

Why Anion Performs Differently than Cation?

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Atomic and molecular anion and cation differ from each other by their charge. The widespread belief in the past was that any discrimination between anion and cation does not exist, that is, in the other words, they manifest themselves in equal manner. This, however, is not true. Precisely: there does exist an asymmetry between them which has been well documented in the literature [1,2] (see also [3]) and manifested in their respect to hydration (p. 12303 of [3]) and the hydrogen-bonded network of water: “anions are stronger than cations at water ordering because of the asymmetry of charge in a water molecule: the negative end of water’s dipole is nearer to the center of the water molecule than the positive end. Therefore, anions see a larger electrostatic potential at the surface of a water molecule than cations see.” The origin of this asymmetry has still been rather unclear and puzzling, and remains unanswered.

The idea of the present work is to show that charged species are differently polarizable. Therefore, the dipole polarizability is precisely that marker which discriminates anion from cation. For clusters, this issue has recently been addressed in [4] which demonstrate that for clusters $(\text{GaAs})_n^Z$ ($n = 2 - 15$, $Z = 0, \pm 1$), the dipole polarizability varies in the order anion > neutral > cation. In the present work this inequality is obtained from the basic principles of quantum structure of atoms.

Being placed in the external electric field, any molecule acquires a dipole moment which magnitude is determined by its polarizability α . Some values of α of atoms and accompanied ions, calculated at the Hartree-Fock level are presented in Table 1. Polarizability of molecule measures a degree of deformation of its electronic cloud or electric charge - a so called ‘softness’ - under the external electric field. Larger this deformation and hence, dipole moment, the larger is polarizability. It is obvious that the electron orbiting on the outer orbital, far from the nucleus, is easier to be distorted. On

the other hand, the electrons which are closer to the nucleus are harder to affect. These facts frame the following

Proposal: For an arbitrary atom A, there obeys the following inequality for different charge states:

$$\alpha(\mathbf{A})^{-1} > \alpha(\mathbf{A})^0 > \alpha(\mathbf{A})^{+1} .$$

Note: In fact, the Proposal is a direct corollary of the statement given in the review [6] and the textbook [7] on p. 387: "... we can expect the polarizability to increase with the radius of the molecule and the number of electrons it contains" resulted from Eq. (12.21): $\alpha \approx N_e e^2 \langle r^2 \rangle / 3 \Delta E$, derived within the mean energy approximation: $\Delta E \approx E_0 - E_n \forall n$, given by the last formula on p. 386 therein.

Table 1. The Hartree-Fock moment $\langle r^2 \rangle$ of atoms and its ions. HF calculations were performed numerically by using a modified version of the MCHF88 program [8]

N	Atom	$\langle r^2 \rangle$	Cation	$\langle r^2 \rangle$	Anion	$\langle r^2 \rangle$
1	H	3.000000E+00	He+	7.500000E-01		Not exists
2	He	1.184828E+00	Li+	4.453206E-01	H-	9.411098E+00
3	Li	6.210689E+00	Be+	2.184887E+00	He-	Not exists
4	Be	4.329693E+00	B+	1.984155E+00	Li-	2.204299E+01
5	B	3.170217E+00	C+	1.611755E+00	Be-	Not exists
6	C	2.298688E+00	N+	1.292088E+00	B-	6.697741E+00
7	N	1.726054E+00	O+	1.047007E+00	C-	3.763417E+00
8	O	1.396080E+00	F+	8.851606E-01	N-	2.790684E+00
9	F	1.137107E+00	Ne+	7.508442E-01	O-	2.085434E+00
10	Ne	9.371844E-01	Na+	6.413168E-01	F-	1.598148E+00
11	Na	2.468703E+00	Mg+	1.273395E+00	Ne-	Not exists
12	Mg	2.467630E+00	Al+	1.439968E+00	Na-	8.768831E+00
13	Al	2.575116E+00	Si+	1.547993E+00	Mg-	Not exists
14	Si	2.304317E+00	P+	1.490252E+00	Al-	5.442423E+00
15	P	2.018319E+00	S+	1.382597E+00	Si-	3.654254E+00
16	S	1.822652E+00	Cl+	1.290169E+00	P-	3.055333E+00
17	Cl	1.625460E+00	Ar+	1.186961E+00	S-	2.539371E+00
18	Ar	1.446355E+00	K+	1.085615E+00	Cl-	2.134647E+00
19	K	2.696392E+00	Ca+	1.644762E+00	Ar-	Not exists
20	Ca	2.828292E+00	Sc+	1.522590E+00	K-	8.078867E+00
21	Sc	2.531655E+00	Ti+	1.393380E+00	Ca-	Not exists
22	Ti	2.279754E+00	V+	9.818491E-01	Sc-	5.283777E+00
23	V	2.065876E+00	Cr+	9.050679E-01	Ti-	4.831737E+00
24	Cr	1.569048E+00	Mn+	1.079381E+00	V-	4.402017E+00
25	Mn	1.722856E+00	Fe+	1.009682E+00	Cr-	4.054543E+00
26	Fe	1.582215E+00	Co+	7.537682E-01	Mn-	3.631870E+00

27	Co	1.458831E+00	Ni+	7.070289E-01	Fe-	3.307697E+00
28	Ni	1.349665E+00	Cu+	6.619639E-01	Co-	3.032958E+00
29	Cu	1.109290E+00	Zn+	7.782334E-01	Ni-	2.796124E+00
30	Zn	1.165970E+00	Ga+	8.411113E-01	Cu-	2.599651E+00
31	Ga	1.321873E+00	Ge+	9.305888E-01	Zn-	Not exists
32	Ge	1.300502E+00	As+	9.536751E-01	Ga-	2.667923E+00
33	As	1.244397E+00	Se+	9.460201E-01	Ge-	1.977157E+00
34	Se	1.210973E+00	Br+	9.380002E-01	As-	1.810812E+00
35	Br	1.157703E+00	Kr+	9.149432E-01	Se-	1.636798E+00
36	Kr	1.098057E+00	Rb+	8.841496E-01	Br-	1.484421E+00
37	Rb	1.844467E+00	Sr+	1.240817E+00	Kr-	Not exists
38	Sr	2.001643E+00	Y+	1.409835E+00	Rb-	5.035675E+00
39	Y	1.881803E+00	Zr+	1.180120E+00	Sr-	Not exists
40	Zr	1.761145E+00	Nb+	9.602729E-01	Y-	4.624850E+00
41	Nb	1.438411E+00	Mo+	9.161552E-01	Zr-	3.147093E+00
42	Mo	1.342584E+00	Tc+	1.022828E+00	Nb-	2.960566E+00
43	Tc	1.469250E+00	Ru+	8.516694E-01	Mo-	2.814297E+00
44	Ru	1.228241E+00	Rh+	8.159940E-01	Tc-	2.612094E+00
45	Rh	1.174441E+00	Pd+	7.809224E-01	Ru-	2.459804E+00
46	Pd	9.265278E-01	Ag+	7.458838E-01	Rh-	2.329904E+00
47	Ag	1.076421E+00	Cd+	8.338709E-01	Pd-	2.216404E+00
48	Cd	1.132523E+00	In+	8.860758E-01	Ag-	2.121380E+00
49	In	1.255189E+00	Sn+	9.621592E-01	Cd-	Not exists
50	Sn	1.260898E+00	Sb+	9.911162E-01	In-	2.131890E+00
51	Sb	1.236581E+00	Te+	9.960425E-01	Sn-	1.769337E+00
52	Te	1.226125E+00	I+	9.999320E-01	Sb-	1.683222E+00
53	I	1.197278E+00	Xe+	9.904429E-01	Te-	1.578097E+00
54	Xe	1.160211E+00	Cs+	9.730267E-01	I-	1.478850E+00
					Xe-	Not exists

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