The Evolution of Chemical Bonding over the Nuclear Transmutation Reaction Path

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Thank you for inviting me!
M. Timm, C. F. Matta; Primary Retention following Nuclear Recoil in $\beta$-Decay: Proposed Synthesis of a Metastable Rare Gas Oxide ($^{38}\text{ArO}_4$) from ($^{38}\text{ClO}_4^-$) and the Evolution of Chemical Bonding over the Nuclear Transmutation Reaction Path; *Applied Radiation and Isotopes*, accepted 10 June 2014.
THE IDEA
• What happens to a chemical bond upon nuclear transmutation?
• Would the compound survive?
• Will it take on new properties?
• How does the electron density evolve following a nuclear event?

POSSIBLE SIGNIFICANCE
• Nuclear transmutation as a synthetic “hot chemistry” route.
• Possible synthesis of thermodynamically metastable compounds, generally difficult to synthesize.
• Synthesis of compounds with unusual oxidation states.
• Sheer intellectual curiosity!
Hot Atom Chemistry: An Obituary

H. Müller; *The rise and fall of hot atom chemistry.*

• Environmental movement.
• Rise of more fashionable fields.
• Moving away of PhD students to areas which can lead to attractive future employment.
• Lack of common language and appreciation between groups working on hot atom chemistry from different vantage points.
• Lack of funding.
Very thin literature on joint investigations of hot atom chemistry & quantum chemistry


Predicting from first principles the chemical evolution of crystalline compounds due to radioactive decay: The case of the transformation of CsCl to BaCl

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In this Brief Report, we use density functional theory to predict the existence of a heretofore unobserved crystalline compound, BaCl, and additionally predict it to be isostructural with NaCl (rocksalt). Due to the chemistry of Ba, which strongly prefers a 2+ charge state, compounds where Ba nominally exhibits a +1 charge (e.g., BaCl) are unlikely to be synthesized via conventional solid-state approaches. However, in considering the chemical evolution of $^{137}$Cs to $^{137}$Ba via $\beta^-$ radioactive decay in a model nuclear waste form CsCl, we find that BaCl may be indeed relevant. The mechanical stability of this surprising structure is confirmed through examination of its elastic constants and phonon-dispersion relations. We have also analyzed the chemical bonding of rocksalt BaCl and found it to exhibit a complex mixture of ionic, metallic, and covalent characters. From our results, we demonstrate that the chemical evolution of crystalline structures due to radioactive decay may be a viable synthesis route for unforeseen materials with interesting properties.

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- Jaing et al.\textsuperscript{1} investigate radioactive decay as a possible synthetic route.
- This is the single example in the literature.
When all Cs has been replaced by Ba, we find only a very small 0.03 eV/atom driving force for the rocksalt BaCl structure to phase separate into a mixture of the orthorhombic structured BaCl$_2$. 

FIG. 1. (Color online) Calculated cohesive energies of Cs$_{1-x}$Ba$_x$Cl compounds in various competing crystal structures. The dashed line denotes the ground-state energy, i.e., the energy of a mechanical mixture of B2 CsCl, bcc Ba, and orthorhombic BaCl$_2$ with the same composition.
FIG. 5. Conduction band-charge density (in $e/\text{Å}^3$) on the (001) plane of rocksalt BaCl.
Hot atom synthesis of ArO$_4$?
ArO$_4$ is the last member of the $N = 50$ $e^-$ isoelectronic and isosteric series of ions:

$$\text{SiO}_4^{4-}, \text{PO}_4^{3-}, \text{SO}_4^{2-}, \text{ClO}_4^{-}.$$
3. Failures

It has been said that "a first-rate theory predicts, a second-rate theory forbids and a third-rate theory explains" (attributed to A. I. Kitaigorodskii). An interesting example, where the isoelectronic principle breaks down is argon tetroxide. A plot of the experimental vibrational frequencies of $\text{PO}_4^{3-}$, $\text{SO}_4^{2-}$ and $\text{ClO}_4^-$ would predict for the next member of the series the frequencies of about 1090, 860, 620 and 430 cm$^{-1}$. Furthermore the "secondary periodicity" (see [15]) could favour $\text{ArO}_4$ over the (unknown) $\text{KrO}_4$, as proposed earlier [16]. Nevertheless, the MP2/6-31G* energy of $\text{ArO}_4$ is 17.3 eV above that of $\text{Ar} + 2 \text{O}_2$, although a minimum is still found at $R = 148$ pm at the MP2 level. The HF curve shows no minimum.
Ab Initio Study of Bonding Trends among Cyanamidophosphates ([PO\textsubscript{4-n}(NCN)\textsubscript{4-n}]\textsuperscript{3-}) and Related Systems

Pekka Pyykkö*\textsuperscript{[a]}

Abstract: Ab initio calculations on the experimentally known anions [PO\textsubscript{n}(NCN)\textsubscript{4-n}]\textsuperscript{3-} are used to show that intramolecular forces are sufficient to determine their existence and structure. Structures are predicted for the analogous cyanamidosulphates and perchlorates. If one of the oxygens of the XO\textsubscript{4}\textsuperscript{4} group is replaced by nitrogen or fluorine, further new anions are obtained. An example is NSO\textsubscript{3}\textsuperscript{3-}. Remarkably, the NArO\textsubscript{3} anion is predicted to have strong inner bonding and is, together with ArO\textsubscript{4}, a candidate for an argon species.

Keywords: ab initio calculations • cyanamide • oxygen • phosphates • pseudochalcogens • sulphates
On the Thermodynamic Stability of ArO₄

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The argon tetroxide molecule, ArO₄, and the isoelectronically associated perchlorate, ClO₄⁻, and sulfate, SO₄²⁻, ions are investigated on different levels of ab initio theory. The equilibrium structures, harmonic vibrational frequencies, and heats of formation are computed applying density functional theory, second order Møller-Plesset perturbation, singles and doubles coupled-cluster with triples corrections, and Brueckner’s doubles coupled-cluster with triples corrections methods in conjunction with various one-particle basis sets. The calculations demonstrate that the description of the bond characteristics in argon tetroxide is sensitive to the applied level of theory. A careful analysis of the global potential energy surface shows that a stationary point exists for the ArO₄ complex corresponding to a local mininium. The calculated equilibrium Ar-O bond distance of 1.48 Å for this structure is slightly longer than the corresponding bond length of the perchlorate ion. Harmonic frequencies for ArO₄ obtained using Brueckner’s doubles coupled-cluster with triples corrections are found to have a similar pattern like those obtained for the isoelectronic series of ions SiO₄⁴⁻, PO₄³⁻, SO₄²⁻, ClO₄⁻. Using the concept of an isodesmic reaction, the enthalpy of formation of ArO₄ is determined to be endothermic by as much as 1246 kJ/mol. The present theoretically predicted strong endothermicity and the large Ar–O bond distance are in conflict with the monotonic trends obtained for the isoelectronic ions, but can be supported by other chemical extrapolation schemes.
To this day, ArO₄ remains to be synthesized.
Proposed synthesis of $^{38}\text{ArO}_4$ from $^{38}\text{ClO}_4^-$

$^{38}\text{Cl}$ is ideal because:

- $t_{1/2} \left( ^{38}\text{Cl} \rightarrow ^{38}\text{Ar} + \beta \right) = 37.24 \pm 0.05 \text{ min}^{[1]}$
- readily produced: $^{[2]}$

$$^{37}\text{Cl}^- (aq) + n \rightarrow ^{38}\text{Cl}^-(aq) + \gamma$$


\[
\text{NaCl} + 3\text{H}_2\text{O} \rightarrow \text{NaClO}_3 + 3\text{H}_2
\]

\[
\text{Cl}^- (\text{aq}) + 3\text{H}_2\text{O}(\text{l}) \xrightarrow{70^\circ\text{C}, \text{H}^+} \text{ClO}_3^- (\text{aq}) + 3\text{H}_2(\text{g})
\]

\[
2\text{Cl}^- (\text{aq}) + \text{H}_2\text{O}(\text{l}) \xrightarrow{>70^\circ\text{C}, \text{OH}^-} \text{ClO}^- (\text{aq}) + \text{H}_2(\text{g})
\]

\[
\text{ClO}_3^- (\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{ClO}_4^- (\text{aq}) + \text{H}_2(\text{g})
\]

\[
^{38}\text{ClO}_4^- (\text{aq}) \rightarrow ^{38}\text{ArO}_4^- (\text{aq}) + \beta^-
\]
\[ {^{38}}\text{ClO}_4^- (aq) \rightarrow {^{38}}\text{ArO}_4 (aq) + \beta^- \]

- But how about the recoil? (from 0 \( \rightarrow \sim \) 5 MeV)
- Would ArO\(_4\) survive?
Ground state of a parent nucleus $\rightarrow$ excited or ground state of a daughter nucleus & $\alpha$-particle. The change in energy of the nucleus is shared as K.E. by the $\alpha$-particle and the recoiling daughter nucleus $\Delta E$ according to the principles of conservation of momentum and of energy. This requires the $\alpha$-particle and the daughter nucleus to move in opposite directions with the same magnitude of $p \rightarrow$ Sharp $p$.

http://www.ohio.edu/people/piccard/radnotes/alphabeta.html
In β-decay there are 3 products: The daughter nucleus, the β-e-, & an antineutrino ($\bar{\nu}$). Thus, conservation of momentum and of energy do not suffice to determine the K.E. of a β-particle, there are too many unknowns. The spectrum of β-K.E. is a broad curve. By conservation of momentum and energy, there will be a maximum K.E. of a β-particle at the limit as the momentum and energy given to the neutrino approach zero. In this case the momentum and energy of only two particles need to be taken into account, giving us the same algebra as alpha decay.

http://www.ohio.edu/people/piccard/radnotes/alphabeta.html
β-emission spectrum of $^{38}\text{Cl}$ with 3 “end points”

Estimation of the yield of primary retention

\[ p_{\text{recoil}} = \sqrt{p_e^2 + p_v^2 + 2p_e p_v \cos \theta} \]

\[ p_e = \sqrt{\frac{E_e^2 + 2E_e m_e c^2}{c^2}} \]

\[ p_v = \frac{E_v}{c} \]

\[ p_{\text{recoil}} = \sqrt{\frac{E_e^2 + 2E_e m_e c^2}{c^2}} + \frac{E_v}{c} + 2\sqrt{\frac{E_e^2 + 2E_e m_e c^2}{c^2}} \frac{E_v}{c} \cos \theta \]

\[ E_{\text{recoil}} = \frac{E_e^2 + 2E_e m_e c^2 + E_v^2 + 2E_v \sqrt{E_e^2 + 2E_e m_e c^2} \cos \theta}{2M c^2} \]

which can be simplified by expressing energies in MeV (1 kcal/mol = 4.336×10⁻⁸ MeV) and masses in atomic mass units (a.m.u.):

\[
E_{\text{recoil}} = \frac{5.36 \times 10^2}{M} \left( E_e^2 + 1.02E_e + E_v^2 + 2E_v \sqrt{E_e^2 + 1.02E_e \cos \theta} \right)
\]

\( E_{\text{recoil}} \) = Recoil energy of transmuted atom (in MeV)
\( M \) = Mass of transmuted atom (in a.m.u.)
\( E_e \) = Kinetic energy of ejected \( \beta^- \) particle (in MeV)
\( E_v \) = Kinetic energy of ejected antineutrino (in MeV)
\( \theta \) = Angle between ejected \( \beta^- \) particle and antineutrino

From this equation, the extreme values of the recoil energy occur for \( \theta = 0 \) (max) and \( \theta = \pi \) (min), leading to:

\[
E_{\text{recoil}} = \frac{5.36 \times 10^2}{M} \left( E_e^2 + 1.02E_e + E_v^2 \pm 2E_v \sqrt{E_e^2 + 1.02E_e} \cos \theta \right)
\]
\[ \theta_{\text{critical}} = \arccos \left\{ \frac{M \times E_{\text{recoil}}^{\text{threshold}}}{5.36 \times 10^2} \right\} - E_e^2 - 1.02 E_e - \left[ \max(E_e) - E_e \right]^2 \]

\[ = \frac{2 \left[ \max(E_e) - E_e \right] \sqrt{E_e^2 + 1.02 E_e}}{2 \left[ \max(E_e) - E_e \right] \sqrt{E_e^2 + 1.02 E_e}} \]

- \( \theta_{\text{critical}} \) = Angular deviation from colinearity between \( \beta^- \) particle and \( \tilde{\nu} \) resulting in a given \( E_{\text{recoil}} \).
- For \( E_{\text{recoil}} \leq E_{\text{recoil}}^{\text{threshold}} \) \( \Rightarrow \theta \leq \theta_{\text{critical}} \).
- \( \max(E_e) \) = Maximum energy of an ejected \( \beta^- \)-particle (the end-point or cut-off value of the bell curved spectrum).
We now impose the energy threshold of recoil (below which the recoil energy is insufficient to cause the dissociation of the daughter molecule).

*Set the upper bound for the recoil energy as:*  
\[ E_{\text{recoil}}^{\text{thresh.}} = \max(E_{\text{recoil}}) = 20 \text{ kcal/mol} \approx 9.1 \times 10^{-7} \text{ MeV (gas-phase).} \]

In other words: This is the highest recoil energy that will leave the ArO₄ molecule intact after the β-decay event.
max($E_{\text{recoil}}$) = 20 kcal/mol

max($E_{\beta\text{-e}}$) = 4.81 MeV

max($E_{\beta\text{-e}}$) = 2.77 MeV

max($E_{\beta\text{-e}}$) = 1.11 MeV

Energy of the ejected $\beta$-electron (MeV)

Maximum angular deviation from colinearity with the antineutrino (°)
\[ \max(E_{\text{recoil}}) = 20 \text{ kcal/mol} \]

\[ (= E_{\text{threshold}}^{\text{recoil}}) \]

\[ \max(E_{\beta^{-}}) = 4.81 \text{ MeV} \]

\[ \max(E_{\beta^{-}}) = 2.77 \text{ MeV} \]

\[ \max(E_{\beta^{-}}) = 1.11 \text{ MeV} \]

Energy of the ejected $\beta$-electron (MeV)

Maximum angular deviation from colinearity with the antineutrino ($^0$)
$\max(E_{\text{recoil}}) = 20 \text{ kcal/mol}$

$\max(E_{\beta-e}) = 4.81 \text{ MeV}$

$\max(E_{\beta-e}) = 2.77 \text{ MeV}$

$\max(E_{\beta-e}) = 1.11 \text{ MeV}$
$$\max(E_{\text{recoil}}) = 142 \text{ kcal/mol}$$

$$\max(E_{\beta-e^-}) = 4.81 \text{ MeV}$$

$$\max(E_{\beta-e^-}) = 2.77 \text{ MeV}$$

$$\max(E_{\beta-e^-}) = 1.11 \text{ MeV}$$
• Applying the derived Eq. over all possible $\beta^-$ energies gives proportion of ejected $\beta^-$ Particles & antineutrinos whose K.E. cancels within the chosen threshold, giving “acceptable” recoil energy less than the threshold and hence insufficient to break the daughter molecule.

• Applying proportions to beta spectrum percentages gives rough percent yield.

$$retention_{\text{gas phase}} (\%) = 0.6 \times 0.534$$
$$+ 1.0 \times 0.158 + 1.9 \times 0.308 = 1.1\%$$

$$retention_{\text{solid phase}} (\%) = 4.1 \times 0.534$$
$$+ 6.7 \times 0.158 + 14.1 \times 0.308 = 7.6\%$$
The 20 kcal/mol threshold
PES of ArO$_3$—O bond dissociation

\[ \Delta \Delta E = 21.5 \text{ kcal/mol} \]

(U)MP2/6-311+G*
PES of $\text{ArO}_3 - \text{O}$ bond dissociation

$\text{ArO}_4 \rightarrow \text{ArO}_3 + \text{O}(^1\text{D})$

$\text{ArO}_4 \rightarrow \text{ArO}_3 + \text{O}(^3\text{P})$

$\Delta\Delta E = 21.5 \text{ kcal/mol}$

(U)MP2/6-311+G*
• ArO₄ exists at a local minimum.
• \textit{Negative} BDE of \( \approx 30 \) kcal/mol.
• Barrier \( \approx 22 \) kcal/mol.
The sudden approximation

The increase in Z from 17(Cl) → 18 (Ar) causes a sudden change in the total energy of the system equivalent to a hypothetical X-ray photon of \( 4.4 \times 10^{17} \) Hz.

Solving the relativistic K.E. equation for the β-particle:

\[
v = c \sqrt{1 - \left[ \left( \frac{K.E.}{m_e c^2} \right) + 1 \right]^2}
\]

we find that \(~ 50\% \) of all ejected e- have speeds of \( > 0.95 \) c.

- At these speeds, a β-e- crosses 1Å in \(~ 3.5 \times 10^{-19} \) s, \( > 2 \) orders of magnitude faster than the period of this photon.
The nuclear transmutation reaction path

\[ ^{38}\text{ClO}_4^- \xrightarrow{\beta^-} ^{38}\text{ArO}_4\left[\@\text{geom}(\text{ClO}_4^-)\right] \rightarrow ^{38}\text{ArO}_4\left[\@\text{geom}(\text{ArO}_4)\right] \]

QCISD/6-311+G(3df)
The nuclear transmutation reaction path

$^{38}\text{ClO}_4^- \xrightarrow{-\beta^-} ^{38}\text{ArO}_4\left[\text{@geom}(\text{ClO}_4^-)\right] \rightarrow ^{38}\text{ArO}_4\left[\text{@geom}(\text{ArO}_4)\right]$

QCISD/6-311+G(3df)
The nuclear transmutation reaction path

$^{38}\text{ClO}_4^- \xrightarrow{-\beta^-} ^{38}\text{ArO}_4 \left[ @\text{geom}(\text{ClO}_4^-) \right] \rightarrow ^{38}\text{ArO}_4 \left[ @\text{geom}(\text{ArO}_4) \right]$
Evolution of QTAIM properties along the nuclear transmutation reaction path:

**Bond Properties**

<table>
<thead>
<tr>
<th>System</th>
<th>B.L.</th>
<th>$\delta$(X,O)</th>
<th>$\rho_b$</th>
<th>$\nabla^2 \rho_b$</th>
<th>$\lambda_1, \lambda_2$</th>
<th>$\lambda_3$</th>
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</thead>
<tbody>
<tr>
<td>ClO$_4^-$</td>
<td>1.442</td>
<td>1.101</td>
<td>0.4005</td>
<td>-1.0204</td>
<td>-0.8153</td>
<td>0.6102</td>
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<tr>
<td>ArO$_4$ (SP)</td>
<td>1.442</td>
<td>1.505</td>
<td>0.4273</td>
<td>-0.5672</td>
<td>-0.8351</td>
<td>1.1030</td>
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<tr>
<td>ArO$_4$ (opt.)</td>
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<td>1.490</td>
<td>0.4158</td>
<td>-0.4929</td>
<td>-0.8035</td>
<td>1.1141</td>
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<table>
<thead>
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<th>$G_b$</th>
<th>$H_b$</th>
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<td>ClO$_4^-$</td>
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<td>0.4328</td>
<td>-0.6879</td>
</tr>
<tr>
<td>ArO$_4$ (SP)</td>
<td>-0.9140</td>
<td>0.3861</td>
<td>-0.5279</td>
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<tr>
<td>ArO$_4$ (opt.)</td>
<td>-0.8800</td>
<td>0.3784</td>
<td>-0.5016</td>
</tr>
</tbody>
</table>

* All entries in this table are in atomic units except bond lengths (B.L.) which are in Å.

QCISD/6-311+G(3df)
Evolution of QTAIM properties along the nuclear transmutation reaction path:

Atomic Properties

<table>
<thead>
<tr>
<th>System</th>
<th>q(Ω)</th>
<th>N(Ω)</th>
<th>E(Ω)</th>
<th>Vol.(Ω)</th>
</tr>
</thead>
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<td></td>
</tr>
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<td>3.9698</td>
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<tr>
<td>ArO₄ (SP)</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>Ar</td>
<td>1.7784</td>
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<td></td>
<td>113.0973</td>
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<tr>
<td>ArO₄ (opt)</td>
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<tr>
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<td>113.5276</td>
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</table>

* All entries in this table are in atomic units.

QCISD/6-311+G(3df)
How can the formation of ArO$_4$ be monitored?
\[ \text{ClO}_4^- \quad 643.7 \]

\[ \text{1152.9} \]
$\text{ArO}_4$

IR Spectrum

\begin{align*}
\Delta \nu &= -70.5 \\
\Delta \nu &= -170.4
\end{align*}

QCISD/6-311+G(3df)
Reviewer #1:

This is an interesting study on a possible way of making the strongly endothermic but metastable molecule.

..........

Summing up, this is a good paper, that should be published after minor changes. No need to re-referee.

*Applied Radiation and Isotopes*, accepted 10 June 2014.
Reviewer #2:

What an original work! Seldomly, I had the pleasure to read such a paper full of original and interesting ideas. Although this is a theoretical study (better: theoretical suggestion or prediction) and it is not fully obvious whether it will be possible to realize the proposed experiment, it is a very interesting piece of work that deserves publication.
Reviewer #2: (Cont’d)

The value of the paper is three-fold. First, it proposes an interesting transmutation reaction to generate the meta-stable, but yet unknown argon tetroxide from an isolectronic perchlorate precursor. Next, it applies QTAIM concepts to study the change in chemical bonding during such a transmutation process, which allows one to relate the known prototypical perchlorate with the unknown and much less stable argon tetroxide. Finally, significant mathematical modelling is done for the assessment of the viability of the transmutation reaction.

*Applied Radiation and Isotopes*, accepted 10 June 2014.
This paper is theoretical chemistry at its best: Rather than descriptive post factum calculations, the authors exploit the full predictive power of the quantum chemical approach. It is my pleasure to recommend this paper for publication.
- Starting from the principle of conservation of momentum, a theoretical framework has been developed to provide quantitative estimates of primary retention yields from the hot-atom chemistry of the $\beta$-decay.

- ArO$_4$ have very unusual properties:
  - Negative BDE
  - Metastable (bound kinetically)

- ArO$_4$ may have other than theoretical interest since it can conceivably be:
  1. a powerful oxidizer
  2. perhaps an energy storage compound
ACKNOWLEDGEMENTS

I have benefited from discussions with (in alphabetical order):

- Axel D. Becke (Dalhousie)
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- Mark Obrovac (Dalhousie)
- Pekka Pyykkö (Helsinki)
- Josef Zwanzinger (Dalhousie)
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- Dalhousie University
- Mount Saint Vincent University
- Canada Foundation for Innovation
- Fonction canadienne pour l’innovation

max($E_{\text{rec}o}$) = 20 kcal/mol
max($E_{\text{exc}e}$) = 142 kcal/mol

0.416
0.433
0.416
1.731

Ar

0.433

O

1.490
Thank You
Extra Slides for Possible Questions
$\text{ArO}_4\text{(aq)} + 4\text{H}_2\text{O} \rightarrow \text{Ar} + 4\text{H}_2\text{O}_2$?
KClO₄ crystallizes without water of crystallization.

4 molecules per unit cell.

The experimental electron density \( \rho(\mathbf{r}) \) of the two isomorphic salts KMnO₄ and KClO₄ was determined by a multipole analysis of accurate X-ray diffraction data at 120 K. The quantum theory of atoms in molecules was applied to \( \rho(\mathbf{r}) \) and to its Laplacian \( \nabla^2 \rho(\mathbf{r}) \). The bonds were characterized using the topological parameters at the bond critical points of the density \( \rho(\mathbf{r}) \), \( \nabla^2 \rho(\mathbf{r}) \), \( G(\mathbf{r}) \) (kinetic energy density), \( V(\mathbf{r}) \) (potential energy density) and \( H(\mathbf{r}) \) (total energy density). According to the classification recently proposed by Espinosa, Alkorta, Elguero & Molins [J. Chem. Phys. (2002), 117, 5529–5542], the K—O and Cl—O bonds have a pure ionic and covalent character, respectively, while the Mn—O bonds show an intermediate behaviour. The results of the topological analysis of the experimental and theoretical (fully periodic Hartree–Fock and density functional calculations) electron density are in good agreement, even on a quantitative level. The atomic charges, determined by performing an integration over the topological basins, are about \( +2 \) e for Mn and Cl atoms. The ionic radius, estimated with the distance of the bond critical point from the nucleus, is in agreement with a charge of \( +2 \) e for the Mn atom.
Unlike the sharp momentum spectra of $\alpha$-decay, $\beta$-decay exhibits continuous momentum / K.E. spectra.
Realizing that \[ E_v = \max(E_e) - E_e \]
then substituting into (*)

\[ E_{\text{recoil}} = \frac{5.36 \times 10^2}{M} \left( E_e^2 + 1.02E_e + E_v^2 + 2E_v \sqrt{E_e^2 + 1.02E_e \cos \theta} \right) \]

(*)

and solving for \( \theta \) we obtain the following expression for the **critical angle**: 
Technical details of the calculations

• QCISD/6-311+G(3df) for geometry optimizations, harmonic vibrational frequencies, and electron densities.
• (U)MP2/6-311+G* for PES scans.

Programs:
  o Gaussian 09 Rev.B01
  o AIMAll/AIMStudio