

Dipole Moments and Ionic Character Exercise - The dipole moments of gaseous NaCl, Acetone and Dimethyl Sulfoxide.*

What about large dipole moments? Ionic salts such as NaCl would be expected to have the largest values. The dipole moment is defined, where e is the charge separation in Coulombs (C) and d is distance (m) between the charges (usually the bond length of the most polar bond of interest), as

$$\mu = e \times d$$

Assume for the moment that the bonding in NaCl is 100% ionic. In this case, the charge on the sodium is a full +1 and the corresponding charge on the chlorine is a full -1 (one unit of charge is 1.6022×10^{-19} C). The bond length of NaCl (actually, the internuclear distance, since this is a crystal lattice) is 236.1 pm (2.361 Å) or 2.361×10^{-10} m. Therefore, the predicted dipole moment is given by

$$\mu = (2.361 \times 10^{-10} \text{ m})(1.6022 \times 10^{-19} \text{ C}) = 3.783 \times 10^{-29} \text{ C-m.}$$

We convert this result to Debye (D) by dividing by the conversion factor, 3.336×10^{-30} C m/D, and obtain μ (100% ionic) = 11.34 D. The experimental value of the dipole moment obtained from microwave spectroscopy is 9.001 D. This is close to 11.34 D. The ratio, $(9.001 \text{ D})/(11.34 \text{ D}) = 0.7937$, indicates that the bonding between Na and Cl in the ionic solid is close to 80% ionic.

Organic Molecules Can Have Ionic Character!

Dimethyl sulfoxide (DMSO) and acetone ($\text{C}_3\text{H}_6\text{O}$) have condensed formulas of $(\text{CH}_3)_2\text{SO}$ and $(\text{CH}_3)_2\text{CO}$, respectively. Both are very polar molecules - the measured dipole moments (μ) for DMSO and acetone are 3.96 D, and 2.91 D. How “ionic” are they? This is the same as asking what the percent contributions of their neutral and charge-separated resonance forms are to the “actual” structure. Work through the following exercises using the above math as a guide.

Acetone – which resonance form is most important?

- Draw the structure for acetone and a valid resonance structure (one that has a negative charge on the oxygen – this is called the charge-separated form).
- Assume for a moment that the “best” resonance structure is the one with charges. Calculate the expected dipole moment be for acetone given the C-O bond length is 121.3 pm
- Now, assume the Lewis structure for acetone which shows no charge separation has a zero dipole moment, then calculate the percent contribution of each resonance form given that the measured dipole moment of acetone is 2.91 D. The calculated percentage of the charge-separated structure represents the percentage that acetone is “ionized”

(*Based on *Discussion on the Polarity of Sodium Chloride*, by Wayne Steinmetz, Pomona College, <http://pages.pomona.edu/~wsteinmetz/handout/dipolemoment.doc>)

Dimethyl sulfoxide (DMSO)

- d. Similar to our treatment of acetone, write the two Lewis structures for DMSO. Since sulfur is in the 3rd row of the periodic table, it can have an expanded octet, so one of the Lewis structures show the sulfur with an expanded octet (and none of the elements shows a formal charge), and the other Lewis structure shows the sulfur with an octet. The second Lewis structure contains formal charges, and is the charge-separated resonance form for DMSO.
- e. Assume for a moment that the “best” resonance structure is the one with charges. What would the expected dipole moment be for DMSO given the S-O bond length is 148.5 pm?
- f. If you assume the Lewis structure for DMSO which shows no charge separation has a zero dipole moment, then calculate the percent contribution of each resonance form given that the actual measured dipole moment of DMSO is 3.96 D.

Conclusion

- g. Finally, given your results from above, for which molecule, acetone or DMSO is the charge-separated resonance form more representative of the actual structure? Which solvent would you predict is more *polar*? Explain.