CHM 2311: Solutions to Homework 1

1. The equation to use is: $E = R_H\left(\frac{1}{n_l^2} - \frac{1}{n_h^2}\right)$ where $R_H = 2.179 \times 10^{-18}$ J

$n_h = 6$, $n_l = 3$

$$E = (2.179 \times 10^{-18} J)\left(\frac{1}{9} - \frac{1}{36}\right)$$

$= 1.816 \times 10^{-19}$ J

$\lambda = hc/E = (6.626 \times 10^{-34}$ J s$)(2.998 \times 10^{8}$ m/s$)/(1.816 \times 10^{-19}$ J$)$
$= 1.094 \times 10^{-6}$ m (x 10^{9} nm/1 m)
$= 1094$ nm

This is in the infrared region

2. Since the 656.3 nm line is in the visible region, we know it is part of the Balmer series, so $n_l = 2$. Now we just need to determine n_h.

First, determine the energy of 656.3 nm:

$E = hc/\lambda = (6.626 \times 10^{-34}$ J s$)(2.998 \times 10^{8}$ m/s$)/(656.3 \times 10^{-9}$ m$)$
$= 3.027 \times 10^{-19}$ J

Use Balmer's equation to find n_h:

$$3.027 \times 10^{-19} = (2.179 \times 10^{-18} J)\left(\frac{1}{4} - \frac{1}{n^2}\right)$$

$$n^2 = 9.00$$

$$n = 3$$

Thus, the electronic transition responsible for the 656.3 nm emission line in the hydrogen atom is the n = 3 to n = 2 transition.

3. (a) The quantum number n emerges in the derivation of the wave function for the particle in the box, and it is this same n that appears in the energy equation. If we look at the wave function, we see that if n = 0, then $\psi = 0$ for all values of x. This would imply that the particle does not exist ($\psi^2 = 0$ at all x, so probability of finding the particle in the box is zero.) This is impossible! Thus, n = 0 is not possible.

   (b) One of the boundary conditions for calculation of a particle in a box requires that $\psi = 0$ at x = a. From this, we determined that sin(ra) = 0 (where r is yet to be defined and a is the length of the box). For the mathematical equality sin(ra) = 0 to hold true, the quantity ra must be equal to an integer multiple of π. In other words, ra = nπ. This is where the quantum number n emerges, and where its possible values are defined. If n were a fraction, then the boundary condition ψ = 0 at x = a would not be met, so it would not be a valid solution.

4. Zero-point energy is the lowest possible energy of a particle (e.g. the particle in the box). For a particle in a box, it is mathematically defined as

$$E = \frac{n^2 h^2}{8ma^2}$$

The lowest value for n is 1. The other values are constants:

h = Planck's constant = 6.626×10^{-34} J s
m = mass of electron = 9.11×10^{-31} kg
a = length of box = 26 pm = 26×10^{-12} m

(Keep in mind that 1 J = 1 kg m^2 s^{-2})

$$E = \frac{1^2(6.626\times10^{-34} kg \bullet m^2 \bullet s^{-1})^2}{8(9.11\times10^{-31} kg)(26\times10^{-12} m)^2}$$

$$E = 8.91 \times 10^{-17} \text{ kg m}^2 \text{ s}^{-2}$$

$$E = 8.91 \times 10^{-17} \text{ J}$$

5. (a). Radial nodes occur when the radial wave function, R, is equal to zero. Therefore we need to set the given radial wave function equal to zero and solve for r (distance from the nucleus). Since r is embedded in the value σ, we start by finding the values for σ at which R is equal to zero.

$$R = \left(\frac{Z}{2a_o}\right)^{3/2} (2-\sigma)e^{-\sigma/2}$$

R = 0 when $2 - \sigma = 0$

(Note: $e^{-\sigma/2}$ can never be equal to zero so we can ignore this term)

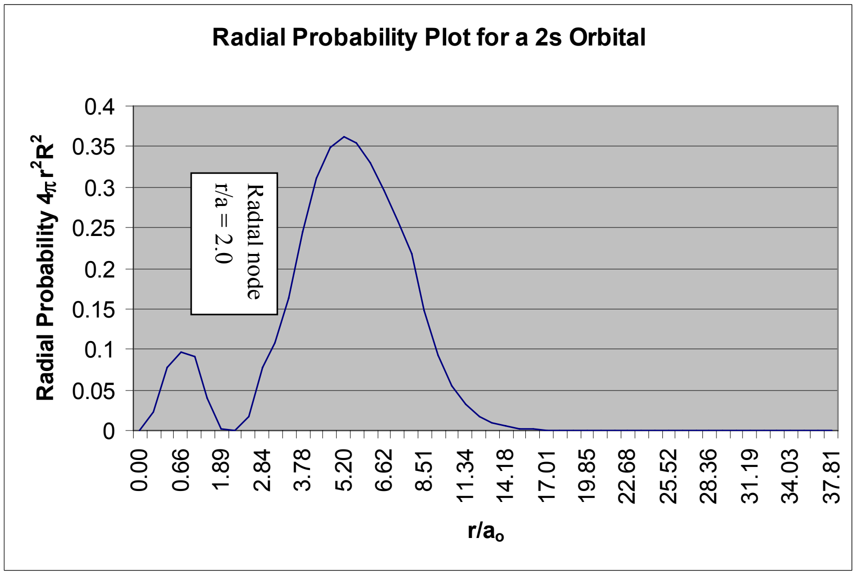
The radial node will be at $\sigma = 2$
$\sigma = 2Zr/na_o$ Therefore, $r = \sigma na_o/2$
For a 2s orbital, $n = 2$

$r =$ (2)(2)(52.9 pm)/2 = **105.8 pm**

(b). A spreadsheet in excel can be set up as follows:

r	r/a_o	$4\pi r^2$	$2Zr/na_o$	R	R^2	$4\pi r^2R^2$
0	0.00	0	0.00	0.005198	2.70205E-05	0
10	0.19	1256	0.19	0.004282	1.83381E-05	0.02303271
25	0.47	7850	0.47	0.003134	9.82429E-06	0.077120685
35	0.66	15386	0.66	0.002499	6.24378E-06	0.096066836
50	0.95	31400	0.95	0.001709	2.92081E-06	0.09171353
75	1.42	70650	1.42	0.000745	5.54745E-07	0.039192758
100	1.89	125600	1.89	0.000111	1.22632E-08	0.001540262
105	1.98	138474	1.98	1.46E-05	2.12266E-10	2.93933E-05
125	2.36	196250	2.36	-0.00029	8.37738E-08	0.016440615
150	2.84	282600	2.84	-0.00053	2.76763E-07	0.078213101
159	3.01	317529.4	3.01	-0.00058	3.38219E-07	0.107394596
175	3.31	384650	3.31	-0.00065	4.22894E-07	0.162666302
200	3.78	502400	3.78	-0.0007	4.88515E-07	0.245430179
225	4.25	635850	4.25	-0.0007	4.87625E-07	0.310056311
250	4.73	785000	4.73	-0.00067	4.44857E-07	0.349213021
275	5.20	949850	5.20	-0.00062	3.8181E-07	0.362662672
300	5.67	1130400	5.67	-0.00056	3.13547E-07	0.354433345
325	6.14	1326650	6.14	-0.0005	2.49024E-07	0.330368244
350	6.62	1538600	6.62	-0.00044	1.92668E-07	0.296438593
375	7.09	1766250	7.09	-0.00038	1.45957E-07	0.257796396
400	7.56	2009600	7.56	-0.00033	1.08672E-07	0.218386796
450	8.51	2543400	8.51	-0.00024	5.78052E-08	0.147021733
500	9.45	3140000	9.45	-0.00017	2.9464E-08	0.092517044
550	10.40	3799400	10.40	-0.00012	1.45388E-08	0.05523886
600	11.34	4521600	11.34	-8.4E-05	6.99346E-09	0.031621606
650	12.29	5306600	12.29	-5.7E-05	3.29547E-09	0.017487731
700	13.23	6154400	13.23	-3.9E-05	1.52679E-09	0.009396471
750	14.18	7065000	14.18	-2.6E-05	6.97379E-10	0.004926983
800	15.12	8038400	15.12	-1.8E-05	3.1471E-10	0.002529764
850	16.07	9074600	16.07	-1.2E-05	1.40551E-10	0.001275445
900	17.01	10173600	17.01	-7.9E-06	6.22054E-11	0.000632853
950	17.96	11335400	17.96	-5.2E-06	2.73132E-11	0.000309606
1000	18.90	12560000	18.90	-3.5E-06	1.19087E-11	0.000149574
1050	19.85	13847400	19.85	-2.3E-06	5.15986E-12	7.14506E-05
1100	20.79	15197600	20.79	-1.5E-06	2.22316E-12	3.37867E-05
1150	21.74	16610600	21.74	-9.8E-07	9.53026E-13	1.58303E-05
1200	22.68	18086400	22.68	-6.4E-07	4.06672E-13	7.35523E-06
1250	23.63	19625000	23.63	-4.2E-07	1.7281E-13	3.39139E-06
1300	24.57	21226400	24.57	-2.7E-07	7.31531E-14	1.55278E-06
1350	25.52	22890600	25.52	-1.8E-07	3.08583E-14	7.06366E-07
1400	26.47	24617600	26.47	-1.1E-07	1.2975E-14	3.19414E-07

1450	27.41	26407400	27.41	-7.4E-08	5.43935E-15	1.43639E-07
1500	28.36	28260000	28.36	-4.8E-08	2.27396E-15	6.42622E-08
1550	29.30	30175400	29.30	-3.1E-08	9.48204E-16	2.86124E-08
1600	30.25	32153600	30.25	-2E-08	3.94438E-16	1.26826E-08
1650	31.19	34194600	31.19	-1.3E-08	1.63712E-16	5.59808E-09
1700	32.14	36298400	32.14	-8.2E-09	6.78069E-17	2.46128E-09
1750	33.08	38465000	33.08	-5.3E-09	2.80292E-17	1.07814E-09
1800	34.03	40694400	34.03	-3.4E-09	1.1565E-17	4.7063E-10
1850	34.97	42986600	34.97	-2.2E-09	4.76345E-18	2.04765E-10
1900	35.92	45341600	35.92	-1.4E-09	1.95878E-18	8.8814E-11
2000	37.81	50240000	37.81	-5.7E-10	3.29702E-19	1.65643E-11



A radial probability plot shows us the probability of finding an electron in a spherical surface of radius r from the nucleus. From this plot we can obtain the following information:

1. Radial node occurs at $r/a_o = 2.0$

2. There is a greater probability of finding an electron after the node.

   (We could determine the radius of maximum probability by taking the first derivative of the radial wave function and setting it equal to zero, but it was not necessary to do this.)

(c) A radial node is a spherical surface at distance r from the nucleus upon which there is zero probability of finding an electron.

6. (a) The number of angular node is equal to the quantum number, l, which is equal to 3 for an f orbital.
   (b) Angular nodes occur when the angular wave function is equal to zero.

$$Y = Cz(x^2-y^2) = 0$$

C is a constant. It cannot be zero because if it were the angular wave function would be equal to zero at all points in space.
Therefore:

$$z(x^2-y^2) = 0$$

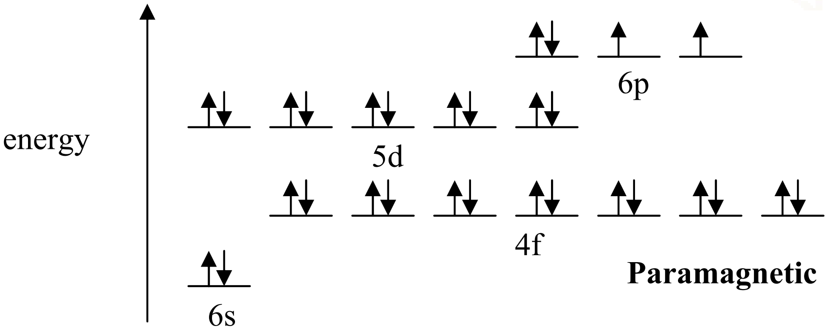
Solving the given equation for the angular wave function, we find the following angular nodes:

$x = y$: This is a plane where $x = y$ for all values of z
$x = -y$: This is a plane where $x = -y$ for all values of z
$z = 0$: This is simply the xy plane

(c) # radial nodes $= n - l - 1$
$= 4 - 3 - 1$
$= 0$
Zero radial nodes

(d) There are 8 lobes

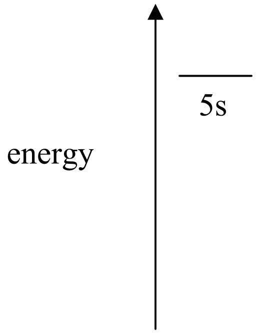
7. **Po: [Xe]$6s^2 4f^{14} 5d^{10} 6p^4$**



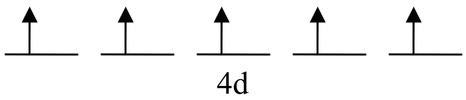
Paramagnetic

Ru^{3+}: [Kr]$5s^0 4d^5$ (electrons are removed from s orbital, ***then*** from d orbitals)

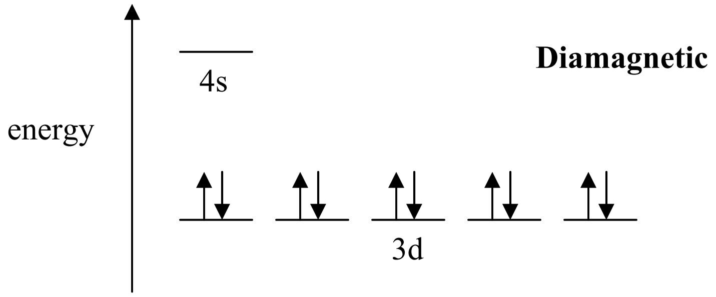
Note that the (n-1)d orbital is ***more stable*** than the ns orbital in the ***cation*** (which is a different order from the neutral atoms). This is why electrons are removed from the s orbital before the d orbital.



Paramagnetic


4d

Ga^{3+}: [Ar]$4s^0 3d^{10}$ (electrons are removed from p, then from s orbitals)



8. Some examples for the calculation of Z_{eff} follow (not complete):

K: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ The highest occupied orbital is 4s

$(1s^2)\ (2s^2, 2p^6)\ (3s^2, 3p^6)\ (4s^1)$

$\sigma = (0.35 \times 0) + (0.85 \times 8) + (1.00 \times 10) = 16.8$

$Z_{eff} = 19 - 16.8 = 2.2$

Ti: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$ The highest occupied orbital is 3d

$(1s^2)\ (2s^2, 2p^6)\ (3s^2, 3p^6)\ (3d^2)\ (4s^2)$

$\sigma = (0.35 \times 1) + (1.00 \times 18) = 18.35$

$Z_{eff} = 22 - 18.35 = 3.65$

Co: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$ The highest occupied orbital is 3d

$(1s^2)\ (2s^2, 2p^6)\ (3s^2, 3p^6)\ (3d^7)\ (4s^2)$

$\sigma = (0.35 \times 6) + (1.00 \times 18) = 20.1$

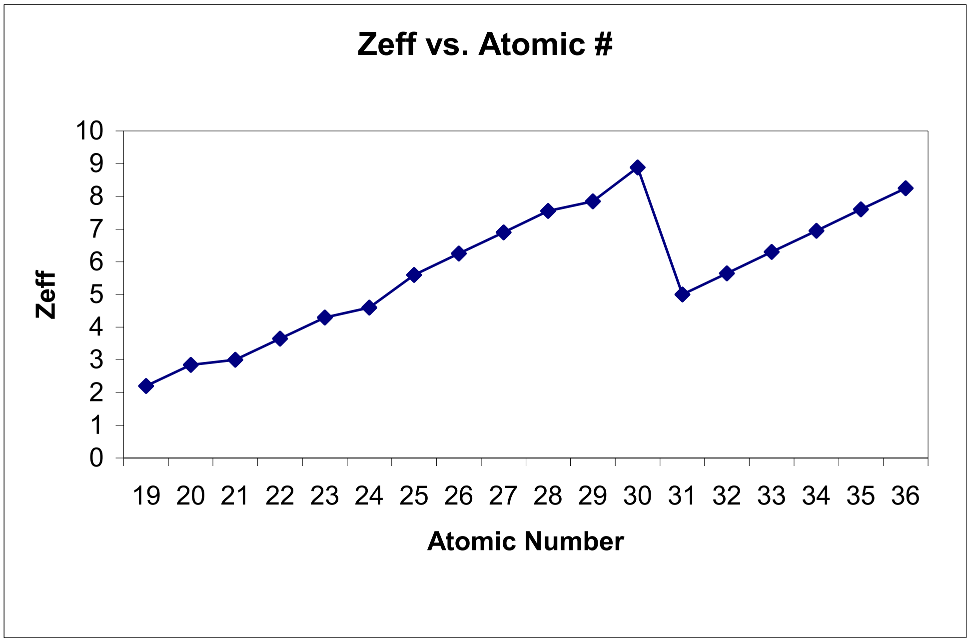
$Z_{eff} = 27 - 20.1 = 6.9$

As: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^3$ The highest occupied orbital is 4p

$(1s^2)\ (2s^2, 2p^6)\ (3s^2, 3p^6)\ (3d^{10})\ (4s^2, 4p^3)$

$\sigma = (0.35 \times 4) + (0.85 \times 18) + (1.00 \times 10) = 26.7$

$Z_{eff} = 33 - 26.7 = 6.3$



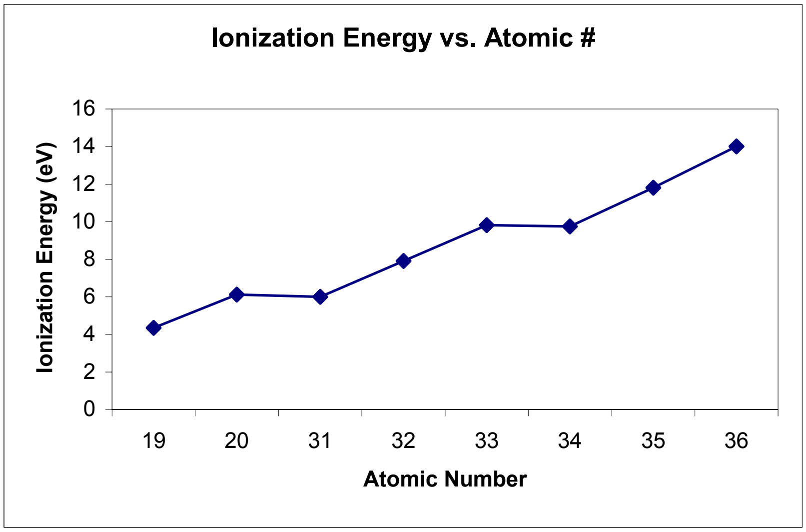
(b). The general trend moving across the period is for Z_{eff} to increase. To understand this trend we should consider two factors:

- electron-proton attraction: this increases moving across the group as the number of protons increases. This contributes toward an increase in Z_{eff}.
- electron-electron repulsions (shielding): this also increases moving across the group as the number of electrons increases.

The electron-electron repulsions considered on their own would cause a decrease in Z_{eff} moving across the group. Z_{eff} actually ***increases*** moving across the group because the attractive forces of the added protons is more significant than the shielding effect of the added electrons. (Thus, according to Slater's rules, each additional proton contributes 1 to Z_{actual}, while each additional valence electron contributes less than one to the shielding factor.)

There is one deviation to the trend. Upon addition of electrons to the p orbital, Z_{eff} decreases. This is due to the filled 3d orbitals now providing a large degree of shielding of the 4p orbital. In addition, these 4p electrons are shielded by the 4s electrons.

9. (a).

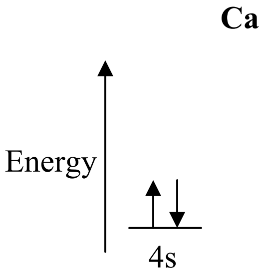


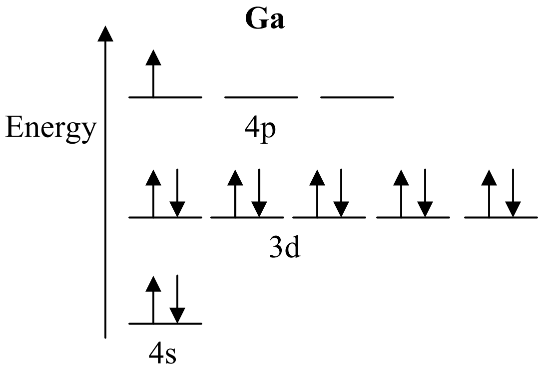
(b) Generally, the trend in ionization energy is the same as the trend in Z_{eff}. This is because removal of an electron will require a greater amount of energy if that electron has a greater attraction to the nucleus.

There two are places where the trend in ionization energy differs from the trend in Z_{eff}.

i. From Ca (20) to Ga (31) Z_{eff} increases, but ionization energy decreases.

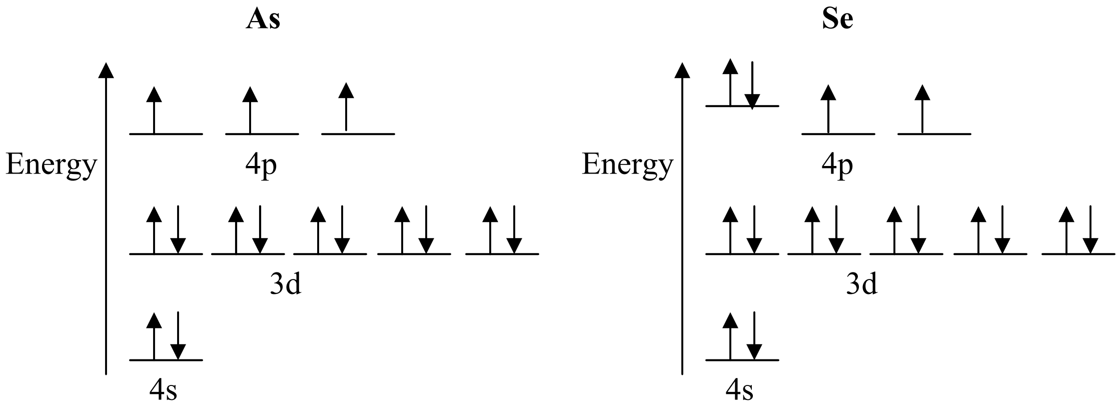
Ga has a lower ionization energy than Ca because the electron in Ga is removed from a higher energy 4p orbital compared to the lower energy 4s orbital in Ca. (A lower energy orbital is more stable, so more energy is required to remove the electron.)





ii. From As (33) to Se (34) Z_{eff} increases, but ionization energy decreases.

In Se, the electron is removed from a doubly occupied orbital, while in As the electron is removed from a singly occupied orbital. A doubly occupied orbital is at a higher energy than a singly occupied orbital due to electron-electron repulsions, thus, less energy is required to remove an electron.



10. (a) Ionization energy – the energy required to remove an electron from the outermost orbital of a gas phase atom.

Potassium: 418.8 kJ mol^{-1}

(b) Electron affinity – the energy change that occurs upon adding an electron to a gas phase atom.

Potassium = -48.4 kJ/mol (note: this is a ***negative*** number)

(c) It is more energetically favorable for a gas phase potassium atom to ***gain*** an electron because this is an exothermic process, whereas losing an electron is an endothermic process.

(d) Chlorine EA = -349.0 kJ/mol

(e) The transfer of an electron from potassium to chlorine can be broken into 2 steps, and Hess's Law can be used to determine the total energy for the process:

i. Loss of an electron from potassium:

$\text{K (g)} \rightarrow \text{K}^+ \text{(g)} + e^-$ $\Delta E = +418.8$ kJ/mol

ii. Addition of electron to chlorine:

$\text{Cl (g)} + e^- \rightarrow \text{Cl (g)}$ $\Delta E = -349.0$ kJ/mol

Overall: $\text{K (g)} + \text{Cl (g)} \rightarrow \text{K}^+ \text{(g)} + \text{Cl}^- \text{(g)}$ $\Delta E = +69.8$ kJ/mol

This result suggests that the transfer of an electron from potassium to chlorine in the gas phase is an endothermic process and, thus, will not be thermodynamically favorable. This might lead one to wonder why, in reality, it happens spontaneously in our practical experience (I hope it makes you wonder this)! Keep in mind that our practical experience generally involves condensed phases (liquids, solids, and solutions). If the newly formed potassium and chloride ions are allowed to combine to form solid KCl, the ionic attractions will cause the overall process to become favorable. In the gas phase, the process is unfavorable because the ions are isolated in the gas phase – there is nothing to stabilize them.