Theoretical study of stable helium complex HeBeO

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Introduction

○Helium molecule? —— Stable helium complex: HeBeO ——

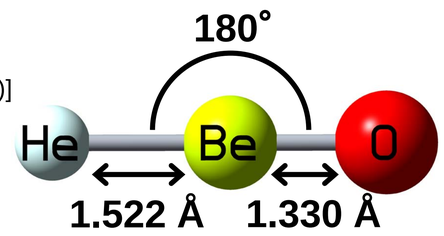
- Ionic molecule (Binding Energy : D_e = 50～100 kcal/mol)
  ex) He_2^+, $HeNe^+$, HeH^+, $HeNa^+$, etc…
- van der Waals molecule (D_e = 0.01～0.30 kcal/mol)
  ex) He-He, He-I_2, He-HCN, etc…

Are there any neutral molecules binding helium strongly??

No. But…

There are several theoretical predictions of neutral helium molecule!!

HeBeO is one of the most stable neutral helium complex predicted by Frenking et al.
[*Chem. Phys. Lett.*, **132**, 330 (*1986*)]



Minimum structure of HeBeO at the CASPT2/aug-cc-pVQZ level of theory.

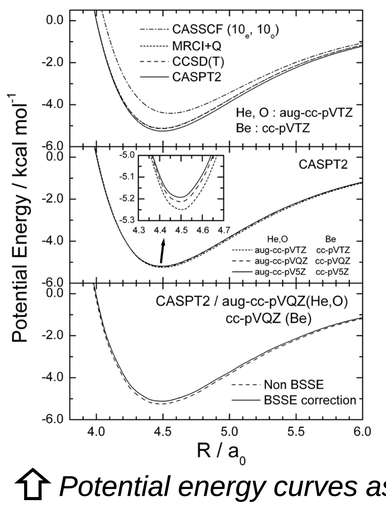
Bond character of HeBeO

- Binding energy ranks with **hydrogen bond**!!
- Charge induce-dipole interaction
- Interaction between He 1s orbital and empty σ orbital of BeO

[Aim of study] ⇨ To answer following questions.

- ☐ Is HeBeO observable molecule?
  ⟶ To investigate vibrational states of HeBeO (anharmonic calc.)
- ☐ Is HeBeO selectively produced in an ultra cold helium cluster?
- ☐ Can several helium atoms attach to BeO in a helium cluster?
  ⟶ To investigate solvation structures in the He_nBeO cluster system.

Computational Method



- Development of 3–D PES for HeBeO
  ⇒ level : CASPT2/aug-cc-pVQZ(Be=cc-pVQZ)
- Calculate vibrational energy levels of HeBeO
  ⇒ Wave packet calculation
- Simulations of HeBeO in ultra cold helium cluster
  ⇒ Path-integral molecular dynamics simulations

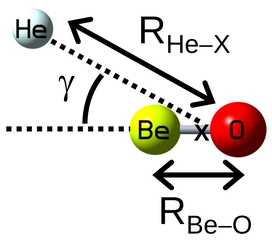
[n_{beads} = 500 T = 2 K
  step = 10,000,000 (~12 ps)]

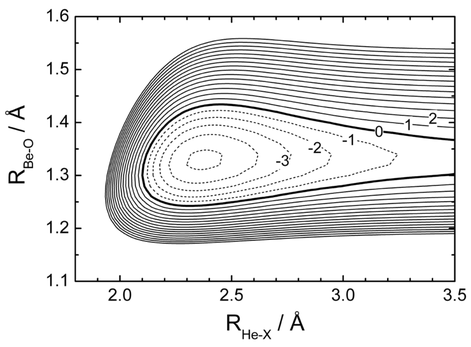
⇧ *Potential energy curves as a function of the distance between He and the center of mass of BeO for determining the appropriate ab initio level.*

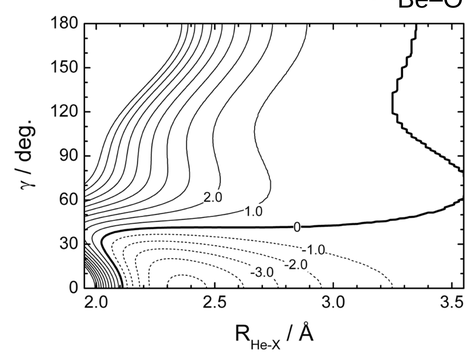
Results and Discussion

○ Potential energy surface for HeBeO

- Helium binding energy is 5.25 kcal/mol
- BeO distance is not affected by He-Be distance
- Attractive region is relatively narrow

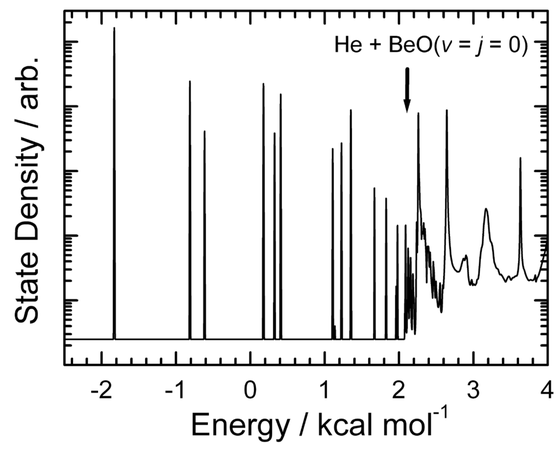




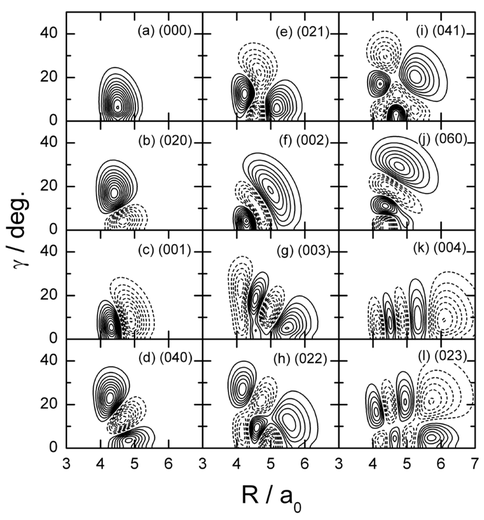


Two-dimensional counter plots of the HeBeO potential energy surface at the CASPT2/aug-cc-pVQZ level of theory.

○ Quantum wave packet calculations



State density profile calculated from three-dimensional wave packet calculations.

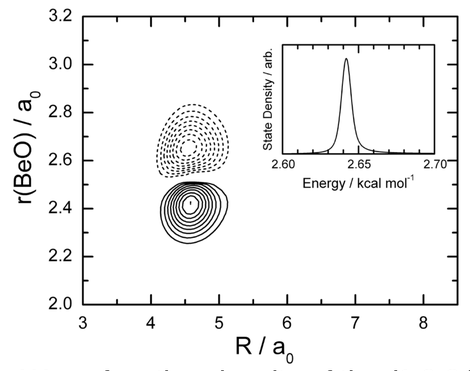


Wave function densities of the HeBeO molecule.

Method	ν_1 Be–O	ν_2 bending	ν_3 He–Be
CASPT2/aug-cc-pVQZ	1573	187	499
Quantum dynamics	1564 (100)-(000)	356 (020)-(000)	424 (001)-(000)

⇦ *Comparison of vibrational frequencies of HeBeO between the ab initio harmonic approximation and quantum dynamics*

**Vibrational quantum numbers (ν_1 ν_2 ν_3) mean BeO stretching, bending , He-Be stretching, respectively.*



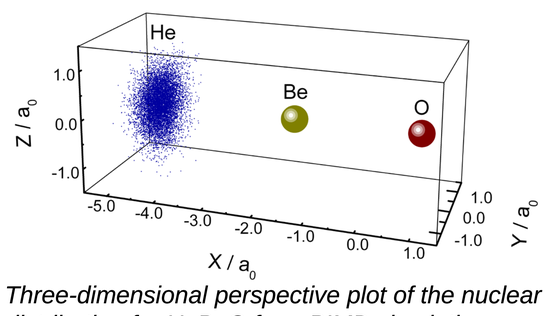
Wave function density of the (1 0 0) resonance state and corresponds to the state density profile.

- HeBeO has 14 vibrational bound states below the He + BeO dissociation level
- The lifetime of the resonance state located at 2.642 kcal/mol is about 2.0 ps
- Anharmonicity is large in He–Be vibrational stretching mode

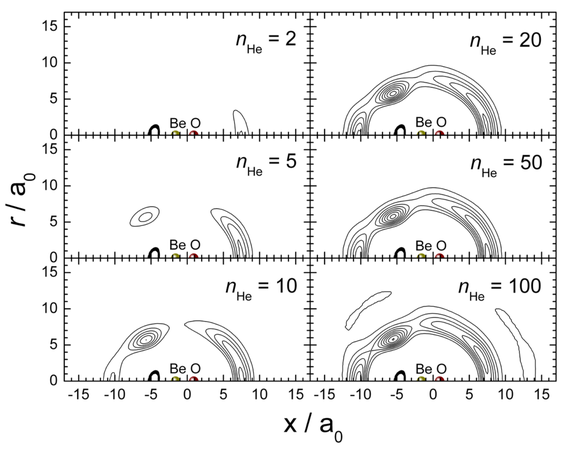
HeBeO has several bound states!!

○ Path-integral molecular dynamics simulations

- HeBeO has nearly linear structures
- The helium motion has a large amplitude due to quantum nature



Three-dimensional perspective plot of the nuclear distribution for HeBeO from PIMD simulation.



Density distribution maps of helium atoms around the BeO molecule calculated by PIMD simulations.

- Only one helium atom is strongly bound to BeO molecule in each size of cluster
- HeBeO is solvated by other helium atoms
- The first solvation shell of the HeBeO has an anisotropic behavior
- The first solvation shell is saturated by 12-14 helium atoms

HeBeO can be generated in helium clusters!!

Conclusions and Future Directions

- HeBeO has several bound states below the lowest dissociation limit
- HeBeO can be presumably generated in large helium clusters
- Extension to other molecules containing helium atom (HeBeNH, HeNiCO etc…)