Methane Clusters at Low Temperatures

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Abstract

Four methane clusters containing 2, 10, 55, 137, 229 molecules: magic numbers for closed shells in different structures

MOTIVATION

- Fundamental properties of symmetrical molecules in a symmetrical environment
- Greenhouse effect & hydrogen storage
- Clathrate [2, 3]
- Beauty

Figure 1. Evaporation of a molecule: Rosen Radev's vision. Monte Carlo simulations of 59 methane cluster at 50K.

OBJECTS - SMALL

Size is always a special-case experience (Fuller)

Why 'small' is different?

Number of connections - a basis for the phenomenon of 'small is different'

Figure 2. Classical and quantum interaction potential.

- Integration of (1) and (2) at a constant total energy using the velocity Verlet algorithm [1] with a time step of 1 fs that keeps the energy constant up to \((10^{-5})\) for 1 ns production runs

Figure 3. Four specific mutual orientations for 2 CH$_4$ molecules (from left to right) - aligned, perpendicular, anti-aligned "1" and anti-aligned "2".

Figure 4. Potential energy per molecule for a methane dimer at 4 different mutual orientations.

The cluster state - liquid or solid - is determined by the radial distribution function \(g(r)\).

Figure 5. Radial distribution function for 55 molecules arranged in a static \(\rho_{\text{se}}\), a static \(\rho_{\text{se}}\), and a "real" structure at \(T = 10\ K\).

Table 1. NN=Nearest-Neighbors; NNN=Next-to-the-Nearest-Neighbors.

<table>
<thead>
<tr>
<th>number of neighbors</th>
<th>NN (3.5-4.1Å)</th>
<th>NNN (4.1-4.5Å)</th>
<th>NNN + NNN (5.5-5.9Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>4</td>
<td>11</td>
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<tr>
<td>2</td>
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<tr>
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<td>9</td>
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<td>11</td>
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<td>0</td>
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</tr>
<tr>
<td>12</td>
<td>0</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>mean</td>
<td>3.85</td>
<td>3.6</td>
<td>7.56</td>
</tr>
</tbody>
</table>

Liquid-solid-like phases are usually distinguishable via the value of the modified Lindemann index \(\delta_{\text{Lin}}\) (the cluster is solid if \(\delta_{\text{Lin}} < 0.08\) [5]):

\[\delta_{\text{Lin}} = \sqrt{\frac{1}{N} \sum_{i,j \neq i} \left( \frac{|r_i - r_j|}{\langle r \rangle} \right)^2} < 0.08 \]

Figure 6. Lindemann index - size effect.

The low-frequency peak in the vibrational spectra at \(T=10\K\) corresponds to a collective surface wave.

CONCLUSION

The most important finding in this study is that dimers of molecules with a specific mutual anti-ferro ordering determine the cluster structure at low temperatures. Obviously, the angular dependence of the classical interaction causes a specific alignment of molecular axes even if the external pressure is zero. The topography of the potential energy surface of clusters of various sizes must be studied as well.

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Production runs: Monte Carlo - Rosen Radev

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References