Global Optimization-Density Functional Theory
Study of Tin Oxide Clusters:
Structures, Energies, and Trends

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Why Global Optimization (GO) of clusters?
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How we do GO.
- Why Global Optimization (GO) of clusters?
- How we do GO.
- Why tin oxide?
Why Global Optimization (GO) of clusters?

How we do GO.

Why tin oxide?

$\text{Sn}_m\text{O}_n$ Results
Why do Global Optimization of cluster structure?
No Lewis theory or VSEPR for clusters
and few structural principles

*but structure is essential!*
Clusters are often

- short-lived,
- found in low concentrations,
- mixed with other stuff,
- part of a broad distribution of size, composition, and structure

⇒ hard to characterize!
Experimental cluster structures possible with

- IR photodissociation spectra (FELIX),
- photoelectron spectra,
- and other techniques . . .

. . . combined with theory $= \text{DFT} + \text{GO}$
DFT/GO, by itself, gives structures $\Rightarrow$ **trends**

Number of isomers for

$\text{Ar}_{13}$: $> 1500$ Chekmarev, PRE 64 (2001) 036703

$\text{Ar}_n$: $\sim 2.8^{n-6}$
How we do GO at York U

R Fournier and A Mohareb, J Chem Phys 144 (2016) 024114
We combine **Evolutionary Computing** techniques

- Taboo Search (TS)
- Simulated Annealing (SA)
- Genetic Algorithm (GA)
- Memetic Algorithm (MA)

and we do

- **concurrent optimization** of many species
pick N values of x (N "points") at random and calculate f(x)
Select low energy points with higher probabilities, and make small changes in x
bad representation of the problem
a GOOD representation
Redundant points (red squares) are rejected.
Big moves early on at high $T$, and gradually smaller moves as $T$ goes down gives a balance between

- *exploration* (global search) and
- *exploitation* (semilocal search)
3 minima: \( f(\text{grey}) < f(\text{red}) < f(\text{magenta}) \)
20 random points, taboo radius = 0.10 (exploration)
slight energy bias, taboo radius = 0.08
medium energy bias, taboo radius = 0.06
strong energy bias, taboo radius = 0.04
very strong bias, taboo radius = 0.02 (exploitation)
Unary and binary operations:

parent A $\Rightarrow$ child C
A + B $\Rightarrow$ child C
Minimizing a model potential (squares) is roughly \((3n-6)\) times cheaper than basin hopping.
Minimizing $U$ each time makes the problem discrete

with $U_{DFT}$ the energy ordering of valleys is perfect

with a bad $U_{model}$ we could get a wrong ordering and miss the global minimum
Why Study Tin Oxide?
• Ionic, but nontrivial

• Bulk: SnO and SnO$_2$. Clusters: ??

• Catalyst

• Gas sensor
Sn$_m$O$_n$ Results
- Gaussian 09
- PBE functional
- SDD pseudopotential and basis sets
- 38 species, \(4 \leq m + n \leq 18\)
- 5 to 12 local optimization per species
- 16,000 GO steps
- \(\approx 10,000\) local optimization steps
Relative Index of Thermodynamic Stability (RITS)

\[ Sn_mO_n \rightarrow mSn + nO \quad AE(m, n) \]

\[ AE(m, n) \approx fit(m, n) = mE(Sn) + nE(O) \]

\[ D = AE - fit \quad (eV) \]

\[ R = D / fit \quad (dimensionless) \]

Fournier & Mohareb, J Chem Phys 144 (2016) 024114
Global Minima: \( \text{Sn}_7\text{O}_7 \approx 7.7 \)
Global Minima: $\text{Sn}_8\text{O}_9 = 8.9$
René Fournier (York University, Chemistry)  Global Optimization-DFT, Sn$_m$O$_n$ clusters
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Global Optimization-DFT, $\text{Sn}_m\text{O}_n$ clusters
RITS vs chemical composition

$(m + n)$ and $(m - n)$
\[ 
\text{Sn}_2\text{O}_3 \text{ and Sn}_3\text{O}_2
\]
The diagram shows a scatter plot with the title $m+n = 7$. The axes are labeled as $RITS$ on the y-axis and $m-n$ on the x-axis. There are four data points represented by blue circles.

This plot likely represents a study or analysis of $Sn_mO_n$ clusters, as suggested by the context provided.
$m+n = 8$
m+n = 9

Diagram showing the relationship between RITS and m-n with m+n = 9.
\[ m+n = 11 \]
$m+n = 15$
$m+n = 16$

The graph shows points at $(m-n, RITS)$ for various values of $m$ and $n$. The coordinates are not explicitly given, but the graph illustrates the relationship between $m-n$ and $RITS$ for $m+n=16$.
Sn\textsubscript{m}O\textsubscript{n} clusters get more stable as

- \((m + n)\) increases
- \(|m - n|\) decreases
- \((m - n) > 0\) is slightly favored over \((m - n) < 0\)
### Table 1: Stability and Reactivity of Species

<table>
<thead>
<tr>
<th>m.n</th>
<th>D (eV)</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.7</td>
<td>-3.58</td>
<td>-0.069</td>
</tr>
<tr>
<td>8.9</td>
<td>-3.94</td>
<td>-0.063</td>
</tr>
<tr>
<td>8.7</td>
<td>-2.88</td>
<td>-0.052</td>
</tr>
<tr>
<td>7.8</td>
<td>-2.89</td>
<td>-0.052</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>6.2</td>
<td>+4.04</td>
<td>+0.145</td>
</tr>
<tr>
<td>3.6</td>
<td>+5.04</td>
<td>+0.147</td>
</tr>
<tr>
<td>2.5</td>
<td>+5.62</td>
<td>+0.208</td>
</tr>
<tr>
<td>2.6</td>
<td>+7.56</td>
<td>+0.243</td>
</tr>
</tbody>
</table>
Stability vs composition ratio
correlation coeff. = 0.81
$s$: same (Sn-Sn or O-O) ; $d$: different (Sn-O)

$d_{ij}$: interatomic distance ; $R_i$: atomic radius

$$S = \left(\frac{1}{N_s}\right) \sum_{i>j}^s \left(\frac{d_{ij}}{(R_i + R_j)}\right)^{-6}$$

$$D = \left(\frac{1}{N_d}\right) \sum_{i>j}^d \left(\frac{d_{ij}}{(R_i + R_j)}\right)^{-6}$$

$$N_s = m(m - 1)/2 + n(n - 1)/2$$

$$N_d = mn$$

$$M_6 = \frac{D}{D + S}$$
Stability vs mixing

correlation coeff. = -0.67
Mixing vs composition ratio

correlation coeff. = -0.75
Global Optimization, what works:

1. a good representation of the problem
2. hybrid methods
3. problem-specific knowledge (e.g. distance constraints)
4. concurrent optimization of many species
Tin oxide clusters $\text{Sn}_m\text{O}_n$:

1. stable when $(m + n)$ is large and $|m - n|$ is small
2. effect of composition: several eV
3. highly mixed clusters are most stable
4. coordination numbers ($CN$) for O: $2 \leq CN \leq 4$
5. Sn has $2 \leq CN \leq 9$
6. many amorphous structures
★ Wesley Paul

★ Stephen Chen

★ NSERC Canada

★ SHARCNET — Shared Hierarchical Academic Research Computing Network

★ the CMMSE 2016 Organizers