Unusual Molecules and Anions: Chemistry Food for Physicists' Thought

Species and Phenomena

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Species made of chemists' elementary particles

What is known about neutral diatomic molecules that include elements up through Rn, Z=86?

For 70% of 3741 diatomics, the ground state term symbols are unknown;

For the majority of the remaining 30%, R_e and D_e are unknown.

==> We still do not know many of the bonding interactions that may occur between pairs of atoms.

So What?

==> In nature, some pairings of atoms may not occur, but we need to know about them to design new materials.

In the year 2000 and beyond, chemistry will emphasize **new materials** whose optical, physical, electrical, and chemical properties can be "designed".

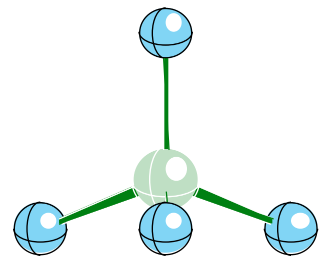
New materials ==> new bonding interactions ==> an area ripe for theory to **guide experiments** by examining **unusual and novel species**.

Our "tools" are now pretty reliable, so it is time for theory to **focus more effort on "discovering" new species and phenomena**.

Species:

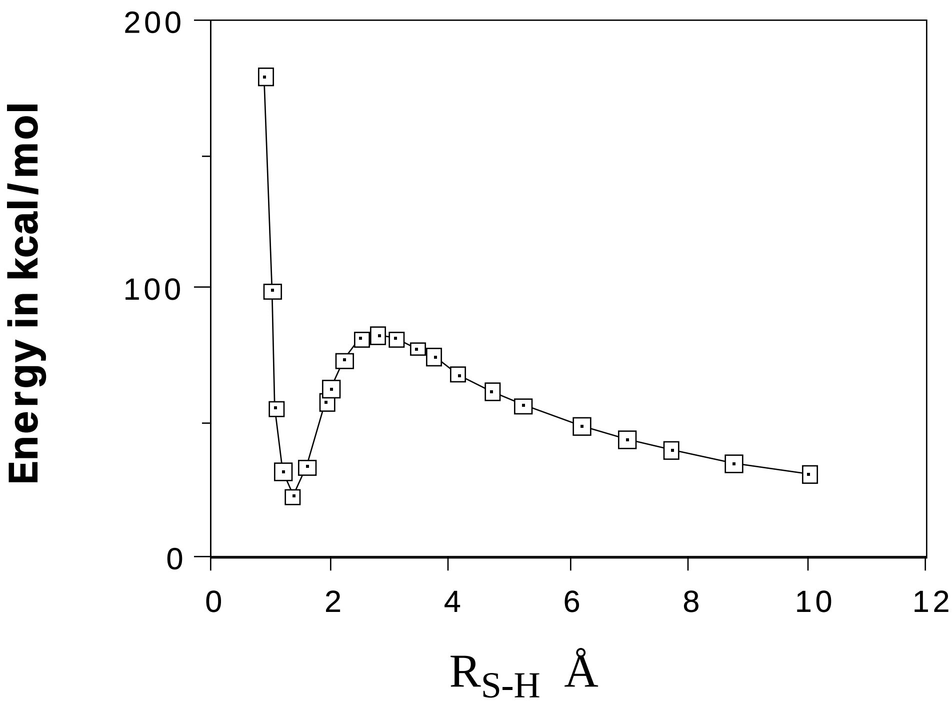
Doubly Charged Ions: AH_n^{2+} and AX_n^{2-}

H_4S^{2+}



has large Internal Coulomb Energy

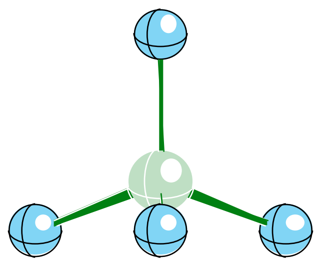
H_4S^{+2} ==> H_3S^{+} + H^{+} + 29 kcal/mol
(barrier is 56 kcal/mol)



But Resonance Delocalization (a quantum phenomenon)
Stabilizes the Repulsion

Species **:Small doubly charged anions** exist too:

$F4Mg^{2-}$



They are geometrically metastable, but with “thick” barriers. They are surprisingly stable (TeF_8^{-2} => TeF_7^- + e^-; 5.8 eV) with respect to electron loss with delocalization again playing a role.

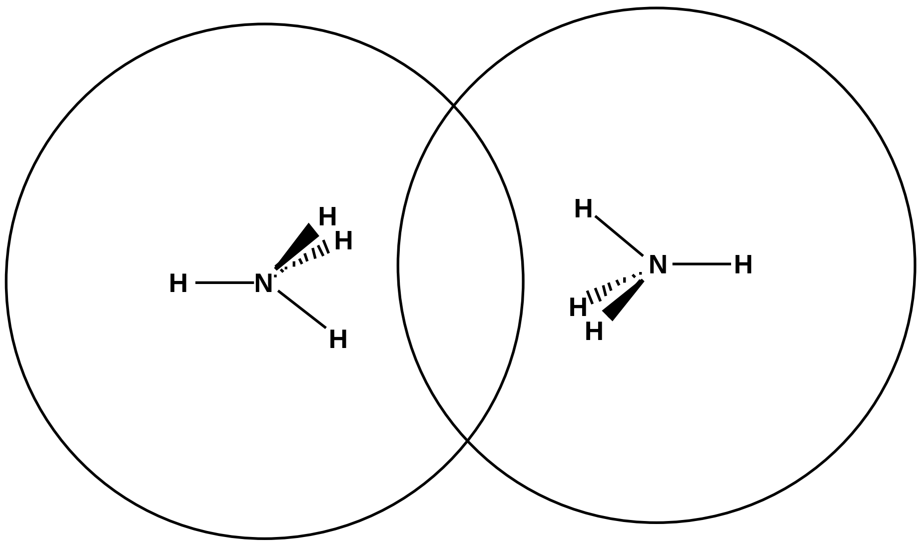
Dissociation Energies (ΔE) and Dissociation Barriers ($E^{\dagger}$) (kcal/mol)

Species	ΔE	$E^{\dagger}$
$H_4O^{2+} \rightarrow H_3O^{+} + H^{+}$	-61	38
$H_3F^{2+} \rightarrow H_2F^{+} + H^{+}$	-111	12
$H_4S^{2+} \rightarrow H_3S^{+} + H^{+}$	-29	56
$H_3Cl^{2+} \rightarrow H_2Cl^{+} + H^{+}$	-67	34
$H_2Ar^{2+} \rightarrow HAr^{+} + H^{+}$	-115	5
$F_4Be^{2-} \rightarrow F_3Be^{-} + F^{-}$	-82	14
$F_4Mg^{2-} \rightarrow F_3Mg^{-} + F^{-}$	-31	24
$F_8Te^{2-} \rightarrow F_7Te^{-} + F^{-}$	-43	> 10
$Cl_8Te^{2-} \rightarrow Cl_7Te^{-} + F^{-}$	-69	> 10
$F_8Se^{2-} \rightarrow F_7Se^{-} + F^{-}$	-75	> 10

A.I. Boldyrev and J.S., J. Chem. Phys. 97, 2826 (1992)
K. O. Christie, et al, J. Chem. Soc. Chem. Comm., 837 (1991).

Phenomena: Molecules can form from bonds comprised not of conventional valence orbitals

$(NH4)_2$ and $(NH4)_2^{+}$



$(NH4)_2 \Longrightarrow 2\ NH_4$; $\Delta E = 8$ kcal/mol

$(NH4)_2^{+} \Longrightarrow NH4 + NH4^{+}$; $\Delta E = 20$ kcal/mol

(Na_2 has a weaker bond than Na_2^{+})

We are now looking into $(NH_4)_2^{-}$ because Na_2^{-} has a strong bond.

A. I Boldyrev and J.S., J. Phys. Chem. 96, 8840 (1992)

Species: Double-Rydberg Anions

NH_4^-, H_3O^-, H_2F^- isoelectronic with Na^-

Na^+ core has $1s^2\,2s^2\,2p^6$ then 3s/3p/4s/3d/...

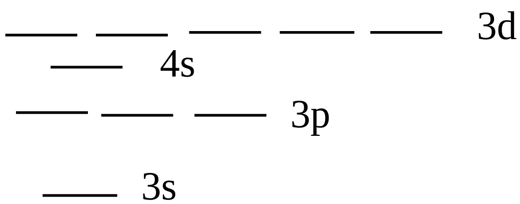
Na^- has two e^-s in the n ≥ 3 orbitals.

NH_4^-, H_3O^-, H_2F^-

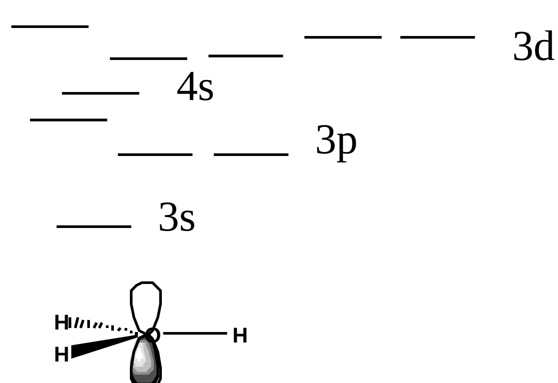
have

NH_4^+, H_3O^+, H_2F^+

cation cores with two e^-s in n ≥ 3 orbitals.

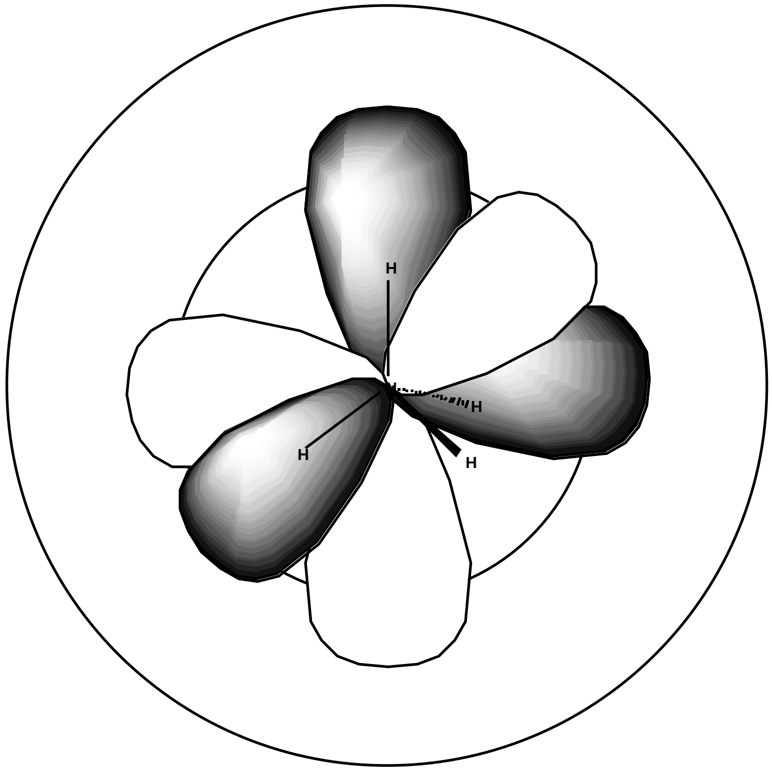


Na^+



H_3O^+

NH_4^- Rydberg Orbitals



NH_4^- $(3s^2)$ ==> NH_4 $(3s^1)$ + e- ; $\Delta E = 0.42$ eV

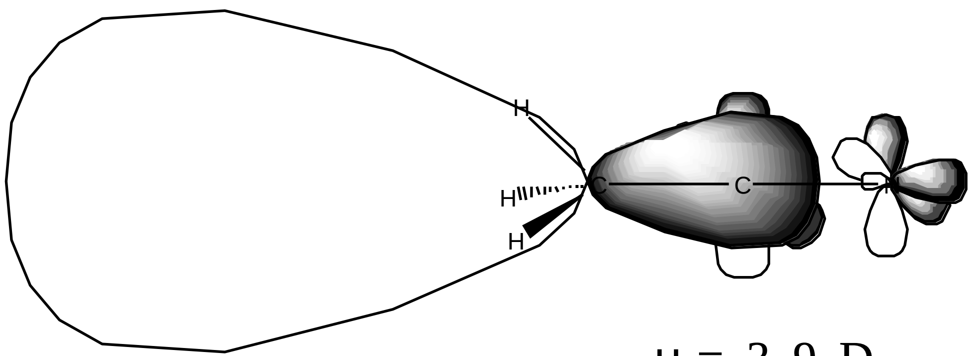
In DR states, the outer e^- pair undergoes strongly correlated motions.

There also exist many excited states
(e.g., NH_4^- $(3p^2)$)which are metastable.

J. S. and M. Gutowski, Chem. Rev. 91, 669 (1991).

Phenomena

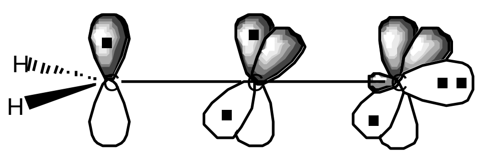
Neutral Molecules With Large Dipole Moments Can Bind an "Extra" Electron Even if They Have No Low-Lying Empty Valence Orbitals

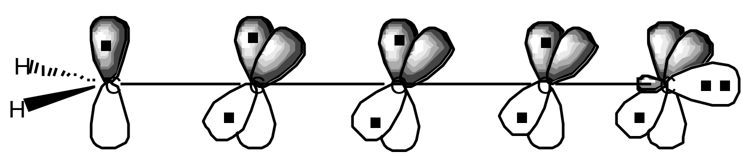


108 cm^{-1}

$\mu = 3.9$ D

$\alpha_{zz} = 5.9$ Å^3





$H_2C{=}C{=}C$
μ = 4.48 Debyes
$\alpha_{par} = 8.9$ A^3; $\alpha_{per} = 4.0$ A^3

173 cm^{-1}

$H_2C{=}C{=}C{=}C{=}C$
μ = 6.40 Debyes
$\alpha_{par} = 22.9$ A^3; $\alpha_{per} = 5.8$ A^3

614 cm^{-1}

$$V = \mu \cos\theta / r^2 + (\alpha_{par} \cos^2\theta + \alpha_{per} \sin^2\theta)/2r^4$$

Our group: Phys. Rev. A1906 (1996).
Lykke, Neumark, Andersen, Trapa, and Lineberger, JCP 87 6842 (1987)

Take home lessons

There are a multitude of new species and interesting phenomena that remain to be discovered.

Diatomic molecules outside the first two rows of the periodic table remain largely uncharacterized.

Doubly charged cations and anions that are geometrically metastable and electronically stable ==> charge delocalization may help make new highly energetic species

Rydberg- bound fragments and **double- Rydberg anions**==> we have to be aware that orbitals other than core and valence orbitals are "available" to electrons

Molecules with large dipole moments have anion states that do not involve valence orbitals and that can undergo rotation and/or vibration induced autodetachment.

4. Electronic structure theory IS FUN!