.36631	0.0153	0.0145	0.0130
C	1.00337	-0.729556	3.36658	0.0141	0.0142	0.0161
C	1.00338	0.729533	3.36658	0.0142	0.0143	0.0160
C	-0.384309	1.18034	3.3663	0.0152	0.0145	0.0130
C	2.34561	-2.59794	0.602493	0.0252	0.0234	0.0256
C	3.19344	-1.42789	0.602616	0.0156	0.0283	0.0280
C	2.96907	-0.701403	1.8541	0.0164	0.0134	0.0102
C	1.97177	-1.43274	2.62576	0.0203	0.0075	0.0107
C	1.58403	-2.60714	1.85335	0.0069	0.0161	0.0133
C	3.19344	1.42786	0.60261	0.0156	0.0283	0.0281
C	2.34568	2.59799	0.602502	0.0252	0.0234	0.0257
C	1.58405	2.60715	1.85337	0.0068	0.0161	0.0131
C	1.9718	1.43273	2.6258	0.0203	0.0075	0.0108
C	2.96908	0.70138	1.8541	0.0164	0.0133	0.0101
C	-0.371081	3.47872	0.603967	0.0186	0.0277	0.0301
C	-1.74668	3.03384	0.604093	0.0148	0.0227	0.0218
C	-1.99091	2.31326	1.85433	0.0134	0.0152	0.0122
C	-0.753966	2.31833	2.62567	0.0252	0.0090	0.0129
C	0.249735	3.04161	1.85439	0.0150	0.0107	0.0073
C	-3.42412	0.72297	0.605057	0.0192	0.0250	0.0266
C	-3.42411	-0.723002	0.605056	0.0191	0.0250	0.0265
C	-2.81693	-1.17847	1.85488	0.0152	0.0111	0.0090
C	-2.4394	-1.26E-05	2.62649	0.0159	0.0089	0.0105
C	-2.81695	1.17845	1.85489	0.0152	0.0111	0.0090
C	-1.74662	-3.03376	0.604084	0.0148	0.0227	0.0218
C	-0.371075	-3.4787	0.603961	0.0186	0.0277	0.0302
C	0.249733	-3.04158	1.85437	0.0150	0.0107	0.0072
C	-0.753958	-2.31831	2.62563	0.0251	0.0090	0.0129
C	-1.99088	-2.31326	1.85432	0.0135	0.0152	0.0122
C	-0.249724	-3.04158	-1.85437	0.0148	0.0107	0.0079
C	0.75397	-2.31836	-2.62567	0.0252	0.0090	0.0126
C	1.99089	-2.31328	-1.85433	0.0134	0.0152	0.0130
C	1.74662	-3.0338	-0.604101	0.0147	0.0227	0.0214
C	0.371094	-3.47884	-0.60399	0.0188	0.0277	0.0289
C	2.81694	-1.17848	-1.8549	0.0152	0.0111	0.0082
C	2.43943	-1.21E-05	-2.62653	0.0159	0.0089	0.0109
C	2.81696	1.17846	-1.85491	0.0152	0.0111	0.0083
C	3.42417	0.722983	-0.60507	0.0192	0.0250	0.0268
C	3.42415	-0.723009	-0.605067	0.0191	0.0250	0.0270
C	1.99091	2.31329	-1.85434	0.0133	0.0152	0.0129
C	0.753977	2.31838	-2.62571	0.0253	0.0090	0.0127
C	-0.249724	3.04161	-1.85439	0.0149	0.0107	0.0079
C	0.371102	3.47886	-0.603995	0.0188	0.0277	0.0290
C	1.74668	3.03387	-0.60411	0.0148	0.0227	0.0214
C	-1.58406	2.60714	-1.85334	0.0067	0.0161	0.0129

C	-1.97186	1.43277	-2.62585	0.0205	0.0075	0.0112
C	-2.96906	0.701382	-1.85407	0.0163	0.0133	0.0100
C	-3.19345	1.42786	-0.6026	0.0155	0.0283	0.0284
C	-2.34574	2.59803	-0.602501	0.0253	0.0234	0.0251
C	-2.96905	-0.701407	-1.85407	0.0163	0.0134	0.0099
C	-1.97183	-1.43277	-2.62581	0.0205	0.0075	0.0112
C	-1.58404	-2.60713	-1.85333	0.0067	0.0161	0.0129
C	-2.34568	-2.59799	-0.60249	0.0252	0.0234	0.0251
C	-3.19346	-1.4279	-0.602604	0.0156	0.0283	0.0285
C	-1.00336	-0.729554	-3.36648	0.0141	0.0142	0.0158
C	-1.00336	0.729531	-3.36649	0.0141	0.0142	0.0159
C	0.384312	1.18034	-3.36625	0.0152	0.0145	0.0128
C	1.24216	-1.22E-05	-3.3669	0.0143	0.0136	0.0174
C	0.384315	-1.18036	-3.36626	0.0152	0.0145	0.0129

Table S3: C_{60}^{+}, DFT-optimized coordinates and partial charges calculated with Mulliken, NBO, and ESP-fit. The partial charge distributions are very similar, the calculated CCS (parameters as used in method 1) are 214.8 $Å^2$ (Mulliken), 214.8 $Å^2$ (NBO), 214.9 $Å^2$ (ESP-Fit)