

A Novel Ab-Initio Based Model for Monitoring Unique Structural Properties of Clathrate Hydrates

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Abstract

Clathrate hydrates are crystalline compounds with guest molecules, such as hydrogen, methane, or carbon dioxide, trapped within cages of hydrogen bonded water molecules. The confined compounds, usually nonpolar or hydrophobic, introduces peculiar physical and chemical properties to the ordinary ice structures. These unique properties can lead to novel applications in alternative energy, climate change control, and nuclear waste storage. However, clathrate hydrates are stable only at low temperature and high pressure, predominantly at the bottom of ocean floors and permafrost regions. This instability causes experimental study of the structures to be difficult. Here we introduce the development of an ab-initio based computer model, known as the Thole-Type Model (TTM), as an alternative to monitor the structural properties of these extraordinary compounds, specifically methane hydrates, in their natural habitat. TTM has been previously shown to be able to accurately and inexpensively describe the interactions between water and halide ions, and the promising results paved the way for its potential to adequately characterize the interactions between water and simple molecules.

Methane Hydrate

Methane hydrates are clathrate compounds in which the guest molecule is solely methane. It is seen as a form of alternative energy due to its ability to be ignited, earning it the nickname fire ice. However, the burning and improper handling of these compounds can result in the release of the captured methane, which are at least 80 times more potent than carbon dioxide as a greenhouse gas in short terms and at least 25 times more potent in long terms, into the atmosphere. Due to their dangerous nature, coupled with its complex structure, methane hydrates are the first to be modeled with TTM. Methane hydrate exists in three types of crystal structures, as shown in Figure 1.

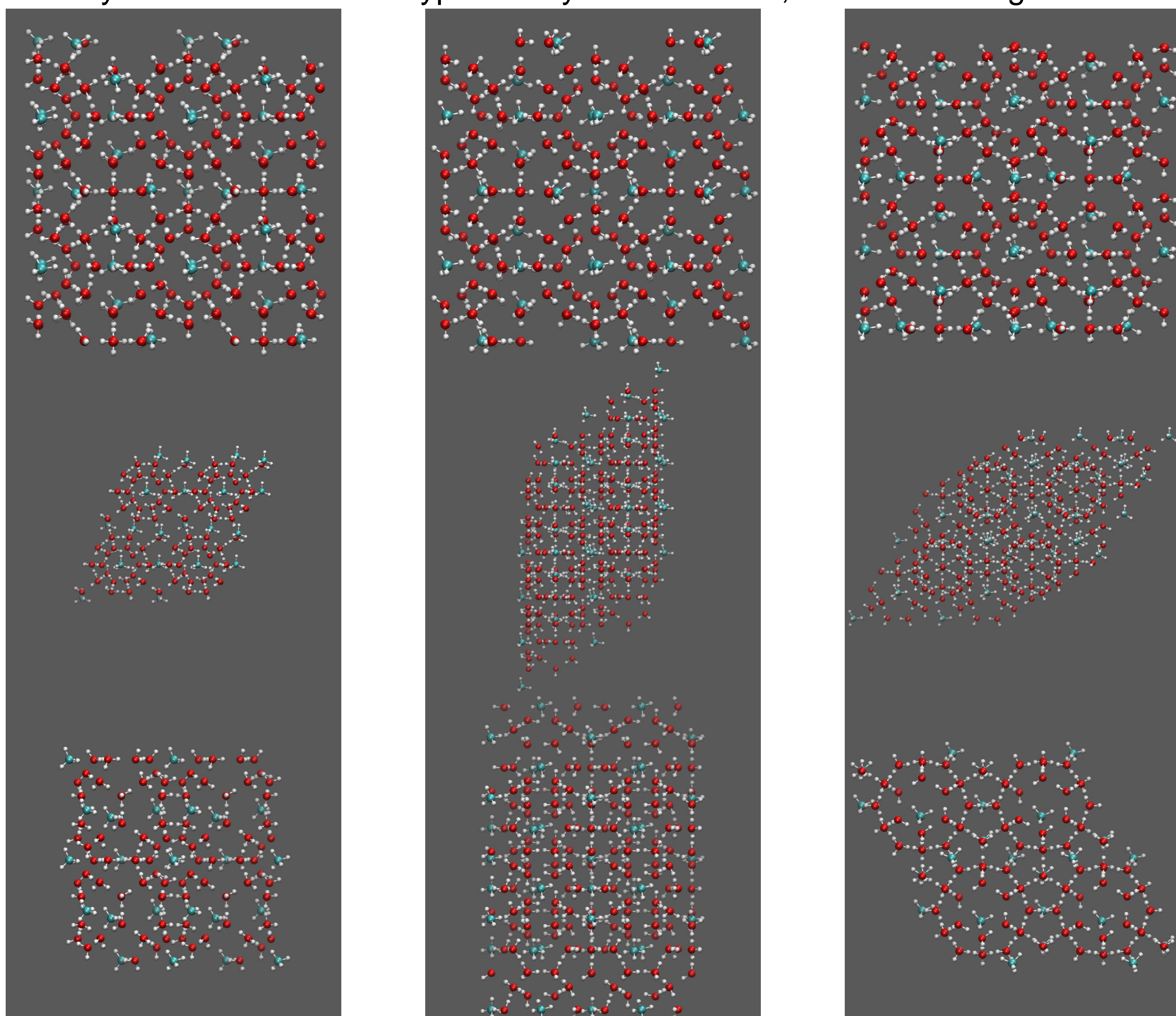


Figure 1. Y-Z, X-Z, and X-Y planar projections (from left to right) of sl, sII, and sH crystal structures (from top to bottom) of methane hydrates. A 2 by 2 by 2 supercell is shown.

Thole-Type Model

The TTM potentials are derived from fits to electronic structure data, and include an explicit treatment of the two-body **repulsion**, **electrostatics**, and **dispersion** energies. Many body effects are represented through classical polarization within an extended TTM. By construction, the TTM potentials are compatible with the flexible and fully ab initio MB-pol potential for water, which is becoming increasingly popular due to its ability to inexpensively produce accurate results when compared to experimental studies.

$$V_{tot} = V_w^{intra} + V_w^{inter} + V^{TTM}$$

$$V^{TTM} = V^{TTM,elec} + V^{TTM,ind} + \sum_{i=1}^n (V_i^{rep} + V_i^{disp})$$

$$V_i^{disp} = \sum_{j=1}^{n-1} \sum_{k=j+1}^n -f(R_{ij}, \delta_{ij}) \frac{C_{6,ij}}{R_{ij}^6} \quad V_i^{rep} = \sum_{j=1}^{n-1} \sum_{k=j+1}^n A_{ijk} e^{b_{ijk}R_{ij}}$$

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Interaction Energy

Interaction energy scans between a methane and a water molecule at different configurations and orientations were performed (Figure 2) by varying the distance between the carbon and the oxygen atom from 2.00 Å to 15.00 Å at intervals of 0.01 Å to obtain the energy at each step of the dimer system through electronic calculations. The calculations were done using the ω B97XD functional with the aug-cc-pvtz basis set. Throughout the process, both molecules were kept fixed at the vibrationally averaged geometry, with $r_{CH} = 1.087736$ Å, $\theta_{HCH} = 109.471^\circ$, $r_{OH} = 0.957367$ Å, and $\theta_{HOH} = 105.052^\circ$. In addition, an equilibrium geometry optimization of both molecules were done at the same level to attain the minimum energy of the structures. The interaction energy can then be calculated by subtracting the minimum energy of the molecules individually from the energy of the dimer system. These scans will be used as the basis to determine the energetic effects of the surrounding water molecules on a methane or vice versa.

$$E_{int} = E_{CH_4-H_2O} - E_{CH_4^{eq}} - E_{H_2O^{eq}}$$

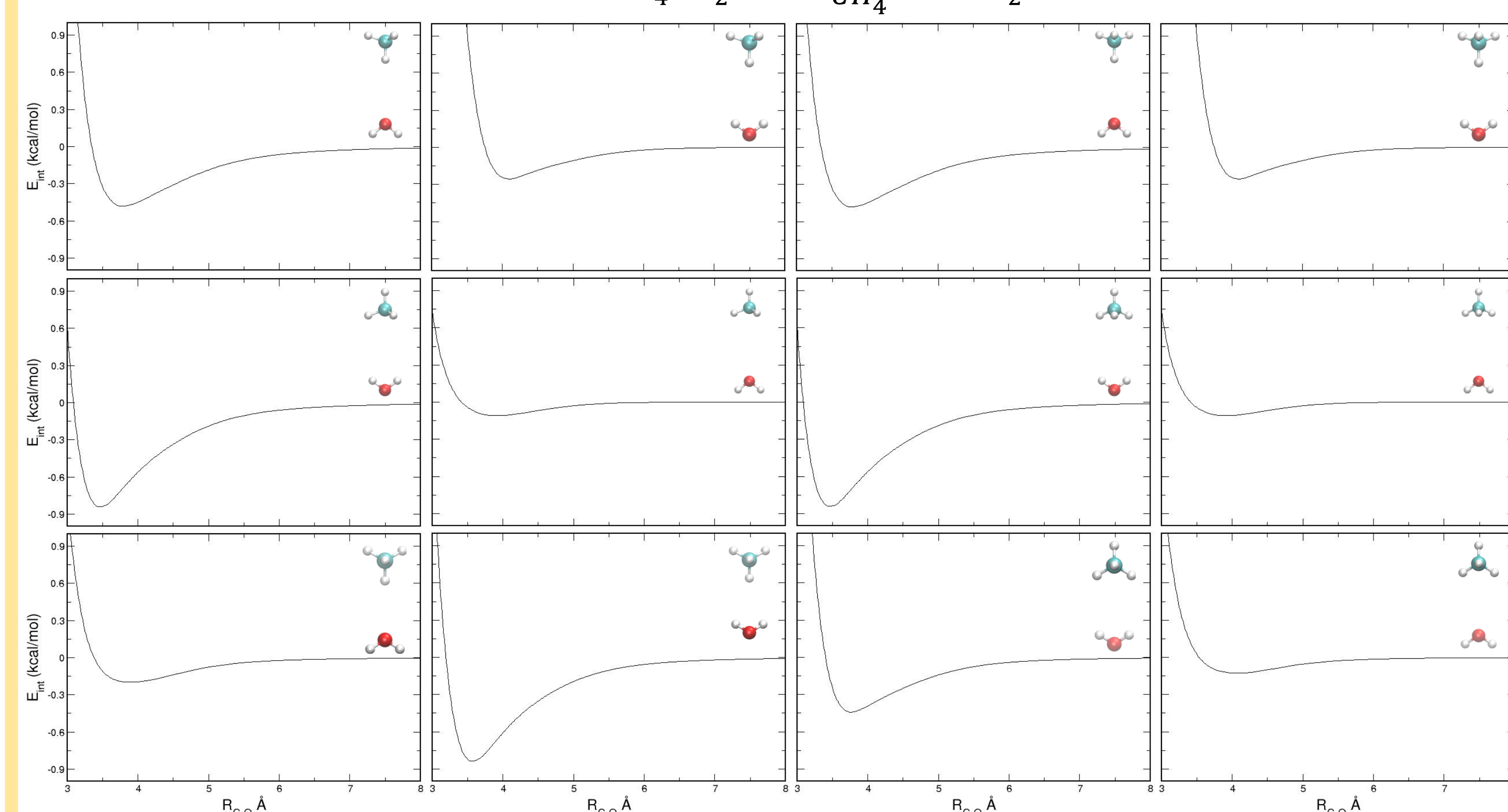


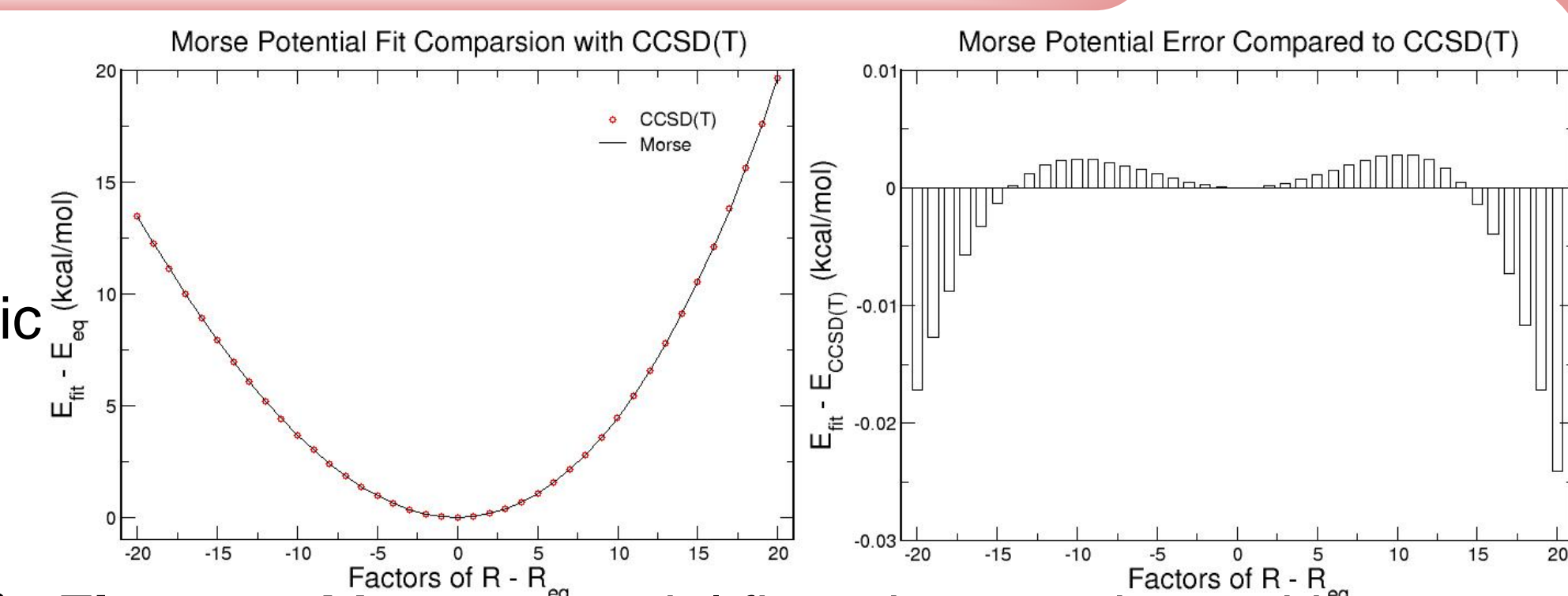
Figure 2. Interaction energy scans between a methane and water molecule at 12 different orientations or configurations as shown schematically on the top right of each graph.

Morse Potential

A Morse potential can be used to fit the vibrational stretching modes of motion for methane as shown in Figure 3. The potential can track the energetic effects on methane as it constantly stretch the bonds with D_e , a , and r_{eq} values.

$$V(r) = D_e(1 - e^{-a(r-r_{eq})})^2$$

Figure 3. Morse potential fit and comparison with reference values obtained from CCSD(T).

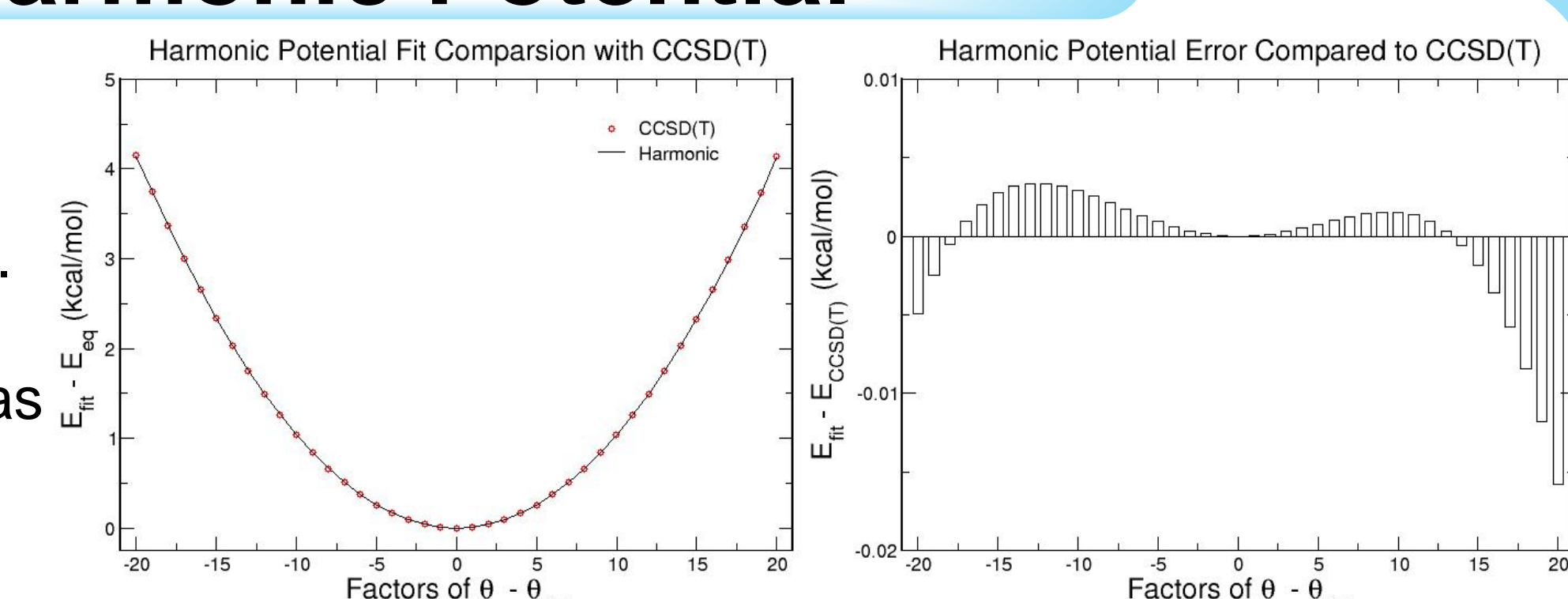


Harmonic Potential

A harmonic potential can be used to fit the vibrational bending modes of motion for methane as shown in Figure 4. The potential can track the energetic effects on methane as it constantly bend the bonds with k and θ_{eq} values.

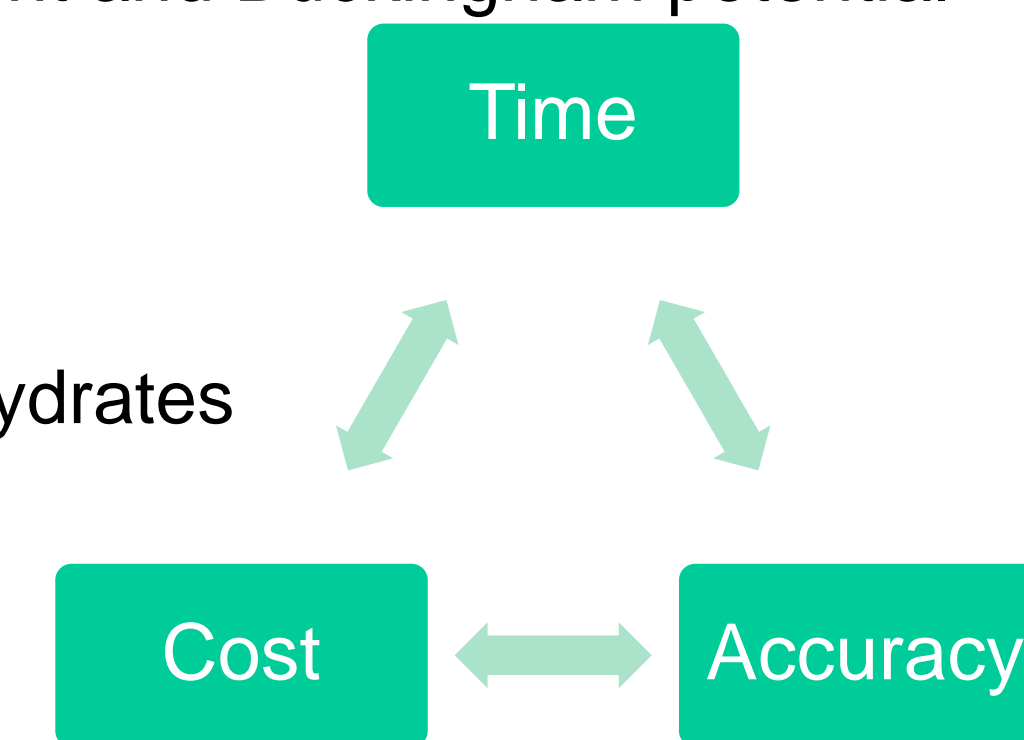
$$V(\theta) = \frac{1}{2}k(\theta - \theta_{eq})$$

Figure 4. Harmonic potential fit and comparison with reference values obtained from CCSD(T).



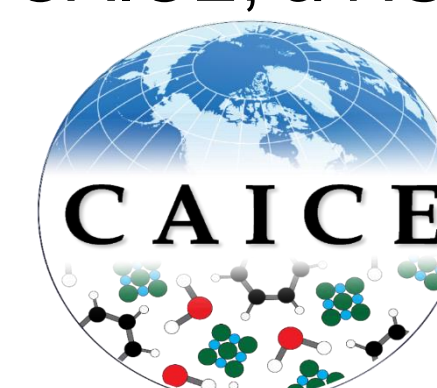
Outlook

- Fit interaction energy using the van der Waals coefficient and Buckingham potential
- Extend model to include flexibility components
 - > Polarizability
 - > Atomic Charges
- Assess and refine the accuracy and cost of the model
- Develop similar models for other classes of clathrate hydrates
 - > Carbon dioxide
 - > Hydrogen
 - > Nitrogen
 - > Xenon



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