And now for something completely different...

(Picture courtesy of Python M)
Theoretical spectra of CaOCa in the two lowest electronic states

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A. Gertych, University of Wuppertal
P. Jensen, University of Wuppertal, Massey University
The general scheme of things

Potential energy surface(s)
Dipole moment surface(s) ...

in general obtained from *ab initio* calculations

Simulated rotation-vibration spectra

**PROGRAMS** MORBID, RENNER, DR, TROVE
Group 2 alkaline-earth $M_2O$ hyper-metallic oxides
## Time evolution of the project

<table>
<thead>
<tr>
<th>Year</th>
<th>Compound</th>
<th>Authors</th>
</tr>
</thead>
</table>

### Future
- **Near future**
  - SrOSr
- **Not-so-near future**
  - BaOHa
- **Rather distant future**
  - RaORa
- **Sometime**
  - Maybe another column of the periodic table?
Motivation

- Study of molecular clusters as a way of understanding the emergence of crystalline properties from molecular properties.
- Elucidation of the stability and structure of metal-rich clusters impacts on the development of new catalytic materials.
General observation

The molecules BeOBe, MgOMg, and CaOCa studied *ab initio* thus far all have electronic ground states and low-lying electronic states.

\[ \tilde{X}^1\Sigma_g^+ \]
\[ \tilde{a}^3\Sigma_u^+ \]

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( T_e(\tilde{a}^3\Sigma_u^+)/\text{cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeOBe</td>
<td>293</td>
</tr>
<tr>
<td>MgOMg</td>
<td>671</td>
</tr>
<tr>
<td>CaOCa</td>
<td>386</td>
</tr>
</tbody>
</table>
CaOCa ab initio calculation

- Calculation of three-dimensional potential energy surface, and the electric dipole moment surfaces.
- Multireference configuration interaction (MRCISD) approach in combination with internally contracted multireference perturbation theory (RS2C) based on full-valence complete active space self-consistent field (FV-CASSCF) wavefunctions with a cc-pwCVQZ-DK basis set for Ca and a cc-pCVQZ basis set for O.
Vibrational energies and $B$ values for $^{40}\text{Ca}^{16}\text{O}^{40}\text{Ca}$ calculated by MORBID

<table>
<thead>
<tr>
<th>$(v_1, v_2, v_3)$</th>
<th>$N_{\text{min}}$</th>
<th>$\tilde{X}^1\Sigma_g^+$</th>
<th>$\tilde{a}^3\Sigma_u^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(0, 0^e, 0)$</td>
<td>0</td>
<td>0.00$^a$</td>
<td>0.00$^b$</td>
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<tr>
<td>$(0, 1^e, 0)$</td>
<td>1</td>
<td>54.84</td>
<td>82.71</td>
</tr>
<tr>
<td>$(0, 1^f, 0)$</td>
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<td>54.84</td>
<td>82.71</td>
</tr>
<tr>
<td>$(0, 2^e, 0)$</td>
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<td>163.73</td>
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<tr>
<td>$(0, 2^e, f)$</td>
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<td>166.39</td>
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<tr>
<td>$(0, 3^e, 0)$</td>
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<td>158.30</td>
<td>244.22</td>
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<tr>
<td>$(0, 3^f, 0)$</td>
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<td>244.22</td>
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<tr>
<td>$(0, 3^f, f)$</td>
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<td>250.96</td>
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<tr>
<td>$(0, 4^f, 0)$</td>
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<tr>
<td>$(0, 4^f, f)$</td>
<td>2</td>
<td>235.39</td>
<td>336.49</td>
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<tr>
<td>$(0, 0^e, 1)$</td>
<td>0</td>
<td>410.29</td>
<td>435.59</td>
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<tr>
<td>$(0, 1^e, 1)$</td>
<td>1</td>
<td>410.29</td>
<td>435.59</td>
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<td>$(0, 1^f, 1)$</td>
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<td>520.38</td>
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<td>474.08</td>
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<tr>
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<td>$(0, 2^f, 1)$</td>
<td>0</td>
<td>804.45</td>
<td>834.68</td>
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<td>$(0, 2^f, f)$</td>
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<td>852.91</td>
<td>914.71</td>
</tr>
<tr>
<td>$(0, 2^e, f, 1)$</td>
<td>2</td>
<td>855.49</td>
<td>915.89</td>
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Simulated spectra of $^{40}\text{Ca}^{16}\text{O}^{40}\text{Ca}$

$\tilde{X}^1\Sigma_g^+$

$T = 15 \text{ K}$

$\tilde{a}^3\Sigma_u^+$

Intensities in units of km mol$^{-1}$, wavenumbers in cm$^{-1}$
Comparison with $^{40}\text{Ca}^{16}\text{O}$-spectrum

$T = 15$ K

Fundamental band of $^{40}\text{Ca}^{16}\text{O}$

$\nu_3$ band of $\tilde{X}^1\Sigma_g^+$ -state $^{40}\text{Ca}^{16}\text{O}^{40}\text{Ca}$

$\nu_3$ band of $\tilde{a}^3\Sigma_u^+$ -state $^{40}\text{Ca}^{16}\text{O}^{40}\text{Ca}$

$\nu_3$ band of $^{40}\text{Ca}^{16}\text{O}^{40}\text{Ca}$ has largest intrinsic intensity
Infrared Spectra of Matrix-Isolated Calcium-44 Substituted Oxides

Lester Andrews¹ and Bruce S. Ault²

Chemistry Department, University of Virginia, Charlottesville, Virginia 22901

The products of $^{44}$Ca atom reactions with ozone and oxygen have been isolated in solid nitrogen at 15 K. An excellent wavenumber fit for four isotopic molecules confirms the diatomic CaO assignment. Calcium and oxygen isotopic data strongly support the observation of rhombic $(CaO)_2$ and isosceles triangular $CaO_2$ and $Ca_2O$ species.
Experiment!

Spectra resulting from reactions of $^{44}\text{Ca}$ with $^{16}\text{O}_3$, and of $^{40}\text{Ca}$ with $^{16}\text{O}_3$ and with $^{18}\text{O}_3$.

The infrared spectra of the reaction products, in the 15 K nitrogen matrix, were recorded in the 400–800 cm$^{-1}$ region.

![Infrared spectra of calcium-ozone and calcium-oxygen reaction products in solid nitrogen at 15 K. Spectra (a) natural $^{44}\text{Ca}$ and $\text{N}_2^{18}\text{O}_3 = 180/1$. Trace (b) $^{40}\text{Ca}$ and $\text{N}_2^{18}\text{O}_3 = 150/1$. Spectra (c) $^{44}\text{Ca}$ and $\text{N}_2^{18}\text{O}_3 = 180/1$. Trace (d) $^{40}\text{Ca}$ and $\text{N}_2^{18}\text{O}_3 = 100/1$, 35% $^{18}\text{O}$ enrichment. Trace (e) $^{40}\text{Ca}$ and $\text{N}_2^{18}\text{O}_3 = 100/1$, 35% $^{18}\text{O}$.](image)
**Experiment!**

Strong peaks attributed to CaOCa by Andrews and Ault:

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<tr>
<td>$^{40}\text{Ca}^{16}\text{O}^{40}\text{Ca}$</td>
<td>476, 486.8</td>
</tr>
<tr>
<td>$^{40}\text{Ca}^{18}\text{O}^{40}\text{Ca}$</td>
<td>461, 472</td>
</tr>
<tr>
<td>$^{44}\text{Ca}^{16}\text{O}^{44}\text{Ca}$</td>
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Simulated spectra of $^{40}\text{Ca}^{16}\text{O}^{40}\text{Ca}$

$\tilde{X}^1\Sigma^+_g$

$T = 15$ K

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No reasonable assignment possible!
Simulated spectra of $^{40}\text{Ca}^{16}\text{O}^{40}\text{Ca}$

$T = 15 \, \text{K}$

\[ \tilde{a}^3\Sigma_u^+ \]

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No reasonable assignment possible!
Conclusion:

- The spectra observed by Andrews and Ault are not due to CaOCa.
- We hope that our calculations will assist in the eventual spectroscopic characterization of CaOCa.